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CONTENT

Plenary Lectures

ADVANCES AND INNOVATIVE PERSPECTIVES OF CHEMICAL SCIENCE

Aldoshin S.M.

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This talk highlights the present state of chemical science from the viewpoint of fundamental research results as well as their possible innovative applications. The modern approaches towards synthesis of compounds and materials for the purposes of high-tech industrial areas, tuning of reaction directions and rates, experimental and theoretical achievements in the studies of compounds to reveal the correlations between structure and properties at all levels of structural hierarchy – macro-, micro-, nano-, molecular, atomic and electronic are demonstrated.

The current level of technology of advanced hydrocarbon conversion is demonstrated, as well as conversion of alternative materials to obtain products for industrial and other applications, novel resource-saving processes of metal production and work, conversion and utilization of technological wastes.

The chemical aspects of ecology, “green chemistry” approaches, and development of novel medical products, biomedical materials, polymeric and composite materials are emphasized.

MEDICINAL CHEMISTRY APPROACHES FOR FOCUSED DESIGN OF INNOVATIVE DRUGS FOR NEURODEGENERATIVE DISORDERS

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In the area of medicinal chemistry of neurologic agents the special attention last decade was focused on the compounds that affect more than one therapeutic target. In the present report the main approaches for design of «multi-target» CNS agents will be analysed. Important place in this area occupy the compounds, which act on different ionotropic glutamate receptors, in particular, positive modulators of AMPA- ("ampakines"), and blockers of NMDA-receptors. In the frame of collaborative research between IPAC RAS and Organic chemistry chair of MSU the directed search, synthesis and study of novel group of multitarget agents acting simultaneously on both these types of receptors was conducted. As a starting point the high-affinity NMDA-receptor antagonist MK-801 having also negative side psychotomimetic effect was used. The virtual design and synthesis of flexible MK-801 bioisosteric analogs was performed. Introduction of "ampakine"-like pharmacophores in the structure of the most active substances resulted in the developing new group of compounds showing anti-NMDA and pro-AMPA activity in electrophysiological tests. On the ground of 3-D docking on different binding sites of NMDA- and AMPA-receptors some hit-compounds have been selected. Behavioral study of cognition-enhancing properties of these compounds permitted to determine the lead-compound, which show strong memory-enhancing activity and has no by-side effect in contrast to MK-801.

As an alternative approach the synthesis and primary testing of compounds, containing additional NO-generating pharmacophore, was performed. It was revealed that such modification leads to a significant change in spectrum of the primary pharmaceutical activity.

ECOLOGICAL RISK ASSESSMENT BY THE APPRAISAL OF INTEGRAL PARAMETERS OF SITES-SPECIFIC ANALYSIS

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Risk assessment is a continuous request coming from thr social and scientific world. Many efforts were in the past devoted to this evaluation. It can be generally said that all the attempts to base on single parameter were unsuccessful due to the sinergism effect of pollutants. This means that integral determinations must preferentially replace differential ones. Here we propose a sensoristic array able to evaluate the total toxic effects or the concentration of species considered as markers of toxicity and/or as representatives of whole classes of compounds. The array contains a respiriometric biosensor based on yeast cells, an algal sensor, an innovartive photosensor. This last combines stability, accumulability and toxicity as properties concurring to the ecological risk. A short discussion will also be addressed to electronic noses and tongues.

S_N^H CROSS-COUPLING REACTIONS OF ARENES AND HETARENES FREE OF ANY CATALYSIS BY METALS

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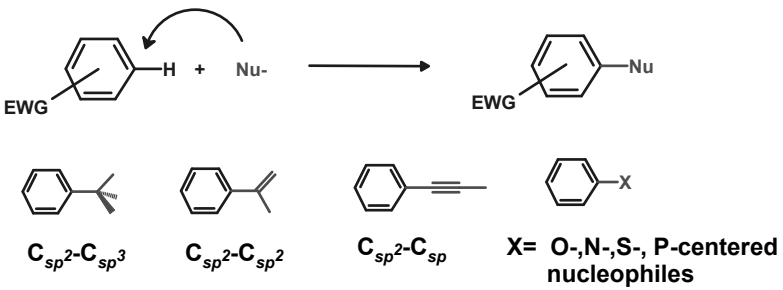
Metal-catalyzed cross-couplings, such as Susuki-Miyaura, Stille, Sonogashira, Negishi or Kumada reactions, are widely used in organic synthesis.[1]

A new synthetic methodology to build C-C and C-X (X= O, N, S, P, etc.) bonds in the series of aromatics has been advanced, which is based on nucleo-philic displacement of hydrogen (S_N^H) in π-deficient aromatic compounds.[2-4] The S_N^H reactions involve a great deal of arenes and a variety of C-, O-, N-, P- and S-centered nucleophiles, thus enabling one to perform nucleophilic alkylation, alkenylation, alkynylation, arylation, amination, hydroxylation, alkoxylation, cyanation, halogenation, as well as carboranylation, ferro-cenylation and other types of reactions.



The data accumulated in the literature during the last two decades demonstrate a common character of the S_N^H reactions, as a good complimentary basis for metal-catalyzed cross-coupling reactions.[2-4]

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DESIGN, SYNTHESIS AND CHARACTERIZATION OF SUPRAMOLECULAR NANOTUBES FROM MACROLACTAMS WITH ALKENES AND ALKYNES INSIDE THE BACKBONE

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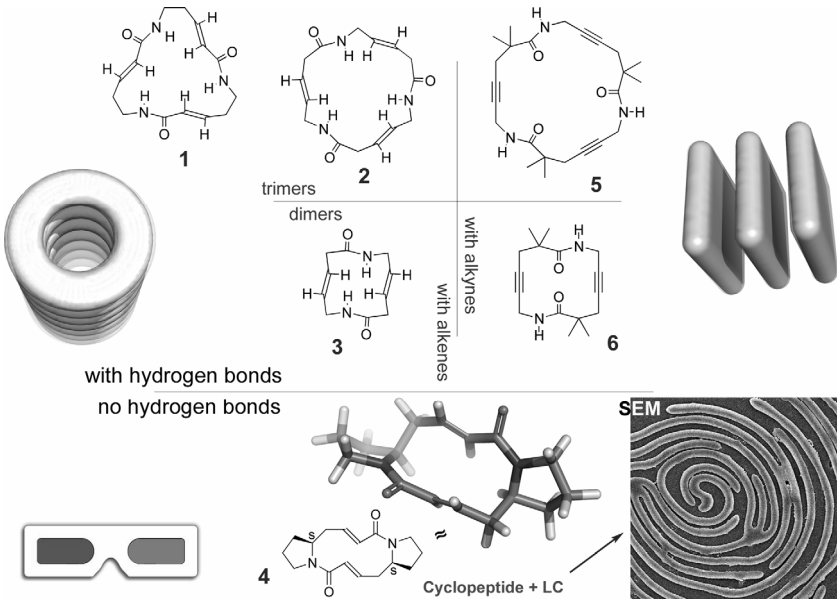
Several lactams 1-6 have been built from secondary amides as well as tertiary amides.



All compounds will alkenes 1-4 in the backbone lead to the formation of supramolecular tubes. The presence of hydrogen bonds is not absolutely necessary to induce tubular assembly, as showed in the case of 4, devoid of secondary amides. This work indicates that alignment of dipoles is sufficient to control the formation of such architectures.

Compounds with alkynes 5 and 6 do not self-assemble as tubes but as supramolecular walls or sheets that further pack much like cellulose does.

NEW ACHIEVEMENTS IN METAL COMPLEX-CATALYZED SYNTHESIS OF CYCLOPROPANES AND MACROCARBOCYCLES

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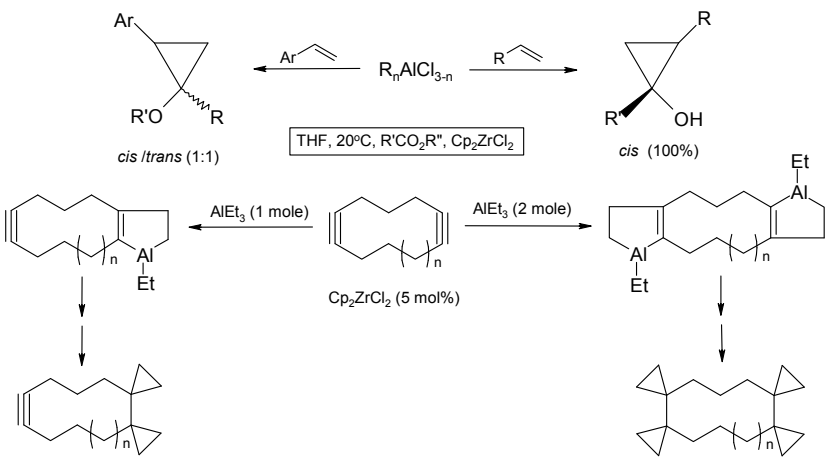
The report presents the results of original research performed by the author and co-workers over the past 5 years on the synthesis and study of properties of cyclopropanes and macrocarbocycles involving metal complex catalysts.

Of particular interest and practical value are the investigations on the development of the catalytic methods to convert olefins and acetylenes into cyclopropanes and macrocarbocycles through the employment of new reactions and organometallic reagents.



Based upon the developed by the authors' catalytic cyclometalaton reaction of olefins, acetylenes, and allenes, the powerful one-pot methodology to synthesize new as well as natural macrocycles and macrolides has been designed and implemented.

In the report, the detailed mechanism of zirconium catalysis of the above reactions is also discussed.

CARBENE ANALOGS OF GROUP 14 ELEMENTS: GENERATION, DIRECT SPECTROSCOPIC DETECTION, REACTIVITY, AND REACTION MECHANISMS

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High reactive carbene analogs of Group 14 elements are the key intermediates of the reactions of organosilicon, organogermanium, and organotin compounds including industrial important ones. Physico-chemical methods are widely used now to study structure, reactivity, and reaction mechanisms of carbene analogs.

Here we report on the generation, direct spectroscopic detection, reactivity and reaction mechanisms of short-lived silylenes, germylenes, and stannylenes studied by laser flash photolysis in the gas phase, matrix isolation as well as DFT and *ab initio* quantum chemical calculations. The main trends in reactivity and mechanisms of incretion and cycloaddition reactions of carbene analogs will be discussed.

Acknowledgements. This work was supported in part by the RFBR (project No. 09-03-00475), the President of the Russian Federation (Presidential program for support of leading research schools, Grant NSh-8242.2010.3), and the Russian Academy of Sciences (Program OX-01).

ELABORATION OF NEW ORGANIC-INORGANIC MATERIALS FOR THE CAPTURE OF DIOXYGEN AND CARBON DIOXIDE

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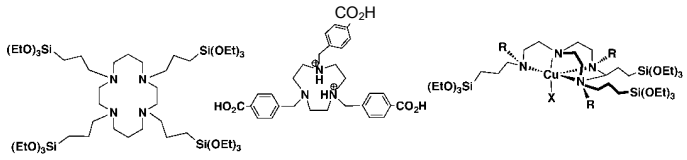
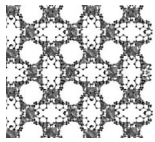
We will describe the use of polyazacycloalcanes - mainly cyclam (1) and triazacyclononane (2) - and tren(3) derivatives for the capture of dioxygen and carbon dioxide.



Firstly, we will describe the methodologies of synthesis used to prepare the polyamine precursors of materials of xerogel type and the incorporation of copper tetraazamacrocycle within a silica matrix. The xerogels incorporating these copper derivatives exhibit a remarkable affinity towards dioxygen due to the reduction of Cu(II) complexes to Cu(I) species during the metalation and the activation step and their confinement in the silica matrix. After several adsorption-desorption cycles, a textural evolution of these materials is observed and the reactivity towards O2 decreases.

This observation prompted us to study a novel class of organic-inorganic nanocomposites named «*Periodic Mesoporous Organosilica*», the PMOs which are described in the second part of our talk. The PMOs exhibit a remarkable regularity of the structure with a homogeneous repartition of the organic moieties in the framework, a high stability of the texture and fine tuned porous diameter. These materials incorporating the above copper complexes show a similar affinity towards dioxygen but in contrast to xerogels their textural properties are almost identical after several adsorption - desorption cycles.

In the third part of the talk, we will show that copper tren complexes exhibit an exceptional affinity towards dioxygen or carbon monoxide. The reactivity of these complexes incorporated in the walls of the silica matrix is drastically different from the one observed when they are grafted into the pores of the mesoporous material.



The fourth part of the talk is related to the study of novel coordination polymers named «*Metal Organic Framework* » (MOF). We have prepared the MOFs by self assembling of TACN with transition metal ions. The microporous hybrid materials are cristalline and exhibit a high specific area (>1000 $m^2.g^{-1}$). The combination of these properties make such a microporous material very competitive as a CO2 selective sorbent for capture applications.

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POLYMER MICELLES FROM BENCH TO THE BEDSIDE

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Polymeric micelles have attracted major attention as nanocontainers for drug delivery. They were first introduced for this purpose in 80'-ies by the work of H. Ringsdorf, K. Kataoka and our group. Initial studies focused on polymeric micelles self-assembled from amphiphilic block copolymers containing hydrophilic and hydrophobic blocks. Such micelles represent small (10 to 100 nm) core-shell structures with the core formed by segregated hydrophobic blocks and the shell formed by hydrophilic blocks. Drug molecules are incorporated into the cores of the micelles either by covalent attachment through cleavable linkers or non-covalently through solubilization. The latter approach is currently the most widespread with several polymeric micellar drug formulations undergoing clinical trials for treatment of cancer and other diseases. Many more polymeric micelle systems are undergoing preclinical development. Latest developments in this field include polymeric micelles with engineered cores that carry hydrophobic drugs, such as paclitaxel, with unprecedentedly high loading capacity of 45% wt. - 100 times greater than loading of commercial Taxol® formulation.[1] Furthermore, ionic drug molecules as well as biomacromolecules are incorporated into micelle cores by electrostatic complexation with block ionomers of opposite charge. Such block ionomer complex micelles have been used for delivery of DNA, siRNA and proteins. The cross-linking of the micelle core or shell by biodegradable cross-links is used to stabilize polymeric micelles in circulation, yet to ensure micelles degradation and payload release in the target cells. Of particular interest are micelles with cross-linked polyion cores, which are swollen in water but collapse upon binding a drug. Such micelles display selective entry in cancer cells but not in normal epithelial cells due differential endocytic pathways in these cells.[2] Following caveolae mediated endocytosis in the cancer cells they bypass the early endosomes and accumulate in lysosomes where they release drug in a pH-dependent fashion. Hence micelles loaded with a cytotoxic

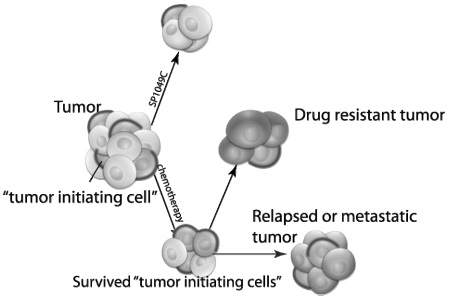

Fig. 1. During regular chemotherapy TIC escape, resulting in tumor relapse and development of MDR. We posit that SP1049C suppresses TIC

drug are toxic to cancer cells but not to normal epithelial cells, where they do not enter.[2] Another remarkable example of phenotypic selectivity of polymeric micelle delivery system is "hypersensitization" of multidrug resistant (MDR) by Pluronic block copolymers. A Pluronic-based micellar formulation of doxorubicin (DOX), SP1049C, has completed Phase II clinical trial and demonstrated high efficacy in patients with advanced adenocarcinoma of the esophagus and gastroesophageal junction.[3] *In vitro* and *in vivo* studies demonstrate that Pluronic block copolymers 1) selectively induce ATP depletion by inhibiting respiration in mitochondria of MDR1 cells, 2) inhibit P-glycoprotein (Pgp) drug efflux pump and 3) activate pro-apoptotic signaling in drug resistant cells in response to the drug. This results in a powerful modality for killing drug resistant tumors.[4] Most recently we discovered that SP1049C is hightly effective against tumor initiating cells (TIC) (also termed "cancer stem cells"), which are known to persist upon regiular chemotherapy and cause tumor relapse and metastasis (Fig. 1). This suggests that SP1049C may have broader spectrum of action that was initially thought, especially in leukemia and breast cancer, where this polymeric micelle drug was already shown to prevent tumor escape during chemotherapy *in vitro* and *in vivo*.[5,6]

ACKNOWLEDGEMENT:

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MATERIALS AND CHEMICAL TECHNOLOGIES FOR AEROSPACE ENGINEERING

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VIAM, a leading material science institute of the aviation industry and the largest scientific center in Russia, is engaged in the development of metallic and nonmetallic materials, based on a variety of classes, types and kinds of chemical products. Due to many researches the institute has established more than 2000 brands of materials for aerospace engineering, which constitute the material basis of domestic aircraft and engines.

Since the first days of its activity VIAM has been working closely with the institutes of RAS, universities, leading industry institutes and enterprises of chemical industry.

An example of effective collaboration of academic, industry and university science (Kurnakov Institute of General and Inorganic Chemistry, FSUE "VIAM" SSC RF and Mendeleev University of Chemical Technology of Russia (MUCTR)) is the development of radically new and highly original "non-fibre" manufacturing technology of high-temperature ceramic composite material such as SiC-SiC.

Jointly with Institute for Energy problems and Chemical Physics of RAS (INEPCP of RAS) and Institute of Silicate Chemistry of RAS there have been established fundamentals, mathematical models of chemical synthesis of complex system, including surface, volumetric and local protection based on carbides, borides, silicides and oxides for carbon composite materials for operation up to 2000 ° C.

At present, the creation of polymer composite materials of a new generation is the most important direction of the development of the Russian economy. For these purposes it is necessary to create new high-tensile, high-module fillers, paying a special attention to carbon fiber manufacturing.

The development of polymer composite materials on various bases and for different purposes requires the creation of polymer matrices - epoxy, phenolic, organometallic, polyimide, polyester, and many others, as well as reinforcing materials.

The future of aerospace engineering, enhancing its competitiveness in the global market is connected with the development of advanced materials based on different classes of chemical compounds, oligomers, polymers with application of nanomodification.

The success in the creation of these materials in many respects depends on the joint efforts of the institutes of RAS, government research centers, universities and interested industry enterprises.

SYNTHESIS AND APPLICATION OF NANOSIZED HETEROGENEOUS CATALYSTS – A PERSPECTIVE WAY OF REALIZATION OF NANOTECHNOLOGIES IN CHEMISTRY AND PETROLEUM CHEMISTRY

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In a number of research sectors, such as nanostructure physics, nanoelectronics, nanobiotechnologies, nanodiagnostics, not only significant applied results are achieved, but also theoretical concepts on occurrence regularities and nature of dimensional effects are substantially developed. At the same time in chemistry and petroleum chemistry, knowledge accumulation mainly takes place, and in only several cases the results are achieved which are important for development and application of nanotechnologies. Thus, it was clearly proved that dimentional effect presents in catalytic, physical and chemical properties of nanosized active component of applied heterogeneous catalysts, nanostructured porous crystals (molecular sieves) in catalytic nanoreactors.

At the same time, few papers are dedicated to study of catalytic properties of nanosized particles synthesized in situ. In particular, the reaction of C-C bond breaking with nanoheterogeneous catalysts synthesized in situ during the process of heavy oil fractions hydroconversion was studied comprehensively. Success of the research was favored by the fact that heavy oil fractions contain native surface-active substances that prevent agglomeration and subsequent deposition of nanoparticles. The achieved hydroconversion rate of heavy oil fractions is 3 degrees higher that one observed in standard industrial processes over a pelleted or microspheric catalyst.

High specific activity of nanosized catalyst particles synthesized in situ is observed in Fisher-Tropsh synthesis. Productivity of iron catalyst nanoparticles reaches the value 517 g_{hydr}/kg_{Fe} h at 80% CO conversion per pass. Comparison of productivity in g_{hydr}/kg_{Fe} h of nanosized catalyst particles and catalyst particles of 30-63 μm shows that productivity is 4-7 times higher when using nanoparticles.

Research of polydienes synthesis over a titan-magnesium catalyst with nanosized particles showed a sharp increase of reaction rate as well, when lowering particle size. If the catalyst particle size is decreased from 120-1000 nm to 15-35 nm, catalyst activity in isoprene and butadiene polymerization is 4-6 times higher. At that a trans-polymer forms at high selectivity (up to 90%wt.).

In this report, on the basis of the inherent studies and analysis of the experimental data from the literature it is shown that in heterogeneous catalysis not only a heavy increase of studies on dimensional effect in traditional areas occurs, but also a new area – nanoheterogeneous catalysis – is forming, which is focused on synthesis, physical, chemical and catalytic properties of nanosized solid particles distributed in liquid medium. For a number of processes, particularly C-C bond formation and breaking, realization of nanoheterogeneous catalysis leads to a sharp increase of the reaction rate and selectivity, including stereoselectivity.

SUPRAMOLECULAR SYSTEMS AS A BRIDGE BETWEEN NONLIVING AND LIVING MATTER

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A comparison of the architectures and functions of synthetic and biological supramolecular systems, consideration of the principles of matter complication during the evolution, and analysis of the profile energy of the basic hierarchical elements in the structural organization of matter allowed one to conclude that supramolecular systems have their own niche in the above hierarchy and precede biological systems, which are a community of functionally differentiated supramolecular systems formed from biomolecules. Therefore, supramolecular systems can be regarded as a peculiar "bridge" between nonliving and living matter. Other issues of matter evolution were considered.

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HIGH TEMPERATURE, ORGANIC FERROMAGNETIC COMPOSITIONS - A LESSON LEARNED FROM DNA SCIENCE

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Materials Science of DNA is in its infant stage although DNA has been enjoying for the past half century the pivotal importance in bioscience and biotechnology. Their unique structural and functional characteristics, however, are teaching us that DNAs can be extremely useful materials that can be advantageously utilized in self-assembly, molecular recognition, molecular wire, formation of metal nanoparticles, optics and optoelectronics, and organic molecular magnets.

This presentation consists of three main parts. In the first part optical and optoelectronic properties of natural and modified DNAs will be discussed. DNA can be chemically modified in various ways to produce versatile materials that can be more easily handled when compared with natural ones. Natural DNAs are water soluble and natural counter ions of DNA phosphate anions are sodium ions (Na^+). If the sodium ions are replaced with long alkyl quaternary onium ions, such as ammonium ions, DNA becomes soluble in common organic solvents and are able to form high quality films. We employed long alkyl ammonium ions containing various terminal functional groups in the alkyl chains in order to render useful optical or optoelectronic properties. Carbazole, styrylpyrene, and chalcone groups[1] are representative examples. We studied fluorescence, this film transistor, and light-emitting diodes properties of such modified DNAs.

In the second part, magnetic properties of natural and modified DNAs[2] will be discussed. Especially, the room temperature ferromagnetism of metal-chelated DNAs and DNAs intercalated with stable organic free radicals will be discussed. Detailed studies of their electron paramagnetic resonance and magnetization were made by EPR spectroscopy and SQUID magnetization measurement, respectively.

In the last part, utilization of organic discotic liquid crystals as mimics of DNA in the development of high temperature ferromagnetic compositions[3] will be revealed. Discotic LCs (DLCs) are composed of columns of

stacked, flat disc-like molecules. When we mixed DLCs with low levels of iron(III) phthalocyanine or stable organic free radicals, the composites were found to be ferromagnetic even at room or higher temperatures. These findings open a new approach in developing high temperatures, organic ferromagnetic compositions that should be able to find applications in modern magnetic data storage and display devices.

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THE RUSSIAN METALLURGY: CONDITION, PROBLEMS, WAYS OF THEIR DECISION

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The share of Russia in total amount of steel production and alloys on the basis of iron is nearby 60 million tons (more than 1.2 billion tons in the world), the Peoples Republic of China has 570 million tons, Japan has more than 87 million tons.

Russia produces the main part of non-ferrous metals such as Al, Cu, Ni accordingly 10 %; 6 % and 6 % from the world volume.

Great achievement of Russian metallurgy in the last years is issuance of pipes with large diameter. It is allowing to refuse from import.

However, as a whole, the level of an iron and steel industry significantly lags behind world parameters. The average wear of the basic production assets has achieved 43 %. The average power consumption of steel is above of the best world parameters up to 20-30 %. A share of waste in the rolling production is in 2 times more. The average labour productivity is in 2,5 - 3 times low. A summarized negative environmental effect is above in 2 times.

The raw material (60 %) and intermediate products (ore, a breakage, coke, cast iron, ingots, bars etc.) are predominated in the export of ferrous metallurgy. Nonferrous metallurgy exports Ni, V, Ti, Al which are necessary for qualitative metallurgy.

For the revival of the Russian metallurgy it is necessary:

- an intensification of scientific researches on perfecting and creation of new technologies and materials on the basis of integration of the academic, high school and applied researches in view of needs of production;
- the forming and financing of special programs on creation leading technologies in metallurgy, creating of new materials with the increased properties;
- the legislative inducing of introduction of innovative development in production.

Examples of an effective utilization of results of basic researches of the academic metallurgical institutes are cited.

PHOTORESPONSIVE ORGANIC AND ORGANOMETALLIC COMPOUNDS AS THE BASIS FOR MOLECULAR SWITCHES, MOLECULAR MEMORIES AND PHOTODYNAMIC CHEMOSENSORS

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The bistable organic, organometallic and metal coordination compounds served as the nanoscale molecular switches represent one of the most important components of the next generation informational and computational systems. Compared with various types of external stimuli that activate switching properties of bistable molecular and supramolecular systems light has many preferences, among which are the fastest response and possibilities of broad variation of energy and intensity of the excitation impulses providing for the optimal conditions for occurrence of the photoinduced transformations.

In the report, a comparative characteristic is given of main classes of photochromic compounds (the compounds prone to reversible rearrangements resulted in significant changes of spectral and other physical properties of the photoisomers), Various applications of photochromes as the molecular switches and molecular memories are reviewed. Special attention is given to the spirocyclic photochromic compounds: spiropyrans, spirooxazines, spiroperimidinecychexadienones and metal chelate compounds, in which the stereogenic spiro-centre is represented by a metal ion M(II). The mechanisms governed the photochemical and thermal reactions of the spirocyclic photochromes are analyzed based on the experimental data of time-resolved spectroscopy and quantum chemical calculations.

The multifunctional hybrid photochromic structures have already found many useful applications in the photocontrollable systems with switchable spectral, magnetic, electrical, mechanical, nonlinear optical, biological and other technically important properties. Illustrative examples of such type structures employed in the molecular devices of three-dimensional optical memory, bio- and chemosensoric systems are considered.

THE DEVELOPMENT OF INDUSTRIAL BULK ORGANIC SYNTHESIS: FROM ZININ UNTIL THE PRESENT TIME

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Basic organic synthesis is a branch of chemical industry whose assortment includes key organic synthesis products and intermediates. The world output of these products is as large as millions of tons. This scale requires the use of not only maximally inexpensive raw materials but also the most selective and energy-efficient processes for converting them into target products. This paper considers the examples of changing the sources of raw materials and developing catalysts and processes to minimize environmental disruption. The majority of these new processes have been introduced into industry well before the appearance of the term *green chemistry*; their development has been stimulated by not only environmental protection but also, essentially, economic reasons. Both economical and social factors give an impact to the formation of new paradigm which is aimed at involvement renewable feedstock into producing chemicals and fuels.

CURRENT ISSUES IN RADIOCHEMISTRY

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The current year is marked with two important occasions for chemists: according to the decision of UN General Assembly this year is declared as "International Year of Chemistry" and the governments of France and Poland declared 2011 as the year of Maria Currie who was twice awarded the Nobel Price. By the coincidence this year is also marked with 25th anniversary of tragic events at the Chernobyl NPP as well as serious accident at the NPP Fukushima-1 in Japan.

During the short period of time that passed from the discovery of radioactive decay by H. Becquerel and introduction of the term "radiochemistry" by Marie Currie for the branch of chemistry that study this phenomenon, radiochemists have accumulated large basic knowledge about the main laws of radioactive decay of nucleus, chemical properties of natural and man-made radioactive elements, methods of their detection, separation and determination, environmental behavior including products of global fallout after nuclear tests. Various technologies for reprocessing of spent nuclear fuel from NPP have been developed and are used currently.

Nowadays the accumulated knowledge gain in special importance as the durable basis for solution of new urgent tasks of radiochemistry connected with the increased demand for the nuclear power production in Russian and in other countries as well as with fast development of nuclear medicine. Among problems that require fast solutions, one would mention the establishment of basically new ways for reprocessing of spent nuclear fuel, methods for partitioning of high level wastes, approaches for safe long-term storage of radioactive substances, design of new waste forms for immobilization of radionuclides, development of new types of natural and engineered barriers that provide safe disposal of spent nuclear fuel and radioactive wastes.

MAIN DIRECTIONS OF THE DEVELOPMENT OF CHEMICAL SCIENCE AND INDUSTRY OF LOWER VOLGA REGION

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The bowels of the earth of the Lower Volga region are rich in minerals: 500 millions of tones of oil, 1.2 trillions cubic meters of gas and 450 millions of tones of gas condensate make nowadays the reserve of hydrocarbons only in Volgograd region. There is also mineral salt, which entire and expected life make (in millions of tones): 365471.1 for bischofite, 4079.0 for common salt, 4507.6 for potassic salt. All these resources have determined the development of chemical and petrochemical industry in the region.

The chemical industry of Volgograd, the venue of the XIX Mendeleev Congress on general and applied chemistry, began at the turn of the XIX-XX centuries. This time there were 140 metalworking and sawing factories, creameries, steammills, tanneries and other enterprises. On the eve of the First World War in 1913 more than 147.0 thousands of tones of steel and 123.3 thousands of tones of rolled metal were smelt[1], the amount of chemical and petrochemical production made only 200 rubles in Tsaritsyn![1] That year all the industry of Tsaritsyn produced products for a sum of 14263.0 thousands of rubbles (by the procedure of calculation in 1966). The city used to be a major transport hub, outrunning such Volga cities as Saratov and Astrakhan in cargo turnover 1.5 times.

In 1879 oil-refining complex of "Nobel" began its work in Astrakhan, and the next year brothers Nobel founded the analogous plant in Tsaritsyn. Oil and oil products were transferred to Tsaritsin from Baku by water. In 1884 Baku transferred about 17.7 millions of poods of kerosene and 12.5 of them were transferred to Tsaritsyn (it makes about 70 %). According to the first five-year plan (1928-1933) Stalingrad Chemical Plant was included into 518 most important objects.[2]

The first professional communities of chemists and engineers in Stalingrad were formed in 1920th -30th. The first province conferences were held at the same time.[3] In the second half of XX century scientific potential of the Lower Volga region increased dynamically. Nowadays in Volgograd region there are 18 members of Russian Academy of Sciences, of Russian Academy of Medical Sciences, of Russian Academy of Agricultural Sciences, of Russian Academy of Architecture and Construction Sciences and more than 850 doctors of science and 3500 candidates of science.

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PHOTOCHEMISTRY AND MOLECULAR PHYSIOLOGY OF VISION

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Photoisomerization of 11-*cis* retinal chromophore (200 fs quantum yield 0.65) within the visual pigment rhodopsin molecule is the only photochemical reaction in vision. Using femtosecond time-resolved laser absorption spectroscopy with two-pulse system, we have studied the coherent 11-*cis*-retinal photoisomerization dynamics [1,2]. Using three-pulse laser system, we were able to demonstrate for the first time the ultrafast photochromic reaction of rhodopsin at room temperature[3]. The result shows that visual pigment rhodopsin molecule can be considered as a prototype of ultrafast molecular photoswitcher.

Physiologically active state of rhodopsin is appeared because of essential conformational changes of its protein part[4]. The visual pigment is able in this state (metarhodopsin II) to bind and activate G-protein, and in consequence to trigger the enzymatic amplification cascade of phototransduction. Rhodopsin is at present the best understood G-protein coupled receptor.

Schiff base linkage hydrolysis and all-*trans* retinal release from the protein part of molecule create the potential hazard of light damage to the retina and aggravation of retina degenerative diseases (photobiological paradox of vision)[5].

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TUMOR IMAGING AND PHOTOTHERAPY: FROM MONOMERS TO NANOPLATFORMS

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Tumors can be detected optically by directing fluorescent molecular beacons to the tumor cells, and the optical imaging of fluorescent markers is a rapidly developing field. Tumor-localizing PS can be fluorescent. This property has been used to guide PDT, and also is being explored to define lesions and margins to guide surgical interventions, however most of the photosensitizers exhibit small Stokes shift between the long-wavelength absorption and emission and are therefore not efficient fluorophores for tumor-imaging.[1] Conversely, highly efficient fluorophores generally do not localize within tumors efficiently, but require some additional moiety or process to provide selectivity, such as attachment of a peptide or other moieties that binds to a targeted receptor with high expression in tumors.[2] However, tumors are heterogenous and may not have a uniform or consistent expression of a particular receptor. In addition to compelling preclinical data, the high response rate of clinical PDT suggests that certain porphyrin-based photosensitizers preferentially accumulate within a wide range of malignancies compared to their normal tissue surroundings. Thus, the photosensitizers can be used as vehicles to deliver the desired imaging agent(s) to tumors, which in turn can help visualize treatment sites.[1]

In recent years, the overall goal of our laboratory has been to develop and characterize multifunctional photosensitizer-fluorophore conjugates[1] or nanoparticle platforms for tumor localization, photodynamic therapy and detection (PET, MRI and fluorescence).[1] Our research involves the synthesis, characterization and pre-clinical validation (including in vivo toxicity) of novel conjugates of tumor-avid PS linked to unique near infrared (NIR) fluorescent dyes or the long half-life PET agent labeled with ^{124}I. Preliminary work shows these conjugates provide very high *in vivo* tumor selectivity, while maintaining PDT efficacy. This "see and treat" approach enhances the scope of image guided therapy. The tumor imaging and therapeutic potential of some of these conjugates and multifunctional biocompatible polyacrylamide-based NPs will be presented.

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PROBLEMS OF CATALYSIS IN CHEMISTRY

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Catalytic technologies are the structuring and innovation basis of the chemical and allied industries in Russia. As a result, development of newest generation catalysts and catalytic processes is the prime problem for the Russian chemical community.

The catalysis science, which is a very fruitful alloy of organic and inorganic synthetic chemistry, physical chemistry and chemical engineering (chemical technology), is strongly affected not only by the logic and progress in the science alone, but also by the economic demand and by the state resource potential.

In the presentation, some examples of strategic problems in the catalysis science, as well as the problems resulted from the current demands in Russia, are discussed. Among the urgent strategic problems are the ones of theoretical and experimental studies of the state of operating catalysts, control of the selectivity of catalytic processes, as well as the *nano* problem, i.e. dependence of catalyst properties on the size of the catalytically active component.

Practical priorities of catalysis in Russia are (i) deep and fine processing of hydrocarbon resources, (ii) inevitable progressive substitution for the resource base of the chemical industry to involve light hydrocarbons and renewable organic materials, as well as (iii) processing of heavy and sulfurous oil. Particular attention is paid to the main factor that retards creation of the Russian basic technologies for large-scale chemical industries.

ATOMISTIC UNDERSTANDING OF HETEROGENEOUS CATALYSIS QUANTUM CHEMISTRY IN CONCERT WITH EXPERIMENT

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Two classes of solid catalysts are considered, zeolites as solid acids used in hydrocarbon synthesis and conversion processes, and supported transition metal oxides as selective oxidation catalysts.

Zeolites are also of interest from a fundamental point of view. With their well-defined crystalline structure they are a perfect example of the active site concept. The interplay of the Brønsted site properties and the framework structure in determining the catalytic function of zeolites is described. The deprotonation energy is used as parameter for characterising the activity of catalysts with different framework structure and composition, and the proton affinity is decisive for whether or not a feedstock molecule forms a stable protonated species in H-zeolites. The example of the tert-butyl carbenium ion1 is used to discuss the relative stability of different protonated alkene species in zeolites. It is shown that progress in computational methodology makes quantum chemical predictions of energy barriers with chemical accuracy possible.2

Based on a detailed mechanism of the oxidative dehydrogenation of light alkanes3 and the oxidation of methanol to formaldehyde,4 the effect of different supporting oxides such as SiO2, Al2O3, ZrO2, and CeO2 on the activity of supported vanadium oxides is analysed. Differently from zeolite catalysts, the surface structure of these powder catalysts is difficult to characterize by experimental techniques alone, and identification of active species by spectroscopy meets assignment problems. The support effect is well-known, but the different factors that may contribute to it and their interplay are not understood: global electronic effects depending on the chemical composition, varying distributions of vanadia species and particles of different size and structure, different role of Lewis and Brønsted acid sites. To compare the catalytic activity of the different materials in oxidation reactions, we calculate the energies of O defect formation that relate to the reaction energy, and the energies of hydrogenation that relate to the energy barrier of the rate-determining step. Our calculations show that the remarkably high activity observed for vanadia catalysts supported on ceria directly relates to a special synergy between the ceria support and the supported oxide (vanadia).5 This is explained by the unique ability of ceria to accommodating extra electrons into Ce 4f states and removing it from V 3d states in the reduced catalyst.

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NEW NATURAL PRODUCTS. STRUCTURES AND BIOLOGICAL ACTIVITIES

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Marine organisms and terrestrial plants are rich sources of new natural products, including those that have unusual chemical structures and show extremely high biological activities. Last years we have isolated several hundreds new natural products from marine micro- and macroorganisms, collected during marine expeditions onboard R/V "Academician Oparin", and from higher plants of the Far-eastern part of Russia. Their structures and absolute stereochemistry were established. There are new alkaloids,[1] steroids and terpenoids,[2] peptides, unusual lipids, poly- and oligosaccharides[3,4] among the isolated compounds. Some of them demonstrate antitumor, cancer-preventive, neurotrophic properties, immunomodulatory, hepatoprotective, and antimicrobial effects.[5-7] Preclinical studies on several substances as potential pharmaceutical leads were carried out. Molecular mechanisms of pharmaceutical action were investigated in some cases.

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GREEN CHEMISTRY FOR SUSTAINABLE DEVELOPMENT

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Over the last century, development of economics as a discipline and the trends in global economy has increasingly, with few exceptions, been dominated by a perception of living in an unlimited world with unlimited resources and pollution drains. Resource and pollution problems in one area were supposed to be solved by moving production or people to cleaner and more resource rich parts of the world. The very hint of an overall global limitation as suggested in the report "*The Limits to Growth*" [Meadows *et al.* 1972] has generally been met with disbelief and rejection by businesses and most economists. However, this rejection was mostly based on false premises.

Sustainable development requires attention to both the demand and supply side. On the demand side there is an urgent need for efficient policy means promoting energy and resource conservation. This includes changes in the institutional and economic framework to compensate for the short comings of the dominating neoclassical economy and the short time horizon of the present market system. On the supply side fossil fuels are becoming a central problem being the dominating global energy source while at the same time presenting serious problems in relation to global warming and limited resources ("peak oil"). Consequently, there is an urgent need to develop alternative strategies and policy means in order to promote sustainable development. In relation to the demand side, the concept of limits to growth on a limited planet must be acknowledged.

Chemists play a key role in providing solutions to many of the major challenges facing the world today, helping to address the Millennium goals. Chemistry is fundamental to our understanding of the world and the cosmos. Moreover, molecular transformations are central to the production of food, medicines, fuel, and countless manufactured and extracted products. Green chemistry is one of the key directions of pollution prevention and pollution control. Since 1990s it has grown into powerful driver of innovations in a global scale. But in our country, due to the collapse of the USSR, the potential of fundamental and applied research in this area was not used by policy makers and business elite.

In the presentation the current trends in green chemistry (on national and global scale) will be analyzed.

PHTHALOCYANINES FOR MOLECULAR PHOTOVOLTAICS

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Porphyrinoids are employed as components of photovoltaic and artificial photosynthetic devices[1-3]. However, synthetic porphyrin analogues such as phthalocyanines[4] have the advantage, as photon harvesters, of exhibiting very high extinction coefficients in a wavelength range that extends to around 700 nm, where the maximum of the solar photon flux occurs. Consequently, Pcs have emerged as excellent light harvesting antennas for incorporation into donor-acceptor systems, mainly in connection with fullerenes as an acceptor moiety. During this talk an overview of the results obtained by our group in Madrid during the last few years will be given.[5-7]

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NANOREVOLUTION IN CHEMISTRY AND TECHNOLOGY

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Nanotechnology is a logical step forward in evolution of the modern fundamental science. This interdisciplinary area includes recent advances in chemistry, physics, biology, mechanics and other classical sciences and is connected with a breakthrough in preparation and analytical methods applied to promising materials. Several parameters are important to design nanomaterials: their chemical composition determining the general properties, a size varying the properties, and also a dimensionality making the particles non-homogeneous and ordering in the system enhancing the properties of an ensemble of the nanoparticles. This is a native feature of nanotechnology: new characteristics can be obtained only in a specially organized at a scale larger than nano although the "nanolevel" always exists in each macroobject and exactly the nanolevel determines the key properties of the material. The main mission of nanotechnology is the search for new highly effective ways of solving a number of global problems including:

- development of new green energy sources;
- enhancement of health and life prolongation;
- maximal increase of agriculture productivity;
- development of information technologies;
- space exploration;
- development of modern interdisciplinary education.

Solving these problems by nanotechnologies predetermines the beginning of original "nanorevolution" in chemistry and technology as a new paradigm of scientific and technical progress.

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CHEMICAL ENGINEERING AND BIOLOGICAL CATALYSIS

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The subjects of the lecture are:

• Discussion of the advances in the study of enzymes – effective, studied in detail and widely applied catalysts.

• Analysis of the structure, architectonics and mechanics of protein molecules. Consideration of the transition from primary amino acid sequence to three-dimensional structure of protein molecule.

• Detailed discussion of the physical chemistry of enzymatic catalysis, including the structure of active sites, the molecular nature of the catalytic activity, and the elementary acts. A fundamental step forward is the quantum-chemical calculation of the energy profiles of the elementary acts of catalysis.

• Discussion of advances in the field of protein engineering of enzymes – the construction of catalysts having specified properties. Significant progress has been made in the study of human enzymes based on the post-genomic research and technology.

• Consideration of the problems of individual molecular polymorphism of enzymes, metabolic stability, new possibilities for designing drugs and personalized medicine.

• Analysis of contemporary biocatalytic technologies: the fine organic synthesis, the analytic applications, the ecobiocatalysis for production of biofuels – energy from renewable sources.

• Discussion of the problems of biomimetics – the construction of catalysts on the principles of enzyme action.

THE AMAZING RIBOSOME

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Ribosomes, the universal cellular machines, act as polymerases that translate the genetic code into proteins with high efficiency. They posses spectacular architecture accompanied by inherent mobility, which facilitate their smooth performance as RNA enzymes in decoding the genomic information and creating nascent proteins.

The peptide bond formation site is located within a universal internal symmetrical region connecting all of the remote ribosomal features involved in its functions. The elaborate architecture of this region is capable of positioning both the amino acylated and peptidyl tRNA substrates in stereochemistry required for peptide bond formation, for substrate-mediated catalysis, and for substrate translocation, hence, enabling the elongation of the nascent proteins.

Adjacent to this site is an elongated tunnel, along which nascent chains progress until they emerge out of the ribosome. This tunnel is involved in gating and chaperoning functions; provides the binding site of the first cellular chaperone that encounters the emerging nascent chain, and hosts a major family of antibiotics that target the ribosome.

RUSSIAN CHEMISTRY: LOOK THROUGH PRISM OF TIME

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Russian Scientific chemistry has been started with Lomonosov; works on general chemistry by Lovits, Reiss and Hess, partially by Severgin and Zakharov, were significant milestones during its first decades. Later, the period of achievements in organic chemistry took place: Zinin, Butlerov and many others. However, studies by inorganic chemist Klaus were remarkable on this background and, of course, most important works by Mendeleev. The end of the XIX century has been characterized, beside others, by the development of physical chemistry and the first (very modest) steps of chemical industry. The first half of the XX century gave many scientific achievements, which have been estimated, sometimes with a delay, by the world scientific community. Creation of chromatography by Tswett, chain reactions by Semenov or preparation of artificial rubber by Lebedev can serve as examples. Powerful chemical industry has been erected, including, e.g., manufacturing fertilizers or – among not so large productions – chemical reagents. Organization of a widespread network of research institutes, conferences, journals and especially the education system (for the preparation of specialists of different levels and applications) played the very significant role. The first half of the XX century has been characterized by the hope on own possibilities and, as a result, by many original scientific, technological and technical decisions. Government decision of May 1958 was an important impact for chemical industry, especially for polymer production. Since the 1970-s, the situation has changed: increasing the scale of chemical industry, organization of manufacturing new products moved along with the large scale buying technologies and equipment abroad. This resulted in decreasing the role of research institutes which often received minor tasks and solved small problems of plants. The period between XX and XXI centuries, that is the last 20 years, was, unfortunately, the time of the fall of chemical industry, the crisis of industrial chemical science, decreasing of the potential of academic chemical science due to low funding. All this factors effected on the position of Russian chemistry in the world, resulted in a decrease in the contribution of our chemical science into the world chemistry. However, we are in opinion that the mentioned negative changes were not irreversible; that the potential of the Russian chemical science is still large enough; that the chemical industry will be the actively developing field.

Section 1

Fundamental problems of chemical science

Chairmen – Academician *O.M. Nefedov*,
Academician *M.P. Egorov*

Oral presentations

INVESTIGATION OF CHEMICAL REACTIONS UNDER SOLVENT FREE CONDITIONS, IN MELTS AND IONIC LIQUIDS

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In recent decades several synthetic approaches were designed to carry out chemical transformations under solvent free conditions towards development of Green Chemical methods. Solid state chemistry and reactions in organic melts represent another fascinating opportunity to enhance the scope and overcome some limitations in this important area. Outstanding activity was shown in the field of ionic liquids utilized for development of new synthetic procedures in recyclable media.

The present lecture will highlight new NMR and MS methods to study solvent-free systems, melts and ionic liquids. Special attention will be paid to address the question of mechanistic studies of organic and catalytic reactions in the alternative media [1,2].

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ACKNOWLEDGMENT

The work was supported by the Russian Foundation for Basic Research (Project No. 10-03-00370) and Programs of Division of Chemistry and Material Sciences of RAS.

SYNTHESIS AND STRUCTURE OF FUNCTIONALIZED NITRO- AND AMINOISOXAZOLES

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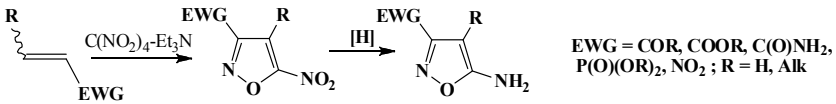
Recently we have elaborated a new efficient method for haterocyclization of electrophilic alkenes by the action of tetranitromethane in the presence of triethylamine which afforded functionalized nitroisoxazoles.[1] X-Ray diffraction method established that nitro group occupies position 5 of the isoxazole fragment. The present investigation deals with reduction of wide series of 5-nitroisoxazoles aimed at the synthesis of functionalized 5-aminoisoxazoles. As isoxazole cycle is known to be labile, we studied various mild reduction systems Zn-NH_4Cl, Zn-AcOH, Zn-HCl, $SnCl_2$, Al-Hg and others. Three types of the products of the nitro group reduction were isolated depending on the reaction conditions: azooxy-, hydroxyamino- and aminoisoxazoles. Target 5-aminoisoxazoles were the sole reaction products when $SnCl_2$-EtOH or Zn-AcOH in i-PrOH were employed.

As a result, we have elaborated a convenient two-step synthesis of functionalized 5-aminoisoxazoles by heterocyclization of commercial available electrophilic alkenes followed by the reduction of 5-nitroisoxazoles.



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NEW INDOLE REACTIVITY PATTERNS THROUGH MOLECULAR ACTIVATION

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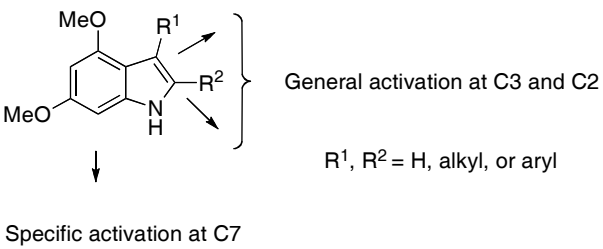
Simple indoles undergo ready electrophilic substitution and addition at C3. Over recent years, we have been investigating the chemical reactions of activated indoles, especially those with methoxy substituents in place to activate the benzene ring. In addition to such specific activation of the benzene ring, there is significant general activation that also affects the C2 and C3 positions. For example, activated 4,6-dimethoxyindoles are capable of being nucleophilic in a variety of positions, including C3, C2, and C7, depending on the overall substitution pattern. The special chemistry of activated indoles allows the formation of diindolylmethanes, triindolyldimethanes, and tetraindolyltrimethanes, and these can further lead to interesting macrocyclic structures. Also, the ambident nucleophilicity enables further ring fusion to take place and generate new heterocyclic ring systems. A selection of new reactions and new ring structures will be described.



PRIMARY STEPS IN PHOTOSENSITIZED REDOX REACTION WITH SUPRAMOLECULAR CYANINE DYES SYSTEM

Chibisov A.K.,[a] Zakharova G.V.,[a] Slavnova T.D.,[a] Görner H. [b]

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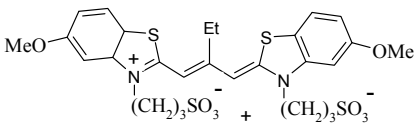
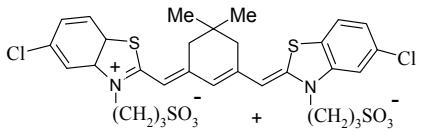
Primary steps of redox reaction photosensitized by thiacarbo- (Dye 1) and thiadicarbocyanines (Dye 2) dimers (supramolecular system) were studied in water by ns-laser photolysis. The formation of the dimers is concluded from the analysis of absorption spectra. Upon laser pulses (532 nm, 10 ns) the triplet state of the Dye 1 dimers (life-time 11.5 μs) is populated. In the presence of electron donor (ascorbic acid, AA) and electron acceptor (*p*-nitroacetophenon, PNAP) at 1×10^{-4} M the dimer triplets are predominantly quenched by PNAP yielding one-electron reduced electron acceptor (the primary step of photosensitization).



Dye 1



Dye 2

Dimeric anion-radical which is formed in the reaction appeared to be unstable and dissociates to the monomer and the dye neutral radical [1]. The secondary step consists of AA oxidation due to electron transfer from AA to the dye neutral radical. In contrast to Dye 1 laser excitation of Dye 2 results in electron transfer between two excited-singlet monomers constituting the dimer and yielding radical pair (the primary step of sensitization). The radical pair further dissociates to neutral and dianion dye radicals which is followed by secondary reactions of one-electron oxidation of AA and reduction of PNAP [2].

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DIAZOCOMPOUNDS: SYNTHESIS AND APPLICATION

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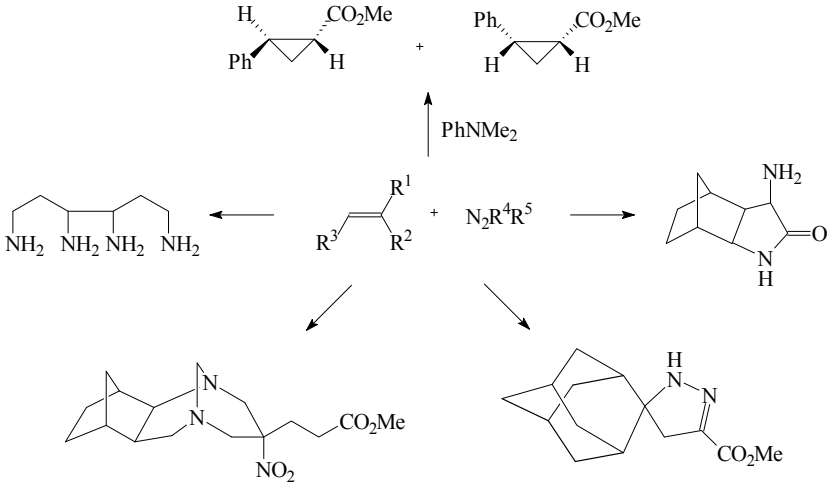
The results of investigation on the development of novel methods for the production of diazocompounds and their application at the synthesis of cyclopropanes, heterocyclic compounds and polyamines are represented. It was shown, that the application of the method of 1,3-dipolar cycloaddition of diazocompounds to olefins and the subsequent catalytic hydrogenation of pyrazolines obtained is an effective approach to the synthesis of 1,3-propylenediamines and pyrrolidin-2-ones. These compounds are interested for the synthesis of pyrrolidine derivatives and analogs of the γ-aminobutyric acid – a basic inhibitor of neurotransmitter in central nervous system Mammalian. Novel effective catalysts of 1,3-dipolar cycloaddition of diazocompounds to a C=C-bound were found which application makes it possible to produce pyrazolines and pyrazols selectively and in high yields.



Among the synthesized heterocyclic compounds the substances possessing an antiarrhythmic, nootropic and antiviral activity were revealed.

This work was financially supported by the Russian Academy of Sciences (Program OCh-01 of Basic Research «Theoretical and Experimental Studies of the Nature of Chemical Bonds and Mechanisms of Important Chemical Reactions and Processes»).

NEW NITROGEN-, PHOSPHORUS CONTAINING ANTIOXIDANTS WITH THE STERICALLY HINDERED PHENOLIC FRAGMENTS

Gibadullina E.M., Shaekhov T.R., Voronina J.K., Burilov A.R., Pudovik M.A., Sinyashin O.G.

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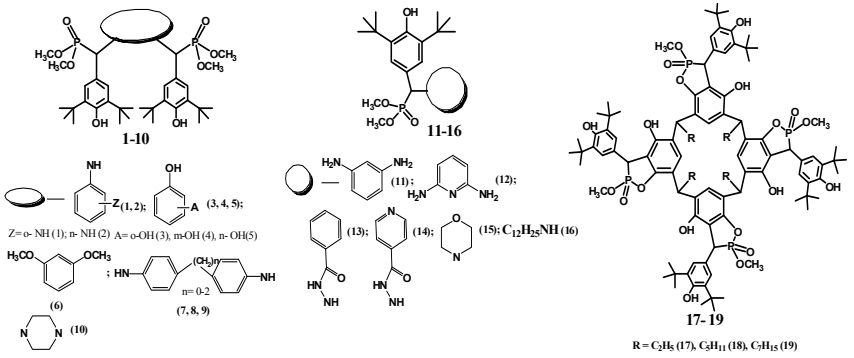
One of the important properties of the polyphenolic compounds that define use *in vivo* and synthetic materials are high antioxidant activity and ability to form stable radicals. This property is most full shown in sterically hindered phenols many of which are used in industry for production of polymeric materials and also in synthesis of drugs. Synthesis of phenolic antioxidants has been carried out by a combinatory principle - by a combination various phenolic, amine, heterocyclic fragments with phosphorylated quinone methide (3,5-di-tert-butyl-4-oxocyclohexa-2,5-dienylidene)-methylphosphonate). As a result we received new nitrogen-, phosphorus containing phenolic antioxidants with the sterically hindered phenolic fragments **1-19.**



The structure of synthesized compounds was proved by NMR ^{1}H, ^{13}C, IR spectroscopy, mass-spectrometry (MALDY) and element analysis.

ACKNOWLEDGEMENT

This work was supported by the Russian Foundation for Basic Research (grant no. 11-03-00416-a), FTP (grant no. П837*).*

THE NEW REPRESENTATIONS ABOUT STRUCTURE AND PROPERTIES OF WATER WITH DIFFERENT ISOTOPIC COMPOSITION

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Data on physicochemical properties of the light water (deuterium concentration is reduced to the ratio D/H = 4 ppm and that of the isotope of oxygen 18 – to the ratio 18O/16O = 750 ppm) have been obtained. They include the melting and boiling points, kinematic viscosity, density, the spin–spin proton relaxation time, self-diffusion coefficients, and the small angle laser light scattering.

The "classical" physicochemical properties of the light water differ from the deionized water having natural isotope composition. It should be stressed that the density of the light and deionized waters to a great extent is determined by the concentration of heavy isotopes of oxygen. The variation of properties of liquid during the reduction of concentration of heavy isotopes testifies the presence of a "control" function of water molecules containing heavy isotopes: one molecule of 1H216O, one molecule of 1H217O and 5–7 molecules of 1H218O fall on ~3000 molecules of 1H216O. Such realization of the isotope effect is possible via the cluster organization of associated liquid. The growing number of tie molecules in light water and its higher "homogeneity" in terms of the structure is corroborated by the variation of its molecular dynamics properties.

In our view the causes of differences in the properties of the light and deionized water can be explained as follows. In earlier papers we put forward a hypothesis on the formation in the water of natural isotope composition of density inhomogeneities of submillimeter range – deuterium stabilized gigantic heterophase clusters (GHC) with the relaxation time of more than one second. These density inhomogeneities of water are stabilized by heavy isotopologues at their probable arrangement on the surface of density inhomogeneities that allows them to implement the "control" function. In terms of a series of physicochemical properties the light water is a new associated liquid that has not been scientifically defined earlier, possible mechanism of implementing the "control" function of heavy isotopologues of water molecules is the formation of density inhomogeneities, i.e., deuterium stabilized gigantic heterophase clusters.

Biological effects of the light water are not related to the ligand dependent toxic effect, but determined by the adaptive reasons.

NEW HOMOGENEOUS OSCILLATING REACTIONS: PROCESS OF C_9-C_{12} CARBONYLATION

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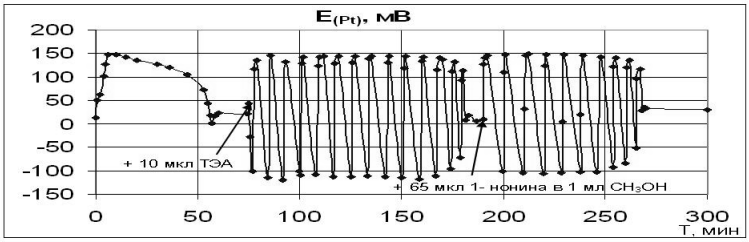
For several years in MITHT investigations of oscillating modes in the oxidative carbonylation reactions of various organic substrates in homogeneous metal complex catalysis in alcohol solutions of palladium salts were conducted. The regimes of developed oscillations in reactions involving phenyl- and methyl acetylene, dimetiletinil-carbinol, propargyl alcohol in the systems PdI_2-KI-CO-O_2-CH_3OH; $PdBr_2$-LiBr-CO-O_2-CH_3OH; $PdBr_2$-LiBr-CO-O_2-$(CH_3)_2CO$-H_2O were found[1-3]. Recently interesting modes of oscillations in carbonylation reactions of 1-nonin, 1-decin and 1-dodecin system PdI_2-KI-CO-O_2-CH_3OH have been found with a number of features depending on the nature of the substrate.



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This work was supported by RFBR (grants № 05-03-33151 and № 09-03-01072).

TELECHELIC POLYMER: SYNTHESIS BY METHODS OF CONTROLLED/LIVING RADICAL POLYMERIZATION. FUNDAMENTAL ASPECTS AND INDUSTRIAL APPLICATIONS

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Telechelic polymers are defined as macromolecules with reactive end groups that have the capacity to enter into further polymerization or other chemical reactions. Such polymers are used as important building blocks for various macromolecular structures, including block- and graft-copolymers, star-, hyperbranched or dendritic polymers.

This report describes the general techniques for the preparation of telechelic polymers by methods of Controlled Radical Polymerization (CRP), including Atom Transfer Radical Polymerization with participation of metallocomplexes, Nitroxide Mediated Radical Polymerization, Quinone Transfer Radical Polymerization and some other methods. The new original organometallic catalytic systems for CRP of various vinyl and acrylic monomers have been analyzed.

Precise control of functionality, molecular weight and molecular weight distribution uniformity can be made by means of controlled radical polymerization techniques. As a result various macromolecular architectures can be obtained.

Industrial interest in telechelics was stimulated by the development of thermoplastic elastomers, which consist of block- and multiblock copolymers. At the dawn of 21^{th} century controlled radical polymerization has become an industrial reality. Telechelic polymers as CRP-polymers will find their place as novel materials that create new high-valued products, rather than as replacement products for existing polymers. A broad spectrum of tailor-made CRP additives with specific properties is awaited in the near future for specific applications as emulsifies, dispersants, sealants, lubricants, adhesives, rheology and surface modifiers, foam control agents, leveling agents, blend compatibilizers, elastomers (thermoplastic), nanocontainers for the encapsulation of actives and etc. CRP-polymers can be used for home care, cosmetics, biomedical, industrial, textile, paints and coatings, airspace and aircraft, automobile and electronics markets.

This work was supported by the Russian Foundation for Basic Research (grant № 11-03-00074).

SELF-PROPAGATING REACTIONS (CHAIN, CYCLIC, OR CASCADE) – A SPECIAL MODE OF CHEMICAL TRANSFORMATIONS OF ORGANIC COMPOUNDS

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Self-propagating reactions of organic compounds are of considerable interest from both theoretical and practical points of view. However an analysis of published results refer to catalytic and initiated reactions substantially complicated by imperfect terminology which used in description concerned at these definitions in the Nomenclature editions[1,2].

In particular such determinations of regeneration stages of the "catalyst" in the case of catalytic reactions and formation stages of the "mediator" of initiated reactions showed some inconclusiveness. In our opinion, in the former term it is needed to introduce mentioning about necessity to create conditions for the formation of the active form of the catalyst. The second term should include a statement that the mediator should be self-reproduced upon completion stage of the concerted reaction. The term "expendable catalyst"[2] contradicted to commonly accepted the term "catalyst"[1] and requires refinement, since on transforming into the inactive form it acts as a simple reactant, which does not enter into the composition of the reaction product. We think that it is not reasonable to use the words "catalytically initiated reactions" in publications. Chain reactions (for example, polymerization) are a particular case of initiated reactions. Cyclic (and cascade) reactions only formally proceed via the catalytic cycle scheme. Self-propagating reactions of this kind represent a specific type of transformations of organic compounds. Both analysis of literature[3] data and our experimental results[4] suggested that for electroinitiated transformations the *criterion* of occurrence of self-propagating reactions is a considerable (much more than 100%) current yield of the target product.

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ALKYNYLCHLOROCYCLOPROPANES IN SYNTHESIS OF FUNCTIONALIZED CYCLOPROPANES AND DIAZAHETEROCYCLES

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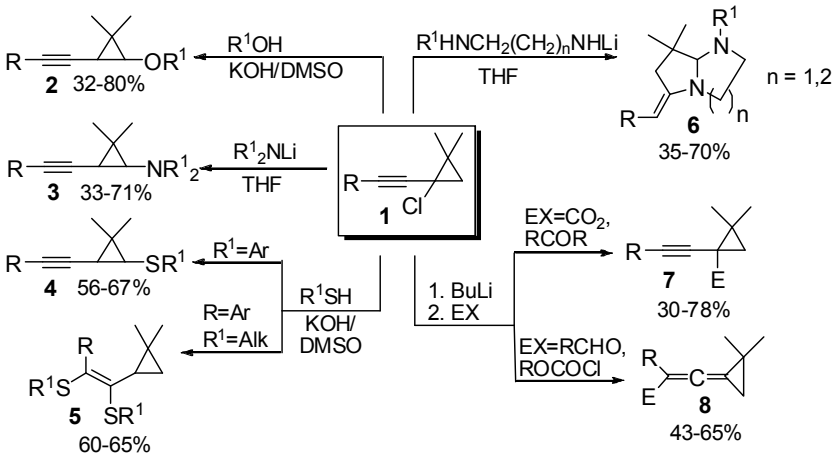
A study of reactivity of alkynylchlorocyclopropanes **1** toward different nucleophilic and organometallic reagents was conducted. It was shown, that reactions of these compounds with alcohols, amines, phenols and thiols in presence of strong bases give previously unknown functional derivatives of ethynyl- and vinylidenecyclopropanic series (**2-5**)[1]. Interaction of **1** with monolithium derivatives of diaminoalkanes as a result of several consecutive reactions leads to the transformation of carbon skeleton of starting molecule, giving bicyclic aminals **6** as final products[2].



Metallation of compounds **1** under action of n-BuLi and subsequent reactions with electrophiles open a pathway to different functionalized ethynyl- and vinylidenecyclopropanes **7** and **8**. Selectivity of formation of the latter is determined by the type of electrophilic reagent used.

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This work was financially supported by the Russian Academy of Sciences (program OKh-01)

CHEMILUMINESCENCE – PHENOMENON OF NUTURE AND METHOD FOR INVESTIGATION OF ORGANIC REACTIONS

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The process of transforming chemical energy into light emission has been an attractive topic of intensive research over the years, in view of its fundamental mechanistic significance and the diversity of practical applications. Bio- and chemiluminescence, the emission of light in biochemical and chemical reaction, is wildly used in technology, biology and medicine. On the other hand, the in-depth knowledge of chemiluminescent systems paves the way for understanding the otherwise difficult to explore "dark" processes associated with such reactions.

In this report, brightly emitting peroxide-based biological systems are illustrated. Relation between fundamental significance of chemiluminescence phenomenon and its practical applications in medicine and biochemistry is demonstrated by the reactions of cyclic peroxides 1,2-dioxetanes, a kind of energy storage system. Special attention is given to the results obtained in laboratory of chemical physics of IOC USC of the RAS in the field of chemistry and chemiluminescence of organic peroxides and singlet oxygen:

- A new type of chemiexcitation for liquid-phase organic reactions is reported (oxygen-transfer chemiluminescence) which is realized during oxidation of saturated hydrocarbons by dioxiranes.[1] A novel mechanisms of light generation in the reactions of peroxides with luminescent lanthanide complexes are described.

– A key role of singlet oxygen, oxidant and important intermediate of chemical and biochemical processes, in freshly discovered light emitting peroxide reactions is demonstrated.[2,3]

– A new promising direction of research is introduced: chemistry and chemiluminescence of pharmacologically valuable peroxides – 1,2,4,5-tetroxanes and 1,2,4-trioxolanes. Achievements and applied perspectives of the area are discussed.[4]

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CLASSICAL AND NON-CLASSICAL AMINOCARBENES: GENERATION AND APPLICATIONS

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Heteroatom-stabilized carbene complexes (e.g., NHC's) have acquired a high importance in modern organic and organometallic chemistry. In particular, these species are prominent in organometallic catalysis for, for instance, hydrosylation of alkenes and diversity of cross-coupling reactions (e.g., Heck, Suzuki–Miyaura, Sonogashira, Kosugi–Migita, and Stille). Two general main approaches for the preparation of such carbene complexes include (*i*) a direct complexation of pre-prepared free carbenes (or typically generated *in situ* from their precursors and a base) to a metal center, and (*ii*) a metal-mediated nucleophilic addition, or a 1,3-dipolar cycloaddition to isonitriles.

This report provides a synthetic, structural, and mechanistic overview of the recent advances in the field of metal-mediated transformations of isocyanides, RNC, with a particular emphasis addressed to the activation of the C≡N moiety toward the addition of protic nucleophiles and 1,3-dipoles.[1] We also report that aminocarbene complexes generated in these reactions exhibit a very high catalytic activity in the Suzuki–Miyaura cross-coupling, at the so-called homoeopathic precatalyst concentrations, and also significant catalytic activity in the Sonogashira reaction.

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APPLICATION OF EXPERIMENTAL CHARGE DENSITY DISTRIBUTION TO ANALYSIS OF PHYSICAL-CHEMICAL PROPERTIES OF FUNCTIONAL MATERIALS

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For the solution of various problems connected with a design of new compounds with the determined physical-chemical properties it is essentially to fetch out what particular intra and inter- molecular and/or ionic interactions are responsible for the realization of these properties. Ranging of the factors influencing or defining a particular property of compound demands not only information on structure and geometrical parameters but also the data about an electronic structure of this compound. However the routine X-ray diffraction methods appear insufficient, as well as quantum-chemical calculations of the isolated molecules and/or small clusters don't allow to describe real systems to the full. For some extent the solution of this problem can be the usage of high-resolution X-ray diffraction investigations which allow to obtain more detailed information on system, including molecular graph, atomic charges, degree of charge transfer between molecular fragments and/or ions, the nature of chemical bonds and intermolecular interactions. The possibility to estimate the energy of specific interactions and coordination bonds is very important from both fundamental and practical points of view. The results of application of high-resolution X-ray diffraction investigations of electron density for a search of the "structure – property" correlation including a analysis of luminescence sensitization of lanthanide ions in their coordination compounds, estimation of nonlinear sensibility of the compounds containing [2,2]-paraciclophane, a study of proton and electron conductivity in organic and organoelement compounds, a phenomena of spin-crossover in the compounds of transition metals etc will be presented.

LAYERED COMPOUNDS OF TETRATHIAFULVALENES AND FULLERENES AS PROMISING MATERIALS FOR ORGANIC ELECTRONICS

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In view of intensely developing nanotechnologies, of special importance is the design of new organic materials with electron systems of lower dimensionality and the study of electronic processes and interlayer transport of charge carriers in them. This can result in principally new effects and new commercial application. The report discusses synthesis, crystal structure, and conducting and magnetic properties of quasi-two-dimensional compounds of the two families.

A series of layered organic metals of the θ-(BEDT-TTF)$_4$*M*X$_4$(Solv) formula, where $[MX_4]^{2-}$ are anions of bivalent metals of tetrahedral geometry and Solv = halogenosubstituted benzenes, based on radical cation salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) has been prepared[1]. The (BEDT-TTF)$_4$*M*X$_4$(Solv) compounds are characterized by metallic behavior of conductivity within the layers and semiconducting one between the layers.

We for the first time prepared a fullerene based unique quasi-two-dimensional metal, $[MDABCO^+](C_{60}^{\bullet-})\cdot$TPC (MDABCO$^+$ is cation of *N-methyl-diazabicyclooctane,* TPC – *triptycene)*, in which the $C_{60}^{\bullet-}$ layers with metallic conductivity coexist with those with antiferromagnetic interaction of spins[2]. No dimerization of $C_{60}^{\bullet-}$ is observed in $[MDABCO^+](C_{60}^{\bullet-})\cdot$TPC with lowering temperature[2], while in most compounds fullerene radical anions dimerize to form diamagnetic dimers $(C_{60}^{-})_2$ that results in drastic changes in magnetic properties [3] and prevents from the appearance of conductivity.

Phase transitions and factors affecting the formation of conducting layers with different properties are discussed.

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The work was supported by RFBR grant № 11-03-01039a and the Program of Fundamental Research of Presidium of RAS №21.

GENERATION AND REACTIVITY OF AZOMETHINE IMINES AND CONGENER STRUCTURES IN IONIC LIQUIDS

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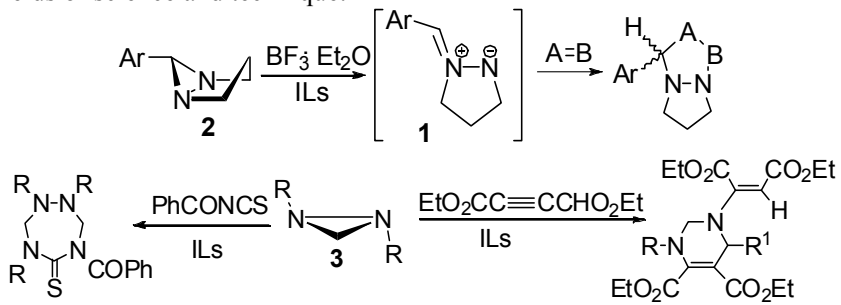
Azomethine imines (AMI) **1** (4-π dipolar systems) are related to mesoionic type of 1,3-dipoles. The significant number of recent publications were devoted to stable AMI, in which positive and negative charges are stabilized by corresponding substitutes. In this work AMI were generated by catalytic *one-pot* opening of diaziridine ring in 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **2** in ionic liquids (ILs) in the presence of different dipolarophiles (nitriles, carbon disulfide, activated alkenes and alkynes, carbonyl compounds), which did not enter in analogous reactions in common organic solvents. Congener dipolar intermediates are generated in similar reactions of monocyclic 1,2-dialkyldiaziridines **3**, resulting in unpredictable structures.

As the results of these investigations new, simple (2-steps) and effective methods for the preparation 1,2,4,6-tetrazepan-5-thiones, tetrahydropyrimidines, 3-(pyrazol-1yl)indol-2-ones, as well as fused heterocyclic structures were developed.[1-3] In latter pyrazolidine ring is condensed with different nitrogen-containing heterocycles: thiazolidine, triazoline, pyrazolidine and pyrazole, including functional substituted those. All reactions are proceeding with high regio- and stereoselectivity. The heterocyclic structures obtained are related to practically important classes of compounds, which are patented for the use in medicine, agriculture and other fields of science and technique.



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NOVEL APPROACH IN BIOORGANOELEMENT CHEMISTRY FOR THE DESIGN OF PROTECTORS AGAINST OXIDATIVE STRESS

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A novel approach for the construction of perspective candidates for the therapy of phatological states induced by oxidative stress is presented. The methodology is based on biomimetic construction of physiologically active biometals complexes and organoelement compounds with analogues of natural antioxidants – tocopherols.

The synthesis, physico-chemical properties and biological activity of novel compounds containing 2,6-dialkylphenols will be discussed. The physiological activity has been evaluated in the *in vitro, ex vivo, in vivo* experiments in peroxidation of lipids in mitochondria, neurons, rat and fish liver and brain homogenates, liposomes and lipids structural fragments, as well as in enzymatic reactions (xanthin oxidase, lipoxygenase, catalase, superoxide dismutase, cytochromes P450). The activity in oxidation reaction, solubility (logD), blood-brain barrier transfer (PAMPA, PAMPA BBB), in inhibition of key enzymes of antioxidative defense system has been studied. The novel membrane-active compounds are perspective candidates as protectors against oxidative stress, mito- and neuroprotectors.

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PROTON RADIOGRAPHY OF FAST PROCESSES

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In recent years studies of shock and detonation wave phenomena at extreme conditions have been conducted at proton radiography facility developed at the ITEP Terawatt Accelerator (TWAC-ITEP). The 800 MeV proton beam intensity in these experiments is about 10^{10} particles per pulse. A single beam bunch consists of four consequent 70 ns long micro bunches with 250 ns intervals between them. The spatial resolution of the facility that was measured in static experiments is about 50 μm. For the generation of shock waves the energy of high explosives (HE) is used, therefore experimental targets are placed within the explosive containment chamber that is certified for the use of up to 100 g of HE in TNT equivalent. The results of latest experiments are presented, including results on explosion and detonation of pressed and emulsion high explosives, shock-induced dense non-ideal plasma of argon and xenon and shock loading of non-uniform metal surfaces.

CATALYTIC OLEFINATION REACTION – NOVEL UNIVERSAL METHOD FOR THE SYNTHESIS OF ALKENES

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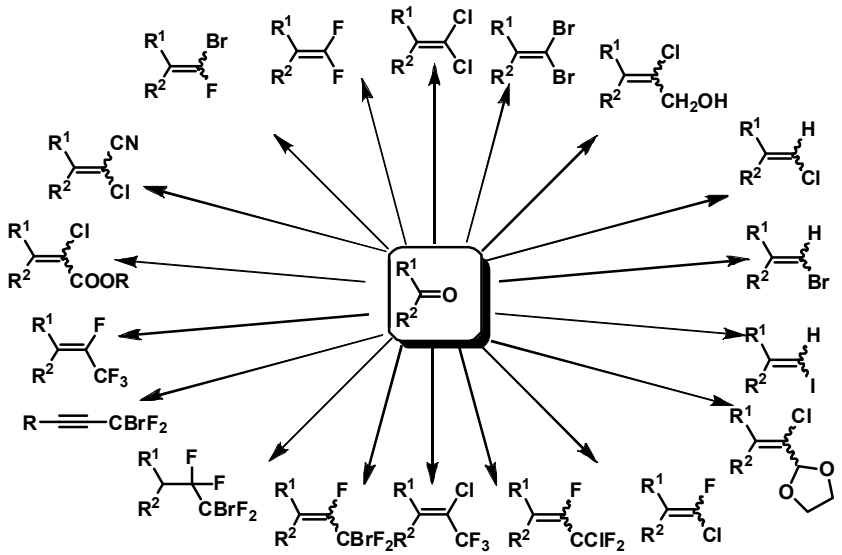
Recently a novel catalytic olefination reaction was found by our group. *N*-Unsubstituted hydrazones of aldehydes and ketones give alkenes $R^1R^2C{=}CXY$ under treatment with $CHal_2XY$ in the presence of catalytic amount of CuCl. Aromatic, heteroaromatic and aliphatic aldehydes and ketones can be involved as a carbonyl component. The reaction has a general character and can be used for the synthesis of a broad variety of alkenes, which are valuable building blocks for the preparation of complex organic molecules, including physiologically active ones.



NEW APPROACHES FOR STEREOCONTROLLED OLIGOSACCHARIDE SYNTHESIS

Nifantiev N.E., Ustuzhanina N.E., Komarova B.S., Krylov V.B., Orekhova M.V., Mironov Y.V., Grachev A.A., Gerbst A.G., Tsvetkov Y.E.

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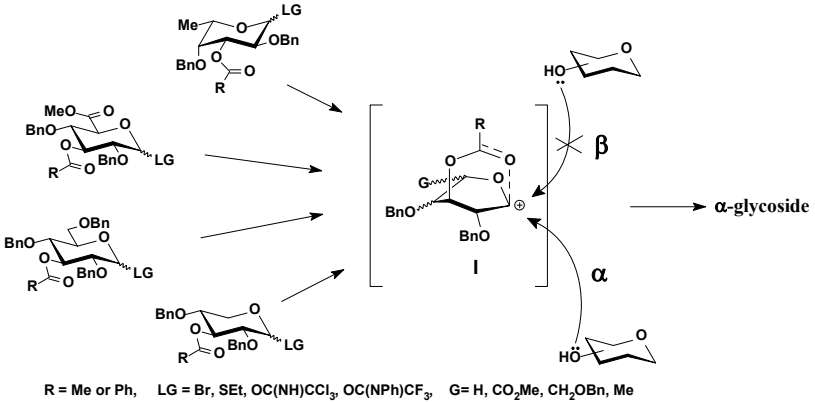
This lecture overviews our recent works towards the development of new approaches for stereoselective synthesis of oligosaccharides. First one is based on the use of intra-molecular participation of remote acyl substituents which control α-glycosylation by the use of *gluco*- and *galacto*-donors. It was shown that the key reaction step is the formation of stabilized cationic intermediates of type **I**, which react with preferential formation of α-glycoside products.



The investigated stereo-controlling method was applied in the synthesis of complex heterosaccharides which correspond to the fragments of the outer core region of the *Pseudomonas aeruginosa* lipopolysaccharide, natural polysaccharides fucoidans, carbohydrate chains of blood-clotting factors VII and IX and other natural compounds.

In addition, the application of mono- and oligosaccharide 2-azido-2-deoxy-selenoglycosides as efficient agents for stereoselective α- and β-glycosylation is discussed as well. These original agents, being described by us recently, were successfully applied for the direct synthesis of heterooligosaccharides, including oncoantigens which are required during the construction of oncovaccines.

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3,4-DIHYDRO-2-ALKOXY-6-BENZYL-4-OXOPYRIMIDINES (DABOS): CREATION ANTHOLOGY AND DEVELOPMENT PERSPECTIVES OF THE HIGHLY POTENT ANTI-HIV AGENTS

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3,4-Dihydro-2-alkoxy-6-benzyl-4-oxopyrimidines (2-alkoxy-6-benzylpyrimidin-4(3*H*)-ones, DABOs) were firstly discovered and characterized as non-nucleoside HIV-1 replication inhibitors by professor Marino Artico group in 1993. The first compounds of this series have been synthesized as the novel regioisomeric analogues of the antibacterial – trimethoprime – an inhibitor of dehydrofolate-reductase. Then, a numerous bioisocteric analogues of these compounds, containing a sulfur (*S*-DABO), nitrogen (*NH*- и *N,N*-DABO) or carbon atom (*C*-DABO or *carbo*-DABO), linked to the C^2 position of the pyrimidine nucleus were described.

Classical DABO-synthesis utilizes 2-arylacetic (or 2-arylpropionic) acids and their nitriles as the starting materials. Successful conversion of the latter into the corresponding alkyl esters of 4-aryl-3-oxobutanoic acids and subsequent condensation with *O*-methylisourea, thiourea, *S*-methylisothiourea, substituted amidines or guanidines leads to the construction of 6-(arylmethyl)pyrimidin-4(3*H*)-one scaffold. An additional pyrimidine C^2 modification results in a variety of DABO-analogues, differing in profile and potency of antiviral activity.

Systematic SAR investigations of the DABO class, led to the identification of their chemical structure elements, being essential for the antiviral activity. They are: the presence of the benzylic moiety at the pyrimidine C^6; an alkyl or cycloalkyl side chain at S, O^2 (for uracils and 2-thiouracils) or N^2 (for isocytosines). An appearance of the lower alkyl fragment (normal or ramified) at the C^5 position of the pyrimidine nucleus is also an important structural feature of DABOs. The substitution of the benzylic portion is a moderator of the antiviral activity, as well.

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SYNTHESIS OF NATURAL ECDYSTEROIDS AND STRUCTURAL ANALOGUES ON THE BASIS OF CHEMICAL TRANSFORMATIONS OF AVAILABLE PHYTOECDYSTEROIDS

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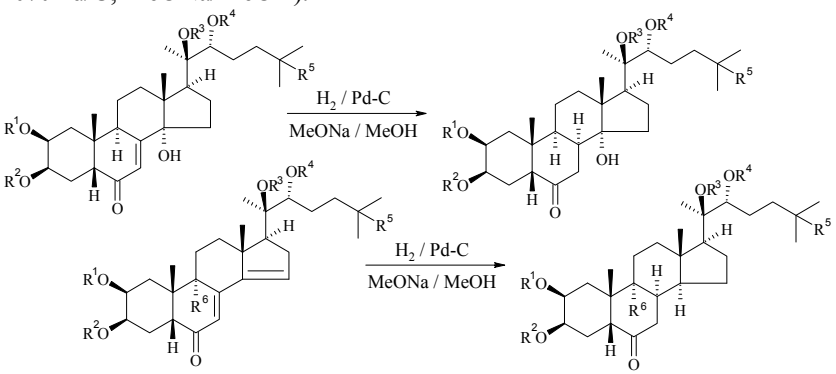
Ecdysteroids are hormones of molting, metamorphosis and diapauses of insects and crustaceans. They are synthesized not only arthropods, but also plants (phytoecdysteroids), and at many times higher concentrations (content in some plant kinds representing 2-2.5%). There are minor phytoecdysteroids at plants along with the basic phytoecdysteroids usually. The most real way to obtain the minor ecdysteroids − a synthesis on the basis of the directed transformations of more available ecdysteroids. Chemical transformations allow to obtain structural analogs of ecdysteroids with new properties. We have developed the transformation of available ecdysteroids of plant *Serratula coronata* (20-hydroxyecdysone and its acetonides) as an approach to the synthesis of less common in nature ecdysteroids. We synthesized shidasterone, stahisterone B, podecdysone B, vitikosterone E, ponasterone A, 2-dehydro-3-*epi*-20-hydroxyecdysone, 25-hydroxydachryhainansterone. From the reactions of ecdysteroids directed to analogues obtaining and study the dependence "structure-property", attention is drawn to the characteristic for ecdysteroids 14α-hydroxy-Δ^7-6-one group transformations. Well-known difficulties of reduction of Δ^7-bond in ecdysteroids. We have developed an effective method of hydrogenation over the Pd-catalyst in alkaline conditions which has made available 7,8α-dihydroecdysteroids. 7,8α-Dihydro-14α-deoxyecdysteroids obtained by hydrogenation of conjugated diene-7.14 ecdysteroids in the same conditions (10% Pd/C, MeONa/MeOH).



R^1, R^2, R^3, R^4=H; R^1+R^2=R^3+R^4=Me_2C; R^5=H, OH; R^6=H, OH

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CHEMISTRY OF TETRAZOLES. ADVANCES AND PERSPECTIVES OF RUSSIAN SCIENTIFIC SCHOOL

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In recent years the number of publications and patents in the area of chemistry of tetrazoles is growing exponentially.[1] Due to the high content of nitrogen in the ring, tetrazoles have extreme values of enthalpies of formation. This property determines the successful application of tetrazoles as components of explosives and propellants. On the other hand, dozens of high-performance drugs, which active pharmaceutical ingredients contain tetrazole cycle, are represented in the global pharmaceutical market.

Russian science in the chemistry of tetrazoles holds one of a leading position. It was made possible due to the success and achievements of the St. Petersburg school of chemists what founded by a student of Dmitrii Mendeleev - Semen Vukolov. Effective and safe methods of synthesis and functionalization of different tetrazoles as well as procedures of a modification of exocyclic functional groups were developed by representatives of this school.

This report reviewed the results of recent research of protolytic equilibria and mechanisms of reactions to lead to the cycle formation, functionalization and transformation of the tetrazole cycle. The analysis of main directions of development of tetrazole chemistry as well as principal aspects of application of these heterocycles as components of advanced materials, especially in polymeric membranes and medical supplies.

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ASYMMETRIC ALKENE CARBO- AND CYCLOALUMINATION BY TRIALKYLALANES, CATALYZED WITH CHIRAL ZR π-COMPLEXES

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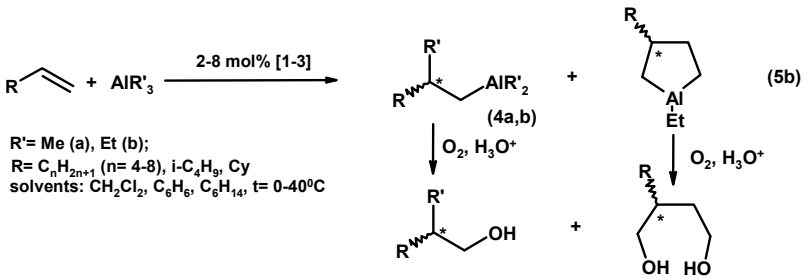
The enantioselectivity of alkene carbo- and cycloalumination by trialkylalanes ($AlMe_3$, $AlEt_3$), catalyzed with chiral zirconocene complexes (p-*S*)(p-*S*)-*bis*[η^5-{1-neomenthylindenyl}] zirconium dichloride (**1**), (p-*S*)-(η^5-cyclopentadienyl)[η^5-{1-neomenthylindenyl}] zirconium dichloride (**2**) and (p-*S*)-(η^5-cyclopentadienyl)[η^5-{1-neomenthyl-4,5,6,7-tetrahydroindenyl}] zirconium dichloride (**3**), has been studied:



It was shown that reaction of terminal alkenes with AlMe3, catalyzed by complex 1, gives predominantly R-enantiomer of 4a with 73% ee. However, reaction with AlEt3 results in S-enantiomers of 4b (68% ee) or 5b (37% *ee*). Alkene cycloalumination by $AlEt_3$, catalyzed with complexes 2 or 3, provides (3R)-(5b) of 7-26% ee. The increase of steric hindrances in terminal alkenes decreases enantioselectivity of carbo- and cycloalumination reactions.

The mechanism of asymmetric catalysis of alkene carbo- and cycloalumination reactions by chiral neomenthyl Zr π-complexes has been proposed. Thus, the dependence of enantioselectivity on the OAC type, catalyst structure and reaction conditions (solvent, temperature) can be attributed to the various ratio of conformers of catalytically active Zr,Al-intermediates, which are formed as a result of π-ligand rotation relative to each other and the zirconium center.

SYNTHESIS AND MAGNETIC PROPERTIES OF MOLECULAR HETEROSPIN SYSTEMS BASED ON BIS-O-SEMIQUINONATO TRANSITION METAL COMPLEXES

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The design of molecular heterospin systems containing different paramagnetic centers is one of the intensely developing branches of chemistry. Systems based on coordination complexes of transition metals with stable organic radicals are very interesting objects. They became widespread in fundamental and applied sciences for investigation magnetic exchange interactions, the search of components of molecular magnets and also for study of intramolecular redox-transfer.

In the present work we have synthesized a series of bis-o-semiquinonato complexes of cobalt, iron and manganese $M(3,6\text{-DBSQ})_2L$ with neutral donor ligand (L = substituted diazadienes, 2,2'-biquinoline, 1,4-diaza-bicyclooctane and pyridine- or thiophen-substituted 3,5-di-*tert*-butyl-benzoxazols and *N*-methylen-1-yl-phenylimines).

Magnetic susceptibility measurements revealed that in most complexes the central metal is in high-spin state (Co(II), d^7, S = 3/2; Fe(II), d^6, S = 2; Mn(II), d^5, S = 5/2) and the antiferromagnetic exchange ligand-ligand or metal-ligand takes place. The exception is manganese complex with 1,4-di-tert-butyl-diazadiene ligand. This complex can be described as low-spin Mn(III) complex with one semiquinonato and one catecholate ligand.

This work was made according to FSP "Scientific and scientific-pedagogical cadres of innovation Russia" for 2009-2013 years (GK P982 from 27.05.2010). We are grateful to RFBR (N 2010-3-00788), President of Russian Federation (grants NSh-7065.2010.3, MK-614.2011.3) for supporting of this work.

FUNCTIONALIZED PHOSPHONIC ACIDS, LIGAND SYSTEMS FOR THE FORMATION OF MONO- AND POLYNUCLEAR, MONO- AND HETEROMETALLIC COORDINATION COMPOUNDS

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Phosphonic acids are polydentate ligands. The functionalization of them with additional electron-donor center with different arrangement in hydrocarbon chain makes it possible to synthesize complex compounds that differ in composition and structure.

We had obtained and investigated in detail earlier new complex compounds of Pd with a number of phosphonic acids. In the crystalline state and in solutions, the formation of mono- (M:L=1:1) and bisligand (M:L=1:2) complexes of cis- and trans-structure, where Pd atom forms a coordination unit of square-planar structure with bidentate (O, O) or (O, N) coordination of ligands, has been established. In aqueous solutions, the formation of anionic complex species of the compositions $[Cl_2PdH_nL]^{(n-m)-}$ and $[Pd(H_nL)_2]^{(n-m)-}$ (m=1, 2, 3, 4) with possible simultaneous presence of four isomers: trans- (syn-, anti-) and cis- (syn-, anti-) isomers has been proved. Under these conditions, not all donor atoms of ligands form bonds to the central atoms, which was utilized by us in the synthesis of heteronuclear (Pd-Cu), (Pd-Co) and (Pd-Ni) containing complexes.

According to the data of IR, electronic, X-ray photoelectron spectroscopy and an X-ray structural analysis, Pd forms in all cases a square-planar coordination unit with bidentate-coordinated phosphonic acid. A peculiarity of the structure of the new compounds is Cu, Co and Ni coordination units. In the first case, Cu forms a quasi-octahedron, which consists of six oxygen atoms: 4 from phosphonic groups and 2 from water molecules with cis- and trans-arrangement of the latter. The Pd and Cu polyhedra are united by the oxygen atoms of the bridging phosphonic group.

In the (Pd-Co) complex, the quasi-octahedral Co unit is formed by 5 oxygen atoms of water and an oxygen atom of the bridging phosphonic group L, which provides a bond to the Pd polyhedron.

In the Ni-containing complex, two Ni atoms form a quasi-octahedral polyhedron. However, in one polyhedron, at the vertices are water oxygen atoms, $[Ni(H_2O)_6]^{2+}$, and in another 4 water oxygen atoms and 2 oxygen atoms, in the cis-position, of the bridging phosphonic group L, which unites the Pd and Ni polyhedra.

ANODIC SUBSTITUTION OF ARENES AS A SPECIAL TYPE OF S_N^H REACTIONS

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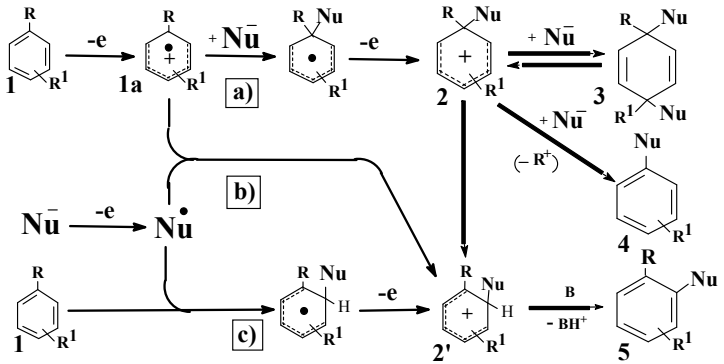
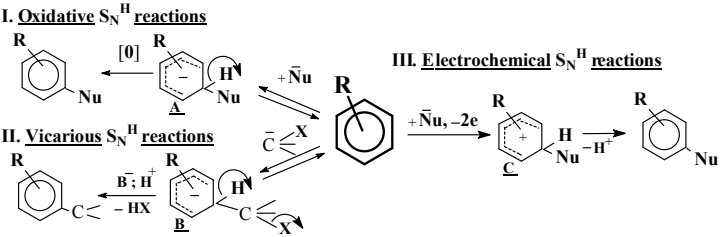
Anodic (electrooxidative) substitution reactions of arenes at the C–H bond are a convenient route to direct formation of C-C, C-O, C-N and other bonds. The results of our studies allow refinement of the general mechanism of these reactions (Scheme 1). It was shown that the realization of routes *a*, *b* or *c*) depends on the nature, oxidation potential of Nu^- and conditions of electrolysis.

SCHEME 1



An idea of the anodic substitution as a special type of S_N^H-reactions has been forwarded. The key problem of the latter is removal of the hydride ion at the aromatization step of the anionic σ^H-adducts **A** and **B** (Scheme 2). The existing solutions of this problem (pathways I and II) are not free from defects.

SCHEME 2



Electrochemical $\mathbf{S_N^H}$ reactions are more versatile, since the hydrogen that is substituted in the cationic σ^H-adduct C is easily removable as a proton (pathway III). As a whole, the electrochemical approach extends the potential of the implementation of $\mathbf{S_N^H}$ reactions and noticeably enriches their arsenal.

FUNDAMENTAL PROBLEMS OF CHEMISTRY OF SUPRAMOLECULAR AND NANOSIZED STRUCTURES

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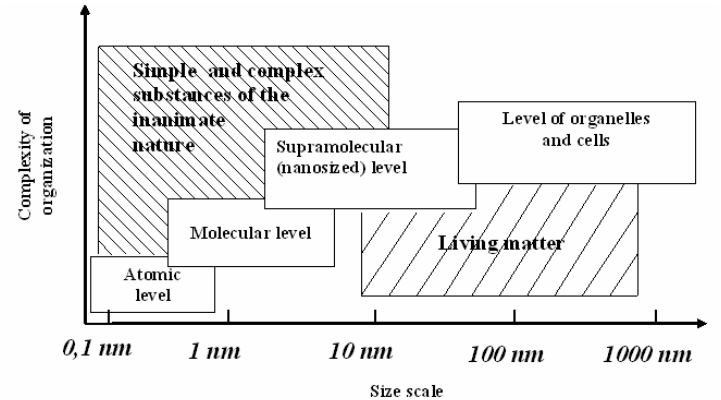
A variety of substances and materials surrounding us in the living and inanimate nature, a quantity of properties and functions which they carry out is caused by their difficult hierarchical structural organization which is realized on several scales of sizes.



Nanosized supramolecular level plays here a key role and opens essentially new approaches to streamlined design of substances and materials within the age-old chemical problem – search of correlations "structure-property".[1,2]

As academician Konovalov A.I. has precisely formulated supramolecular systems are the bridge from the inanimate to living matter.[3] For the last 2–3 decades two complementary new directions in chemistry – supramolecular chemistry and nanochemistry were generated.

In the report the retrospective review of the most significant achievements in this field of chemistry and its modern trends are given.

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A SMALL MOLECULE PROBE APPROACH FOR STUDYING 2-OXOGLUTARATE DEPENDENT OXYGENASES

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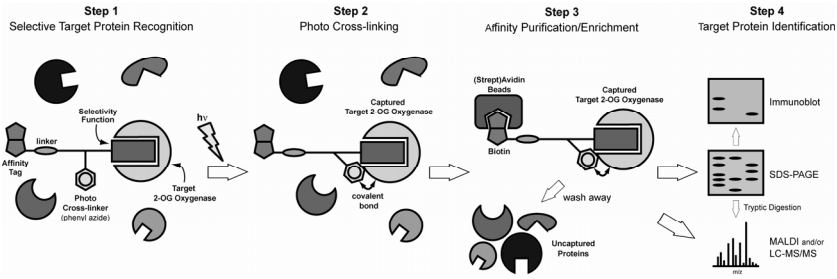
2-Oxoglutarate (2-OG) dependent oxygenases catalyze a range of hydroxylation and *N*-methyl demethylation reactions that are important in oxygen sensing and the epigenetic modulation of gene expression.[1] These enzymes are being targeted for inhibition by small molecules as novel potential therapeutic targets for the treatment of anemia, ischemic diseases and cancer. We report a small-molecule probe for 2-OG oxygenases that employs an hydroxyquinoline template coupled to a photoactivable cross-linking group and an affinity purification tag. Following studies with recombinant proteins, we demonstrate that this probe-based approach is useful for the identification of 2-OG oxygenases present in human cell extracts, including to proteins at endogenous levels, and for identifying 2-OG oxygenases that interact with inhibitors.



The approach was validated by studies on a transcription factor 2-OG dependent hydroxylase (PHD2, EGLN1)[2] and by the finding that the probe binds to, and inhibits the N^{ε}-methyl lysine histone demethylase FBXL11 (KDM2A).[3] We also demonstrate the potential of this photo cross-linking small-molecule probe-based approach to "capture" the 2-OG oxygenase (PHD2) substrate HIF-1α, suggesting that it may be useful in substrate capture and in target discovery studies.[4]

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ASYMMETRICAL OXIDATION OF POLYFUNCIONAL SULFIDES

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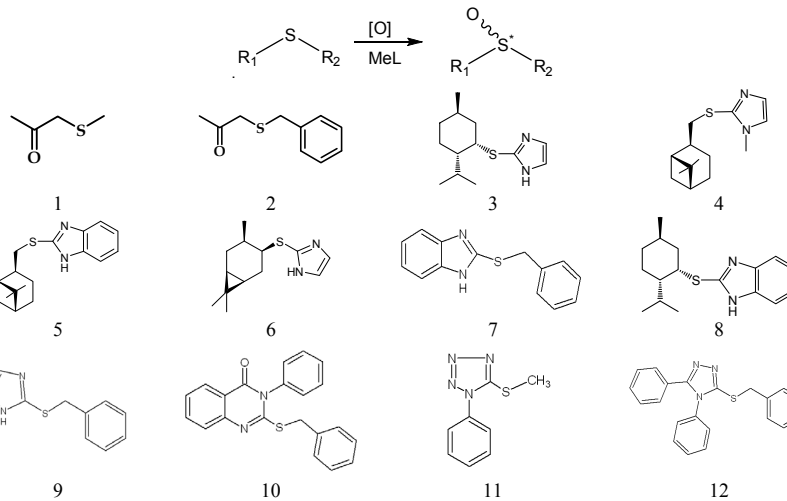
Chiral sulfoxides are widely applied in asymmetric synthesis[1]. Interest to optically active sulfoxides is caused by their high biological activity as antioxidants, antidepressants and inhibitors a gastric acid[2].

Asymmetrical oxidation of ketosulfides, triazole-, tetrazole-, imidazole-, monoterpenile-containing sulfides (1–12) catalyzed by complexes of titanium and vanadium (system Bolm, Sharpless and Fujita) is carried out.



Sulfoxides in high yield (up to 97 %) and with high enantioselectivity (*ee* up to 99 %) are received.

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AZOLOANNULATED 1,2,4-TRIAZINES – NEW CLASS OF ANTIVIRAL COMPOUNDS

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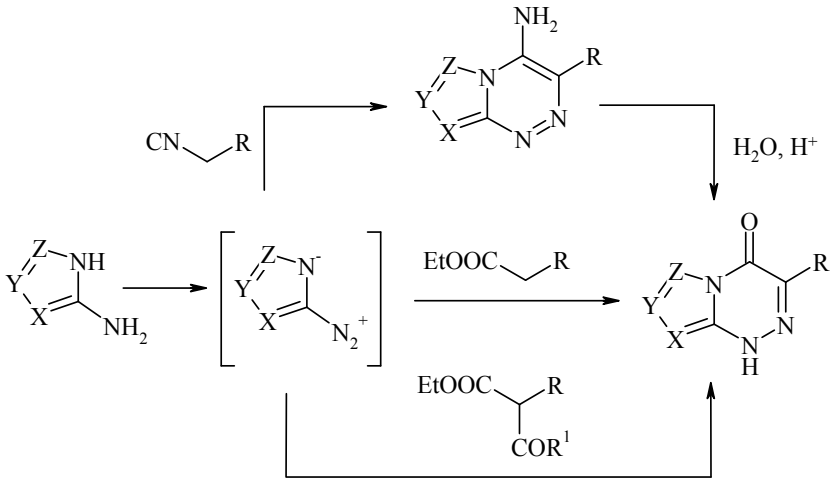
We discovered new class of compounds with antiviral activity – azolo-1,2,4-triazines with bridge atom of nitrogen. Being structurally similar to biogenic purines, pyrozolo-, imidazolo-, 1,2,4-triazolo[5,1-c]-1,2,4-triazinones are capable of imitating them in metabolic processes, and it is this capability that determines their antiviral activity.

Main techniques for synthesis of such bicyclic structures include annulating of azine cycle into azole one as it allows to use a wide range of aminoazoles and accessible syntones – derivatives of acetic acid, acetonitrile, acetoacetic acid and acetylacetonitrile.



R = H, F, Cl, Br, I, NO_2, CN, COOEt, Alk, Ar, Het;
X,Y,Z = N, CH, CR^2

These compounds are proven to be effective against infections caused by influenza viruses, including H1N1 strain, parainfluenza, vernal encephalitis, and other viral infections.

Based on this class of compounds, we developed antiviral drug triazavirin which underwent a series of clinical trials in 2011.

POLYFLUORINATED 2-(HET)ARYLHYDRAZONO-1,3-DICRABONYL COMPOUNDS: SYNTHESIS, STRUCTURE AND THEIR CHEMICAL TRANSFORMATIONS

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2-(Het)arylhydrazono-1,3-dicarbonyl compounds represent an extensive class of organic substances combining a 1,3-dicarbonyl fragment and a (het)arylhydrazone substituent in their structure. The diversity of 2-(het)arylhydrazono-1,3-dicarbonyl compounds is provided by facile and convenient methods for their preparation. The key method is azo coupling of 1,3-dicarbonyl compounds with (het)aryldiazonium salts in which substituents in any molecular fragment can be varied. Structural features account for the abundant synthetic potential of these derivatives. Unlike 1,3-dicarbonyl compounds, they can react not only at the 1,3-dicarbonyl fragment, but also at the active NH group of the hydrazone residue thus generating heterocyclic systems of various classes. Besides, 2-(Het)arylhydrazono-1,3-dicarbonyl compounds, their open-chain and heterocyclic derivatives are of interest as polydentate ligands for complexation. The practical applications of 2-(het)arylhydrazono-1,3-dicarbonyl compounds and products of their transformation are diverse; of these, especially valuable are heterocyclic derivatives having a broad spectrum of physiological action.[1]

In this report we discuss the chemistry of fluorinated 2-(het)arylhydrazono-1,3-dicarbonyl compounds, which has the significant differences from the chemistry of non-fluorinated analogues.

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NEW FEATURES OF FEMTOCHEMISTRY

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In recent years, a new area of chemistry research is successfully developed. It is femtochemistry. The main research tool of femtochemistry is laser pulses of femtosecond duration. The present report discusses three areas of femtochemistry: 1 the investigation of mechanisms and dynamics of physical and chemical processes on the femtosecond time scale; 2 coherent chemistry, which represents a new type of chemical transformation, based on regular and synchronized motion of the nuclei in molecules; 3 physicochemical processes initiated by multiphoton absorption of femtosecond laser pulse. The first two areas of femtochemistry were developed over 20 years. In the framework of the first area the dynamics and mechanisms of physical and chemical processes occurring on ultrashort time are investigated, that before it was experimentally impossible to carry out. The second area of research is coherent photochemistry, which is based on the fact that excitation by femtosecond pulse leads to quantum interference of nuclear wave functions that manifests as nucleus regular motions. Coherent photochemistry makes possible to control the dynamics of chemical processes and the yield of chemical product in multi-channel reactions. Coherent photochemistry enables to determine the frequency of the vibrational modes involved in the chemical act too.

The third area is just developing. It is due to the fact that multi-photon absorption transitions can be effectively excited by femtosecond pulses even with a small energy of the pulse. As a result of the multiphoton absorption the molecule is formed in the high excited electronic states in which there are various physical and chemical processes leading to the breakdown of the molecules and the destruction of the material. These processes have not been sufficiently explored, but their use has led to the development of practically important areas of research: multiphoton polymerization (manufacturer of polymer nanostructures and objects); dissection of biological objects, microsurgery of cells and embryos, etc.

We have developed the holographic setup with multiple optical beams (traps) formed a continuous and femtosecond lasers. Novelty of the made setup is a possibility to use simultaneously a several "femtosecond" optical beams to implement the various physical and chemical processes initiated by multiphoton absorption of light at different points in space. We performed experiments on multiphoton polymerization, dissection of various biological objects, as well as we investigate cloned embryonic stem cells.

KINETIC AND THERMODYNAMIC ASPECTS OF DIHYDROGEN BONDING AND PROTON TRANSFER TO TRANSITION METAL HYDRIDES

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Proton transfer involving transition metal hydrides and/or heterolytic splitting of dihydrogen are important steps in many catalytic processes, including ionic hydrogenation and reduction of H^+ to H_2. Protonation of metal hydride complexes is generally recognized as the most common method of $[M(\eta^2\text{-}H_2)]$ preparation.[1] Detailed studies of the mechanism of proton transfer to transition metal hydrides have firmly shown that, in spite of its apparent simplicity, the process involves several steps and proceeds via various hydrogen bonded intermediates of molecular or ionic type (Scheme).[2,3]

$$\text{M-H + H-A} \rightleftharpoons \underset{\text{molecular complex}}{\text{M-H}\cdots\text{H-A}} \rightleftharpoons \underset{\text{hydrogen bonded ion pair}}{[M(\eta^2\text{-}H_2)]^+\cdots A^-} \rightleftharpoons \underset{\text{solvent separated ion pair}}{[M(\eta^2\text{-}H_2)]^+ \,//\, A^-}$$

The analysis of recent results on proton transfer to transition metal hydrides will be presented. The balance of the transition metal atom electron richness and of ligand electronic and steric properties determines the proton transfer pathway and structure of the intermediates and of the reaction products. The relationships of kinetic and thermodynamic parameters of dihydrogen bonding, MH···HA, of proton transfer yielding $[M(\eta^2\text{-}H_2)]$ species, and subsequent steps such as $[M(\eta^2\text{-}H_2)]$ to $[M(H)_2]$ isomerization or H_2 evolution will be analyzed.[4]

Hydrogen bond strength, hydride ligands proton accepting ability will be shown to correlate with the kinetics and thermodynamics of the proton transfer. The experimental data backed up by the theoretical results allow discussing the possible types of potential energy profiles and factors, which determine stability of the species involved. The knowledge acquired opens the possibility for tuning the reactivity of hydride and dihydrogen complexes and for governing the reaction pathway.

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The work was supported by the Division of Chemistry and Material Science of RAS and the Russian Foundation for Basic Research (№11-03-01210)

RADICAL TEMPLATE POLYMERIZATION OF IONIC MONOMERS IN SOLUTION OF OPPOSITELY CHARGED SURFACTANTS AS A WAY OF CONTROLLED SYNTHESIS OF POLYELECTROLYTE

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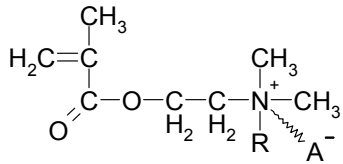
Radical template polymerization of quaterny salts of 2-(Dimethylamino)ethyl methacrylate



where – R is CH_3; CH_2–CH_3; CH_2–C_6H_5; A is Cl; Br; OSO_3CH_3

in micellar solutions of sodium alkylsulfate (sodium octylsulfate, sodium decylsulfate and sodium dodecylsulfate) in a wide interval of surfactant concentration and in a wide ratio of monomer – surfactant were studied.

It was shown that coefficient of polydispersity of polyelectrolytes obtained by template radical polymerization is less than coefficient of polydispersity of polyelectrolytes obtained by conventional radical polymerization.

Moreover it was found that the polymerization of water-soluble ionic monomers in the presence of oppositely charged surfactants is an alternative to the preparation of polyelectrolyte–surfactant complexes and makes it possible to obtain water-soluble complexes noticeably enriched with surfactant ions.

The study was supported by Russian Foundation of Fundamental Researches (grant 09-03-99006_r_ofi).

COORDINATION CHEMISTRY OF POLYOXOMETALATES

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Lacunary derivatives of polyoxometalates (POM) are excellent ligands for coordination to mononuclear, polynuclear and cluster cations. They offer almost unlimited possibilities of incorporating desired building blocks in order to introduce catalytic centers, biological activity, luminescence, paramagnetism etc. In this contribution we will present new important developments in this field:

– new ways of incorporation of noble metals, in particular, of Rh and Ir into polyoxometalates;

– possible synthetic application of these complexes, with a particular emphasis upon C-H activation and formation of Rh-C and Ir-C bonds;

– use of POM platforms for stabilization of unusual oxidation states and bonding, such as Ir_2^{4+} or Ir(VI);

– introduction of chirality into polyoxometalates;

– incorporation of metal-metal bonded and cluster building blocks into POM;

– designed synthesis of giant, nano-sized polyoxometalate complexes with well-defined stoichiometry and structure.

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SELECTIVE PEROXIDATION OF DI- AND TRICARBONYL COMPOUNDS AND THEIR HETEROANALOGS

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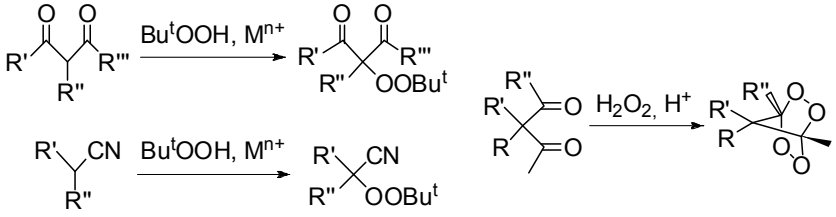
In the last two decades, organic peroxides have received considerable attention from researchers in medical chemistry and pharmaceutics in relation to the drug design for the treatment of important parasitic diseases in human population, such as malaria and helminthiases. At present the wide row of methods exists for peroxide synthesis based on monocarbonyl compounds. Peroxidation of di- and tricarbonyl compounds is known much worse; practically, selective methods for their peroxidation are absent.

We have proposed two principally different approaches for di- and tricarbonyl compounds peroxidation: acid-catalyzed reaction of hydrogen peroxide using carbonyl groups and peroxidation of α-position with application of the system *tert*-butylhydroperoxide / transition metal.



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SYNTHESIS OF CHIRAL COMPOUNDS WITH OXIDOREDUCTASES

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Chiral compounds are widely used in pharmaceutical industry as synthons for drug preparation. According to requirements of Food and Drug Administration of the USA enantiomeric excess (ee) for such compounds has to be 99% or more. Enzymes are unique biological catalysts and are actively used for chiral synthesis. Many oxidoreductases catalyse synthesis of compounds with chiral center from non-optically active precursors with very high chemo-, regio- and stereoselectivity. For example, alcohol dehydrogenase makes only one "stereochemical mistake" per 10^9 cycles in synthesis of optically active alcohols from ketones. In present time the largest enzyme process of synthesis of chiral compounds is the industrial production of *tert*-L-leucine using dehydrogenases. This process was established by Degussa company. Many reactions with oxidoreductases require second substrate – reduced coenzyme NADH or NADPH. For low cost production processes of chiral synthesis with oxidoreducatases use the second reaction of regeneration of NAD(P)H. In this laboratory new generation of biocatalysts for regeneration of NADH and especially much more expensive NADPH were developed. These biocatalysis were successfully tested in different process of preparative synthesis of chiral alcohols, chiral lactones (Baeyer–Villiger reaction with monooxigenases) and stereoselective hydroxylation with cytochromes in two-phase system water – *n*-hexane with yield >95% and enantimeric excess 99%. Detailed experimental data will be presented in report.

This work was supported by Ministry of Education and Science of Russian Federation, contract 16.512.11.2148 and Russian Foundation for Basic Research, grant 11-04-00920.

FROM STUDY OF ORGANIC REACTIONS – TO NOVEL FUNCTIONAL MATERIALS

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Fundumental study of organic reactions provides reliable ways to creation of novel functional materials for recording and storage information, optoelectronics, sensor technologies.

It is shown, that reaction of photodehydrogenation of aryl(hetaryl)pyrazolines works not only for preparation of related pyrazoles.[1] This reaction goes smootly in polymer films as well and can be used as a source of acidity which is capable to generate active forms of laser dyes possessed of very intensive fluorescence. The result leads to creation of novel media for recording and storage of information with superhigh density.

It was found that complex formation of organic π-donors with halogens (iodine, bromine) undergo not only in organic solvents, but in polymers as well. This reactivity provides reliable way to formation of bilayer films which possess of electrical conductivity, high sensitivity to strain and pressure, different sensor properties.

Study of isomerization transformations of coumarin derivatives and their analogs provided several structures, which increase their fluorescence in much extent in the presence of some proteins. Study of mechanism of the protein-fluorophor interaction leads to creation of novel fluorescent markers for biochemical research.[2,3]

Some of the results are represented for patent application.

Research is done under financial support of the RFBR, projects 07-03-00936, 08-03-12124-ofi, 09-03-12199-ofi_m, 10-03-00734-a.

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PROSPECTS OF COMPUTATIONAL CHEMISTRY IN THE XXI CENTURY

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Computational and quantum chemistry have always been extremely interested in high-and resource-intensive calculations. Currently, researchs in the field of chemistry and interdisciplinary sciences, as a rule, are ineffective without carrying out of similar calculations for the solving of problems of the most different classes using a super-powerful supercomputer installations or distributed regional and global computer polygons.

In the report the major trends and prospects of development of the computational chemistry, formed during the first decade of the 21st century, are analyzed. The newest methods of the solving of challenging tasks of various types in the field of computational and quantum chemistry by carrying out of large-scale calculations in the conditions of geographically distributed computational GRID environments and on high-efficiency supercomputer facilities are shown. Various aspects of application of methods of parallel and distributed computing are shown, the original authoring technologies developed for carrying out of quantum-chemical calculations are described.. The fundamental role of quantum chemistry in hierarchical modeling of the material objects from the quantum to the macro levels is considered. The similar hierarchy is based on the simulation of molecular and nano systems by the methods of quantum chemistry and molecular dynamics with usage of parallel and distributed computing technologies.

On an example of the IPCP computing center and the Russian and international GRID-polygons integrated with it various variants of implementation and perspective of development of computing services in the field of quantum chemistry and modeling molecular and nanostructures are shown. Developed in the IPCP computing technologies allow computing problems to solve fundamental and applied in the field of chemistry of local computing resources. The computing technologies developed in the IPCP RAS allow to solve computing tasks of fundamental and application-oriented character in the field of the chemical sciences, not previously available due to limited capacity of local computing resources.

This project was supported by the RFBR, grant № 11–07–00686-a.

ASYMMETRIC ORGANIC CATALYSIS: FROM PROLINE TO HIGHLY EFFICIENT IMMOBILIZED ORGANOCATALYSTS

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In this contribution achievements and prospects of the asymmetric organic catalysis, which is an intensively developing area of chemical science, are discussed. Proline is the first and still the most available organocatalyst of asymmetric reactions. Modern catalysts derived from amino acids, peptides, alkaloids, etc., having higher activity and selectivity and a wider scope than proline, are rather expensive, and hence an issue of their regeneration arises.

We developed an efficient strategy for the immobilization of chiral organocatalysts by modifying them with ionic liquid or ionic polymer units. New catalysts bearing α-amino acid (proline, serine or threonine), α-amino amide or β-hydroxyamine fragments tagged to the imidazolium, triazolium or pyridinium cation were synthesized. In the presence of α-amino acid or α-amino amide-derived ionic catalysts ($\leq$ 15 mol. %), prochiral ketones react with aldehydes in organic or aqueous media affording chiral aldols with extremely high enantioselectivity (up to 99% *ee*), which is similar to enzymatic reactions. Furthermore, varying the catalyst structure, it is possible to obtain deliberately either *anti*- or *syn*-aldols (up to 99:1 *dr*). The latter can be easily transformed to polyols with the *syn*-configuration of all hydroxyl groups incorporated into hydrocarbons and some other natural compounds. In the presence of α, α-diarylprolinol-derived ionic catalysts (10 mol. %) α, β-unsaturated aldehydes react with C- (dialkylmalonates and nitroalkanes) and N-nucleophiles (O-protected hydroxyl amines) yielding respective Michael adducts with very high enantioselectivity (up to 99% *ee*). Using this methodology, we synthesized key intermediates for the preparation of the most active enantiomers of medications (Paroxetine, Phenibut, Baclofen, Rolipram) for CNS-disorders and important β-amino acids (β-phenylalanine, β-tyrosine, β-DOPA). Unlike the known, the developed ionic catalysts can be multiply used in the studied reaction without any decrease in product yields and *ee* values.

The work was financially supported by the Ministry of Education and Science of the Russian Federation (contract No 02.740.11.0630) and by the RFBR (grants Nos. 09-03-00384 and 09-03-12164).

Poster presentations

PALLADIUM-CATALYZED AMINATION OF DIHALOPYRIDINES WITH ADAMANTANEAMINES

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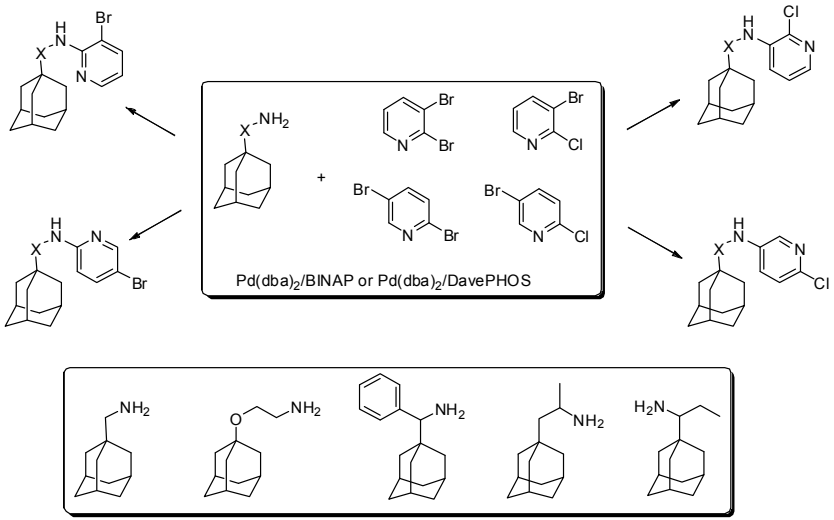
Pd-catalyzed amination of 2,3-dibromo-, 2,5-dibromo-, 3-bromo-2-chloro- and 5-bromo-2-chloropyridines with various adamantaneamines was studied. Almost in all reactions exclusive or prevailing substitution of the bromine atom in the presence of chlorine atom was observed. Depending on the nature of dihalopyridine and amine $Pd(dba)_2$/BINAP or $Pd(dba)_2$/DavePHOS catalytic systems should be used. In the case of 2,3-dibromo-, 2,5-dibromo- and 3-bromo-2-chloropyridine the best yields (up to 66%) were achieved by the use of bulky amines due to more selective amination. In the case of 5-bromo-2-chloropyridine the yields of the products with all amines ranged from 34 to 48%.



The work was supported by the RFBR grant N 10-03-01108.

SYNTHESIS OF 7,8β-DIHYDROPONASTERONE A–MINOR PHYTOECDYSTEROID FROM THE NEEDLES OF THE JAPANESE YEW, *TAXUS CUSPIDATA*

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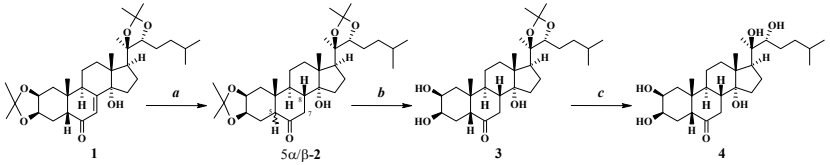
As previously reported a new phytoecdysteroid 7,8β-dihydroponasterone A have been isolated from the needles of japanese yew *Taxus cuspidata* (Taxaceae) with the yield $1.2 \cdot 10^{-4}$%. The synthesis of this minor ecdysteroid is not yet described.

The newly formed chiral center of a 7,8-dihydroecdysteroid has 8α-H configuration at the hydrogenation under palladium and at reduction by lithium aluminum hydride. We found that the reduction of diacetonide ponasterone A **1** by lithium in liquid ammonia leads to diacetonide 7,8β-dihydroponasterone A **2** as a mixture of 5α- and 5β-epimers. After the partial hydrolysis of later the resulting mixture of 5α/β-20,22-acetonides was separated by the column chromatography. The hydrolysis of individual 5β-acetonide 3 has led to the target phytoecdysteroids 4, NMR data of which were identical to those for the natural 7,8 β-digidroponasterona A given in [1].



Reagents and conditions: *a*. Li/liq.NH_3, THF, -35˚C; *b*. 10% $HClO_4$/MeOH, SiO_2; *c*. 10% $HClO_4$/MeOH.

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STABLE COMPLEX OF SYSTEM Na, K,Ca//F, WO_4

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One of the main tasks of modern technics is creation of materials with a complex of the set properties. The decision of the given problem assumes research of multicomponent systems (MSS) in which course the information about heterogeneous равновесиях is represented. Research of three- and more componental systems the labor-intensive process including studying of topology and modeling of phase complexes and reactions of an exchange, a complex formation and firm solutions and their interference and interaction. For this purpose perfection of tool and methodological maintenance is necessary. The theory of differentiation of the MSS, i.e. splitting of an initial phase complex into components taking into account features of interaction of components in elements ограпения and number of components in system [1,2]. Is now there is a prospect developed. And at the same time there is a prospect even more to simplify its ways re-shenija. We with that end in view investigate fourfold mutual system Na, K, Ca//F,WO4 in which course its differentiation taking into account topological feature and with use of computer technologies for modeling of elements of a phase complex [3] is spent. Stable cells - phase individual blocks (PhIB) the given system are

CaF_2-$CaWO_4$-$Na_4F_2WO_4$-$NaKWO_4$

K_2WO_4- CaF_2- $Na_4F_2WO_4$-$NaKWO_4$

K_2WO_4- CaF_2- $CaWO_4$- $NaKWO_4$

Na_2WO_4- $CaWO_4$-$Na_4F_2WO_4$-$NaKWO_4$

NaF- CaF_2- $Na_4F_2WO_4$-$NaKWO_4$

NaF- CaF_2- $CaWO_4$- $NaKWO_4$ and NaF-K_2WO_4- CaF_2- $NaKWO_4$

Thus, the revealed compositions can be object of research for reception of perspective inorganic materials with the set properties on the basis of the multicomponent systems which are a basis of modern materials technology.

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NOVEL NIR-FLUORESCENT COUMARIN-FUSED BODIPY DYES

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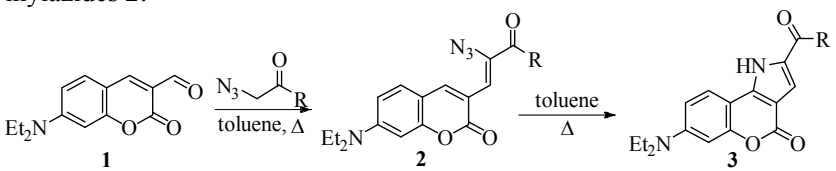
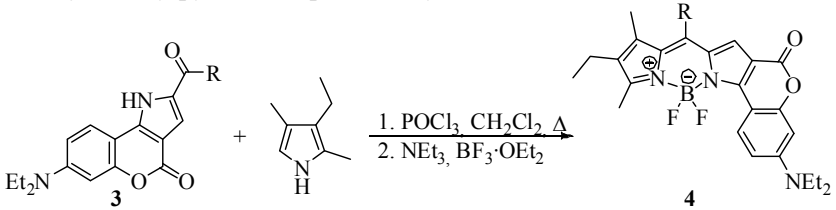
4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene derivatives (BODIPY dyes) have many application fields, such as fluorescent labels, laser dyes, photovoltaics, etc. BODIPY-dyes, annulated with various rings, usually show NIR-fluorescence. Recently, an annulated BODIPY with highest ever known for BODIPY derivatives emission wavelength (830 nm) was reported[1].

We have developed synthesis of novel BODIPY-dyes, in which one of the pyrrole ring of BODIPY core is annulated with coumarin fragment.

Earlier reported methods for synthesis of 2-benzoylchromeno[4,3-b]pyrrol-4(1H)-one core were unsuccessfull for 7-diethylamino-derivatives **3**. For synthesis of **3** we used an approach based on thermal cyclization of vinylazides **2**:



The target dyes **4** were obtained by reaction of compounds **3** with 2,4-dimethyl-3-ethylpyrrole in up to 70 % yields.



R=Ph, 4-$MeOC_6H_4$, 4-BrC_6H_4

Compounds **3** and **4** are new and were characterized by ^{1}H- and ^{13}C-NMR- and mass-spectra. Absorption maxima of **4** range between 600–650 nm and fluorescence emission maxima lie in the near-infrared (NIR) region (up to 780 nm).

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KINETICS OF REACTION URACIL DERIVATIVES WITH HYDROGEN PEROXIDE

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Reactivity of uracil derivatives in reaction of chain termination on the peroxyl radicals has been studied in sufficient details to date [1-3]. However, information about the uracils reactivity in their reaction with peroxide compounds is very scarce. Therefore, in the work presented here kinetics of reaction hydrogen peroxide - simplest representative of hydroperoxide compounds with the following uracil derivatives: 5-hydroxy-6-methyluracil (I), 5-bromo-6-methyluracil (II), 5-amino-6-methyluracil (III), 5-nitro-6-methyluracil (IV) was studied.

The kinetics of reaction uracils with hydrogen peroxide was explored using the method of kinetic spectrophotometry at 348 K. Water and 1,4-dioxane were used as the solvent.

It was found that the reaction order for uracil is the first. We have assumed that the reaction order for hydrogen peroxide is the first too. Thereby, bimolecular rate constants of reaction uracil derivatives with hydrogen peroxide for compounds (I) and (III) in 1,4-dioxane ($k \cdot 10^2$, $mol \cdot l^{-1} \cdot c^{-1}$) are (0,37±0,03), (2,01±0,22), respectively; for compounds (I), (II), (III) and (IV) in water ($k \cdot 10^2$, $mol \cdot l^{-1} \cdot c^{-1}$) are (2,50±0,3), (1,13±0,27), (0,47±0,14), (0,13±0,03), respectively.

Temperature dependence of the bimolecular rate constants of reaction uracil derivatives with hydrogen peroxide was studied in the temperature range from 333 to 360 K. This dependence has the form:

$$\lg k = (12{,}4 \pm 2{,}0) - (96 \pm 26)/\Theta \quad \text{(I)}$$

$$\lg k = (13{,}2 \pm 2{,}6) - (103 \pm 33)/\Theta \quad \text{(III)}$$

$$\lg k = (9{,}4 \pm 1{,}8) - (83 \pm 16)/\Theta \quad \text{(IV)}, \qquad \Theta = 19{,}1 \cdot 10^{-3} \cdot T, \text{ J/mol}$$

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CHEMOSPECIFIC HETEROCYCLIZATION OF BIFUNCTIONAL AMINES WITH ALDEHYDES AND H_2S

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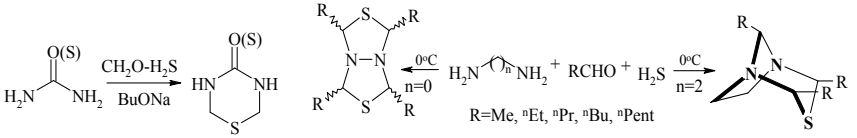
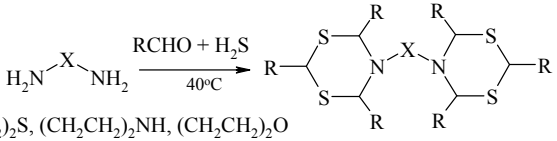
In recent years, we have studied multicomponent reactions of aldehydes and H_2S with organic compounds, which have mobile hydrogen atoms (NH-, OH-, SH-, CH-acids). These *one-pot* reactions lead to the saturated *N,S*-containing heterocycles.[1-5]

This report presents different pathways of the multicomponent reaction of bi- and heterofunctional amino-containing substrates with aldehydes and H_2S, namely: route **A** - intramolecular heterocyclization in the synthesis of monocyclanes and annulated bicyclanes;

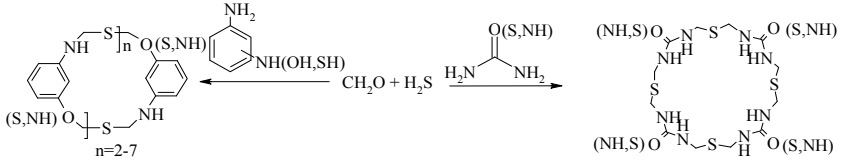


route **B** – locally-directed *N*-heterocyclization through NH-bond activation of the amino terminal group in the synthesis of bicyclanes with isolated rings;



X=(CH_2)n, n=2-5; $(CH_2CH_2)_2S$, $(CH_2CH_2)_2NH$, $(CH_2CH_2)_2O$

route **C** - intermolecular heterocyclization in the synthesis of macrohete-rocycles.



Chemospecificity of the heterocyclization reaction of hydrazine, aliphatic and hetero-chain (O, S, NH) diamines, anilines and (thio)ureas is also discussed.

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BORATE LITHIUM-IRON – CATHODE MATERIALS OF LITHIUM-ION BATTERY

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In order to find new materials that can be used as cathode materials for lithium batteries Li_2O-MO-B_2O_3 (M = Mn, Fe, Co) system was investigated. It was caused by growing interest to structures containing metal cations and polyanions.

We have synthesized and studied $LiFeBO_3$ as a cathode material for lithium-ion batteries. Samples were prepared by solid-phase, sol-gel and electrochemical methods. Carbon was added to the structure of $LiFeBO_3$ to improve the conductivity of the electrode. Thin carbon layer provides electronic conductivity without blocking the path of lithium ions' diffusion. The optimum amount of carbon depends on the microstructure and operational conditions of the cathode and usually it is in the range 2-10 wt.%. A detailed study showed that the addition of carbon does not influence on the phase composition and structure. The results of electron microscopic examination of the received materials showed their nanoscale.

The cyclic voltamogramm of the lithium battery with a composite electrode on the basis of $LiFeBO_3$ have been studied to investigate the electrochemical response of the system.

One of the positives $LiFeBO_3$ is the stability of the material, which allows you to create batteries maintaining much more cycles of discharge/charge current batteries. Another significant advantage of $LiFeBO_3$ is their stability under extreme conditions, particularly at high temperature influence. Structure of materials can easily withstand heat up to 300^0C.

Studies show that $LiFeBO_3$ is a promising cathode material for lithium-ion batteries. Application of this material will significantly reduce the cost of lithium batteries and increase the stability and duration of their work as well.

NONEQUILIBRIUM THERMODYNAMICS

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The Born-Oppenheimer adiabatic approximation states that motion of electrons in a molecule is fast compared with the nuclear motion and allows electrons to regroup instantly with any change of a nuclear configuration, and the nucleuses interact not with an individual electron, but with whole “electronic cloud” distributed in the molecular space with a certain density. For nonequilibrium systems the concept of density of energy and entropy are introduced.

We propose a new thermodynamic function, i.e. the Gibbs function normalized to the total number of electrons, $\Delta\overline{G}^{\circ}_{298}$, which is calculated by dividing the Gibbs energy of formation of a compound by the total electrons number in a chemical compound. This value defines the density of the free energy of formation of a compound having single electron. The physical meaning of $\Delta\overline{G}^{\circ}_{298}$ is based on the definition of a chemical bond as a collective effect of the electron-nuclear interaction. $\Delta\overline{G}^{\circ}_{298}$ is an intensive value.

Gibbs function normalized to the total number of electrons, interpretation in chemical potential, permission calculated affinity by T. de Donde - motive forces of chemical reaction.

The electronic density of the energy appears function of only temperature. The Gibbs function normalized to the total number of electrons is a function of temperature, so temperature is determined by the transformation of the initial components into final products. The temperature difference between the transformations of the initial components in the final product is presented as a thermodynamic force and found the value of the thermodynamic stream.

Based on this approach identified the production and entropy stream. According to transition state theory based on the chemical potential calculated activation energy, entropy of activation, the reaction rate constant.

Irreversible process evolves to the most probable state. The values of the thermodynamic "likelihood" of Boltzmann are calculated. Based on all these data, calculated the rate of entropy production and the degree of completeness of reaction by T. De Donde and I. Prigozhine.

TRENDS IN KINETIC STABILITIES OF METAL COMPLEXES OF DIPYRROMETHENES IN THE REACTIONS OF ACIDIC DISSOCIATION

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The kinetic resistance of dipyrromethene metal complexes and their derivatives in organic solvents has been studied in reactions of acidic dissociation. Relevance of the work caused by the necessity of multifactor analysis of the stability of the compounds, allows to optimize the search for compounds leaders with a set of practically valuable physical and chemical properties. On the example of palladium (II), zinc (II), nickel (II) and other metals, as well as borfluorin complexes with alkylated dipyrromethenes and bis-derivatives - biladien-a,c the reactions of protolytic and solvoprotolic dissociation studied. Qualitative and quantitative composition of protonated mixtures (C_6H_6-CH_3COOH, C_6H_6-CF_3COOH, C_2H_5OH-CF_3COOH, C_2H_5OH-H_2SO_4) was selected experimentally based on the optimal conditions for studying the kinetics of processes using absorption spectroscopy and fluorescence spectroscopy. All reactions produce the protonated forms of ligands, ie protolytic reaction scheme (solvoprotolic) dissociation is (for complex $[ML_2]$): $[ML_2] + 4H^+...A^- \rightarrow 2H_2L^+...A^- + MA_2$, (here $H^+...A^-$ and $H_2L^+...A^-$ - donor of the proton (acid) and protonated form of the ligand, respectively). The kinetic parameters indicate that, in most cases, the studied reactions proceed in accordance with the first order on metal complexes and the second order on the acid, ie in the rate-limiting step is two-fold protonation of the nitrogen atoms of coordination nod. The experimental data and identified trends of mutual nature of the metal, ligand and other factors on the kinetic stability of the compounds are discusses in this report

This work was supported by grant of the President of the Russian Federation for young Russian scientists - candidates of sciences (№ MK-401.2011.3) and the Federal Program "Research and scientific-pedagogical cadres Innovative Russia" for 2009-2013 (State contract № 14.740.11.0617).

APPLICATION OF DENSITY FUNCTIONAL THEORY TO THE DICRIPTION OF DISPERSION INTERACTION IN WEAK-BONDED SYSTEMS "XENON+AROMATIC MOLECULES"

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Modelling of biochemical systems at the molecular level has some methodic difficulties. To understand the processes taking place in systems with xenon accurate calculations of weak dispersion interactions are needed. Density functional theory combined with QM/MM approach seems to be the most comprehensible method for modelling of complex biosystems.

We were investigated systems, which contain xenon atoms and aromatic molecules (phenol, tyrosine, tryptophan and others). The calculations of geometry and binding energies were carried out with DFT with addition of empirical correction on dipersive intercation by Grimme [1], implemented in program package GAMESS(US). We were examined a set of exchange-correlation functionals (B3LYP, BLYP, PBEOP, X3LYP, M05-2X, PBEVWN and others) to reproduce standard values, which were obtained from perturbation theory MP2 calculations with cc-pVTZ basis. It was shown that the calculations with B3LYP functional and 6-31G* basis provide good geometrical structures and binding energies of main isomer (phenol+xenon). At the same time some local minima not corresponding to ab initio MP2 calculations were presented. Using of bigger basis (cc-pVTZ) instead of small (6-31G*) didn't improve situation much. That problem shows that using the Grimme's technique is limited. Thus for modelling of biochemical systems using DFT method thorough choosing of initial geometries is required and admissible description of weak despersive interaction is expected.

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The authors thank RCC of MSU for providing computational resources.

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CONFORMATIONAL ANALYSIS OF THE HIV-1 THIRD VARIABLE (V3) LOOP: MODELING OF 3D STRUCTURES AND DETERMINATION OF THE PATTERNS IN V3'S SPATIAL ORGANIZATION

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The V3 loop on gp120 from HIV-1 is a focus of many research groups involved in anti-AIDS drug development because this region of the protein is the principal target for neutralizing antibodies and determines the preference of the virus for T-lymphocytes or primary macrophages. Although the V3 loop is a promising target for anti-HIV-1 drug design, its high sequence variability is a major complicating factor. Nevertheless, the occurrence of highly conserved residues within the V3 loop allows one to suggest that they may preserve their conformational states in different HIV-1 strains and, therefore, should be promising targets for designing new anti-HIV drugs.

In this work, the 3D structural models for the consensus amino-acid sequences of the V3 loops from the HIV-1 subtypes A, B, C, and D were generated by bioinformatics tools to reveal common structural motifs in this functionally important portion of the gp120 envelope protein. To this effect, the most preferable 3D structures of V3 were computed by homology modeling and simulated annealing methods and compared with each other, as well as with those determined previously by X-ray diffraction and NMR spectroscopy. Besides, the simulated V3 structures were also exposed to molecular dynamics computations, the findings of which were analyzed in conjunction with the data on the conserved elements of V3 that were obtained by collation of its static models.

As a matter of record, despite the high sequence mutability of the V3 loop, its segments 3-7, 15-20 and 28-32 were shown to form the structurally invariant sites, which include amino acids critical for cell tropism. Moreover, the biologically meaningful residues of the identified conserved stretches were also shown to reside in β-turns of the V3 polypeptide chain. In this connection, these structural motifs were suggested to be used by the virus as docking sites for specific and efficacious interactions with receptors of macrophages and T-lymphocytes. Therefore, the structurally invariant V3 sites found here represent potential HIV-1 weak points most suitable for therapeutic intervention.

SYNTHESIS AND PHOTONICS OF ZN(II) COMPLEXES WITH ALKYLATED 3,3'-*BIS*(DIPYRROLYLMETHENE)S

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For the first time Zn(II) complexes with a number of alkylated *bis*(dipyrrolylmethene) involving $[Zn_2L_2]$ constitution were synthesized. The influence of chromophores molecular structure and medium nature on the fluorescence properties was studied and perspective directions of fluorophors practical use were established. It was revealed that $[Zn_2L_2]$ complexes give the intense fluorescence, fluorescence quantum yield amounting 0.9 in a polar, slowly polar and aromatic hydrocarbons (heptane, hexane, cyclogexane, benzene, toluene, o-xylole). Fluorescence efficiency of the $[Zn_2L_2]$ decreases as for as 500 times in nonpolar solvents (chloroform, DMFA, DMSO, pyridine, acetone, ethanol, 1-propanol) and approaches 0 in acetonitrile. The fluorescence quantum yield decreases two times in the 1-propanol – cyclohexane mixtures with the volume fraction of alcohol $\varphi \sim 0.17$ and 8 times with $\varphi \sim 0.50$. Decreasing the amount of alkyl substitutions in helicands from 10 to 4 result in the considerable hypsocromical shift of complexes $[Zn_2L_2]$ absorption and fluorescence maxima and reduction Stokes shift for approximately 4 nm. The first laser data for generations in cyclohexene under excitation by 2^{nd} harmonic of Nd:YAG laser (532 nm) are given. It was established that ethanol solutions of the analyzed compounds reduce nonlinearly the laser radiation power (W=200 MW/cm^2) at 355 nm. In both frozen solutions the phosphorescence around 750 nm and slowed fluorescence (542 – 546 nm) with approximately the same intensity are observed. The possibilities of using $[Zn_2L_2]$ helicates in new technologies (laser media, laser limiters, optical sensors of medium polarity) are discussed.

The work was supported by the Federal Target Programme ‘‘Research and Research-Teaching Stuff of Innovative Russia’’ (2009–2013 years).

CORALLOID URINARY STONES AND METHODS OF THEIR STUDYING

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The index of constantly increasing of annual incidence of urolithiasis in the world ranges from 0.5 to 5.3% and the proportion of coral-like nephrolithiasis, when the stone can reach sizes of several centimeters and fully occupy the entire kidney, accounts for between 0.02 to 0.6%. Within a year, the likelihood of recurrence is 10%, and within 5 years - 50% in the absence of adequate treatment. The treatment of this disease requires advanced knowledge of the composition of rocks and their formation processes, which now is virtually non – existent.

Of 453 urinary stones we have studied by complex of modern physicochemical methods (IR spectroscopy, spectrophotometry, the use of X-ray and synchrotron radiation X-ray microanalysis, scanning electron microscopy) the proportion of staghorn stones is about 3%. They are phosphates (typically struvite and hydroxylappatite) - 30%, urate (dihydrate and anhydrous uric acid and its salts: ammonium lithate more acidic, which is typical for these stones) - 30%, oxalate (usually wewellite, the most common for other urinary stones) - 15%, urate - and phosphate - calcium oxalate mixtures - 25%.

The center and the periphery of the stones differed in protein, elemental and phase composition. As a rule, for urates there is dihydrate on the periphery, and in the center there is anhydrous uric acid, for oxalate there is wewellite + weddellite outside and in the center there is wewellite for phosphates on the periphery there is poorly educated apatite or struvite, and inside there is crystal carbonate (hydroxyl) apatite. The characteristics for oxalates and urates dense interweaving of crystals and outside individual crystals – inside, and in phosphates there are amorphous formations in the center and crystal – in the periphery, which leads to greater hardness of the periphery of the stone compared to the center in the first case and vice versa – in the second. Based on the results of the proposed mechanisms of stone formation: the growth of oxalate and urate occurs slowly, by deposition on an organic matrix, and phosphates are formed from colloidal aggregates.

ANTIOXIDATIVE ACTIVITY OF BICYCLIC PYRROLIDINE DERIVATIVES

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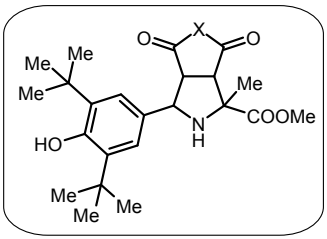
Antioxidants of different chemical nature are promising agents for pharmacological correction of oxidative stress. Numerous scientific groups are involved in synthesis and study of antioxidative properties of novel compounds possessed of increased potency and decreased side effects in comparison with existing agents.

In the present work we performed synthesis of novel pyrrolidine derivatives (**I-VI**) contained fragment of sterically hindered phenol and evaluated their influence on oxidative destruction of lipid *cis*-9-octadecene carboxylic acid structural fragment.



X = 2,6-diMePhN (**I**); 2,3,5,6-tetraFPhN (**II**); PhN (**III**); 4-MeOPhN (**IV**); (naphthalen-1-yl)N (**V**); 4-BrPhN (**VI**)

Oxidation experiments were conducted in thermostat equipment during 5 h under steady air barbotage at 37°C и 65°C in the presence of 1 mM of synthesized compounds. Addition of pyrrolidines (**I-VI**) to *cis*-9-octadecene carboxylic acid inhibited it's oxidation. Concentrations of primary lipid peroxidation peracidic products (R'OOH) as well as secondary lipid peroxidation carbonyl products are considerably decreased in the presence of pyrrolidine antioxidants. Compound (**IV**) was identified as the most effective agent during the whole oxidative process. In conclusion, high antioxidative activity of novel bicyclic pyrrolidine derivatives has been demonstrated in explored model lipid peroxidation system.

The research was supported by the Federal program "Scientific and scientific-teaching personnel of innovative Russia" on 2009-2013 years (state contract N 16.740.11.0441 from 30.11.2010), RFBR grants 11-03-00389-a, 09-03-92011-HHC_a.

EFFECT OF ANTIMONY(V) COMPLEXES WITH REDOX ACTIVE LIGANDS ON THE LINOLEIC ACID PEROXIDATION

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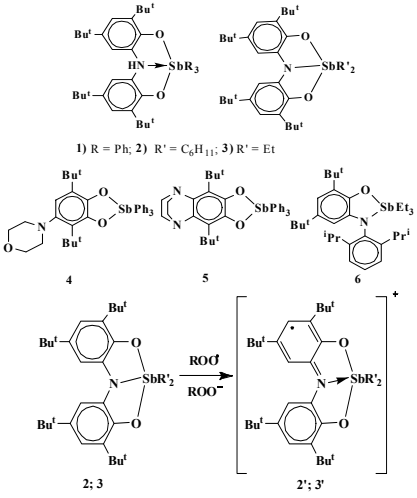
In this work, the autooxidation of linoleic acid was studied in the presence of five-, six-coordinated antimony(V) complexes containing redox active ligands (**1-6**), Ph_3Sb(**7**) and ionol (**8**).



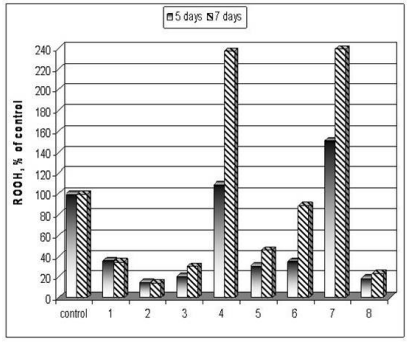


Fig. 1. Relative content of ROOH in linoleic acid during 5 days, 7 days of oxidation (25°C; $C_{additives} = 10^{-3}$ mol L^{-1}).

Effect of additives of complexes was estimated by changes in the concentration of ROOH as well as the accumulation of TBARS. The comparative data on the inhibiting activity of the target compounds in the process of linoleic acid peroxidation are shown in Figure 1. Complexes **1-3**,**5**,**6** exhibit an inhibitory effect throughout the experiment. Antioxidant activity of compounds is caused by the presence of redox-active fragments which are involved in the scavenging of active ROO-radicals. During the experiment for complexes of **2**,**3** a change of solution color is occurred, that points out the accumulation of monocation forms – **2'**,**3'**. Compounds **4**, **7** provide promoting effect. It has shown that complexes **2**,**3** show the same inhibitory activity as well-known phenolic antioxidant – ionol.

The work was financially supported by FCP (GK № 16.740.11.0441), RFBR (№ 11-03-00389-a, 10-03-00921-a), grants of the President of the Russian Federation (MK-1156.2011.3, MK-614.2011.3).

PERCULIARITIES OF PROCESSES IN THE REACTION SYSTEM "FURFURAL – H_2O_2 – H_2O – CATALYST" DEPENDING ON CATALYST NATURE

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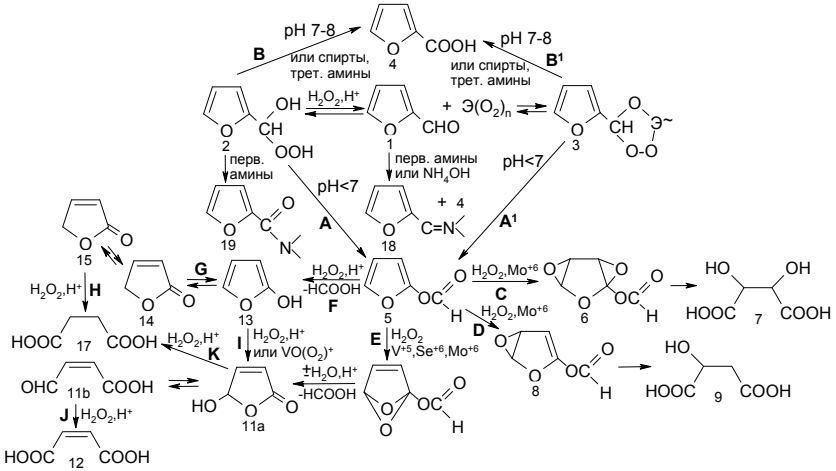
Various stages of multi-directed process of furfural oxidation with hydrogen peroxide under conditions of acid autocatalysis or in the presence of V^{+4}, V^{+5}, Nb^{+5}, Mo^{+6}, Cr^{+6}, Se^{+4} as catalysts together with autocatalysis have been studied. The oxidation goes through peroxide 2 or peroxide 3 formation, and then through Bayer-Villiger rearrangement of peroxides 2 and 3 to ether 5. Further the autocatalytic reaction goes on directions F, G, H and I, J, K to form mainly lactone 14 and acid 17. The catalyst added considerably accelerates the process and changes its purposefulness. Epoxydizing activity of peroxocomplexes of catalysts with H_2O_2 brings about directions C, D, E. Radical hydroxylation during lactol 11a formation from compounds 5 and 13 in the presence of V^{+4}, V^{+5} is not excludes.



At pH>7 peroxides 2 and 3 lead to acid 4 formation. Addition of amines or aqueous ammonia into reaction mixture in the presence of V^{+5} or without it also leads to azines 18 and amides 19 formation.

APPLICABILITY OF THEORETICAL MODEL OF TRANSFER OF ENERGY IN NON-AQUEOUS SOLUTIONS OF SALTS OF ALKALINE AND ALKALI-EARTH ELEMENTS

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Earlier authors developed and showed applicability of theoretical model of transfer of energy in water solutions of electrolytes in frameworks plasma conformable to the concept. In the given report values of heat conductivity of salts of alkaline and alkali-earth metals in alcohols (methanol, ethanol, propanol and butanol) are designed at various concentration (0,0001-0,1 mol/l) and temperature (288-323 K). Additionally numbers of solvation, radii and masses of ions in non-aqueous solutions of salts of alkaline and alkali-earth elements were found.

The developed theoretical model of transfer of energy is based that solutions of electrolytes are considered as the systems of charges described by a plasma oscillatory mode of balance "dissociation solvated ions - recombination in molecular solvates" with appropriate energies and speeds and takes into account characteristics separate solvated ions and properties of solvent (a dielectric constant, energy of intermolecular interactions, dipole the moment, radius and molar mass). Also one of fundamental problems of the theory of solutions is the problem of mobility of ions and molecules as basic parameter of research of dissipative properties.

The results received on considered theoretical model, will well be coordinated with available literary values and confirmed with experiment. The conclusion that, using one theoretical model approved on aqueous solutions, it is possible to obtain data on heat conductivity of solutions of electrolytes in non-aqueous solvents, in particular alcohols, is made.

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BROMINATION OF 4-ALLYLTHIOQUINAZOLINES

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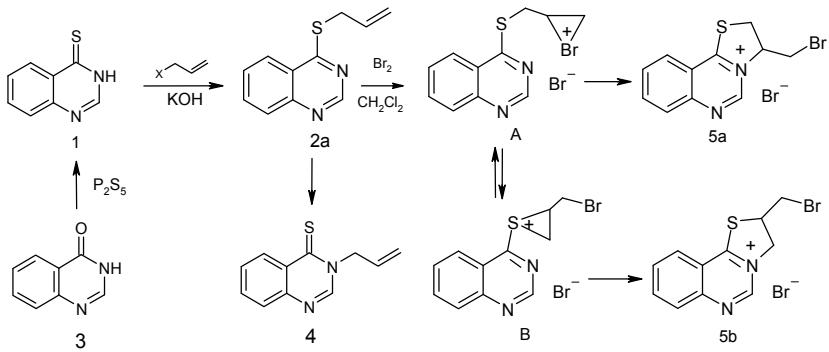
4-Allylthioquinazoline (2a) and 4-(2-methyl-2-propen-1-il)thioquinazoline (2b) were obtained by interaction of 3H-quinazoline-4-thione (1) with allyl bromide and 2-methyl-3-chloro-1-propene respectively. Compound 1 was obtained by thionation of 3H-quinazoline-4-one (3) under the influence of pentasulphide phosphorus in pyridine.

The compound 2a was shown to undergo Claisen rearrangement giving 3-allyl-quinazoline-4-thione (4) by heating.

We studied bromination of allylsulphide 2a in dichloromethane and found bromocyclization leads to formation of two compounds. Using ^{1}H NMR we found one of the products to be a 3-bromomethyl-2,3-dihydrothiazolo[2,3-c]quinazolinium bromide (5a), and the second one to be a 2-bromomethyl-2,3- dihydrothiazolo[2,3-c]quinazolinium bromide (5b). Hereby, bromide 5a seems to be formed through bromonium ion (A), whereas bromide 5b is formed through thiiranium ion (B).



^{1}H NMR spectrum of bromide 5a has a proton on NCH groups forming multiplet at 6.08 ppm which is characteristic of such dihydrothiazoloquinazolinium systems. 5-H proton of bromide 5a is shifted to lower field on 0.5 ppm in comparison with corresponding 2-H proton of initial compound 2a, that explained by appearance of the positive charge on nitrogen atom.

The bromination of metallylsulphide 2b takes place in similar way.

KINETICS OF FORMATION REACTIONS OF URETHANES WITH DIPHENYLOLPROPANE AND ITS DERIVATIVES

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Interaction of isocyanate group with hydrogen labile atom is a principal reaction of polyurethane formation. Competence in kinetic regularities gives an opportunity to form polymer structure and decide the issues related to the process of intensification and their production.

The present work shows the results of kinetic studies of reactions of phenylisocyanate and diphenylolpropane and their derivatives, aromatic diols. The latter was suggested as chain extenders in the polyurethane materials synthesis. Research studies were carried out in the cyclohexane medium in the presence and without catalyst in the temperature range of 25 – 60°C. Dibutylaurat tin and triethylamine were used as catalysts. Reagents quantity was calculated to provide the equimolar ratio of isocyanate and hydroxyl group. Reaction process control was accomplished at isocyanate groups consumption by means of titration of the reaction mixture amount with diethylamine in acetone solution. Discussed transformations on the main kinetic areas follow the equations of second order reactions for irreversible processes. According to the values of effective reaction rate constants and their activation energies, aromatic diols reveal greater reactivity in comparison with diphenylolpropane. Introduction of catalyst allows increasing reaction rate significantly. Thereby, organotin catalyst accelerates the interaction with aromatic diols on a larger scale than the similar transformation with diphenylolpropane. On the contrary, in the presence of amine catalyst, reactivity of alcohol hydroxyl group exceeds the reactivity for phenyl group.

Research studies were financially supported by Federal purpose program “Scientific and scientific-pedagogical personnel of innovation Russia” for 2009-2013, ГК № П729

SYNTHESIS AND SOME CHARACTERISTICS OF CHLORO-SULFONYLISOCYANATE AND ITS DERIVATIVES

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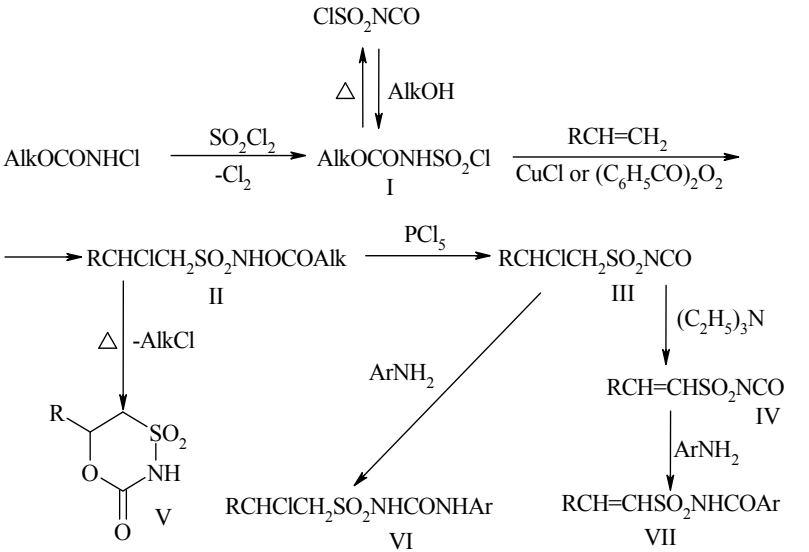
Chlorosulfonylisocyanate known as isocyanate of "Graf" is obtained by very laborious method1. A new, easy method of its synthesis was proposed using an interaction of accessible alkyl ethers of N-chlorocarbamic acid with sulphuryl chloride2. Obtained alkyl ethers of N-chlorosulfonylcarbamic acids under heating give N-chlorosulfonylisocyanate in 90 % yield. Alkyl ethers of N-chlorosulfonylcarbamic acids were found as the valuable products for obtaining adducts II, isocyanates II and IV, derivatives of oxathiosin-2,4,4-trione V and ureas VI, VII. The latest were interesting as potential antidiabetic agents.



A structure of obtained compounds (I-VII) was confirmed by an element analysis, NMR, IR-spectroscopy.

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SELF-ASSEMBLY OF SUPRAMOLECULAR STRUCTURES IN L-CYSTEINE AND SILVER NITRATE BASED DILUTE AQUEOUS SOLUTIONS

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Nowadays the amount of research in the field of processes of self-assembly of supramolecular structures in solution is continuously growing. The lack of strong chemical bonds between the interacting components is the universal distinctive feature of these structures. There several factors, which drive its formation. They are electrostatic and Van der Waals interactions, hydrophobic effects, hydrogen and weak donor-acceptor bond. The low concentrated gels constitute a separate field of research.

Scientists of the Department of Physical Chemistry of Tver State University were the first to discover the process of gelation in low-concentrated aqueous solution of L-cysteine and silver nitrate. In the first, place hydrogel is a unique model system for studying the processes of self-organization in dilute aqueous solution (concentration of 0,1% and below). Secondly, the presence of silver in the system makes it possible to use it in medicine.

The aim of this work was to study the process of structuring of cysteine-silver solution (CSS) and hydrogel using optical and others methods. The results of this research are essential for a more informed approach to the production of hydrogels with desired properties.

In the course of research, the formation of clusters of silver mercaptide (SM) at the initial stage of the synthesis of L-cysteine-based hydrogel and silver nitrate was established through optical and microscopic methods. The dependence of the size and number of clusters (particles) SM from the ratio between AgNO3 and L-cysteine was founded. The dependence of numerical concentration of the particles on mass concentration of dispersed phase in CSS was determined too. The studies by dynamic light scattering method confirmed the results of optical studies of CSS and of hydrogels; the molecular weight distributions of different samples, the clusters and gel network formation kinetic mechanism was found. We succeeded in finding temperature-time ranges of formation of system based on L-cysteine and silver nitrate with high viscous-elastic properties, using rheological methods. Correlation of rheological data and optical method data allowed to determine the structural-property dependence for the studied hydrogels. It allowed to introduce some adjustments to the base of theory describing the formation of hydrogel based on L-cysteine and silver nitrate.

This study was supported by a Analytical Departmental Special Purpose Program "Development of higher school scientific potential (2009–2010 years)", project № 2.1.1.6867

INVESTIGATION OF THE SAMPLES OF PEKMEZ EATH GATHERED FROM NIGDE CITY FOR THE RESIDUES OF PESTICIDES AND POLYCYCLIC AROMATIC HIDROCARBON (PAH)

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Fruit juice concentrate (Pekmez), a traditional Turkish food, is a concentrated and shelf-life extended form of mulberry or grape juice formed by boiling without adding sugar or other food additives. Adding pekmez earth in production of grape pekmez decreases the titratable acidity to below 1% and increases the pH to more than 5. The pekmez earth also contributes to a decrease in turbidity. This is evident as the absorbance value at 520 nm declines to 0.522 of liquid pekmez after adding 20% pekmez earth, compared to 1.602 of liquid pekmez without adding pekmez earth. Amount of the earth to be used may vary according to its amount of $CaCO_3$ content. Thus, in theory, 0.1 to 1.0 kg earth should be added to a 100 kg of fresh grape-juice.

In this study, PAH (Policyclic Aromatic Hydrocarbon) and pesticide residues in samples of pekmez earth were investigated. For this purpose, 37 samples were collected from pekmez earth. Samples were analyzed. Naphthalene was found in eight samples[1-3]. In addition, benzo[a]anthracene found in three samples. Analysis, GC / MS was performed. Such types of pesticides as procymidone, azoksitrobin, cypermethrin, deltamethrin, Lambda-cyhalothrin were found in earth samples. The type of pesticide residue that was researched (limit of quantification is 10 ppb for GC-MS) was not found at a detectable level. However, in the study conducted to search the polycyclic aromatic hydrocarbons, naphthalene was detected in four samples and benzo[a]anthracene was detected in one sample above the limits specified.

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SINTHESIS OF PYRAZOLE DERIVATIVES BASED ON METHYL-4-(N-PHTHALYL)BUTA-2,3-DIENOAT

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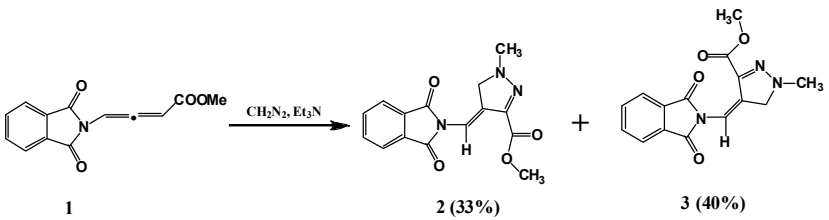
Pyrazole derivatives are widely used in pharmacology as an antidiabetic, antiviral, antimicrobial, antibacterial and anticancer drugs [1,2], which stimulates the search for and develop effective ways of their receiving.

One of the most effective approaches to the synthesis of substituted pyrazoles is the reaction of 1,3-dipolar cycloaddition of diazo-derivatives to unsaturated compounds. We have investigated the interaction of propadiene (**1**) with excess of diazomethane in the presence of triethylamine as a catalyst. As a result of reaction formes isomers of pyrazole derivative (**2,3**), containing phthalimidic fragment.



1 **2 (33%)** **3 (40%)**

The structure of the compounds is established by physical and chemical methods of analysis.

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This work was supported by the grant of the President of the Russian Federation for support of leading scientific schools (NSH-3756.2010.3) and the Federal Target Program "Scientific and scientific-pedagogical specialists of Innovative Russia" for 2009-2013 (State contract № 14.740.11.0367).

SYNTHESIS AND ION SELECTIVE PROPERTIES OF DERIVATIVES OF TETRAPHENYL[(O-PHENYLENE)OXYMETHYLENE]-DIPHOSPHINE DIOXIDE

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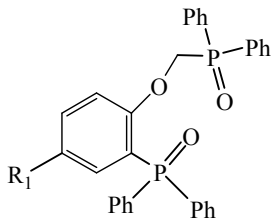
The new derivatives of tetraphenyl[(o-phenylene)oxymethylene]diphosphine dioxide were synthesized and investigated as the active components of the plasticized polymer membranes of the ion selective electrodes (ISE). These compounds are quite simple to synthesize and they posses low toxicity ($LD_{50}\geq 2000$ mg/kg) and high affinity to the polymer materials.



I

R_1=H, Et

The electroanalytical parameters of the ISEs were measured and their selectivity constants were determined. The compositions of the ISEs membranes for the determination of Ca^{2+} cations in aqueous solutions were developed. The complexes of Cu^{2+}, Ca^{2+}, и Er^{3+} with these compounds have been obtaned in the solid state and their structures were determined on the base of IR-spectroscopy, DTA/DTG analyses and X-ray diffraction data.

Financial support from the Presidium of the Russian Academy of Sciences through a project “Development of new chemical substances synthesis techniques and new materials” is gratefully acknowledged.

SYNTHESIS AND TRANSFORMATIONS OF ADAMANTANE CONTAINING ALLYL ARYL ETHERS

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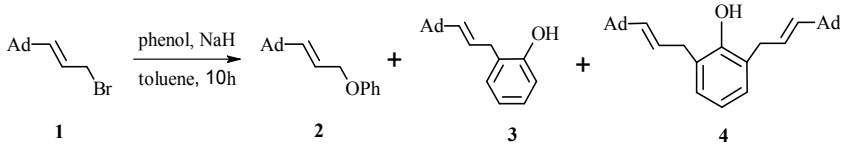
The study of molecular rearrangements of allyl aryl ethers containing bulk adamantane fragment can help to use this type of reaction for a wide number of compounds. The complication of the allylic fragment and the introduction substituents into the aromatic ring probably will influence on the directions of rearrangemens.

Starting ethers (**2, 5**) have been prepared by reaction of allyl bromide (**1**) with *o*-R-C_6H_4-OK (where R = H (**2**), $COOC_2H_5$ (**5**)) in acetone. In case of the reaction of compound (**1**) with sodium phenolate in hot toluene we have found two products (**2, 3**) which are formed. Continuous heating of the reaction mixture gave the additional bis-allyl product (**4**).



1 **2** **3** **4**

Thermal rearrangement of the ether (**2**) in diethylene glycol has led to *o*- and *p*-adamantyl allyl phenols (in 3:1 ratio) and a significant amount of adamantyl allyl diethylene glycol monoether and phenol. This fact is the evidence of the intermolecular pathway of the rearrangement. Thermal rearrangement of the ether (**5**) in ethyl salicylate leads to migrating allyl fragment from oxygen atom into *ortho*-position.

The study was financially supported by the Federal Program «Scientific and pedagogical staff of innovative Russia in 2009-2013».

NEW ORGANIC N,S-CONTAINING LIGANDS AND THEIR COORDINATION COMPOUNDS - CATALYSTS OF REDOX REACTIONS

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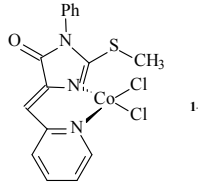
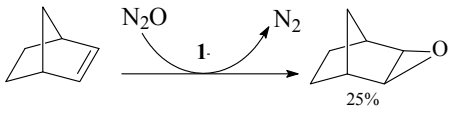
Transition metal complexes with organic N,S-containing ligands are in recent years widely studied as models of metalloenzymes and catalysts of redox reactions. Getting the low-molecular analogues of natural metalloenzymes is current trends in modern bioorganic and bioinorganic chemistry. Enzymes containing in the active site of transition metal ions, catalyze different chemical transformations: oxidation, hydroxylation, amination, epoxidation, cyclopropanation, oxidation of sulfides, etc. In this case, catalysis is carried out at atmospheric pressure and room temperature, with high selectivity and yield.

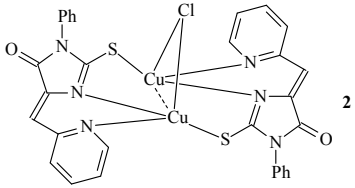
In this report the synthesis of new N,S-containing organic ligands - derivatives of 2-tiogidantoinov, thio-substituted amides, amines and imines, complex compounds of Ni(II), Cu(II) and Co(II) on their base and the results of a study of catalytic properties of the coordination compounds in the oxidation of organic substrates and the reactions of alkylation is described. Among the investigated model reactions - oxidation processes under the action of N_2O, the only byproduct of which is N_2, for example:



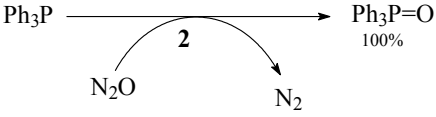
1



CH_3CN, 25°C, *4 часа*



2



In addition, we studied the complexing reaction of transition metal ions with ligands, adsorbed on the gold surface (gold electrode or gold nanoparticles) to form a "metallocomplex surfaces", combines the advantages of homogeneous and heterogeneous catalysts.

This work was supported by RFBR, project № 10-03-00677.

AZOCOUPLING REACTION OF 3H-FURAN-2-ONES AND CONVERSIONS OF THEIR PRODUCTS UNDER ACTION OF NUCLEOPHILIC AGENTS

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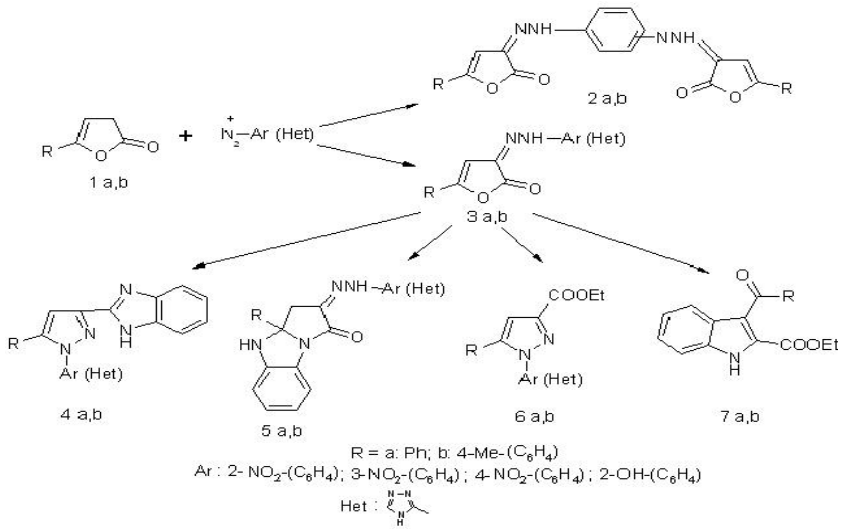
The synthesis methods of 3-(het)arylhydrasono-3H-furan-2-ones, based on azocoupling reaction of 5-R-3H-furan-2-ones with the (het)aryldiazonium and tetrazonium salts were developed.



A large library of compounds based on certain reactions was used for obtaining different heterocyclic systems given structure.

It was shown that the studied systems reacts easily with mono- and bi-nucleophilic reagents giving rise to series of pyrazole compounds, substituted tricyclic structures, and they indolizes under conditions of Fischer rearrangement.

It was found that bishydrozonoderivates of furanones are tetradentate ligands in complexation reactions.

Structures of the newly synthesized compounds were proved with attraction of IR, ^{1}H and ^{13}C NMR spectroscopy data.

The study was carried out with a financial support from the Russian Foundation for Basic Research (grant no. 10-03-00640-a).

NEW N-SILOXYCARBONYL REAGENT

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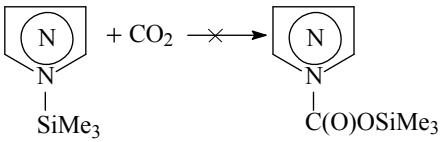
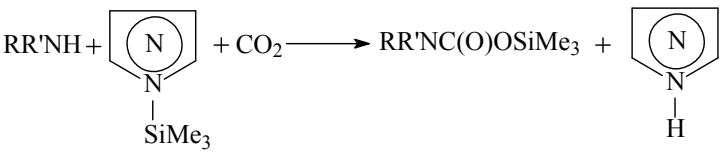
Having high silylating power, N-trimetilsilyldiazoles used as silylating reagents in fine organic synthesis. At the same time they do not absorb carbon dioxide in the reactions of carboxylation.



The combination of these two factors has led to the suggestion that the N-trimetilsilil derivatives of diazoles can be used as N-siloxycarbonyl reagent in conjunction with carbon dioxide. It was found that, indeed, this couple can successfully receive valuable in terms of application of O-silylurethanes from both the primary and the secondary amines.



Discovered a new N-siloxycarbonyl reagent of N-trimetilsilyl derivatives diazoles / carbon dioxide makes it possible to carry out the process without the use of a catalyst for dramatically reduce response time and increase the yield of target products.

METHYLPHEOPHORBIDE *A* AND ITS ANALOGUES IN THE SYNTHESIS OF POLYFUNCTIONAL CHLORINS

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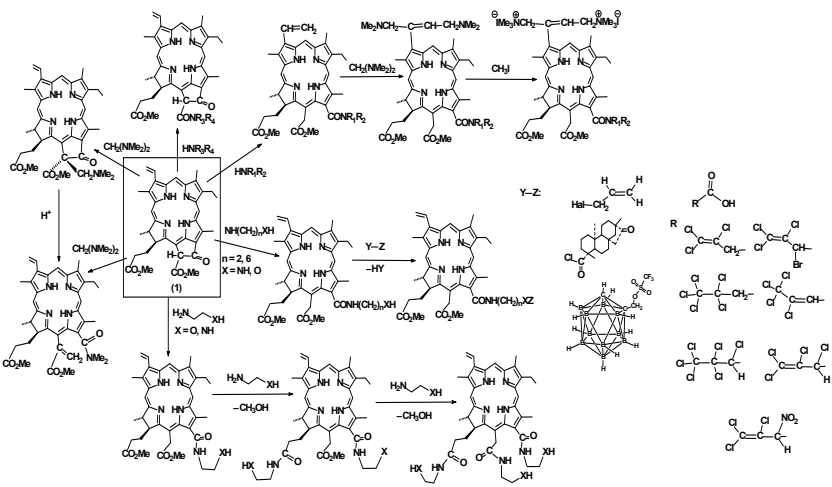
The chemical transformations of chlorophyll *a* derivatives, such as methylpheophorbide *a* **1** (Scheme 1), are important because chlorins obtained are perspective as antitumoral medication, biological models and other. From the viewpoint of structure-biological activity study and new biologically active compounds synthesis the development of simple and effective methods for chlorophyll derivatives chemical modification is of a great interest. The review of methyl pheophorbide *a* and its analogues chemical transformations (Scheme 1) carried out in our institute in 2003-2011 should be presented.



Scheme 1

IONIC AND RADICAL REACTION OF ACTIVATED HYDROGEN SULFIDE WITH ORGANIC COMPOUNDS

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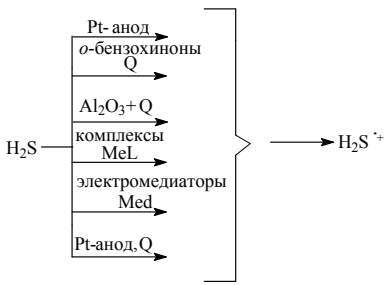
To date, the reactivity of H_2S has been studied quite extensively. However, studies on the activation of hydrogen sulfide by means of one-electron transfer are extremely small.

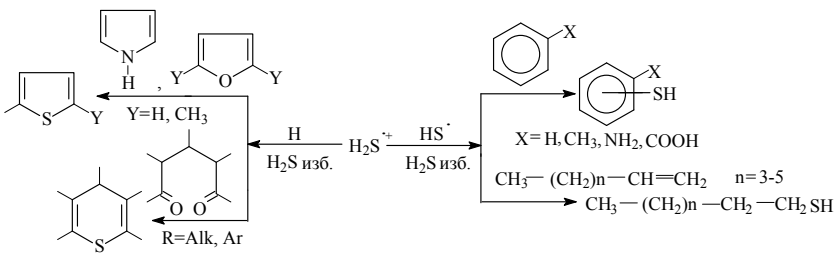
This research studies a number of synthetic methods required for the activation of H_2S to the radical cation in reactions with organic compounds at room temperature. These synthetic methods include electrochemical and/or chemical means of oxidation of molecules H_2S, increasing its reactivity. The fragmentation of the unstable radical cation H_2S can generate a proton and thiyl radical initiating ionic and radical reaction of hydrogen sulfide with organic compounds.

The reactions of H_2S with activated aromatic, unsaturated, heteroaromatic and 1,5-dicarbonyl compounds can be represented in general by the scheme:

Activation:



Initiation of reactions:



This work was supported by RFBR (grant № 09-03-00677a), FTP (НА № 16.740.11.0441, 13.11.2011)

SEQUENCE OF TRANSFORMATIONS OF FURAN TO POLYTHIOPHENES IN THE PRESENCE OF ACTIVATED HYDROGEN SULFIDE AND ELEMENTAL SULFUR

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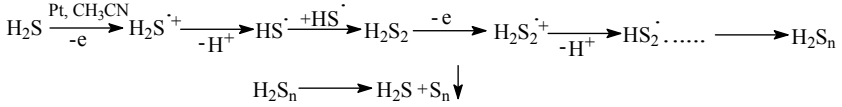
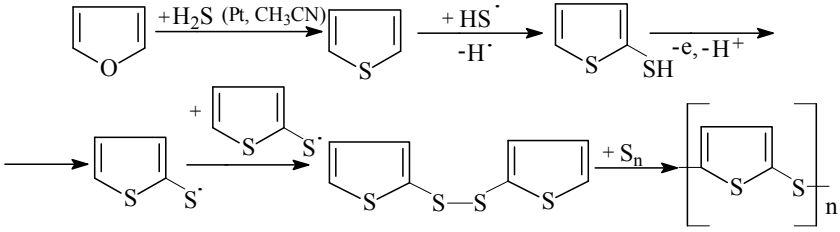
It is known that polythiophenes are used in electric supply sources, memory of data storage and light-emitting devices as well as in electrochemical sensors. The main aim of this research is working up a low-temperature (t = 23 ÷ 50 °C) method of obtaining of the polythiophenes based on reaction between furan and H_2S. The process of electrochemical oxidation of H_2S is a single stage with the formation of radical cation. The oxidation of molecule H_2S leads to the generation of unstable polysulfanes that disproportionate with the formation of elemental sulfur:



In the electrochemical reaction of furan with H_2S are obtained: thiophene (34%), 2-tiofentiol (20%), bis (2-thienyl) disulfide (28%) and sulfur. The increasing of reaction's time leads to the formation of polythiophenes (14%).



The replacement of the anode to oxidizer of H_2S – 3,5-ditret.butyl-*o*-benzoquinone contributes to obtaining an amorphous polymer (24%, t_{mel}= 55 ° C) with disulfide links. The yield and viscosity of the polymer depend from the quantity of sulfur produced in the reaction.

This work was supported by RFBR (grant № 09-03-00677a), FTP (HA № 16.740.11.0441, 13.11.2011)

SOLVATION OF BLOOD PORPHYRINS IN THE SOLVENT MEDIA MODELING PROTEIN-LIPID SURROUNDING

Berezin D.B.[a], Kustov A.V.[b], Smirnova N.L.[b], Karimov D.R.[a], Krest'yaninov M.A.[b], Berezin M.B.[b]

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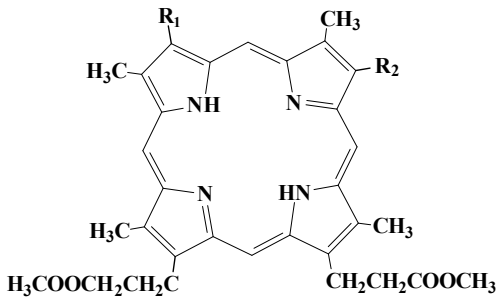
Study of preferential solvation of asymmetrically substituted periphery of biomolecules like porphyrins of chlorophyll and blood groups (fig.) are required for understanding of their behavior in living systems upon ones interaction with a protein and lipid surrounding in processes of dioxygen fixation during photosynthesis, tissue respiration and photodynamic therapy of tumors. In addition, some of above processes suggest passive transport of macromolecules through cell membranes.

Present work is devoted to the study of the influence of polar ester fragments of the molecules of blood porphyrins on the character of solvation processes with their participation in the medium of solvents modeling inner side of proteins (N,N-dimethylformamide) or hydrophobic part of cell membranes (1-octanol).



To solve this problem the IR-spectral and thermochemical investigations of solvation of blood bioporphyrins and their model fragments as ethylacetate are carried out. The predominantly universal type of solvation of biomolecules as well as the absence of compensation of energy expenses for the destruction of their crystal lattice during solvation process is observed. It is found that in the mixed solvent DMF – 1-OctOH the solvate shells of ester fragments are enriched with amide component. It attests in favor of higher degree of their affinity to the protein models compare to lipid ones owing to strong dipole-dipole interactions.

The financial support of this work by grant of Russian Foundation for Baric Research (project *№ 10-03-00020-a)* is gratefully acknowledged.

THE SYSTEM ANALYSIS OF INNOVATIVE POTENTIAL OF THE BRANCH CHEMICAL SCIENCE (1990-2009)

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The branch science is the basic motive power of technical progress of the Russian industry. Preservation and development of this major component of scientific potential of Russia is possible at purposeful support by the state controls (Ministry of Industry and Trade and Ministry of Education and Science of Russian Federation).

It is shown, that from all sectors of a science (academic, university, branch) the strongest losses were incurred with branch (enterprise) sector. However, despite of the minimal state support, today in this sector it is concentrated 1,5 times more personnel and material resources, than in the academic and university sectors of science taken together, and volumes of R&D 2 times above.

From 1993 to 2010 within the contracts of Ministry of Industry and Trade and Ministry of Education and Science of Russian Federation there were carried out researches of innovative resources of a branch science on an example of leaders of branch scientific research institutes of the chemical and petrochemical industry of the state and joint-stock forms of ownership (83 organizations). Information base are data of statistical documents "2-science" which are annually represented by all scientific research institutes to the state controls.

For carrying out of the system analysis of innovative resources the information system was developed and introduced in the state controls where parameters of innovative resources have been divided into 3 groups: intellectual, financial and material. Each of these groups represents set of the subgroups including corresponding indicators. For example, the group of intellectual resources included subgroups of personnel and scientific resources, and also a subgroup of indicators on preparation of the scientific staff (postgraduate study).

One of the major elements of the system analysis of innovative resources of branch scientific research institutes of a chemical complex is the developed methodology of the rating analysis.[1] It allowed to determine correctly a position of each scientific research institute in innovative potential of branch.

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Work with financial support from Ministry of Industry and Trade of Russian Federation, project 8411.0816900.13.057

INFLUENCE OF DIAMAGNETIC REFERENCE IN ANALYSIS OF PARAMAGNETIC SHIFTS BY MEANS OF NMR SPECTROSCOPY OF (PORPHYRINATO)(PHTHALOCYANINATO) LANTHANIDES

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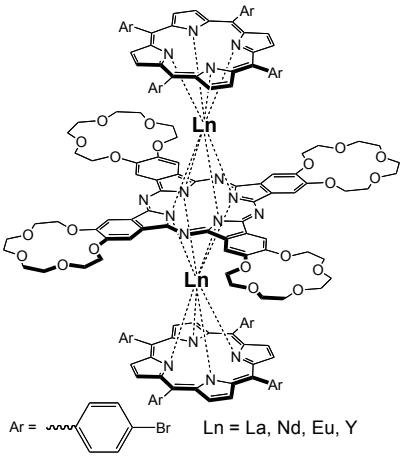

Series of investigated triple-decker complexes $Ln_2[Br_4TPP]_2[(15C5)_4Pc]$

Analysis of lanthanide-induced paramagnetic shifts (LIS) of resonance peaks in ^{1}H-NMR spectra of series of heteroleptic triple-decker lanthanide (porphyrinato)(phthalocyaninates) allows to determine the isostructurality[1] and structural parameters[2] of investigated series in solutions.

Previously we have determined the isostructurality of the series of heteroleptic complexes of general type $Ln_2[Por]_2[(15C5)_4Pc]$ (Ln = La-Eu)[2]. Nevertheless lanthanide contraction within the series should results in decrease of interligand distance and alternation of conformations of *ms*-substituents of porphyrin ligands. In order to evaluate the influence of the lanthanide contraction onto accuracy of results of LIS analysis the related diamagnetic complexes $[Br_4TPP]M[(15C5)_4Pc]M[Br_4TPP]$ (M = La, Y) and their paramagnetic analogues (M = Nd, Eu) were synthesized. It was found that chemical shifts of signals in spectra of diamagnetic complexes do not coincide, revealing the structural deviations of the compounds. Analysis of LIS with application of La and Y data produced different results, revealing the influence of the diamagnetic reference. LIS analysis is found to be insensitive to structural changes, determined by lanthanide contraction.

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SYNTHESIS AND CATALYTIC ACTIVITY OF COPPER COMPLEXES WITH AND POLYARENAMIDOPHOSPHITIC AND POLYARENPHENYLPHOSPHONITIC LIGANDS

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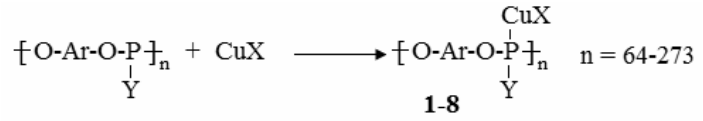
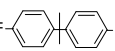
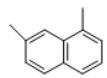
Previously, we have reported about the synthesis and structure of polymer arenamidophosphites and arenphenylphosphonites[1].

In furtherance of this investigation we have studied the complexation of synthesized[1] polyarenamidophosphites and poliarenphenylphosphonites. It was established that the synthesized polyamidophosphites and polyphenilphosphonites at 60^0C in o-xylene form with salts of Cu (I) polymeric coordination compounds:



Ar =  , Y = NEt_2 , X = Cl (**1**); X = Br (**2**) X = I (**3**)

Ar =  ; Y = NMe_2 , X = Br (**4**); Y = NEt_2, X = Cl (**5**); X = Br (**6**); Y = Ph, X = Br (**7**)

Ar =  ; Y = NEt_2 , X = Br (**8**)

It is shown that in the resulting metal complexes copper is coordinated by the phosphorus atom, as evidenced by strong-polar shift ($-\Delta\delta p$), the magnitude of this shift is a function of electron acceptor properties of the halogen (X) (I <Br <Cl), type of substituent at the phosphorus atom (Y) and the structure of the arene fragment (Ar).

The synthesized metal complexes (5,6) were examined for catalytic activity in cyclopropanation of olefins and hydrogen transfer, conversion CCl_4 in $CHCl_3$. We have found that the coordination compounds (5,6) are effective catalysts of chemical processes.

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ASSYMETRICAL MACROCYCLOARENEPHOSPHAMIDES

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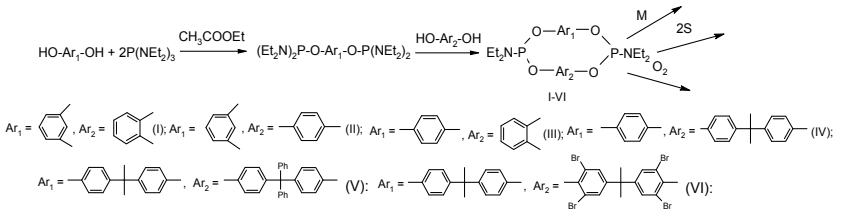
Now different arene phosphorous-containing macrocycles[1] are actively investigated. And the most interesting of them (from the standpoint of synthesis, structure and properties) are macrocyclic arenephosphamides[2,3] .

In this regard we have synthesized by the method of "molecular construction" (with different combination of two-atomic phenols) and have investigated several new macrocyclic phosphamides bearing asymmetrical aromatic fragments:



Compounds I-VI were investigated in reactions of complexation with transition metals, with sulfur and air oxygen by developed method[4]. Synthesized phosphates and thion-phosphates present perspective objects for supermolecular and synthetic organic chemistry[1]. For obtained macrocyclic phosphates and thion-phosphates antimicrobial activity was founded in 2-4 times higher, than furacilin, but this substances are found to be harmless for E.coli.

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SYMMETRICAL AND ASSYMETRICAL MACROCYCLOARENEPHENYLPHOSPHONITES

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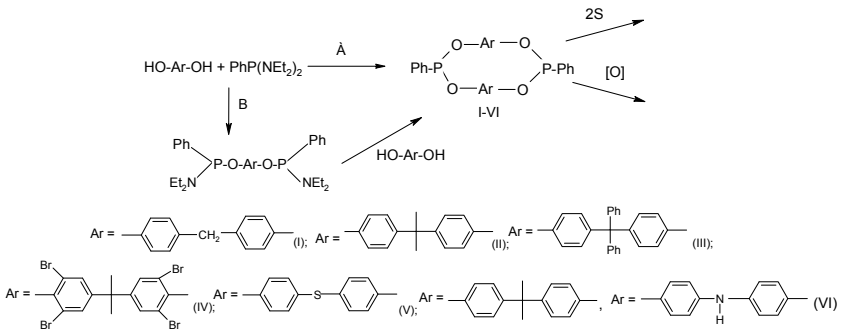
The first representative of symmetrical macrocycloarenephenylphosphonites was obtained by direct synthesis (A) and by method of «molecular constriction» (B) on the basis of two-atomic phenol with hydroxyl groups separated in space, specifically 2,2'-bi(p-hydroxyphenyl)propane (DIAN) and tetraethyldiamide of phosphonic acid[1,2].

Further we have synthesized (A,B) macrocyclic arenephenylphosphonites using different two-atomic phenols. Thus, both symmetrical (I-V) and asymmetrical (VI) by aromatic fragments macrocycloarenephenylphosphonites were synthesized, which under specific conditions were sulfurisized and oxidized:



It has been established, that from P(III) to P(V) change of macrocycle's conformation is observed, accompanied by a corresponding change in the spatial arrangement of phosphorus atoms and the substituents at it.

The possibility of complexaton of macrocycloarenephenylphosphonites synthesized with transition metals was revealed.

Also the impossibility of macrocyclisation with resorcinol and tetraethyldiamide of phenylphosphonic acid were shown.

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NEW ANTIPARASITIC PRODUCTS ON THE BASIS OF AVERMECTIN

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This work is devoted to the development of new antiparasitic drugs on the basis of the products of acylation avermectin anhydrides vicinal dicarboxylic acids. We have selected techniques of production and examined the antiparasitic activity of some acyl derivatives of avermectin.

It is shown that the antiparasitic effect of the product obtained by acylation of avermectin succinic anhydride exceeds by 10-25% the effect of the known drug abermectin. The new drug is low-toxic and in comparison to the well-known drugs this one is a very weak antibiotic that allows you to save microfauna and microflora in the stomach of the animals and humans being treated.

Currently, in order to optimize the compound - the leader (hemisuccinate avermectin) some methods of producing derivatives that belong to different classes of organic compounds (esters, amides, etc.) are being developed. In addition, the technology for hemisuccinate avermectin is being improved in order to achieve solvent recycle, to reduce response time and the amount of succinic anhydride.

AMPHIPHILIC LIQUID CRYSTALLINE DENDRIMERS: NANOSTRUCTURATED AND SELF-ASSAMBLED SYSTEMS.

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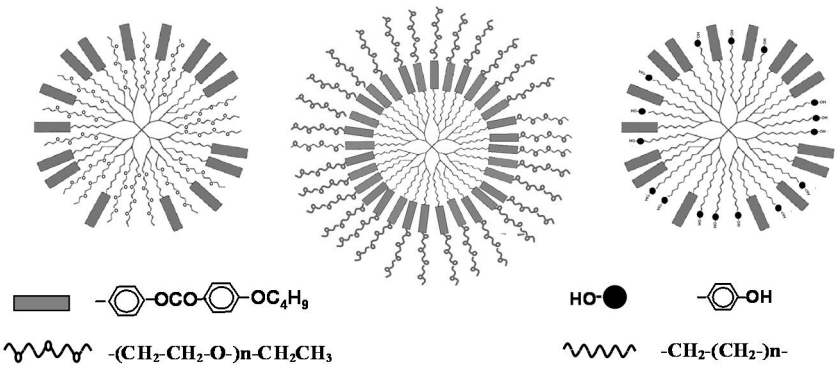
Unusual molecular topology of liquid crystalline (LC) amphiphilic dendrimers combining structural units capable of forming LC mesophases (hydrophobic mesogenic groups) and hydrophilic fragments thus yielding surface-active molecules, causes in recent years an increased interest in studying the processes of "self assemble" of such compounds in the solid phase and at the interface. This interest is due, primarily, to the possibility of obtaining thin-film materials with nanoscale self-organization in a combination with anisotropy of physical properties.

The work presents results of the synthesis and study of new amphiphilic carbosilane LC dendrimers from first to fifth generations of different architectures with terminal mesogenic phenylbenzoate, hydrophobic aliphatic and hydrophilic (phenolic, oligoethyleneglycolic) groups:



Phase behavior, molecular and supramolecular structures of synthesized amphiphilic dendrimers are discussed. The influence of dendrimer molecular organization (generation number, type and nature of hydrophilic groups) on the formation of a monolayer at the water/ air interface and the structure of LB films are considered.

GEM-DIHALOCYCLOPROPANES AS SYNTHONES FOR SYNTHESIS OF ISOXAZOLES

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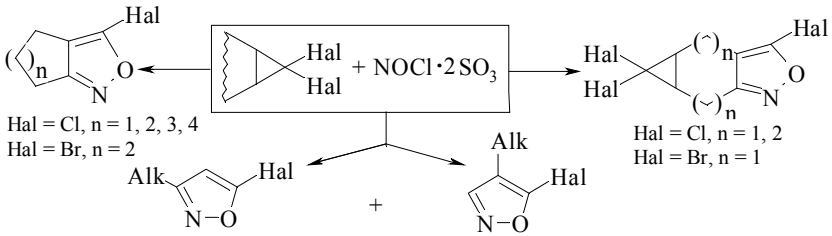
A variety of problems facing modern society require chemical science to create rational technologies. That is why it is important to accumulate theoretical and synthetic knowledge and review it in the light of industrial purposes. One of the goals here is to find synthones and create the data-bases of such compounds. The main requirements for synthones are their availability and ease of conversion into products with valuable chemical or physico-chemical properties. g*em*-Dihalocyclopropanes are among them. Easily accessible, they differ by great structural variety and are used for conversion into other classes of organic compounds.[1-2]

In this work, we used *gem*-dichloro- and *gem*-dibromocyclopropanes as synthones for the synthesis of 5-chloro(bromo)isoxazoles under the action of adduct of nitrosyl chloride with sulfur trioxide.



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This work is supported by the Russian Foundation for Basic Research, project no. 08-03-00707 and by the Presidium of the Russian Academy of Sciences (the program of "Development of Methods for Synthesizing Chemical Compounds and Creating New Materials").

ORGANOALUMINUM CO-CATALYSTS FOR TWO NEW PHENOXYIMINE ZIRCONIUM COMPLEXES (ETHYLENE POLYMERIZATION)

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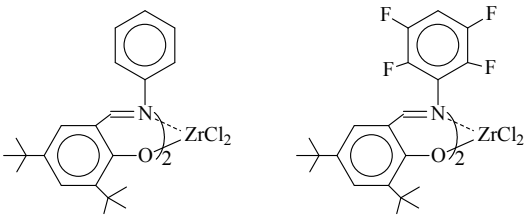
Catalytic properties of two new phenoxyimine (FI) complexes of zirconium:



1 **2**

have been studied in ethylene polymerization with different organoaluminum cocatalysts: commercial polymethylalumoxane containing ~ 35 mol% of trimethylaluminum (MAO (TMA)), MAO released from TMA ("dry" MAO) and "classical" OAC - TMA and triisobutylaluminum (TIBA). Complex **1** exhibits a high activity upon activation with cocatalysts containing aluminum trialkyls (AlR_3), but it is not active with "dry" MAO (A (kg PE/(mol of Zr h atm): ~ 13,000 (MAO (TMA)), 5000 (R = ^{i}Bu), 3000 (R = Me)). Complex **2** is active with MAO (TMA) and "dry" MAO (A ~ 10,000), but under the action of TIBA it shows only a trace activity (A ~ 30). When activated with AlR_3, **1** forms multi-site systems, which give rise to low molecular weight polyethylenes (M_n = 3000-7500) with polymodal GPC curves what is especially pronounced for R = ^{i}Bu. Complex **2** forms high molecular weight polyethylenes (M_n = 170000-300000) with low values of the coefficients of polydispersity (M_w/M_n ~ 2), typical for single-site systems. It is of interest that PE produced by the low-active system **2**/TIBA has the same molecular weight characteristics as PE formed by the highly active **1**/TIBA system. That is, for complex **1** AlR_3 are more effective activators than MAO, while for the fluorinated complex **2** reactions with AlR_3 resulting in the formation of several types of active sites are hindered.

MOLECULAR LOGIC GATES - THE FIRST STEP ON THE WAY TO "CHEMICAL" COMPUTER?

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The modern computers are based on semi-conductor transistors. Reduction of the transistor size (so-called "Moore's law") inevitably comes to physical and technological limits, below which development by "top-down" principle is impossible. Therefore, now new trend in chemistry is growing, which, possibly, will lead to creation of a "chemical" computer (CC) constructed using "bottom-up" approach. CC can be defined as hierarchically organized molecular system in which information processing occurs by means of chemical reactions. Due to this, CC will possess the minimal sizes and the maximal performance.

Creation of CC includes several stages: development and research of the basic working elements - molecular logic gates (MLGs), interconnection of MLGs to create complex circuits where different MLGs could communicate with one another, the organization of an interface - systems for the information input and output, etc.

The first step on a way to CC is already done – many molecular systems, including specially synthesized, capable of performing MLG function, are investigated. In the report the general block-diagrams and principles of MLG functioning, as well as algorithm of MLG designing, will be considered. The examples of various MLGs will be discussed, which can perform logic operations "AND", "OR", excluding "OR" ("XOR"), "INHIBIT", etc., and more complex functions of the half-adder and half-subtractor, based on reversible chemical reactions.

The second step on the way to CC is an integration of individual MLGs into supramolecular ensembles - analogues of microcircuits. It is more difficult task; the main problem here consists in organization of the directional signal transfer from one MLG to another. It is necessary to provide for homogeneity of the input and output signals. In part this problem is solved due to reconfigurability and superposability - unique properties of MLG, unattainable for semi-conductor analogues, when the same molecular system performs various logic operations.

The work is supported by the Russian Foundation for Basic Research (grant 10-03-00751).

A THEORETICAL STUDY OF REACTIONS OF N-HETEROCYCLIC CARBENES WITH ALDEHYDES

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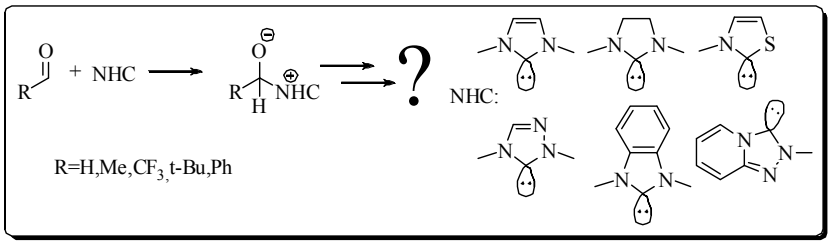
The report will be summarized the results of a quantum-chemical study of the reaction of N-heterocyclic carbene (NHC) with aldehydes (Scheme 1).



Scheme 1.

Various quantum-chemical methods (B3LYP, MP2, MP4(SDQ), CISD(T), basis sets *aug-cc-pVTz*, 6-311++G(*2d,p*)) calculated the geometric and electronic characteristics of the reactants, products, intermediates and transition states.

DIRADICAL MECHANISM OF PERFLUOROCYCLOPROPANES AND PERFLUOROOXIRANES PYROLYSIS

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The time dependences of light absorption intensivety of initial diradical intermediates (λ=250 nm) and secondary difluorocarbene (λ=271 nm) under pyrolysis of the perfluorometylcyclopropane and perfluorooxiranes (C_3F_6O and C_4F_8O) were found using the kinetic spectroscopy method under strictly homogeneous conditions of the free-piston adiabatic compression set-up. The experimental temperature dependences for pyrolysis final products were found by GLC method.

The experimental data were used for determination of the Arrhenius parameters of elementary stages formation and disappearance of the mentioned intermediates. Qualitative agreement energy diagrams for 1+2-cycloelimination of perfluorometylcyclopropane (Fig.1A) and perfluorocyclopropane (Fig.1B) is evidence of the diradical mechanism this process. Analogous results were found under experimental study of the perfluorooxiranes pyrolysis.

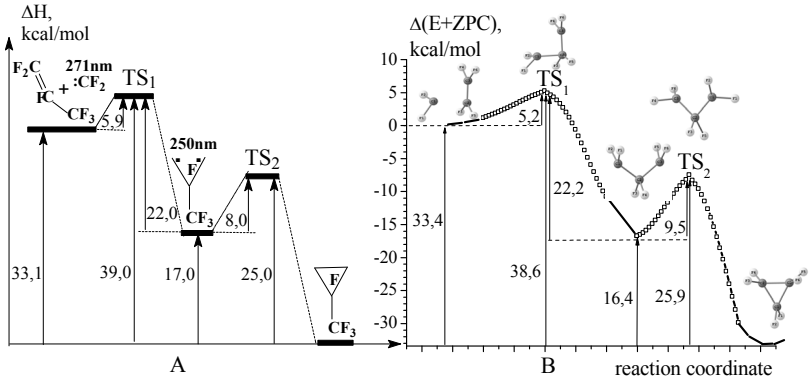

Fig.1. Energy diagrams for 1+2-cycloelimination:
A – perfluoromethylcyclopropane using the results of experimental data working;
B – perfluorocyclopropane using the results of MP2/6-31G* calculations.

SYNTHESIS OF 3- AND 5-DI(TRI)FLUOROMETHYLSUBSTITUTED 1-(β-GLYCOPYRANOSYL)PYRAZOLES

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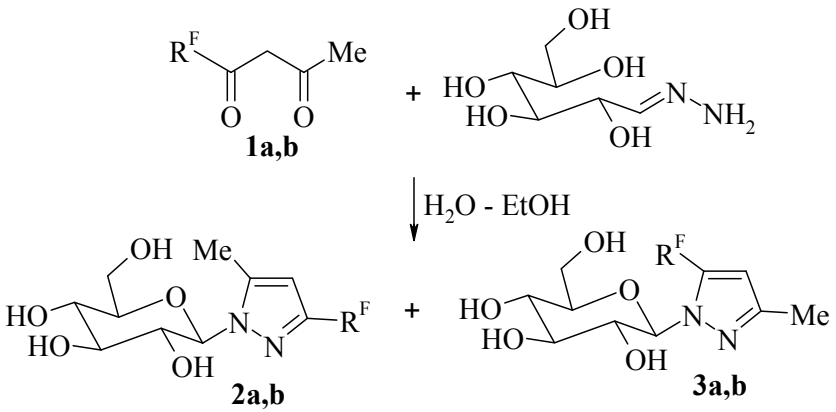
To obtain polyfluoroalkylsubstituted glycosylated pyrazoles we have been used the cyclocondensation of 1,3-diketones **1** with hydrazone glucose synthesized from hydrazine and glycose[1]. The reaction was carried out in a water-alcohol medium at room temperature. We obtained mixture of isomers of **2** and **3**, in which 1-(β-glycopyranosyl)-3-methyl-5-polyfluoroalkyl-1*H*-pyrazole **3** was dominated.



1,2,3: $R^F = HCF_2$ (**a**), CF_3 (**b**)

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NEW RECEPTOR SYSTEMS BASED ON CALIX[4]RESORCINARENES

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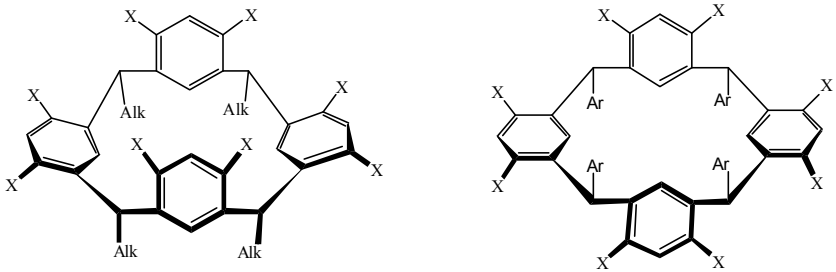
Calix[4]resorcinarenes are convenient base for the design of receptor systems with set number and definite orientation of functional groups immobilized on the hydrophobic matrix.

We obtained new octafunctionalized resorcinarenes **2-4** with triflate, thiocarbamoyl, and alkylaminogroups at the periphery of the molecule. Because of using resorcinarenes **1** in *boat* and *chair* conformations as basic compounds, functional groups included in modified derivatives **2-4**, had different orientation toward each other and to the plane of macrocycle.



boat *chair*

X=OH (**1**); $OS(O)_2CF_3$ (**2**); $OC(S)N(CH_3)_2$ (**3**); $N(C_4H_9)_2$, NHC_6H_{13} (**4**)

The interaction of **1** with trifluoromethanesulfonic acid anhydride was carried out in pyridine at 20-25°C. The reaction of **1** with dimethylthiocarbamoyl chloride was performed in acetone at 50-55°C. The yields of perfunctionalized resorcinarenes **2, 3** were 60-80%. Aminoalkyl derivatives **4** were synthesized by direct amination in microwave reactor CEM «Discover» (50-150 W, 2455 MHz) at 110°C with the yields 45-60%.

The work was supported in part by the Russian Foundation for Basic Research (project no. 09-03-00201a).

SYNTHESIS OF ADAMANTYL-CONTAINING ISOCYANATES

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Organic isocyanates, containing in their composition adamantyl fragment are promising intermediates for the synthesis of biologically active substances, as well as monomers for the synthesis of polymers with improved properties.

As part of our research effective methods for single stage synthesis of adamantly-containing mono- and diisocyanates , as well as amines and urethanes based on them were developed. These methods allow us to obtain the target products in high yield and selectivity, relatively mild conditions without the use of catalysts. At the same time preparation of these substances by other methods used to produce isocyanates is either impossible, or requires multi-step synthesis.

We first derived isocyanates containing within their structure the 1,3 - dimetiladamantyl fragment.

The interaction of 1,3-dehydroadamantane with aliphatic mono- and diisocyanate, aromatic and adamantil-containing isocyanates were investigated. Application of 1,3-dehydroadamantane essentially reduces and simplifies the synthesis, allowing us to produce rare isocyanates containing adamantyl radical in α-position in one stage. For the first time a systematic study of reactions of 1,3-dehydroadamantane with various isocyanates were carried out.

The resulting products can be used to synthesize a wide range of compounds with potential biological activity due to the presence of the reactive groups and the adamantyl radical in the molecule. The main application area of the obtained isocyanates - is synthesis of hydrochlorides of amines based on them. As part of the work an effective alternative method for obtaining hydrochloride 1-amino-3,5-dimethyladamantane (international generic name "Memantine"), which is currently used in medical practice for the treatment of Parkinson's disease, Alzheimer's disease, neurodegenerative diseases, glaucoma, etc was developed.

SYNTHESIS OF BIOLOGICALLY ACTIVE COMPOUNDS ON THE BASIS OF INTERACTION ARYLMETHYLIDENE 3H-FURAN (PYRROLE)-2-ONES WITH N-, S-NUCLEOPHILES

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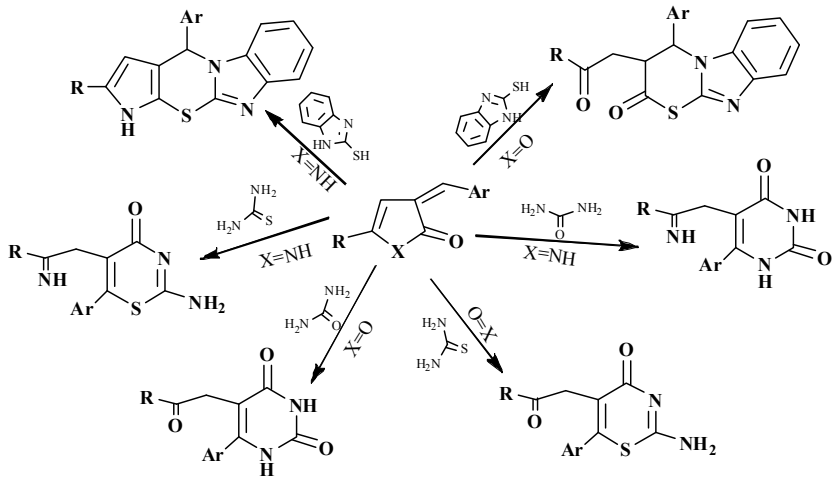
Arylmethylidene derivatives of 3H-furan (pyrrole)-2-ones are of interest as intermediate, which combine the properties of esters and unsaturated carbonyl compounds and can react with substances that have mobile hydrogen atoms. It is known, compounds, which containing in the structure benzimidazole, pyrimidine, thiazine fragments, have wide utilized.

It was studied by us the interaction arylmethylidene derivatives of 3H-furan (pyrrole)-2-ones with 2-mercaptobenzimidazole, urea, thiourea.



It was shown, that in all cases the reaction proceeds with opening of the heterocycle on the position C2-X, against the nature of the heteroatom and leads to formation of different polyheterocyclic compounds. The structure of products was confirmed by spectral dates. A series of previously unknown potentially biologically active substances was obtained.

This work was supported by RF Presidential grant for state support of young Russian scientists № МК-2054.2011.3. and RFBR grant 10-03-00640-a

ADAMANTANE DERIVATIVES IN SUPRAMOLECULAR CHEMISTRY

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The report examines the application of various adamantane derivatives in supramolecular chemistry. Examples of using the compounds of adamantane as "guests" in the structure of the "hosts", as well as the templo commuting agents are given.

The synthesis of various macrocycles - "hosts", linking the cations and neutral molecules is discussed. This is primarily crown ethers, cryptands, sferandy, calix [*n*] arenes, containing in their structure adamantyl radical.

Particular attention is paid to the formation of complexes of α-, β-, and γ-cyclodextrins - "hosts" with various "guests"- adamantane derivatives: amines, acids, esters, amides and other compounds, some of which are medicinal substances. The question of thermodynamic stability of such complexes is discussed.

The use of adamantyl-containing compounds in the formation of supermolecules - gathering and synthetic self-assembling systems such as catenanes, pseudorotaxanes and rotaxanes; gelicates is shown. The considerable amount of adamantyl group allows to use adamantane derivatives to create a blocking group in the structure of pseudorotaxanes and rotaxanes.

Information on the synthesis of adamantyl-containing macromolecular compounds - dendrimers, as well as polypseudorotaxanes and polyrotaxanes is provided.

The examples of a variety of supramolecular devices, such as devices for converting light, photochemical and electrochemical sensors, molecular electronic devices: switches, wires, rectifiers, molecular machines based on catenanes and rotaxanes are studied.

In conclusion, the chemical reactions of **[**3.3.1**]**propellane to obtain various adamantane derivatives used in supramolecular chemistry: monomers to obtain cyclodextrin supramolecular polymers, pseudorotaxanes, rotaxanes, and others are given.

POLYHEDRAL EXPANSION REACTIONS IN CLOSO-NONABORATE ANION $[B_9H_9]^{2-}$ BY INTERACTIONS WITH VIIIB-METALS COMPLEXES

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Results of experimental investigations of polyhedral expansion reactions in $[B_9H_9]^{2-}$ anion are discussing in the report. Similar processes are representative for structurally-nonrigid higher polyhedral boron hydrides from carboranes [1], but for $[B_9H_9]^{2-}$ anion only one example alike processes is known [2].

We have success to made polyhedral expansion reactions by interactions of $[B_9H_9]^{2-}$ anions salts with VIIIB-metals complexes.

Particularly using this technique we have made syntheses boranes of metals with polyhedral cage $[MB_9H_9]$ when organic ligands (acetonitrile, triphenylphosphine, acetylacetone, cyclooctadienyl etc.) are coordinated by the metal atom.

Products when chelatation of metal is possible or when there is additional π-binding appears are most stable. Any peculiarities of metals including in nine-vertexes cage processes behavior is noted.

Also it is shown that reaction with Co and Rh complexes result in formation of both possible isomers. At the same time, are generating boranes of metals both with metal in vertex and with metal in equatorial position. When temperature increasing (> 60 ^{0}C) rearrangement with exceptionally apical form formation make place.

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THEORETICAL STUDY OF UNIMOLECULAR GAS-PHASE DECOMPOSITION MECHANISMS OF NITROALKANES

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In present time there is numerous kinetic data regarding gas-phase unimolecular decomposition of nitroalkanes. Nevertheless, availability of experimental data does not allow to favor one mechanism. This can be explained by contribution of several simultaneously proceeding processes to experimentally obtained rate constant. Therefore, theoretical estimation of activation energies and rate constants using modern methods of quantum chemistry are of great interest.

Values of activation enthalpies for four main decomposition mechanisms: hemolytic C-N bond rupture, β-elimination of nitrous acid, nitro-nitrite rearrangement and formation of aci-form were calculated employing DFT levels of theory together with precise G3, G4, G3B3, CBS-QB3 composite techniques and hi level QCISD, CCSD *ab initio* methods. Isomerization reactions were studied till formation of simple compounds. Rate constants for homolytic bond cleavage reactions as well as activation enthalpies and entropies were found by localizing transition state corresponding to maximum energy on free energy surface. Theoretically estimated kinetic data was used in discussion of competitive decomposition reaction pathways.

QUANTUM-CHEMICAL DESIGN OF TEMPLATE SYNTHESIS OF MACROCYCLIC METALCOMPLEXES INTO GELATIN-IMMOBILIZED MATRIX SYSTEMS

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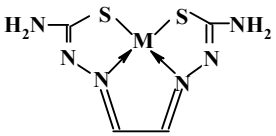
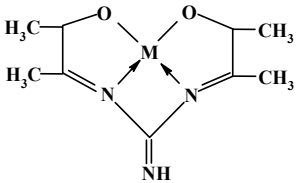
The results of quantum-chemical calculations of molecular structures of a series of **(545)-**, **(555)-**, **(565)-**, **(656)-**, **(666)-**macrotricyclic and **(5555)-**, **(5656)-**macrotetracyclic metalcomplexes of 3*d*-element ions M(II) with (NSSN)-, (NOON)- and (NNNN)-coordination to complexator, that really or in principle, may be formed at template synthesis in the M(II) ion– N,S-containing organic compound– mono- or dicarbonyl-containing compound into metal(II)hexa-cyanoferrate(II) gelatin-immobilized matrices (M = VO, Mn, Fe, Co, Ni, Cu, Zn), among their number of **I (555), II (545)** and **III (5656)** types, by **DFT B3LYP 6-31G(d)** method and Gaussian03 program have been generalized.



I



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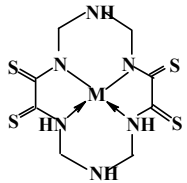

III

Coordinates of all atoms having in the complexes, inter-atomic distances, valence and torsion angles, and, also, their electric moments of dipole and standard thermodynamic parameters have been calculated. The series of examples of structure of such complexes have been presented. It has been noted that complexes of **(545)**, **(555)** and **(5555)** types are practically plane whereas ones of all other types, are to some extent non-coplanar.[1-3]

Quantum-chemical calculations were carried in the Kazan Branch of Supercomputer Centre of RAS.

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NEW FLUORINE-CONTAINING TETRAKETONES

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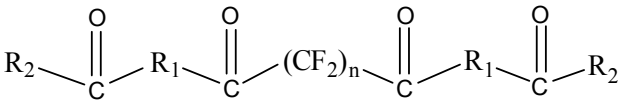
Fluoroorganic polycarbonyl compounds are initial substances for preparation of peroxide[1] and heterocyclic compounds, besides they have wide spectrum of biological activities that show their exploitability as using qua pharmaceuticals for curing of different diseases[2].



n=4,5,6

R_1= CH_2,$CHCH(CH_3)_2$,$CHCH_2CH_3$

R_2=Me, Ph, t-Bu

One of possible ways for preparation of polyfluorinated tetracarbonyl compounds is a condensation reaction. However for above-mentioned polyfluorinated structures emerged a necessity of searching new conditions for realization of the process[3].

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THE RESEARCH OF RELATIVE VOLATILITY ISOLINES IN THREE-COMPONENT SYSTEMS WITH BIAZEOTROPIC BINARY PARTIAL

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The changing of components relative volatility (α) of base mixture is traditionally considered for estimation of rectification separation possibility of difficult mixtures in the presence of additional substances with different volatility. We [1] have offered to analyze the features of relative volatility isolines (α-lines) course to all pairs of components.

In the present work by means of modern software the mathematical models of vapor-liquid equilibrium in the triple systems formed by biazeotropic binary partial (butyl propionate (BP) – propionic acid (PA), or butyl butyrate (BB) – butyric acid (BA), or isobutyl acetate (IBA) – acetic acid (AA)) and additional substances: acetophenone (AF), mesityl oxide (MO), methyl ethyl ketone (MEK), acetone (A) – are received. As carbonic acids are inclined to dimerization and even polymerization in vapor phase, its nonideality is considered in computing researches.

For systems BP–PA–AF, BB–BA–AF, IBA–AA–AF, BP–PA–MO, BB–BA–MO, IBA–AA–MEK, IBA–AA–A the set of diagrams with nottrivial course of relative volatility isolines which are projections of α-surface characterized by availability of extremum of different type (minimum, maximum, minimax) is revealed.

The offered approach allows predicting the quality of products of extractive and reextractive rectification that confirms by calculations of these processes.

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The work is carried out at financial support of the Russian Fund of Basic Researches (the project № 11-03-00295a).

THERMODYNAMICS OF COMPLEX FORMATION REACTIONS OF 18-CROWN-6 ETHER WITH SOME AMINO ACIDS IN WATER-DIMETHYLSULFOXIDE MIXTURES

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As a prosecution of our studies on the influence of nature and composition of solvents on the thermodynamics of complex formation reactions, we present the results of the effects of water-dimethylsulfoxide mixed solvents (H_2O-DMSO) on the stability and energetics of molecular complex formation reactions of 18-crown-6 ether (18C6) with D,L-alanine (Ala) and glycine (Gly).

Thermodynamic parameters of complex formation reactions of [Ala18C6] and [Gly18C6] complexes (Log$K$, $\Delta_r H$, $T\Delta_r S$) in H_2O-DMSO mixed solvents at X_{DMSO} = 0,0 ÷ 0,3 molar fraction were obtained from calorimetric titration experiments carried out by means of the TAM 2277 (Thermometric, Sweden) and TAM III (TA Instruments, USA) microcalorimeters at T = 298.15K.

In water and in its mixtures with DMSO, the [Ala18C6] complex is less stable than [Gly18C6]. Possibly, the smaller stability of [Ala18K6] is caused by the presence of the $–CH_3$ group of Ala which is a steric obstacle to the interaction of the amino acid functional groups with the macrocyclic ring taking place. Transition from pure water to H_2O-DMSO solvent at X_{DMSO} = 0,3 is accompanied by the increase of LogK [Ala18C6] from 0,32 to 1,58, and LogK [Gly18C6] from 0,63 to 1,92. The increase of the exothermicity of formation reactions of [Ala18K6] and [Gly18K6] from X_{DMSO}=0 to X_{DMSO}=0.3 is approximately 20 kJ/mol.

The analysis of solvation characteristics of reaction formation participants of [Ala18K6] and [Gly18K6] complexes has shown that the increase of exothermicity of reactions with increasing DMSO content in solvent is to be ascribed mainly to the changes in the 18C6 solvation state.

This work was supported by the program "Development of Scientific Potential of Higher School (2009-2010)" projects 2.1.1/5594, 2.1.1/5593, and the Federal Program "Researchers and Scientific-Pedagogical Staff of Innovation's of Russia" for 2009-2013 (State number 02.740.11.0253).

THE ORGANOCHLOROGERMANES SYNTHESIS THROUGH THE DICHLOROGERMYLENE

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Authors' investigation results of thermal reactions of $GeCl_2$ generated in $GeCl_4 – Si_2Cl_6$ and $GeCl_4 – Ge$ systems with aryl-, alkyl- and alkenylchlorides, methyl-substituted benzene and unsaturated compounds have been summarized. Possible routes of organochlorogermane formation discussed.

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CATALYTIC DIRECTED SYNTHESIS OF CHIRAL TERPENOPHENOLS

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Terpenophenolic compounds are widely used as antioxidants of organic materials, as initial components in synthesis of antiseptic preparations, insecticides, fragrant substances. Last decades the significant attention has been given to chiral substances which are of great importance for medicine. For this reason researches of chiral phenolic antioxidants in racemic and enantiomeric forms gain in strength. Usually terpenophenols obtains by alkylation of phenols with various terpenes at presence of acid catalysts. However propensity of terpenes to skeletal rearrangements in the acid conditions, increasing variations of alkylation products, brings additional complexity in choice of selective catalysts for the given reactions. Therefore search of effective industrial catalysts for terpenophenols obtaining is an actual problem.

In the report results of studying of laws and optimization of conditions of selective alkylation of phenols two-nuclear phenols and naphthols by terpenoids at presence of various catalysts will be presented. As catalysts aluminium phenolates and alkoxides, bimetallic alkoxides, heterogeneous acid catalysts have been investigated.

Ways of direction regulation of alkylation of phenolic compounds by monoterpenoids are as a result established. Selective methods of directed synthesis of various structural type semisynthetic terpenophenols which are perspective antioxidants and stabilizers of different purpose are developed. Chromane type ethers and optically active terpenophenols are obtained at alkylation of phenol by pinenes. Preparative resolution of salicylic aldehydes and also terpenophenol containing isobornyl substituent on enantiomers is carried out.

The study was carried out under a financial support of the Russian Academy of Sciences (grant no. 09-П-3-1010) and the Russian Foundation for Basic Research (grant no. 10-03-01129-a).

COMPLEX FORMATION OF COPPER(II) AND COBALT(II) CHLORIDES WITH (1*H*-BENZO[D]IMIDAZOL-2-YL) (3,3-DIMETHYL-3,4-DIHYDROIZOQUINOLINE-1-YL)METHANON

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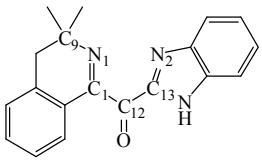
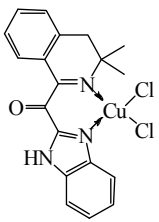
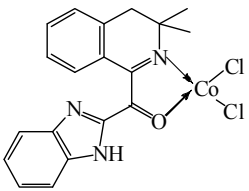
1*H*-benzo[d]imidazole-2-yl)(3,3-dimethyl-3,4-dihydroizoquinoline-1-yl)methanon (L) and its complexes $[CuLCl_2]$ (I) and $[CoLCl_2]$ (II) were synthesized and investigated. The structure of molecule L is defined by X-ray method on single crystals. It was established that in a free (non co-ordinate) state L crystallizes in the form of an isomer in which the chemical bonds C(1)=N(1) and C(12)=O are in *trans*-position relating to the exo-cyclic bond C(1)-C(12).



Dihydroizoquinoline and benzoimidazole fragments of the molecule L lie approximately in mutually perpendicular planes. Bond lengths N(1)=C(1) (1.278(3)Å), C(1)-C(12) (1.526(3)Å), C(12)-C(13) (1.451(4)Å), N(2)=C(13) (1.327(4)Å) and C(12)=O (1.218(3)Å) testify about insignificant π-conjunction. This also correlates with the position of ν(C=O) in the IR-spectrum of L (1681 sm^{-1}).

Complexes I and II were synthesized from ethanol. According to IR-spectroscopy (ν(C=O) 1742 (I) and 1640 (II) sm^{-1}) their structures differ from each other.





SYNTHESIS OF POLYETHERISOCYANURATEDIMETHYLSILOXANES USING MACROINITIATORS OF ANIONIC NATURE

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Obtaining dimethylsiloxaneuretane copolymers is an important problem of polymer science and technology. Such polymers possess gas-separating properties and biocompatibility. Polyaddition of dimethylsiloxane cycles to a macroinitiator and the development of narrow-meshed structures is a new trend in the field of synthesis and research of organosiloxane polymers, it allows to change the technology of their obtaining and to find new spheres of their usage.

Hydrolytically stable polymers were synthesized on the basis of 2,4-toluenediisocyanate, octamethylcyclotetrasiloxane and block copolymer of propylene and ethylene oxides which contain potassium alcoholate and hydroxyl groups. The ratio of initial agents and the influence of temperature conditions on polymer properties were investigated.

It was established that when aromatic isocyanates, octamethylcyclotetrasiloxane and block copolymer of propylene ethylene and oxides interact a molecule of aromatic isocyanate is joined to potassium alcoholate chain of the block copolymer, then the end O- polyisocyanate chain starts the polyaddition of octamethylcyclotetrasiloxane.

The leading role of isocyanurates in the formation of cross-links of three-dimensional network of synthesized polymers was proved. It was shown that if there is substantial excess of isocyanate the polyisocyanurates being a component of permeating polymer networks are formed.

The synthesized polymers were tested as gas-separating membranes for biogas. It was determined that the developed polyetherisocyanuratedimethylsiloxane polymers are capable of sorbing polar molecules of carbon dioxide and of leaking out nonpolar molecules of methane.

The possibility of using synthesized polymers as solid-state active media of configurable lasers was shown.

QUANTITATIVE DETERMINATION OF INTERACTION CHARACTERISTICS OF N,N-DI(2-CARBOXYETHYL)-3,4-XYLIDINE WITH SURFACTANTS

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In the present work quantitative characterictics of interaction of N,N-di(2-carboxyethyl)-3,4-xylidine **(**KDK) at different surfactant concentrations in aqueous solutions (anionic surfactant - sodium dodecylsulphate (SDS), cationic - cetyltrimethylammonium bromide (CTAB)), including in the presence of zinc(II) sulphate (C=1.4 g/l) have been obtained. Previously we found that zinc sulfate increases fluorescence of protonated and unprotonated KDK in the presence of CTAB and protonated reagent in SDS medium, although zinc ions do not form complex with KDK.

Critical micelle concentration (CMC) of these surfactants have been determined in the presence of KDK and zinc salt from the changes in the absorption spectra. It is found that reagent interaction with surfactants occurs at surfactant concentrations below its CMC.

Binding constants between KDK and micelles for quantitative estimation of reagent interaction with surfactant micelles, including in the presence of zinc(II) sulphate, have been calculated from data obtained by fluorometric method [1].

Absorbance and fluorescence spectra of solutions were made with «Fluorat-02-Panorama» spectrofluorimeter.

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This work was carried out at equipment of CCU «Ural-M» and was supported by grants of Presidium of UB RAS (program 09-P-3-1022) and Ministry of Education and Science of Russia (GK 14.740.11.0364).

A NEW METHOD OF STUDING PROPERTIES OF THE PROTOTROPIC FORMS OF ORGANIC ACIDS IN DILUTED SOLUTIONS

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Information about ionized and solvated volume represents a particular significance in biochemistry for assessment pharmacodinamic parameters *in vivo*[1].

In this work a new method of study of acidic-basic equilibria of different classes of organic compounds in diluted solutions is developed, using experimental facts about their molecular volumes defined by ionization ratio.

A Brensted-Lowry theory is used as a theoretical fundamental, based on that five particles are formed in dissociation process: A^-, H_3O^+, OH^-, AH, H_2O.

It is supposed that observed molecular volume V_S of compound under study in solution depends on its ionization ratio χ:

$$V_S = \chi \cdot V_i + (1 - \chi) \cdot V_0,$$

V_i and V_0 – volumes of ionized particles A^-, H_3O^+, OH^- and AH,H_2O – volumes of solvated particles. A value of observed molecular volume in solution calculated as:

$$V_S = \frac{M}{N_a} \cdot \left(\frac{1}{\rho w} - \frac{1}{\rho_s w} + \frac{1}{\rho_s} \right)$$

ρ – is a density of solution at 20°C; ρ_s – is a density of water at 20°C; w – is a mass content of the dissolved compound, M – its molecular weight, N_a – Avogadro constant.

For assessment of validity of supposition concerning the correlation ionization ratio χ *vs*. observed molecular volume V_S a set of measurements were performed. Dependences of density and acidity of many organic acids *vs*. their mass content in solution were registered. Also an ionization ratio was directly and independently determined by spectrophotometric method.

The analysis of the above experimental dependences allows one to conclude that the above supposition is valid. The obtained values of thermodynamic dissociation constants for organic compounds under study differ from corresponding values in literature[1,2].

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ELECTRON-RICH d-ELEMENTS 1,10-PHENANTHROCYANINES: SYNTHESIS AND INTERACTION WITH *DNA*

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We worked out the method of synthesis and examined coordination compounds of a new structural cyanine class – *electron-rich* supramolecular 1,10-phenanthrocyanines of transitional metals with definite electron configuration – **d^8 Ni(II), Pd(II), Pt(II); d^7 Co(II); d^6 Rh(III); d^3 Cr(III) and d^{10} Zn(II), Cd(II), Ag(I).** These compounds are *glassy* in solid state and *colloidal* in solutions. The synthetic methods are based on *metal-promoted* **direct C*H*–C*H-coupling*** of 1,10-phenanthrolines, coordinated to transition metal ions. 1,10-Phenanthrocyanines of d-elements are chromophoric complexes with cations: **$[A_2M^{n+}$(μ-1,10-phencyanine)$M^{n+}A_2]^{2n+}$,(N-N)M^{n+}(μ-1,10-phencyanine)M^{n+}(N-N)$^{2n+}$, $[(N\text{-}N)_2M^{n+}$(μ-1,10-phencyanine)$M^{n+}(N\text{-}N)_2]^{2n+}$** and *electron-rich* bridging 1,10-phenanthrrocyanine ligands **(μ-1,10-phencyanine)** with valence-isomeric, tautomeric forms of dihydro-bi-1,10-phenanthroline **C–C** dimmers.

Electron-rich 1,10-phenanthrocyanine complexes have more complicated C–C dimmer binuclear structure and specific *electron-rich* chromophoric fragments composition in comparison to 1,10-phenanthroline precursors, that is characterized by advanced affinity to polymeric substrates, as well as *redox*-sensitivity.

Complexes are expected to have high selectivity in binding biological targets, including *DNA* and to participate in *redox*-processes. It was determined, that *DNA* binding to 2,9-dimethyl-1,10-phenanthrocyanine Pd(II) complex leads to *stack-looking* supramolecular structure formation. Unique physic-chemical properties allow to attribute these complexes as promising pharmaceutical agents of a new generation, that forms templates with *DNA*, inclinable in biological processes penetration, that provides *redox*-mediated antibacterial, antiviral and antitumoral effect.

The work is fulfilled with RFFI support (project № 04-03-32932) and departmental specific program “High School Scientific Potential Development” RNP.2.1.1.1277.

SYNTHESIS OF POLYNUCLEAR HETEROCYCLIC COMPOUNDS BASED ON THE DERIVATIVES OF 9,10-ANTHRAQUINONE

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The general approaches based on intramolecular cyclization of the derivatives 9,10-anthraquinone of the required structure polynuclear heterocyclic compounds (PHC) are worked out. PHC, containing angular-annelated azyne cycle, are prepared in acid-catalyzed reaction of 1-aminoanthraquinone with aldehydes or kethones, which are capable to crotonate condensation[1].

Angular- or linearcondensed pyrane- or pyrrole- cycles are obtained in the intramolecular cyclization of ethynylsubstituted anthraquinones, containing hydroxy- and aminogroup in ortho-position[2]. By the similar way β-anthraquinonylacrylic acid is able to form PHC, containing pyrane or azyne cycle.

The salts α-aminoanthraquinone containing ortho-alkyl substitute (methyl-, benzyl- and etc.), under conditions of homolytic process are decomposed, but azo-group is preserved. This reaction leads to the derivatives of [2,1-*d*]pyrasole[3]. Perycondensed PHC synthesis are based on the inner-molecular cyclization with participation of carbonyl group on the one hand and containing heteroatom group which is in the position one on the other hand.

The derivatives of anthra[1,8-bc]pyrole are obtained with thermolyse (200-250^{o}) of 1-N,N-dialkylaminoanthraquinone in polar solvents[4,5]. Isomeric anthra[9,1-bc]pyrroles may be obtained by means of the reduction of 1-aroyl-9-anthraquinoneoxymes or reduced amination of 1-aroylanthraquinones by means of Leykhart-Vallach reaction[6].

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Zr-CATALYZED REACTION OF α-OLEFINES WITH Et_3In

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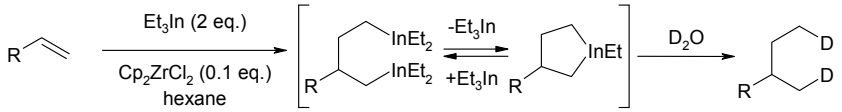
Carbometallation of alkenes and alkynes is a convenient method for the formation of carbon-carbon bond. Catalytic carbomagnesiation have found wide application in synthetic organic chemistry. Zr-catalyzed interaction of alkynes and alkynes with alkyl derivatives of magnesium and aluminum is complex and, depending on the conditions proceeds as carbometallation, cyclometallation or hydrometallation. In 1980, the reaction of catalytic cyclomagnesiation of α-olefins with Et_2Mg was found. The phenomenon of cycloalumination catalytic cyclomagnesiation of α-olefins with Et_3Al was observed for the first time in 1989. At the same time, Cp_2ZrCl_2 catalyzed reaction of Et_2Zn with α-olefins gave only products of carbometallation. Thus, the nature of the metal plays a significant role in this reaction. In order to develop new methods of synthesis organoindium compounds, as well as studying the effect of the nature of the metal on the product ratio of carbo-and cyclometallation, we investigated the reaction Et_3In with α-olefins in the presence of catalytic amounts of Cp_2ZrCl_2.



R = *n*-C_9H_{19} (a), *n*-C_6H_{13} (b), $PhCH_2$ (c)

1a (84%)
1b (67%)
1c (81%)

It was established that the reaction of α-olefins (1-octene, 1-undecene, allyl benzene) with 2 equivalents of Et_3In in the presence of Cp_2ZrCl_2 (10 mol. % to the olefin) in hexane at 40 ^oC for 6 hours gives after deuterolysis dideuterium substituted hydrocarbons **1a-c** in high yield. When using 1 equivalent of Et_3In, the yield of **1a** decreased to 43% that indicates the equilibrium between 2-alkyl-1,4-diindiumbutane and indiumcyclopentane. Thus, we carried out catalytic cycloindination of α-olefins for the first time.

PECULIARITIES OF "HEPTACYCLIC" REACTIONS OF 1,5-DIKETONES WITH HYDROGEN SELENIDE

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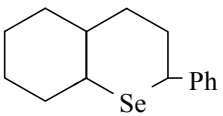
In the course of the reaction of 1-phenyl-3-cyclohexanonilpropane-1-one and 1-phenyl-3-cyclopentanonilpropane-1-one with hydrogen selenide in situ in the medium of acetic and hydrobromic acids or 10-11 N solution of hydrogen chloride in methanol, the process does not stop on the stage of selenopyrans formation, the selenopyrylium salts being produced. The cyclization of the selenocyclohexanes was only supposed in such conditions of reaction[1].

When conducting a similar reaction in the ethereal solution of hydrogen chloride, after the salts of 2-phenyl-5,6-tetramethyleneselenopyrylium being separated, the ethereal extracts have been analyzed by means of gas chromatography/mass spectroscopy method. As a result, the composite mixture of products was found to possess the signals of two isomers 2-phenyl-5,6-tetramethyleneselenocyclohexane 1 (one isomer as admixture: less than 0,7 %), two isomers of dehydroselenodecalin 2, three isomers of 2-phenyl-10-chlorine-seleniumdecalin 3, which can be formed in case of joining a hydrogen chloride molecule to the corresponding 4H-selenopyran and some other selenium-containing compounds, their structure having been failed to determine.



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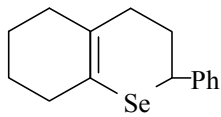

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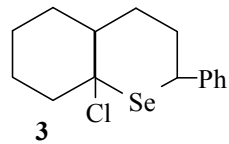

3

It should be noted that formation of α-chlorine derived selenocyclohexanes while cyclization of glutaric aldehyde at low temperatures was the basic process.

The conditions of the reaction under investigation are referred to in the RF patent.

Thus, for the first time the first representatives of a new class of heterocyclic compounds – selenodecalins – have been identified.

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METHODOLOGY FOR THE SYNTHESIS OF PHOSPHINIC PEPTIDES

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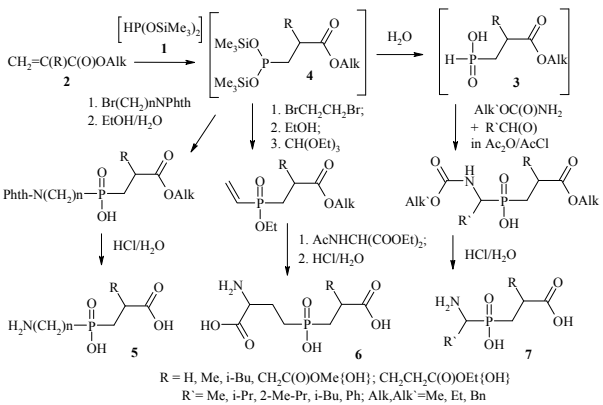
Phosphinic pseudo-peptides, an important class of protease inhibitors, are peptidic isosters containing the chemically stable phosphinic moiety $P(O)(OH)CH_2$ which mimics the transition state of tetrahedral geometry of scissile peptide bond during enzymatic hydrolysis[1]. Known method for the construction of phosphinic acid analogues of peptides usually consists in the synthesis of N-protected aminoalkylphosphonous component of pseudo-peptide followed by the addition to acrylates and formation of desired pseudo-peptide molecules.[2] However, the need of protection and deprotection for N and P atoms of P^{III} - building blocks leads to complication and lengthening of common process.[2]



We propose a new methodology for the synthesis of pseudo-dipeptides with the *reverse construction* of desired molecules,[3,4] consisting in the addition of the bis(trimethylsilyl)hypophosphite **1** *in situ* to corresponding α-R-substituted acrylates **2** and the formation of phosphonous acids **3** containing structural isostere of aminoacid, or its silyl esters **4** followed by the addition of aminoacid function. The results of study of the synthesis of pseudo-γ-aminobutanoyl- **5**, and pseudo-γ-glutamylpeptides **6**, and pseudo-α,α`-dipeptides **7** in according to the proposed methodology are discussed.

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COHERENT EFFECTS IN ELECTRON TRANSFER REACTIONS IN THE MODIFIED ZUSMAN'S APPROACH

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As is known, the Zusman's model[1,2] of theory of electron transfer in a polar solvent, does not account for coherent effects with the nuclear degrees of freedom, although the evolution of electronic degrees of freedom is considered coherently. This disparity essentially limits the applicability of this approach in the study of phenomena, where it is necessary to consider both types of coherence. It has recently been pointed out the principle possibility of such modification[3] of the Zusman's stochastic approach, in which the completely coherent description is possible.

In this paper, in the frames of the modified stochastic approach, the reaction of the photoinduced electron transfer in the environment polar solvent has been considered. Coherent passage regime of crossing point of electronic terms has been studied.

The proposed approach is also used to study the influence of magnetic field on quantum yield of photoinduced charge separation and is the straight continuation of the previous article[4]. In this paper, the so-called, Δg – mechanism was examined[5]. The comparison with results obtained in the Zussman's model (incoherent dynamics) was fulfilled. The values of parameters that lead to maximal difference between these models have been determined.

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THERMAL REARRANGEMENT OF THIO- AND SELENOPYRYLIUM SALTS

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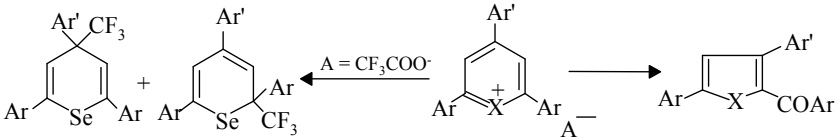
4H-(Thio-, seleno)pyrans and thiopyrilium salts are known to be oxidized into the corresponding aroylfurans, -thiophenes, and -selenophens[1-3]. Besides, when analyzing pyrylium, thiopyrylium, and selenopyrylium perchlorates by the GC-MS method, we have found that the compounds under analysis mass spectra and retention times on the chromatogram are completely identical to those of aroylselenophens, -thiophenes, and -furans[4].

Seleno(thio)pyrylium perchlorates applied to alumina are found to transform into the corresponding aroylselenophens and -thiophenes on heating to 300 °C in the inert atmosphere[5].

It should be noted that the reactions with selenopyrylium salts are slightly more selective than those with thiopyrylium salts. When using the corresponding pyrylium perchlorates, aroylfurans in the individual state were not isolated.

Heating selenopyrylium trifluoroacetates in the presence of an adsorbent gives trifluoromethylselenopyrans.



Selectivity of 2(4)-(trifluoromethyl)-2,4,6-triarylselenopyrans formation is the highest if heteroaromatic cations with electron donor substitutes in heterocycle C_2 and C_6 positions of are used.

Thus, the direction of the reaction depends on the nature of the anion, substitutes of heteroaromatic cation and heteroatom.

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SYNTHESISG THE FIRST REPRESENTATIVES OF NEW SERIES OF HETEROCYCLIC COMPOUNDS – 7,8-BENZO-3,4,4A,5,6,10B-HEXAHYDROSELENOCHROMENE

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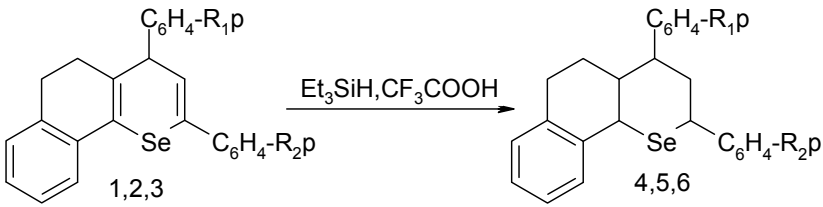
For the first time 2,4-diaryl-7,8-benzo-3,4,4a,5,6,10b-hexahydroselenochromene were synthesized by us from 2,4-diaryl-7,8-benzo-5,6-dihydro-4H-selenochromene using method of ion hydrogenation. The reaction was carried out in the presence of trifluoroacetic acid, the latter being a protoning reagent and solvent.



1,4 R_1=R_2=H; 2,5 R_1=H, R_2=Cl; 3,6 R_1=Cl, R_2=H

As a result, 2,4-diaryl-7,8-benzo-3,4,4a,5,6,10b-hexahydroselenochromenes **4, 5, 6** have been synthesized in 88%, 80% and 82% yields, respectively, the structure of the obtained compounds was determined by GC-MS method, ^{1}H NMR spectrometry and elemental analysis.

While analyzing the compound **4** by means of the GC-MS method, it was found out that hydroselenochromene exists in the form of two isomers (a molecular ion has m/z = 404, for Se^{80}) which are formed in of 44,2 % and 44,5 % yields respectively (detemined by chromatography).

While analyzing ^{1}H NMR spectrum of 2,4-diphenyl-7,8-benzo-3,4,4a,5,6,10b-hexahydroselenochromene **4**, two doublets at 4,61 and 4,50 ppm were ascertained to possess constants of spin-spin interaction (10 and 14 Hz, correspondingly), this proving axial-axial interaction of protons. In this case the two doublets overlap the other signal pointing to the fact of axial-equatorial reaction.

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INFLUENCE OF MOLECULAR WEIGHT AND CHARGE DENSITY ON REGULARITIES OF FLOCCULATION WITH BINARY COMPOSITIONS OF CATIONIC POLYELECTROLYTES

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Development of approaches for task-oriented choosing of chemical structures and molecular-mass characteristics of polyelectrolytes with high flocculation ability is a very actual task. Using of combined reagents, for example two different polyelectrolytes, allow to find additional possibilities to increase the efficient control of the sedimentation and aggregation stability of the model and real dispersed systems.

Influence of molecular weight, charge density of polyelectrolytes, an order of polyelectrolytes addition on rate of sedimentation, size, density, form and size distribution of floccules of model and real dispersed systems were studied using a set of physicochemical methods. Samples of cationic polylectrolytes with different molecular mass based on [2-(methacryloyloxy)ethyl]-thrimethylammonium methyl sulfate were synthesized via atom transfer radical polymerization and conventional radical polymerization. Dispersions of clay, ochre and iron oxide were using as model dispersed systems.

From results of research it is possible to note that there is the expressed influence of order of polyelectrolytes addition into dispersion. Rate of sedimentation of different dispersions can be increased when two polyelectrolytes with definite molecular weight and charge density are adding synchronous in 2-4 times. Moreover turbidity of supernatant can be decreased on 40-50 %. We believe that more difficult mechanism of flocculation is demonstrated .

The study was supported by grant of the President of the Russian Federation for support of leading schools (project 5459.2010.3)

PHENYL-SUBSTITUTED PLANAR BINUCLEAR PHTHALO- AND NAPHTHALOCYANINES: SYNTHESIS AND INVESTIGATION OF THEIR PROPERTIES

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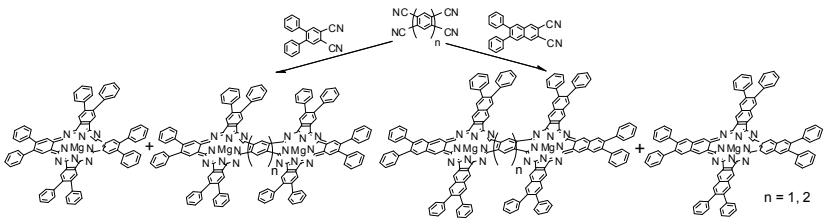
The presence of absorption in the near IR region determines the interest to the binuclear phthalo- and naphthalocyanines with extended π-conjugation system. In the present work two main approaches to the expansion of π-system were investigated: the expansion of the aromatic bridge and the expansion of the peripheral π-system. The pyromellitonitrile and naphthalene-2,3,6,7-tetracarbonitrile were used to synthesize the macroheterocycles with benzene and naphthalene bridges respectively. 1,2-Dicyano-4,5-diphenylbenzene and 6,7-diphenylnaphthalene-2,3-dicarbonitrile, which were obtained using Suzuki reaction, were chosen as a second component in cyclization.



During the expansion of peripheral π-system the binuclear naphthalocyanine complexes shows the 100 nm bathochromic shift of absorption band in comparison with phthalocyanine analogues. The shift of absorption band to the near IR region is observed during the transition from naphthalene to benzene ring. Thereby the intensive absorption in the near IR-region and about 200 nm red shift of the Q-band for the planar binuclear phthalo- and naphthalocyanine complexes in comparison with their mono-analogues was found. This absorption achieves 960 nm in the case of the planar binuclear naphthalocyanine magnesium complex sharing a common benzene ring. Spectroelectrochemical measurements showed the thermodynamic reversibility of the redox properties. The "brick-wall" arrangement of the macroheterocycles was investigated using the ROESY NMR and AFM methods.

POLYNUCLEAR OLEFIN-CARBOXYLATE PALLADIUM COMPLEXES: SYNTHESIS AND TRANSFORMATIONS

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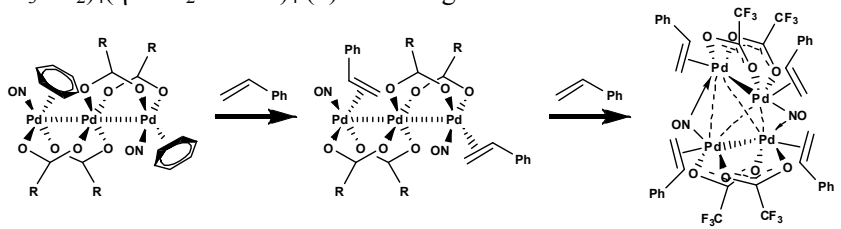
Palladium carboxylate complexes are widely-used catalysts for transformations of unsaturated organic molecules. Recently we have studied the cyclopropanation of alkenes catalyzed by palladium carboxylate compounds.[1] It was shown that catalytically active compounds are most likely polynuclear and contain both olefin and carboxylate groups coordinated on the palladium. So we started investigations of palladium olefin-carboxylate complexes with some palladium centers.

An interaction of $Pd_3(NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}C_6H_5Me)_2$ (**1**) with alkenes has been studied.[2] A replacement of η^2-coordinated arene by various olefins has been found to result in complexes of different nuclearity, $Pd_3(NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}L)_2$ (L = $Me_3CCH{=}CH_2$ (**2**), $CH_2{=}CHPh$ (**3**)), $Pd_4(\mu\text{-}NO)_2(\mu\text{-}CF_3CO_2)_4(\eta^2\text{-}CH_2{=}CHPh)_4$ (**4**) according to the scheme:



Complexes **3** and **4** have been characterized by an X-ray diffraction analysis. Complex **4** represents a new type of nitrosyl carboxylate tetrahedral palladium cluster. Also an unusual 6-nuclear palladium complex was obtained by the reaction of $Pd_4(NO)_4(CF_3CO_2)_4$ with neohexene. The reaction was carried out on the air in CH_2Cl_2 and result in compound $Pd_6(\mu\text{-}Cl)_2(\mu\text{-}CF_3CO_2)_4(\mu^2\text{-}Me_3C\text{-}C(=O\text{–})CH_2\text{–})_4$ (**5**), which contains acetonyl and cholride ligands. It's quite clear that chloride-anions formed from methylene chloride, while acetonyl groups are a result of oxidation of neohexene by oxygen of air. Thus, complex **5** can be considered as a model of intermediate of olefins' oxidation processes (including Waker-process).

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HUMIC FERTILIZERS AS THE POWERFUL ENHANCERS OF AGRICULTURAL PRODUCTION EFFICIENCY

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Humic substances are the complex multicomponent mixtures of high-molecular organic compounds as products of biochemical transformation of differently composed biogenic materials. Humic substances are formed both by broad spectrum of microorganisms and enviromental factors alike[1-3].

High physiological activity of the humic substances is defined by the presence of highly varied natural active components, thus allowing them to be used in production of high quality «green» agricultural products. This factor becomes utterly important in the wake of the fact that Russian Federation is expected to become a member of Worldwide Trading Organization in the next few years. Thus, agricultural usage of humic preparations will allow our products to comply with the strict certification terms.

The authors of this report have conducted long-term research projects on evaluation of chemical composition of brown coal and peat organic matter originating from different regions of Russian Federation. We also have developed unique humic fertilizer production technology. Our humic fertilizers have been field-tested throughout many regions of RF and in many adjacent countries as well.

Humic fertilizer preparation usage increases harvest yield per 10 to 45% while improving many biochemical qualities of the end-line product.

Humic fertilizers reduces consumption of mineral fertilizers per 20 — 30% yet reducing harvest maturation period per 10 — 14 days. Humic preparations can be much more than just fertilizers. They have their uses in medical science, ecological applications like soil remediation tasks and different technological processes.

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SYNTHESIS OF NOVEL *MESO*-MONO AND DIPHOSPHORYLPORPHYRINS

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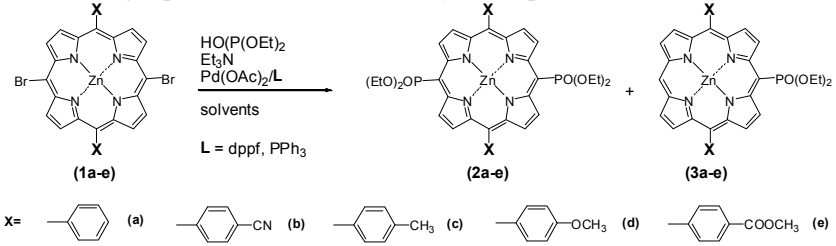
Phosphoryl-substituted porphyrins including different functional groups at the periphery of molecule are promising compounds for elaboration of highly ordered supramolecular systems and materials.

Previously [1,2] we have developed the efficient pathway towards polyphosphorylporphyrins. The optimization of the conditions of cross-coupling reactions between starting compounds **(1a-e)** and diethylphosphite afforded target products **(2a-e)** with the yields up to 86%.



It was shown that co-products, which were isolated with the yields less than 10%, were mono-phosphorylated zinc porphyrins **(3a-e)**. All complexes were characterized by UV-Vis, NMR, IR-spectroscopy and MALDI TOF mass-spectroscopy. The optimal conditions of crystal growth for these compounds were found and its structures were studied by means of X-Ray diffraction analysis.

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RELATIONSHIP OF STRUCTURE AND REACTIVITY IN THE INTERACTION URACIL WITH HYDROGEN PEROXIDE

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It is known that the properties of compounds depend largely on their structure. We have previously studied the reactivity of uracil derivatives in the reactions of chain termination by peroxyl radicals. However, to the number of active centers in a chain reaction of oxidation also include peroxide compounds, providing a degenerate chain branching. In this regard we have studied the relationship of the kinetics of the interaction of the hydroperoxide hydrogen - the simplest representative of hydroperoxide compounds on the structure of uracil. The objects of study were the following compounds: 5-hydroxy-6-methyluracil (I), 6-methyluracil (II), 5-bromo-6-methyluracil (III), 5-nitro-6-methyluracil (IV).

Kinetics of the reaction of uracil with hydrogen peroxide was studied by kinetic spectrophotometry at 348 K. As a solvent twice-distilled water was used.

With the help of monitoring the concentration of the compounds it was shown that the reaction first order of uracil. Assuming first-order reaction with respect to hydrogen peroxide were calculated bimolecular rate constant for the interaction of uracil derivatives with hydrogen peroxide, which were found to be $k \cdot 10^2$, $l \cdot mol^{-1} \cdot s^{-1}$ = (2,50 ± 0,3), (2,30 ± 0,23), (1,13 ± 0,27), (0,13 ± 0,03) for compounds (I), (II), (III) and (IV) respectively.

It was found that the studied compounds obey the Hammett equation $lgk = lgk_o + \rho\sigma^*$ (Fig. 1), where ρ – constant of reaction series for a given reaction, σ^* - Hammett constant.

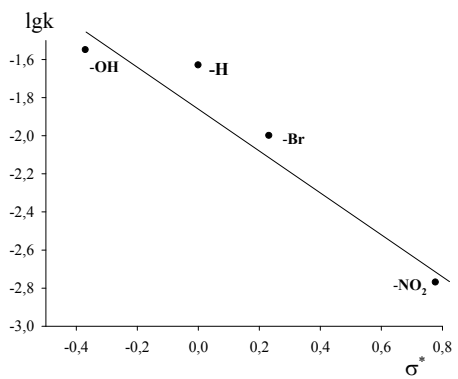

Fig.1 Dependence of the logarithm of the bimolecular rate constants of the Hammett inductive constant

CYCLOPENTAANNELLATION OF α-HALO LEVOGLUCOSENONE DERIVATIVES

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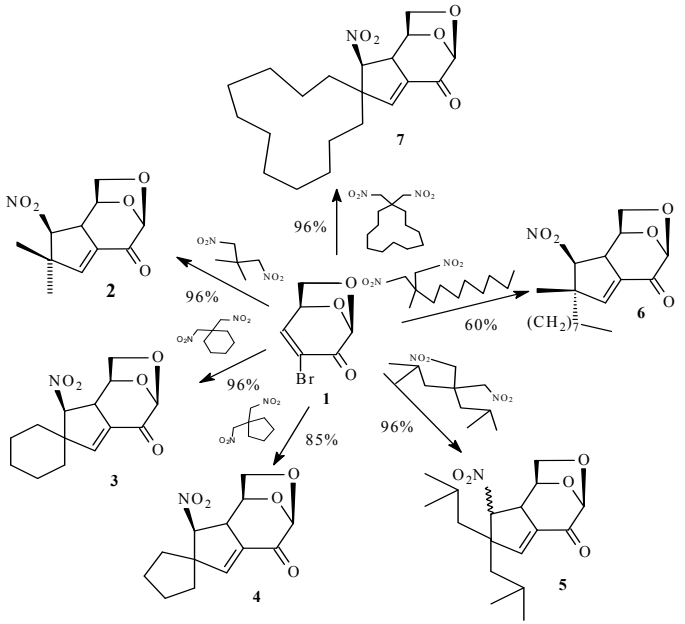
The limits of the use of a previously [1] developed method of cyclopentaannellation of α-halo derivatives levoglucosenone [2] with dinitro compounds [3] are expanded. Spiro and hem dialkil derivatives with the piece of carbohydrate are obtained.



Regents and conditions: K_2CO_3, toluene, ultrasonic, cat.

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The study was carried out under a financial support of the Russian Foundation for Basic Research (grant no. 08-03-97033-p_povolzh'e_a», of the Council for grant of the President of Russian Federation (program NSh-1725.2008.3), and Scientific and scientific and pedagogical staff of the innovation Russia, state contract № 14.740.11.0367.

EFFECT OF TRIMETHYLALUMINUM ON ETHYLENE POLYMERIZATION BY CATALYTIC SYSTEM BIS-[N-(3,5-DI-TERT-BUTYLSALITSILIDENE) -2,3,5,6-TETRAFTORANILINATO] TITANIUM (IV) DICHLORIDE/METYLALYUMOXANE

Fayngold E.E.,[1] Mukhina E.V.,[1] Bravaya N.M.,[1] Gagieva S.Ch.,[2] Tuskaev V.A.,[2] Bulychev B.M.[2]

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By phenoxyimine (FI) titanium complexes with fluorine substituents in ortho-position of the chelating ligand = N-Ph is shown an increased interest as catalysts of "living" polymerization of olefins, capable of promoting the process even at high reaction temperatures (50-75 ° C) [1] . We have previously shown [2] that in a prolonged polymerization (ethylene, propylene) and a high concentration of methylaluminoxane (MAO) catalyst of the class activated by MAO can form high molecular weight polyolefins with large values of the polydispersity index ($M_w/M_n>>1$) . The assumption on the impact of trimethylaluminum (TMA) contained in MAO on the catalytic properties of activated FI complexes has been made.

The results of ethylene polymerization with the catalyst activated by different MAO samples containing different amount of TMA (5 ("dry" MAO), 25, and 35 mol %) are presented in the work. It is shown that the "living" polymerization of ethylene on FI titanium catalyst can greatly complicated by the presence of TMA contained in MAO. The presence of TMA leads to a significant reduction of polyethylene molecular weight in comparison with the system activated by the "dry" MAO, the appearance of bimodality and the broadening of the GPC curves. The assumption of a reversible outer-coordination of TMA to the active site slowing growth of the polymer chain has been made.

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The work was supported by the Russian Foundation for Basic Research (project № 10-03-00926-a) and Rosnauka. (project № 02.740.11.0646).

INFLUENCE OF AGGREGATION PROCESSES ON THE LUMINESCENT PROPERTIES OF β-DIKETONATES OF BORON DIFLUORIDE

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Luminescence of some β-diketonates of boron difluoride crystals and solutions of various concentrations was investigated, by the stationary and time-resolved luminescent spectroscopy methods. It was foud that increase of a luminophor concentration resulted in batichromic shift of the luminescent spectrum and transition from solutions to crystals this shift increased and might achive 100 nm.

Analysis of the luminescent excitation spectra showed that aggregation had several stages: (fig. 1): individual molecule (M) ($C=10^{-6}$ mol/L) – dimers (D) and H-aggregates ($C=5\cdot10^{-6}$ - 10^{-5} mol/L) – J-aggregates ($C=10^{-4}$ – 10^{-3} mol/L) – excimers ($C=10^{-2}$ - 10^{-1} mol/L).

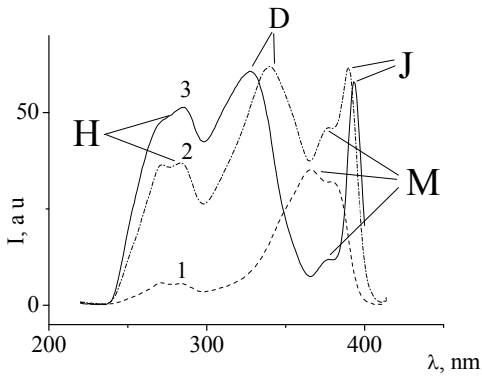

Figure 1. Luminescence excitation spectra of the dibenzoylmethanate of boron difluorides in chloroform: 1 - $C=1\cdot10^{-5}$ mol/L; 2 - $C=5\cdot10^{-5}$ mol/L; 3 - $C=1\cdot10^{-4}$ mol/L

For the most of the β-diketonates of boron difluoride intensive π-π staking interaction was observed. As it was shown by the quantum chemical calculations, the attractive forces prevail and luminescence of excimers and J-aggregates is observed while the intermolecular distance in the β- diketonates of boron difluoride crystals achieved 3,6-3,45 Å. If the intermolecular distance is less then 3,45 Å, repulsive forces predominate in intermolecular interaction and luminescence of individual molecules is observed. In this case, the luminescence spectrum of the crystals coincides with that of the individual molecule.

NITROGEN FIXATION UNDER MILD CONDITIONS

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Since the 60-s of the last century a lot of attempts have been made in different countries to find catalyst systems to fix nitrogen under mild conditions according to the reaction which occurs naturally and may be described by general equation:

$$3C^{*} + N_2 + 3H_2O = 2NH_3 + 3CO_2 \quad (1),$$

where C is a carbon atom in an organic substance with the oxidation number (+2).

However, the system having stable reduction of nitrogen to ammonia has not been found yet.

We have shown in [1-3] that platinum metals carbonyl complexes having low oxidation number are able to react as in (1) invariably according to general equation:

$$3CO + N_2 + 3H_2O = 2NH_3 + 3CO_2 \quad (2),$$

Reaction (2) proceeds at room temperature and atmospheric pressure.

The report includes the theory of reaction (2) and the experimental data.

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NUCLEOPHILIC TRANSFORMATIONS OF 3-SUBSTITUTED CHROMENE-2-ONES

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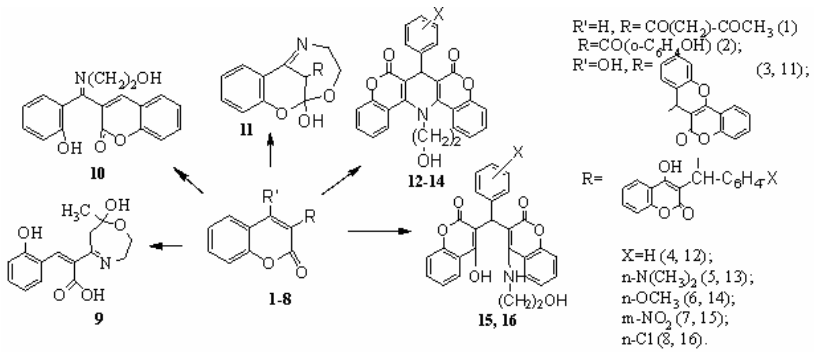
Introduction of pharmacophoric fragments, in particular, chromene-2-one peculiar to natural and synthetic biologically active substances and medicines, is a topical task of the modern design of valuable condensed heterocyclic compounds. This is also important from a position of solving fundamental questions of reactivity studies of the appearing heterosystems of a new type.



For the first time we studied reactions of a series of 3-substituted chromene-2-ones with ethanolamine as a nucleophilic agent and revealed structure-reactivity regularities. In the case of 3-acetoacetyl substituted 2H-chromene-2-one (1), decyclyzation of the lactonic fragment occurs with subsequent formation of oxazepine (9). For 3-(2-hydroxybenzoyl)-2H-chromene-2-one (2), nucleophilic attack of the conjugated carbonylic group of the substrate takes place to form chromenone 10. Introduction of an enolic hydroxyl to the fourth position changes the character of these transformations. E.g., the interaction of complex-built polyoxocompounds (3) proceeds to form condensed chromanooxazepine (11). Aryl*bis*chromene-2-ones react depending on the substituent's nature to form N-substituted dihydropyridines (12-14) or enethanolamines (15, 16). Tautomeric transformations of the substrates and reaction products were studied by means of NMR^{1}H, UV spectroscopy (MILCA software).

STEREOELECTRONIC STRUCTURE OF 2-ALKOXYPHENYLTRICHLOROSTANNANES WITH PENTACOORDINATED TIN ATOM USING AB INITIO CALCULATIONS

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The ^{35}Cl nuclear quadrupole resonance (NQR) spectra at 77 K of 2-alkoxyphenyltrichlorostannanes indicate the intramolecular interaction of tin atom and alkoxy-group oxygen atom closing four-membered ring in these compounds.[1] In order to study stereoelectronic structure of their molecules, nature of intramolecular interaction of Sn and O atoms in them, the influence of substituents on strength of the Sn←O coordination bond, calculations of molecules as per the Gaussian 03W program using RHF, MP2 and B3LYP methods and the 3-21G* basis set have been made. The results of calculations have been compared with NQR experimental data.

The calculations have shown that the Sn←O intramolecular interaction in 2-alkoxyphenyltrichlorostannanes takes place as a result of which the tin atom becomes pentacoordinated and its coordination polyhedron has distorted trigonal bipyramidal structure. The electronodonor substituents in aromatic ring as well as replacement of methoxy- by ethoxy-group enhance the strength of the Sn←O coordination bond. Only one O atom partakes in this interaction with the Sn atom in 2,6-dimethoxyphenyltrichlorostannane. At the Sn and O atoms interaction in 2-alkoxyphenyltrichlorostannanes the electron density from C and H atoms of alkoxy-group as well as from the Sn atom passes to the atoms of coordination polyhedron of the latter. At that, the electron density of the O atom participating in this interaction increases also.

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This work has been completed with financial support of the Russian Fund of Fundamental Researches, project No. 10-03-00131a, and of the fundamental research program executed in the Ural Branch of the RAS jointly with researchers from Siberian and Far-East Branches of the RAS.

SYNTHESIS, STRUCTURE AND THERMOPHISICAL PROPERTIES OF DIANIONIC ORTHOCOMPOUNDS $AZr_2(TO_4)_X(PO_4)_{3-X}$ (A – ALKALI METAL, T − As, V)

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New mixed orthocompounds and solid solutions of the composition $AZr_2(TO_4)_x(PO_4)_{3-x}$ (A = Li, Na, K, Rb, Cs; T = As, V) were received, and their structure and thermophisical properties (heat capacity and thermal expansion) were studied. The samples were prepared by precepitating method. The synthesized phases were characterized by X-ray powder diffraction, infrared spectroscopy and electron microprobe analysis, calorimetry.

Continuous solid solutions with the kosnarite (NZP, NASICON) type structure are formed in the arsenate-phosphate systems with A = Li, Na, K, Rb, Cs. In the series with A = Li there is an irreversible phase transition from $P2_1/n$ (scandium tungstate) to $R\bar{3}c$ space group (kosnarite) at 960°C. The crystal structures of arsenates $AZr_2(AsO_4)_3$ (A = Li, Rb, Cs) and mixed arsenate-phosphates $AZr_2(AsO_4)_{1.5}(PO_4)_{1.5}$ (A = Li, Na, K, Rb, Cs) were refined. The framework of the arsenate-phosphates $[Zr_2(AsO_4)_x(PO_4)_{3-x}]_{3\infty}$ structure was constructed from statistically occupied tetrahedra by arsenic and phosphorus atoms and ZrO_6-octahedra connected by tops. They formed a stacked (NZP) or parquet ($Sc_2(WO_4)_3$) packing. Alkali metal atoms occupy the extraframework position structures. Limited substitutional solid solutions with the kosnarite (A = Li, Na, K, Rb, Cs, $0 \le x \le 0.2 - 0.5$) and scandium tungstate (A = Li, $0 \le x \le 0.75$) type structures formed in the vanadate-phosphates rows. Structures $NaZr_2(VO_4)_{0.4}(PO_4)_{2.6}$ and $LiZr_2(VO_4)_{0.75}(PO_4)_{2.25}$ were confirmed by the Rietveld method.

Using high temperature X-ray diffraction (20–800°C) the thermal expansion of arsenate-phosphates with the A = Na, K, Rb, Cs and x = 1.5, 3.0 was studied. An average linear coefficient of thermal expansion value of arsenate-phosphates was $(0.35-3.9)\cdot10^{-6}°C^{-1}$. They are classified as medium- and low-expansion compounds. Due to smooth heat capacities running $NaZr_2(AsO_4)_3$ and $AZr_2(PO_4)_3$ (A = Na, Cs), we concluded that there were no phase transitions in the temperature range 7−650 K.

This work was supported by the Russian Foundation for Basic Research (project № 11-03-00032).

THE MECHANISMS OF CATALYTIC REACTIONS WITH NORBORNADIENE

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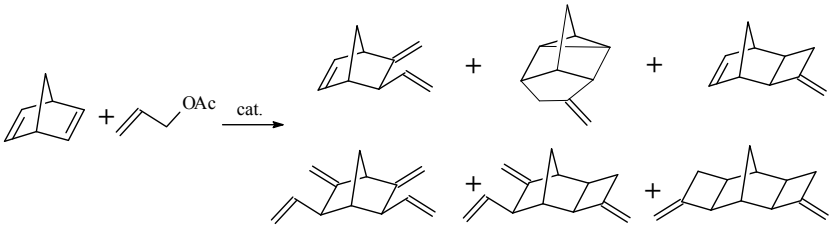
Catalytic processes with norbornadiene are promising for the synthesis of a wide range of strained polycyclic hydrocarbons. The effective use of such synthetic approaches, as dimerization, co-dimerization and non-conventional allylation of a wide range of norbornens and norbornadienes allows the development of unique synthetic approach for the obtaining of carbocycles with methylene, vynil and methylenecyclobutane fragments.



The selectivity problems in multiroute reaction with NBD and its derivatives are very important. Using the allylation of NBD and norbornenes as an example, the possibility of control of selectivity and the rate of the reaction is shown. The ways of formation of nickel and palladium catalysts are studied. The key intermediates are found by spectral methods, the kinetics is studied and the mechanisms are proposed. The quantum-chemical simulation of the processes with NBD was performed. The factors, influencing for the routes of reaction are established, they allow obtaining the individual stereoisomers. Selectivity and a number of catalytic cycles are dependent on the composition of catalytic system and the effective charge on metal atom. The series of novel unsaturated compounds is synthesized, possessing with a set of double bonds with different reactivity and interesting in production of modified resins.

The comparison of effectiveness of homogeneous and heterogeneous metal complex catalysts is performed; the similarities and differences in reaction mechanisms were established.

The work was performed with financial support of RFBR (grant № 11-03-00662-a).

SYNTHESIS AND CHEMICAL TRANSFORMATIONS OF 3-DIAZOPYRROLIDIN-2-ONES

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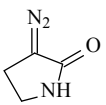
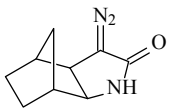
Nowadays wide attention is paid to the search of new regio- and stereoselective methods for building pyrrolidine cycle, which is a pharmacophoric group of various pharmaceutical products (piracetam, oxyracetam, phenotropyl) and physiological active compounds (domoic acid, oxazolomicin).

In the present work new 3-diazopyrrolidin-2-ones **1,2** were synthesized by interaction of corresponding 3-aminopyrrolidones with *i*-amylnitrite at the presence of AcOH, and their chemical transformations were investigated.

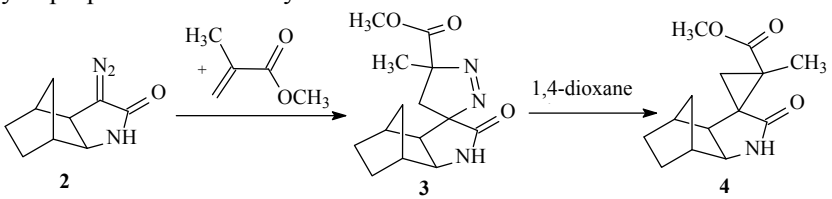


1



2

1,3-Dipolar cycloaddition of diazolactams **1,2** to the electron-deficient olefins (methylvinylketone, methylacrylate, methylmethacrylate) in CH_2Cl_2 at room temperature leads to the formation of spiropyrazolines. Heating of the compound **3** in 1,4-dioxane promotes dediazotization giving spirocyclopropane **4** with 99% yield.



2 **3** **4**

It was found, that 5-diazo-*ekzo*-3-azatricyclo[5.2.1.$0^{2,6}$]decan-4-one **2** in the presence of $Rh_2(OAc)_4$ interacts with methyl and allyl alcohols resulting in the products of insertion into OH-bond.

This work was financially supported by the Presidium of the Russian Academy of Sciences (Program for Fundamental Research «Development of Methods for the Synthesis of Chemical Substances and Design of New Materials», Subprogram «Development of Methodology of Organic Synthesis and Design of Compounds with Valuable Applied Properties»).

THE TOPOLOGY AND THE THERMOCHEMISTRY OF Li,Na,K//Cl,NO_2,NO_3 SYSTEM

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On the merits, the physical and chemical analysis is "a geometrical method of research of chemical transformations". The topology modeling and the thermochemistry of complex systems are the actual problems of the given direction. We chose the Li,Na,K//Cl,NO_2,NO_3 fivefold mutual system as an object of our research. By studying of its geometrical polytope structure we found that its combinatory type is "Д", characterized by the presence of three free tops (LiCl, KNO_2,$NaNO_3$). They form the lateral branches in the singular star cycle. By splitting the polytope on simplexes we gave the description of stable and metastable complexes. According to the results of estimating the thermochemical criteria and studying the basic elements and exchange reactions it was shown that the system belongs to Д ↔E type and its basic triangles are $LiNO_3$-$NaNO_2$-KCl and $LiNO_2$-NaCl-KNO_3, total heat content, according to the exchange reactions, where the given salts are formed, makes 32,84 and 29, 93 kJ / (mole*eq), accordingly. By the calculation of conditional total thermal effect of each salt generation we received the series, where they were located in the decreasing order of its values (KCl→$LiNO_2$→$LiNO_3$→NaCl→$NaNO_2$→KNO_3). It characterizes their rank and influence on the physical and chemical processes in the system. As the additional criterion characterizing the basic triangles, the sum $\sum Q_i$ was calculated for the salts forming them, values of which are 64,225 and 61,315 kJ / (mole*eq). The calculation and comparative thermochemical analysis, and experimental study of basic elements and exchange reactions as well allowed proving the splitting and the system type. According to the set of the results of studying of some similar systems we suggested the method of modeling the topology and thermochemistry of 3K//3A systems. It allows raising the forecasting effectiveness of phase-generation and the estimation of the heat content of the polytope elements. It is important for searching the materials with the set properties.

The paper was written with financial support according to the thematic plan of the Ministry of Education and Science, the project 1.1.08-11.

THE PHASE COMPLEX OF LI,NA,CA,BA//F,WO_4 SYSTEM

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The melts with halogenides and tungstates of alkaline and alkaline-earth metals are perspective for working out of chemical and technological processes of high-temperature revelation of scheelytic ores and concentrates, chains of tungsten refinement, using as electrolytes in high-temperature chemical current sources, etc. The tungstates possess catalytic, semi-conductor and luminescent characterisitcs.

The purpose of our work consisted in studying the physical and chemical properties and revealing the features of fluoride-tungstate exchange and phase-formation in Li,Na,Ca,Ba//F,WO_4 fivefold mutual system.

For the first time, with the help of the whole complex of modern methods of the physical and chemical analysis, we experimentally studied 2 double (Li,Ca//WO_4, Li,Ba//WO_4), 3 triple (Li,Na,Ca//WO_4, Li,Na,Ba//WO_4. Li,Ca,Ba//WO_4), 2 three-component (Li_2F_2-CaF_2-$CaWO_4$, Li_2F_2-$CaWO_4$-$BaWO_4$), 2 triple mutual (Li,Ba//F,WO_4, Li,Ca//F,WO_4), 1 fourfold (Li,Na,Ca,Ba//WO_4), 1 fourfold mutual (Li,Ca,Ba//F,WO_4), 2 five-componental (Li_2F_2-Na_2F_2-CaF_2-D_3-$BaWO_4$, Na_2F_2-BaF_2-CaF_2-D_3-$BaWO_4$) systems ingressed in Li,Na,Ca,Ba//F,WO_4 fivefold mutual system. The received structures with melting temperatures of 450-760 ^{0}C can be used as heat-storages and working materials for chemical current sources .The structures rich with tungsten are perspective for electrochemical releasing of the tungsten. The exchange reactions in the given mutual systems are effective for the synthesis of refractory tungstates where fluorides play the role of the inorganic solvents. The given paper shows the way, how on the basis of our research on studying the phase system complex is possible to solve the applied problems on revealing the compositions with regulated properties, on the basis of volume figures representing the diagrammes of condition and structure of MCS. The generalized information on the phase-formation processes in these systems allowed revealing their features and mutual interference on the topology and properties.

The paper was written with financial support according the thematic plan of the Ministry of Education and Science, the project 1.1.08-11.

DIRECTED SYNTHESIS OF FUNGITOXIC STEREOISOMERIC 2-THIOCARBAMOYL-3-ARYL-3,3A,4,5,6,7-HEXAHYDROINDAZOLS

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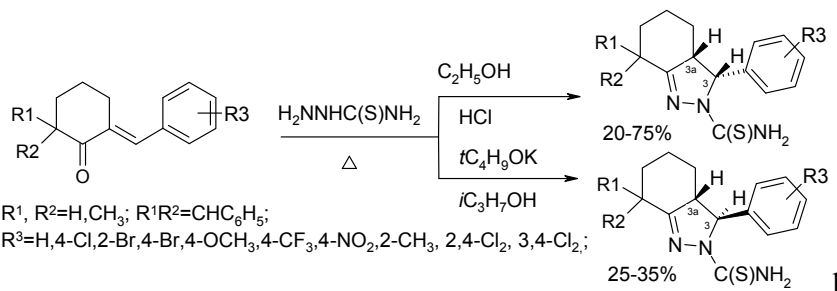
Design of novel fungicides is an important task because of the generation of the formed resistant pathogenic fungi. A number of used stereochemical pure agrochemicals and drugs is increasing. As a result the elaborated method of synthesis of individual stereoisomers of biological active compounds is a very actual aim.

The condensation of 2-alkyl-6-arylidenecyclohexanones with thiosemicarbazide or N'-substituted thiosemicarbazides with the presence of acid catalysis gave 2-thiocarbamoyl-3-arylhexahydroindazols. *N*-Unsubstituted 2-thiocarbamoyl derivatives exhibit highest fungicidal activity. Mainly they were obtained in the form *cis*-isomers.[1]



R¹, R²=H,CH_3; R¹R²=CHC_6H_5;
R³=H,4-Cl,2-Br,4-Br,4-OCH_3,4-CF_3,4-NO_2,2-CH_3, 2,4-Cl_2, 3,4-Cl_2; h

The selective condensation with the presence of base catalysis of potassium *tert*-butoxide gave *trans*-isomers of 2-thiocarbamoyl-3-arylhexahydroindazols. Relatively low fungitoxic *N*-arylthiocarbamoyl-3-aryl hexahydroindazols in the form *trans*-isomers were prepared alternatively in the two steps.[2]

We have elaborated the methods of the stereodirect synthesis of *^{3}H,^{3a}H-cis*- and *trans*- 2-thiocarbamoyl-3-arylhexahydroindazols. The prepared compounds showed the strong fungicidal activity.

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DIHALOGENALKYL PROPARGYL ETHERS: SYNTHESIS AND PROPERTIES

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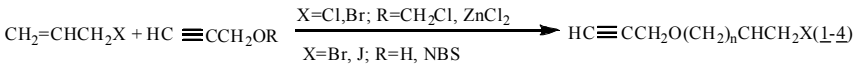
Dihalogen ethers of acetylene spirits practically haven't been studied. Nevertheless, they are important as basic combinations for organic synthesis as well as in applied aspect [1,2].

We've developed efficient (up to 70% output) mono staged methods of obtaining of two types (1,2 & 3,4) dihalogen ethers of propargyl spirit with equal and various by nature atoms of halogen included in

– catalytic addition ($ZnCl_2$) of propargyl oxymethylchloride to allylhalogens (X= Cl,Br);

– bromoalkoxylation of allylhalogens (X= Br) by propargyl spirit and bromosuccinimide (NBS)



X=Cl(1), Br(2,3) J(4);
Y=Cl(1,2), CH_2Br (3,4);

n=2(1,2), zero (3,4).

It has been defined that dihalogen ethers (1-4) in the concentration of 01÷1,0% are the effective antimicrobe additives to lubricating oil (M-10). In this case the degree of suppress or growth microorganisms in the oil alters in the order (1)< (2)<(3)<(4), i.e. it grows with the increase of halogencontain in the molecular with more large atom number.

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CALIXRESORCINES, MODIFIDED BY AMINO GROUPS – TRANSPORT FACILITIES FOR NOOTROPIC BASED ON PHOSPHORYLACETIC ACIDES HYDRAZIDES

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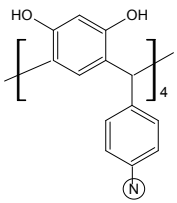
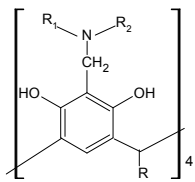
Calix[4]resorcines – resorcinol aldehydic macrocyclic tetramers – show possibility for further funshionalization on resorcinol ring and a radical of an aldehydic fragment. Such multipurpose possibility of modification allows to create supramolecules possessing multicenteric points of recognition of inclusion compounds, including medical products.

Using two approaches the calixresorcines 1-6, modifided with various aminocontaininmg fragments were synthesised:



1 Ⓝ = $NH_3^+Cl^-$
2 Ⓝ = $(CH_3)_2NH^+Cl^-$



3 R=*n*-$CH_3C_6H_4$ R_1=CH_3; R_2=CH_3
4 R=*n*-$CH_3C_6H_4$ R_1= C_2H_5; R_2= C_2H_5
5 R=*n*-$CH_3C_6H_4$ R_1=*n*-C_3H_7; R_2=*n*-C_3H_7
6 R=*n*-$CH_3C_6H_4$ R_1=CH_3; R_2=CH_2-C_6H_5

Results of toxicological research of compounds 1-6 have shown that calixresorcines 2 and 4 are not toxic. Their inclusion ability was studied in "host-gest" reactions with derivatives of phosphorylacetic acids hydrazides: [2-(diphenylphosphoryl)acetohydrazid] (phosenazid) **7**, hydrochloride [2-(diphenylphosphoryl)acetohydrazid] (phosenazid hydrochloride) **8** and 2-[4-(dimethylamino)phenyl]-[(2-chloroethoxy)phosphoryl] acetohydrazid (CAPAH) **9**. Acetohydrazides 7-9 are known to possess a complex of psychotropic effects, promoting function of a brain. Studying of pharmacological activity of the molecular complexes has shown essential increase of nootropic actions of an initial drug.

The financial support of grant of the President of the Russian Federation for the state support of young Russian scientists (64832.2010.3)

SYNTHESES BASED ON 1,2,4-TRIAZOLINE-3-THIONES

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The outstanding role of nitrogen-containing heterocycles in nature, medicine and technology leads to intensive research in the synthesis of these compounds, modification of their properties by varying the structure. Five-membered heterocycles with three nitrogen atoms – 1,2,4-triazoles and their sulfur derivatives – 1,2,4-triazoline-3-thiones are of particular practical and theoretical interest.[1, 2] Triazolinethione structure contains two nucleophilic centers – the exocyclic sulfur atom and the endocyclic nitrogen atom. This fact allows to use sulfur atom or nitrogen atom as well as both reaction centers depending on the nature of the attacking reagent and reaction conditions. Both centers are used in the reactions with various bifunctional electrophiles and new heterocyclic systems are formed herewith. So, we synthesized new dicyanocontaining benzothiazoles by the reaction of 1,2,4-triazoline-3-thiones, substituted at 5 position by different aromatic rings, with highly activated bifunctional electrophile – 4-bromo-5-nitrophtalonitrile.[3] These compounds were used in the hexazo*cyclane* synthesis on the base of which mono- and bifluorophore having intense fluorescence were obtained.

In order to obtain new compounds with potentially useful properties we also investigated the reactions of 5-substituted-1,2,4-triazoline-3-thiones, containing fragments of arylsulfonyl(sulfanyl)alkanecarboxylic acids, with such bifunctional electrophiles as 1,2-dibromoethane, monochloroacetic acid, epichlorohydrin and others.

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EMPIRICAL AND NON-EMPIRICAL APPROACH TOWARDS THE PREDICTION OF ^{13}C NMR CHEMICAL SHIFTS IN OLIGOSACCHARIDES

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Automatization of structure elucidation of organic compounds by their NMR spectrum is an important task of the modern chemistry. This specially applies to the field of polysaccharide investigations. These naturally occurring substances possess a range of peculiar properties including pharmacological ones, hence their structural studies are performed in many scientific centers in the world.

Previously, a method was proposed by the authors, that allowed for the computer assissted analysis of natural fucopolysaccharides (fucoidans) with the use of artificial neural networks (ANN) [1]. To provide its work, data on the chemical shifts of model oligofucosides corresponding to the principal structural motifs of fucoidans are needed (so called training set). This technique was developed and tested on a set of chemical shifts of synthetic oligofucosides possessed by the authors.

However, oligofucosides that model structurally important fragments of fucoidans are not always readily available for investigation. In the present work molecular modelling methods were studied to obtain the values of chemical shifts in oligosaccharides on the example of fucosides. Two approaches were employed, the empirical one, also based on the use of ANN, and the non-empirical, which included quantum chemistry calculation of the chemical shifts. The comparison of the results showed the maximum error in the case of non-empirical approach to be significantly lower than in the case of the empirical one.

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PHOSPHOLIPASE A2 - PHOSPHATIDYLCHOLINE INTERACTION UNDER UV-IRRADIATION

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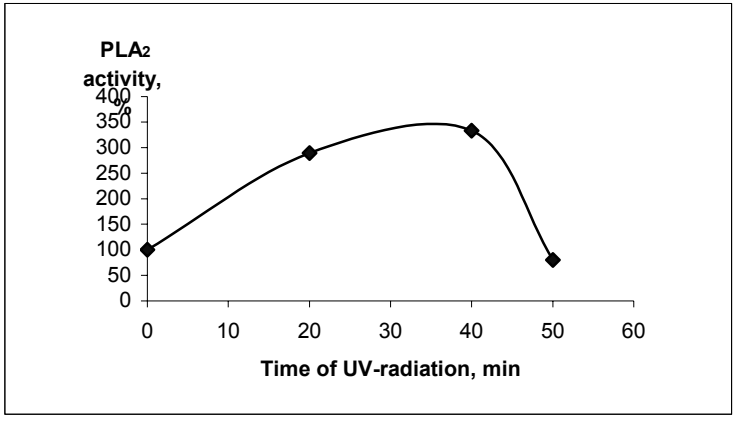
The selective removal of oxygenated fatty acid residues from the phospholipid component of cell membranes by phospholipase A_2 (PLA_2, EC 3.1.1.4) with subsequent its replacement by the new fatty acids with participation of acyl-CoA transferase is one of the ways of functioning of cell antioxidant system.

Lipid peroxidation, in turn, promotes to pancreatic PLA_2 activation [1]. In this connection, PLA_2 investigation is of special interest since this enzyme is very sensitive to interface defects and may be used as an indicator of its structure changes under the influence of various factors, including UV radiation.



It is shown that PLA_2 activity towards the substrate undergoing UV-radiation is increased during first 40 min and then declined (Figure).

This can be explained by the fact that PLA_2 is activated by removing of the primary products of lipid peroxidation (hydroperoxides of fatty acids, etc. in the lipid phase), while during the stage of secondary products formation (malondialdehyde and other carbo-and carboxy-derivatives of decomposed fatty acids), its activity falls down.

Thus, one can register the moment of transition of primary products of lipid peroxidation into the secondary ones, as well as estimate the oxidation extent of phospholipid's fraction of the membrane by the increased activity of phospholipase A_2.

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INFLUENCE OF COMPOSITION AND NATURE OF AQUEOUS-ORGANIC SOLVENTS ON COMP0LEXATION OF SILVER(I) WITH GLYCINATE-ION

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The purpose of the present work is to establish influence regularities of reagents solvation on silver(I) complexation with glycinate-ion in wide composition range of aqueous organic solvents.

The stability constants of silver(I) complexes with glycinate-ion were determined by potentiometric method in aqueous solutions of ethanol, isopropanol, acetone, dimethylsulfoxide. The change of enthalpies of silver(I) glycinate formation in aqueous solutions of ethanol and dimethylsulfoxide were obtained by calorimetric method. Gibbs transfer energies of glycine and glycinate from water to aqueous-dimethylsulfoxide solvents were determined by method of interfacial distribution between two immiscible phases.

It was found, both the concentration and nature of organic solvent have an influence on change of silver(I) complexes stability. While decreasing water concentration the largest rising of complexes stability was observed in the case of aqueous acetone solvents and the least rising of complexes stability was noted in case of aqueous dimethylsolfoxide solvents.

It was discovered anomalous enthalpies ratio of stepped formation reactions of mono- and bis-complexes of silver(I) with glycinate-ion in water and aqueous ethanol solutions: addition of the second ligand is more than two times more exothermic than coordination of the first one. It is shown that increase of dimethylsulfoxide concentration in solution results in inverse ratio of stepped enthalpies.

It was established that the rising of stability of silver(I) complexes with glycinate-ion in aqueous organic solvents and change of exothermicity of complexation reactions are in general determined by resolvation energy of glycinate-ion in mixed solvents. In one's turn glycinate-ion desolvation depends on acid-base properties of aqueous organic solvents to a considerable extent.

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EXPERIMENTAL AND THEORETICAL STUDY OF PORPHYRINO METAL COMPLEXES STRUCTURE

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The molecular structures of 2,3,7,8,12,13,17,18-octamethylporphyrins of nickel (NiOMP), copper (CuOMP) [1], tin(II) (SnOMP) were studied by gas phase electron diffraction method and density functional theory calculations using the B3LYP and PBE functionals with cc-pVTZ basis sets (Gaussian 03). The structures of ZnOMP, NiP, CuP, ZnP, SnP were studied by QC calculations.

Nickel and copper porphyrins are planar (Fig.1a). Doming distortion of the macroheterocycle is typical for tin complexes (Fig.1c). In case of nickel complexes, availability of ruffling distortion (Fig.1b) is not excluded. Structural regularities depending on metal nature were found.

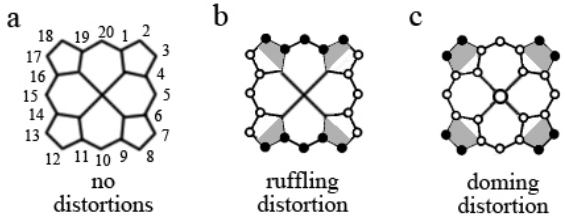

Figure 1. Kinds of macroheterocycle distortions in porphyrin complexes (light fragments are located over the plane, dark fragments are located under plane)

The evaporation of NiOMP, CuOMP, SnOMP was studied at the temperature 668, 674 и 707 K, respectively. The every mass spectrum consists of two groups of peaks corresponded to single and double charged parent ion and ions formed by consecutive removal of groups CH_3 by an electron impact (U=50 V).

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ALKALI METAL FLUOROPHOSPHATE ZIRCONATES (HAFNATES)

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In our earlier papers, we presented the class of fluorosulphate metallates (titanates, zirconates, hafnates) with one-, two- and tri-valent elements. Fluorophosphates (FP) with one- and tri-valent cations are known. No FP for Zr and Hf have been revealed before. The studies were conducted without heating along sections of the systems $MeO(NO_3)_2$–$MF(HF)$–H_3PO_4–H_2O, where Me–Zr, Hf, M–K, Rb, Cs, at molar ratios (m.r.) HF/Me = 0, PO_4^{3-}/Me = 0.5, 1.5–1.8, MF/Me =1–5, and also at m.r. HF/Me = 2–6; PO_4^{3-}/Me = 0.5, 1.6; M/Me = 1–3. All the isolated compounds (Table) have been studied by using crystallooptic, XPA, element analyses, TA and IR spectroscopy.

Table. Compounds composition

K	Rb	Cs
Fluorophosphates		
Acidic		
-	-	$CsHZrF_3PO_4$
$K_3H_3Me_3F_3(PO_4)_5$	$Rb_3H_3Me_3F_3(PO_4)_5$	$CsMe_2(PO_4)_3{\cdot}2HF{\cdot}1.5H_2O$
Medium		
-	-	$CsMe_2F_6PO_4{\cdot}(3\text{-}4)H_2O$
-	$RbMeF_2PO_4{\cdot}0.5H_2O$	α-$CsMeF_2PO_4{\cdot}0.5H_2O$
-	-	β-$CsZrF_2PO_4{\cdot}0.5H_2O$
-	$RbZr_3F_4(PO_4)_3{\cdot}1.5H_2O$	$CsZrF_2PO_4{\cdot}H_2O$
-		$CsZrF_2PO_4{\cdot}H_2O$
$KHf_2F_3PO_4{\cdot}2H_2O$	-	$Cs_2Zr_3F_2(PO_4)_4.4.5H_2O$
Basic		
-	$Rb_2Zr_3OF_6(PO_4)_2{\cdot}2H_2O$	$Cs_3Zr_3O_{1.5}F_6(PO_4)_2{\cdot}3H_2O$
-	-	$Cs_2Zr_3O_{1.5}F_5(PO_4)_2{\cdot}2H_2O$ conv
-	-	$Cs_3Hf_4O_2F_6(PO_4)_3{\cdot}6H_2O$
-	-	$Cs_2Zr_3O_2F_4(PO_4)_2{\cdot}3H_2O$ conv
-	$Hf_3O_{0.5}F_5((PO_4)_2{\cdot}6H_2O$	$Zr_3O_4(PO_4)_{1.33}{\cdot}6H_2O$ conv

Table. Compounds composition

K	Rb	Cs
Fluorophosphatoonitrates		
-	$MeF_4 \cdot Rb(PO_4)_{0.33} \cdot RbNO_3$	-
$K_4Zr_4O_{1.5}F_8(PO_4)_2(NO_3)_3 \cdot 7H_2O$	-	$Cs_2Hf_3O_{1.5}F_7(HPO_4)_4 \cdot 3CsNO_3 \cdot 5H_2O$*
$KZr_3O_{0.5}F_3(PO_4)_2(NO_3)_3 \cdot 3H_2O$	$RbZr_3OF_3(PO_4)_2(NO_3)_2 \cdot 5H_2O$ conv	$CsZr_3O_{1.25}F_4(PO_4)_2(NO_3)_{0.5} \cdot 4.5H_2O$
$K_2Zr_3O_2F_2(PO_4)_2(NO_3)_2 \cdot 2H_2O$	$Zr_3OF_3(PO_4)_2NO_3 \cdot (7\text{-}8)H_2O$ conv	-

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SYNTHESIS OF TERMINAL ACETYLENE AZIDES AND AMINES MODELS

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Process of oxidation and hydrolysis of lipids are an integral part of the regulatory mechanism of cell. Lipids and polyunsaturated fatty acids (PUFA), enzymatically converted by living organisms into the eicosanoids, hydroxyl unsaturated acids (HETE), epoxyeicosatrienoic acid (EET), lysophospholipids, cannabinoids, sphingosine-1-phosphate and sphingosylphosphorylcholin affect the course of many cellular reactions, including cell growth and cell death, as well as an inflammation. Bioactive lipid mediators are generated by enzymes such as lipoxygenase (LOX), cyclooxygenase (COX), cytochrome P-450 dependent monooxygenase, lipase. The study of the catalytic features of lipid oxidation enzymes and variety of bioregulators formed seems to be relevant.

To research the interaction of animal lipoxygenase with fatty acid substrates useful approach was chosen. There was covalent affinity labelling of substrate-binding sites of the enzyme using synthetic photo-affinity probes (azidoderivatives of unsaturated fatty acids). For this purpose procedures of azide obtaining were developed as an example the synthesis of short-chain acetylene models. Also in the frames of the research short-chain terminal acetylene amines were obtained. The amines can be used as matching when you create a modified nucleoside analogs and other natural compounds with pharmacological activity.

The strategy of synthesis is based on the sequence of reactions: 1) the preparation of terminal 1-chloropent-4-in from 1-bromo-3-chloropropane with sodium acetylide, 2) the substitution of chlorine by the azido group with sodium azide at room temperature, which led to preparation of 1-azidopent-4-in. Its subsequent reduction with triphenylphosphine has led to 1-aminopent-4-in. Using alkynylchloride and lack of heating has increased the yield of the azide and an amine at 10-15% compared with the method based on the use of terminal acetylene mesylate on the steps of introducing azido group (Y.Saito, Tetrahedron, 2008).

The work was supported in part by grant of Russian Ministry of Education and Science (№ 2.1.1/2889).

THERMAL STABILITY OF FIVE-MEMBERED HETEROCYCLES

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The proposed [1] method of the low-temperature solidification of rubbers with dinitroiloxides was certainly developed [2], after the stable at the room temperature and sterically screened benzodinitriloxides were synthesized. The large-scale use of this effective method of solidification depends on the thermal stability of izoxazaline ring, which is formed as a fragment of cross link at the addition of dinitroxides to olefins.

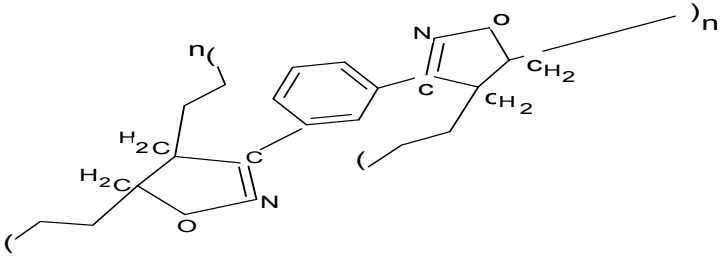

Fig.1 Scheme of five-member cycles formation between macromolecules

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It is shown that stability of cross link depends on a structure of screening fragments around nitriloxide groups on the whole. RSA has shown that strongly screening fragments hardly fix five-member ring at an angle 90 degrees to a plane of a benzene ring, and the weak screening make it possible to heterocycle to be disposed in one plane with a benzene ring.

The mechanism of isoxazoline ring thermal decomposition itself depends on a mutual arrangement of the rings. In a case of the strong screen the decomposition occurs on biradical way but in case of weak screen - on the monomolecular one. Kinetic parameters of reactions are received.

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RESEARCHING OF THE REACTION OF HALOGENNITROBENZO[1,2,5]OXADIAZOLES WITH DERIVATIVES OF NITRIC AND NITROUS ACID

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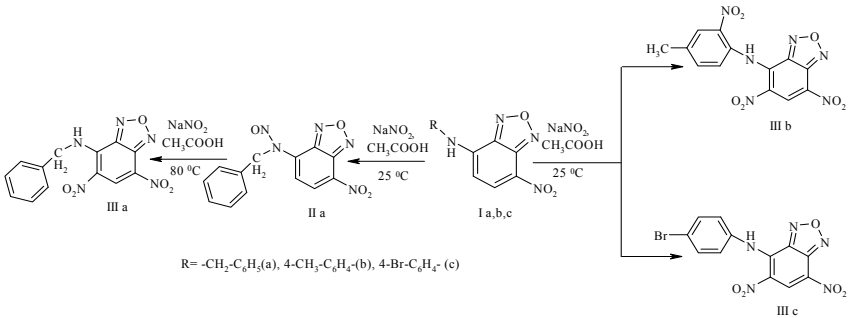
It is known that carbocycles of benzofuroxans are sensitive for the action of nitratings agent. There is not enough information about nitration of amino substituted 2,1,3-benzooxadiazoles in the literature.

We have studied interaction of 4-R-amino-7-nitro-2,1,3- benzooxadiazoles with derivatives nitric and nitrous acid.

Treatment of substrates (I a-c) by sodium nitrite in acetic acid is leading to appropriate nitroderivatives (III a-b), however the place of incoming nitro group is defined by substitute structure.

Although, this reactions proceed with the participant N- nitrososubstances.



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CONFORMATION AL ANALYSIS OF OLIGOGLUCOSIDES STRUCTURALLY RELATED TO CELL WALL B-(1→3)-D-GLUCAN OF YEASTS, INCLUDING *CANDIDA* AND *ASPERGILLUS*

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β-(1→3)-D-Glucan is the principal cell wall part of many pathogenic yeasts, including *Candida* and *Aspergillus* and exhibits high immunological activity. We perform systematic conformational analysis of synthetic oligosaccharides related to the glucan structural fragments for the detection of epitopes determining immunological activity of the polysaccharide.

The series of linear oligo-β-(1→3)-D-glucosides and their 3,6-branched derivatives with the number of monosaccharide units varying from three to thirteen was studied in this work. The conformational analysis was performed by means of NMR spectroscopy (interproton nuclear Overhauser effect (nOe) and Spin-Spin Coupling Constants (SSCC)) and theoretical molecular modeling (molecular mechanics calculations and molecular dynamic simulations with the use of MM3 force field). The modeling was performed with different solvation models, including continuum solvent model SASA and explicit solvent model (H_2O molecules).

The use of the explicit solvent model allowed for the good coincidence between experimental and theoretical values of nOe and SSCC, that evidenced the usefulness of this model. It was shown that conformational properties of disaccharide fragments in linear oligo-β-(1→3)-D-glucosides did not depend critically neither on their position in the chain nor the length of the chain; the introduction of 3,6-branching points in β-(1→3)-D-glucoside chain did not significantly change its conformation. The possibility for the studied oligoglucosides to form self-assembled di- and trimer clusters in water solution was also shown.

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FINITENESS OF MENDELEEV'S PERIODIC SYSTEM

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All the elements of a famous part of Periodic system are divided into four families (s-, p-, d- and f-elements), that simplifies analysis of laws as inside of every period as when passing from one period to another. Assessment of minimal specific energy of nuclear nucleon connection allows restricting Periodic system above[1]. Law analysis of structure nucleon change of nuclear allows assessing saturated element number locking the System for each of separated atoms families.

On the basis of derived assessments of maximum elements numbers, taken to different families, Periodic system structure of Substance atoms elements, taking with a glance to its finiteness, which contains 172 elements, 7 classes and 12 periods. Class is a new structural unit of Periodic system, proposed by the author.

Analysis of nucleon nuclear structure change for different elements systems as inside of periods as when passing from one period to another on the basis of which assessments of nucleon and isotope structure of today's unknown 54 elements are presented. These obtained assessments are consistent quite well with assessments of atoms nucleon nuclear structure of unknown elements.

Ratios describing elements distribution according to periods of a given System, which in fact are a mathematical record of a law about periodicity are set.

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THE FORMATION OF SUPRAMOLECULAR STRUCTURES IN ORGANIC FLUIDS. EXPERIMENT AND THEORY

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It is well known that some new absorption bands appear in IR spectra of organic compounds at the transaction from gas to liquid state. This concerns medium as well as high frequency region. It is obvious that these bands can be connected with the intermolecular interactions appearing in the condensed state.

The comparison data of FTIR spectra analysis in 2400-1400 and 4500-2800 cm^{-1} regions of a number of the often used in preparative practice organic solvents such as the halogensubstituted methanes CX_3H (X = Cl, Br), CH_2X_2 (X = Cl, Br, I), functional methane derivatives CH_3X (X = NO_2, CN, I), benzene and its derivatives C_6H_5X (X = H, Cl, Br, NO_2), aliphatic hydrocarbons C_6H_{10}, C_7H_{16}, C_8H_{18} and their deuterated analogs were presented in our work.

The revealed in liquid phase bands shift at deuteration of investigated compounds. The isotopic shifts (ν_H/ν_D=1.25-1.36) are in good agreement with the theoretical values for harmonic oscillator. This results prove that the observed bands assign to fundamental modes of hydrogen atoms but not to overtones or combination bands.

The 2400-1400 cm^{-1} region is typical for the motion of bounded proton. Since the location of the mentioned bands correlates with the halogen nature (in case of halogen derivatives), it can be assigned to the stretching of intermolecular hydrogen bonds, existing between mobile hydrogen atom and halogen atom of neighboring molecules. The bands in high frequency region (4500-2800 cm^{-1}) may be assigned to modes of dihydrogen bonds analogically to H-H stretching in hydrogen molecule.

In the case of aromatic systems we suppose the formation of intermolecular π-hydrogen bonds. This assignment is verified not only by the isotopic shift of the described bands, but also by the expected splitting of bands in substituted benzenes due to non-equivalence of hydrogen atoms in benzene derivatives.

In the spectra of organic solvents such as aliphatic hydrocarbons the broad multicomponent band in the 4500-3800 cm^{-1} region, having the expected isotopic shift (ν_H/ν_D=1.29-1.35), is observed. The location of this band and its sensitivity to deuteration indicates the dihydrogen bond formation.

This experimental data allow to conclude that the strong intermolecular interactions may appear in liquid phase not only for polar, but also for non-polar solvents.

DO WE NEED A TRIS(HYDROXYMETHYL)PHOSPHINE?

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The answer can only be positive. Unfortunately, according to data available investigation of possible tris(hydroxymethyl)phosphine (TGMF) application in Russia is terminated. However the polymeric materials with reduced flammability and extragents of rare earth and transuranium metals have been previously obtained on the base of TGMF. Nevertheless, overseas TGMF now found application in chemical technology for creating water-soluble metal complex catalysts of hydrogenation, in biology and biotechnology as crosslinking agents to obtain immobilized forms of enzymes in medicine in the form of complex compounds as anticancer drugs or diagnostic radiopharmaceutical.

TGMF can be obtained by the reaction of phosphine with formaldehyde in the presence of chlorides of *d*-metals, preferably Pt, Pd and Rh.[1-2]

$$PH_3 + 3\,CH_2O \rightarrow P(CH_2OH)_3$$

Slow speed of the process limits the ability of obtaining it, therefore, a more efficient method of obtaining TGMF is proposed.[3-4] The method is based on the use of effective catalytic systems - the salts of nickel or cobalt, activated by primary aliphatic amines, which are characterized by high selectivity and activity.[5-6]

The reaction proceeds at high speed, with yield of the product to 96-98%. The results obtained allow to recommend the process of synthesis TGMF for pilot testing and to expand to possibility of its use.

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BIOACTIVE COMPLEXES OF SILVER(I) WITH *O*-DIPHENOL DERIVATIVES OF THIOGLYCOLYC AND 3-MERCAPTOPROPIONIC ACIDS

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Synthesis and investigation of physico-chemical properties of Ag(I) coordination compounds are always topical due to their unique qualities and potential possibilities of being used in medicine, catalysis and optics.[1] We have synthesized crystalline complexes of Ag(I) ions with the ligands: 2-(4,6-di-*tert*-butyl-2,3-dihydroxyphenylsulfanyl)acetic acid (**I**) и 2-(4,6-di-*tert*-butyl-2,3-dihydroxyphenylsulfanyl)propionic acid (**II**). Elemental composition (corresponding to the general formular AgL_2), physico-chemical characteristics and structural peculiarities of the Ag(I) complexes were determined. According to the results of IR spectra analysis, oxygen atoms of carboxylic group and carboxylate ion are involved in forming coordination polyhedral of Ag(I) complexes.[2] As the ligands **I** and **II** are potential reductants for Ag(I), their complexes were investigated by EPR spectroscopy method in order to find out whether it was possible that paramagnetic particles were formed during their synthesis. In the EPR spectra of Ag(I) complexes there is a singlet signal with *g*-factor of 2,003-2,004 which belongs neither to phenoxyl radical nor to silver atoms Ag(0) or paramagnetic Ag^{2+} ions, but can be indicative of a partial charge transfer (PCT) complex being formed, involving orbitals of the ligand **I** (or the ligand **II**) and Ag(I).[3] Pharmacological screening revealed a high antimicrobial activity of Ag(I) complexes comparable with that of standard antibiotics (tetracycline, streptomycin, terbinafine and amphotericin B), but with a broader spectrum of action due to the fact that these complexes combine both antibacterial and antifungal activities.

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THERMODYNAMIC QUANTITIES OF PROTOLYTIC AND COORDINATION EQUILIBRIA FOR SOME COMPLEXONES RELATED TO ETHYLENEDIAMINETETRAACETIC ACID

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This work presents results of potentiometric, spectrophotometric and calorimetric investigations of the acid-base equilibria for trimethylenediamine-N,N,N',N'-tetraacetic, 2-hydroxypropylene-1,3-diamine-N,N,N',N'-tetraacetic, tetramethylenediamine-N,N,N',N'-tetraacetic, ethylenediamine-N,N'-diacetic-N,N'-dipropionic, N-(β-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acids and the complexation of those with zinc(II), cadmium(II), nickel(II), cobalt(II) ions in aqueous solutions. Thermodynamic quantities (logK, ΔG, ΔH, ΔS) for the relevant equilibria have been determined at 298.15 K and ionic strength values of 0.1–1.0 M. The results obtained were compared with the reference data on related compounds: imino-N,N-diacetic, N-methylimino-N,N-diacetic, N-(β-hydroxyethyl)imino-N,N-diacetic, nitrilo-N,N,N-triacetic, ethylenediamine-N,N,N',N'-tetraacetic and ethylenediamine-N,N'-disuccinic acids. The influence of background electrolyte character and concentration on the protolytic and coordination equilibria was under consideration. The standard thermodynamic quantities (logK°, ΔG°, ΔH°, ΔS°) have been evaluated for the corresponding reactions.

As ancillary part of this study, the spatial, electronic and energy parameters for isolated molecules and ions of these complexones have been computed. The data obtained were compared with results of structural and thermochemical investigations for the relevant complexones in an aqueous solution and crystalline state.

This work was supported by the federal target program "Scientific and Scientific Educational Personnel of an Innovative Russia" for 2009-2013 (No. 02.740.11.0253 and P-1360).

RUTHENIUM CARBORANE COMPLEXES AS EFFECTIVE CATALYSTS FOR CONTROLLED RADICAL POLYMERIZATION

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The synthesis of polymer materials with desired molecular-weight parameters and properties is an actual task for modern polymer chemistry. The controlled radical polymerization is one of the most efficient ways of it solution. That's why the development of novel systems capable to conduct polymer synthesis in the controlled mode is under careful attention in the leading scientific centers all over the world.

We have established that systems based on ruthenium carborane complexes are effective catalysts for controlled radical polymerization and allow to obtain polymers of methyl methacrylate, styrene and a number of other monomers. The use of the proposed systems allows to synthesize polymer samples with the molecular weights ranging from 2 to 150 thousands and polydispersity index of 1.1-1.3.

During the investigation of the influence of structure of ruthenium carborane complexes on the polymerization it was established that the complexes with chelate diphosphine ligands are the most effective catalysts. The mentioned compounds are real catalysts of the polymerization and may be reused after polymerization.

The use of systems based on ruthenacarboranes opens wide opportunities for macromolecular design, namely allow to synthesize block-copolymers based on different monomers.

It was shown that the use of additives of aliphatic amines has an activating influence on polymerization: allows to carry out controlled radical polymerization with rates, which are typical for conventional radical polymerization and allows to decrease the time of ultimate conversion up to 2-4 hours. This fact has a great influence for further applications of the obtained results.

The work was supported by RFBR (project № 11-03-00074)

MATHEMATICAL FOUNDATIONS FOR PHYSICAL-CHEMICAL MODELS OF SUBSTANCE TRANSFORMATION

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It is known that chemistry has acquired a mathematical and physical basis since the emergence of quantum mechanics and transferring the developed principles to molecular systems. As was revealed by Planck, an absolutely black body emits energy in portions. De Broglie established an association between the wave and corpuscular properties of matter. Heisenberg proposed a matrix approach to atom mechanics. Schrodinger described the systems in microcosm to develop an apparatus for wave mechanics. Dirac and von Neumann have proposed a mathematical substantiation for quantum mechanics by revealing the identity of the wave and matrix approaches, and rely on vector transformations in Hilbert space [1]. Chemical characteristics of an object can be obtained by solving a mathematical problem, yielding a vector in the orthonormal Hilbert space whose value gives a dimensionless probability for physical characterization of the object. Transition to the physical parameters proper occurs under the action of value operators on the vectors obtained. Metrization is performed on the basis of empirical law. The phenomenological approach to the description of molecular systems behaviour, called chemical thermodynamics, was developed within the bounds of physical thermodynamics and substantiated in statistical physics. The problem of mathematical justification of statistical mechanics is posed, and substantially solved, within the conception of the probability theory [2]. By further developing this approach it may be possible to develop a rigorous justification of fundamental physical and chemical regularities of multi-molecular systems movement, while remaining within the fairly abstract set, measure, and probability and avoiding any special assumptions about the character of objects under investigation.

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SYNTHESIS OF CYCLOPROPANE CONTAINING COPOLYMERS AS THE PHOTOSENSITIVE MATERIALS

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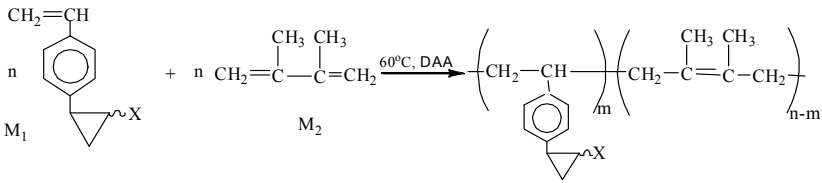
Now before the researchers there is a problem of not only improvement of the technological characteristics of photoresists used in photolithography, but preparation of new polymer photosensitive materials, and also revealing of the optimal conditions of their use.

This work has been devoted to the development of method of synthesis of polymer light-sensitive compounds with the aim of creation of new negative photoresists on their base. The light-sensitive compositions on the basis of copolymers of 2-(substituted)paracyclopropylstyrenes (PCPS – M_1) with 2,3-dimethylbutadiene-1,3 (M_2) were taken as an object of investigation.

The copolymerizations were carried out in mass and in solution of benzene in the presence of DAA.

The compositions and structures of the synthesized copolymers have been established on the basis of data of the spectral and elemental analyses. The structures of polymers showed that the polymerizations of PCPS proceed only on vinyl group.



X: -CO_2Et, -COOH, gem-dichlor, -CH_2OCH_3.

The copolymerization constants of the investigated comonomers have been determined and Q-e parameters have been calculated. It has been shown that in all cases 2,3-dimethylbutadiene-1,3 shows larger activity in comparison with PCPS, i.e. $r_2>r_1$(r_1 and r_2 – copolymerization constants of M_1 and M_2).

It has been revealed that the synthesized polymers possess high lithographical characteristics and can be used as high-sensitive photoresists of negative type. In addition, these polymers are optically transparent substances and show high physical-mechanical and heat-physical properties.

ELECTROCHEMICALLY AND CHEMICALLY INITIATED CYCLIC REACTIONS OF FORMATION AZODERIVATIVES FROM N-ARYLSUBSTITUTED HYDROXYLAMINES

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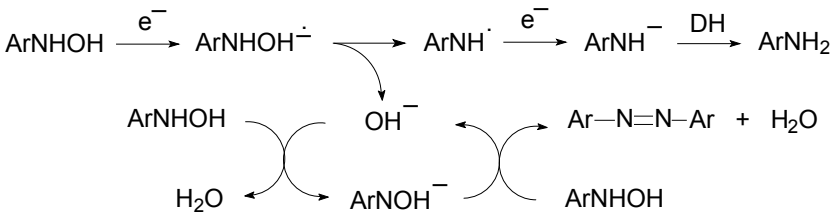
It was shown at first time, that in DMF solutions of 4-nitrophenylhydroxylamine passing of 0.1 F electricity causes its 70-80% conversion to corresponding azoderivative – 4,4′-dinitroazobenzene. Earlier we have found, that electroreduction of nitrophenylhydroxylamines gives rise to hydroxide anions formation[1]. It allows one to assume, that hydroxide anion acts both as an initiator and a mediator of cyclic reaction, and general mechanism of process is described by the scheme:



Really, the addition of small amounts of Et_4NOH to solutions of 3- and 4- nitrophenylhydroxylamines, selective formation of azoderivatives is observed (without passed of electricity).

This new reaction presents an interesting example of cyclic reaction, which can be initiated both chemically (as a result of proton transfer) and electrochemically (as a result of electron transfer).

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The work was supported by the Federal Targeted Program "Scientific and Scientific Pedagogical Personnel of the Innovative Russia in 2009—2013" (government contract 02.740.11.0636).

MODELING OF BUTADIENE-1,3 POLYMERIZATION USING NEODYMIUM CATALYST COMPLEX

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1,4-*cis*-Polybutadiene obtained by using the neodymium metal complex system is important raw material for rubber and tyre industries. Methods of obtaining a number of high stereoregular polybutadienes in the presence of various catalytic systems based on the compounds of titanium, cobalt, nickel are known. Alongside with that, 1,4-*cis*-polybutadienes synthesized by using neodymium catalysts turned out to be the most promising in terms of ecological cleanness of production. The issues of obtaining and using neodymium 1,4- *cis*-polybutadiene are based on the structural features of the neodymium catalytic system. First of all, it is polycentricity of a catalyst, which contains several points of anionic coordination polymerization differing by their activity. Therefore, to investigate the possibility of rubber properties regulation by controlling the molecular structure is an important scientific and practical issue.

The majority of models suggest that the reaction of polymerization takes place in the active centers of unified nature, i.e. a monocenter model of polymerization is accepted. In this study the mechanism of polymerization kinetics of butadiene-1,3 initiated by neodymium metal-complex system was identified.

Kinetic models of ion-coordination polymerization of butadiene-1,3 were suggested, these models allow to solve both the primal problem of defining molecular characteristics and inverse problem of searching kinetic constants. The values of kinetic constants of rates of all elementary stages of the process were defined, adequately describing experimental values of average molecular weights and molecular weight distribution. The mathematical software was developed as a complex of algorithms and programmes of solving primal and inverse problems for the systems of differential equations describing the kinetics of ion-coordination polymerization of butadiene-1,3, which can be used when the analysis of related catalytic reactions is performed.

THE MODIFICATION OF HETEROCHAIN POLYMERS WITH GELS BASED ON THE THERMODYNAMICALLY INCOMPATIBLE OLYGOMERS

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The synthesis of organic-inorganic gels based on the tetraethoxysilane and thermodynamically incompatible olygomers - oligooxyethylene glycol and oligodimethyl siloxane - is worked out. The experimental research was aimed at overcoming incompatibility of inorganic and organic components, that is the main problem of obtaining materials based on the sol-gel technology.

It was established that the fractal clusters of silica are formed in the bulk of the oligomer matrix. Owing to the associates lability silica gel is spread in reactive oligomers with the subsequent forming of silica network in the bulk of polymeric matrix. The silica fractal clusters were researched as nanostructure forming modifiers of polymers based on aromatic isocyanates in order to improve their performance properties.

It was determined that the modification of heterochain polymers by organic-inorganic gels caused the formation of additional intermolecular interactions. Consequently the significant increase of physical-mechanical properties in the area of very low concentrations was observed. Temperature dependence of dielectric loss tangent and atomic-force microscopy results showed the significant effect of the organic-inorganic gel modification on the microphase separation process.

TAGUCHI APPROACH TO INVESTIGATE THE RATE CONSTANT OF ACID-CATALYZED HOMOGENEOUS ESTERIFICATION REACTIONS

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The law of mass action states that rate constant is independent of concentration but dependent on catalyst, temperature and other factors. However, the effect of reaction parameters (mainly catalyst, reaction temperature, and molar ratio) on the rate constant in homogeneous catalysis is not fully understood.[1] Sulfuric acid catalyzed esterification of free fatty acids (50% oleic acid in oil) with methanol was carried out to understand the relations of rate constant to the reaction parameters. Taguchi method of statistical analysis has been used to quantify the relations.[2] For this method, L9 (3^4) orthogonal array of experiments (9 experiments, 3 parameters, 3 levels) were conducted. Taguchi method minimized the number of experiments and enabled study of many parameters simultaneously. It also facilitated the understanding of effect of reaction parameters on rate constant, overall reaction kinetics, and interaction of the parameters. Experimental data of kinetics fitted best with second order reversible rate equation.[3] Taguchi analysis of apparent rate constant and analysis of variance led us to redefine the rate constant which was found to be absolutely independent of molar ratio and only dependent on catalyst loading and temperature. Based on the re-defined rate constant, a method was developed to predict reaction kinetics of the remaining 18 experiments from full factorial design of 27 experiments and good agreement was found with experiments. A reaction mechanism has been also proposed from these results. Furthermore, investigating to relate the rate constant to Maxwell-Boltzmann distribution (for energies), i.e., fractional number of particles ($CH_3OH_2^+$–FFA) occupying a set of state $\boldsymbol{i}$ possessing energy $\boldsymbol{E_i}$. It would allow predicting kinetics at various %FFA level.

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STUDY ON HETEROCYCLIZATION OF 3-MERCAPTO-4-METHYL-1,2,4-TRIAZOLE AND ITS S-DERIVATIVES

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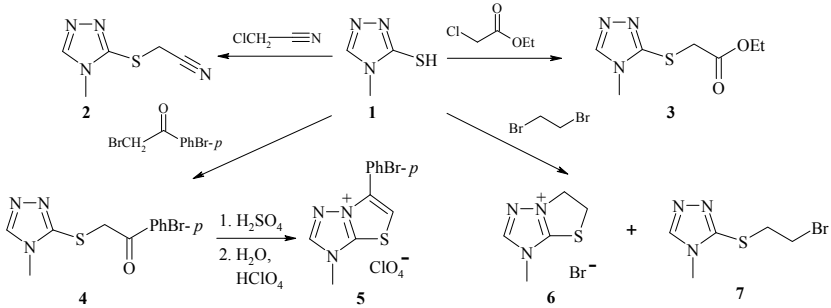
In this study, we aimed at the synthesis of new derivatives of thiazolo[3,2-*b*][1,2,4]triazole and so herein we report the interaction between [(4-methyl-1,2,4-triazol-3-yl)thio]acetonitrile (**2**), ethyl[(4-methyl-1,2,4-triazol-3-yl)thio]acetate (**3**) and 1-(4-bromophenyl)-2-[(4-methyl-1,2,4-triazol-3-yl)thio]ethanone (**4**) with acids and also the reaction of 3-mercapto-4-methyl-1,2,4-triazole (**1**) with 1,2-dibromoethane.

Parent compounds **2-4** were synthesized by the reaction of mercaptotriazole **1** with chloroacetonitrile, ethyl chloroacetate and *p*-bromophenacyl bromide, respectively, in 2-propanol in the presence of sodium isopropylate (method A) and in alcoholic alkali solution (method B).



It was found that compound **4** undergo heterocyclization in acid medium that resulted in 6-(4-bromophenyl)-3-methyl[1,3]thiazolo[3,2-*b*][1,2,4]triazolium chlorate (**5**), whereas compounds **2** and **3** do not react with the acid. Boiling of compound **1** with 1,2-dibromoethane in 2-propanol in the presence of KOH afforded the mixture of cyclization products, 3-methyl-5,6-dihydro[1,3]thiazolo[3,2-*b*][1,2,4]triazolium bromide (**6**), and S-alkylation product, 3-[(2-bromoethyl)thio]-4-methyl-1,2,4-triazole (**7**).

The structure of synthesized compounds was confirmed by mass spectra, IR and ^{1}H NMR.

O-QUINONATO AND O-IMINOQUINONATO NONTRANSITION METAL COMPLEXES IN REACTIONS WITH SMALL MOLECULES

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The combination of complex nontransition metal and redox-active ligand which is capable to reversible oxidation and reduction being in a metal coordination sphere permits to model a behavior of transition metal complexes. The reactions of small molecules and atom groups addition carrying out with retention of nontransition metal oxidation state but with change of redox-active ligand oxidation state are possible in such type of complexes.

It was found that catecholate and *o*-amidophenolate Sn(IV), Pb(II), Mg(II), Zn(II) and Cd(II) complexes react easily with nitrogen mono- and dioxides and halides yielding corresponding *o*-semiquinonato and *o*-iminosemiquinonato derivatives. Some of these derivatives were isolated in solid state and were characterized using different physicochemical methods including X-ray analysis.

The reactions between bis-*o*-semiquinonato/bis-*o*-iminosemiquinonato Zn(II), Cd(II) and Pb(II) complexes and nitrogen monoxide were investigated using EPR method. It was found that these complexes bind reversible NO at temperature lowering, in this process one of two *o*-semiquinonato/*o*-iminosemiquinonato ligands is oxidized to form a coordinated *o*-quinone/*o*-iminoquinone.

This work was made according to FSP "Scientific and scientific-pedagogical cadres of innovation Russia" for 2009-2013 years (GK P982 from 27.05.2010). We are grateful to RFBR (№ 10-03-00788), President of Russian Federation (grants NSh-7065.2010.3, MK-614.2011.3), Russian Science Support Foundation (I.E.V.) for supporting of this work.

MECHANISM OF CATALYTIC EFFECT OF ONIUM SALTS AND ALLIED COMPOUNDS IN ALKYLATION REACTIONS OF COMPOUNDS WITH MOBILE ATOM OF HYDROGEN REPORTED IN LITERATURE AS PHASE-TRANSFER CATALYSIS

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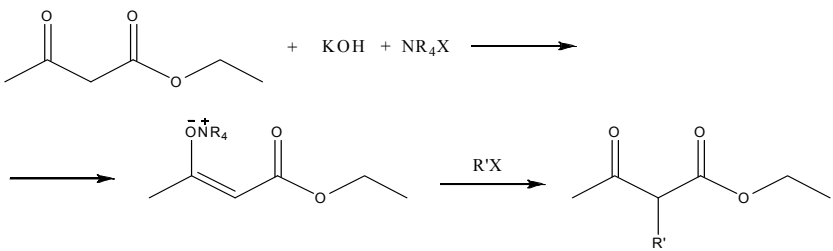
The purpose of the research was to reconsider the present ideas about the role of onium salts and allied compounds with mobile atom of hydrogen, reported in literature as "phase-transfer catalysis", in reactions occurring in the area of contact between two phases. We concluded that the role of aforementioned compounds is the formation of low-dissociated intermediates, which leads to final products of reaction under the influence of alkylated compounds.[1,2]



USING THE TODD-ATTERTON REACTION UNDER CATALYTIC ACTION OF ONIUM SALTS IN THE SYNTHESIS OF A LARGE RANGE OF ORGANOPHOSPHORUS COMPOUNDS

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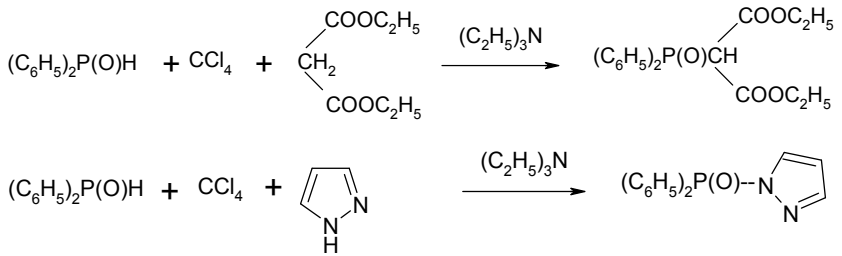
Todd-Atherton reaction was discovered by Atherton at al. in 1945[1]. The reaction consists of interaction of hydrophosphorylic compound with carbon tetrachloride, an amine and a tertiary organic base.

This reaction was carried out in the presence of catalytic quantity of onium salts with a large number of different-constructed nucleophiles – phosphines, mercaptances, alcohols, β-dicarbonyl compounds, acetylene, vinylacetylenes, diines, azoles, pyrimidines, etc.



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ON MECHANISM OF INTERACTION SUBSTITUTED N-ARYLSULPHOXYIMIDES AND BASES

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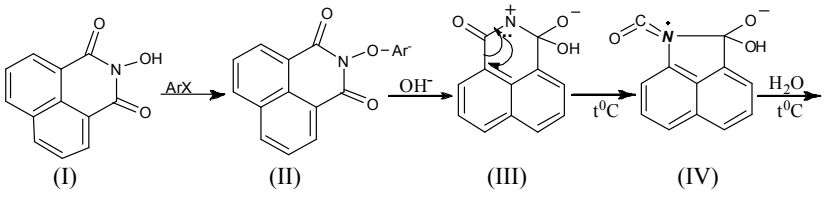
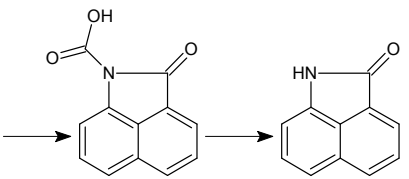
Lately naphthostyryl (VI) (lactam of 1,8-aminonaphthoc acid) has been attracting still close attention of many investigators. Of special interest has been naphthostyryl since the beginning of the60s of the 20th century [1]. There are several methods of production of (VI) industrially: oxidation of naphthaloimide with sodium hypochlorite (Hofmann rearrangement), alkaline fusion of 1,8-cyanonaphthalene sulphonic acid. The available methods of production (VI) have a number of disadvantages; low product output of a volume unit and love output of (VI), or it is necessary to use toxic product such as salts of hydrocyanic acid.

The method of producing naphthostyryl and its substitutes has been proposed, which proceeds from easily available N-oxynaphthaloimide (I) by changing its N-aryloxy- or N-arylosulphoxynaphthaloimides (II) when interacting with water-alcohol solution of alkali or organic base. There by the reaction undergoes a number of intermediate stages (III, IV, V), resembling sextet rearrangement of Lossen, Curtius, Schmidt [2].



(I) (II) (III) (IV)



(V) (VI)– *naphthostyryl* (VI)

Rearrangement (II) runs without opening an imides ring but by transferring electron pairs whit forming isocyanate (IV), the structure of it has been proved correct by NMR-Spectrums by changing the compound (V) into esters and amides.

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STUDYING REDUCTION REACTIONS OF ARYL-SUBSTITUTED 4H-SELENOPYRANS

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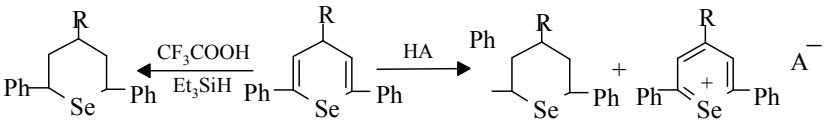
The aryl-substituted 4H-selenopyrans are known to form the corresponding selenanes during the reduction in the disproportion[1] or ion hydrogenation[2] reactions.



During the process of the disproportion reaction in the presence of deutero-trifluoroacetic acid, the constant of proton spin-spin interaction in α-position of selenane ring was determined to be more than 11 Hz. It means that phenyl substituents at the same carbon atom are located equatorially.

In the course of studying the reaction products obtained by means of chromatography/mass spectroscopy method, it was found that selenanes are mainly produced as a single isomer in which all the substitutes are located equatorially. However, there are admixtures of other isomers in the reaction mixture, these isomers disappearing during recrystallization.

For example, to connect the heterocyclic ring with methyl substitute in C_4 position there have been revealed three isomers in the quantities of 92,5 %; 6 % and 1,5 %. The predominance of the main isomer in the disproportion reaction for other compounds was much more expressed.

The isomeric composition of the compound in the ion hydrogenising was similar to the composition obtained in the previous experiments, the content of the main isomer being considerably less in the compound with p-methoxyphenyl substitute in C_4 position of the heterocycling ring.

The obtained results can be explained with running along with the basic process isomerization reaction of 4H-selenopyran into its 2H-isomer as it has been described before[3].

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THE NEW IN CHEMISTRY OF MONOTERPENE SEVEN-MEMBERED LACTONES

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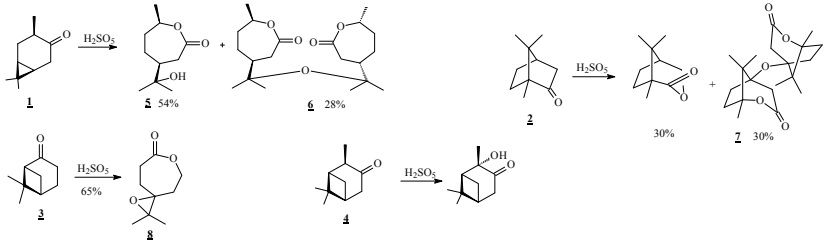
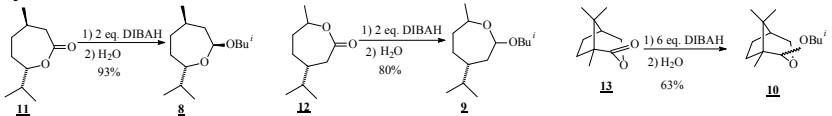
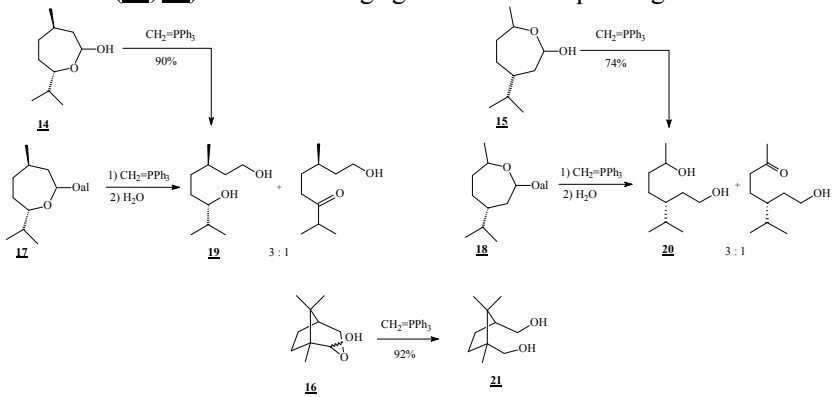
Using Caro's acid in the Baeyer-Villiger oxidation, we have performed the synthesis of a number of seven-membered lactones (**1**-**4**) resulting from oxidative and skeletal rearrangement of bicyclic monoterpene ketones (**5**-**7**) and proposed a possible mechanism for their formation.



A new reaction has been found in chemistry of aluminum organic compounds, that is the formation of lactol O-isobutyl derivatives (**8**-**10**), in the process of the low-temperature (-70°C) reduction of monoterpene seven-membered lactones (**11**-**13**) by excess diisobutyl aluminum hydride in methylene chloride.



It has been revealed that methylentriphenylphosphorane (19-21) in reactions with a number of seven-membered lactols [(-)-mentholactole (**14**), carvomentholactole (**15**), 1,8,8-trimethyl-3-oxabicyclo[3.2.1]octan-2-ol (**16**)] and their aluminates (**17**, **18**) can be reducing agent to the corresponding diols.



CONTROLLED RADICAL POLYMERIZATION OF VINYL MONOMERS AND METAL COMPLEXES

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Radical polymerization is one of the most important commercial processes to produce polymer materials. At present two important trends of controlled synthesis – "living" radical polymerization and complex-radical polymerization – have been developed rapidly. The use of metal containing substances in polymerization processes advance new promises on a path leading to well-defined polymers. The goal of this study is search and investigation of new types of metal complexes of different nature, their combination with each other or with heteroatom containing derivatives and development of effective initiating systems on their base for carrying out the radical polymerization of vinyl monomers in controlled manner.

For the first time azinyl derivatives of ferrocene, semiclathrochelates and clathrochelates of Fe(II) containing ferrocenyl fragments (and without them), porphyrins of titanium (IV), zirconium (IV), iron (III) and cobalt (III) as modifying additives for the radical polymerization of vinyl monomers were proposed. Common and peculiar features of methyl methacrylate and styrene polymerization in the presence of novel initiation systems based on metal complexes were shown. The correlation between the composition of initiating systems and their reactivity in polymerization processes were found. Dependences of molecular characteristics and thermo stability of polymers obtained by the use of metal complex additives on synthesis conditions were established. The effect of stereoregulation in MMA radical polymerization on the base of new initiating systems was found. The most probable mechanisms of vinyl monomers polymerization processes in the presence of metal complex additives were proposed. The most effective initiating systems among a hundred studied systems were singled out.

This work was supported by the Russian Foundation of Basic Research (grants No. 10-03-00027-a and 10-03-00967-a).

PECULARITIES OF GEOMETRIC AND ELECTRONIC STRUCTURE OF HEMIHEXAPHYRAZINES

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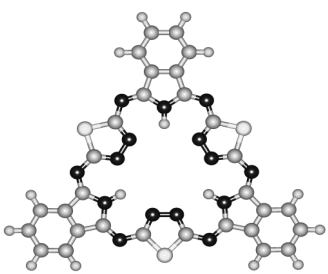
A synthesis of analogues of hexaazaporhyrinoids (*hemihexaphyrazines*) has been carried out [1, 2] and their structure was determined for the first time: in the gas phase, by gas-phase electron diffraction combined with high-level quantum-chemical computations [3], and in the solid phase, by X-ray crystallography [4].

It has been found that the framework of the molecules is planar and contains a formally conjugated system whose number of π-electrons (30) corresponds to the Huckel's rule (4n+2). At the same time experimental and theoretical investigations have shown that these macrocyclic molecules do not exhibit aromatic character. A detailed analysis of global and local aromaticity of hemihexaphyrazines and some model compounds has been performed using geometrical and magnetic criteria. It has been shown that intramolecular three-centered hydrogen bonds play a crucial role in formation and stabilization of the non-aromatic framework of the molecules. Denstity functional theory calculations have been used to study intramolecular proton transfer.



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ULTRAFAST PHOTOINDUCED CHARGE SEPARATION AND CHARGE RECOMBINATION

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In the report the results of experimental and theoretical investigations of ultrafast photochemical processes obtained last decade have been generalized and systematized. Comprehension of the fact that ultrafast processes proceed in parallel with an nuclear relaxation and, as a rule, in the conditions of strong nonequilibrium nuclear subsystem is one of the most important results in this field.[1-3] The basic regularities of such processes are discussed, in particular, dependence of an quantum yield of products on characteristics of reactants and properties of solvents.[1,4] The models capable quantitatively to describe kinetics of ultrafast processes are considered and critically analysed. Making use of the revealed regularities, approaches are formulated how to control a quantum yield of products. Results of these researches are important not only for the decision of traditional problems of chemical kinetics, but also for working out of molecular elements of electronic devices,[5] creation of molecular structures for effective photovoltaic units.

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This work was supported by the Ministry of Science and Education of Russian Federation, contracts P1145 and 14.740.11.0374.

NOVEL METHOD OF FORMATION PERYLENE CRYSTALLINE LAYER AT THE SURFACE OF POLYCARBONATE FILM

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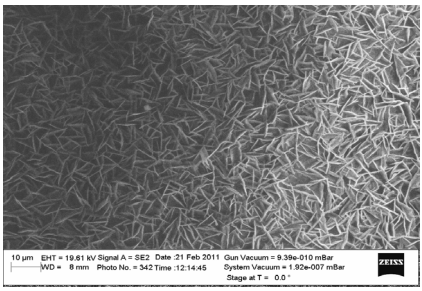
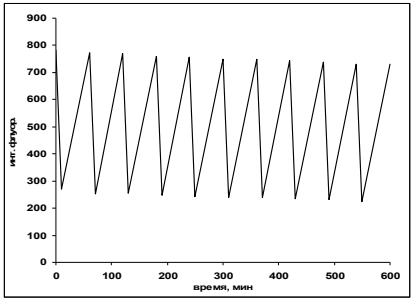
We found that the complex formation of perylene with iodine can be applied to the formation of crystalline perylene layer on the surface of a polycarbonate film. This is achieved by chemical deposition method[1-2] of complex after treatment of polycarbonate films containing dissolved perylene with iodine – solvent vapors. Crystalline layer of perylene on the surface of polycarbonate film is studied by Scanning Electron Microscopy (SEM-image is shown on the left) and Attenuated Total Reflectance IR-spectroscopy (ATR IR-method).





Novel belayer films perylene on polycarbonate behave sensor properties to vapors of iodine, which is appeared in the reversible changes in both spectral properties (enhancing absorption intensity at 700-800 nm and decreasing fluorescence intensity at 500 nm – image shown on the right) and electrical conductivity of the surface layer.

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This work was supported by RFBR, project N 09-03-12199-ofi_m and N 11-03-93984-ИНИС_а.

ALKYLATION OF POLYFLUOROALKYLSUBSTITUTED PYRAZOLES 4-BROMOBUTYL ACETATE

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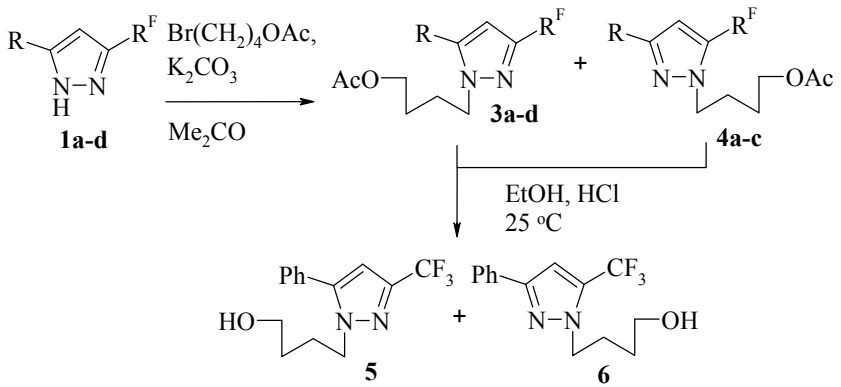
To synthesize non-natural nucleoside analogs we have studied the reaction of alkylation of pyrazoles **1** by 4-bromobutyl acetate, simulating a fragment of nucleoside reverse transcriptase inhibitor - abacavir. The reactions in refluxing acetone in the presence of potassium carbonate lead to the formation of 4-acetoxybutylsubstituted isomers **3** and **4**, the ratio of which depends on the nature of the substituents. Acyl protection was removed by acidic hydrolysis. Isomers **3**, **4** and **5**, **6** were separated by HPLC.



1,3,4: $R^F = CF_3$, R = Ph (**a**); $R^F = (CF_2)_2H$, R = Me (**b**), Ph (**c**), $(CF_2)_2H$ (**d**)

This work was supported by the Russian Foundation for Basic Research (project № 09-03-00274a), the Ministry of Education and Science of the Russian Federation (State contract № 02.740.11.0260), Ural Branch of Russian Academy of Sciences (№ 09-I-3-2004), a program of state support of leading scientific schools (grant № SS-65261.2010.3).

SYNTHESIS OF BIANTENNARY NEOGLYCOLIPIDS

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The development of new gene delivery systems is an actual problem of modern gene therapy. Because of potential danger of viral delivery systems alternative transport "containers" on the basis of cationic lipids are widely applied. Lipid gene delivery systems are nonimmunogenic, nontoxic, biodegradable, but they possess a low selectivity, reducing its delivery efficiency. For improving lipid carriers targeting ligands are included in their structure to promote effective penetration of a genetic material into target cells. Peptides, antibodies and mono -, oligo - and polysaccharides are commonly used as targeting ligands.

Galactose-containing lipid transport systems are selectively recognized, bound and merged by hepatocytes, exhibiting asialoglycoprotein receptors on its surfaces. It is known that the affinity of transport system to receptors increases with the increasing of the galactose quantity in a lipid molecule.

We carried out synthesis of the cluster neogalactolipids possessing increased affinity to hepatocytes. The structure of neogalactolipids includes two galactose moieties, bound to the lipid domain (cholesterol or ditetradecylglicerol) into a single molecule by means of L-glutamic acid. An attachment of targeting ligands to glutamic matrix was carried out with spacers on the basis of 6-aminohexanol and oligoethyleneglycol. Obtained carbohydrate clusters were conjugated with COOH-containing lipid components in conditions of classical reaction of amid bound formation. Structures of the neoglycolipids have been confirmed by means of nuclear magnetic resonance spectroscopy and mass spectrometry.

Work is supported by Federal Program «Scientific and pedagogical human resources for innovative Russia 2009-2013» (the state contract № P715) and the Russian Foundation for Basic Research (№ 10-03-00995-a).

SYNTHESIS OF NEW NEOMENTHYL CONTAINING COMPOUNDS

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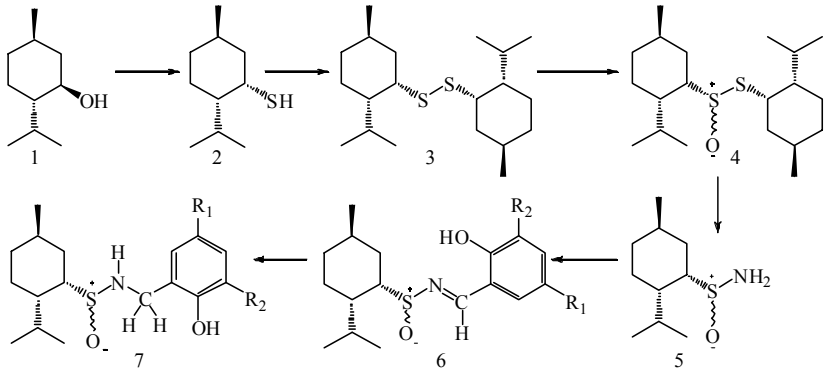
Sulfur containing terpene derivates possess valued physiological properties. High antiparasitic, antibacterial and nematocidal activities as well as moderate antitumoral effect for some terpenic sulfinyl containing matters are detected. Terpenic thiols are of interest in organic synthesis of new potential biologically active organosulfur compounds: sulfoxides, thiosulfinates, sulfinyl and sulfonyl amides et al.

Based on *l*-menthol, we carried out the synthesis of neomenthyl thiol (**2**), dineomenthyl disulfide (**3**), dineomenthyl thiosulfinates (**4**), sulfinyl imines (**6**) and sulfinyl amides (**5**), including *N*-substituted ones (**7**)**.**



1. R_1=R_2=H; 2. R_1=Cl, R_2=H; 3. R_1=R_2=Br

The thiol (**2**) was obtained via tosylate and isothiouronic salt of menthol in two steps. The synthesis occurred with the inversion of a configuration. **3** formed in a quantitative yield as a result of the oxidative dimerization of the thiol (**2**) by I_2. The oxidation of **3** by various oxidants (*m*-CPBA, TBHP, CHP) was studied. The individual sulfinyl amide (**5**) was obtained via nucleophilic substitution in **4** by potassium amide. New sulfinyl salicyl aldimines (**6**) with *trans*-position of substituents at the double bond are synthesized via condensation of **5** with salicyl aldehide and its derivatives. Reduction of sulfinyl imines (**6**) by $NaBH_4$ or $LiAlH_4$ gave the corresponding *N*-substituted sulfinyl amides (**7**).

The work was supported by the Russian foundation for basic research (grant 10-03-00969).

BIOLOGICALLY AND SURFACE-ACTIVE DERIVATIVES OF OXANE-4-OLE

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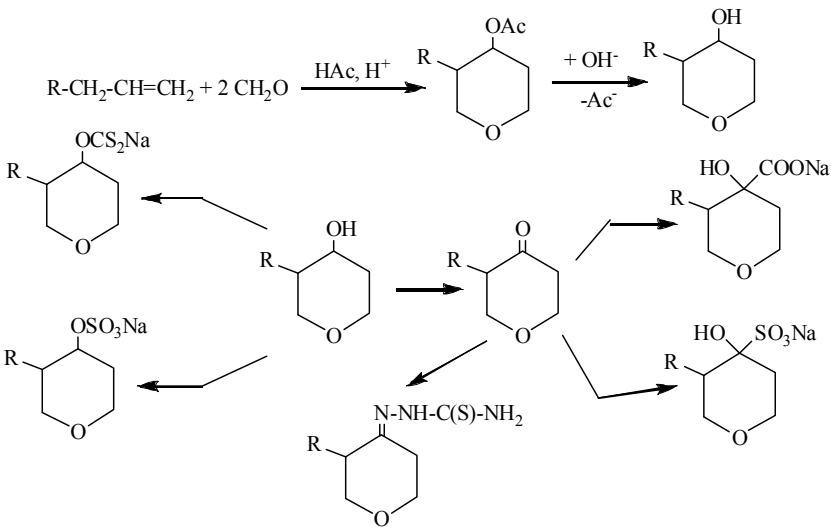
The oxane-4-ole derivatives[1], synthesized under the scheme, are the biologically and surface-active compounds and can by used in practice as flotation reagents[2], depressants[3] for pumping hydrocarbons and growth factor of plants in phytotechnology[4].



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Work with financial support of the Ministry of Education and Science of Republic Kazakhstan.

1, 3-DEHYDROADAMANTANE IN REACTIONS WITH AROMATIC COMPOUNDS

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Adamantyl-containing aromatic compounds are used in various fields of science and technology. Therefore, the synthesis of these compounds is relevant. Known methods of obtaining aromatic compounds containing the adamantane framework based on using as adamantyl-containing agents halogen - and hydroxy-adamantane and its derivatives. Promising adamantyl-containing agent in reactions with aromatic compounds is 1,3-dehydroadamantane (DHA)**.**

The purpose of this study was to investigate the reactions of DHA with aryl alkanes, polycyclic aromatic compounds, phenols and naphthols, as well as with benzoic acid and its derivatives.

Investigated the catalytic and non-catalytic reaction of DHA with aryl alkanes: toluene, ethylbenzene, cumene, *o*-, *m*- and *p*-xylenes, 1,3,5-trimethylbenzene and 1,2,4,5-tetramethylbenzene. Established that non-catalytic addition of DHA to the aryl alkane occurs by α-carbon atom side chain, which is unusual for fatty aromatic hydrocarbons. In this form the aromatic compounds in which the adamantyl radical is linked to the aromatic ring methylene bridge. Reaction of DHA on the methylene group with aromatic compounds such as acenaphthene, tetralin, fluorene also point to the unusual course of these interactions. Non-catalytic reaction of DHA with phenols occur mainly on the hydroxyl group with the formation simple adamantyl ethers of phenols.

Catalytic reactions (catalyst-sulfuric acid) of DHA with these aromatic compounds of benzene and of a series of phenol results in predominantly the adamantylation products into the aromatic ring.

In the reactions of DHA with benzoic acid and its derivatives selectively formed adamantlyl ethers in a relatively short time (30-60 min) under mild conditions and in the absence of a catalyst.

STUDY OF THE POSSIBILITY OF SYNTHESIS OF THE POLIBOROPHENILSILOXANES BY MECHANOCHEMICAL ACTIVATION

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The interaction poliphenilsiloxanes with boric acid under the conditions of mechanochemical activation at initial ratios Si/B, equal to 1:1 and 2:1 have been investigated. Mechanochemical activation was carried out in Planetary Mono Mill "Palverisette 6" at a frequency of 10Hz and the ratio of the activating packing to effective load equal to 1 : 1.8. The activation time from 1 to 5 minutes.

Reaction mixture after mechanic-chemical activation was divided into all syntheses into soluble and insoluble fractions by a toluene extraction in a Soxhlet apparatus. Soluble fractions - glassy substance from white to pale yellow. Insoluble - powdery substance gray-white color. Composition of the fractions were studied by elemental analysis, infrared spectroscopy, X-ray diffraction and X-ray analysis, gel - chromatography.

Insoluble fractions are mainly a mixture of boric acids, including unreacted orthoboric acid. Insoluble fraction depended little on the time of activation, but decreased with increasing initial ratio of Si / B.

Soluble fractions, according to research, represented poliborophenilsiloxanes, with a relative molecular weight ≥ 5000.

In all of the soluble products ratio Si / B is close to two.

For received poliborophenilsiloxanes set composition: $[(PhSiO_{1,5})_xBO_{1,5}]_n$. Depending on the initial ratio of Si / B and the activation time value of X changed as follows:

The initial ratio Si / B = 1/1: X = 2,1 (1 min.) X = 2,1 (3 min.) X = 2,0 (5 min.). The initial ratio Si / B = 2/1: X = 2,3 (1 min.) X = 2,3 (3 min, X = 2,2 (5 min.).

It was proposed that the composition obtained in a mechanochemical activation products depends on the nature introduced into the siloxanes chain heteroatoms, and not the initial ratio of Si / B. Ratio of Si / B = 2:1 may be evidence of a stable structure cyclolinear borosiloxanes fragments. X-ray diffraction analysis showed the amorphous nature of products, increased interchain distances with increasing boron content in the polymer chain.

OXIDATION OF ALKANOLS BY SYSTEMS H_2O_2 - Ce(III) – MBR AND H_2O_2 - Ce(IV) – MBR

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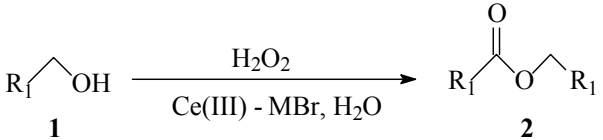
Oxidation of alcohols is one of the fundamental reactions of organic chemistry. The problem of development is new, simple, and selective methods for oxidation is always urgent.

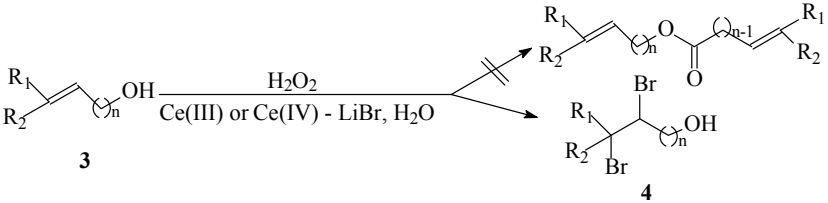
A new oxidation system was proposed, namely, salt Ce(III)(cat.) - MBr(cat.) - H_2O_2(stoichiometric oxidant), under the action of which primary alkanols (**1**) C_6 - C_9 are transformed into esters (**2**) in the reaction zone with very low concentration of H_2O_2. At the molar ratio **1** : $Ce(NO_3)_3$: MBr : H_2O_2 = 1 : 0.5 : 1 : 10, the selectivity of formation of esters **2** is ~ 98% and conversion of **1** is ~ 90%. Transformation **1** → **2** occurs in the cyclic process, and $Ce(NO_3)_3$ and MBr act as redox catalysts (Ce(III)/Ce(IV); $Br^-/Br^\bullet$).



1 **2**

R_1 = alkyl C_5 – C_8; M = Li, Na, K

Under the same conditions, unsaturated alkanols (**3**) are oxidized by systems H_2O_2 – Ce(III) and H_2O_2 – Ce(IV) combined with LiBr.



3 **4**

R_1, R_2 = H, alkyl C_1-C_3; n = 1–4; Ce(III) = $Ce(NO_3)_3$; Ce(IV) = $Ce(NH_4)_2(NO_3)_6$

α-Methylene group in alkenols **3** is not oxidized with bromine generated from LiBr. Bromine adds to the double bond to form only vicinal dibromoalkan-1-ols (**4**) in 80-90% yield.

This work was financially supported by the Russian Foundation for Basic Research, project no. 09-03-00292a.

OLIGO-AND POLIMERIZATION OF ETHYLENE IN THE PRESENCE OF CATALYTIC SYSTEMS BASED ON SOLUBLE FORMAZAN COMPLEXES WITH Ni(II), Cr(III) AND Ti(IV)

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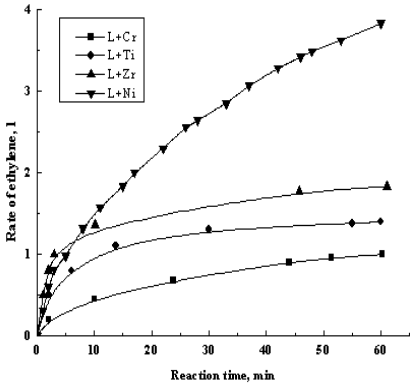
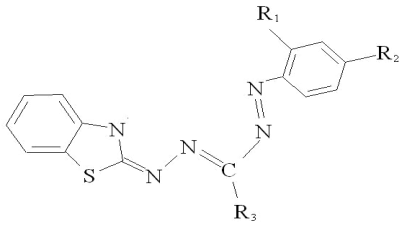
Application of homogenous catalysts based on organometallic complexes of nickel, titanium, chromium and zirconium in conjugation with the organoaluminum compounds in oligomerization processes is the most common in the chemical industry.





L) **R_1=Cl, R_2=H, R_3=C_4H_9**

Fig. 1. Kinetic curves of consumption of ethylene in the reactions of oligo- and polymerization of olefins. T = 60^0C, toluene 50 ml, [Me] = $1\cdot10^{-5}$ mol/ml, $Al(C_2H_5)_3$ = $3{,}6\cdot10^{-4}$ mol/ml, $P_{ethylene}$= 2 MPa

This work concerns the study of catalytic activity of different formazans with transition metals Cr(III), Ti(IV) and Ni(II) in oligo- and polymerization processes of olefins and the influence of reaction conditions. It is shown that the conjugation of formazans with Cr and Ti forms ultra-high molecular weight polymer, while the usage of Ni results in oligomers formation(C_4-C_{12+}).

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THE STABLE PHOSPHORYLATED AZIRIDINIUM SALTS AND THEIR SOME REACTIONS WITH NUCLEOPHILES

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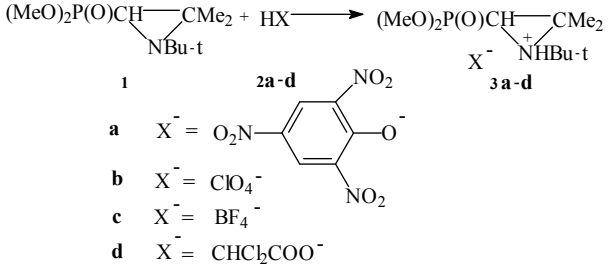
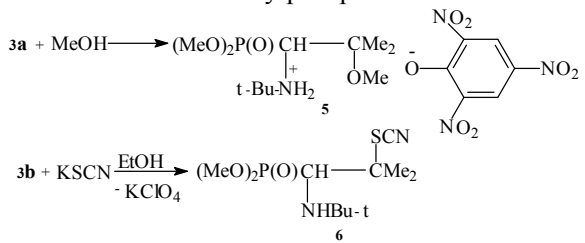
We have found that an interaction of O,O-dimethyl(1-*tert*-butyl-3,3-dimethylaziridin-2-yl)phosphonate 1 with acids 2a-c led to the formation of the stable salts 3a-c, which were isolated in individual state.

When the reactions between compounds 1 and 2b-c were carried out in dioxane the solvate complexes 4b-c of the salts 3b-c with dioxane were formed in ratio 2:1.



The aziridinium salts 3 react with nucleophiles to form the polyfunctional organic phosphorus derivatives. For example, a salt 3a reacts with methanol and 3b reacts with potassium thiocyanate. The new salt 5 and the thiocyanato substituted 1-aminoalkylphosphonate 6 were formed.



The composition and structure of the new compounds 3a-c, 4b-c, 5 and 6 synthesized were confirmed by elemental analysis, ^{1}H and ^{31}P NMR spectroscopy and mass spectrometry.

This study was financially supported by the Federal purpose programme «Scientific and pedagogical personnel of innovation Russia for 2009-2013» (The state contract P-1108).

THE REACTIONS OF O,O-DIMETHYL-1-(*TERT*-BUTYLAMINO)-2-METHYL-2-CHLOROPROPYLPHOSPHONATE WITH SOME NUCLEOPHILES

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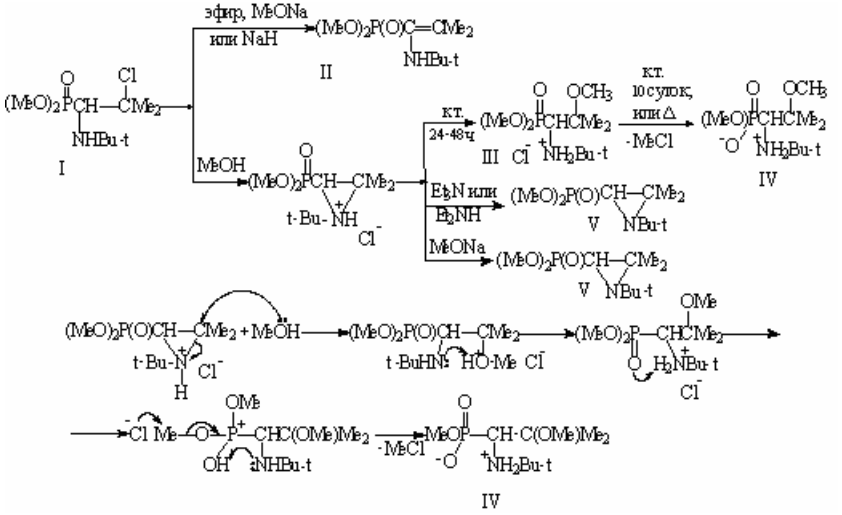
For the purpose of synthesizing of the polyfunctional N-containing phosphoryl compounds the reactions of O,O-dimethyl-1-(*tert*-butylamino)-2-methyl-2-chloro-propylphosphonate (I) with some nucleophiles (methanol, sodium methylate and hydride, secondary and tertiary amines) were studied.

We have found that the rout of an intrection of the compound (I) with sodium methylate depends on the solvent nature: enamine (II) and aziridine (V) were formed in ether and alcohol solutions, respectively.

When the mixture of the compound (I) with methanol was allowed to stand for 48 hs, the lowstable 2-methoxy-1-(tert-butylamino)propylphosphonate hydrochloride (III) was formed. In 10 days standing or by short time boiling the salt (III) transformed into betain (IV). By the treatment of the compound (I) with methanolic solution of diethyl- or trielthylamine aziridine (V) was the main reaction product.

We propose the following reaction schemes:



This study was financially supported by the Federal purpose programme «Scientific and pedagogical personnel of innovation Russia for 2009-2013» (The state contract P-1108).

DIRECTED SYNTHESIS OF AMINO SULFIDES THROUGH AMINOMETHYLATION OF THIOLS

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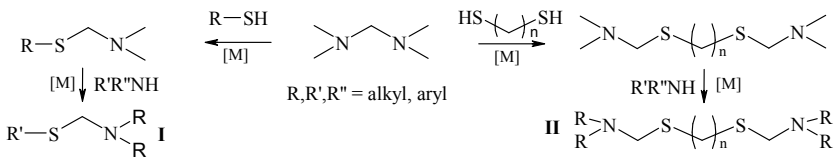
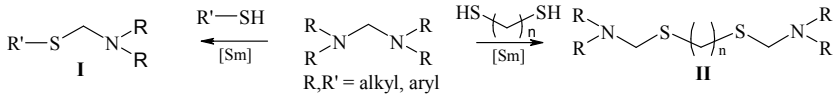
The Mannich aminomethylation reaction mediated by formaldehyde and secondary amines is recognized as the classical method to produce amino sulfides[1].

This report represents new methods for the selective synthesis of amino sulfides through aminomethylation of thiols with *gem*-diamines under the action of the Lewis-acid catalysts.

Thus, amino sulfides, previously obtained from *N,N,N′,N′*-tetramethylmethanediamine and thiols, were found to react with secondary amines under the action of $ZnCl_2 \cdot 2H_2O$ or $FeCl_3 \cdot 6H_2O$ as catalysts under reaction conditions ($CHCl_3$, 60 ºC, 6 h) with the selective formation of amino sulfides **I** and **II** in 65–95% yield. Without a catalyst, the yield of the target products did not exceed 25%.



The alternative approach to the selective synthesis of amino sulfides **I** and **II** via aminomethylation of mono- and α,ω-alkane dithiols with *gem*-diamines mediated by $FeCl_3 \cdot 6H_2O$ as acatalyst, under the same conditions, but within 1.5 h, is also discussed.



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This work was financially supported by Russian Foundation for Basic Research (Grant 08-03-00789a).

SELECTIVE ETHYLENE OLIGOMERIZATION TO HEXENE-1 BY THE HOMOGENEOUS CATALYST SYSTEM $Cr(EH)_3$–DMP–$AlEt_3$–MODIFYING AGENT

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Union Carbide Co researchers had previously detected hexene-1 formation on the catalyst system Cr-(ethylhexanoate)$_3$–polyisobutylaluminoxane for ethylene polymerization.[1] The different homogeneous catalyst systems based on Cr(III) have been studying in recently 20 years. Some of these systems, which consist of complex Cr-(ethylhexanoate)$_3$ showed in table 1.

Table 1. **Catalyst systems of selective ethylene oligomerization**

Catalyst system	T, °C	$P_{ethylene}$, MPa	Selectivity of C_6-1, wt.%	Ref.
$Cr(EH)_3$–PIBAO–1,2-dimethoxyethane	95	2.8 – 3.5	74	2, 3
$Cr(EH)_3$–pentaphenylcyclopentadiene–TEA–C_2Cl_6	120	5.0	76	4
$Cr(EH)_3$–dimethylpyrrole–TEA–chloro-compound*	90	3.5	no less 80	5

* 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 2,2-dichloropropane, 1-chloroheptane, chloroform.

We had also observed hexene-1 formation during the polymerization of ethylene using Cr(acetylacetonate)$_3$–$AlEt_3$ catalyst system.[6]

The data about influence of temperature, monomer pressure, modifying agent/Cr molar ratio and solvent type to the catalytic activity and selectivity of system $Cr(EH)_3$–2,5-DMP–TEA–modifying agent will be represented in our reporting as the continuation of last investigations. The selectivity to hexene-1 obtained 93 wt.% under optimal conditions. The process kinetic performance was calculated for this catalyst system.

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REGIOSELECTIVE REDUCTION OF 2-PERFLUOROALKANOYLCYCLOHEXANE-1,3-DIONES AND THEIR ENAMINO DERIVATIVES

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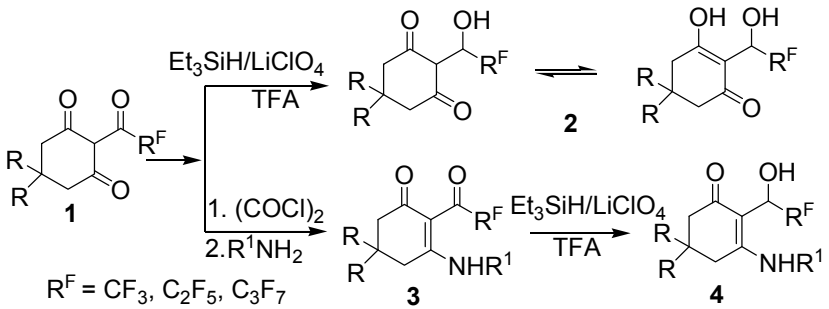
2-Perfluoroalkanoylcyclohexane-1,3-diones[1] and their enamino derivatives present significant interest as the versatile "building blocks" for introducing polyfluoroalkyl groups in various carbo- and heterocyclic systems. Unlike nonfluorinated cyclic β,β'-triketones chemistry of these compounds is studied unsufficiently and investigation of their chemical transformations, in particular, in reduction, is an important problem for the chemistry and the synthetic use of these polyfluorinal compounds.



The ionic hydrogenation of nonfluorinated 2-acylcycloalkane-1,3-diones and their *endo*-cyclic enamino derivates is known to proceed with hydrogenolysis of keto group in the side acyl chain to give the methylene group. We found that the reaction of ionic hydrogenation of 2-perfluoroalkanoylcyclohexane-1,3-diones **1** under the action of triethylsilane in trifluoroacetic acid in the presence of catalytic amounts of lithium perchlorate proceeded regioselectively with reduction of *exo*-cyclic carbonyl group to hydroxy one to afford diketoalcohols **2** in high yields. Under the conditions of ionic hydrogenation enamino diketones **3**, containing secondary amino group, afforded enamino ketols **4**, while enamino diketones **3**, containing tertiary amino group, were subjected to a deacylation to afford enamino ketones.

SYNTHESIS OF POLYFLUOROALKYL-CONTAINING 7-(4-PHENYL-1*H*-1,2,3-TRIAZOL-1-YL)-6,7-DIHYDRO-1*H*-INDAZOL-4(5*H*)-ONES

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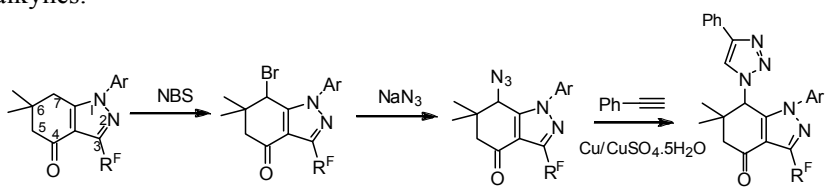
Indazoles constitute an important class of heterocyclic compounds, many of them possess anti-inflammatory, analgesic, antipyretic, anti-tumor, antiviral activity and others kinds of biological action.

On the basis of synthesized recently polyfluoroalkyl-containing indazolones **1**[1] we have synthesized new 1-aryl-3-polyfluoroalkyl-7-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-6,7-dihydro-1H-indazol-4(5*H*)-ones **2** with using as a key stage a Huisgen 1,3-dipolar cycloaddition reaction between azides and alkynes.[2]



R^F = CF_3, C_3F_7
Ar = C_6H_5, 4F-C_6H_4

7-Bromo derivatives **3** were obtained by refluxing fluorine-containing indazolones **1** with N-bromosuccinimide (NBS) in dry CCl_4 for 15 h. A treatment of **3** by fourfold excess of sodium azide in refluxing acetone for 48 h afforded 7-azide substituted indazolones **4**. A reaction between azides **4** and phenylacetylene in mixture tert-butanol/H_2O (2:1) in the presence of $Cu/CuSO_4 \cdot 5H_2O$ at 50°C for 8 h resulted selectively to target products **2**.

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The work was financially supported by the Belarusian Republican Foundation for Fundamental Research, grant X10JIAT-005 Belarus

AMIDINATION OF ADAMANTANES WITH ORGANIC NITRILES MEDIATED BY Mn, V AND Mo CATALYSTS

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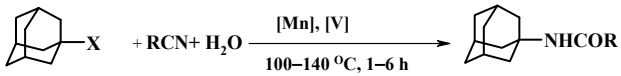
Amidination of adamantane **1** and its 1-chloro-(**2a**), 1-bromo-(**2b**), and 1-hydroxy-(**2c**) derivatives with organic nitriles catalyzed by Mn, V, and Mo complexes has been implemented in aqueous media.

Nature and structure of nitrile do not significantly influence the selectivity and yield of target N-(1-adamantyl)amides **3a–g**.



2a–c X = Cl, Br, OH **3 a–g**

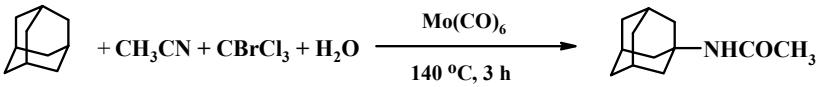
R = (3a)CH_3 (99%); (3b) C_2H_5 (48%); (3c) Ph (95%); (3d) 4-CH_2Ph- (75%); (3e) CH_2CN (95%); (3f) CH_2=CH- (85%); (3g) $(CH_2)_4CN$ (78%)

[Mn] = $MnCl_2$, $MnBr_2$, $Mn(acac)_3$, $Mn_2(CO)_{10}$

[V] = $VO(acac)_2$

A method to prepare N-(1-adamantyl)acetamide (**3a**), directly from adamantane (**1**) is recognized to be the most promising from the practical point of view.

In this report, the results of direct amidination of adamantane with acetonitrile successfully performed in the presence of $Mo(CO)_6$ catalyst and bromotrichloromethane reagent are also presented and discussed.



1 **2a (95 %)**

This work was financially supported by Ministry of Education and Science of the Russian Federation (Contract No. 02.740.11.0631).

SYNTHESIS AND STUDY OF NEW MIXED-LIGAND COMPLEX COMPOUNDS OF SOME LANTHANIDES WITH O-PHENANTHROLINE AND SALICYLIC ACID

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Coordination compounds of rare earth metals with organic ligands have found an application in electrical engineering, electrotechnology due to their ability to luminescence (luminesce).[1] Certain complex compounds with heterocyclic compounds - Schiff bases are received (obtained)[2]. We have synthesized new mixed-ligand complex compounds of some lanthanides with O-phenanthroline and salicylic acid of the composition $[Ln(Phen)Sal](NO_3)_2$, where Ln= La, Nd, Sm, Eu, Gd. It was shown preliminarily by spectrophotometry, that mixed ligand complexes are generated in spirit solutions.

The synthesis was conducted by extraction (emission) of sparingly soluble compounds from reagents alcoholic solutions which are taken in the ratio Ln:Phen:Sal=1:1:1. For this purpose, alcoholic solutions of lanthanide nitrates were mixed with ligands solutions and and evaporated on a water bath until precipitation, that was separated and dried in a vacuum - desiccator. The evolved complexes are powdery substances, which colors are typical for the respective rare-earth element (REE). Received compounds are characterized by chemical, infrared analysis (infrared spectroscopy) data, as well as X-ray diffraction and thermogravimetric analysis. Basing on analysis of received IR – spectra the hypothesis is made *about* the coordination of O- phenanthroline nitrogen atoms with metal high-frequency shift of the absorption bands of vibrations of C = N bond in 1600 cm^{-1}), and participation in the coordination of carboxyl group oxygen atoms of salicylic acid. *The* TGA and IR - spectroscopy data also indicate the absence of water molecules in the complex. On the base of received data the possible structure of the synthesized compounds is suggested.

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NEW POTENTIAL INHIBITORS OF THE BASIC ELECTROGENIC SYSTEM OF HIGHER PLANTS

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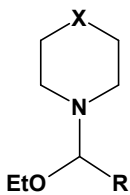
There are a great number of enzymes which catalyze various biochemical processes in cells of plants. Among these enzymes the special place belongs to superficial membrane H^+-ATPase. The given fermental system hydrolyzes molecules of ATP, using the energy released as result of hydrolysis for carrying over through cellular membrane of ions of hydrogen and by that supporting pH cytoplasm close to the neutral. Also H^+-ATPase creates on membrane potential difference, defining electrical properties of higher plants. H^+-ATPase is the integrated protein, whose polypeptide chain ten times crosses plasma membrane. Inhibitors of H^+-ATPase suppress its work and eliminate metabolic component (contribution of H^+-ATPase in formation of trans-membrane potential difference).[1]

According to PASS computer program 1-(1-ethoxyalkyl)piperidine and 4-(1-ethoxyalkyl)morpholine can be effective inhibitors of H^+-ATPase (EC 3.6.3.6) with high probability of 65.1-84.7 %.



X = -O, -CH_2

R = Me, Et, i-Pr, n-Pr

The given compounds are optically active. Spatial and electronic structure of optical isomers of compounds is investigated for the first time by methods of quantum chemistry; physicochemical properties are calculated for the first time with the use of applied programs.

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STUDY ON NOOTROPIC EFFECTS OF MECHANICAL OF 5-HYDROXYNICOTINIC ACID AND L-GLUTAMIC ACID AND D-, L-ISOMERS OF AMPASSE

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To study the role that play different components in nootropic effect of the caltsium salt of 5-hydroxynicotinoyl-L-glutamic acid (Ampasse®) we have evaluated antiamnestic properties of the mixture of 5-Hydroxynicotinic acid and L-glutamic acid and its components in comparison with the activity of the whole compound and its D-and L-isomers. Antiamnestic effect was evaluated by experiments with rats according the standard amnesia of passive avoidance (APA) reflex test induced by maximum electroshock (MES). The studied compounds were injected 30 min before the passive avoidance learning. During the experiments was proved that only L-isomer of Ampasse decreases amnesic action of MES increasing average to group period of latent entering the dark chamber to 63,7±5,8 sec (Mann-Whitney criterion) and part of the rats being able to demonstrate APA to 63% ($P \leq 0,05$, Fisher criterion). Thus the nootropic feachers are obtained only be the whole molecule of the L-isomer of Ampasse, but not by the separated components.

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NEW CROWN-CONTAINING QUINONES: SYNTHESIS AND COMPLEX FORMATION WITH ALKALI AND ALKALINE-EARTH METAL CATIONS

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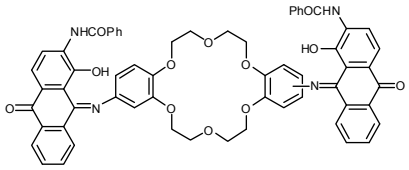
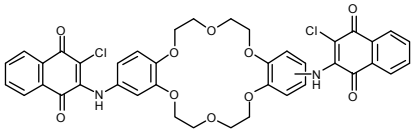
The novel derivatives of diaminodibenzo-18-crown-6 ethers containing two anthra- or naphthoquinone chromophore fragments were synthesized. The derivatives of 9,10- anthraquinone-9-imine (1a,b) were obtained by photoirradiation of mixtures of diaminodibenzo-18-crown-6 ethers with photochromic 1-aryloxy-9,10-anthraquinones. In compounds 1a,b, the crown ether fragment is directly connected to the imine moiety of the chromophore. The crown-containing naphthoquinones 2a,b were synthesized by substitution of one of the chlorine atoms in 2,3-dichloro-1,4-naphthoquinone by arylamino group of the corresponding diaminodibenzo-18-crown-6 ether.



1a,b



2a,b

The complex formation of chromogenic crown ethers 1a,b and 2a,b with Group Ia and IIa metal perchlorates in MeCN and DMSO was investigated by spectrophotometric titration method. There was shown quantitative dependence of the efficiency of complex formation on the type of a chromophore system and the relative spatial arrangement of the groups participating in coordination. For compounds 1a,b that are characterized by the imine–enamine tautomeric interconversion, the contribution of each of the tautomeric forms to the complex formation process was estimated. The structures of the complexes of 1a,b and 2a,b with metal cations were studied by quantum chemical simulation using DFT method.

It was found that chemosensors 1a,b in MeCN effectively bind Mg^{2+}; the complexed cation is coordinated with the imine nitrogen atom, OH-group and the carbonyl oxygen of the benzoylamino group ($\lg K = 4.4$). The other cations interact preferably with the crown ether moiety of 1a,b; in this case the complex stability constant decreases in the sequence $Ba^{2+} > Sr^{2+} > Ca^{2+} > Na^{+}$.

REASON OF PERIODICITY OF THE PERIODIC TABLE

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The strict quantitative explanation of periodicity of modification chemical and physical properties of elements has appeared extremely challenging task. To this day there isn't a mathematical reason of periodicity of the Periodic table.

Despite deviations of separate chemical elements from the normal form conceived by the Nature, apparent inconsistency because of realization of rigid physical conditions, in complication of electron shells stable, accurate correspondence to the minimum complication of the first elementary operations of Ideal mathematics[1] is observed:

Addition of one number (electron)	*a*
Multiplication "by two" numbers	*aa*
Combination "by two out of three"	*ab,ac,bc*
Arrangement "by two out of three"	*aa,ab,ac,bc,ba,ca,cb,bb,cc*
Arrangement "by two out of four"	*aa,ab,ac,bc,ba,ca,cb,bb,cc,ad,bd,cd,dd,da,db,dc*

Accurate observance of sequence of combinations "by two" of mathematical operations repeats in each following phase, repeatedly. Moreover, each previous operation by all its combinations is permanently put in all subsequent. Recurrence, eligibility ***of sequence of combinations "by two" became a mathematical reason of periodicity*** of the Periodic table by Dmitri Mendeleev and a basis of first four stages of formation of chemical elements, up to the 118th.

Representation of following stages (5th..10th) developments of chemical elements is fulfilled on a basis of the 5th..10th operations of Ideal mathematics.

Thanks to the revealed combinations, periodicity becomes obvious, more evident and true as confirms the fact of usage of regularities of Ideal mathematics with the Nature, and after it – u n c o n s c i o u s – chemists and physicists. It is offered to direct a maximum of creative energy on the further r e a l i z e d perfection of chemistry and physics new (11th etc.) operations of Ideal mathematics.

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MACROTRICYCLES COMPRISING CYCLEN, CYCLAM, AZA- AND DIAZACROWN ETHER MOIETIES

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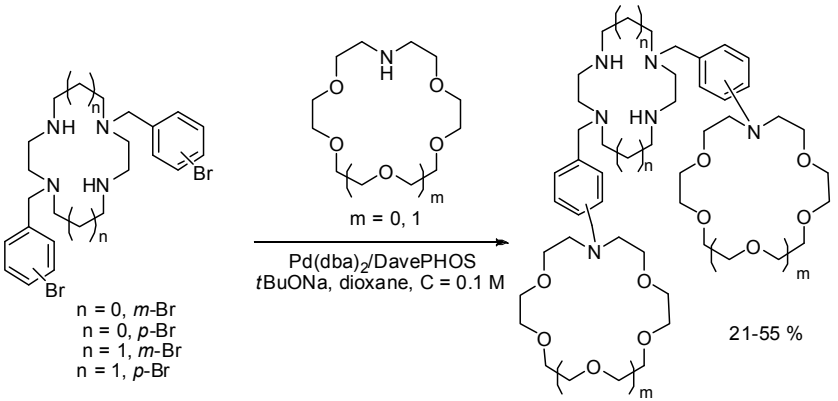
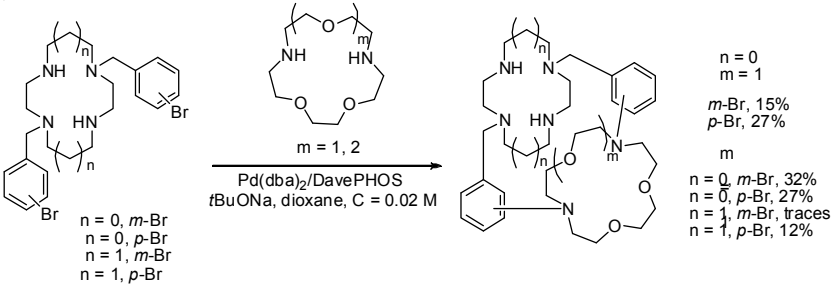
Pd-catalyzed amination was employed for the synthesis of macrotricyclic compounds comprising one fragment of cyclen or cyclam and two fragments of azacrown ethers. We have established the dependence of the yields of target products on the nature of tetraazamacrocycles and azacrown ethers and revealed the formation of side macrobicycles due to the catalytic reduction of bromine.



Similar reactions with diazacrown ethers in dilute solutions led to the formation of macrotricycles of cryptand type. We have established scope and limitations of this reaction for various combinations of tetraazamacrocycles and diazacrown ethers.



The work was supported by the RFBR grant N 09-03-00735.

RESEARCH OF THE INFLUENCE OF THE OUTLET FITTING GEOMETRY ON THE PROCESSES IN THE CENTRIFUGAL SEPARATOR

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Deep and effective clearing of the gas from the droplets of a disperse phase is necessary in various branches of the modern industry and technology. Ever-increasing requirements of environmental safety of chemical production, the purity of final products, waste technologies require further research in this area

In the research laboratory of Moscow State University of Environmental Engineering has been studied the influence of the outlet fitting geometry on the processes processing in the centrifugal separator. It is follows from the results of the studies of various outlet fitting configurations and lengths that under certain conditions the outlet fitting has an effect on the flow behaviour within the cyclone. This in turn can result in poor increase of swirl flow in the crucial region of the cyclone and substantially reduce the efficiency.

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NUCLEOGENIC TREE-COORDINATED CATIONS OF ELEMENTS OF THE 14-TH GROUP

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Chemical consequences of β-decay are of great interest for various areas of chemistry. As a result of these investigations, new methods of synthesis of previously unknown compounds, such as, for example, oxygen, fluorine and organic derivatives of xenon have been developed. One of the most interesting aspects of chemical changes under β-decay of tritium that is a part of molecules is its use for the preparation of intermediate reactive speashes (reaction intermediates) and the study of their rearrangements.

Three-coordinated cations of elements of the 14-th group (C, Si, Ge, Sn, Pb) having a charge on the central atom +1 and the external sextet electron shell are attributed to such reactive intermediates.

Typical processes for these particles are their specific reactions with neutral molecules (ion-molecululars reactions, IMR) that play an exceptionally important part in radiation, plasmo-, astro-, organic and organometallic chemistry.

The interpretation of mechanisms of processes occurring with the participation of these particles requires the knowledge of their behavior in a broad diapason of experimental conditions: from isolated molecules to condensed phases. The nuclear-chemical method worked out by us and based on processes of tritium β-decay in molecules and its consequences opens unique opportunities for the study of IMR between charged particles and molecules in the gas, liquid and solid phases.

The application of this method for the generation of cations R_3M^+ (M=Cl, Si, Ge, Sn) and study of their rearrangements in reactions with representatives of various classes of compounds will be discussed in the talk.

This work supported by RFBR (grant 09-03-00439a)

PROBLEMS AND PERSPECTIVES OF METAL/CABONIC NANOSTRUCTURES SYNTHESIS DEVELOPMENT IN POLYMERIC MATRIXES NANOREACTORS

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The appearance of nanochemistry among chemical sciences considerably changed the direction of investigations in the trend of fundamental chemical disciplines.

Nanochemistry may be represented as the sphere of chemical science which is devoted to the investigation of transitional states and nanosystems self organization processes, as well as the investigations of composition and structure of nanostructures and nanosystems.

In these cases the conditions are created for rapid and directional transition from reagents through transitional state to products with definite composition and structure. This transition is possible when the processes are realized in nanoreactors from which nanoreactors in polymeric matrixes are perspective. Our investigations show the possibility of metal/carbonic and metal/carbonpolymeric nanocomposites synthesis in nanoreactors of such polymers as polyvinyl alcohol, its mixture with polyethylene polyamine, polyvinyl acetate and polyvinyl chloride.

The investigations introduced the prognosis of interactions of polymeric matrixes nanoreactors fragments with fragments of metal containing phases using the programs of quantum chemistry. The calculating experiment contributed to the selection of pairs “inner walls of nanoreactor–metal containing phase”, relations of components which participated in interaction, forms and sizes of nanoreactors and also prognosticated composition, size and forms of nanocomposites formed.

After that the experiments in liquid or solid phases resulted on the first stage to color gels formation which were investigated by means of complex of methods including optic and atomic force microscopy, X-ray photoelectron spectroscopy and IR spectroscopy. Thus the sizes and forms of nanoreactors with metal containing phase were determined.

On the next stage, the reactions of monomeric, dimeric and trimeric nanostructures formation by energy action on reactive mass depending on the value and duration of energy impulse are carried out.

The nanostructures were obtained as metallic clusters defended by films of carbon fibers. The sizes of clusters change from 7 to 25 nm depending on the metal nature.

SOLVENT STRUCTURE NEAR SINGLE WALL CARBON NANOTUBES

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Carbon nanotubes (CN) have a series of unique properties due peculiarities their electronic properties. These electronic properties in turn are sensitive to local surroundings. A properties of CN change as in presence of gases and free radicals, ions as well. An influence of compounds in nearest arrangement of CN depends on their nature and chirality. Despite of many theoretical and experimental works in this field, the influence of functional groups and chirality of nanotubes is not enough studied. This is the main aim of this work. In this work , CN with different chirality (6,0), (6,4), (6,5), (7,0), (7,5), (10,0), (13,0) in aqueous electrolyte solutions have been studied by MD simulation. The simulation was carried out using standard procedure with program package "GROMACS 4.0.4" in NVT ensemble at temperature of 300 K. The local density distribution in axial and radial directions has been calculated for analysis of atomic density near nanotubes. The local density in direction of nanotube axis at distances of 0,25 (УНТ–Н), 0,41 (УНТ–ОН) и 0,61 нм (УНТ–СООН) decreases while polarity of functional groups increases. Nanotube in liquid system has an effect on structural and dynamical solvent properties. The first peak on RDF O-H decrease, but second one increases in comparison with net solvent. The average number of hydrogen bonds per one oxygen for all considered systems is 1.77 and average coordination number is 4.06, what is lower than in liquid water.

This work has been supported by RFBR No. 11-03-00586-a, 11-03-00122-a

PENTATSIALNYE DERIVATIVES DIHYDROQUERCETIN WITH BIOACTIVE AMINO ACIDS

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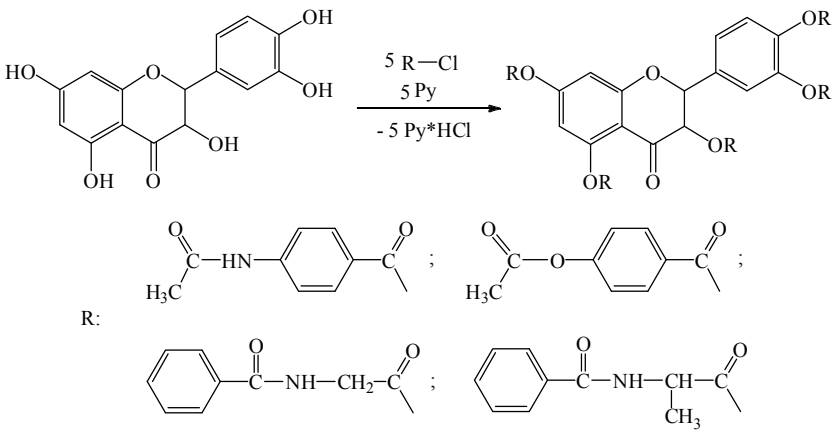
In current medical practice, a large number of antioxidants, possessing anti-inflammatory action. In addition, special interest medicines derived from natural substituted polyhydric phenols. One such means is troxerutin – (3',4',7-trihydroxyethoxyrutin), which has a high angioprotective and anti-inflammatory activity.

In contrast to the above preparation, including matrix kvertsetinovuyu its closest structural analog dihydroquercitin for the synthesis of anti-inflammatory and antioxidant drugs to date has not been used.

In this regard, we have developed a method for obtaining previously unknown fully acylated derivatives dihydroquercetin with potential antioxidant and anti-inflammatory activity.

Synthesis proceeds as follows:



Thus, it was the synthesis of derivatives of *n*-aminobeyzoic acid, glycine and alanine: 3,3',4,5,7-penta-*O*-paraacetylaminobenzoyl-2,3-dihydroquercitin (I), 3,3',4',5,7-penta-*O*-paraacetylhydroxybenzoyl-2 ,3-dihydroquercitin (II), 3,3', 4',5,7-penta-*O*-benzoyl aminoacetyl-2,3-dihydroquercitin (III) and 3,3',4',5,7-penta-*O*-benzoylaminopropionyl-2,3-dihydroquercitin (IV). The resulting compounds are currently being investigated for anti-inflammatory and antioxidant activity.

THE ADDUCTS OF Pr, Gd, Ho FERROCENOYLACETONATES AND Eu CYMANTRENOYLACETONATE WITH BIPYRIDYL. SYNTHESYS, STRUCTURE, MAGNETISM, SOLID STATE THERMOLYSIS

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Chelate β-diketonates have been known for a long time; they found various applications. The derivatives of organometallic β-diketons are relatively scantily studied. The data on the derivatives of such substances and REE are especially poor.[1,2]

Isostructural ferrocenoylacetonates $[Ln(FcCOCHCOMe)_3(bpy)]\cdot MeC_6H_5$ (Ln = Pr (**1**), Gd (**2**), Ho (**3**), (Fc – ferrocenyl; bpy – 2,2'-bipyridyl) (**1**) and cymantrenoylacetonate $[Eu(CymCOCHCOMe)_3(bpy)]\cdot 0.5MeC_6H_5$; Cym = $(\eta^5\text{-}C_5H_4)Mn(CO)_3$)) (**2**) were prepared. In the crystal lattice of **1-3** two molecules form quasi-dimeric structure due to stacking interactions. Magnetic behavior of **2** corresponds to the presence of high-spin Gd^{3+} in the molecule. Thermal decomposition of the compounds was studied by means of DSC and TGA. According to X-ray powder analysis data the final products of thermolyses of **1-3** under air contain perovskite-like antiferromagnetics $LnFeO_3$, **4** under the same conditions forms ferroelectric $EuMn_2O_5$.

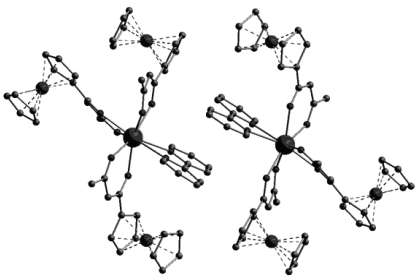

Fig 1. The structure of 2.

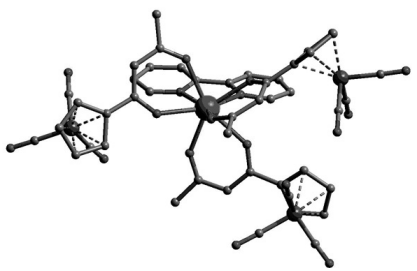

Fig 2. The structure of 4.

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THE METALL - CATALYZED SYNTHESIS OF POLYVINYLCHLORIDE AND ITS COPOLYMERS

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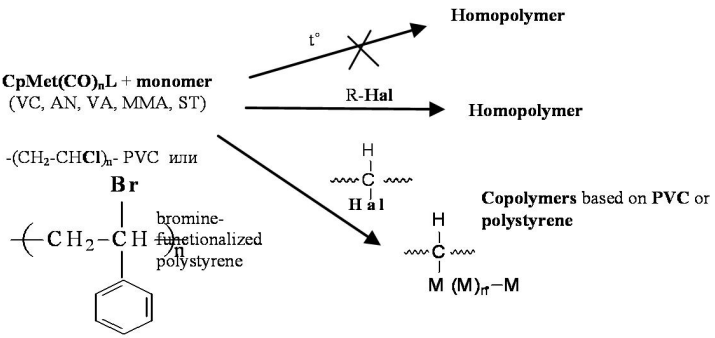
Polyvinyl chloride (PVC) is one of the major large-capacity polymers produced in the chemical industry today. Different methods of graft and block copolymerization apply for modification of properties of PVC and allow to obtain the materials based on it with a range of new features: enhanced heat resistance (methyl methacrylate, styrene), elasticity (vinyl acetate), impact resistance on solvents and other chemical reagents (acrylonitrile).

It was established that the iron derivatives ($[CpFe(CO)_2]_2$, $CpFe(CO)_2Br$) and manganese complex ($CpMn(CO)_2$styrene) in combination with alkyl halides (CCl_4, ethyl-α-bromizobutirate, etc.) at temperature 50-80˚C allow synthesis of PVC to deep conversion within 30 hours.



The synthesis of graft copolymers of PVC-PVA was performed. It was determined that the efficiency of grafting depends on the nature of the initial polymer. The influence of temperature and the ratio of initial components (polymer macroinitiator – PVC or PST-Br) on the composition, molecular-weight characteristics and the temperature of glass transition of the synthesized copolymers were studied.

In summary the studied metallocomplexes initiate the radical polymerization of VC in a wide range of temperature. Moreover, they provide an opportunity to modify the mechanical properties of formed PVC via its copolymerization with a range of monomers, that promote the synthesis of new polymer materials with desired characteristics and properties.

This work was supported by the program "Development of scientific potential of higher education"

CATALYSIS AS A PHENOMENON OF ENERGY EXCHANGE BETWEEN THE CATALIST AND REAGENTS

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The phenomenon of catalysis should be considered from the standpoint of physical and chemical processes occurring in the energy exchange between the catalyst and reagents. Quantum exchange in the form of electromagnetic fields is possible when the ratio of the Bohr holds: $\Delta E = hv$, where ΔE is the difference between the energies of two quantum states, h-Planck's constant, v-frequency. The sequence of activation of reactant's groups with characteristic frequencies v_i, determines the scheme of the reactions. Possibility of activation of these groups provides by resonant energy exchange between the catalyst and excited groups in the frequency range lying in the infrared spectrum.

The ability of substances to emit electromagnetic waves of frequencies required, corresponding to their chemical composition, identifies their basic catalytic properties for the excitation of groups of frequency v_i. Thus, to support the process of catalysis is necessary a source of energy, including the desired frequency range exciting catalyst, which has a selective absorption and emission with the frequency of coherent oscillation frequency of the activated atoms or groups in the reagents.

Theoretical foundations of the interaction of radiation with substance described by A.Einstein in 1916. Development of this theory in heterogeneous catalysis - "radiation" theory, is reflected in the works of I.E. Adadurov and G.K. Boreskov. This approach allows choosing the chemical composition of catalysts and temperature parameters of heterogeneous catalysis.

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VECTOR CORRELATION ANALYSIS FOR THE F+HD CHEMICAL REACTION

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In the last years all over the world arises a great interest to anisotropy that arises in chemical reactions[1]. This research is of a great significance for laser chemistry, physics of chemical reactions, astrophysics, and also can be claimed in nanotechnologies.

In the present work, theoretical study of elementary process F+HD(v=0, j) -> H+FD(v', j'), (D+HF(v', j')) has been proceeded, translational energy of reactants is 0.078 eV. Using results of previous authors[2], angular distributions of chemical reaction products were obtained for two reaction channels DF+H and HF+D. Also, total reaction cross-sections have been calculated for all vibration quantum numbers. Calculations were made by using S-matrices obtained by Italian co-workers. These results present good correspondence with experimental data[3] that illustrate possibility of using this potential energy surface.

Also, the calculations of anisotropy transferring coefficients have been produced. Particularly, orientation and alignment angular dependences of reaction product angular momentum were obtained and investigated. These results are important for understanding of chemical reaction dynamics. Also, the influence of angular momentum polarization on differential and total cross section of chemical reaction was studied

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"2,4-CYCLOHEXAANNELATION" OF LEVOGLUCOSENONE

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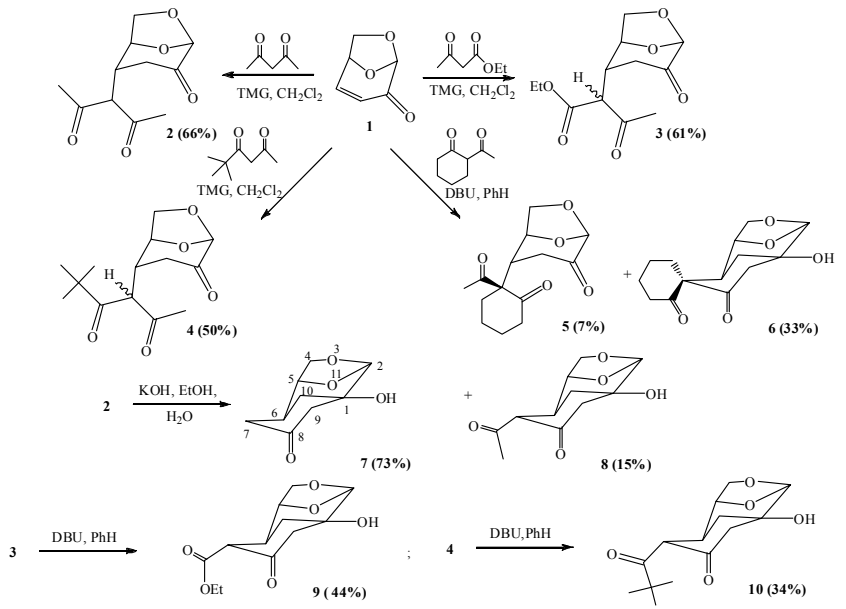
For the first time carbocyclization of Michael adducts of levoglucosenone with acetylacetone, acetoacetic ester, 5,5-dimethylhexa-2,4-dione and 2-acetylcyclohexane is carried out with obtaining 2,4-annelated cyclohexanes with carbohydrate fragment. In case of adducts with acetylacetone reaction of intramolecular aldol condensation is accompanied by simultaneous proceeding of deacetylation and formation of compound 7.



This work was supported by the Federal Program "Research and scientific-pedagogical cadres Innovative Russia" for 2009-2013. State contract № 14.740.11.0367

REGIOSPECIFIC AND REGIOSELECTIVE SYNTHESES OF NON-SYMMETRICALLY 2,6- AND 2,8-DISUBSTITUTED GLYCOLURYLS

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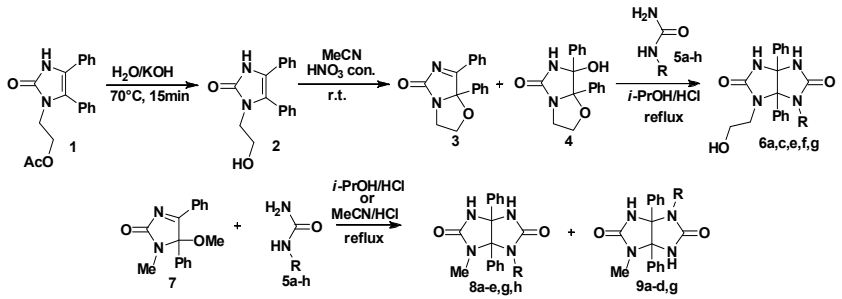
With a view to design regiospecific and regioselective syntheses of non-symmetrically disubstituted glycoluryls we undertook a comparative assessment of the properties of compounds **3,4** and **7** in reactions with monosubstituted ureas. For that, we synthesized starting **1**[1] and **7**[2] by literature procedures and developed synthetic procedures for **2**-**4**. A research on the interaction of ureas **5à-h** with compounds (**3+4**) and **7** indicated that the regiospecificity of the synthesis of glycoluryls **6** via the fist route relied on the structure of the formed carbcation where the amino group enabled ureas to approach merely the carbon atom Ñ(7). In the second instance, glycolurils **8** and **9** were produced with a varying ratio of regioisomers (from 1:1 to 1:0) due to an equally probable ureas' approach realized by the amino group to the carbcation reaction sites Ñ(4) and Ñ(5), which is why the regioselectivity is likely to be related to the urea structure.



5. R = Me (**a**), c-Hex (**b**), CH_2COOH (**c**), $(CH_2)_2COOH$ (**d**), $(CH_2)_3COOH$ (**e**), $(CH_2)_2OH$ (**f**), $(CH_2)_2N(Me_2)$*HCl (**g**), (*S*)-$(CH_2)_3CH(COOH)NH_2$ (**h**).
6,8,9. R = Me (**a**), c-Hex (**b**), CH_2COOi-Pr (**c**), $(CH_2)_2COOi$-Pr (**d**), $(CH_2)_3COOi$-Pr (**e**), $(CH_2)_2OH$ (**f**), $(CH_2)_2N(Me_2)$*HCl (**g**), (*S*)-$(CH_2)_3CH(COOH)NH_2$ (**h**).

The structure of prepared compounds **2-9** was ascertained by ^{1}Í and ^{13}Ñ NMR spectra. Also, x-ray diffraction was performed for **6f**.

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SYNTHESIS OF OLIGO (POLY) TERPHENYLEN PHTALID BLOCKS GIVEN LENGTH AND BASED ON THEM THREE-BLOSCK POLYARYLENE PHTALIDES

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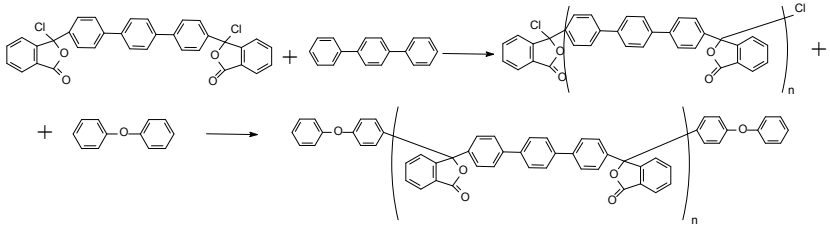
The approach to the controlled synthesis of oligo- and poliarilen phtalides terphenilen series with acil chloride and diphenyloxide groups at both ends of the chain for the three block polyarylene phtalides, based on tracking (by TLC and UV spectroscopy) for the content dichloride in the reaction mass.



To determine the composition and length of politerfenilen phtalid blocks used difference and derivative UV spectroscopy colored sulfuric acid solution polycondensation products, taken in the course of the reaction and the method of C-13 NMR spectroscopy of the final polymers.

It showed that the full and complete use of dichlorineanhydride is mandatory when obtaining terphenylphtalide blocks of the given structure and length with reaction of pseudodichloranhydride -4',4"-bis-(2-carboxybenzoyl)terphenyl with n-terphenyl. Otherwise, dichloranhydride having not entered polycondensation, reacts with diphenyloxide (that happens at the stage of limiting the polymeric chain) generating improper product, i.e. block-copolyarylenphtalide of the opposite composition (если обратный состав имеет значение структуры, то тогда structure).

It has been established that due to diffusion limitations caused by a high viscosity of reaction system, it is possible (apart from terphenylphtalide blocks with diphenyloxide end group) to generate regular-and-alternate copolymer of a periodic structure where terphynylphtalide blocks are bound together by diphenyloxide links. Variation of technological parameters during the synthesis , i.e. stirring speed, order and duration of reagents dissolving, can influence the obtaining of predominately one of the end products. Oligoterphenylphtalide block of various length (n=8, 20, 29) and diblockcopolyarylenphtalides with different ratio of terphenylphtalide and diphenylenoxidephtalide (diphenyloxidephtalide and diphenylensulphidephtalide) links with diverse length of the second block have been synthesized.

This work was supported by the RFBR project 09-0301160a.

THE NEW MECHANISM OF SOLID-PHASE CHAIN REACTION PROPAGATION

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The potential way of energy transformation, which is given by energetic materials decomposition, together with dissipation in heat, is an electron-hole (e.h.) pairs multiplication. This circumstance leads to energetic chain reaction (CR) evolution[1]. This study objective is formulation and testing of the new mechanism of chemical reaction propagation along the heavy metal azides crystals, differing from known detonation and burning.

This mechanism based on the branched solid-phase CR from[1]. The main new mechanism hypothesis is energized reaction products generate by deactivation two e.h. pairs in reaction zone (perhaps, electrons are localizing at the formed anion vacancies) and one e.h. pair at the r_0-neighbourhood of reaction proceeding elementary act area. This fact consequence is a considerable (more than order) increasing of the critical initiation energy of an explosive decomposition (H_c) under the decreasing of irradiation area diameter $d = 1000 \div 10$ μm. On the other hand chemical energy transmission from reaction zone leads to decreasing of an exponential increase effective constant (K_p) of CR velocity (with d variation under the same limits). Comparison with an experiment leads to value of chemical energy transmission effective length $r_0 = 55 \pm 5$ μm for $H_c(d)$ and $r_0 = 60 \pm 5$ μm for $K_p(d)$. Practically equality of obtained values let us consider the both effects as $K_p(d)$ decrease as $H_c(d)$ increase with the irradiation area diameter decrease (on the 2 orders) are determined by the same reason – reaction energy transmission from irradiation zone to a non reacted crystal area.

On the base of model taking into account new propagation mechanism and getting r_0 values mathematical modeling of CR wave forming and propagation along the crystal was done. Getting velocity value of propagation chemical reaction wave is $V \approx 1.5$ km/s, that is in a good agreement with the experimental data.

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MECHANISMS OF THE SOLID STATE CHAIN REACTIONS

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Heavy metal azides are the unique energetic materials because of their capability to show one of it in case of different initiating agent. The main purpose of this article is to analyze the different types of the explosive decomposition models for the heavy metal azides initiated by laser pulses, and compare the results of this analysis with the experimental data. In case of stationary radiation, the main argument for the thermal explosion models is a strong explosive criterion dependence on the temperature [1]. In case of pulse radiation the explosive criterion does not depend on the temperature, this is the typical sign of the chain process. In according with experimental data:

For the case of short pulse initiation of the heavy metal azides explosive decomposition was proposed a branched chain reaction model. The chain's nature of the process most important consequence is the critical energy density dependence on the sample size and the radiation wave length. Critical energy density rises considerably when the crystal size value or the reciprocal value of the absorption coefficient is commensurable to the charge carriers (electron excitations) diffusion length. The effect's cause is the the inhibitory surface action and has the same reason as it is in the gas chain reactions. It was shown that this chain model gives the reasonable initiation's criteria values and could clearly explain it's dependence on the pulse duration. All considered regularities – critical criteria values dependence on the pulse duration, induction time dependence on the energy initiation density, size effects (critical energy density dependence on the sample size, irradiation diameter, and coefficient of absorption), velocity and time-space process parameters are in complete agreement with experimental data.

SYNTHESIS AND STRUCTURE OF ISOMERIC (FUNCTIONALLY) SUBSTITUTED AZOLOQUINAZOLINES

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Nitrogen-containing heterocycles (quinazolines, azoles) play an important role among those heterocyclic compounds whose fragments are part of known medicine preparations and natural substances.

We have developed ways to obtain azoloquinazolines containing linearly bonded (het)arylic substituents, on the basis of 1,3-bielectrophilic substrates — α,β-unsaturated ketones I,II (mono-, diene derivatives of cyclohexane), 1,3-dioxo compounds III (diethyl-2-aryl-4-hydroxy-4-methyl-5-oxocyclohexane-1,3-dicarboxylates) and polydentant reagents (3-amino-1,2,4-triazole, 5-amino-1,2,3,4-tetrazole, 2-aminobenzimidazole).

Regularities and features of reactions for each type of the reagents have been established. When substrates I and II react with azoles, isomeric triazolo-, tetrazolo-, benzimidazoloquinazolines with various types of ring connection are formed as a result of primary nucleophilic substitution of a carbonylic group or conjugated 1,4-addition. Dienones II of asymmetric structure form regioisomeric azoloquinazolines whose ratio determines variations of the terminal substituents. E.g. for thienylaryl-containing, furyl-containing and 5-nitrofuryl-containing substrates II, four, two and one isomers, respectively, are spectrally detected. In some cases, the regioisomers of linear structure were separated from the angular ones (by recrystallization) and isolated as pure compounds (HELC).

The regiospecificity of formation of functionally-substituted thiazolo-, triazoloquinazolines of linear structure only is a peculiarity of the interaction of β-ketoesters III with 3-amino-1,2,4-triazole and 2-aminothiazole.

Key signals have been resolved in NMR spectra (^{1}H, ^{13}C, NOESY, HMBC) for determination of the ring connection type, the regioisomer ratio, the position of nitrogen atoms in the azole cycle.

The newly synthesized azoloquinazolines are promising with respect to their biological activity.

RECEIPT OF THE NEW HETEROCYCLIC COMPOUNDS ON THE BASIS OF 1,3-DIKETONES WITH ADAMANTINE MOIETY

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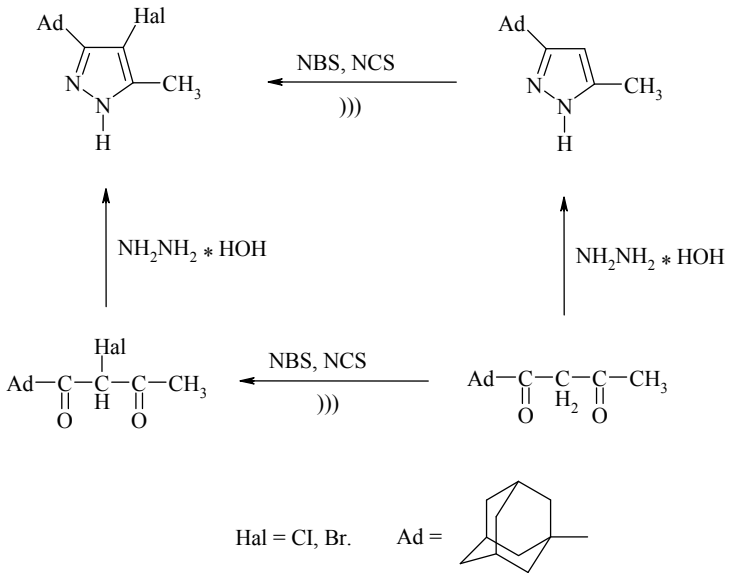
N-halogenides, such as NBS, NCS are effective halogenating agents for the multitude numbers of organic compounds[1], including 1,3-diketones with adamantine moiety and for heterocycles on their basis.



4-Halogen substituted pyrazoles with adamantine moiety we receipted by us by interaction between NBS or NCS and 1,3-diketones with adamantine moiety and further cyclization with formation of halogenated pyrazoles with adamantine moiety.

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SELECTIVE ACYLATION OF DIHYDROQUERCETIN

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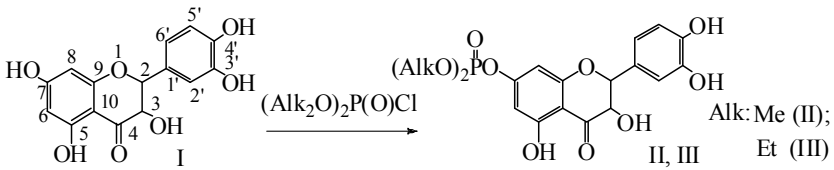
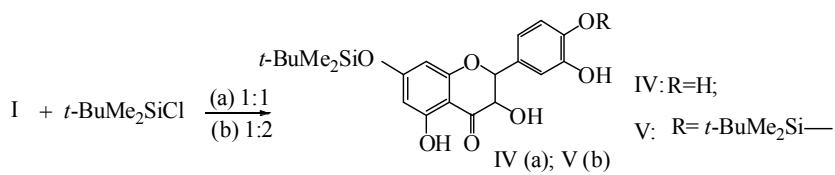
A possibility of selective acylation of dihydroquercetin (DHQ) has been studied to create new biologically active compounds. DHQ is an effective natural bio-oxidant widely used in producing medicines.

Acylation of DHQ with phosphorous chloroanhydrides (ratio 1:1), which are known to be active phosphorylating agents, resulted in a number of more or less substituted derivatives. These derivatives demonstrating similar physicochemical properties, it was impossible to isolate individual compounds.

Phosphoric chloroanhydrides and the reactant ratio 1:1 being used, phosphorylation proceeds selectively in position 7of the DHQ molecule.



Silylation of the flavonoid involved was carried out using tert-butyldimethylchlorosilane with the ratios (a) 1:1 and (b) 1:2. In case (a) under mild conditions the 7-monosubstituted product is obtained. In case (b) under similar conditions disilylated derivative (positions 7-OH and 4'-OH) is formed.



Hence, composition and structure of products in acylation of DHQ are shown to depend substantially on the structure of acylating agent.

THE STAGENES AND BIFURCATION WITHIN THE FLAME MONOFRONT

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On the basis of the postulate on concurrence of two mechanisms of fuel conversion within the flame front, - A – low temperature autocatalysis and T – high temperature auto acceleration, we have proposed the method of measuring the degree of flame stages of the designed combustible mixture S. The corresponding predominance zones of each of these mechanisms, the activity of which depends on the initial values of fuel concentration C_0, temperature T_o and pressure P, have been revealed. The quantitative method of measuring the value S is finding the ratio of maximum reaction rates of consumption of oxygen or fuel and formation of water in zones A – (^AK_i) and T – (^TK_i) from the data of mass spectral probing of the flame front. The values $S < 1$ respond to the monofront (before bifurcation), $S > 1$ respond to the bifront (after bifurcation point). Bifurcation point occurs due to the increase in NTC at the moment when difference $^AK_i - {}^TK_i = \varepsilon$ shifts to the range of positive values which is the criterion of bifurcation. At $\varepsilon \leq 0$ between A and T zones, there increases the zone of negative temperature coefficient of rate (NTC) on the curves of rate profiles of fuel and oxygen consumption and formation of water. At $\varepsilon > 0$, the monofront changes to bifront.

It is stated that the influence of T_o growth on the form of the curves of formation and accumulation rate of other combustion products, which are typical for T zone except O_2, fuel and water, is little or absent. For the first time, experimental data on mass spectral probing of combustible mixtures of pentane $\alpha = 1.4$; 1.5 and 1.7 were presented. The results on calculation of S are presented on the basis of the earlier published data on probing the front of hydrocarbon flames $C_1 – C_6$. The value S for all flames is shown to be a smoothly changing function of C_0 before bifurcation point. The dependency of S on T_0 is negative. The flames with similar values of S are identical.

OXIDATIVE TRANSFORMATIONS IN DIRECTED MODIFICATION OF UNSATURATED FATTY ACIDS

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Oxidized form of fatty acids are often reparative-regenerative, mild cardiotonic, antispasmodic and anti-inflammatory effect. There is information about the antibiotic and antitumor activity of oxygenated fatty acids. Because natural sources are allocated in small amounts, is important to search for synthetic methods for introducing a molecule of oxygen-containing fatty acid groups of different polarity, which increase the lipophilicity and the permeability of biological membranes.

The methods for the oxidative transformation of oleic, linoleic and linolenic acids in the allyl position of the double bond, allowing to enter oxo-function (action SeO_2) and hydroxyl-group (catalyzed hydroperoxide oxidation). It was investigated the influence of solvent, including ionic liquids, temperature and reactant on the efficiency of the reaction of epoxidation of linoleic and linolenic acids at the efficiency of the reaction with *meta*-chloroperbenzoic acid. It was found that the introduction of one oxirane ring in the molecule of linoleic acid in almost equal amounts formed epoxides on C9-C10 and C12-C13, while a further epoxidation gives diepoxide under the provisions of C9-C10 and C15-C16. With the use of 1H and 13C NMR spectroscopy and quantum chemical calculations in approximation MPW1PW91/6-311 G (d, p) explained by the inertia of the double bond at position C15-C16 fatty acid in relation to *meta*-chloroperbenzoic acid in monoepoxidation. Conditions are found for the selective introduction of epoxy groups on C12-C13, consisting of an action on a molecule of linolenic acid, *t-Bu*-hydroperoxide in the presence of $MoCO_6$. Controlling the direction of the reaction in this case is the steric factor.

TRANSFORMATIONS OF CHROMENO[3,4-*c*]- AND [3,2-*c*]PYRIDINES UNDER THE ACTION OF ACTIVATED ALKYNES

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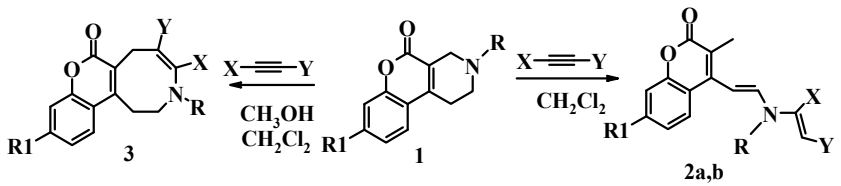
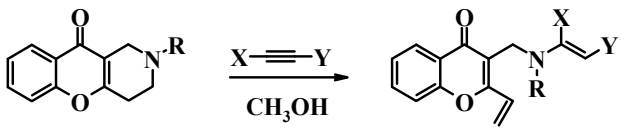
Natural derivatives of chromene and coumarins exhibit a wide range of biological activities the most interesting of which are antibacterial, antiallergenic and antispasmodic. Our work on the studying of the behaviour of chromenopyridines under the action of activated alkynes resulted into obtaining new functional substituted chromenes and coumarins. It was shown that the reactions of tetrahydrochromeno[3,4-*c*]pyridines **1** with methyl propiolate or acetylacetylene depend on the solvent and lead to the formation of substituted coumarins **2a**, **b** or chromeno[4,3-*d*]azocine **3**.



1, 2a,b, 3: R=Bn; 2a, 3: X=H, Y=CO_2Me; 2b: X=H, Y=COMe; R1=OCOMe

We carried out the analogous experiments with chromeno[3,2-*c*]pyridines **4a**, **b**. In this case under the action of activated alkynes chromeno[3,2-*c*]pyridines undergo Hofmann-like cleavage of the tetrahydropyridine ring thus leading to vinyl substituted chromones **5a-e** in high yields (70-90%)



4a,b **5a,b,c,d,e**

1a, 2a, b,c: R=Bn; 1b, 2c,d: R= Me; 2a,d: X=Y=CO_2Me; 2b,e: X=H, Y=CO_2Me
2c: X=H, Y=COMe

The study was supported by the grant of the President of the Russian Federation for young scientists (MK-1048.2010.3).

POLYNUCLEAR METAL COMPLEXES BASED ON TRI- AND FOUR-COORDINATED PHOSPHORUS DERIVATIVES

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New types of heterocyclic polynuclear complexes – polymeric, dimeric, tetrameric and clusters linked via bridged molecules of ligands in 2D- or 3D- polymeric nets, were synthesized based on P-ligands – derivatives of tri- and four-coordinated phosphorus,{^{III}P-E (where E=O, N, S), ^{IV}P(S)S}, with transition d-metals [Cu(I), Cu(II), Co(II)]. By means of X-ray single crystal diffraction different types of mutual arrangement of the P-N-, P-O-, P-S-, S-P-S- и S-S- structural fragments were revealed at the complexation due to the disproportionation or other transformations of P-ligands in metal coordination sphere, what determine the structure, coordination mode as well as physical and chemical properties of complexes.

Thus, the realization of certain structures, variety of stoichometries and configurations in complexes studied depend not only on the stereoelectronic factors in ligand, but on the conditions of transition metal – ligand bond formation as well.

The investigations performed are perspective in terms of the synthesis of new P-ligand complexes, metal containing cyclothiophospates, precursors for the building of new bridged (via metal) dimers, trimers or coordination polymers as well as for the study of various aspects of their biological, magnetic and catalytic properties.

The grants of RFBR (09-03-00006a) and DCSM RAS (Pr.6) are gratefully acknowledged

QUANTUM CHEMICAL CALCULATIONS AND KINETICS OF 1,2-DIALKYLDIAZIRIDINES FORMATION

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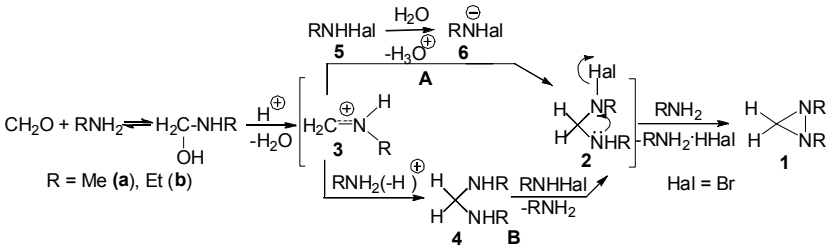
In this work new evidences of formation of 1,2-dialkyldiaziridine **1** precurror - halogenaminal **2** were obtained. This process is result of amination of iminium cation **3** (pathway **A**) together with parallel halogenation of hemdiamine **4** (pathway **B**)[1] (see Scheme).

It was found by UV-spectroscopy, that decrease of MeNHBr **5a** concentration in this reaction was best described by equation for two parallel reactions of first order $C_r = C_{01}e^{-k_1\tau} + C_{02}e^{-k_2\tau}$, in which the constants velocity k_1 and k_2 at 20 ^oC were differed in three times at using of MeNHBr **5a** and in 10 time at using of EtNHBr **5b.** Calculated value of charges on nitrogen atoms for anion **6a** was -0.634 a.e. and -0.563 for anion **6b**, that evidently was reason of k_1 at transfer from MeNHBr **5a** to EtNHBr **5b.**

Heat efficiency of without barrier reaction of aminal **4a** formation was 18.74 kcal/mol and aminal **4b** – 22.71 kcal/mol. Activation barrier of halogenaminal **2a** formation through MeNHBr **5a** by pathway **B** was 32.31 kcal/mol, and halogenaminal **2b** through EtNHBr **5b** by pathway **B** was 35.4 kcal/mol. This result is evidence of second process limits a formation velocity of intermediate **2** by pathway **B** and explains fourfold decrease k_2 at use of EtNHBr **5b** instead of MeNHBr **5a.**



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STRUCTURE OF Co(II), Cu(II) AND Zn(II) COMPLEX WITH BIS(α-PYRIDYL)BISPIDINOAZA-14-CROWN ETHER

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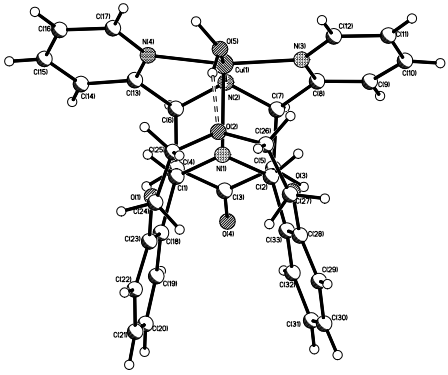
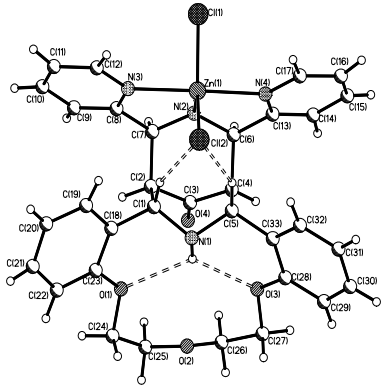
New complex compounds of Co(II), Cu(II) and Zn(II) with bis(α-pyridyl)bispidinoaza-14-crown-4 ether (L) were obtained. X-ray analysis data show the coordination of the neutral molecule L with the atoms of metals as N,N,N,N-tetradentate- (in case of Co(II) and Cu(II)) or N,N,N,N-tetradentate- chelating ligand (in case of Zn(II)).



a



b

Coordination polyhedra of the cobalt atom in the complex $[Co(L)(H_2O)]\cdot[CoCl_4]$ is the octahedra, of the cuprum atom in the complex $[CuL(H_2O)](ClO_4)_2 2H_2O$ – distorted tetragonal pyramid (fig. a), of the zinc atom in the complex $[ZnCl_2L]C_2H_5OH$ – trigonal bipyramid (fig. b).

IR-spectroscopy data, physical-chemical properties and the structures of the obtained complex compounds are discussed.

THE SYNTHESIS AND BIOSCREENING OF NEW INDOLE DERIVATIVES*

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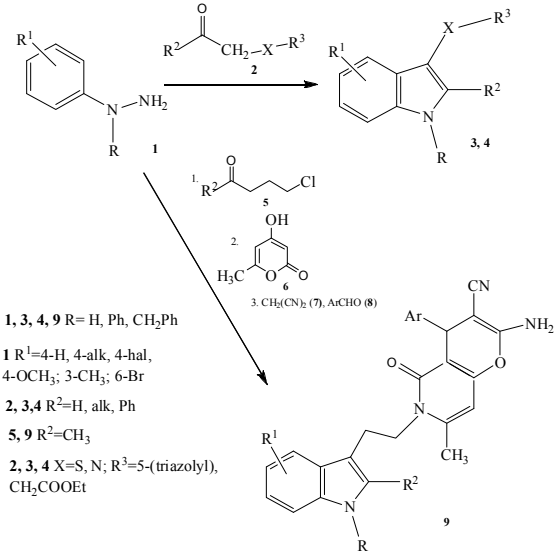
In the course of further studies on the synthesis of biologically active compounds[1, 2] the methods for obtaining new indole derivatives **3**, **4**, **9** have been developed. Heating ethanol solutions of arylhydrazines **1** and compounds with the carbonyl group **2** in the presence of acid leads to indoles **3**, **4** (yield 40-75 %), many of which have revealed marked auxine activity. The reaction with chloroketone **5** as the carbonyl compounds results in tryptamines (Grandberg's reaction[3]), which interact with pyrone **6** forming the corresponding pyridones**.** The interaction of the latter with malononitrile **7** and aromatic aldehyde **8** leads to pyranopyridones **9**, which are potential cytotoxic compounds according to the program PASS.



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*Dedicated to the memory of professor I.I. Grandberg

CATALYTIC COAL LIQUEFACTION

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Coal liquefaction processes in hydrogenous solvent enviroment are to be studied and developed since it opens us new sources of high-grade motor fuels. This task is vital and should not to be underestimated because it allows worldwide energy system to become more independent from oil refining industry[1,2].

Intermediate metal formiates can decompose at 200°C yielding thin suspended metal particles which then can serve as an effective catalytic system.

Aluminium stearate as a hard Lewis acid that allows n-alcane isomerisation processes as well alkylation and realkylation processes resulting in significant improvement of motor fuel quality.

Coal organic mass conversion degree as well as liquid product yield have been measured. Structural and group composition of resulting disel fraction have been determined as well as it's cetane number.

We have determined that aluminium stearate and Ni(II) formiate serve as the most effective liquefaction catalysts for the brown coal we studied. The process we developed allows us to convert up 70% of coal organic mass into liquid products that consist of isoalcanes, cycloalkanes and arenes which allows to use them as motor fuels as well as raw materials for further organic compound and petrochemical production.

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MAGNETOSTRUCTURAL CORRELATIONS IN THE COPPER(II) COMPLEXES WITH N,N'-*BIS*-(3-FORMYL-5-*TERT*-BUTYLSALICYLIDENE) 1,3-DIAMINOPROPAN-2-OL

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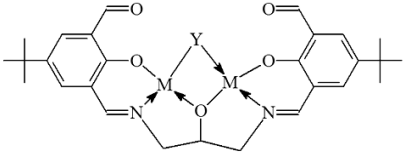
Novel ligand system N,N'-*bis*-(3-formyl-5-*tert*-butylsalicylidene) 1,3-diaminopropan-2-ol (H_3L) and binuclear Cu(II) and Ni(II) complexes on its basis with composition [$M_2L(Y)$] were synthesized. Structure and properties of the obtained substances were studied by IR-, ^{1}H NMR spectroscopy, TG/DTA, magnetic susceptibility measurements and single crystal XRD. Presence of two free formyl groups in the molecule opens possibility to obtain heterobridged binuclear complexes and, moreover, to further fictionalization of the ligand by condensation reaction with amines and hydrazines to develop two additional chelating centers for metal ions coordination.



M = Cu(II), Ni(II)
Y = CH_3COO, CH_2ClCOO, CCl_3COO, CF_3COO, Pyr

Protolytic properties of the *bis*-azomethine were studied by potentiometry. Quantum-chemical modeling within DFT method (B3LYP/6-311G(d,p)) was performed. Calculation results are compared with the experimental IR spectra and pKa values. Exchange interaction between paramagnetic centers was studied. Lower values of the experimental exchange parameters when compared with earlier studied copper(II) complexes with N,N'-*bis*-(salycilidene) 1,3-diaminopropan-2-ol can be explained by noticeable structural changes in binuclear unit. Influence of the Y bridging group on the exchange interaction does not match the magnetostructural correlations obtained for earlier studied complexes[1].

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This work was financially supported by the Ministry of Education and Science of Russia according to the Federal Program "Scientific and Pedagogical Personnel in Innovative Russia" for 2009–2013 (П1362).

REVISITED INTERACTION BETWEEN CHLORINS AND NUCLEOPHILIC AGENTS

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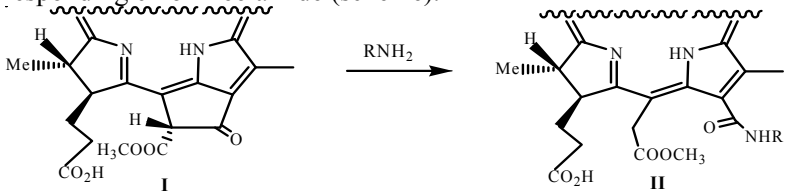
Application of porphyrins and chlorins as photosensitizers in various areas of science, medicine and technology is determined their structural and physic-chemical properties. It is known that the increasing of photosensitizer's hydrophobicity may for example enhance the degree of the growth inhibition for microorganisms or increase insecticidal efficiency. The degree of hydrophobicity of porphyrins and chlorins can be increased by introduction of alkyl residues.

In the present research natural chlorin – pheophorbide *a* (I) was modified by means of ring V cleavage by amine action with the formation of corresponding chlorin e6 amide (scheme).



I **II**

Fatty amines with various alkyl chain length (butylamine, dodecylamine, octadecylamine) were used in nucleophilic substitution reaction as amine that allowed to obtain hydrophobic derivatives of chlorin e6 (II). The effect of primary aliphatic amine structure and of conditions during it's reaction with pheophorbide a and methylpheophorbide a (solvent, the presence of tertiary amine and the reaction time) on the yield of the end product (II) is displayed. Increasing of the amine's chain length from C4 to C18 lead to decrease reaction rate and the yield of the end product. Similar developments fatty amine's nucleophilic properties were in axial coordination reactions between metallo-porphyrins(chlorines) with amins, wherein axial complex's stability constants may be as a degree of nucleophilic properties for corresponding amine.

Complexing compound /metalloporphyrin or metallochlorine/	+	***Ligand*** $H_2N(CH_2)_nCH_3$	⇌	***Axial complex***

The research was supported in part by Grant № 2.1.1/2889 (АВЦП "Развитие научного потенциала высшей школы").

OXIDATION OF 3-METHYL-2-MERCAPTOQUINAZOLIN-4-ONE BY CHLORINE DIOXIDE

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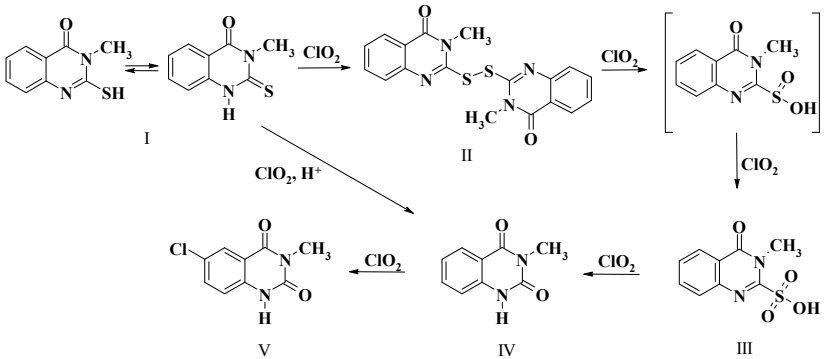
3-Methyl-2-mercaptoquinazolin-4-on (I) are quinazoline derivative, being structural fragment of quinazoline alkaloids, which possess a wide range of pharmacological activity. Therefore, an addition of new functional groups to a structure of this compound class, are of great interest both with medical and with chemical points of view. Oxidation of organic compounds is a method of sinthesis of new derivatives.

The oxidation transformation of 3-methyl-2-mercaptoquinazolin-4-one (I) under the influence of chlorine dioxide depending on reaction conditions such as temperature, type of solvent and mole ratio of reacting agents was investigated in this research. Benzene, dichloromethane, acetic acid, acetonitrile, methanol, pyridine and diethyl amine were used as solvents. The optimal conditions for synthesis of various reaction products (II-V) were selected.



The study was supported by programs of basic researches of Department of Chemistry and Materials Science (the project 09-T-3-1015).

CHLORINE DIOXIDE OXIDATION OF SUBSTITUTED PHENOLS

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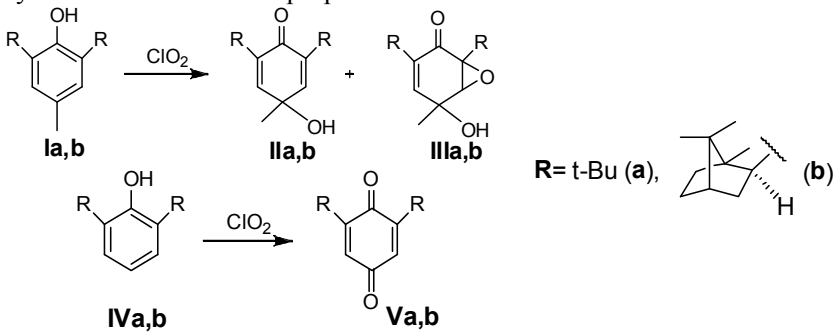
In recent years, the scope of quinones, which were initially used in the manufacture of dyes, actively extends. Quinones are used as reagents for synthesis, polymer modifiers and stabilizers, antioxidants, organic materials, catalysts of chemical reactions. Quinone derivatives have taken a strong place in arsenal of medicines for treatment of ischemic heart disease, muscular dystrophy, heart poisons in case of poisoning, as antibiotics, anticancer agents. Development of methods for quinones obtaining based on sterically hindered phenols is of practical interest. Chemistry of phenols oxidation by various oxidants has been studied quite extensively. Known to use chlorine dioxide ClO_2 for the oxidation of 2,6-substituted phenols [1-3].

In this paper, a convenient way of oxidation of phenols Ia,b and IVa,b by chlorine dioxide have proposed.



It is shown that chlorine dioxide oxidation of sterically hindered phenols having a methyl group in the *para*-position relative to the hydroxyl group leads to the formation of 4-alkyl-p-quinolyl **IIa,b** with yields of up to 78%. Oxidation of phenols with free *para*-position leads to the formation of 1,4-quinones **Va,b** and 80%.

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PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF GROUP 4 METAL COMPLEXES. APPLICATION FOR CATALYSIS

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Early-transition metal metallocenes $(\pi\text{-L})_2MX_n$ have been a cornerstone in the development of modern coordination organometallic chemistry and catalysis. Despite a number of promising commercial and fundamental applications, a principle relation "structure – properties", as well as patterns of reactivity of this important organometallic family remains unresolved.

The present contribution will provide an overview of novel experimental and theoretical data on photophysics and photochemistry of d^0 group IV metallocenes with respect their prominent use in homogeneous catalysis. [1-4] We have developed first photophysical approach to estimate orbital nature of rare long-lived ligand-to-metal charge transfer excited states and also coordinative interaction of basic components of catalytic systems for polymerization: metallocene complexes and unsaturated hydrocarbon substrates. In the similar way, the photophysical approach will be highlighted to enable studying fine intermolecular interactions in homogeneous systems with catalytic concentrations of metal complexes that cannot be achieved by other conventional (e.g. NMR) methods. The approach to estimate the orbital nature of extremely long-lived ligand-to-metal charge transfer excited states and to reveal coordinative interactions of basic components of polymerization catalysts (d^0 bent metallocenes and unsaturated hydrocarbon substrates) will be discussed.

In summary, a combined photophysical and theoretical approach made it possible to carry out study of the phenomenon of monomer coordination in practical catalytic or near-practical conditions, that may be of crucial importance for understanding mechanism and prediction of a multistage catalytic process of unsaturated compounds polymerization with organometallic complexes, particularly, d^0 metal complexes.

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TRIPLET – TRIPLET ABSORPTION OF d^0-COMPLEXES

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Triple states, based on organometallic compounds, are of special fundamental interest. Phosphorescence study is of importance for triplet state theory advance. Rare ligand-to-metal charge-transfer (LMCT) excited states, based on d^0-metallocenes of titanium group, were revealed to be highly emissive and long-lived.[1] We have obtained first group 4 metal π-complex (*rac*-$C_6H_{10}(IndH_4)_2ZrCl_2$), having high phosphorescence quantum yield (Φ up to 0.41) and lifetime ($\tau = 10^{-7}$–10^{-5} s.) in fluent solutions at room temperature.[2]

In this work, triplet – triplet (*T*–*T*) absorption of d^0 metal complexes was for the first time revealed and studied by means of pulse photolysis and *T*–*T* energy transfer. *T*–*T* absorption of d^0 metal complexes was studied with the use of representative complex *rac*-$C_6H_{10}(IndH_4)_2ZrCl_2$ dissolved in methylcyclohexane (MCH), toluene, *t*-butylmethyl ether (BME), CH_2Cl_2, $CHCl_3$, CCl_4 and also in THF and 2-methyltetrahydrofuran (MTHF). *T*–*T* absorption maxima at 20°C are located at ~540 nm (in MCH), ~545 nm (in toluene), and ~550 nm (in BME). At photolysis of the target zirconocene dissolved in chlorine-containing hydrocarbons, THF, and MTFH, a fast photochemical decomposition occurs and photolysis products are accumulated that does not allow determination of *T*–*T* absorption of the complex. The rate of photolysis of the complex in chlorine-containing hydrocarbons increases in the sequence: CH_2Cl_2<$CHCl_3$<CCl_4. In the similar way, pulse photolysis of Cp_2ZrCl_2 solutions was revealed to yield the fast photochemical decomposition already in toluene that does not permit quantitative estimate for *T*–*T* absorption of the simplest zirconocene representative Cp_2ZrCl_2.

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The study was financially supported by Russian Academy of Sciences and the Russian Foundation for Basic Research (project N 09-03-00379).

DEXTER ENERGY TRANSFER: UNRAVELING EFFECTS OF ORGANIC DONOR STRUCTURE AND MEDIUM

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Triplet – triplet energy transfer (*TET*) is the most common and important type of energy transfer involved in chemical and biochemical processes. Transfer of triplet excited-state energy plays a crucial role in the operation of electrophosphorescent and optical memory devices. Influence of the molecular structure of donor and acceptor on the efficiency of electron-exchange (Dexter) resonant energy transfer is poorly studied. Presently, we reveal effects of energy donor structure employing aromatic amines as the phosphorescing donors and α-olefins as the energy acceptors. The aromatic amines studied in this work are structurally similar, which is important for comparative analysis (Table 1).

Table 1. **Energies of 0–0 transition, phosphorescence maximum, and the critical radii of *TET* from the aromatic amines to hexane-1 in glassy ethanol at 77 K.**

Energy donor	$E_{0\text{-}0}$, cm^{-1}	E_{max}, cm^{-1}	R_0, Å
aniline	27300	24000	10.8
diphenylamine	25600	23600*	7.8
N-methyldiphenylamine	25300	23400*	6.6
carbazole	24900	22900*	6.9
N-ethylcarbazole	24900	22900*	6.1
ditolylamine	25000	23000*	6.4
4,4’-di(dimethylbenzyl)diphenylamine	25300	23350	5.7
triphenylamine	24900	24200*	5.6

Our data demonstrates that the critical radius of *TET* sphere (R_0) substantially depends on the molecular structure of energy donors and organic media and reflects the degree of orbital and chemical interactions in solutions. The tendency of the reduction of the *TET* sphere radius with increase of steric hindrances in the energy donor molecule was demonstrated in ethanol and less polar but more specific ethers as the glassy media.

The study was financially supported by Russian Academy of Sciences and the Russian Foundation for Basic Research (project N 09-03-00379).

USE OF WATER-FUEL EMULSIONS FOR IMPROVEMENT OF ECOLOGICAL SITUATION IN BIG CITIES

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Water-fuel emulsions (WFE) in diesel engines reduce the smoke of exhaust gases as well as the content of nitrogen and carbon oxides (1).

Researchers of our Institute have developed fire-proof diesel fuels (water-fuel micro emulsions), for instance, fire-proof summer grade of diesel fuel (PBD-L) TU 38.40130-88 which reduces the probability of inflammation by 50% and more. The stand tests of fuel PBD-L in different types of engines showed that concentration of nitrogen and carbon oxides in exhaust gases (EG) is reduced by 30% and 15% respectively, the smoke of exhaust gas is reduced by three times. Composition of fuel PBD-L includes: commercial diesel fuel, summer grade (77%wt), water(15% wt) and surface-active substance- emulsifier" AmIcrom"(8% wt) providing the formation of stable reverse micro-emulsion , type "water-in-oil' with the size of water drops less than 1 micron. The developed fire-proof diesel fuel is prepared by simple mixing of components in available technical means of fuel storage and transportation (storage tanks, tank truck and refuellers) be means of available fuel pumping facilities in conformity with the Instruction on preparation and use of Fuel PBD-L.

Fuel PBD-L (Permission for production and use No 763/415 of 16-th April, 2001) ensures fire-safety of vehicles, improves ecological characteristics of exhaust gases and may ве recommended for use in city conditions.

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POLYMERIC MICELLES WITH SEGREGATED CORONA

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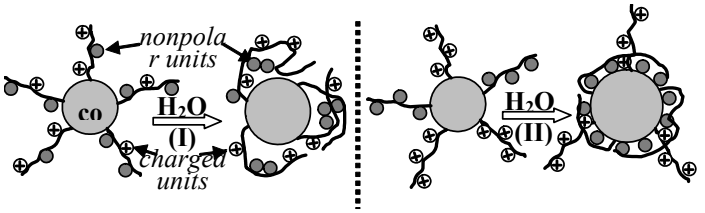
Amphiphilic block and graft copolymers in selective media self-assemble into micelles with lyophobic core and lyophilic corona. One of the important tasks of contemporary chemistry is the design of multicompartment polymeric micelles with the core and/or corona further segregated onto a number of smaller domains. Such micelles mimic natural protein globules with their heterogenic microstructure and can form the basis of novel class of polymer nanocontainers.[1]



Current presentation deals with peculiarities of self-assembly of the simplest type of such systems – the polymeric micelles with the homogenic hydrophobic core and heterogenic corona from polyelectrolyte and hydrophobic units, distributed statistically (I) or in a block manner (II).

It is shown, that in aqueous media the formation of both "statistically distributed" (I) or "segregated" (II) hydrophobic domains in the charged corona of such micelles is possible. The structure of micelles, their dispersion stability, solubilization and complexation properties are the function of the ratio and the character of distribution of charged and nonpolar units within the polymeric corona.[2]

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SINTHESIS ADAMANT-1-YL SUBSTITUTE AZOLES WITH APLICATION OF 1,3-DEHYDROADAMANTANE

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Among the adamantane derivatives, of great interest is had adamantil contenting heterocyclic compounds, including pyrazoles which are interesting as a therapeutically active substances with a broad spectrum of action. For example, pyrazoles, containing in its composition adamantyl radical and highly basic amino group exhibit antiviral activity[1].

Interesting way of synthesis of N-adamantil containing pyrazoles is to use as a initial reagent bridge strained [3.3.1] propellane - 1,3-dehydroadamantane (DHA), which has a great affinity to the proton, given that the pyrazole (pKa pyrazole = 14) and pyrazole derivatives exhibit properties of weak acids.

We first performed adamantilation by DHA of 1H-pyrazole and the series of azoles: pyrazole; 3(5)- и 4- substituted pyrazoles; 3,5 –disubstituted pyrazoles; 3,4,5-trisubstituted pyrazoles; N-substituted pyrazoles; 3-amino-5- methylisoxazole.

Initial 1H-pyrazoles had various nature and number of substituents, which made it possible to widely influence on their acid-base properties. 1H-pyrazoles contained electron donor (methyl-, 1-adamantyl-) and electron acceptor substituents: phenyl, trifluoromethyl-, bromo-, nitro, hydroxy, and others, as well as the amino group.

We have found that the structure obtained in specific cases adamantilpyrazoles depends on the structure of the initial pyrazole and its acid-base properties, the presence of tautomeric transformations, reaction conditions, the nature of the solvent.

Thus, developed a convenient non-catalytic (in the case of 1H-pyrazoles) and catalytic (in the case of N-substituted pyrazoles) one-step method for obtaining 1 - (adamant-1-yl)-substituted pyrazoles in high yields, under mild conditions.

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THE PHASE COMPLEX OF THE Li_2MoO_4-$LiPO_3$-MoO_3SYSTEM

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The saline and oxide-saline melts are used as high-temperature greasing, heat-carriers and catalyzing environments in some processes of the organic and petrochemical synthesis, for obtaining the semiconductor materials.

The purpose of the given paper is studying the phase-formation in Li_2MoO_4-$LiPO_3$-MoO_3 three-component oxide-saline system. In the system 25 internal cuts are investigated with the methods of the thermal analysis. Te polytherm projection of the system crystallization on the triangle of structures shows that mono-variant curves converge in eight non-variant points, parameters of which (see the table) are defined by constructing the projection of curves of the mono-variant balance on Li_2MoO_4-$LiPO_3$ side of the structure triangle.

Table. **The characteristics of non-variant-points of Li_2MoO_4-$LiPO_3$-MoO_3 system**

The point character	Symbol	t,^{0}C	Structure, mole %		
			Li_2MoO_4	$LiPO_3$	MoO_3
Eutectics	E_1	480	20	32	48
Eutectics	E_2	500	32	6	62
Eutectics	E_3	505	26	10	64
Eutectics	E_4	605	12	82	6
Peritectics	P_1	515	30	5	65
Peritectics	P_2	520	20	43	37
Peritectics	P_3	656	25	59	16
Peritectics	P_4	968	63	21	16

In the system ten crystallization fields are limited: of three initial components (Li_2MoO_4, $LiPO_3$, MoO_3) and of seven double compounds ($MoO_3 \cdot 3LiPO_3$; $MoO_3 \cdot LiPO_3$; $MoO_3 \cdot Li_2MoO_4$; $2\,MoO_3 \cdot Li_2MoO_4$; $3\,MoO_3 \cdot Li_2MoO_4$; $3\,LiPO_3 \cdot Li_2MoO_4$; $LiPO_3 \cdot 3\,Li_2MoO_4$).

The investigated system is of interest for revealing the peculiarities of formation of the new phases from its melts in thermo- and electrochemical modes, including moly-bronzes, which are the perspective non-organic materials.

The paper was written with financial support according the thematic plan of the Ministry of Education and Science, the project 1.1.08-11.

FORMATION OF DISSIPATIVE STRUCTURES AT OXIDATION OF ELEMENTARY BIOSUBSTRATA IN THE HOMOGENEOUS ENVIRONMENT

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It is known that at a process of chemical reactions in homogeneous environments there are no restrictions for complexity of behavior of intermediate connections in time and in space.

The results of regular studies of the character of fluctuations of concentrations realized at oxidation of such biosubstrates, as naphtodiol, leucoriboflavin, leucomethylene blue, amber and lipoic acids, glutathione and ubiquinol in the presence of coordination compounds of transition metals with dimethylglyoxime, the nitrogenous basis and molecular oxygen are presented in this message.

At the end result of the spent researches the following results are received:

• the new class the liquid-phase oxidation-reduction reactions proceeding in an oscillatory mode is found;

• on the basis of discrete transformation of Fure, flikker-noise spectroscopy, reconstruction of the dynamics of process on time numbers, calculations of indicators of Lyapunov and entropy of Kolmogorov-Sinai there was established that observed oscillations are the result of the course of chemical reactions, i.e. deterministic dynamics is displayed;

• probable mechanisms of proceeding processes are proved and offered;

• the reasons of the loss of stability by the system are established on the basis of approaches on nonlinear and nonequilibrium dynamics.

• the number and stability of decisions, the character of bifurcation, concentration limits of the reagent and catalyst at which the oscillatory mode of the course of processes is realized are determined at the end of qualitative analysis and numerical integration of systems of differential equations presented as mathematical models.

This work is executed by financial support of the Russian Federal Property Fund, the project 09-03-96621 р_юг_а

NEW MECHANISM OF N-ALKYL-N'-METHOXYDIAZENE OXIDES THERMAL DECOMPOSITION

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Potential energy surfaces have been determined for N-methyl-N'-methoxydiazene-N'-oxide and N-ethyl-N'-methoxydiazene-N'-oxide by density functional theory methods (DFT) GGA PBE/L11 and wB97XD/6-31(2df,p). Reactants, transition states and products have been localized; reaction pathways to connect them have been obtained for a number of alternative methods of thermal decomposition. The process has been shown to occur through sigmatropic rearrangement related to shift of methyl group from methoxy oxygen atom to N-oxide oxygen atom with further N-N bond disruption in the N-N=O group formed. Decomposition of N-alkyl-N'-methoxydiazene-N'-oxides with alkyl group hydrogen atom in β-position occurs through corresponding olefine elimination, whereas β-hydrogen migrates to N-oxide oxygen atom.

ELECTROCATALYTIC HYDROGENATION OF PYRIDINE CARBOXYLIC ACIDS

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Among the saturated N-heterocyclic compounds manifesting a biological activity and used in production of medicinal preparations, the derivatives of piperidine carboxylic acids occupy one of the important places. Depending on the complexity of structure they are obtained or as a result of multistep synthesis, or by the reduction of unsaturated analogues. In the work the opportunity of piperidine carboxylic acids preparation by electrocatalytic hydrogenation (ECH) of pyridine carboxylic acids (PCA) on the copper cathode activated by skeleton catalysts in the water-alkaline solutions of catholyte is investigated. The experiments have been performed in electrocatalytic diaphragm cell at a current intensity 2A, 40^{o}C, 1 g of skeleton catalyst (Ni, Co, Fe, Zn, Cu) and 0,55 g (0,0046 mole) of initial compound in 60 ml of catholyte (Table 1).

Table 1. **The influence of catholyte composition and the nature of catalysts on electrocatalytic hydrogenation of *2*-, *3*- and *4*-PCA**

Catholyte	Catalyst	*2-PCA*		*3-PCA*		*4-PCA*	
		α, %	W(α= 0,5)	α, %	W(α = 0,5)	α, %	W(α = 0,5)
2% Na_2SO_4	Ni skel.	100	9,6	68	2,7	100	9,5
0,5% NaOH	Ni skel.	97	9,6	77	3,5	100	7,0
1% NaOH	Ni skel.	100	9,2	65	3,4	98	7,4
2% NaOH	Ni skel.	95	8,7	62	3,1	97	6,3
2% NaOH	Co skel.	99	6,1	75	4,5	100	4,5

α – it is a degree of transformation of initial compound, W – a rate of the process at α= 50%

According to the presented data, the ECH processes of *2*- and *4*-isomers of PCA proceed the most intensive and with high conversion in a solution of sodium sulfate and in low-alkaline catholyte on Reney nickel. *3-PCA* is better hydrogenated on skeleton cobalt, however not achieving a full conversion. At the use of Fe, Zn, Cu catalysts, and also by the electrochemical reduction on the copper cathode in specified conditions the hydrogenation of all the three PCA does not go. After a separation from cathalyte the substance yield of *2*-piperidine carboxylic acid makes up 95% (on Ni catalyst) and 98 % (on Co catalyst). Furthermore, the electrocatalytic hydrogenation of *2*, *3* and *4-PCA* is studied under the influence of such factors, as current intensity, weight of catalyst (skeleton Ni) and initial concentration of hydrogenated PCA.

SYNTHESIS AND ESTERASE PROFILE OF ORGANOPHOSPHATES WITH FLUORINE-CONTAINING LEAVING GROUPS

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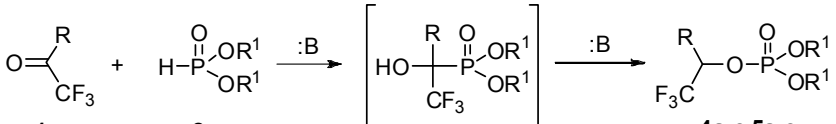
Our previous studies showed that introduction of CF_3-containing substituents into one of the *O*-alkyl groups of trialkylphosphates transforms the formerly unreactive alkoxy group into an electron-withdrawing fluoroalkoxy leaving group.[1-2] The aims of the present work were to synthesize organophosphates with various fluorine-containing leaving groups and to determine their esterase profiles. The synthetic route used to obtain the titled compounds is outlined in the scheme:



1a-c **2a-c** **3** **4a-c 5a-c 6a-c**

1a, **4**: R = Ph; **1b**, **5**: R = CF_3; **1c**, **6**: R = C(O)OEt
For all, R^1 = Me (**a**), Et (**b**), Bu (**c**)

The esterase profiles of phosphates **5-6** were determined by measuring their inhibitory activities against 4 serine esterases: acetylcholinesterase (AChE), butyrylcholinesterase (BChE), carboxylesterase (CaE) and neuropathy target esterase (NTE). Kinetic studies showed that phosphates **4-6** were irreversible progressive inhibitors for all the studied esterases except reversible inhibition of CaE by phosphates **4**. The *O*-alkyl groups, along with the substituent in 1-position in the leaving group, determined potency and selectivity of the phosphates as inhibitors of AChE, BChE, CaE and NTE.[2-3] Some selective inhibitors of BChE and especially CaE were found.

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COORDINATION COMPOUNDS OF PALLADIUM (II), RHODIUM (III), IRIDIUM (IV) AND PLATINUM (IV) WITH PURINE AND PYRIMIDINE BASES

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Research of complex compounds of transition elements with amino acids and DNA heterocyclic bases provides data for biological catalysts exploration and further development of biologically active substances for medical and agricultural applications.

Means of potentiometric titration revealed conditions complex formation of Pt(IV), Ir(IV), Rh(III) and Pd(II) with adenine ($C_5H_5N_5$), cytosine ($C_4H_4N_3O$) and hypoxanthine ($C_5H_4N_4O$), their composition and constants of formation.

Ligand	**Constants of formation, lg K_1**			
	Pd(II)	**Rh(III)**	**Pt(IV)**	**Ir(IV)**
Adenine	-	8,96	9,57	9,41
Hypoxanthine	-	6,81	-	8,27
Cytosine	10,70	10,93	10,44	-

Complex compounds of Pd(II) with adenine and hypoxanthine show little solubility in water, that's why it was impossible to determine related constants.

Taking in account all the research we conclude that metals of platinum group form most strong coordination compounds with cytosine.

The following complex compounds were extracted from aqueous solutions: $[Pd(Hyp)_2Cl_2]$, $[Pd(Ade)_2Cl_2]$, $[Pt(Ade)H_2O]Cl_4 \cdot H_2O$, $Pt(Ade)_2Cl_4 \cdot 2H_2O$, $Pt(Ade)_3Cl_4 \cdot H_2O$, $Pt(Cyt)Cl_4 \cdot H_2O$, $[Pt(Cyt)_2Cl_2]Cl_2 \cdot H_2O$, $Pt(Cyt)_3Cl_4 \cdot H_2O$, $[Ir(Hyp)Cl_4]$, $[Ir(Hyp)_2Cl_2]Cl_2$, $[Ir(Ade)Cl_4] \cdot 2H_2O$, $[Ir(Ade)_2Cl_2]Cl_2 \cdot 2H_2O$, $Rh(Ade)_2Cl_3$, $Rh(Hyp)Cl_3 \cdot 2H_2O$, $Rh(Cyt)_3Cl_3$.

Chemical and thermo-gravimetric analysis, X-Ray-diffraction, Infrared spectroscopy and ^{13}C NMR studies proved the composition and structure of the obtained complexes.

We came to conclusion that it is a same type of interaction of metal-ions with the ligands in all the complexes, nucleobases acting as bidentate ligands (atoms N3, N7 of heterocycles and atoms of O and N of exocyclic groups).

CONJUGATED PROCESS OF SULFUR DIOXIDE CONVERSION UNDER THE EFFECT OF RADICAL-CHAIN REACTIONS OF METHANE AND HYDROGEN OXIDATION

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The processes of sulphur dioxide conversion in the environment of chain reaction of methane and hydrogen slow combustion at T = 450 ÷ 510°C and P = 120 ÷ 200 Torr under the conditions when peroxy radicals are the main leading active centres have been realized. Peroxy radicals oxidize SO_2 into SO_3.[1-2] The direction of chemical transformation of SO_2 changes at law pressure of hydrogen oxidation (P = 20 ÷ 80 Torr) because active species – H, O and OH – become leading active centres instead HO_2. Conjugated process in this case leads to elementary sulfur formation.[3-4] Depending on gas flow rate (or contact time - τ) the rare flames can turn to "intermittent" flames accompanied with sharp light flashes. Observed phenomena were explained on the basis of fundamental statements of chain reaction theory.

The probable kinetic scheme based on the competition reactions of leading active centres – hydrogen atom – was proposed:

1) $H + O_2 \rightarrow OH + O$ – chain branching, 2) H + wall → chain termination, 3) $H + O_2 + M \rightarrow HO_2 + M$ – chain termination, 4) $H + SO_2 \rightarrow HSO_2$ (OH + SO) – first step of SO_2 conversion following by the reactions of sulfhur formation.

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DIPYRRIN METALLOCOMPLEXES AND HYBRID MATERIALS BASED ON THEM. ANALYSIS OF SPECTRAL AND PHOTO-PHYSICAL PROPERTIES, THERMAL AND PHOTOSTABILITY

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Dipyrrins (the members of linear oligopyrrole family) and complexes based on them are the compounds of great interest today. Chromophoric properties of these compounds are due to the presence of easily polarizable aromatic system in dipyrrins and the ability to form stable metallocycles leads to large number of different coordination compounds. It is able to modify optical properties of dipyrrin coordination compounds by varying the ligand structure (the nature of substitution in dipyrrin fragment), the nature of complex-former and the nature of solvatation media (solvent or polymeric matrice). Results of mentioned factors influence on chromophoric and fluorescence properties of dipyrrin complexes are discussed in the report. Solvatocromic properties of investigated compounds lead to the variations in absorption and fluorescence maxima positions in spectra, Stokes shifts and fluorescence quantum yields. The correlations of abovementioned parameters with solvent nature (polarity, polarizability, donating properties and acid-base properties) discussed in the report are made for zinc and boron difluoride complexes. The influence of polymeric matrice on thermal and photo stability of discussed compounds in the hybrid materials is also discussed in the report.

This work was supported by the Council for Grants of the President of the Russian Federation for Support of Young Scientists – candidates of science (grant no MK-401.2011.3) and the Federal Targeted Program "Scientific and Scientific–Pedagogical Personnel of the Innovative Russia in 2009–2013" (States no 14.740.11.0617).

KINETICS OF SOLID PHASE CHEMICAL REACTIONS WITH DIFFUSION OVER THE SPECTRUM OF REACTION STATES

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The kinetics of cage reactions in solid phase is considered, depending on the efficiency of mixing of reaction states, and the proper diffusion equation with constant coefficient D of spectral diffusion in the spectrum of the rate constants k of the reaction system is analyzed. The exact solution of spectral-diffusion equation for chemical reaction is compared with its approximate solution and with empiric features of reaction kinetics in solid polymers and frozen liquids. The exact solutions give various kinetic curves coincident with experimental curves: exponential $lnC(t) \sim -t$, or sum of two or more exponentials, or classical dispersive kinetics when a part of kinetic curve is fitted by equation $C(t) \sim lnt$, or square root kinetics when kinetic curve is fitted by equation $lnC(t) \sim -t^{1/2}$, depending on the initial conditions and value of D.

In the most important case of a broad range of rate constants, that may be considered as unrestricted space, the simple equation for reaction kinetics has been obtained:

$$C(t)/C(0) = \sum_{n=1}^{\infty} a_n \exp(-k_n t), \qquad (1)$$

where $k_n = D^{1/3} r_n$, $-r_n$ are zeros of the first derivative of Airy function $Ai(x)$, and coefficients a_n are related to initial distribution function $\rho(k)$ by relationship:

$$a_n = \pi (D/k_n)^{1/2} \rho(k_n)$$

The equation (1) has been shown to describe well the above-listed features of solid phase reaction kinetics, depending on D and $\rho(k)$. The method of spectral diffusion analysis has been proposed in order to determine the spectral diffusion coefficient, invariant parameters of initial distribution and steady-state rate constant of reaction, derived from experimental kinetic curves. The application of this method is illustrated by the examples: reaction of abstraction of atom H by methyl radical in methanol at 77-87 K and reaction of benzophenone triplet state decay in PMMA at different temperatures in a wide range of temperatures from 77 to 420 K. The coefficient and activation energy of spectral diffusion, width of distribution and lifetime of mixing of reaction states have been determined for reactions studied.

OXIDATION OF ISOTACTIC POLYPROPYLENE MODIFIED BY INTRODUCTION OF SIDE CYCLOHEXYL GROUPS INTO THE MAIN CHAIN OF POLYMER

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Random copolymers of propylene and vinylcyclohexane (VCH) with VCH content up to 0.37 mol % obtained by homogeneous copolymerization at 60°C have been examined. Some characteristics of oxidation of copolymers obtained have been measured: the induction periods τ for the consumption of oxygen and the rate constants k of termination of peroxyl macroradicals determined by chemiluminescence of copolymers.

The introduction of low amounts of side cyclohexyl groups (CHG) into the main chain of PP has been shown to increase substantially (to 5 times) the induction period of PP oxidation.

Chemiluminescence of PP is a useful probe to explore the molecular mobility which effect on polymer reactions. It is important that this method explores the mobility in the areas where reaction centers of polymer are localized. Initial increase in k has been found with increase in content of CHG that indicates the increase in molecular mobility induced by the disturbance of regular sequences in the main chain of PP due to introduction of CHG. Correspondingly the induction period is increased.

The complex dependence of kinetic parameters of oxidation of copolymers on content of CHG has been found. The induction period of oxidation and the rate constant of radical termination go through a maximum with increasing content of side groups at low levels of CHG. Under the further increase in the comonomer content the induction period of oxidation is increased and the rate constant of radical termination is decreased. These results indicate that effect of side cyclohexyl groups on copolymer oxidation can occur via two mechanisms: on the one hand they disturb the lengths of regular sequences in the main chain of crystallizing PP, leading to a decrease in ordering of molecules and an increase in their mobility, but on the other hand a structure-forming effect of side groups becomes important with increasing their concentration that leads to formation of physical network and to corresponding decrease in molecular mobility and oxidation rate.

HETERONUCLEAR LANTHANIDE TRISPHTHALOCYANINATES, CONTAINING TWO DIFFERENT PARAMAGNETIC IONS

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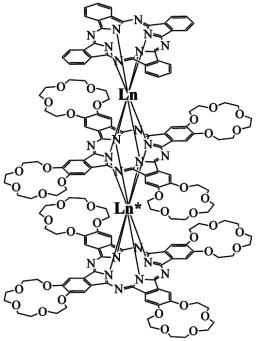
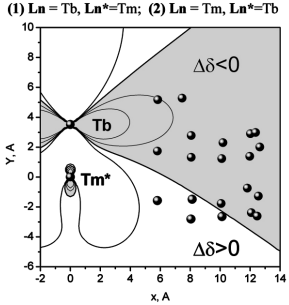
Specific feature of triple-decker lanthanide complexes with tetrapyrrolic ligands is a relatively short distance between Ln^{3+} ions (~3.5Å), which provides efficient *f-f* interaction between paramagnetic centers. Therefore, these compounds may act as perspective components of molecular magnets [1].



(1) Ln = Tb, **Ln***=Tm; **(2) Ln** = Tm, **Ln***=Tb



Distribution of dipolar LIS contribution in complex **(1)**

The pair of isomeric heteronuclear crown-phthalocyaninates, containing two different paramagnetic nuclei (Tb^{3+} and Tm^{3+} ions), namely $[(15C5)_4Pc]Ln^*[(15C5)_4Pc]Ln(Pc)$, was firstly prepared with the application of unsubstituted lanthanum diphthalocyaninate – efficient donor of phthalocyaninato-dianion (Pc^{2-}), found previously [2,3]. The presence of two different paramagnetic ions and their relative positions were supported by MALDI TOF MS and ^{1}H-NMR respectively.

The studies of lanthanide-induced shifts (LIS in NMR spectra of synthesized complexes were performed in terms of analysis of dipolar (through space) LIS contribution. The investigation of its distribution in the space around two paramagnetic nuclei afforded the explanation of the presence of both up- and down-field shifted resonance signals in ^{1}H-NMR spectra which result in very broad spectral window (46 ÷ -73 ppm). Complete assignment of resonance signals was performed within the purely dipolar shift approximation.

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HALOGENIDES OF IVB GROUP ELEMENTS – EFFECTIVE INDUCTORS OF NUCLEOPHILIC SUBSTITUTION IN CLUSTER BORON ANIONS

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Introducing different functional groups into cluster boron anions is an important step in the process of obtaining compounds for ^{10}B-NCT. Using the reactions of electrophile-induced nucleophilic substitution (EINS) allows to obtain various functional derivatives of cluster boron anions [1].

We have investigated the interaction of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions with the wide range of nucleophilic reactants (nitriles, ethers, alcohols, carbamides and their thioanalogs) in the presence of different Lewis acids – halogenides of IVB group elements ($TiBr_4$, $ZrCl_4$, $HfCl_4$). It was shown that the first step of the substitution process was formation of cluster boron anion complexes with the Lewis acids of type $[B_nH_n^{2-} \cdot L]$ or, in case of excess of the inductor, $[B_nH_n^{2-} \cdot 2L]$. Earlier we investigated similar processes in reactions with carbocations [2]. These complexes then react with nucleophiles in mild conditions, the respective substituted derivatives $[B_nH_{n-1}Nu]^-$ or $[B_nH_{n-2}Nu_2]^0$ (n=10, 12) being formed. Composition and structure of the derivatives were verified via physical-chemical analysis methods [3].

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INTERACTION OF 2,4-DICHLORO-2-PENTENE-1,5-DIONE WITH NUCLEOPHILIC AGENTS IN THE CONDITIONS OF BIDZHINELLI'S REACTION

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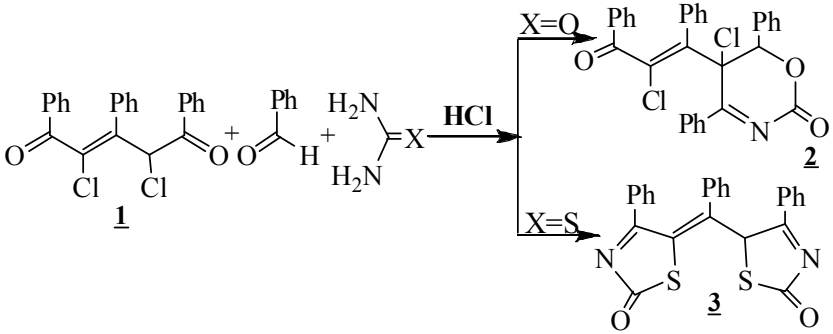
Previously we found that the reaction of 2,4-dichloro-1,3,5-triphenyl-2-pentene-1,5-dione **1** with urea and benzaldehyde in a three-component condensation formed 5-chloro-4,6-diphenyl-5-(1,3-diphenyl-2-chloro-3-oxopropan-1-yl)oxazalid-2-one **2.** This is a product of heterocyclization in the presence of α-chloropropanonile fragment [1].

Using thiourea as a nucleophilic reagent, substrate **1** turn into a (5-phenyl-3-thiazol-2-one-4-ylidene)-phenyl-(5-phenyl-3-thiazol-2-one-4-yl)methylene **3** in yield of 58%.



Realization of the reaction in an aqueous acidic medium contributes the conversion of thiourea from thiocarbonyl to thiol, and in the last step - hydrolysis of present imine groups to carbonyl.

In case of interaction 1 with a thiourea both fragments participate: α-chloropropenonyl and α-chloropropanonyl. They also form bis-product **3**.

The composition and structure of compounds **2**, **3**, is found on the basis of elemental analysis, IR and NMR spectroscopy.

Thus, behavior researches of dichloropentendione **1** allowed to open new sides of the reactivity of dichlorine-substituted unsaturatted 1,5-diketones with urea and thiourea in conditions of Bidzhinelli's reaction.

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THE EFFECT OF ACTIVATING COMPLEXATION IN *O*-QUINONE (*O*-IMINOQUINONE) – 12-13 GROUP METAL HALIDES SYSTEM

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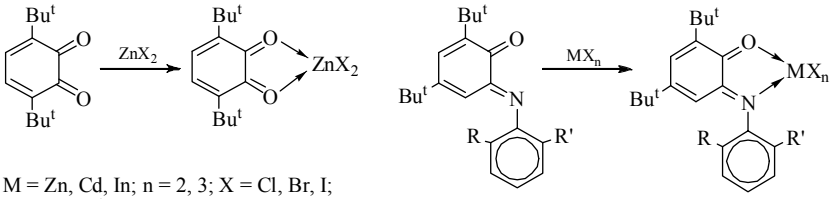
The interaction of different *o*-quinones with metal halides includes one-electron transfer from Lewis acid to ligand. The mechanism was proposed in order to explain this redox reaction, which is carried out between two electron acceptors. In accordance with this mechanism, the complexation between Lewis acid and neutral *o*-quinone takes place at the first step of the reaction. The oxidative ability of *o*-quinone increases in this complex due to the partial transfer of electron density from ligand molecule to metal. This effect was named as the activating complexation.

The number of complexes of zinc(II), cadmium(II) and indium(III) halides with unreduced substituted *o*-iminobenzoquinones and 3,6-di-tert-butyl-*o*-benzoquinone were synthesized in order to prove proposed mechanism.



M = Zn, Cd, In; n = 2, 3; X = Cl, Br, I;
R = R' = Pr^i; R = R' = Me; R = R' = Et; R = Me, R' = Et

The complexes obtained were characterized by IR-, NMR- and UV-Vis spectroscopy, X-ray structure analysis and voltammetry. The effect of activating complexation was demonstrated giving examples of obtained complexes interaction with metallic zinc, cadmium, indium and mercury and with ferrocene.

We are grateful to the Russian Foundation for Basic Research (grant 10-03-00788-a), Russian President Grant (grants NSh-7065.2010.3, МК - 614.2011.3) and FSP "Scientific and pedagogical cadres of innovation Russia" for 2009-2013 years (GK-P982 from 27.05.2010) for financial support of this work.

2(5)-(1-HYDROXYCYCLOALKYL)- AND 2(5)-(1-CYCLOALKENYL)-2,2'-BITHIOPHENES IN THE VILSMEIER-HAACK REACTION

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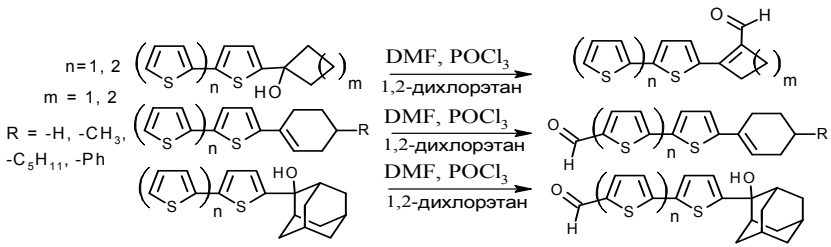
Derivatives of 2,2'-bithiophenes with exocyclic nitrogen and oxygen atoms have fluorescent, semiconducting and nonlinear optical properties.[1] Cyclohexylbiphenyls are the basis for liquid crystals[2], the heteroanalogues of which are derivatives of 2,2'-bithiophene.

Grignard reaction of 2-thienyl- and 5-bithienyl-2,2'- magnesium bromides with cyclobutanone, cyclopentanone and 2-adamantanone leads to the formation of stable tertiary alcohols. However reaction with cyclohexanones, accompanied by water elimination at decomposition of magnesium alkoxides, leads to corresponding cycloalkenyl derivatives (**3-6**).

Tertiary alcohols (**1**) and (**2**) in the reaction with $POCl_3$-DMF mixture are dehydrated to cycloolefins, which formed corresponding α,β-unsaturated aldehydes (**8, 9**). At the same time formylation of cyclohexenylthiophenes and 2,2'-bithiophenes (**3-6**) passes into 5' (5) position of heterocycle unit (**10-13**).



The research work focused on the development of new organic luminophores allowed us to convert the aldehyde group into carbonitrile and dicyanoethylene moieties. The appearance of intense luminescence of 5-(2"-hydroxyadamantyl-2")-2,2'-bithiophene (**7**) and its formyl- (**14**) and carbonitrile derivatives was noted. The obtained compounds (**1-14**) have luminescence properties in the wavelength range from 400 to 550 nm with quantum yield up to 0,5.

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STUDY *fac*-[Co(mea)$_3$]·3H$_2$O NMR SPECTROSCOPY

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Complex compounds of cobalt with monoethanolamine are studied for a long time. In works Stepanenko O.H. shown that in the ^{59}Co NMR solution *fac*-[Co(mea)$_3$]·3H$_2$O, where mea = $NH_2C_2H_4O^-$, there are two signals with equal integral intensity that was consistent with the finding that the proportion of octahedral and prismatic forms in a crystal same.[1] Based on studies in the ^{59}Co NMR solution *fac*-[Co(mea)$_3$]·3H$_2$O fixed one resonance line $\delta(^{59}Co)$ = 2,030 ppm, which indicates the presence in solution of one octahedral fac-isomer. X-ray diffractometry data confirmed the single *fac*-[Co(mea)$_3$]·3H$_2$O.[2] Thus, our data do not confirm the existence of trigonal-prismatic *fac*-isomer. In the spectrum of ^{1}H NMR in solution *fac*-[Co(mea)$_3$]·3H$_2$O (in D$_2$O), we observe a few sets of multiplet signals (figure), in the field of 2 - 4 ppm. It means that in a solution probably equilibrium existence *fac*- and *mer*-izomerov. This suggests that in solution probably the equilibrium existence *fac*- and *mer*-isomers.

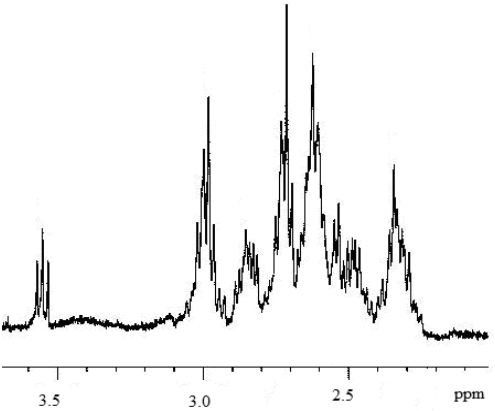

Figure. Spectrum of ^{1}H NMR a solution *fac*-[Co(mea)$_3$]·3H$_2$O in D$_2$O.

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MODELING OF BORDER Ni,H_2/ SOLID STATE ELECTROLYTE

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New solid polymer electrolyte «H^+- SEL» based on the sulfosalicylic acid, distributed in the matrix of polyacrylonitrile was received. Border Ni,H_2/«H^+- SEL» with hydrogenated micro porous Ni was investigated by impedance. The equivalent circuit for calculating the impedance spectra (Fig. 1) contains a branch of the elements belonging to the major charge carriers - hydrogen ions H^+. Reversibility of Ni electrodes for hydrogen ion was investigated.

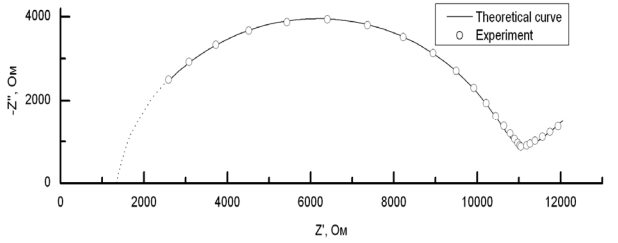

Fig. 1. impedance spectra

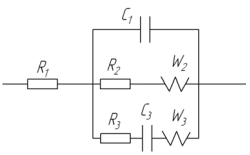

Fig. 2. The equivalent circuit for calculating the impedance spectra

Complex impedance Z_1 has mathematics expression according to the model adopted:

$$Z_1 = \left\{ j\omega C_1 = \left[R_2 + (1-j)W_2\omega^{-1/2} \right]^{-1} + \left[R_3 + \left(j\omega C_3 \right)^{-1} + (1-j)W_3\omega^{-1/2} \right]^{-1} \right\}^{-1}, \quad (1)$$

where R1 - resistance «H+- SEL»; C1 - capacitance of the electrical double layer; W2, W3 - warburg constant; C3 - adsorption capacity; R2, R3 - resistance; j - imaginary; ω - angular frequency.

The calculated values of circuit elements are presented in the table.

Table 1. Electrochemical parameters of border Ni,H_2/«H^+- SEL»

T, K	C_3, pF/cm^2	W_3, Ω·cm^2/s$^{1/2}$	R_3, Ω·cm^2	W_2, Ω·cm^2/s$^{1/2}$	R_2, Ω·cm^2	C_1, pF/cm^2	σ_0, Ω^{-1}·cm^{-1}
298	50,7	973300	1,1197	115000	9341,4	25,6	2,607 ·10^{-2}

Equivalent circuit parameters were obtained using the method of computer optimization, fitting the theoretical curve to experimental data using the program EIS Spectrum Analyser.

CONTROL OF PHOTOINDUCED CHARGE TRANSFER IN SUPRAMOLECULAR SYSTEMS

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Processes of electron transfer in donor-acceptor complexes attract significant attention of researchers since they, firstly, play a key role in many chemical and biochemical processes, and secondly, are promising components of molecular devices. The central problem of ultrafast reactions of separation and transfer of charges in such systems is the control of their rate and the quantum yield of products. The most promising methods of control are based on a variation of the spectral characteristics of the exciting pulse.

A detailed analysis of the influence of the spectral characteristics of the exciting pulse (the carrier frequency and its duration), as well as dynamic properties of the solvent on the kinetics of the processes of ultrafast photoinduced transfer and recombination of charges in donor-acceptor complexes included in supramolecular systems is given.[1-3] The principal possibility of controlling the efficiency of photochemical reactions of charge transfer in donor-acceptor complexes occurring in a nonequilibrium mode is demonstrated.

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MESOMERISM OF β-DI-, β,β′-TRICARBONYL COMPOUNDS, THEIR ANIONS AND ENOL DERIVATIVES. REPRESENTATIONS — COMPUTATIONS — EXPERIMENT

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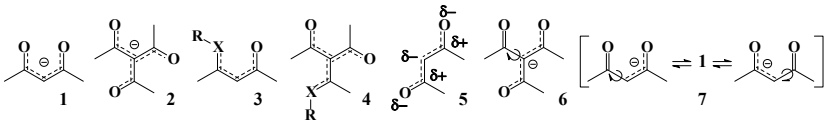
β-Di-, β,β'-tricarbonyl compounds (β-di-, β,β'-TriCC) and their enol derivatives are large and diverse group of organic substances.[1] β-Di-, β,β'-triCC are widely represented in natural objects from microorganisms to higher plants and mammals, and carry out important biological functions during their vital functions.[2] These substances are important reagents for laboratory and tonnage organic synthesis.[3] The combining factors of compounds of these series are 1,3- or β-dicarbonyl fragment,[1] the phenomenon of prototropii or tautomerism (*keto-enol-enolic* and *keto-enolic* of anions)[4] and mesomerism.



According to existing representations anions, enols and enol derivatives of parent compounds of this series — acetylacetone (acac) and triacetylmethane — are graphically represented by pentad **1**, **3** and heptad **2**, **4** mesomers (where X = O, N, S, R = H, Alk, Ar, Aralk), accordingly. Thus if for an anion acac quantum-mechanical modelling admits pentad mesomer in W-conformation with alternation of a charge **5**, that for an anion triacetylmethane is admitted only pentad mesomer with acyl removed of a conjugation plane **6**, that testifies to lability as heptad **2**, **4**, and pentad **1**, **3**, **5**, **6** mesomers. The data on a H/D-exchange of β-di-, β,β'-TriCC[5-7] testify, that the specified compounds exist in the form of balance triad-pentad mesomers **7**.

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DISSIPATION OF SUBSTANCE, THROWING BY THE CORE OF AN VORTICAL OBJECT IS THE SOURCE OF ORIGIN OF THE CHEMICAL ELEMENTS IN THE UNIVERSE

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The modern state of one of fundamental and complicated problems of science on the origin of the chemical elements was examined.

Some processes of synthesis of atoms of the chemical elements in different objects of the Universe are treated.

The new model of formation of the chemical elements in different objects of the Universe is proposed. It is considered that their origin is occurred by the internal dynamics of the homogenous viscous liquid substance of the vortex of any size of the object of the Universe and, it is caused by dissipation of substance thrown by its core at ejection of its surplus of energy, derived by excitation.

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SOME NEW PHYSICAL CHARACTERISTICS OF ATOMS OF THE CHEMICAL ELEMENTS OF THE PERIODIC TABLE OF D.I.MENDELEEV

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Considering the modern Periodical Table of Elements of D.I.Mendeleev, one can notice that not the mass of the atom as it was assumed by the author of the Table, but the value of a positive charge of a nucleus of the atom, of which the charge is equal to the ordinal number of the element, is agreed as the main characteristic of an atom. [1] By this the positive charge of the nucleus is balanced by the total charge of electrons rotating around the nucleus. A number of electrons surrounding the nucleus is equal to the ordinal number of the element; and, it is considered that the atom is electrically neutral as a whole.

The investigations fulfill by us of the experimental data on different kinds of interactions show that the atom of the chemical element may be considered as a spherical self-closing vortex rotating around own axis; which is composed of a homogenous viscous liquid substance.[2-3] The vortical state of substance is not a hypothesis. It was experimentally discovered by Oersted in 1820, but nonetheless, it is not realized up to now.

Using the previously found the expression for a charge Q, the characteristics of atoms of the Periodic Table of Elements were analyzed. [2-3] The new physical characteristics of atoms of the chemical elements: (a) a gravitational charge Q_G; (b) the velocity υ of motion of substance in vortices, forming the atoms of the chemical elements; (c) a value of circulation of a velocity of transfer of substance $(\upsilon \cdot r)$ in atoms, which is being of one of the basic fundamental characteristics of atoms, and which is responsible for appearing of periods in the Periodic Table of Elements of D.I.Mendeleev were obtained. [2-3]

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NEW ABOUT STRUCTURE OF ATOMS, CHARGE AND THEIR INTERCONNECTION WITH SPECTRA OF RADIATION

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In the given work the structure of an atom of any element of the Periodic Table of Elements of D.I.Mendeleev was considered from the position of a model proposed by us of the basic form of existing of masses of substance of different objects in the kind of a liquid homogeneous rotating self-closing spherical vortex.[1-2]

The emphasis was on the internal structure of an atom, neutron, proton, electron and their interconnection with a charge as a radiation coming outside the field of the outer shell of the atom-vortex and being a component of the pulsated separated jets of substance of the atom; which consists of the convective cells of substance as photons of certain length of wave transferring the mass and which are responsible for different kinds of interactions between different objects.[1-4]

The interpretation of the physical essence of a Rydberg constant for an atom of hydrogen is first given.

The association of the spectral characteristics of radiation of the atom of hydrogen with the internal dynamics of substance in the atom is shown.

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MICROWAVE IRRADIATION IN THE PHOSPHORUS CONTAINING ADAMANTANE DERIVATIVES SYNTHESIS

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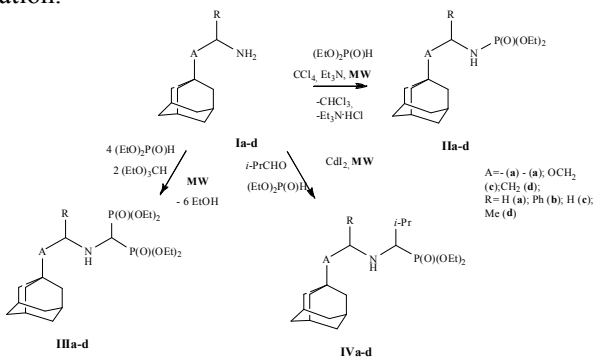
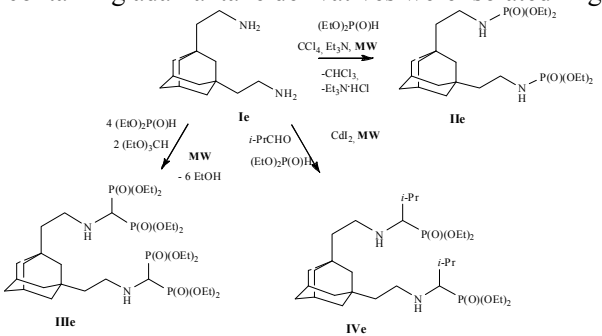
Microwave irradiation is widely used in synthetic organic chemistry to decrease the reaction times and to increase the selectivity and the product yields. We applied this convenient approach to the synthesis of biologically phosphoramidates (**IIa-d**), α-aminophosphonates (**IVa-d**) и aminomethylenebisphosphonates (**IIIa-d**), containing adamantyl fragment under microwave irradiation.



Reactions were carried out under microwave irradiation. The target phosphorus containing adamantane derivatives were isolated in good yields.



All adamantane containing compounds were adequately characterized by means of ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and elemental analysis. Some of the phosphorus containing admantane derivatives were explored as a medicine for osteoporosis treatment

SCHIFF BASES IN ADDITION AND CYCLOADDITION REACTIONS

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Organic compounds with carbon-nitrogen double bond frequently occurring in scientific and patent literature under the titles “Schiff bases“, “Azomethines”, “Aldimines”, “Ketimines”, “Imines” and “Aniles” are successfully used as basic models in crucial theoretic problem investigations and come-atable reagents in innovative activity of practically significant compounds.

Chemistry of this compounds is one of the most intensively developed fundamental branches of modern fine organic synthesis.[1-8]

Schiff Base’s addition and cycloaddition reactions will be reviewed.

Considerable attention will be given to the convenient routes into cyclic and heterocyclic systems and Schiff Base’s reactions referring to substituents at carbon and nitrogen atoms of double bond.

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HYDRODYNAMIC METHOD INTENSIFICATION OF SYNTHESIS AND ADJUSTING OF MOLECULAR CHARACTERISTICS OF STEREOREGULAR POLYDIENE

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Along with traditional factors that influence the activity of microheterogeneous catalytic systems for dienes polymerization and their molecular characteristics (modifier addition, temperature and time catalyst exposure) there is a possibility of controlling the polymerization process by changing size of the catalyst particle under hydrodynamic impact[1]. The present paper is devoted to detailed study of the influence of hydrodynamic effects on particle sizes of titanium catalyst.

Fractionation catalyst $TiCl_4$-$Al(i\text{-}C_4H_9)_3$ shows that it's represented by particles whose size varies widely. There are three particles groups: nano (30 – 100 nm), submicron (100 nm – 3 μm) and micro particles (3 – 45 μm). Single hydrodynamic impact in turbulent reactor result in complete disappearance of the particle sizes of 3-45 μm, due to the fragmentation of large catalyst particles under the influence of the kinetic energy of turbulent flow. As a result, increases the fraction of particles in the submicron range.

Occurring under hydrodynamic impact redistribution of catalyst particles in size result in increase activity in the dienes polymerization and make for additional opportunities for more adaptable control over their molecular characteristics.

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CHEMICAL PROPERTIES OF GRAFTED LAYER OF HYDROXYAPATITE MODIFIED WITH PHOSPHONIC ESTER

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Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is one of the most important biological materials – it is a main mineral of human and animals bones. At the same time, any bone is a composite, therefore, there are interfaces mineral-protein in any bone. Thus, if we can change properties of the surface of either mineral or protein component of the composite, we can influence the properties of the bone.

As was shown in [1], a treatment of HAP with *n*-butylphosphonic acid diethyl ester can result in HAP with grafted butyl groups, attached on the surface by pyrophosphate group:

$$(HAP)P(O)OH + n\text{-}BuP(O)(OEt)_2 = (HAP)P(O)OP(O)Bu$$

Pyrophosphate group is rather reactive and able to interact with a variety of nucleophils. In our case, nucleophils can interact either with phosphorus atom of HAP, or with phosphorus atom of grafted phosphonic group. The first reaction will result in HAP with grafted nucleophil, the second – in formation of phosphonic acid derivative and restoration of initial HAP surface.

We studied the interaction of phosphonic-modified HAP with a number of nucleophils. The samples obtained were studied with combustion analysis and solid-state MAS-NMR ^{1}H and ^{31}P. It was shown that octyl alcohol reacts with phosphonic phosphorus atom, giving bare HAP. On the other hand, the interaction of *tert*-butylamine and piperidine with phosphonate-grafted HAP results in reaction with HAP-phosphorus atom and gives amines attached on the surface through the surface P-N bond.

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THE NEW ABILITY OF THE CHROMOGENIC SYSTEMS ON THE BASE OF HOST-GUEST COMPLEXES

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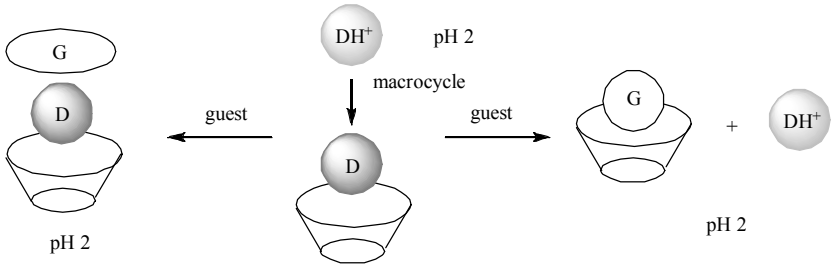
The idea of the new chromogenic systems is based on the stabilising in host-guest associates of the dye forms differs from ones presenting in the bulk solution.[1] The host molecules in such systems are presented by amphiphilic calix[4]resorcinarenes, existing in solution in the monomer form or as aggregates.

The variation of the degree of aggregation of the amphiphilic macrocycles as well as the buffer composition is able to be the instrument of influence on the receptor properties of calixarenes. The introduction of the third component which can compete for binding of host molecule changes the form of dyes, i.e. the color or other spectral characteristics. This is the way that chromogenic systems are able to visualize the phenomenon of molecular recognition as indicator system as well as in the processes of solubilization and sorption.



The aggregation characteristics of the macrocycles bearing ammonium groups on the upper rim of cavity and different hydrophobic groups on the lower rim were determined by NMR DOSY. The photolytic properties of the dyes (methyl yellow, methyl orange) in the presence of macrocycle were studied by UV-VIS spectroscopy.

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EPR SPECTROSCOPY AND ELECTRONIC STRUCTURE OF THE OPEN-SHELL FULLERENE DERIVATIVES

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Advances of high-resolution EPR spectroscopy for elucidation of electronic structures and reactivity of the open-shell fullerene derivatives are considered. The attention is focused on the comparison of experimental spectroscopic charascteristics of the open-shell species with characteristics calculated using modern quantum chemical methods and on the application of the data for determining molecular and electronic structures of such type molecules. In this study, free radicals $^{\bullet}C_{60}F$ and $^{\bullet}C_{70}F$ and the paramagnetic endometallofullerene molecules were isolated in sold argon matrices at cryogenic temperatures. High resolution anisotropic EPR spectra of the isolated molecules at temperature 5 K have been obtained for the first time. [1, 2].

Hyperfine coupling constants characterizing Fermi contact interaction and electron-nuclear-magnetic-dipole interaction have been derived from the experimental ESR spectra. We used these parameters for testing the validity of the various computational methods to predict an electronic structure of such type species. Based on the comparison of the measured hyperfine constants with those estimated by the quantum chemical calculation, the electron spin distribution and reactivity of the radical $^{\bullet}C_{60}F$, various regioisomers of $^{\bullet}C_{70}F$, and endometallofullerenes $M@C_{82}$ (M = Sc, Y, La) are characterized. The metal–fullerene cage interactions in the endometallofullerenes $M@C_{82}$ are discussed based on the spectroscopic EPR data and theoretical calculations.

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This work was supported by Russian Foundation for Basic Research (Grant №. 10-03-00065 and Russian Academy of Sciences (Program OKh-01).

SYNTHESIS AND CHEMICAL PROPERTIES OF 1,3-DIKETONES WITH ADAMANTANE MOIETY

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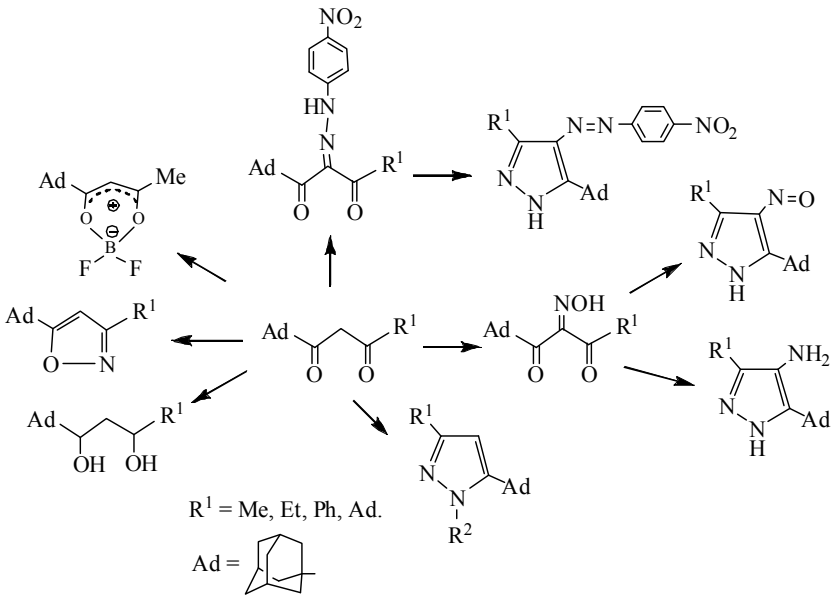
Derivatives of adamantane already found their practical use as an antiviral drugs in medicine. The research of interconnection between the structure of derivatives of adamantane with their antiviral activity has a big practical importance. 1,2-Diazols are using as a pirazolones dyes, materials for optoelectronics, pesticides, drugs. These compounds are of great interest because of a big variety of their chemical transformations. Many drugs such as amidopyrine, analgin, celebrex, antipyrine are heterocyclic derivatives of 1,3- dicarbonyl compounds[1].

On the basis of 1,3-diketones with adamantine moiety we have synthesized a big amount of compounds, having the potential biological activity[2-3].



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WAVE ISOTOPE SYSTEMATICS

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We define the binding energy of any isotope dependence $E(A,Z)=[Zm_p+(A-Z)m_n+ Zm_e-M(A,Z)]c^2$, where the Z-number of protons, A-mass number, $(A-Z)$-the number of neutrons, m_p, - the mass of the proton, m_n - the mass of the neutron, m_e - the mass of the electron, $M(A,Z)$- the mass of the isotope, c-light speed in vacuum. Using data on isotopes, for example, as annexed to[1], you can display them graphically in a coordinate system «*XOY*» (figure 1). At the same time was for each isotope: $X=E(A,Z)/c^2Y$, $Y=(A-Z)/Z$. This choice of coordinate system follows from the comparative analysis of several articles[2-4]. Every single isotope in figure 1 represents a point of intersection of two lines: «i» and «j», belonging to two groups of curves. The first group of lines can be represented by a pencil of lines with center at point A (figure 2). Analysis of the curves of the second group (figure 2) allows us to assume that their nature can be modeled by the equation of Lame for normal waves in an elastic layer of finite thickness. Each curve of the second group can be associated with the parameter $f=A-2Z$. For the curves of the second group (figure 1) $f= -2, -1,0,1,2, ..., 56,57$. Curve $f=0$ coincides with the axis O_1X_1 and approximated hyperbole. Other curves seem to waves with dispersion.

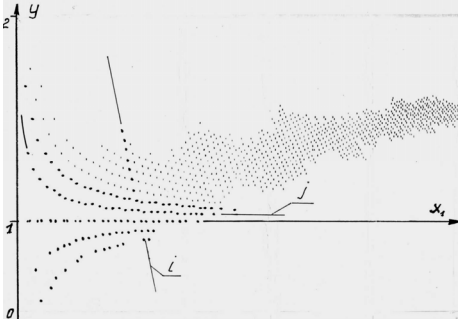

Figure 1

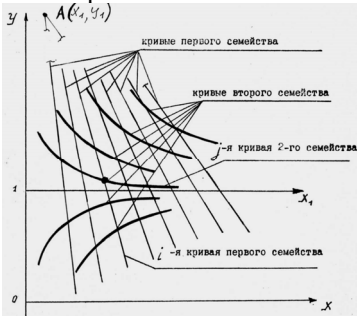

Figure 2

As wrote the D.I. Mendeleev[5], periodic law expressed continuously so what they do in number theory. The above confirms this.

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1,3-DEHYDROADAMANTANE AS STARTING REAGENT FOR SYNTHESIS OF DIFFERENT ADAMANTANE DERIVATIVES

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As a result of systematic investigations carried out was developed a new perspective scientific direction, based on investigation of chemical reactions of 1,3-dehydroadamantane (DHA) and it's homologs, which are related to strained bridged [3.3.1]propellanes – very slightly investigated type of compounds, and discovering of new methods for synthesizing of number of adamantane derivatives.

It is shown that DHA and it's homologs are able to undergo reaction with a wide number of strong and weak CH-acides: α-, β- and γ-dicarbonyl compounds, aldehydes, ketones, esters, nitriles and carboxylic acid's N,N-dialkylamides with cleavage of C-H bond at α-carbon atom of these substrates. An ability of DHA to alkylate alkylaromatic compounds at C-H bond of their alkyl side chain is discovered.

Found, that DHA and it's homologs may react with different halogenated substructs with cleavage of carbon-hydrogen or carbon-halogen (F, Cl, Br, I) bonds. Using of Br- and I-containing compounds leads to cleavage of their C-Br (C-I) bonds and foundation of 1,3-disubstituted adamantane derivatives.

It is shown that DHA and it's homologs are able to undergo reaction with ammonia, amines and NH-containing heterocycles, and also with amides and imides of carboxylic acides, that was unusual for another types of propellanes.

The reactions of DHA with H_2S and several thioles, catalytic and non-catalytic reactions with aromatic compounds and phenols are also investigated.

For the first time were carried out the reactions of DHA with diaryldiselenides and di- and trisulphides, proceeding with cleavage of element-element bond and foundation of 1,3-disubstituted adamantane derivatives.

In the report possible mechanisms of the reactions utilizing DHA, and intermediates (cation, radical, cation-radical), generated from it in presence of different substrates are discussed.

ALKYLATION OF AMINES BY ALCOHOLS USING NICKEL AND COBALT NANOPARTICLES AS CATALYSIS

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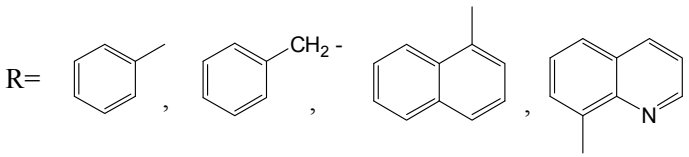
Discovered an ability of direct aromatic and aliphatic amines alkylation by alcohols using nickel or cobalt nanoparticles as catalysts. It was found, that by this reaction secondary and sometimes tertiary amines may be obtained.



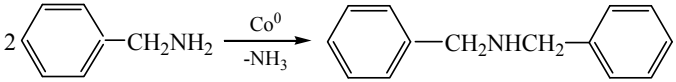
R^1= C_6H_{13} , C_8H_{17} , $C_6H_5CH_2$

Reaction proceeds at 150ºC and higher temperatures, and discovered method is applicable at laboratory conditions for high-boiling amines and alcohols.

Structures of obtained secondary amines are proved by NMR and CMS.

The possible mechanism of alkylation is so-called “hydrogen borrowing”, postulated for analogical reactions, using iridium or palladium complexes as catalysts.

It is shown, that using of nickel and especially cobalt nanoparticles besides primary aliphatic amine alkylation leads to side reaction of their disproportionation. This is proved by disproportionation of benzylamine in absence of alcohol.



The method for synthesizing of secondary amines is high-promising because high surface area of nanoparticles makes possible using smaller amounts of them, and nanoparticles themselves can be easily prepared from simple metal salts, and may be synthesized *in-situ*.

THE REDUCTION OF NITROARENES BY HYDRAZINE HYDRATE CATALYZED BY METAL NANOPARTICLES

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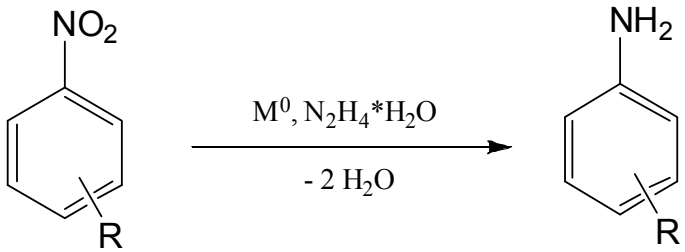
Discovered a method for reduction of nitrobenzene and it's derivatives by means of hydrazine hydrate in presence of different metal nanoparticles. Synthesis of nanoparticles and reduction of nitroarenes can proceed in one reactor and the same conditions. Metal chlorides and nitrates were used as starting materials for obtaining of catalysts.

The reaction proceeded by gradually addition of nitroarene to suspension of metal nanoparticles in 2-propanol and hydrazine hydrate at 20-80 ºC, and the alkylation of aniline with 2-propanol was not occured. The yield of aniline is close to quantitative, content of aniline in purified product is 100% (GLC).



$M^0 = Fe^0, Co^0, Ni^0, Cu^0$

R= H, o-CH_3, o-NH_2, p-NH_2

The reduction proceeds the same way, but less exothermically. The yields of products of 2-nitrotoluene, 2- and 4-nitroaniline reduction were 78 - 83%.

Catalysis by ferromagnetic colloidal solution of iron nanoparticles in the reduction of nitrobenzene was investigated. The yield of aniline was 94%.

In difference with iron and nickel, catalysis by cobalt nanoparticles lead to obtaining except aniline N-phenynhydroxylamine as by-product. Reduction of nitrobenzene was conducted also in presence of copper nanoparticles with yield of aniline 92%.

It was shown, that metal nanoparticles doesn't need stabilization during reaction and can be used several times without loss of catalytic activity.

STUDYING OF STRUCTURAL CHANGES OF MICELLES OF CETYLTRIMETHYLAMMONIUM BROMIDE

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movchan@phyche.ac.ru

Studying of structural changes of micelles of cetyltrimethylammonium bromide (CTAB), in particular, transferring of the spherical form in cylindrical, represents scientific and practical interest. Scientific interest is caused by the lack of both theoretical, and experimental data about the sizes and the form of micelles in wide area of concentration and temperatures, and practical - wide application in various technological processes CTAB. Definition of structural changes of micelles in solutions of ionic Surfactants is based on fixation of points of a break in concentration dependences of some parameters (viscosivity, electroconductivity, activity, etc.).

The aggregation properties in micellar solutions of bromide Cetyltrimetylammonium in wide areas of concentration c=($1\cdot10^{-5}$ – 0.4) M and temperatures (T) - ($27\text{-}60^0$)C have been studied by capillary viscosimetry, electroconductivity and Dynamic Light Scattering (DLS) methods.

The concentration area indicating the process of micellar transition was experimentally discovered for water CTAB solutions. Results of researches have found out infringement of linearity on curves $\eta_{rel} = f(c)$ at concentration 0.2-0.32 M. The sharpest increase in viscosity and critical increment of energy began at with = 0.32M (for T=27^0C) and with 0.4M (for T=60^0C). On dependences of equivalent conductivity of CTAB in the field of the structural changes maxima are found out. The micellar parameters of CTAB solutions of different concentrations including hydrodynamic radius, aggregation numbers micelles and degrees of counterion binding micelles have also been found.

CARBAMOYLATED HEXAFLUOROISOPROPANOLES AS NEW SELECTIVE INHIBITORS OF CARBOXYLESTERASE

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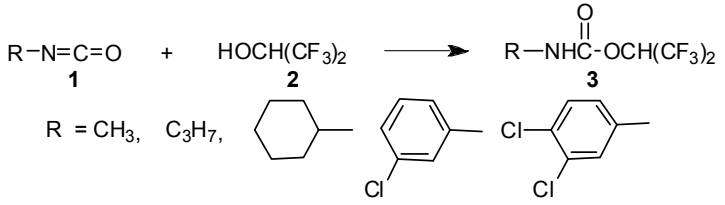
Previously, we synthesized a series of *O*-phosphorylated 1-hydrohexafluoroisopropanoles. Their antiesterase activity was studied in detail, demonstrating availability of using hexafluoroisopropoxy fragment as a leaving group. A high selectivity for carboxylesterase was shown.[1-2]

The purpose of this work was to synthesize the previously unknown *O*-carbamoylated hexafluoroisopropanoles and to study their inhibitor activity against three serine esterases: human erythrocyte acetylcholinesterase (AChE, EC 3.1.1.7), horse serum butyrylcholinesterase (BChE, EC 3.1.1.8) and porcine liver carboxylesterase (CaE, EC 3.1.1.1). Carbamates **3** were obtained with quantitative yield by interaction of isocyanate **1** with 1-hydrohexafluoroisopropanole **2** at 20°C in benzene.



Kinetic studies showed that carbamates **3** did not inhibit AChE, weakly inhibited BChE and exhibited selective inhibitor activity against CaE, the structure of R determined their efficiency and selectivity. Thus, we propose a new type of innovative inhibitors of CaE which can be used as modulators of drugs and insecticides.

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This work was supported by the Program of Russian Academy of Sciences "Biomolecular and Medicinal Chemistry" and grant RFBR 11-03-00581-a.

NEW SYNTHESIS OF THIOPHENE-, FURAN- AND PYRROLE CARBOXYLATES

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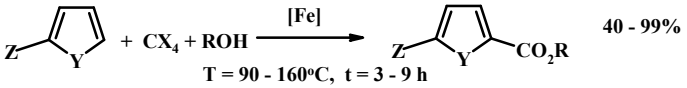
Thiophene-, furan- and pyrrolecarboxylic acids are widely used in the synthesis of medicinal preparations, dyes and polymers.

The known methods to synthesize heterocyclic carboxylic acids are complicated, multistage, require expensive reagents, and have a low yield.

This report presents the convenient method developed for the insertion of the ester moiety in the 5-membered heterocycle molecule of thiophenes, furans and pyrroles via the reaction of said heterocycles with halogen methanes (CX_4, X = Cl, Br) and alcohols in the presence of Fe catalysts.

The reaction is general in nature. It involves different heterocycles such as thiophene, furan, and pyrrole, their alkyl, halogen, acetyl, and carboxy derivatives, as well as *N*-substituted pyrroles and benzo[*b*]furan.



Y = S, O, NH, N-R (R = CH_3, Ph, 4-Cl-Ph) **CX_4 = CCl_4, $CBrCl_3$, CBr_4**

Z = H, CH_3, $COCH_3$, COOH, CO_2CH_3 Cl, Br, I **R = Me, Et, *i*-Pr, *n*-Pr**

[Fe] = $FeCp_2$, $Fe(acac)_3$, $FeBr_2$, $Fe(OAc)_2$

As a result, esters of thiophene-, furan- and pyrrolecarboxylic, and dicarboxylic acids are formed in 40–99% yield depending upon the reaction parameters such as temperature, duration of the reaction, nature of heterocycle, alcohol, halogen methane, and catalyst.

The plausible mechanism of the reaction is proposed to proceed through the generation of trihalogenmethyl radicals from halogen methane under the action of a catalyst on the first stage. Akylation of heterocycle occurs on the next stage aided by CX_3 radical. And subsequent alcoholysis of trihalogenmethyl derivative leads to the formation of appropriate heterocyclic carboxylate.

This work was financially supported by Russian Foundation for Basic Research (grant 09-03-00472-a) and by grant of the President of Republic of Bashkortostan (2011).

NEW APPROACHES TO SELECTIVE SYNTHESIS OF *N*-ARYL-1,5,3-DITHIAZEPINANES, DIOXAZEPINANES AND DITHIAZOCINANES

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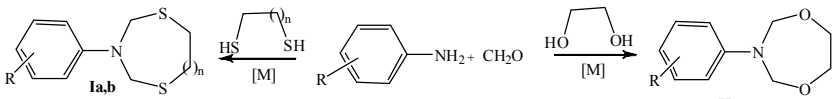
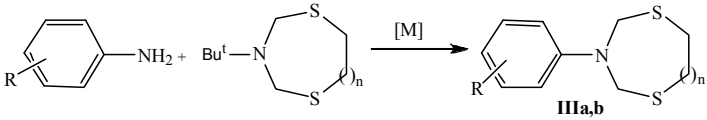
Sulfur- and nitrogen-containing heterocycles represent high interest in medicine and agriculture. The literature data on the methods for the synthesis of *N*-substituted 1,5,3-dithiazepinanes and dioxazepinanes are limited. In this report, the new approaches for the synthesis of *N*-aryl-1,5,3-dithia(ox)azepinanes and dithiazocinanes in the presence of the catalysts based upon transition and rare-earth metals are discussed.

Thus, the heterocyclization reaction of primary arylamines with formaldehyde and 1,2-ethanedithiol or ethylene glycol under optimized conditions ($Sm(NO_3)_3 \cdot 6H_2O$, 20 °C, 0.5 h) leads to the formation of corresponding *N*-aryl-1,5,3-dithiazepinanes **Ia** or dioxazepinanes **II** in 65–97% yield. Heterocyclization of arylamines with formaldehyde involving 1,3-propanedithiol in the presence of the $Co(acac)_3$ catalyst at 20 °C for 0.5 hours affords *N*-aryl-1,5,3-dithiazocinanes **Ib** in 60–95% yield.



n = 1 (**Ia**), 2(**Ib**); M=Sm,Co; R=H, *o-*,*i-*,*i*- CH_3, OCH_3, NO_2

The synthesis of *N*-aryl-1,5,3-dithiazepinane **IIIa** and N-aryl-1,5,3-dithiazocinanes **IIIb** via the transamination reaction of *N*-*tert*-butyl-1,5,3-dithiazepinane and *N*-*tert*-butyl-1,5,3-dithiazocinane with *N*-arylamines at 20 °C for 3 hours in the presence of the $Sm(NO_3)_3 \cdot 6H_2O$ catalyst was also successfully implemented in 66–92% yield. Non-catalytic reaction affords heterocycles **I–III** in low yields (less than 10%).



R = H, *o-*,*i-*,*i*- CH_3, OCH_3, NO_2, M = Sm; n = 1 (**IIIa**), 2(**IIIb**)

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SYNTHESIS OF NOVEL PYRIMIDINE NUCLEOSIDES

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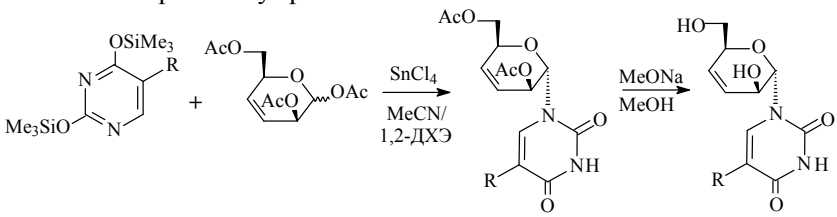
Synthetic analogues of nucleosides have found wide application in medicine. It is known, that some 3′-deoxynucleosides shows high antiviral activity [1]. For the purpose of searching of nucleosides with potential antiviral activity we have studied glycosylation of pyrimidine bases by levoglucosenone derivative, containing no 3′-OH group.

Synthesis of nucleosides were carried out by Vorbruggen modification of Hilbert-Johnson method [2]. Sylilated uracils **1a-c** interacts with 1,2,6-tri-O-acetylhex-2-enopyranose (**2**) – in 1,2-dichloroethane or acetonitrile in the presence of $SnCl_4$ with formation of N-1-α-nucleosides **3a-c,** which gives target compounds **4a-c** after deacylation by MeONa. Structure of **3a-c** and **4a-c** was proved by spectral methods.



1a-c **2** **3a-c** (60-94%) **4a-c** (58-76%)

R = H (**a**); F (**b**); Me (**c**)

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FLUORINATED ALKENES IN THE SYNTHESIS OF CARBO- AND HETEROCYCLIC COMPOUNDS

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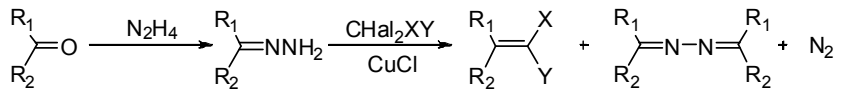
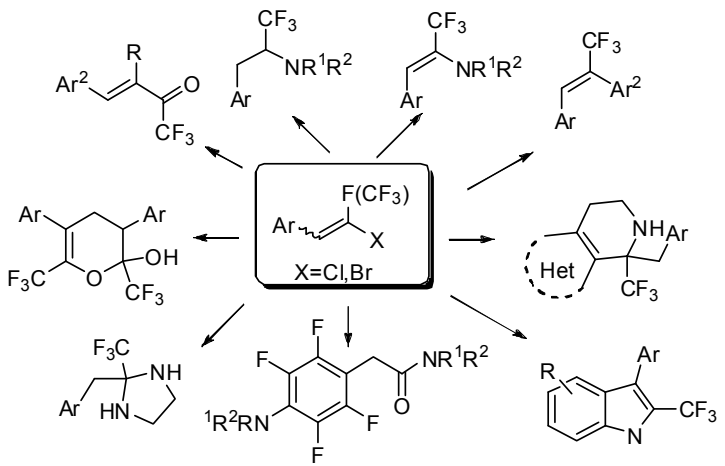
The introduction of fluorine or fluorine substituents into organic compounds results in dramatic change of their properties, leading often to appearance of biological activity. Thus, a lot of trifluoromethylated heterocycles were applied as drugs. At the same time, known methods of direct introduction of fluorine do not posses enough selectivity and effectiveness. Hence, there is a great demand for the elaboration of new synthetic methods in organofluorine chemistry.

Recently a novel catalytic olefination reaction was found by our group. *N*-Unsubstituted hydrazones of aldehydes and ketones give alkenes $R^1R^2C{=}CXY$ under treatment with $CHal_2XY$ in the presence of catalytic amount of copper salts, giving a variety of alkenes, including fluorinated ones.



It was also found, that nucleophilic vinylic substitution in β-halogen-β-trifluoromethylstyrenes $ArC(H){=}C(Hal)CF_3$ proceeds easily, allowing to synthesize fluorinated alkenes with different functional groups. These fluorinated building blocks were successfully used in the synthesis of fluorinated compounds, which are very interesting for medicinal chemistry.



PROBLEMS OF DIVISION OF ISOTOPES OF LUNGS AND AVERAGE ELEMENTS A METHOD OF A CHEMICAL ISOTOPE INTERCHANGE

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Coefficient of separation of isotopes (α) lungs and average elements inevitably should differ from unit and consequently the question of possibility of division almost coincides with a problem of search of optimum systems for division of isotopes of these elements.[1]

Applicability of this or that system for division of isotopes is defined first of all by its two characteristics: in size of coefficient of separation of isotopes (α) and speed of course of reaction of an isotope interchange. Size of coefficient of separation which is taking place at reaction of an isotope interchange between two any connections of the given element, are defined as the relation so-called β- factors of these connections: $\alpha = \beta_1 / \beta_2$

β - factors are characterize in the exhaustive image thermodynamic possibilities of connections concerning division of isotopes. [2-3]

Selection of chemical systems for division of isotopes is carried out empirically or semiempirical as there are possibilities quantum – statistical calculations of coefficient of separation. The fundamental role of power characteristics of molecules for chemical processes of division of isotopes is defined, but the practical appendix of corresponding kinetic positions is limited by a number of circumstances.

We consider methods which can be successfully used in calculations β – factors and coefficient of separation of isotopes in systems with ionic crystals. They represent geochemical interest and their knowledge β – factors opens new possibilities for geochemical researches.

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NEW TETRAPYRAZOLYLPORPHYRINS WITH AMPHIPHYL PROPERTIES

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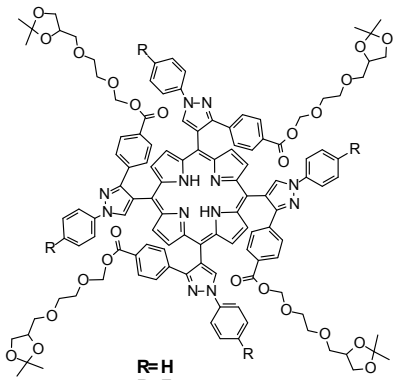
The porphyrins that contain heterocyclic groups in meso-positions can widely be applied in various areas, such as photodynamic therapy and diagnostics, catalysis, transformation and solar energy transfer, modeling of various biological processes and creation of supramolecular structures.

Investigated in the real work tetrapyrazolylporphyrins possess a number of advantages in comparison with widely studied TPP. In addition to the raised solubility in the majority of organic solvents, an electronic spectrum of absorption of mezo-pirazolylporphyrins with shift in the red area, the fluorescence quantum yield essentially increases with heterocyclic group introduction. We synthesized a number of the substituted porphyrins. Mezo-tetrapyrazolylporphyrins may be modified easily. It is possible to change physical, chemical and structural characteristics of received por-



phyrins by addition of various donor and acceptor substituents in pyrazolyl ring, getting substances with valuable properties. For increase in solubility of received porphyrins hydrophyl groups were introduced in the form of long chains of modified glycerine. The porphyrins thus modified have the raised solubility in water and organic solvents.

COMPLEX OXIDES OF SUBMICRON DISPERSITY WITH SPECIAL ELECTROPHYSICAL PROPERTIES

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Purposeful search of new materials based on complex oxides with a structure of perovskite (ABO_3, where A is Y or Ln; B is transition metal) and its analogues, which have special electrophysical properties (dielectric, highly or superconductive), is realized by means of varying of their cation composition. The actual problem is not only improvement of properties of known oxide materials, but also development of progressive efficient technologies for obtaining of these materials in the form of highly-dispersed powders. The technologies involve synthesis form solutions, like sol-gel method (citrate method) or coprecipitation.

The work is dealt to synthesis and investigation of complex oxide compounds based on cobalt, nickel and copper: $La_{1-3x}Li_xM_{2x}CoO_{3\pm\delta}$ (M = Ca, Sr, Ba), $YBa_2Ni_{3-x}Zn_xO_{7\pm\delta}$ ($2{,}0 \le x \le 2{,}5$), Bi(Ln)2212, Bi(Ln)2223, Ln123 and Ln124; their phase analysis has been performed, the elementary cell parameters have been determined; morphology and electrophysical properties have been researched.

The particle size of cobaltites ($La_{1-3x}Li_xM_{2x}CoO_{3\pm\delta}$, where M = Ca, Sr, Ba), which had been obtained with a coprecipitation method using Na_2CO_3 and $H_2C_2O_4$, were within the interval of 100 – 900 nm and depended on radius of rare-earth metal ion. The transition of metal→dielectric is realized within the homogeneity field ($x \le 0{,}1$), when the temperature decreases. Nickelates of $YBa_2Ni_{3-x}Zn_xO_{7\pm\delta}$ ($2{,}0 \le x \le 2{,}5$), which have been obtained using a citrate method, demonstrate dielectric properties. The polycrystallite grains show dielectric properties, the grain shape can be related to timber-like with a size up to 2 μm. The transition into superconductive state have been found for copper-containing systems of Bi(Ln)2212, Bi(Ln)2223, Ln123 and Ln124 at substitution degree of $x \le 0{,}1$. The cuprates are compact nonporous ceramics with average particle size of less than 1 μm.

Thus a decrease of ceramic grain was found in the order of synthesis methods, which looks as follows: ceramic – citrate – coprecipitation. Electrophysical properties are determined by a size of transition ion.

The work was performed within the framework of the program № 11BF037-01 supported by Taras Shevchenko Kiev National University.

QUANTUM CHEMICAL MODELING OF CATALYTIC OXIDATION OF METHANE TO METHANOL IN THE PRESENCE OF GOLD QUERCETIN COMPLEXES

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Recently it was found that gold quercetin complexes can catalyze the oxidation of methane to methanol by oxygen air at room temperature and atmospheric pressure. However the structure of an active site and the mechanism of reaction have not been ascertained experimentally. The goal of this work is to determine of the structure of gold quercetin complexes and to study mechanism of methane hydroxylation in mild condition using density functional theory. All calculations have been performed by means of PRIRODA program using the nonempirical PBE functional and the extended basis set for SBK pseudopotential.

To reveal the nature of catalytic active cite in water solution the structure and the energy of various mono- and binuclear Au complexes with quercetin were studied. The most probable oxidation state of Au in the systems is Au^{+1}. Bidentant coordination site for gold(I) is formed by carbonyl group of A ring and hydroxo group of C ring of quercetin. Mononuclear gold(I) complex contain additional ligand which is a molecule of water. Aurophilic interaction and formation of strong internal hydrogen bonds lead to association of mononuclear gold(I) complexes with energy release, and binuclear complexes with short Au-Au distance were formed. It was found the most stable binuclear Au complex can activate C-H bond methane with formation of methyl derivatives. The process of heterolytic C-H bond cleavage with proton transfer on the oxygen atom of quercetin ligand via water molecule is the most probable. This reaction has moderate activation energy, which provides its possibility in mild condition. Further process of O_2 molecule coordination with subsequent reactions of its protonation leading to alkyl-hydroperoxo complex and hydrolysis with formation the products, alcohol and H_2O_2.

The authors express their gratitude to the Ministry Education and Science of RF for financial support of this work under State Contract 0646. Quantum chemical calculations have been done using the facilities of Joint Supercomputer Center of the Russian Academy of Sciences.

INVESTIGATION OF COMPLEX FORMATION BETWEEN POSITIVE CHARGED NANO SIZED ALUMOXAN PARTICLES WITH NEGATIVE CHARGED POLYMERS IN AQUEOUS SOLUTION

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The formation of complex between positiv charged alumoxan particles with high (sodium salt of poly(4-vinilbenzolsulpho acid) and weak (poly(acrylic acid), polyelektrolytes in aqueous solutions, and copolymers of acrylamide and acrylic acid have investigated.

Size, molecular weight distribution and geometric parameters of the alyumoxan particles have determined by small-angle X-ray scattering[1].

The composition of formed polymer-colloid complexes are determined by UF-spectroscopy, viscometry, sedimentatin analysis and complexonometric methods. Optimum conditions of preparing water-soluble polymer-colloid complexes are determined.

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THERMODYNAMICAL PROPERTIES OF IONS IN N-METHYLPYRROLIDONE – WATER MIXED SOLVENTS

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Standard partial molar heat capacities (at constant pressure) of dissolved electrolytes $\bar{C}^0_{P2}$, are sensitive probes for certain types of solution phenomena, providing similar information to that obtained from the far more widely studied partial molar volumes, $\bar{V}^0_2$. Apart from their intrinsic interest as a fundamental thermodynamic parameter, heat capacities are .also important for understanding the nature of thermal processes in solution and for modelling industrial processes which involve significant temperature changes. However, unlike $\bar{V}^0_2$, heat capacities of electrolytes have received relatively little theoretical attention to date and their relationships to solvent and ion properties are not well understood.

Heat capacity C_p and density ρ of alkali metal halides solution in N-methylpyrrolidone (MP)–water mixed solvents at 298,15 K were experimentally investigated. For measurement the precision calorimetric and densimetric installation were used. The standard partial molal heat capacities $\bar{C}^0_{P2}$ and volumes $\bar{V}^0_2$ of electrolyte in MP–water mixed solvents at 298,15 K were determined by the extrapolation of concentrated dependences of apparent molal values to the state of infinity dilution. For their separation on ion constituents $\bar{C}^0_{Pi}$ and $\bar{V}^0_i$ the linear dependences (1,2) were used:

$$\bar{C}^0_{P2(i)}(\text{МП-H}_2\text{O}) = a_C \bar{C}^0_{P2(i)}(\text{H}_2\text{O}), \quad (1)$$

$$\bar{V}^0_{2(i)}(\text{МП-H}_2\text{O}) = a_V \bar{V}^0_{2(i)}(\text{H}_2\text{O}), \quad (2)$$

where $\bar{C}^0_{P2(i)}$ and $\bar{V}^0_{2(i)}$ values of standard partial molal heat capacities and volumes of electrolytes and ions in MP-water mixed solvents and in water, a_C, a_V - empirical constants (Table).

Table. **Values of the *a* coefficient in Equations. (1,2) (*r* is the correlation coefficient)**

Parameter	$X_{МП}$					
	0,10	0,10	0,10	0,10	0,10	0,10
a_c	0,852	0,182	-0,129	-0,510	-0,584	-0,602
r_c	0,999	0,999	0,986	0,995	0,995	0,999
a_v	1,066	1,100	1,011	0,923	0,856	0,784
r_v	0,992	0,996	0,999	0,966	0,970	0,999

On the base of analysis of different contribution to the values $\overline{C}^0_{Pi}$ and $\overline{V}^0_i$ the special features of solvation of the ions were discussed.

CATALYTIC TRANSFORMATIONS OF FLUOROCHLORO-CYCLOPROPANES BY ACTION OF COPPER (I) CHLORIDE. PREPARATION OF FUNCTIONAL FLUOROALKENES

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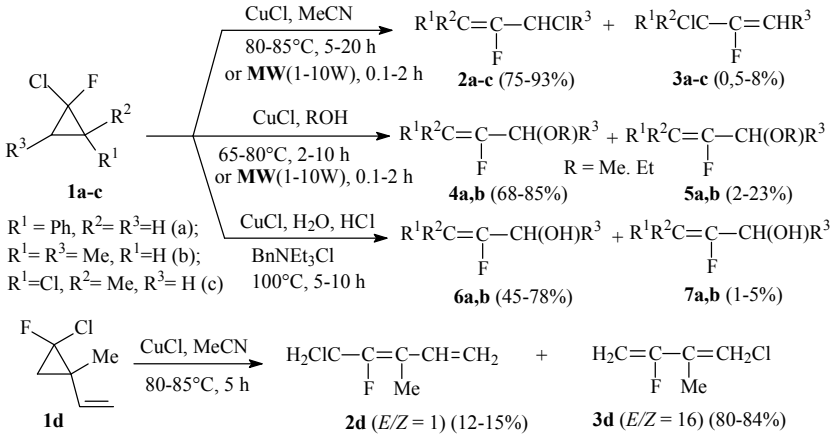
Ability of cuprous chloride to catalyze ring-opening transformations of *gem*-fluorochlorocyclopropanes **1a-d**, easily prepared by addition of fluorochlorocarbene, generated from $CHCl_2F$ under phase-transfer catalysis conditions, to corresponding alkenes was found. It was shown that fluorochlorocyclopropanes **1a-d** by heating in acetonitrile in the presence of CuCl undergo catalytic rearrangements with formation of fluorochloroalkenes **2a-d** and **3a-d** as a result of ring-opening accompanied by chlorine migration.



Heating of **1a,b** in methanol or ethanol gives corresponding alkoxyfluoroalkenes **4a,b** and **5a,b** *via* ring-opening followed by alkoxydechlorination. Similar transformations of **1a,b** in aqueous medium in the presence of HCl and $BnNEt_3Cl$ proceed with formation of fluorinated allylic alcohols **6a, b** and **7a, b**.

Microwave irradiation leads to significant acceleration of *gem*-fluorochlorocyclopropanes transformations.

REACTIONS OF DONOR-ACCEPTOR CYCLOPROPANES WITH 1- AND 2-PYRAZOLINES

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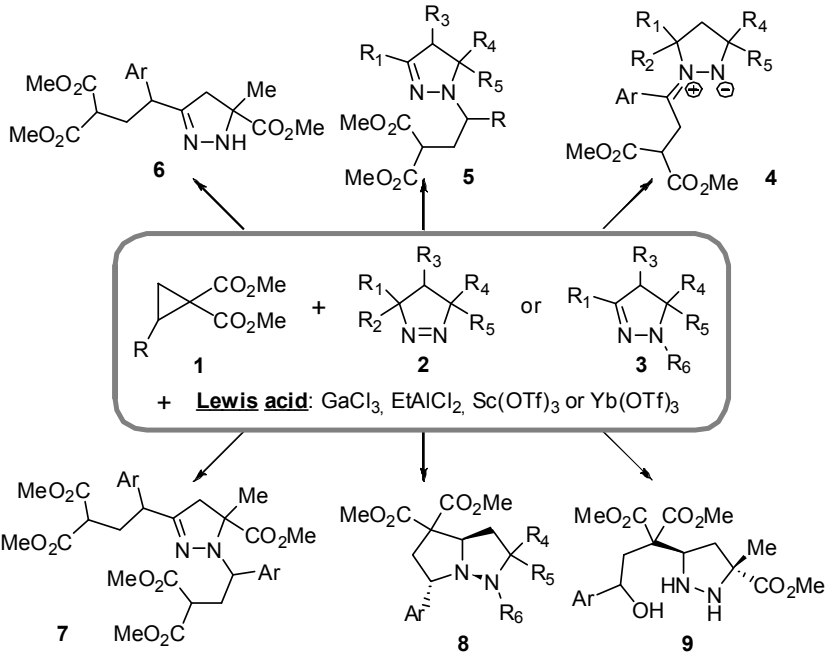
Reactions of donor-acceptor cyclopropanes **1** with 1- and 2-pyrazolines (**2** and **3**) are efficiently catalyzed by Lewis acids to give compounds **4–9** as the major products (yields 20–99%). We have found six primary ways of these processes, which can be controls by varying temperature, ratio of reagents, substituents in starting substances and Lewis acid.



Possible reactions mechanisms are suggested. We have shown, that the main role of Lewis acid concludes in activation σ-bond of cyclopropane ring; formed dipolar intermediate attacked the most nucleophilic or sterically accessibly atom of nitrogen or carbon in 1- and 2-pyrazolines with the following transformation in target product.

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CARBO[3+3]CYCLIZATIONS

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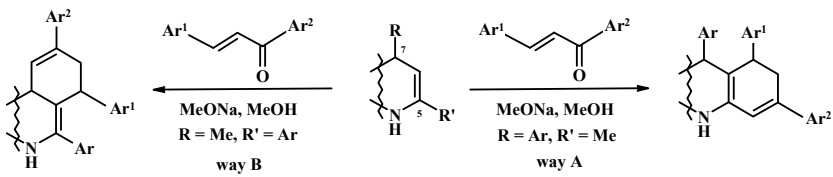
Novel methods of C–C-bonds formation are one of the fundamental problems of organic chemistry. A few data, known from literature, which deals with carbo[3+3]cyclizations (or -cyclocondensations), resulting in formation of annelated cyclohexane (-ene, -diene and aromatized) derivatives are observed. They involve such typical reactions, as Knoevenagel and Kostanecki reactions. There are some single examples, relative to similar cyclization of compounds combinations: α,β-unsaturated ketones, their precursors, enamines, 2-methylindole and related structures.

We found new group of reactions of unsaturated aromatic ketones and azolodihydropyrimidines, which play role of heterocyclic enamines. The presence of methyl group in position 5 (way A) or 7 (way B) result in quick cyclocondensation of Michael adduct, formed at first stage, to the new azoloquinazoline systems with different state of hydrogenation. The state of hydrogenation depends on electron properties of azoles, aromatic ketone rings and reaction conditions. Aromatization may be avoid by activation of process by ultrasonic irradiation.

Derivatives of Biginelli compounds – 4-aryl-6-methyl-3,4-dihydropyrimidin-2(1H)-ones – have similar behavior. Their interaction with chalcones in MeOH/MeONa system results in 3,4,5,6-tetrahydro-2(1H)-quinazoline derivatives formation. Interestingly, that these partially hydrogenated compounds are stable as in air, as well in solutions and in storage.



SYNTHESIS OF 4*H*-1,3,2-BENZOXATHIAPHOSPHININE 2-SULFIDES

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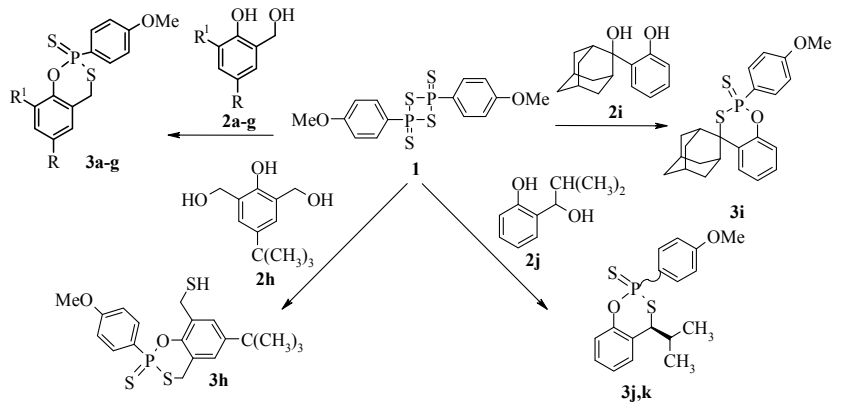
Lawesson's reagent along with P_2S_5 is widely used for the introduction of sulfur atom in various organic compounds: aldehydes, ketones, amides, alcohols, nitrogen-containing heterocycles, etc.[1] At the same time, the reaction of Lawesson's reagent with the polyfunctional substrates having two nucleophilic or one nucleophilic and one electrophilic centers may lead to heterocyclic rings incorporating part of Lawesson's reagent.[2]

We have shown that the interaction of salicylic alcohols **2a-j** with Lawesson's reagent in *o*-xylene at reflux formed 4*H*-1,3,2-benzoxathiaphosphinine 2-sulfides **3a-k**, which are of interest as possible herbicides.



a R = Br, R^1 = H; **b** R = Cl, R^1 = H; **c** R = R^1= $C(CH_3)_3$; **d** R = NO_2, R^1 = H; **e** R = CH_3, R^1 = 1-Ad; **f** R = 1-Ad, R^1 = Br; **g** R = R^1 = H

The main competing process reducing the yield of target 4*H*-1,3,2-benzoxathiaphosphinine 2-sulfides is the formation of 2-mercaptomethylphenols from the initial alcohols.

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The study was financially supported by the Federal Program «Scientific and pedagogical staff of innovative Russia in 2009-2013».

AUTODEHYDROGENATION REACTION OF HYDRAZINOSUBSTITUTED DERIVATIVES OF PHOSPHONIUM SALTS AND PHOSPHINE OXIDES

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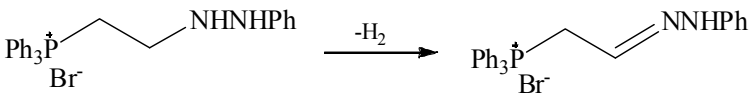
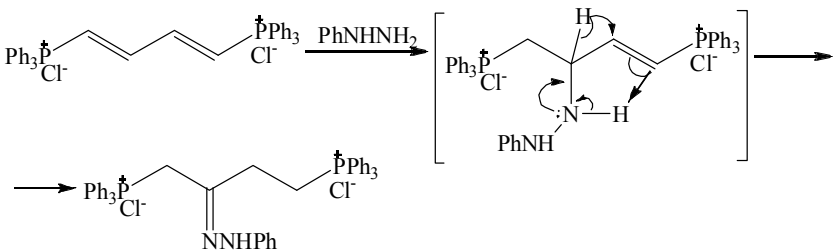
We have established that NH-CH- group containing β-hydrazinoethyl- and δ-hydrazinobut-2-enylphosphonium salts and phosphine oxides of similar structure in mild heating conditions in acetonitrile or alcohol, and sometimes already by room temperature, undergo an autodehydrogenation in formation of appropriate hydrazonoderivatives[1,2]. For example:



On the basis of our investigation results we have proposed a cyclic reaction mechanism with participation of hydride ion.

Recently we have found, that 1,4-bis(triphenylphosphonium)but-1,3-dienedichloride reacts with phenylhydrazine in formation of 2-phenylhydrazonobutane-1,4-diyl-bis(triphenylphosphonium)chloride. Reaction proceeds possibly on dehydrogenaton-rehydrogenation scheme[3].



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2,2-DINITROMALONONITRILE IN THE SYNTHESIS OF AZAHETEROCYCLIC COMPOUNDS

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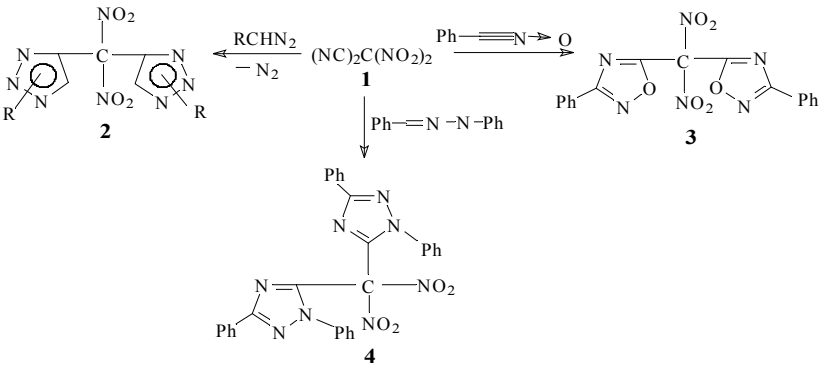
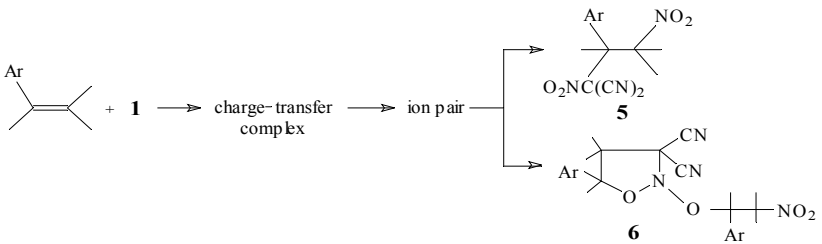
2,2-Dinitromalononitrile **1** is a promising compound for obtaining on its basis multifunctional substances that have practically important properties.

The presence in its molecule dipolarophilic nitrile groups allowed to carry out the reactions of 1,3-dipolar cycloaddition with a range of active nitrous 1,3-dipoles: diazoalkanes, benzonitrile N-oxides, diphenylnitrilimine that led to 1,2,3-triazole **2**, 1,2,4-oxadiazoles **3** and 1,2,4-triazole **4**.



The reaction of compound **1** with arylethenes is accompanied by denitration, in this case aryletenes act as nucleophilic reagents. As a result 1-nitro-1,1-dicyanoalkanes **5** (the products of C-alkylation) and 3,3-dicyanoisoxazolidines **6** (the products of O-alkylation) are formed.



In this work the regularities and schemes of reactions are discussed. The structure of the compounds is established by IR spectroscopy, ^{1}H and ^{13}C NMR, mass spectrometry, and the composition is confirmed by elemental analysis.

TRANSFORMATION OF HYDROXO COMPLEXES OF IRIDIUM (III) AND (IV) IN ALKALINE SOLUTIONS

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Complex of physical and chemical methods were studied processes flowed in strongly alkaline solutions of hydroxo comlexes of iridium (III) and (IV). Showed role of oxygen in reactions of formation of strongly colored complexes of iridium, which are binuclear dioxygen compounds of iridium – $[(OH)_5Ir^{IV}(\mu\text{-}O_2^-)Ir^{IV}(OH)_5]^{3-}$ и $[(OH)_4Ir^{IV}(\mu\text{-}O_2^{2-})(\mu\text{-}OH)Ir^{IV}(OH)_4]^{3-}$.

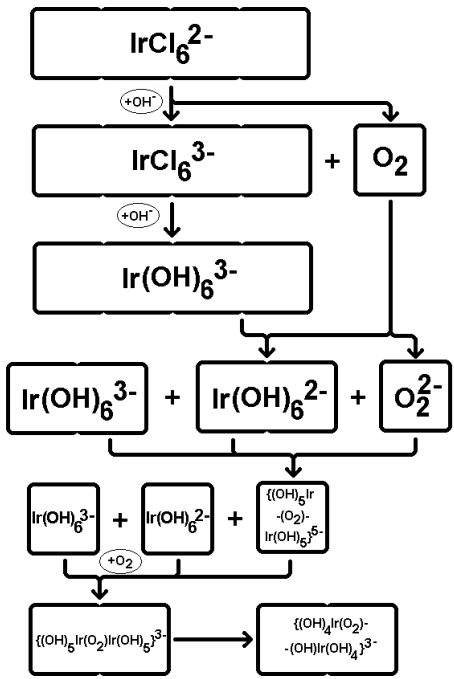

Fig. Scheme of transformations of iridium compounds in alkaline solutions (the area of each block is proportional to the number of participating in the reaction of substance)

This work was supported by the Russian Foundation for Basic Research (project №№ 09-03-01041, 10-03-01198)

ENERGY OF CHEMICAL BONDS: METHODOLOGY OF CALCULATION

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A general methodology of calculation of the bond energies is developed. It includes the following stages: 1) the choice of objects of investigation and allocation the basic compounds (e.g. methane, silicomethanes etc), generation and systematization of the structures (on the basis enumeration theory of graphs); 2) the analysis state of data on the enthalpies of formation ($\Delta_f H^o$) and enthalpies of atomization ($\Delta_a H^o$) molecules and free radicals, the mean bond energies (ε) and bond dissociation energies (D) for given compounds: their gathering, examination, puting in order to the series of similar molecules etc; 3) the selection of calculation methods; 4) the realization of numerical calculations; 5) the establishment of regularities of bond energies (ε, D_{298}); 6) the formation of banks of data.

On the basis of developed by us the phenomenological concept of binary and more complex interactions of atoms[1] (*atom-atomic approach*) the end-working formulas for estimation and prognosis of and the bond energies in the compounds of type $EH_{4-l}X_l$, $EH_{4-l-m}X_lY_m$, ... ; $EH_{3-l}X_l$, ... ; $EH_{2-l}X_l$, ... ; (E = C, Si, Ge, Sn, … ; X,Y, … = D, T, F, Cl, Br, I, CH_3, NO_2, ...) are received. The bond dissociation energy for series $ЭH_{4-l}X_l$, if we take into account the binary atom-atomic interactions, appeared to be quadratic function of the number substituents (l) [1-2]

$$-D^{l}_{Э-H} = d_0 + d_1 l + d_2 l^2 \quad (l = 0, 1, 2, 3),$$

$$-D^{l}_{Э-X} = đ_0 + đ_1 l + đ_2 l^2 \quad (l = 1, 2, 3, 4).$$

Here d_0, d_1, d_2, $đ_0$, $đ_1$, $đ_2$ are parameters expressed by bonded and non-bonded interactions.

The numerical estimations of the mean bond energies and bond dissociation energy are led. The calculation results are in accord with experiment. The predictions are done. The analysis of experimental (and design) data on the bond energies of various classes of organic (and other) compounds is given.[3] The systematization of the data is carried out. Some regularities are revealed.

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SYNTHESIS OF BUTENOLIDE PRECURSORS OF 4,8-INTERPHENYLENE 11-DEOXY-10-OXAPROSTANOIDS OF E SERIES

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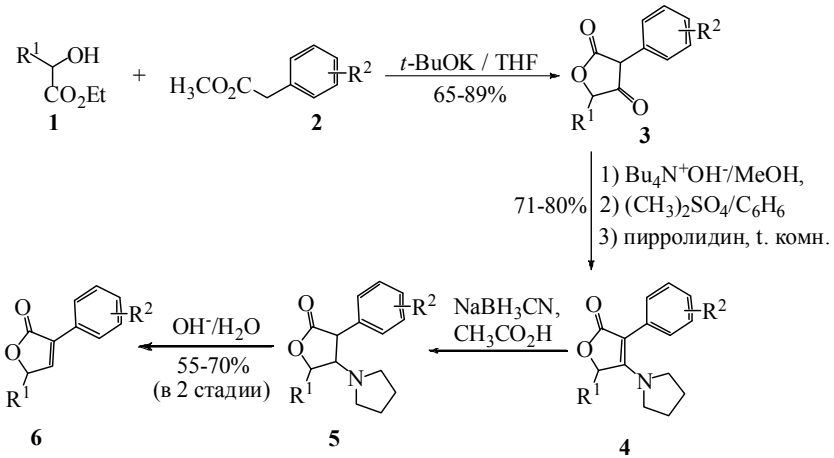
On the basis of 3-aryltetronic acids **(3)**, obtained from esters of α-hydroxy- **(1**, R^1=H,CH_3**)** and arylacetic acids **(2**, R^2=C_1-C_4-fragment of α-prostanoid chain**)** according to the method[1] synthesis of butenolide precursors of new 4,8-interphenylene 11-deoxy-10-oxaprostanoids of E series has been realized employing the scheme analogous to that described by us earlier[2].



3-Arylbutenolides **(6)** are obtained during alkaline work-up of 3-aryl-4-aminolactones **(5)**. The latter are formed by means of reduction of the conjugated double bond of the heterocycle in the enamino derivatives **(4)** of tetronic acids. It's worth noting that in contrast to the compounds **(5)** their 3-alkyl analogues are transformed into the corresponding butenolides only at reflux in toluene in presence of silica gel[2].

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SYNTHESIS OF 4,8-INTERPHENYLENE HETEROPROSTANOIDS OF B SERIES

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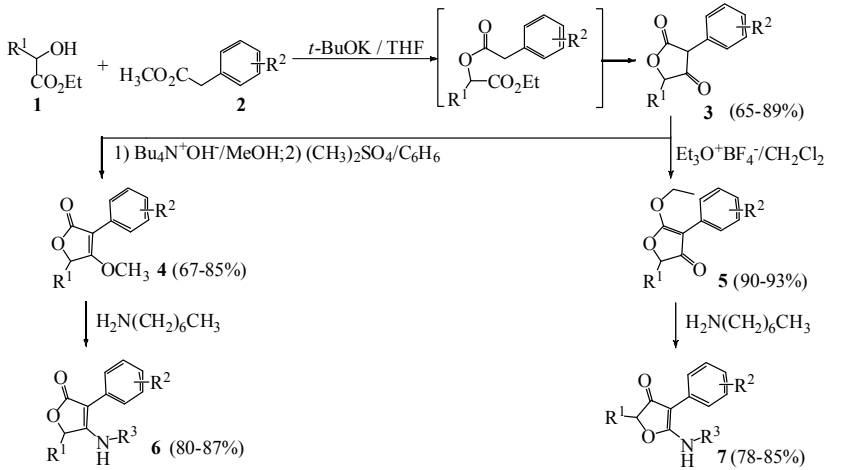
Among bioactive prostaglandin analogues the compounds containing prostanoid chains modified by aromatic moiety are of particular interest. Such prostanoids have found application for the treatment of stomach ulcer, pulmonary arterial hypertension and peripheral arterial deseases, open angle glaucoma. They are also used for fertility control and in veterinary practice.

Herein we describe the synthetic scheme for new 4,8-interphenylene 10-oxa-13-aza- **(6)** and 11-oxa-13-azaprostanoids **(7)** of B series on the basis of readily available α-hydroxyacid esters **(1**, R^1=H, CH_3**)** and arylacetic esters **(2)**, containing C_1-C_4-fragment of α-prostanoid chain as the R^2-substituent.



1 **2** **3** (65-89%) **4** (67-85%) **5** (90-93%) **6** (80-87%) **7** (78-85%)

The scheme includes 3-aryltetronic acids **(3)** preparation according to the method[1], selective O-alkylation of the compounds **(3)** and reaction of the regioisomeric enolethers **(4,5)** thus obtained with amines.

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THE MECHANISM OF THE INHIBITING ACTION OF HALOGENIDES ON THE ACID-CATALYSED STYRENE EPOXIDE TRANSFORMATION AND OXIDATION IN ALCOHOL SOLUTION

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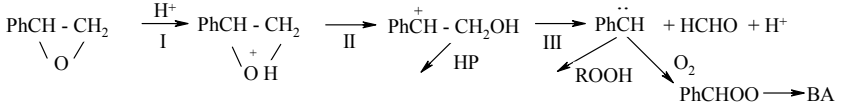
Acid-catalyzed transformation of styrene epoxide (SE) follows two main routes, of which the major route (~95%) is non radical consumption of SE mediated by an acidic agent. Concomitant to this route, there is the pathway accompanied by oxygen absorption (~5%) yielding benzaldehyde (BA) and hydrogen peroxide. In the absence of oxygen, this route manifests itself in the decomposition of hydroperoxides added to the binary system (BS) styrene epoxide + p-toluenesulfonic acid (SE+TSA). The kinetic relationships for the rates of overall consumption (heterolytic reaction), for the rates of oxygen uptake, the buildup of oxidation product and hydroperoxide degradation as a function of the [TSA] and [SE] are the same, $V_j = k_j [SE]^0 [TSA]^1$ in accordance with scheme



The inhibiting action of potassium iodide and bromide, of tert-alkylammoniums chlorides and of tert-butyl hypochlorite on the transformation of the bynary system SE+TSA was revealed. Halide salts added to the bynary system SE+TSA retard the overall SE consumption as good as O_2 uptake and BA buildup processes they retard. It was inferred that inhibition in this case is connected with the stage II retardation (see scheme). The retardation of the carbonium ion formation results in decreasing of oxidation and of ROOH destroying rates. Hypochlorite (HP) addition to SE+TSA system don't retard SE overall consumption but effective inhibits oxidation reaction. In triple system SE+TSA+HP kinetic relationship for the rate of HP consumption is identical to that for SE+TSA+ROOH, $V_{HP} = k_{HP} [SE]^0 [TSA]^1 [HP]^0$. Oxygen do'nt prevents consumption as regards ROOH in SE+TSA+ROOH system. It may be inferred that HP in triple system reacts rapidly with carbonium ion preventing stage III resulting in the inhibition of oxidation reaction, see scheme.

NEW METHODS OF SYNTHESIS 2-SUBSTITUTED BENZOTHIO- AND SELENOPHENES ON THE BASIS 4-ARYL-1,2,3-THIA- AND SELENADIAZOLES

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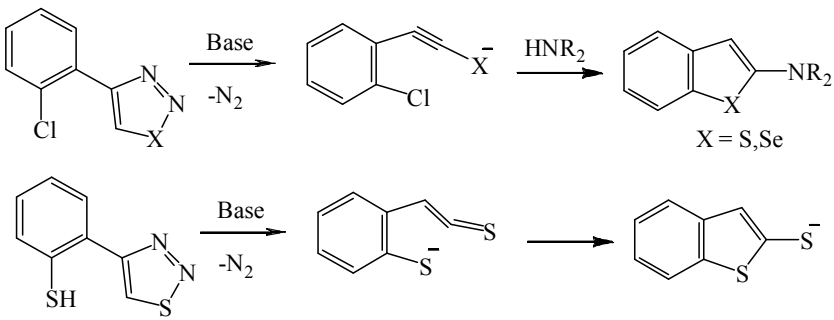
2-Aminobenzothiophene derivatives are important intermediates in the synthesis of the selective estrogen receptor modulators – raloxifene and its analogs. [1,2] We offer new methods of synthesis 2-substituted benzothio- and selenophenes on the basis of transformations easily accessible 4-aryl-1,2,3-thia- and selenadiazoles.

4-(2-Chloroaryl)-1,2,3-thia- and selenadiazoles decompose under the action of bases and the subsequent nucleophilic ipso-cyclization of intermediates in excess of amine converts into 2-dialkylaminobenzothio- and selenophenes. 4-(2-Arylthiol)-1,2,3-thiadiazoles decompose under the action of bases and the subsequent alkylation of intermediates converts them into 2-alkilsulfanilbenzothiophenes.



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Work with financial support of the RFBR, the project 08-03-00383.

CHEMICALLY MODIFIED HUMIC ACIDS AS AN EFFECTIVE SORBENTS FOR ACTINIDES

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Carboxyl, phenolic, methoxyl, quinoid and amino groups as well as O-, N- and S-consistant heterocycles of humic acids play significant role in actinide sorption processes.

We have developed different methods of chemical modification of humic acids, allowing us to control the nature and quantitive correlation of abovementioned functional groups. Actinide sorption processes have been studied. All samples of modified humic acids serve as more effective actinide sorbents compared to nonmodified ones. Yet at the same time there is a significant difference between kinds of actinides. Thus, Pu and U are better sorbed by oxymethylized humic acids while Am and Np(V) are having high affinity to carboxylated humic modificates. Moreover, Np(V) sorption rates for the studied humic preparations significantly exceed those of U and P while being equal to those of Am. The fact of modified humic preparation having increased sorption rates in comparison to native humic substances seems to be very interesting for further studying. Consequently, the advancement of abovementioned methods in order to obtain highly selective humic sorbents in relation to different actinides is vital scientific task.

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EFFECT OF THE ANIONIC SURFACTANT ON THE COLLOIDAL STABILITY OF BUTADIENE-STYRENE AND NATURAL LATEXES

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Questions of colloid stability regulation of latex in the presence of electrolytes attract attention in connection with their using for new waterproofing materials based on the compounds of bitumen and latex aqua dispersions, their dispersive medium is nanostructured aqua solution of surfactant. Process of latex electrolytic coagulation determines features of bitumen-latex films formation.

Adsorption of anionic surfactant from aqua solution on the surface of butadiene-styrene (BSL) and natural (NL) latexes was studied with adsorptive titration method. Characteristics adsorptive titration of the anionic surfactant on BSL and NL were calculated. It was established adsorption of the anionic surfactant on the interface polymer / water results from the hydrophobic interaction, that brings about formatting the monomolecular layer on the surface of latex particles.

Colloid stability of BSL and NL in the presence $MgCl_2$ and $CaCl_2$ with coagulation titration method was studied. It was established that BSL and NL lose the colloid stability in the presence $CaCl_2$, while $MgCl_2$ is coagulating agent for only NL. It was found out, that BSL is coagulated under the action $MgCl_2$ in the presence anionic surfactant, this results from the modifying of adsorption layer.

Critical coagulation concentrations and Hamaker constants were calculated based on the results of turbidimetric titration $CaCl_2$ of BSL and NL in the presence anionic surfactant. It was established, that providing increasing of anionic surfactant concentration the values of critical coagulation concentrations increase and Hamaker constants decrease. It means that colloid stability of the latexes increases. It is concerned with decreasing of Van der Waals interaction between latex particles due to increasing of hydration shell thickness with degree of adsorption saturation of latex surface.

This study was developed at financial support of Belarusian Republican Basic Research Fund, project №X10M-152.

SODIUM-22 PRODUCTION

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Sodium-22 is widely used as a radioactive label due to its rather long half-life (about 2.6 years) and hard γ-radiation, which accompanies its decay (about 1275 keV with the yield of 99.9%).

Besides, it is used in positron radiation sources for researching positron properties and the mechanism of their interaction with a material, for antihydrogen production, in positron synchrotron radiation sources, for positron microscopy, etc. [1-4]

A method of Sodium-22 production from the targets made of aluminum and its alloys and irradiated in an accelerator in the city of Troitsk has been developed at the SSC RF-IPPE. It includes:

– target dissolution in a strong hydrochloric acid;

– precipitation of aluminum and impurity cations with ammonium carbonate;

– sorption purification of the target Sodium-22 on cation-exchange resin;

– conditioning of Sodium-22 solution in acidity and concentration activity.

Commercial shipments of Sodium-22 as a solution and sealed sources are made.

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PHOTOCHEMISTRY OF QUINOLONE ANTIBACTERIALS

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Fluoroquinolone (FQ) antibiotics are widely described synthetic agents with a broad spectrum of antibacterial action. The reaction of proton and electron transport in aqua under the UV-irradiation is the important part of FQs chemical transformations. It let us to observe the primary photochemical reactions of FQs. The contrastive analysis of time-resolving spectroscopy and quantum-chemical data made us possible to observe the characteristics of proton and electron transfer processes.

We estimated the radiant quantity intervals among the S_1*-levels of different protolytic forms FQs. We showed that this values are rather close – their difference is 1,5 – 5,0 kkal/mol. As so as the activation barrieres of the transition from one protolytic form to another are low it lets us to surmount this barriers by the little forces (hυ, T). Electron and proton transfer along the H-bonds realizes in ground and excited states. It was found out that the transfer of different protolytic forms of FQs in excited S_1*-state leads to electron density redistribution between the compound's fragments. After the electron transfer at the time interval 10^{-13} – 10^{-10} sec it goes the proton transfer. This process may be registrated by the time-resolved method at the nanosecond diapason.

We revealed that for the fluoroquinolone antibiotics excitation to the S_1* level accompanes both by the returning of some molecules to the ground state without any structural changes and by the phototransformation to the other protolytic forms and by the photodecomposition. For the neutral forms such excitation is accompaned by the opening of quinolone ring and by the removing of the C_2H_5 (C_3H_5)-group. As for the zwitterion form such excitation is accompaned by the opening of piperazine ring and by the removing of the carboxyl group. There were discussed general and specific functions of H-bonding for protolytic forms of FQs. It was established the important role of H_2O molecules for the transfering of electron density in water solutions of DA complexes of fluoroquinolones.

Grant FEBRAS № 04-I-OXHM-07.

α,α-DIFLUOROAZIDES – REAGENTS FOR NITROGENCONTAINING HETEROCYCLIC COMPOUNDS SYNTHESIS

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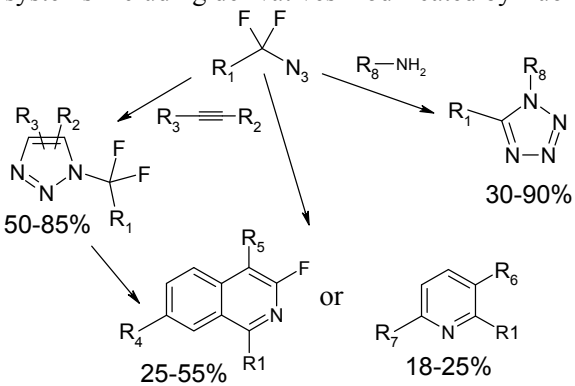
Nitrogen containing heterocyclic compounds keep a special place among all the groups of biologically active substances. A structure of this type of compounds is complicated every year. Thus, one of the main objects of bioactive substances chemistry is a development of effective synthetic methodologies for heterocyclic systems construction.

On the other hand it is well known that the introduction of fluorine into original molecules is one of the efficient methods for modification of their biological activity. Thus, fluorine containing derivatives of known heterocyclic bioactive substances attract considerable attention as potential highly active pharmaceutical compounds.

Oxidative fluorinating reagents – α,α-difluoroazides (RCF_2N_3) – are stable safe and reasonably priced compounds which are easily prepared, for example, from fluorolefins and fluorohalogenides.[1-2] We have found that these reagents may be used for construction of various nitrogen containing heterocyclic systems including derivatives modificated by fluorine.[3-4]



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BINUCLEAR CU(II) COMPLEXES WITH HETEROCYCLIC AZOMETHINE LIGAND: SYNTHESIS, STRUCTURE AND MAGNETO-STRUCTURAL CORRELATIONS

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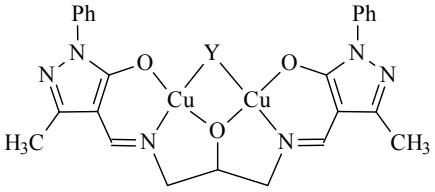
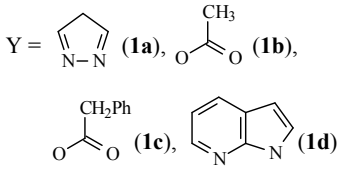
Series of binuclear Cu(II) complexes (type **1**) with *bis*-azomethine – condensation product of 1-phenyl-3-methyl-4-formyl-5-hydroxypyrazole with 1,3-diaminopropanol-2 were synthesized. Their composition and structure were studied by single crystal XRD, IR spectroscopy, temperature varied magnetic susceptibility measurements and TG/DTA.





Exchange interaction between Cu^{2+} in the binuclear metalchelates **1** depends on the nature of the exogenous bridging group Y and geometry of the exchange fragment Cu-O(Y)-Cu. The main geometric factor influencing on the exchange sign and strength in the complexes of this type is the value of the α angle in the Cu–$O_{(alcoxo)}$–Cu fragment.[1] Found 2***J*** values in **1a-d** complexes are –449, –168, –213 and +30 $см^{-1}$, α angles Cu–$O_{(alcoxo)}$–Cu are 125.82º, 104.77º, 104.96 and 105.33º correspondingly. Distinctive feature of **1b-d** complexes is considerable folding of the exchange fragments and presence of the axially coordinated DMSO molecules. Reverse sign of the exchange interaction in **1d** complex is explained both by the small valence angle value and the effect of the counter-complimentarity of the bridging azoindolate anion and alcoxo oxygen atom orbitals. Exchange parameters of the complexes were calculated by broken symmetry approach (B3LYP/6-311G(d)) and reasonable agreement with experimental ones is found.

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SYNTHESIS OF 1,3-DICARBONYL COMPOUNDS CONTAINING DIPHENYLOXIDE FRAGMENT

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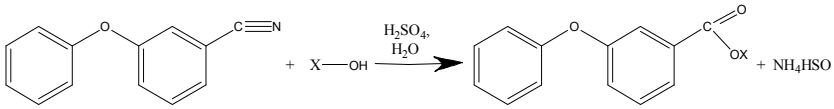
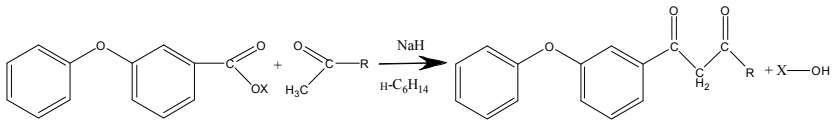
1,3-Dicarbonyl compounds have a wide application for solving the practical problems of inorganic and analytical chemistry. 1,3-Diketones have also been important intermediates in organic synthesis because of their high reactivity.[1]

The dicarbonyl system was carried out by the condensation reaction of carbonyl compounds with the esters of carboxylic acids[2]. The esters of 3-phenocsybenzoic acid were obtained by interaction of nitrile, containing the diphenyloxide fragment, with alcohols at heating in the presence of concentrated sulphuric acid:



X = - CH_3, - CH_2 - CH_3 55-84%

As a result of condensation of methyl ketone with esters containing 3-phenoxyphenyl fragment in the presence of sodium hydride in n-hexane produced 1-phenoxyphenyl derivatives of 1,3-alkandiones:



X = - CH_3, - CH_2 - CH_3; R = - CH_3, - CH_2 - CH_3, - C_6H_5 56-61%

Received 1,3-dicarbonyl compounds, except an independent importance, are reactive synthons for the synthesys of five- and six-members oxygen- and nitrogen-containing heterocycles.

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HYDROGENATION OF SOME UNSATURATED SUBSTANCES BY MEANES OF CATALYSIS BY METAL NANOPARTICLES

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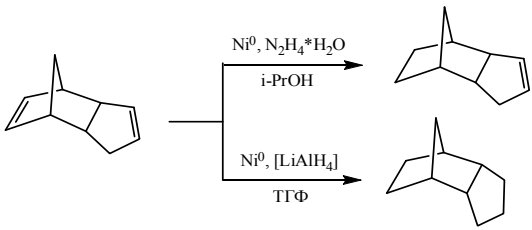
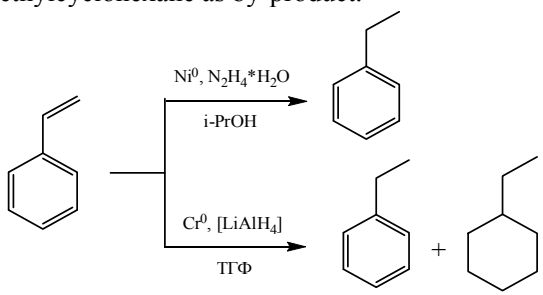
An ability of *in-situ* generated metal nanoparticles to catalyze hydrogenation of cyclic and aromatic alkenes by hydrazine hydrate or complex metal hydrides is discovered.

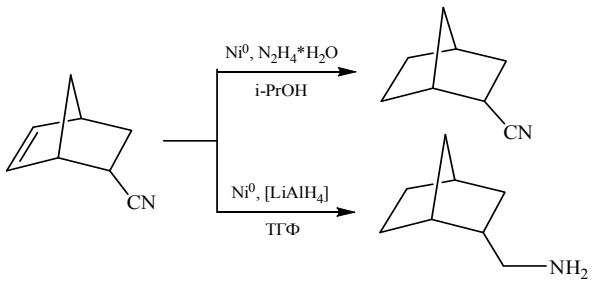
Reaction conditions for full or partial hydrogenation of substances are found. For example, dicyclopentadiene is hydrogenated by hydrazine hydrate to dihydrodicyclopentadiene, but using hydrogenating system metal salt - lithium alumohydride, with gives in turn metal nanoparticles, AlH_3 and LiCl, leads to *endo*-tetrahydrodicyclopentadiene.



The hydrogenation of styrene shown, that using of $CrCl_3$ and $LiAlH_4$ gave a 2% of ethylcyclohexane as by-product.



Hydrogenation by hydrazine hydrate has advantages when selective hydrogenation in presence of functional groups is needed.



SYNTHESIS OF HETEROCYCLES COMPOUNDS FROM NITRILES, CONTAINING DIPHENYLOXIDE-MOIETY

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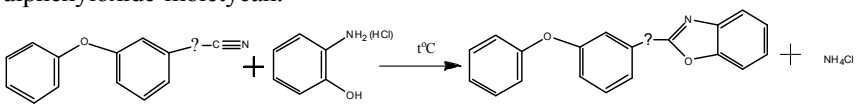
At use of such derivatives diphenyloxide as chloride 3-phenoxybenzyl acid, 3-phenoxybenzaldehyde, 3-phenoxyphenylmethylketon, 3-phenoxybenzilhlorid, 3-phenoxybenzyl alcohol and 3-phenoxybenzylamin have been synthesized 3-phenoxybenzoilacetonitrile, 3-(3-phenoxyphenyl)acrilonitrile, 3-(3-phenoxyphenyl)-2-butenonitril, 3-(3-phenoxyphenyl)propionitrile, 3-(3-phenoxybenzylamino)propionitrile, 3-(3-phenoxyphenylmethoksy)propionitrile, 3-phenoxyphenilacetonitriel and 2-methyl-2-(3-phenoxybenzoat)propionitrile.[1-3]

The synthesized nitriles derivatives of interest as syntons for production of five- and six-membered nitrogen-contaning heterocycles.

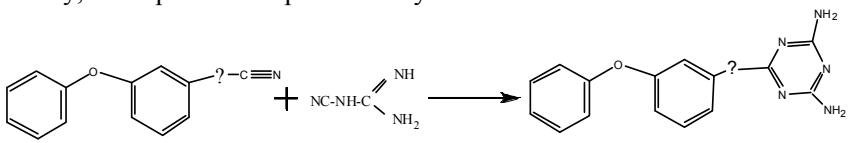
The formation of 2-(3-phenoksiphenil-substituted)benzoxazoles by heating in a sealed tube mixture o-aminophenol hydrochloride and nitriles containing diphenyloxide-moietycan:



X = одинарная связь, -CH=CH- ; - C(CH3)=CH- ; - C(=O)-O-C(CH3)2- ; -CH2-CH2-; -CH2-; -CH2-NH-CH2-CH2-; CH2-O-CH2-CH2-.

56-80 %

2-(3-Phenoxyphenyl-substituted)-4,6-diamino-*simm*-triazines was obtained by the reaction of dicyandiamide with nitriles, containing diphenyloxide-moiety, in the presence of potassium hydroxide:



X = одинарная связь, -CH=CH- ; - C(CH3)=CH- ; - C(=O)-O-C(CH3)2- ; -CH2-CH2-; -CH2-; -CH2-NH-CH2-CH2-; CH2-O-CH2-CH2-.

63-88 %

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THE REACTION OF ALKYLHALOGENIDS WITH 2,4-PENTANEDIONE BY CATALYSIS WITH COPPER NANOPARTICLES

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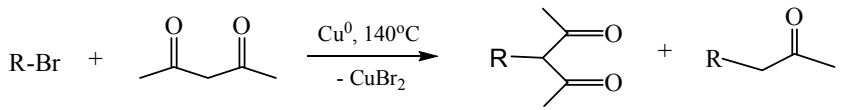
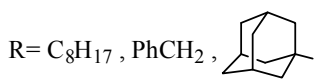
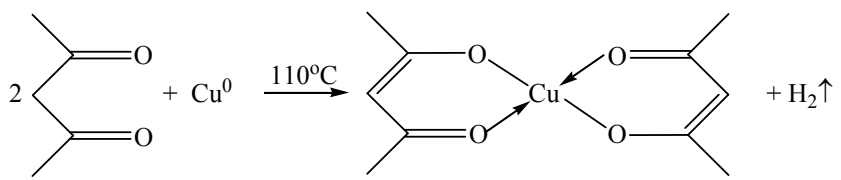
The reaction of halogenoalkanes and 2,4-pentanedione in presence of equal quantity of copper nanoparticles leads to obtaining of corresponding 3-alkyl-2,4-pentanediones. The reaction proceeds at 130-140єC during 8-12 hours.





It was found, that reaction in this conditions leads not only to desirable 3-alkyl-2,4-pentanediones (40-45%), but also to corresponding monoketones (45-55%). Using benzyl chloride as reagent gave 80% of benzylacetone and only 5-7% of 3-benzyl-2,4-pentanedione. These facts may be explained by destruction of the alkylated β-diketones in reaction conditions.

It was found, that reaction proceeds over obtaining of copper β-diketonate as intermediate, it's formation was proved by direct reaction between copper nanoparticles and 2,4-pentanedione.



The yield of copper β-diketonate was close to quantitative. The reaction investigated may be used as method of mono- and diketones combined preparation.

THE MODIFICATION OF LEUCKART-WALLACH REACTION BY USING OF COPPER NANOPARTICLES CATALYSIS

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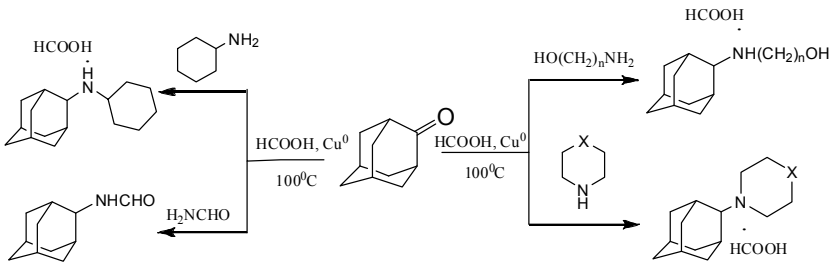
It is found, that number of cyclic ketones undergoes Leuckart-Wallach reaction in softer conditions comparing with traditional methods by means of using of catalysis by copper nanoparticles, giving homogenous colloidal solution in reaction mixture.

As starting ketones were used cyclopentanone, cyclohexanone and adamantanone-2, as starting amines – primary and secondary amines and formamide.

The reaction was carried out at molar proportion of ketone : amine : HCOOH 1:3:5-6 at 100ºC in presence of catalytic quantity of copper nanoparticles during 3-8 hours. Syntheses utilizing adamantanone-2 are shown on the scheme:



X= CH_2, O, NH; n=2,3

The products of reaction were formates of amines, but not corresponding formamides, that makes easy obtaining of free amines.

An attempts to carry out the reaction of acyclic ketones and D,L-camphor with piperidine and formic acid in such conditions were unsuccessful.

Basing on these investigations was discovered a modification of the Leuckart-Wallach reaction, which allows obtaining of hydroamination products of number of ketones, including ketones with low reaction ability, with high (70-90%) yields in softer conditions. The catalyst used is accessible, and may be synthesized in reaction mixture *in-situ*.

RESEARCH OF REACTIONARY ABILITY OF IMIDOYL CHLORIDES CONTAINING ADAMANTANE

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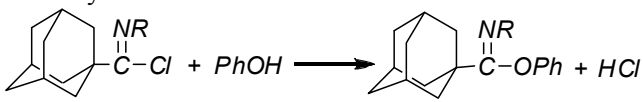
The research is devoted to studying the kinetics and the reactions mechanisms of imidoyl chlorides containing adamantane with O-nukleophilic reagents.

It is known, that imidoyl chlorides are convenient objects for solving some theoretical problems of organic chemistry as it is typical of these compounds to change mechanisms of reactions provided that there are small structural changes in reagents and depending on the polarity solvent.[1]

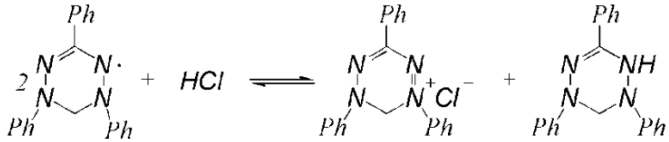
We have studied the kinetics of the reaction of imidoyl chlorides with phenol by verdazyl method:



A B

R = Ph; C_6H_4-Me-o, -m, -p; C_6H_4-NO_2-p

The method is based on application of triphenylverdazyl which quickly and quantitatively reacts with hydrogen chloride which is a co-product of the reaction:



In this reaction the balance is practically totally shifted towards the products. The kinetic researches were carried out in toluene at the low concentrations of verdazyl ~$1 \cdot 10^{-4}$ the mol/l, which were measured on change of the absorption intensity at the appropriate characteristic frequency: for triphenylverdazyl (*Y-Vd·)* - 720 nanometers, for salts triphenylverdazyl (*Y-Vd^+Cl)* - 540 nanometers.

It has been found out, that in not polar solvent the reaction can proceed in two parallel routes: the second order (k_o, $l \cdot mol^{-1} \cdot min^{-1}$) and the third order ($k_b$, $l^2 \cdot mol^{-2} \cdot min^{-1}$) under catalytic assistance of the second phenol molecule: $r = k_o \cdot C_A \cdot C_B + k_b \cdot C_A \cdot C_B^2$.

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SOME SPECIAL FEATURES OF INTERREACTING OF IMIDOYL CHLORIDES CONTAINING ADAMANTANE WITH O-NUCLEOPHILES

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The research is devoted to studying the reactions mechanisms of imidoyl chlorides containing adamantane with phenol using the quantum-chemical calculation by method AM1.

It has been found out by the kinetic researches, that in non-polar solvent for the reaction of imidoyl chlorides containing adamantane with phenol the dependence of the reaction rate on the concentration of phenol changed from the total first and second orders to the second at the transition from electron-donating to electron-accepting substituents at the nitrogen atom. The kind of substituting groups influence on the reaction rate tells about essentially different types of transitive conditions at limiting stages.

To establish the reaction mechanism, we have studied the electronic structure of imidoyl chlorides by the semi-empirical quantum-chemical method AM1. At the calculations we used the unlimited Hartree–Fock method as it allows to estimate the energy of the structures under investigation more reliably.

According to the calculations the Z-form with a non-planar configuration is the steadiest one. In addition the difference in the general potential energy between Z- and E- isomers makes from 4,83 to 5,25 kcal/mol.

We have also calculated the catalytical complexes of imidoyl chlorides with phenol which can be formed between the hydroxyl hydrogen in a molecule of phenol and free electronic pair of the nitrogen atom or the chlorine atom in a molecule of imidoyl chloride.

The calculations have shown that the complexes on the nitrogen atom are the steadiest ones. In all cases the general potential energy of such a complex is less than the general potential energy of the complexes on the chlorine atom from 0,45 to 1,75 kcal/mol.

The data obtained in the present work together with the results of the kinetic stidies allow us to offer the proved mechanism of nucleophilic replacements among imidoyl chlorides containing adamantane.

3-ALKOXYALKYL-7-(2-PHENYLETHYL)-3,7-DIAZABICYCLE[3.3.1]NONANS AS POTENTIAL ANALGESICS

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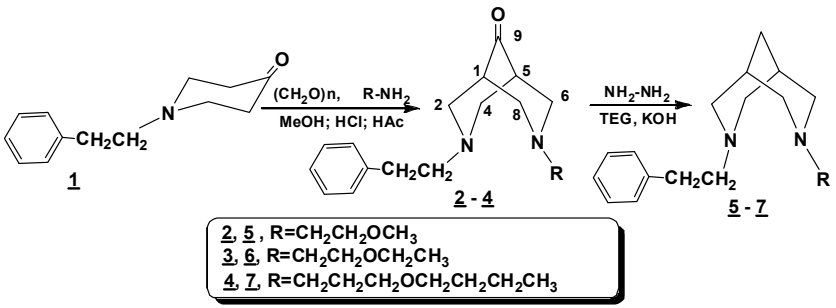
Modification of piperidones-4 with hydrogens situated in α-position to carbonyl group, gives an opportunity to complicate the initial molecule in which fragments of N-alkoxyalkylpiperidine and N-(2-phenylethyl)piperidine will be mixed. The last one is constructing a structural skeleton of active neuroleptanalgesic - fentanyl.

By the simultaneous condensation of Mannich reaction 1-(2-phenylethyl) piperidine-4-on (**1**) with paraform and various amines – 2- methoxyethylamine, 2-ethoxyethylamine and 3-buthoxypropylamine, in acetic acid + methanol solution 3-(2- phenylethyl)-7-(2-methoxyethyl)-(**2**), 3-(2-phenylethyl)-7-(2-ethoxyethyl)-(**3**) and 3-(2-phenylethyl)-7-(3-buthoxypropyl)-3,7-diazabicyclo[3.3.1]nonan-9-ons (**4**) with yields of 41,0–92,6 % are synthesized.



Reduction of 3,7-diazabicyclenonan-9-ones (**2** - **4**) via Kizhner-Wolf reaction by hydrazine hydrate in triethylene glycol leads to corresponding 3,7-diazabicycle[3.3.1]nonanes (**5**-**7**).

It is found, as expected, that analgesic properties are inherent to 3-alkoxyalkyl-7-(2-phenylethyl)-3,7-diazabicycle[3.3.1]nonanes, the most strong analgesic is oxalate 3-(2-phenylethyl)-7-(2-ethoxyethyl)-3,7-diazabicyclo[3.3.1]nonane, which is exceeding on duration of the general analgesic in 1,4 times of tramal. Moreover in the experiment on animals the progress of comprehensive analgesia of tramal is not observed, while the duration of that for HA-158 makes up 105 min.

SOME APPROACHES TO SYNTHESIS OF PHARMACOGICALLY ACTIVE BISPIDINE ANALOGS

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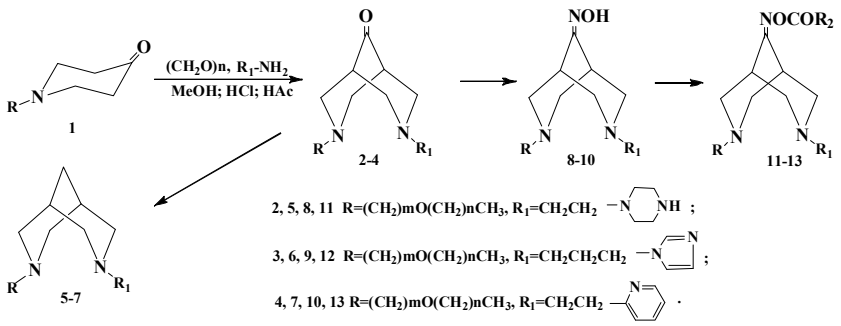
AS «Institute of Chemical Sciences named after A.B. Bekturov», Kazakhstan, Almaty, Walikhanov Str., 106, e-mail: praliyev@rambler.ru

Bicyclic analogs of natural alkaloid bispidine, which structure consist of two condensed piperidine cycles, possess of a wide spectrum of pharmacological activity, including anti-arhithmic, spasmolytic, anti-bacterial, anti-tuberculous, immunopotentiating, anti-opiate, analgesic activity as well as non-narcotic ones.

1-Alkoxyalkyl-4-oxopiperidines were used as a basic syntone of carried out investigations on synthesis potentially biologically active compounds. By the interaction of piperidones-4 with formalin and 2-piperazinoethylamine, 3-indolylopropylamine and 2-pyridinoethylamine in the conditions of Mannich reaction in one step 7-heterocyclylalkyl-3-alkoxyalkyl-9-oxo-3,7-diazabicyclo-[3.3.1]nonanes **2–4** have been synthesized with 54–62% yields.

By the reduction of novel 3-alkoxyalkyl-3,7-diazabicyclo[3.3.1]nonan-9-ones **2-4** with hydrazine hydrate in the presence of KOH corresponding bicyclic amines **5-7** have been obtained.



The treatment bispidinones **2-4** with hydroxylamine hydrochloride followed by acylation of obtained oximes **8-10** have led to *O*-acyl-derivatives **11-13**. «Chair-chair» conformation of bicyclic ketones, relative oximes and 3,7-diazabicyclo[3.3.1]nonanes has been defined for the reason vicinal coupling constants of cycle proton.

NEW HYDROXY- AND AMINOMETHYL SUBSTITUTED DERIVATIVES OF MONO- AND BISORGANOPHOSPHORUS ACIDS AS PERSPECTIVE LIGANDS AND ANTIOXIDANTS

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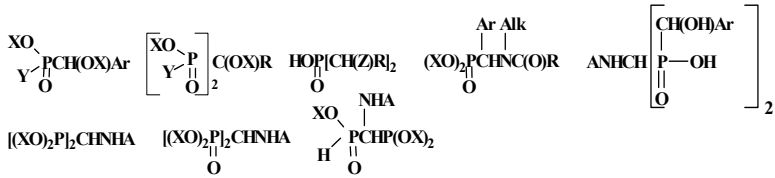
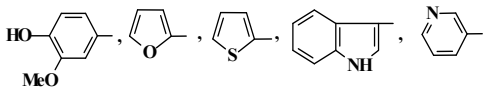
Functionalized hydroxy- and aminomethyl substituted derivatives of mono- and bisorganophosphorus acids are well-known organophosphorus analogs of hydroxy(amino)carbonic acids and natural pyrophosphates. These compounds are widely used as effective chelating ligands and various bioactive substances[1]. We have developed the convenient methods of synthesis of new types of these compounds using the starting reactive synthons such as the trimethylsilyl esters of several trivalent phosphorus acids and functionalized carbonyl compounds including heterocyclic, aromatic, and unsaturated fragments[2].



R = MeCH=CH, Me(CH=CH)$_2$, PhCH=CH, Me(CH$_2$)$_7$CH=CH(CH$_2$)$_7$, Ph, 4-MeOC$_6$H$_4$, Py;

Ar = Ph , 4-FC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-Me$_2$NC$_6$H$_4$, 4-MeOOCC$_6$H$_4$, 2-HOC$_6$H$_4$, 4-HOC$_6$H$_4$, 2-HOOCC$_6$H$_4$,



X = H, Et, Me$_3$Si, Na; Y = H, OX, (CH$_2$)$_2$Ph, (CH$_2$)$_2$Py, (CH$_2$)$_2$COOX, (CH$_2$)$_n$  , n = 1,2;

Z = OH, NHR, N(R)Ac, N(R)C(O)(CH$_2$)$_7$CH=CH(CH$_2$)$_7$Me; A = H, Me$_3$Si, Ar.

The presented compounds are of great interest as perspective polydentate ligands and new antioxidants with the significant routes of their antioxidantive activity.

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Prishchenko A.A., Livantsov M.V., Novikova O.P., Livantsova L.I., Petrosyan V.S. *Heteroatom Chemistry* , 2008, **19**, 352; 2009, **20**, 319; 2010, **21**, 361.

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MAGNETOPOSITRONIUM IN SEMICONDUCTORS

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Magnetopositronium – new quasiparticle – can be formed at an irradiation of semiconductors by positrons at ultralow temperatures in strong magnetic fields [1]. In this connection within the limits of the theory [2] probabilities λ_s and width Γ_N of process of two-quantum annihilation of and are calculated. It has appeared that λ_s and Γ_N extraordinary strong anomalies that allows to hope to detect and are inherent in sizes, at least at as much as possible achievable fields in laboratory $H \sim 100$ Tl. The contribution of own magnetopositronium annihilation in the general annihilation process in a case KI makes size of an order of 96 %, and in a case MgO - size of an order of 81 %. Size $\tau_s^{tot}(KI) = 2.842 \cdot 10^{-10}$ s closer to value in, and size with closer to value $\tau_1(KI) = (2.16 \pm 0.13) \cdot 10^{-10}$ c in MgO [1]. Thus, in oxyd semiconductor and KI crystal supervision of magnetopositronium in very strong magnetic fields seems quite real. One more possibility of supervision of magnetopositronium value of parameter of the theory λ_0 [1] characterizing to a certain extent degree one-dimensionality of magnetopositronium in very strong magnetic fields [3,4] can sharp increase. As extreme criterion of one-dimensionality the one-dimensional model of magnetopositronium with potential $V = -e^2 / \varepsilon z$ can serve. In this case according to model of Ludona [3], one-dimensional atom of hydrogen size $\lambda_0 \to \infty$, so basically in semiconductors probably supervision of times of life with $\tau_s << \tau_s^0 = 1.25 \cdot 10^{-10}$ s – life time of synglet positronium. These positronium states with short time of life have the big scientific interest.

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FLOCCULATION OF OCHER, TITANIUM DIOXIDE, AND BENTONITIC CLAY BY ACRYLAMIDE (CO) POLYMERS

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Flocculation behavior of polymers has been the subject of a considerable number of works devoted to the flocculation mechanism and the use of flocculants in the division technology of coarsely dispersed, micro heterogeneous and ultra micro heterogeneous dispersions. This study systematizes active parameters and their influence on the aggregative and sedimentation stability for model and real dispersed systems (DS), related to the solution of actual and future challenges in modern theory and research of flocculation processes.

Flocculation kinetics with a dosed introduction of acrylamide (co) polymers of different chemical nature in the water-salt media (I = 0,06 N) has been studied for model suspensions of ocher with a charge density (ζ=–44mV) and the average particle size ($\overline{R}$ = 9,25·10^{-6} м), of titanium dioxide (ζ=–63mV) and ($\overline{R}$ = 25,1·10^{-6} м), as well as a real suspension of bentonitic clay (ζ=–26mV) and ($\overline{R}$ = 7,28·10^{-6} м). Ionic polyacrylamide flocculants with molecular mass (M>1·10^6), with low and similar in magnitude concentrations of ionic groups (β <20%), as well as non-ionic polyacrylamide with M = 8.7·10^6 served as water-soluble polymer flocculants.

It has been determined that flocculation activity of polymer additives for ocher, TiO2 and bentonitic clay suspensions depends on various factors, such as the chemical nature of repeating units and the composition of macromolecules of the (co) polymer, flocculant concentration, and the combination of chemical, physical-chemical and physical properties of the dispersed phase and dispersion medium (pH, nature and the ionic strength of electrolyte, surface-active substances (SAS)). It has been shown that flocculation parameters demonstrated higher values in the presence of an anionic copolymer owing to the difference in the flocculation mechanism (bridging or neutralization), when compared to cationic and nonionic samples. Kinetics and unique characteristics of ionic polymer adsorption on solid adsorbents have been investigated. The size of resultant “superfloccules” was defined by means of optical microscopy. During floccules formation the parameters, characterizing the specific nature and dynamics of the changes in DS have been revealed. Finally, the correlation between the flocculation parameters of ionic PAAF and the stage of sediment dehydration has been determined.

EFFECT OF SUBSTITUENT NATURE IN AROMATIC RING ON SYNTHESIS AND ISOMERIZATION OF *O*-(CYCLOPROPYLMETHYL)PHENOLS

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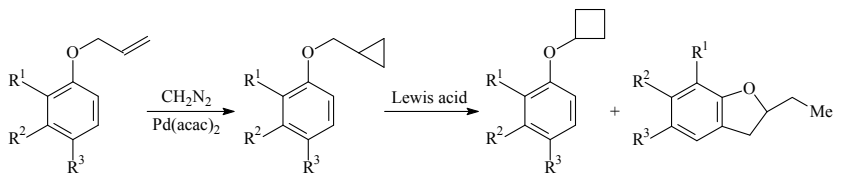
Cyclopropane containing compounds are widely used for the organic synthesis as practically significant compounds and synthetic intermediates. The rearrangement of allyl phenyl ethers into allyl phenols (Claisen rearrangement) is a prototype of many pericyclic reactions. But in the literature some information on the isomerization of *O*-(cyclopropylmethyl)phenol and its derivatives is absent.

In the given work the effect of the substituent nature in an aromatic ring on the reaction of *O*-allyl phenols with CH_2N_2 in the presence of $Pd(acac)_2$ and the subsequent isomerization of forming cyclopropane containing phenol derivatives were studied.

It was found, that *ortho*-, *meta*- or *para*-*O*-allyl cresols **1a-c**, react with diazomethane in the presence of $Pd(acac)_2$ in Et_2O at 5–10°C to form corresponding cyclopropane containing compounds **2a-c** in the yields 69-73%. The insertion of bromine atom into aromatic ring increases the yields of the cyclopropanation products **2d,e** up to 81-88%.



1a-e **2a-e** **3b-e** **4a-c**

a) R^1 = Me, R^2 = R^3 = H; b) R^1 = R^3 = H, R^2 = Me; c) R^1 = R^2 = H, R^3 = Me; d) R^1 = Br, R^2 = R^3 = H; e) R^1 = R^2 = H, R^3 = Br.

It was shown, that the isomerization of bromine containing derivatives of *O*-(cyclopropylmethyl)phenols **2d,e** in the presence of Lewis acids ($BF_3 \cdot OEt_2$, $AlCl_3$, $SnCl_4$) at –10°C in CCl_4 leads to 2-brom- and 4-brom-*O*-(cyclobutyl)phenols **3d,e**. At the presence of the methyl substituent in the aromatic ring the reaction proceeds mainly as a Claisen rearrangement with the migration of cyclopropylmethyl substituent into the aromatic ring and the subsequent formation of 2-ethylcoumaranes **4a-c**.

COORDINATION PROPERTIES OF PORPHYRINS WITH NONPLANAR STRUCTURE OF THE MACROCYCLE

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The interest towards porphyrins and their complexes is caused by the tremendous importance of two major " complexes of a life » - heme and chlorophyll for wildlife in whole. Macrocycle structures of metaloporphyrin molecules in majority of nature objects now were found out to be nonplanar. [1].

Researches of the influence of deviation from a plane structure (deformation) of tetrapyrrole macrocycle on physical and chemical properties and reactivity of porphyrins in processes of metaloporphyrin complex formation and dissociation, so as axial coordination of additional ligands were performed by the use of synthetic porphyrins with two structural types: polysubstituted and spatially hindered.

Deformation of porphyrin macrocycle was found out to be the reason of reactivity sharp increase in electron-donating solvents and of its sharp decrease in electron-acceptor solvents independently of the electronic nature of peripheral substituents. Deformation effect can change coordination reaction rate in any way more than in 10^4 times at respective alteration of activation parameters. Kinetic stabilities of Mn (III), Co (II), Cu (II) and Zn (II) complexes with spatially distorted porphyrins in proton-donor media were under investigation. Kinetic stability of metaloporphyrins appropriately decreased with the growth of deformation of tetrapyrrole macrocycle. Due to this effect solvoprtolitic dissociation rate can be increased in tens thousand times at the decrease of process activation energy in 2 - 3 times. The stability of metaloporphyrin extracomplexes with nitrogen- and oxygencontaining molecules also decreases with the increase of porphyrin fragment deformations.

Thus, the change of the character and porphyrin macrocycle deformation degree were shown to be one of the most effective ways of the regulation of physico-chemical and coordination properties of porphyrins and their complexes, and that opens new ways for obtaining of materials with specified properties.

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ELECTRONIC STRUCTURE AND REACTIVITY OF ANIONS GENERATED FROM PYRIMIDINE COMPOUNDS

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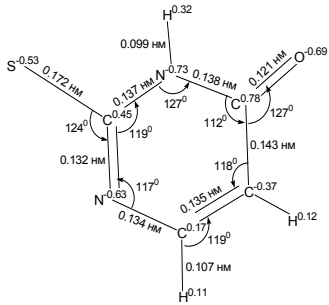
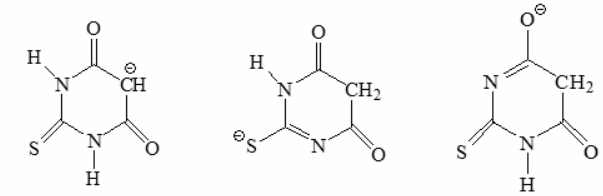
Geometrical and electronic structures of anions from 6-methyl-2-thiouracil studied by ab-intio method[1]. This is shown under:



Substation reactions of halogen in R Hal (Hal = I, Br, Cl; R = Bn, Bn(*м*−OPh), Bn(*n*-Ad), Pr, All, Et, Bn(*n*-SOF_2), Bn(*o*-Br), Bn(*n*-Br), Ad)R Hal (Hal = I, Br, Cl; R = Bn, Bn(*м*−OPh), Bn(*n*-Ad), Pr, All, Et, Bn(*n*-SOF_2), Bn(*o*-Br), Bn(*n*-Br), Ad) go in water-dioxane solution (30–50 ^{0}C, 15–60 min) with participation of S-anions. Yield is72 – 99 %

Full energy (Kcal/mol) of possible anions from thiobarbituric acid is equal:



CH- Anions with R Hal react badly (CH- anions have «dense» solvated cover in water-dioxane solution).

But CH- anions and aromatic aldehydes react easy with formation of 5- aryliden-2- thioxodihydropyrimidine-4.6 (1H,5H)-dienones with yield 92-93 %[2].

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TRANSITION METAL CATALYZED ENANTIOSELECTIVE MICHAEL ADDITION TO SUBSTITUTED NITROSTYRENE

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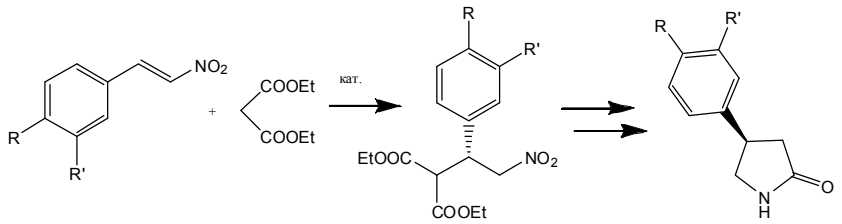
The development of asymmetric Michael additions for carbon-carbon bond formation is an important challenge in organic synthesis. We report the highly enantioselective catalytic addition of diethyl malonate to substituted nitrostyrene in the presence of diamine chiral Ni(II), Co(II,III) and Mn(II,III) complexes.



1a-c **2** **3a-c** **4a-c**

1, **3**, **4**: R = H, R′ = H (**a**); R = Cl, R′ = H (**b**); R = MeO, R′ = *cyclo*-C_5H_9O (**c**)

Catalyst design was based on the hypotetical catalytic cycle included 1,3-dicarbonyl enolization following nucleophilic attack of acetylacetonate type ligand on nitrostyrene. The two diamine ligands in this systeme each play a distinct role: one serves as a chiral ligand to provide stereoinduction in the addition step while the other functions as a base for substrate enolization. Octahedric structure of transition acetylacetonate complexes is a necessary condition for catalytic activity. We shows the effect of catalyst structure and metal on the reaction time and enentioselectivity. The reaction of nitrostyrenes **1a-c** with malonate **2** in the presence of 0.2 – 2 mol. % (*S*,*S*)-diamine complexes afforded (*R*)-nitroesters **3a-c** with 40 – 92 % *ee*, following reduction and decarboxylation result chiral pyrrolidine-2-one **4a-c**.

The work is supported by Russian Ministry of Education and Science (16.512.11.2011).

PREPARATION, STRUCTURE AND COLLOIDAL PROPERTIES OF BIOACTIVE GELS

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One of the main tendencies in the technology of cosmetic compositions production is introduction of bioactive ingredients into formulations and antioxidant products creation. An actual problem is the search for new effective additives with antioxidant and UF-protective properties. Cosmetic and medical gels are new perspective products. However, the mechanism of bioactive ingredients interaction with gels components and their influence on gel structure and formation processes still remain unclarified.

In our work gel formulations with bioactive ingredients were developed. We have used N-(ß- hydroxyethyl)-4,6-dimethyl-2-dehydropyrimidone and dithiooctanic acid as anti-inflammatory ad antioxidant additive. Synthetic gelators as Carbopol were used in optimized concentrations.

The rheological properties were done with Reotest reometer at 25^{o}C. The investigation was shown to reveal the effect of nature and concentration of bioactive ingredients on gels structure and thixsotropy. Optimal formulations with good thixsotropy properties for application in cosmetic production were created. All gels demonstrate a rheological behavior of Bingham fluid, which is typical for gels. It was established that mechanical properties can be varied largely by the substitution of small amounts of nonionic surfactants. The influence of temperature on gels stability and rheological properties was analyzed.

The effect of gels structure and bioactive ingredients presence on their biological access by means of penetration threw cellophane membrane was studied. It was shown that the surfactants intense the penetration. The synergism between bioactive ingredients and other components of cosmetic formulations has been revealed. The measurements of antioxidant activity by means of voltamperometric technique and the study of UVA protection showed that adding of dithiooctanic acid leads to obtain compositions with high antioxidant activity and the including of N-(ß- hydroxyethyl)-4,6-dimethyl-2-dehydropyrimidone allow to develop UF-protected gels.

FORMATION AND ACCUMULATION OF CARBONATES IS ONE OF FUNDAMENTAL PROBLEMS OF HYDROCHEMISTRY

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Process of formation of carbonates occurs in many modern reservoirs, but the most interesting it is in Balkhash lake, which the scientific interest and discussions haven't stopped till now about.[1] For Balkhash lake, which the drainage of waters of different types and concentration accumulates, during a long-term cycle (since 1958) the characteristic horizontal stratification of a mineralization (increase in 4-7 times) and ionic composition (increase unequal, in 2-15 times, and for ions Ca^{2+} - decrease in 2-4 times) remains. The vertical stratification is shown very seldom owing to strong wind mixture of the water masses saturated by O_2 and colloidal particles. This fact distinguishes continental reservoirs from those of hymid zones.[2] Another unique feature is strongly pronounced metamorphization of chemical compound, leading to course of polytypic processes with appreciable participation of all ions, except Na^+ and Cl^-. The carbonate formation especially intensively proceeds (in 10 times more intensively, than in other reservoirs of arid zones). From water to deposits annually get about 4,5 million tons of $CaCO_3$ which in condition of small maintenance of CO_2 or its absence remain at the bottom of reservoir. The processes of metamorphization have not lost their intensity even in condition of strong anthropogenic influence.

The sequence of sedimentation of carbonates is specified and added. The quantity of these salts which are get owing to evaporation, forms 0,05-0,11 %, and owing to polythermal cooling does 0,12 - 0,46 % of the general stock of salts. Owing to cation exchange 0,45% of carbonates precipitated. Biochemical reactions resulted in precipitation of 0,8 g of carbonates from 1 l of lake water.

Features of conditions of formation carbonates supersaturated of waters of reservoirs-coolers of Ekibastuz state district power stations-1,2 are revealed.

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STUDIES OF PROCESSES OF COMPLEX FORMATION OF D-METALS WITH AZODYES BASED ON METHYLPHLOROGLUCINOL

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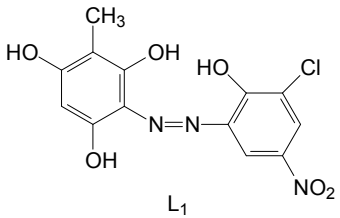
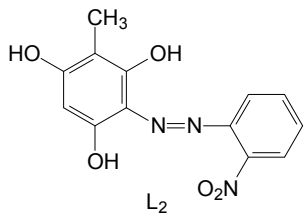
The basic share of explosives for utilization is 2,4,6-trinitrotoluene (TNT). One of the directions of chemical synthesis in order to transformate explosives into products of civil use and of practical application is the reaction of transformation of TNT into 2,4,6-trihydroxytoluene (methylphloroglucinol, MFG) and its further use as an azo-coupling component in the reaction of synthesis of azo-dyes[1]. As far as solution of metallic salts are actively used in the processes of dying, studies of complex formation is rather actual. In this paper, the results of studies of processes of complex formation of a series of d-metals with two azoderivatives of MFG are presented:



L_1



L_2

Processes of deprotonation and complex formation of L_1 and L_2, are studied by spectrophotometric titration. It was shown that the character of changes of electronic absorption spectra is identical in both two processes. Constants of deprotonation of ligands are calculated, the composition and formation constants of complexes are determined in ethanolic solutions. Quantum-chemical modeling of co-ordinate chelate ring is performed. The composition and structure of complexes obtained in the crystalline form are discussed.

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SYNTHESIS OF 2-ACYLCYCLOPENTANE-1,3-DIONE DERIVATIVES FROM CYCLOHEXANE β-TRIKETONES

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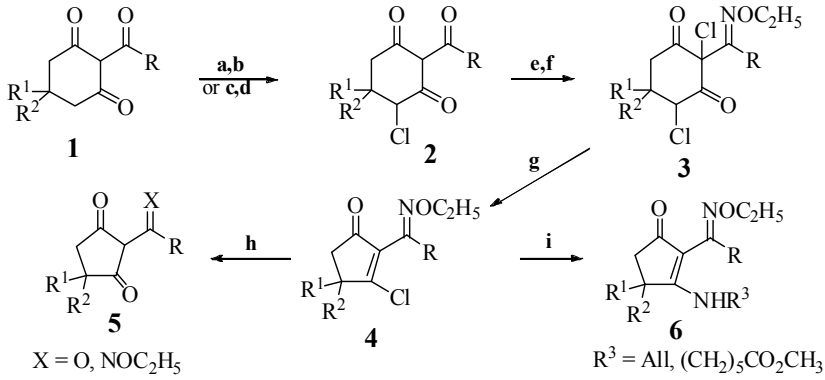
2-Acylcyclopentane-1,3-diones are widely used in synthesis of prostaglandins, phytoprostanes and their analogues. The availability of cyclohexane β-triketones with a diverse variation of substituents at any position of the six-membered cycle makes these compounds attractive synthones for the development of synthetic schemes for substituted cyclopentanoids.



R = C_2H_5, C_3H_7, $(CH_2)_5CO_2CH_3$, $(CH_2)_6CO_2CH_3$; R^1, R^2 = H, CH_3, 2,4,6-$(CH_3)_3$Ph

$R^1 = R^2 = CH_3$ **a**) t-BuOCl, **b**) DMF•HCl (65-80%);
R^1 = H, R^2 = H, 2,4,6-$(CH_3)_3$Ph **c**) $(NH_3)_2SO_4$, K_2CO_3, **d**) NaH, $(CH_3)_3SiCl$, t-BuOCl (50-60%);
e) $H_2NOC_2H_5$ (95%); **f**) t-BuOCl, **g**) K_2CO_3 (60-70%); **h**) 20% H_2SO_4 (60-90%);
i) NH_2R^3 (80-85%)

It has been shown, that β-triketones **1** can be transformed with good yields into cyclopentane chlorovinyl ketones **4**. The scheme includes the stages: introduction of chlorine atom into *4* position of a cycle, then transformation of the side chain acyl group into ethoxyimine one, then synthesis of 2,4-dichloro derivative **3** and cycle constriction, which occured by the action of anhydrous potassium carbonate. Chlorovinyl ketones **4** have been converted by acidic hydrolysis into ethoxyimino diketones **5** (X = NOC_2H_5) or triketones **5** (X = O), and by reaction with amines into enamino ketones **6**.

PHOSPHORYLATED 1-HYDROPERFLUOROISOPROPANOLS AS EFFICIENT INHIBITORS OF MICE PLASMA CARBOXYLESTERASE *IN VIVO*

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Preclinical studies are carried out commonly in rodent models. The carboxylesterase (CaE) activity in rodent plasma was reported to be significantly higher than in humans. So, the ester and amide-containing drugs undergo rapid degradation in rodent plasma. In this connection there is the task of creating an adequate model in mice for the study of pharmacologically important compounds. The application of CaE inhibitors possessing low acute toxicity in the experiments *in vivo* may represent a viable model. Our previous *in vitro* studies showed that phosphorylated 1-hydroper-fluoroisopropanoles (PFP) of general formula $(RO_2)P(O)OCH(CF_3)_2$, where R=Alkyl, exhibit the selectivity to the CaE in comparison with acetylcholinesterase (AChE) and butyrylcholinesterase (BChE).[1-2]

The aim of this study was to investigate the inhibitory activities of two compounds, diEt-PFP (R=Et) and diBu-PFP (R=Bu), against AChE, BChE and CaE in mice blood after a single i.p. injection. We found that diEt-PFP (R=Et) and diBu-PFP have the high inhibitory activities against mice plasma CaE (EC_{50}=25.0±1.0 and 3.08±0.27 mg/kg, respectively), lower anti-BChE activities (EC_{50}=46.8±1.5 and 15.7±1.8 mg/kg, respectively) and no activity against AChE. These compounds were shown to have a low acute cholinergic toxicity (diEt-PFP LD_{50}=200 mg/kg, diBu-PFP LD_{50} >2500 mg/kg, i.p.). Thereby, the studied compounds, especially diBu-PFP, can be used as new highly efficient *in vivo* inhibitors of plasma CaE in the study of pharmacologically important drugs containing ester or amide groups in the experiments on mice.

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METAL COMPLEXES OF DIPYRRINES AND THEIR *BIS*-DERIVATIVES: PHYSICAL-CHEMICAL PROPERTIES AND FUNCTIONALIZATION

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This report is devoted to the generalization of research considered the physical-chemical properties and directed functionalization methods of linear oligopyrroles (dipyrrines and their *bis*-derivatives), their complexes and hybrid materials based on them for solving different theoretical and practical tasks. Differing several intramolecular or extramolecular parameters (the structure of di- and tetrapyrrolic ligand or they complexes with a large variety of metals; the nature of solvent media (in solutions) or polymeric matrices (in hybrid material) is a very effective instrument for searching of practically useful materials for optic, medicine, nanotechnologies. Linear oligopyrroles metal complexes are the great example of compounds combining high flexibility of aromatic π-system of pyrrole rings with linkers and the ability to form very kinetically and thermodynamically stable six-member metallocycles. A wide variety for constructing different types of complexes (homo- and heteroleptic, mono- and polynuclear) allowing us to accurately tune the spectral and photo-physical properties of investigated compounds under the exact task. The methods of hybrid material synthesis by incorporation of investigated compounds into organic or inorganic polymeric matrices with the formation of spatial grid which differs from the initial structures but saving common motives and functionality are especially effective.

The results of the investigation will be presented in report in detail.

This work was supported by the Council for Grants of the President of the Russian Federation for Support of Young Scientists – candidates of science (grant no MK-401.2011.3) and the Federal Targeted Program "Scientific and Scientific–Pedagogical Personnel of the Innovative Russia in 2009–2013" (States no 14.740.11.0617 and 02.740.11.0253).

STUDIES OF THE REACTIVITY OF HYDROXYLS WITH DIFFERENT TYPE OF ASSOCIATION IN ACETALIZATION OF POLY(VINYL ALCOHOL) WITH BUTANAL

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Poly(vinyl butyral) (PVB) is obtained by reacting of the poly(vinyl alcohol) (PVA) hydroxyl groups with butanal in the presence of an acid catalyst.

The kinetics of the acetalization of PVA, might be complicated due to the different specific peculiarities of the reagent – strong inter- and intramolecular association of hydroxyls, chain effects, neighbouring group effects. During the acetalization of PVA composition and structure modifications of macromolecules occur. It can`t but has an influence on the character of listed effects and hence on the kinetics. Therefore, the aim of our study was to find out correlation between the hydroxyls` molecular organization in the polymer chain and their reactivity.

Using computer simulation methods it was shown, that with increase of the acetalization degree of PVA the content of hydroxyl groups, involving into intermolecular HB, decreases because of the increasing content of hydroxyls involving into intramolecular HB and HB between hydroxyl groups and H_2O.

The parameters of such HB were determined by using quantum-chemical calculations. It was shown that hydroxyl groups with intermolecular association show less reactivities in the acetalization reactions. To prove this data three systems, modeled different types of HB in macromolecules, containing 2-butanol/chloroform/butanal, 2-butanol/H_2O/chloroform/bu-tanal and 1,3-butandiol/chloroform/butanal were investigated kinetically. In accordance with calculated rate constants it was determined, that hydroxyl groups with intramolecular HB and HB between hydroxyl groups and H_2O are more reactive. With respect to the obtained data, based on both - computer simulation methods and kinetics it was guessed, that reactivity of the residual hydroxyl groups must increase at definite degree of PVA conversion.

THE DIRECT CHEMICAL AND ELEKTROCHEMICAL SYNTHESIS OF AMINO ACIDS COMPLEXES OF METALS

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There have been implemented a complex chemical and electrochemical study of stoichiometric interactions in normal and compact powder 3d-metals (copper, iron and manganese) with natural and synthetic α-and β-amino acids in two-, three-and four-component systems in aqueous and organic media, and in the absence of solvent.

Established the active role of oxygen in the reaction of 3d-metals with amino acids that act as coordinating agents and oxidants superoxide anion.

The effect on the efficiency of the chemical interaction of transition metals with amino acids, the dielectric constant, polarity, donor number and amount of solvent, temperature and reaction time, the solubility of amino acids and their metal complexes, metal ratio - an amino acid, the presence of additional oxidants and chelating agents, the composition of the medium and the acidity of the solution. This gave the opportunity to predict the reaction to the transition metals with amino acids in the liquid phase and to optimize their conditions.

Based on the interaction of copper powder with a stoichiometric amount of amino acids suggested an effective method of direct synthesis of chelate compounds of copper(II) with glycine, alanine, valine, serine, lysine, asparagine and β-phenyl-β-alanine in water and organic solvents (dimethylformamide, dimethyl sulfoxide , acetonitrile), as well as directly by heating metals with amino acids. Synthesis metallochelates can be made by boiling the reaction mixture for an hour (yield 25-80%), as well as a storage for 10-20 days at room temperature (yield 40-90%). Introduction to hydrogen peroxide significantly intensify t he reaction, thus reducing her time to one hour and increase the yield of the complexes.

SYNTHESIS OF PYRAZOLONATE COMPLEXES OF LANTHANIDES BY REACTION OF METALS WITH PYRAZOLONE

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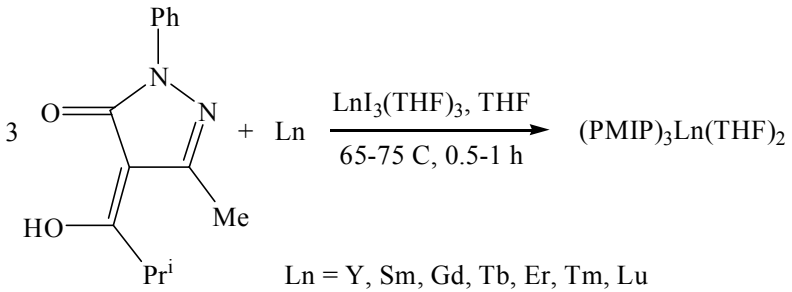
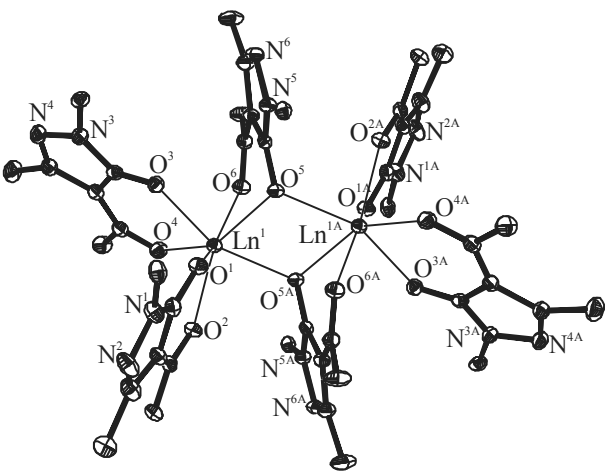
Interaction of 1-phenyl-3-methyl-4-isopropylpyrazolone-5 (PMIPH) with excesses of lanthanide metals in THF at 65-75°C in the presence of $LnI_3(THF)_3$ (5 mol%) was found to complete in 1-1.5 h with the formation of $(PMIP)_3Ln(THF)_2$ in high yields:



The composition of $(PMIP)_3Ln(THF)_2$ was confirmed by elemental analysis and IR-spectroscopy. The coordinative THF eliminates from the complexes in vacuum at 100ºC. The compounds was found to sublime at 230-270°C (10^{-2} – 10^{-3} Torr). X-Ray analysis revealed that sublimed complexes have a dimeric structure $(PMIP)_6Ln_2$, in which lanthanide atoms are linked by pyrazolonate bridges. The compounds $(PMIP)_6Ln_2$ (Ln = Y, Er, Gd, Tb) are isostructural.



PECULIARITIES OF THE ADSORPTION OF 1,3,4-OXADIAZOLES FROM SOLUTIONS ON THE SURFACE OF POROUS GRAPHITIZED CARBON AT HENRY'S FIELD

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In recent years porous graphitized carbon (PGC) has found application in the adsorption separation of geometric and positional isomers, diastereoisomers, and, in addition, amino acids, peptides, carbohydrates, nucleosides, etc. However, studies on the adsorption from solution on its surface are not considered physical chemistry of the process. Therefore in this work the peculiarities of adsorption in the Henry's field of 1,3,4-oxadiazoles from solution on the surface of PGC was studied by high performance liquid chromatography. The comparison of the characteristics of adsorption on the surface of the this adsorbent, octadecylsilica gel, and unmodified hyper-cross-linked polystyrene was conducted.[1,2]

Results of the study show that a significant importance in the adsorption of 1,3,4-oxadiazoles from solution on the surface of PGC has a planar arrangement of the molecules with respect to the adsorbent surface. In the case of PGC along with the dispersion interactions π- and electrostatic solute – adsorbent are realized. In general regularities of adsorption of the compounds are identical, regardless of the nature of the solvent. At the same time, according to a comparison of experimental data with calculations at the level of theory IEFPCM by B3LYP/6-31++G(*d,p*), preferential solvation of the solute molecule with acetonitrile leads to deviations from the linear relationship of molecules – adsorption.

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SYNTHESIS OF CONDENSED AZOLES BY THE SMALL RING OPENING REACTIONS

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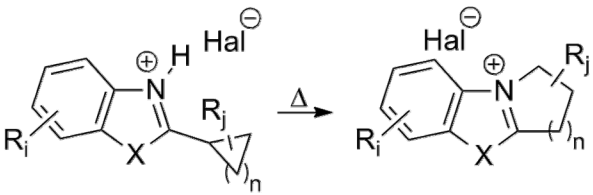
The cyclopropyliminium rearrangement was discovered by Cloke in 19291 but did not find a wide application in organic synthesis. By present it has been studied for only ketimines and thiomethylimidates. We found that the reaction takes place in the case of azoles that have a cyclopropyl substituent in □-position to the nitrogen atom as well.2 So, we developed a pathway to the synthesis of pyrrolinoimidazoles and pyrrolinothiazoles. For the first time it was revealed that analogous transformations take place in the conditions of thermolysis of cyclobutyl substituted azoles to form tetrahydropyridinoazoles. The study of these reactions has a practical value since some of the products we have obtained are either analogs or precursors of many biologically active compounds.



R = H, Alk, Ar, MeO, NO_2; X = NH, NBz, S; Hal = Cl, Br, I; n = 1, 2

We have systematically studied the rearrangement of azoles containing small cycles and revealed the regularities of influence of substrate structure, temperature, counter ion nature and solvent polarity on the reaction mechanism and rate. We have studied the reduction transformations of the thiazolium salts which form at the cyclopropyl and cyclobutylthiazoles rearrangement into neutral compounds.

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PREPARATION OF HIGH UNSATURATED CARBOXYLIC ACIDS BY CHEMICAL AND MICROBIOLOGICAL METHODS

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The high-unsaturated functional compounds containing double and triple bonds in molecule have large synthetic possibilities for preparation of various carbocyclic, heterocyclic and polyunsaturated structures incoming in molecule of many natural biologically active substances [1, 2]. In this plan one of the fundamental directions of organic synthesis is the preparation of high-unsaturated carboxylic acids and investigation of their properties [2]. Continuing the systematic investigations in this direction [3, 4], we have developed the chemical and microbiological methods of preparation of new polyunsaturated carboxylic acids having double and triple bonds in molecule and their properties have been studied. The developed chemical method of preparation of high-unsaturated acids (allylacetylene, dienine, di- or triine series) has been based on oxidation of the corresponding primary alcohols in the presence of oxidative mixture consisting of chromium anhydride and sulphuric acid.

For development of microbiological method of preparation of high-unsaturated carboxylic acids the biosynthesis of polyacetylene acids with basidial fungi (*Ganoderma lucidum, Pleurotus ostreatus, Trametes hirsute, Laetiporus sulpherus*), detected in forests of various ecological zones of Azerbaijan has been investigated. As a result of the carried out experiments the methods of preparation of some polyacetylene acids have been established.

Thus, the chemical and microbiological results confirm that the prepared high-unsaturated acids possessing biologically active properties open up possibilities of their further application for preparation of preparations which can be used in medicine.

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MECHANISM OF AUTOCATALYTIC REACTION OF METHANOL WITH LINEAR ASSOCIATES

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Interaction between isocyanates and alcohols underlies in production of polyurethanes, large-scale polymer materials. Polyurethanes are one of the most significant polymer materials. Their production volume and range of application increase every year. At the present time inverse process acquires distinction. It is decomposition of carbamates into isocyanates and alcohols known as the principal reaction of isocyanate production.

By quantum mechanical method B3LYP/6-311++G (df,p) autocatalytic reaction of methylisocyanate with methanol monomer and dimer was studied. N-methylcarbamate molecules form pre-reactive complexes with methanol monomer and dimer. They have better electron-donating properties in comparison with free molecules of methanol. It results in increased activity of carbamates-alcohols complexes in reaction with isocyanate. New molecules of carbamate and azomethinenol are the products of autocatalytic reaction. Transformations pass through coordinated asymmetric transition states. Isomerization of azomethinenols into carbamates is catalyzed by molecules of alcohols and their associates. Autocatalytic reaction with alcohols becomes possible due to the capacity of alcohols to catalyze this isomerization.

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REACTIONS ARYLISOCYANATES WITH LINEAR ASSOCIATES OF METHANOL

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By *quantum mechanical* method B3LYP/6-311++G (df,p) the mechanism of joining of linear associates of methanol (monomer, dimer, trimer) to aryl isocyanates by their C = N bond and C = O was studied. Regardless of the electronic nature of substituents in the aromatic ring of isocyanates, all reactions proceed through a concerted asymmetric late transition states. Accession to the C = N isocyanate is much more preferable than the accession of the C = O. The reason for this is less destructive energy C = N bond in the isocyanate as compared with the fracture energy of C = O. In the reactions with individual isocyanates in all cases with increasing degree of association of alcohol increases the kinetic and thermodynamic preference transformations. The analysis of various factors determining the relative reactivity in the test series was made. In describing transformations become important intermolecular donor-acceptor interaction between the reactants. They lead to the emergence in the studied reactions, the phenomenon of anomalous selectivity.

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REACTION OF VINYLCYCLOPROPANES WITH BROMTRICHLORMETHANE AND SYNTHESIS OF CHLORINE-CONTAINING TRIENS AND EPOXY DIENES

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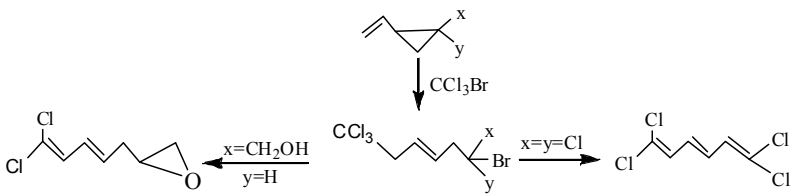
The radical additions of various addends to compounds, where a conjugation of double bond with three-membered cycle is possible show that vinylcyclopropanes (VCP) react with simultaneous opening of both groups with formation of 1,5-adducts [1,2]. In this work the interaction of bromtrichlormethane (BTM) with gem-dichlor- and hydroxymethyl substituted VCP has been studied. It has been established that the composition of the forming reaction products mainly depends on ratio of BTM:VCP and nature of functional substituent in three-membered cycle. In particular, at ratio of BTM:VCP > 5 a monoadduct of composition 1:1 is the unique reaction product. In decrease of content of BTM in the initial mixture along with monoadduct the dimers and other telomers have been isolated.



The analysis of NMR-spectra of monoadducts allowed to isolate signals of separate configuration isomers, to refer them to *cis*- and *trans*- series, and on integral intensities of corresponding signals to determine a relative content of isomers. It has been established that monoadducts are mixture of two geometrical isomers.

The dehydrohalogenation of the synthesized adducts in the presence of various amines has been carried out and it has been shown that the process goes up to the end with formation of chlorine-containing triens and epoxy dienes.

It has been shown that the dehydrohalogenation reaction proceeds exothermally and practically is finished for 1.0–1.5 ч.

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NEW MULTI-STAGE MECHANISMS OF C-NITRO COMPOUNDS THERMAL DECOMPOSITION

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The paper presents results of theoretical investigation of new multi-stage mechanisms of nitroalkanes, nitroalkenes, and nitroarenes gas phase decomposition.

A new mechanism of nitromethane two-stage nitro-nitrite rearrangement (NNR) through singlet biradical transition stages and intermediate has been found. This alternative of nitromethane NNR can compete with CN bond homolytic decomposition.

For α-nitroolefins, it has been found that the mechanism of their monomolecular thermal destruction is a complex multi-stage process. Its main channel is formation of different oxazete oxides at the initial stage. For nitroalkenes, which have a hydrogen containing substituent in their cis-position, an alternative thermal decomposition mechanism is possible, 1.5-sigmatropic shift of hydrogen atom from hydrogen substituent to nitro group oxygen at the initial stage. Significant increase of nitroethylene thermal decomposition process in liquid phase in comparison with monomolecular processes in gas phase state has been explained. It is related to auto-catalytical mechanism, including dimer formation as a result of [4+2] cycloaddition reaction with further decomposition according to biradical scheme.

For nitrobenezene and a number of its multifunctional derivatives, it has been found that depending on temperature, two channels of thermal decomposition compete, radical mechanism and NNR. During gas phase monomolecular decomposition of o-substituted nitrobenzene with hydrogen containing substituent (o-nitrotoluene, o-nitroaniline, o-nitrophenol), a minimum barrier can be observed for reaction of intramolecular hydrogen shift from hydrogen containing substituent to nitro group. For o-dinitrobenzene, 1,2,3- and 1,2,4-trinitrotoluenes and hexane-nitrobenzene, the most energetically profitable is the process of bicyclic intermediates formation with their further decomposition according to biradical scheme.

It has been shown that processes of thermal gas phase decomposition of C-nitro compounds cation radicals occur with significantly (2-8 times) lower energy barriers. Mechanisms of thermal decomposition for molecules and their cation radicals, however, may differ.

SUPRAMOLECLAR ASSOCIATION OF TETRAMETHYLEN-SULFONATOCALIX[4]RESORCINEARENE AND THEIR COMPLEXES IN THE BULK SOLUTION AND ON THE SURFACE

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At the first time the physical immobilization of macrocycles **H1** and **H2** on the surface of anion exchange resin **Amberlite IRA 900 Cl** was carried out.

It was defined that the binding of parent substances of drugs - Xymedon® and Dimephosphon® - by immobilized macrocycles significantly differs from that observed in the bulk solution. In the binding of **Xym** and **Dmph** for immobilized **H1** and **H2** the effect of cooperative hydrophobic cavities, that they form, is come out. This effect influences on the selectivity, rate and degree of the binding of the investigated substrates.

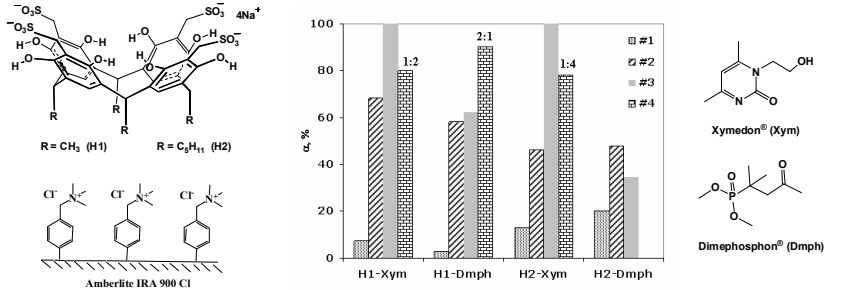

Fig.1. The comparison diagram of the **Xym** and **Dmph** binding by macrocycles **H1** and **H2** in the aqueous solutions and in the immobilized state on the surface. #1 - in a diluted solution (4.5 mM) and #2 - in concentrated solution (200 mM (**H1**), 10 mM (**H2**)), #3 and #4 - in immobilization on the surface in equimolar and not-equimolar ratio of macrocycle:substrate.

Immobilized on the surface complexly organized structures are an example of the creation of new functional surfaces that are able to concentrate various substrates.

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POSSIBILITIES OF FORMATION OF CYCLOHEPTANE FRAGMENT CORE OF GUAIANE TYPE FROM LEVOGLUCOSENONE

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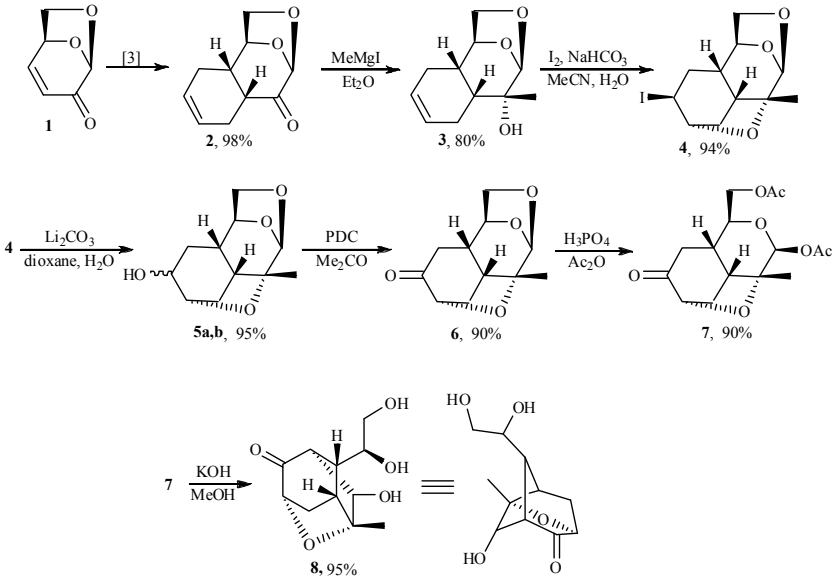
Seven-membered carbocyclic skeleton is the characteristic structural fragment of guaiane sesquiterpenoides[1], gibberellins[2], also other biologically active natural compounds. In order to study possibilities of formation of seven-membered carbocyclic matrix from levoglucosenone **1** we was developed an effective scheme of synthesis of bicycle[3.2.1]octane **8** based on aldol intramolecular cyclization of the derivative of levoglucosenone adduct with butadiene **2**



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SONOLUMINESCENCE OF METAL COMPOUNDS IN AQUEOUS SOLUTIONS

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The works discussed in this communication, solve two problems of sonochemistry. First, elucidation of the mechanism of non-volatile compounds participation in the reactions taking place in the cavitation bubbles, and second, detection of sonolysis products distribution in the field of these bubbles, arising under the action of ultrasound on liquids.

Luminescence of alkali-metal atoms was first observed at sonolysis aqueous alkali-halide salt solutions of more than 70 years ago.[1] In subsequent works such sonoluminescence (SL) was obtained for the compounds of alkaline earth and some other metals. Observation of gas-phase metal lines indicated the close relationship of radiation with bubbles (formation of excited metal atoms either inside or directly at the bubble/liquid interface).[2] Furthermore, in addition to the alkali metals, SL of lanthanides ($LnCl_3$) in solutions was discovered. This SL is connected with the radiative deactivation of the ions (Ln^{3+}), but not atoms.[3] Results of researches show that the electronic excitation of Gd^{3+}, Tb^{3+}, Dy^{3+}, Eu^{3+} also caused by direct interaction of metal with bubbles.

Two main models are presented that explain the penetration into a bubble and the electronic excitation of metal atoms and ions. This is a model of the hot shell and the model of microdroplets injection. The proofs a validity of a droplets injection model are obtained.[4,5] The results of studies to identify the spectral-spatial distribution of two types bubbles are presented. These symmetric "hot" or deformed, containing a metal, "cold" bubbles arise in acids and aqueous solutions of sodium and terbium compounds during sonolysis in a known regime of multi-bubble SL, as well as the regimes of the new varieties multi-bubble SL (multi-cluster and poly-center SL).

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DUAL ROLE OF BASE IN SUZUKI REACTION

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One of the features of reaction between aryl halides and aryl boronic acids called Suzuki-Miyaura reaction[1] is the compulsory presence of base excess. Both exiting hypothesis concerning base role come to involvement of organoborate anion or Pd intermediate containing basic counter ion that are formed in situ under the base action in transmetallation step of Suzuki reaction catalytic cycle[2]. These hypotheses have no experimental evidences at the moment.

Kinetics of interactions of a set of palladium complexes with $PhB(OH)_2$ or $[PhB(OH)_3]^-$ has been studied. It has been established that reaction rate increases considerably using $PhB(OH)_2$ instead of $[PhB(OH)_3]^-$. It points to involvement of neutral acid molecule, but not borate anion, into transmetallation step. On the other hand it has been established that using Pd complexes containing less basic counter anion results in significant reaction deceleration (rate decrease in the order OAc>Br>>I). The results are indicating of the most important role of counter ion in Pd compound that react with $PhB(OH)_2$.

Hereby, the kinetic data obtained point to neutral phenylboronic acid and Pd compound containing basic anion react in transmetallation step. Consequently, base plays dual role in Suzuki-Miyaura reaction. On the one hand base participates in unwanted borate anion formation; on the other hand it provides formation of catalytic cycle intermediates that are able to participate in transmetallation.

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NEW ASPECTS OF CHEMISTRY POLIGETEROATOMIC HYDROAZOLES AND AZINES

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It was carried out systematic study of the reactions of inter-and intramolecular heterocyclization a wide range of carbonyl and thiourea substrates, which are different by nature of the carbon skeleton, degree of saturation, the nature and position of substituents with the formation of 5,6-membered polyheteroatomic systems and molecular assemblies, including several heterocyclic fragments.

On the basis of the methodology of cascade processes, domino reactions and tandem reactions, it was designed single stage procedures of preparing of spiro-, condensed, functionalized thiazolic, thiadiazolic, pyroazolic, dihydropyrimidinic, dihydrothiazinic, hexahydroindazolic compounds.

It were discovered the optimal conditions, which allow obtain desired product with yields of up to 90%. It was found regiodirection of reaction depending on the nature of the substrate and reagent, such as activation and interaction conditions. It were revealed features of heterocyclization saturated and conjugated β-aminoketones different series.

It was shown, that the interaction monoenones with C-nucleophiles in the presence of organic base leads to formation form adducts with Michael.

It has been designed alternative approach to the synthesis of spirocyclic thiopyrimidines by interaction dienones with thiobarbituric acid in the condition of double Michael addition reaction or the domino process Knevenagel-Diels-Alder reaction.

Stereo structure of products and scheme interactions were discovered on the basis of data NMR ^{1}H, ^{13}C, and two-dimensional NMR spectroscopy, GC-MS and quantum chemical calculation.

It was obtained data about the biological activity of compounds of that series as an effective regulator of plant morphogenesis and immunomodulators of basic grains, vegetables, forage and forestry crops

MODELS OF AGGREGATION WORK FOR IONIC MICELLES IN THERMODYNAMICS AND KINETICS OF MICELLIZATION

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An approach to thermodynamics of molecular aggregates of nonionic surfactants and to kinetics of micellar relaxation in polar solvents, developed recently[1-2] with the help of methods of the nucleation theory, has been extended to ionic micellar solutions. New expression for the aggregation work of ionic micelle has been obtained and relations between this work and the chemical and electrochemical potentials and the aggregation numbers of surfactant ions and counterions have been established.[3-4] On the basis of computer molecular dynamics simulation of micellar solutions of ionic surfactants, one-dimensional curves and two-dimensional surfaces of the equilibrium distribution of aggregates and the work of aggregation are found and analyzed as functions of aggregation numbers of surfactant ions and counterions.[5] Thermodynamic and statistical procedures of "dressing" ionic micelles have been considered. Coefficients of the counterion binding to ionic aggregates of different sizes have been calculated at several total concentrations of surfactant in solution. Fundamental equations and key statistical and thermodynamic relations with electrochemical potentials for ideal and real ionic micellar systems have been derived with elimination of existing inaccuracies. The differential equation for the osmotic pressure in the system of ionic aggregates has been derived. Specific contributions to the aggregation work of ionic micelle have been commented on and several approximations for the electrical contribution as a function of aggregation number of surfactant ions at the most probable number of associated counterions have been considered.

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This work was supported by the program 6 RAS "Chemistry and physicochemistry of supramolecular systems and atomic clusters" and the Program of development of St. Petersburg University (project 0.37.138.2011).

SYNTHESIS AND REACTIVITY OF 5-METHYLIDENEHEXAHYDROPYRROLO[1,2-*A*]IMIDAZOLES AND 6-METHYLIDENEOCTAHYDROPYRROLO[1,2-*A*]PYRIMIDINES

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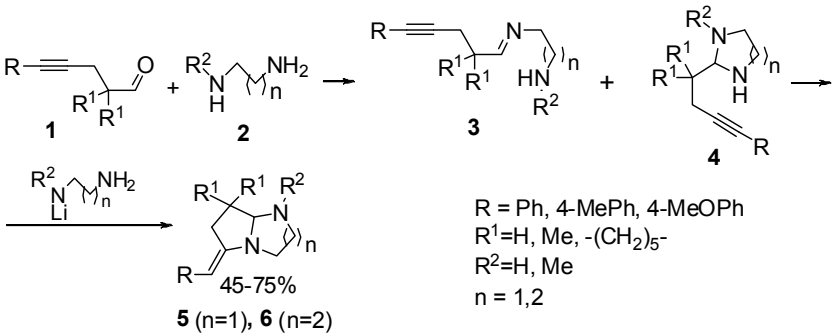
We have revealed[1], that interaction of 1-alkynyl-1-chlorocyclopropanes with lithium derivatives of 1,2- and 1,3-diaminoalkanes gives previously unknown methylidene-substituted hexahydropyrrolo[1,2-a]imidazoles **5** and octahydropyrrolo[1,2-a]pyrimidines **6**. The results, obtained by the study of mechanism of these unusual reactions, allowed us to suggest a new general method for synthesis of bicyclic enaminals **5** and **6**, which is based on the reaction of alk-4-ynals **1** with excess of corresponding diaminoalkane **2** and subsequent intramolecular cyclization of adducts **3** and **4** under action of strong bases. This process can be performed without isolation of compounds **3** and **4** with overall yields 45-75%



Compounds **5** and **6** are the first representatives of diazabicycloalkanes with enaminal fragment. Their reactions with hydrogen in the presence of Pd-catalysts proceed with retaining of starting bicyclic system, whereas reduction with complex metal hydrides leads to the selective cleavage of one C-N - bond.

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This work was financially supported by the Russian Academy of Sciences (program OKh-01)

CATALYTIC ACTIVITY OF CARBON CONTAINING NANOPARTICLES NI, CU, FE IN THE PROPANE'S CRACKING.

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In the present work to study the conversion of propane were studied samples of furfural-activated carbon black (FAS) and FAS with deposited nanoparticles of metals Cu, Ni, Fe. Cracking reaction of propane (99.98% wt.) studied in stationary conditions in a flow catalytic apparatus at atmospheric pressure. The main products of cracking were methane, ethane, ethylene, propylene. Using FAS as a catalyst would enhance the conversion of propane α, compared with non-catalytic reaction, an average of 10% and matrixing FAS nanoparticles of iron or nickel significantly increased the α. High catalytic activity and selectivity of FAS may be associated with participation in the decomposition of propane carbon particles in the surface during catalyst preparation. Despite the increase in E_a in a series of Ni/FAS - Fe/FAS - Cu/ FAS, selectivity to olefins increased, probably as a result of growth in the number of active centers of the catalyst surface, as indicated by the increase Lnk_0. The use of bi- and three-metal systems has not changed the qualitative composition of the reaction mixture. For all samples, the effective rate constant (k_{eff}) catalytic conversion many times greater than k_{eff} homogeneous decomposition. Most k_{eff} had FAS, however, due to the high values of apparent E_a conversion of propane was not great. Comparison of the calculated E_a, Lnk_0, k_{eff} and the maximum degree of conversion of mono-, bi-, and three- metal systems showed that the introduction of copper lowers the k_{eff} and α_{max} respectively, due to blocking of some of the active centers of the catalyst surface. When you add iron or nickel in the monometallic samples of similar relations were observed. Higher selectivity to olefins on copper-bearing monometallic catalyst and the activation energy close to the value of activation energy of non-catalytic process that could indicate the predominance of radical-chain mechanism in this sample. The introduction of the second component decreased the E_a and suppression of this mechanism.

SELECTIVE FUNCTIONALIZATION OF LOWEST ALKANES UNDER MILD CONDITIONS BY THE Au-BIOFLAVONOID COMPLEXES

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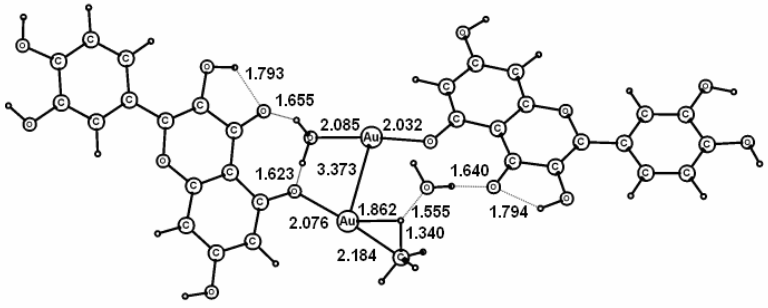
With discovery of Shilov reaction on Pt (II) complexes, new prospects for the functionalization of alkanes by metal complex catalysis appear. In this aspect, there are much interest in complexes of gold in view of easy auraion of aromatic hydrocarbons. Recently, it was first found that in the biomimetic system HAuCl4-rutin-NADH catalytic centers are formed, which are capable to activate C-H bond of methane under mild conditions with formation of methanol under the action of atmospheric oxygen. The zero order with respect to the catalyst is achieved in the system already at low concentrations of gold that greatly complicates the study of reaction mechanism. The system tests showed that from a wide range of bioflavonoids only rutin and quercetin support methane oxidizing function. In catalytic oxidation of simplest alkanes alcohols - methanol, ethanol and isopropanol are selectively formed. The yield of products per one mole of Au at 25 ^{o}C (30, 140, 220) grows amongst C_1-C_3 alkanes. Analysis of the kinetic parameters of the reaction allows us to estimate that only a small part of Au, less than 0.01, participates in the formation of active centers. Instead of O_2, also H_2O_2 and $K_3[Fe(CN)_6]$ may perform the role of an oxidant.

To elucidate the molecular nature of the active site and a probable mechanism of the process quantum-chemical modeling of reactions of light alkanes with quercetin complexes of gold (I) was used. As an example, the figure shows the structure of the transition state of methyl complex formation with concerted proton transfer to the ligand through the H_2O molecule.



This work was supported by Federal Program "Scientific and scientific-pedagogical personnel of innovative Russia" for 2009-2013, "State contract № 02.740.11.0646.

^{13}C-^{15}N COUPLING CONSTANTS AS A NEW TOOL FOR STUDIES OF THE STRUCTURE OF FUSED TETRAZOLES

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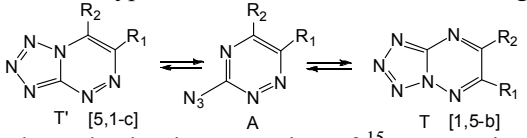
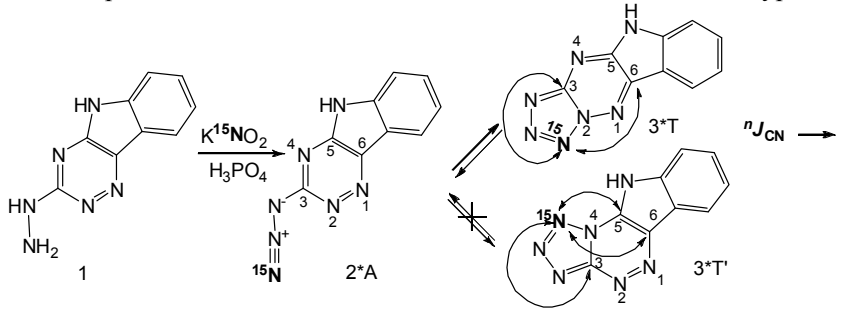
Cyclization of the azido group attached to 1,2,4-triazines **A** at the position between nitrogen atoms can result in formation of two different fused tetrazoles **T** and **T'**. In this case X-ray is the unique approach allowing unambiguous determination of the fusion type between tetrazole and triazine rings.



We found, that selective incorporation of ^{15}N atoms in the azole rings of tetrazolo-1,2,4-triazines and subsequent analysis of ^{13}C-^{15}N J coupling constants provide alternative method to determination of the fusion type.



For example, cyclization of the azide **2*A** leads to compound **3*T**, but not **3*T'** as it has been reported earlier. This conclusion is confirmed by presence of ^{13}C-^{15}N splitting for the C3 and C6 signals in 1D ^{13}C NMR spectrum of **3*T**.

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This work was supported by the State contract P2444, RFBR (project № 10-03-01007) and grant from President of Russian Federation (NSh-65261.2010.3)

CRYSTAL STRUCTURE AND VIBRATIONAL SPECTRA OF $[Fe(D_2O)_6]^{3+}(ClO_4^-)_3\ 3D_2O$

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Crystal structure of a coordination compound of water, $[Fe(D_2O)_6]^{3+}(ClO_4^-)_3\cdot 3D_2O$ (I), is determined by X-ray diffraction method. The compound crystallizes in the trigonal crystal system. The unit cell is hexagonal with the following parameters: $a = b = 16.098(2)$ Å, $c = 11.435(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$; $Z = 6$, $\rho_{calc} = 2.005$ g/cm^3, $R\bar{3}\,(S_6)$ space group, R1 = 0.0548 (2257 reflections with $I > 2\sigma(I)$).

In complex cation $[Fe(D_2O)_6]^{3+}$, six molecules of water are located on the corners of the octahedron around the Fe^{3+} ion. Metall–oxygen distances and octahedron angles are close to ideal: average length of the Fe–O bond is 1.994 Å and the angles O–Fe–O lie within the interval 89.22 to 90.87º. Independent complex cations $[Fe(D_2O)_6]^{3+}$, in the partial position 3 each, with outer-sphere molecules of heavy water and anions ClO_4^- (in the common position) form a complex net of hydrogen bonds. The inner-sphere molecules form short D–bonds (O…O 2.65Å) with the oxygen atoms of outer-sphere water molecules, while D–bonds of the same molecules with the oxygen atoms of ClO_4^- are longer (2.74–2.80Å). Each outer-sphere molecule form D–bonds with disordered perclorate-ions, the bond length lying in the interval 2.76–2.85Å. Polycrystal samples of (I) were analyzed using IR and Raman spectroscopy methods. Two sets of bands are clearly distinguished. The first one refers to stretching vibrations OD of the inner-sphere molecules. The second one is due to similar vibrations of the outer-sphere molecules. As an effect of short D–bonds, the first set of bands is shifted in relation to the second one to the low frequencies. Moreover, it is characterized by an exclusively large breadth of profiles due to a synergy action of multiple effects.

SELF-ORGANIZATION EFFECTS IN SOLUTIONS OF CATIONIC POLYELECTROLYTES AND ANIONIC SURFACTANTS

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Self-organization in mixed solutions of polyelectrolytes with micelle-forming surfactants results in formation of highly organized supramolecular structures - polymer-surfactant complexes. The structure and properties of such complexes are determined by polyelectrolyte and surfactant chemical nature as well as by the nature of solvent.

Methods of ion-selective potentiometry, viscometry, spectrophotometry and dynamic light scattering have been used for study of how the composition and nature of aqueous-organic medium influences self-organization of various cationic polyelectrolytes (quaternized poly-4-vinylpyridine, poly-N,N-dimethyl,N-benzylammoniummethylmetacrylate chloride and chitozan) with anionic surfactant (sodium dodecylsulfate) in mixed aqueous-alcohol (methanol, ethanol, isopropanol) solutions.

The composition of aqueous-organic media has been shown to exert the dominant influence on formation of supramolecular structures. Small ethanol and isopropanol additives (20 vol. % of ethanol and 10 vol. % of isopropanol) promote binding of sodium dodecylsulfate by polyelectrolytes. Methanol additives up to 30 vol. % do not cause any changes in surfactant binding comparing aqueous solutions.

Opposite effect is demonstrated by media with alcohol content above 30 vol. %. Polyelectrolyte-surfactant interaction becomes less active, so does the stability of associates. Concentration limits for association initiation shift to higher surfactant concentrations. Alcohol content above 60 vol. % is the area of substantially inhibited polyelectrolyte-surfactant interaction because of decreased dielectric permittivity and increased affinity of aqueous-alcohol solvents to nonpolar fragments of a polymer chain and surfactant molecules.

A correlation between self-organization processes in studied systems with structural characteristics of mixed solvents is discussed.

INTERACTION BETWEEN THE COMPONENTS IN LIQUID HETEROGENEOUS SYSTEM WITH PHOSPHORIC ACID

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Application of phosphoric acid in various sectors of the economy does not detract from attention to researchers from the standpoint of fundamental science. Physico-chemical methods studied for more than 30 systems of phosphoric acid - an organic component - non-aqueous solvent. The organic components were used different classes of organic substances.

The influence of various factors (temperature, concentration, environment, nature of the organic component) on the mutual solubility of substances in ternary liquid systems, as well as the strength of the resulting compounds of phosphoric acid with an organic reagent. The results allowed to determine the conditions for the formation of critical solutions of the highest order. Developed a method for determining the critical point of solubility of the highest order in multicomponent liquid systems. The method is based on the electrometric measurement systems, new liquid phase which is considered as the contact phase of the membrane properties. Found part of compounds of phosphoric acid in the formation of third liquid phase in the ternary liquid systems.

Investigated the permeability of the fourth component, calcium chloride, a new liquid phase in the system 2,6 - lutidine - water - heptane and in the phosphoric acid - m-cresol - n-octane.

The results can be compared with the transition through biological substances, in particular, the basal membrane, in which the process of hardening and thickening.

The experiment showed the presence of labile variable structure in the ternary systems, the formation of which involved the connection of phosphoric acid with an organic component.

The work was performed as part of training of scientific personnel of highest qualification:

- In the Tver State University (PhD, Scientific School prof. Krupatkin I.L., has long led the regional board of the WMO. Mendeleyev and awarded a medal for this work Mendeleev.
- The Bucharest Polytechnic Institute, Scientific School prof. Sternberg S.

PREPARATION OF OPTICALLY ACTIVE GLYCIDYL ACETATE

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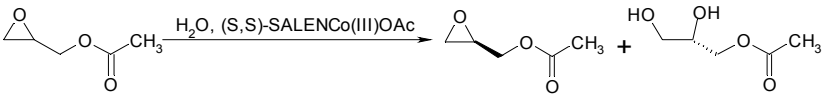
Lately great attention is paid to chiral synthons consisting of three carbons. A number of drugs and the most important natural substances contain chiral glycerol building block, for example, adrenoblockers, antiviral drugs such as cidofovir, lysophospholipides, MAO inhibitors and many others. Glycidyl acetate, chiral derivative of glycerol, is of high reaction activity, so it is very perspective for synthesis drugs, containing chiral three carbon fragment.

Nowadays the only method that allows to obtain optically active glycidyl acetate is acetylation of optically active glycidol [1], which is produced in several stages.

We have used the method of hydrolitic kinetic resolution [2] to develop simple way of obtaining optically active glycidyl acetate from the appropriate racemate.



By hydrolisys of the racevic sample with enantiopure (*S*,*S*)-salen complex of Co(III) we obtained product with 99% purity an 96% ee, based on the GC data. Optical rotation of the sample was -30.32° at 589 nm and 20°C (-29.37° at 22°C; lit. -29.9° at 22°C [1]). Despite high hydrolytic lability of acetic group, we haven't found the products of its hydrolysis in the reaction mass. The yield of (*R*)-glycidyl acetate was 60%.

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SYNTHESIS OF THE PARTIALLY HYDROGENATED NITROGEN-CONTAING HETEROCUCLES: HOW DOES RITTER-TYPE HETEROCYCLIZATION PROCEED?

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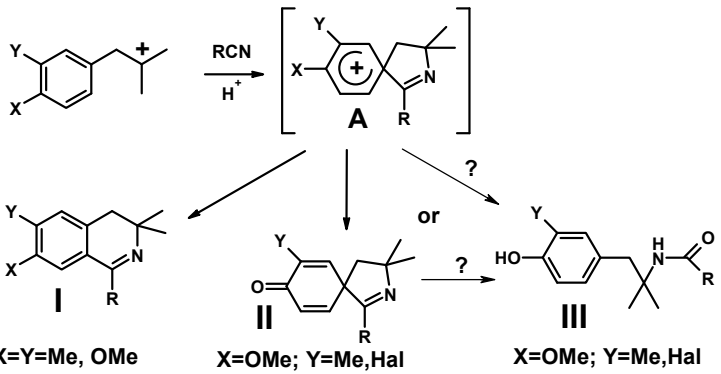
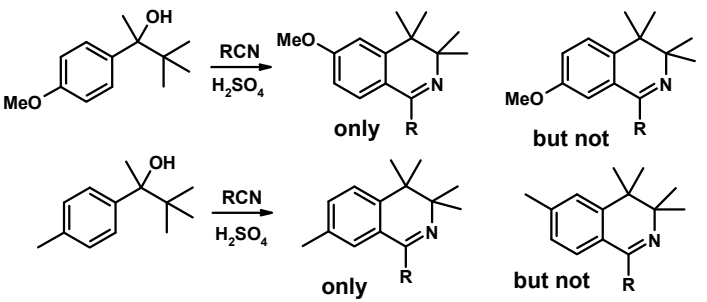
The report summarizes the author's works on synthesis of 3,4-dihydroisoquinolines (**I**), spiropyrrolines (**II**), polyhydroindoles (**IV**), neospiranes (**V**), polyhydrocarbazoles (**VI**) and classical products of Ritter reaction (**III**) as well. Basing on the obtained data there has been done an assumption that all the Ritter-type heterocyclizations proceed trough the *ipso*-σ-complex of **A**-type generation, the 1,2-sigmatropic shift in which results in isoquinolines **I** formation. Water addition to complex **A** produces spiropyrrolines **II**, the dienone-phenol rearrangement of which gives rise to amides **III**.



There has been demonstrated that carbenium-ion generation via retro-pinacolin rearrangtment completely excludes the possibility of spiropyrrolines **II** formation even for anisoles.



The work was financially supported by Russian Foundation for Basic Research (project no 10-03-00138), by RAS Presidium's programs (nos 18, 21) and by programs of collaboration between of the UB and SB RAS scientists.

SYNTHESIS OF MANNOSE-CONTAINING TARGETED MODULE AS THE STAGE IN THE DEVELOPMENT OF ANTINEOPLASTIC VACCINES ON THE BASIS OF DENDRITIC CELLS

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Anticancer vaccinotherapy is the medical and preventive method of specific immunotherapy which based on the using of tumoral antigens themselves or their complexes with an adjuvant for the augmentation of the antineoplastic immune response. Anticancer vaccinotherapy uses vaccines on the basis autologous or allogenic tumoral cells, synthetic polyvalent vaccines, dendritic cells, macrophages, B- lymphocyte, etc. Dedritic cells are a key of the immune response regulation and attract a great interest as a feasible adjuvant for immune therapy of various pathologies. The principal function of dendritic cells is the presentation of antigenes to T-cells, therefore they possess an ability to capture various antigenes from environment by means of phagocytosis, pinocytosis or receptor-mediated endocytosis.

At present the new approach named genetic immunization is developed. This approache allows to induce the immune response without the antigene introduction into organism by delivery of gene encoding antigenes. There are receptors on the surface of antigene-representing cells which recognize mannose resdues. Hence, mannose ligands can be used for targeting of genes on the dendritic cells. We carried out the synthesis of mannose-containing neutral amphiphile for liposomal delivery of nucleic acids into dendritic cells. The target compound consists of two functional domains; the lipidic "anchor" is represented by ditetradecylglycerol and the targeting ligand is represented by mannose residue. Both structural domains were connected by urethane, amide and glycoside linker through hexamethylene spacer groups.

Work is supported by ***Federal Program*** «***Scientific and pedagogical*** human resources for ***innovative Russia*** 2009-2013» (the state contract № P715) and the Russian Foundation for Basic Research (№ 09-03-00874-a).

ON THE ORIGIN OF DISSYMMETRY AND HOMOCHIRALITY OF NATURAL OBJECTS

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Understanding of surprising specificity and selectivity of the processes in wildlife is closely related with resolution of a problem concerning the origin of homochirality – one of the central problems of modern natural sciences. Carroll[1] believes rightly that originating life and originating homochirality is unified event.

In the present work existing hypotheses about the origin of homochirality of natural objects are critically analyzed and own approach to this problem is developed. It was shown that for creation of dissymmetric compounds two conditions are necessary: 1) dissymmetry of medium, vacuum, originating dissymmetry of fundamental particles; 2) translation of dissymmetry from nuclei to electron shells of the atoms, molecules, crystals etc. with its amplification. According to Shubnikov,[2] vacuum dissymmetry may be described by the dissymmetric group $\underline{\infty}/\infty$ with set of the infinite order anti-axes which are crossed in each point of vacuum and are the simple axes of the same order simultaneously. Mechanisms of the dissymmetry translation and amplification provide for magnetic spin effects, chiral radiation action, non-equilibrium and nonlinear effects at alias. Proposed approach is compared with Davankov views[3,4] included idea of chirality as inherent property of fundamental particles and photons.

On the examples of the ternary systems copper(II) – oligopeptide – *D*/*L*-histidine the dissymmetry influence of the coiled conformations of the di- and tripeptides on the complex formation stereoselectivity is demonstrated. Important role of metal-coordination in amplification of the enantiomer enrichment of primary set of amino acids in the process of the prebiotic evolution was revealed.

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METALLOCENES IN COMPLEX-RADICAL POLYMERIZATION OF VINYL MONOMERS

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Polymerization studying of vinyl monomers (styrene and methyl methacrylate) shows that in the presence of metallocene Cp_2Fe, $(C_5Me_5)_2Fe$, $(CH_3COO)_2Fe$, Cp_2ZrCl_2, Cp_2TiCl_2 and $(C_5Me_5)_2ZrCl_2$ with benzoyl peroxide or azoisobutylnitrile (AIBN) affects the rate of polymerization , the yield of stereoregular polymer smoothing gel-effects, as well as the conversion depending curves of molecular weights and MWD curves. In the presence of metallocene observed the effect of prolonged postpolimerization. After a brief UV irradiation the polymerization process proceeds until the complete consumption of monomer, containing small amounts of metallocene. Polymer is formed as a result is able to initiate polymerization of a new portion of monomer. These facts shows that the general role of metallocenes associated with participation in the formation of radical centers, which not only initiate the polymerization (along with free radical), but also participate in the stage of the chain growing, as a result is smoothing the of the gel-effect. So, it is creates an opportunity to participate several types of active centers (free and complex-bound) in the polymerization. They are differ kinetic parameters of propagation and limitation the chain, called the kinetic heterogeneity of active centers. This fact is confirmed by computer calculation solving of the inverse task of MWD. The kinetic heterogeneity calculated by the method of Tikhonov regularization. Obtained distribution curves for the kinetic heterogeneity had two peaks corresponding two types of active centers.

Obtained data allows us to managing polymerization not only in terms of its kinetics, but also, and most importantly - control the molecular characteristics of and consequently the properties of polymers.

This work was supported by the Federal Program " **Research** and **Pedagogical Cadre** for **Innovative Russia** " (project № 02.740.11.0648).

SYNTHESIS OF TRANSITION *D*-METALS COMPLEXES WITH 5,15-BIS(DIETHOXYPHOSPHORYL)-10,20-BIS(*P*-CARBOXYMETHYL) PHENYLPORPHYRIN

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Phosphonate and carboxylic groups are attractive as peripheral functional groups in porphyrins because they can form strong metal-ligand coordination and hydrogen bonds. Simultaneous attachment of both groups to porphyrin molecule is a promising way towards coordination polymers.

In current work we obtained new complexes of 5,15-bis(diethoxyphosphoryl)-10,20-bis(*p*-carboxymethyl)phenylporphyrin with transition *d*-metals Cu(II), Cd(II) and Ni(II). All compounds were synthesized by the reaction between free-base porphyrin and salt of corresponding metal. Copper (II) and cadmium (II) complexes were obtained at room temperature in the solvent mixture $CHCl_3$-MeOH using acetates. Nickel (II) complex was synthesized by refluxing in 1,2-dichlorobenzene using nickel acetylacetonate.

M=Cu(II), X=OAc, $CHCl_3$-MeOH, RT, τ=50 min, η=87%
M=Cd(II), X=OAc, $CHCl_3$-MeOH, RT, τ=2h 20min, η=47%
M=Ni(II), X=acac, DCB, 180^{0}C, τ=5 min, η=99%

All new complexes were characterized by means of physicochemical methods: UV-vis spectroscopy, ^{1}H, ^{31}P NMR-spectroscopy. Based on the results of this work we found out the influence of metal nature on the conditions of formation of complexes with 5,15-bis(diethoxyphosphoryl)-10,20-bis(*p*-carboxymethyl)phenylporphyrin.

This work was performed in the framework of French-Russian Associated Laboratory "LAMREM" supported by ARCUS 2007 Burgundy-Russia project, Russian Foundation for Basic Research, the CNRS and Russian Academy of Sciences.

NEW EFFECTIVE INHIBITORS FOR CARBON DIOXIDE AND HYDORGEN DISULFIDE CORROSION BASED ON ELEMENTAL PHOSPHORUS AND SULFUR, INDUSTRIAL ALCOHOLS AND AMINES

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Corrosion of oil field equipment in various types of hostile environment is a grand problem in oil and gas field deposits exploitation. One of the most effective ways of protection of mild steel from corrosion is the use of corrosion inhibitors. Despite a number of inhibitors are already available now, the range of reagents, which would effectively solve the problem of steel protection in corrosion fluids containing both hydrogen sulfide and carbon dioxide, is rather limited, so the development of new efficient and versatile inhibitors for hydrogen sulfide and carbon dioxide steel corrosion is an actual problem.

New ammonium salts of O,O'-dialkylditiophosphoric acids were synthesized on the basis of available materials: substituted alkylene glycols and monohydric alcohols (ROH, where R = *i*-Bu, *i*-Oct, *i*-$C_{12\text{-}14}H_{25\text{-}29}$, *i*-$C_9H_{19}C_6H_4$, *i*-$C_9H_{19}C_6H_4(OCH_2CH_2)_n$), various amines ($NEt_3$, $C_{12}H_{25}NH_2$, $Me_2NC_{12\text{-}14}H_{25\text{-}29}$, $H_2NCH_2CH_2OH$, $HN(CH_2CH_2OH)_2$, $N(CH_2CH_2OH)_3$), elemental phosphorus (P_4) and sulfur.

$$(RO)_2P(S)\bar{S}\ \overset{+}{H}NR'R''_2$$

The obtained compounds demonstrate high inhibiting properties to carbon dioxide and hydrogen sulfide corrosion of steel (over 90%) in a wide range of operating temperatures (30 - 80 ^oC), their effectiveness being as that of the basic range of domestic and imported reagents. At present time, the works on the optimization of marketable forms of reagents based on the obtained compounds as well as bench testing of inhibitors in different oilfields in Russia and CIS are in progress.

Financial support from Russian Foundation for Basic Research (grants no. 09-03-00006-a, 08-03-12004 ofi) is gratefully acknowledged.

SYNTHESIS OF C2′-β-FLUORO-SUBSTITUTED NUCLEOSIDES

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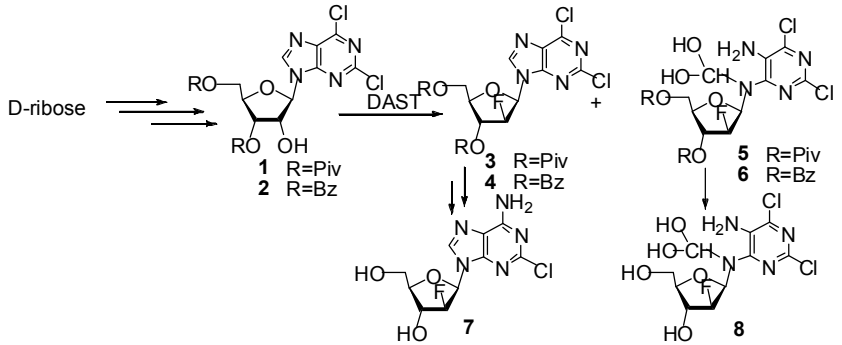
Nucleosides bearing fluorine at C-2′ possess chemical and metabolic stability and display different biological activity.[1] C2′-β-Fluoro purine nucleosides are of special interest as chemotherapeutic agents.[1-2]



With the aim of preparation of anticancer agent clofarabine 7, the approach to the synthesis of C2′-β-fluoro-substituted purine nucleosides 3-4 was studied via the DAST fluorination of 3′,5′-di-O-acyl derivatives of 2,6-dichloropurine β-D-riboside 1-2 prepared from D-ribose. Under fluorination it was established that modification of heterocyclic base of nucleosides 3-4 takes place with the formation of pyrimidine nucleosides 5-6 as the result of a by-side reaction.

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SPECTRAL CHANGES IN HEMOGLOBIN INDUCED BY SECONDARY PRODUCTS OF LIPID PEROXIDATION

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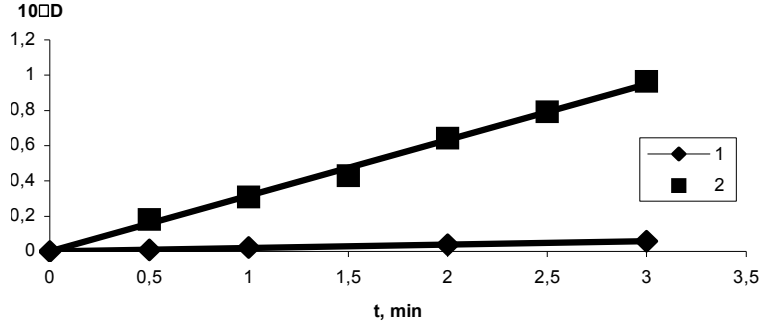
It is known that destruction of oleic acid under UV-light might cause appearance of c_9-derivatives (aldehyde, acid) and azeloil derivatives of phosphatidylcholine (PC) as secondary products of lipid peroxidation, both of them being able to convert hemoglobin to hemichrom [2].

We have previously shown that the native PC does not affect the spectral properties of hemoglobin [1]. However it is also known, that up to 60% in the second position of PC glycerol skeleton is represented by oleic acid.

Therefore, the aim of the present work is to study spectral changes in hemoglobin induced by UV-radiated PC (the source of UV-radiation - mercury-quartz lamp PRK-4 with the radiation range 180-400 nm). The lipid peroxidation (LPO) extent was assessed by determination of accumulated malondialdehyde (MDA) using thiobarbituric acid test.

The kinetics of the interaction of hemoglobin with mixed micelles of PC and sodium deoxycholate, DOC (1:3, mol/mol) (1) and PC, passed UV-radiation during 60 min are shown at figure (2).



Thus, UV-radiation of PC for an hour can instigate hemoglobin-hemichrome transition. By observing the spectral changes in hemoprotein it is possible to detect the generation of lipid peroxidation products and thus characterize the extent of oxidation of the lipid phase.

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DETERMINATION OF SERUM ANTIOXIDANT POTENTIAL USING LIPID PHASE

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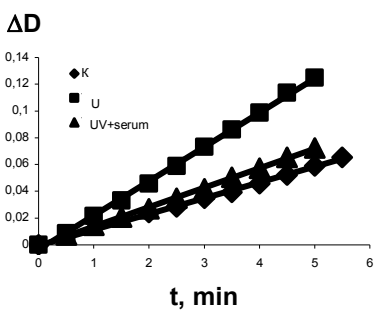
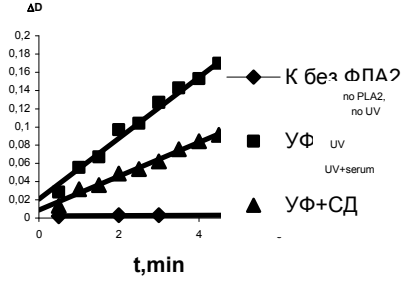
Individual components of the blood total antioxidant system are distributed between the aqueous and lipid phases. Utilization of the products of membranes lipid peroxidation (LPO) is performed by phospholipase A_2 (PLA_2) and glutathione peroxidase. It is known that phospholipids containing hydroperoxide fatty acid residues are more preferable substrates for PLA_2 than normal non-oxidized phospholipids [1], and consequently, changes in the activity of this enzyme towards the LPO-modified substrate, will indicate both on the intensity of LPO and an antioxidant effect of the tested sample (donor serum, for example).

UV-radiation micelle phase of the substrate was chosen as a factor causing lipid peroxidation. A mercury-quartz lamp PRK-4 and the radiation range 180-400 nm were used. Changes in enzyme activity were monitored in kinetic mode using hemoprotein method [1] by recording spectral changes in hemoglobin at the Soret band under the influence of phospholipolysis products.





The kinetic curves obtained during the control PLA_2-reaction towards mixed micelles of phosphatidylcholine and deoxycholate, on UV-radiated micelles, and UV- radiated ones in the presence of serum of a healthy donor (a) are shown in the figure. Kinetics of interaction of methemoglobin with radiated and un-radiated micelles PC-DOC (1:3, mol/mol) in the absence of PLA2 (b) are also shown.

To quantify the antioxidant potential of biological liquids, we used water-soluble analogue of tocopherol (vitamin E) - trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid). The antioxidant capacity of serum in terms of trolox was determined from the calibration curve.

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INFORMATION AS STATISTIC THERMODYNAMIC FUNCTION RESEARCHES OF AQUEOUS SYSTEMS

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Law of energy conservation has different forms. Any system has such properties as an order and randomness, this give the way to express the total energy (E_{tot}) as a sum of the organized motion energy (E_{org}) and the chaotic form energy (E_{chaos}):

$$E_{tot} = E_{org} + E_{chaos}$$

Quantitative characteristic of the system randomness is a statistic thermodynamic function *entropy S. Information I* is proposed as a statistic thermodynamic function, which is corresponded to the system order. The value of the system information can be calculated as $\Delta I=\Delta G/T= E_{org}/T$ (p,T=const), where G is free energy on Gibbs, or $\Delta I=\Delta F/T= E_{org}/T$ (V,T=const), where F is free energy on Helmholtz.

It is correctly for stationary state:

$$I + S \geq \text{const, or } \Delta I + \Delta S \geq 0$$

Entropy-informational process is a spontaneous change of system stationary state to other one, accompanied by the change of a level of organizing (I/S), which is resulted from a conjugated displacement of internal energy (U) between U_{org} and U_{chaos}, initiated by definite value of an intensive parameter (p, T, c) or a weak physical fields, at approximately the same value of total internal energy ($\Delta U\approx 0$).

Self-organizing as well as self-destruction is typical for water, so the method proposed in our work can be effectively applied to the investigation of different aqueous systems.

Water is an open, dynamic, irreversible, structurally differentiated, polyvibrating supra-molecular system, which has the intermolecular continuum of a hydrogen bond unite network.

Entropy-informational processes in an aqueous systems are the base for a reagentless change of acid-base, also redox and comlexiting properties of water. These phenomena are resulted from formation of a clathrate of water molecules, also its ions and radicals. Given reactions are the reasons of self-purification of water (real or pseudo).

DESIGN OF MOLECULES AND CRYSTAL STRUCTURES

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In present investigation a new approach for a design of system of chemical bonds in molecules and crystals – geometric conception of chemical bond (GCCB) - have been used. In GCCB the term „chemical bond“, the shape of atoms and a relative dimensions of valent orbits of atoms are determinated strictly in initial postulates that allow to obtain a full collection all possible valence configurations of atom. This configurations of excited atoms and use as elements for design of crystal structures.

Design of structure of chemical bonds in anorganic and organic molecules, in which the interpretation of the chemical bonds between atoms is discussing (O2, CO, Be2Cl4, B2H6, IF7, [Be(CH3)2]n, allene, cyclopropane, benzene, isomers and homologues of benzene, graphene, etc.), has been realized.

By using the models of crystal structures the phenomenon of polymorphism in the simple substances under temperature and high pressure has been investigated. As rule, the polymorphic transition is escorted by the change of the type and the structure of chemical bonds in crystal frame. The peculiarities of polymorphism in berillium, cerium, carbon, alkaly and rare-earth metals have been examined.

Models of systems of chemical bonds in based structural types of ionic compounds (NaCl, CsCl, ZnS, NiAs, CaF2, Na3As, TiO2, CaTiO3, Al2MgO4 and outhers) have been created. Analysis of the models is show that each structural type consists of a few subtypes with different systems of chemical bonds. Each system of chemical bonds is characterizing by a single relation of radii of cations and anions. Models allow to calculate the real ionic radii of atoms strictly from the parameters of crystal structure. The polymorphic transitions in ionic compounds are connected with the change of valent state of anions (electronic excitation ↔ orbital excitation). If this transition isn't full, politypes of this structure form.

Analogous investigations for widely-distributed structural types intermetallic compounds ((Cr3Si, CsCl, MgCu2, MgNi2, MgZn2, CaCu5, CaB6 и др.).

This suggested approach can be used both in chemical education and for solution of scientific problems in chemistry and material sciense.

FLUORINE-CONTAINING 1,4- AND 1,5-BISELECTROPHILIC REAGENTS FROM ACYLIMINES OF HEXAFLUOROACETONE AND METHYLTRIFLUOROPYRUVATE

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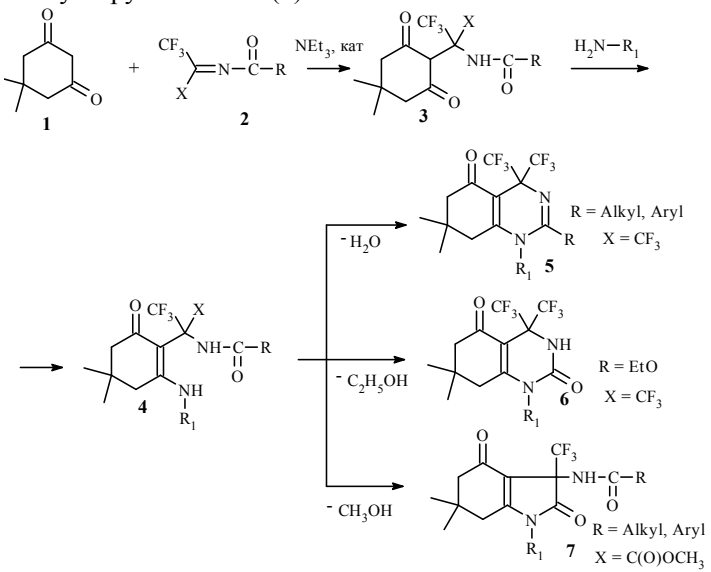
We have obtained a sufficiently large number of examples[1-3] of the cyclocondensation reactions of N-acylimines (2) of hexafluoroacetone and methyltrifluoropyruvate) allowed to propose a new approach to the synthesis of trifluoromethyl-containing five- and six-membered heterocycles.

Based on the dimedone (**1**) and N-acylimines (**2**) we have obtained previously unknown 1,4- and 1,5-biselectrophylic reagents - 1-substituted N-(2,6-dioxocyclohexyl)-2,2,2-trifluoroethylamides (3) and studied their transformations in cyclocondensation reactions with primary amines, which, depending on the nature of N-acylimines lead to three types of heterocycles: 1,4-dihydropyrimidines (**5**), 1,,4-dihydropyrimidinones (**6**), and 1,3-dihydropyrrol-2-ones (**7**):



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NEW APPROACH TO MOLECULAR DESIGN OF FLUORINE-CONTAINING FIVE-MEMBERED AZAHETEROCYCLIC SYSTEMS

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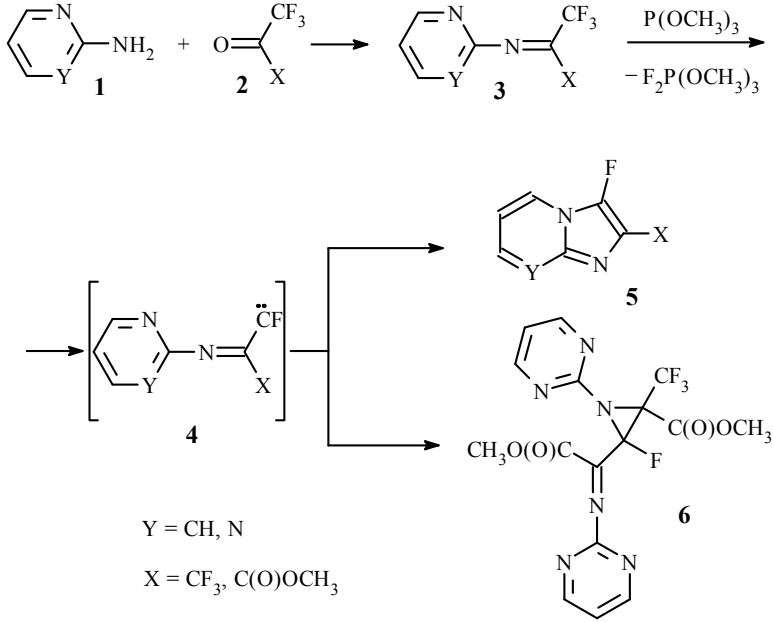
The purpose of this study was the molecular design of new fluorine-containing five-membered azaheterocyclic systems based on systematic investigation of cyclodefluorination N-heterylimines of methyltrifluoropyruvate and hexafluoroacetone by generation of carbenoid systems with trialkylphosphites as defluorinating agents.



Depending on the nature of the N-heterylimine and condition of the reaction, condensed fluoroimidazoles **5** or substituted fluoroaziridines **6** (at 0 ^{o}C) are formed. Structures of compounds obtained were proved by NMR and mass-spectrometry and confirmed by chemical transformations.

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SPECTRAL STUDIES OF SUPRAMOLECULAR INTERACTIONS OF ANTIRADIKALS AND BIOPOLYMERS AND THEIR COUPLED OXIDATION REACTIONS

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Serum albumins are the most abundant proteins in blood plasma. One of the most important biological functions of albumin is their ability to transport drugs, endogenous and exogenous substances. This fact may be useful in drug design. Previously it was shown that decay product of heme bile pigment bilirubin in addition to toxic effects is one of the most important antioxidants in organism. The results of our studies [1] show that the binding of bilirubin to albumin leads to a decrease of antiradical activity and its manifestation of the «protein protection». It is also shown that the manifestation of antiradical activity of some substances such as ascorbic acid, hydroquinone and *meso*-tetrakis (*p*-sulfophenyl)porphin in coupled oxidation reactions of bilirubin is closely linked with the formation of supramolecular complexes with the protein. Thus, the supramolecular interaction of antiradicals and biopolymers largely determine the antiradical activity. In this paper studies of the supramolecular interactions of antiradicals and biopolymers, including the coupled oxidation reactions on the example of a number of antioxidants with albumin were considered. Spectral studies allowed us to determine the mechanism of oxidation reactions, to identify a number of thermodynamic and kinetic characteristics of the interaction reactions of antioxidants, biopolymers, and oxidants. More details are presented in the report.

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This work was (partially) supported by a grant of the President of the Russian Federation for young Russian scientists - candidates of sciences (№ МК-401.2011.3) and the Federal Program "Research and scientific-pedagogical cadres for Innovative Russia" for 2009-2013 (State contract № 14.740.11.0617).

CHEMICAL SYNTHESIS OF DIAMOND FROM ACTIVATED GAS MEDIA

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Diamond application in the scientific and industrial practice for a long time was hampered by its limited natural resources, as well as by technical difficulties in the synthesis at ultrahigh pressures. And it is not surprising that the problem of diamond's synthesizing at low pressure, using concepts and techniques of chemistry, physics and physical chemistry, remains vital. That is why totally new methods of diamond synthesis in the field of its thermodynamic metastability have been proposed and developed by researchers of the Institute for Physical Chemistry and Electrochemistry RAS (formerly - Institute for Physical Chemistry of the USSR Academy of Sciences). In this area, our science has the absolute world priority. The report will give a brief overview of the results on thermal and electrical activation of carbon-containing gas media for the synthesis of diamond nanocrystals and diamond films (DF) and its thick layers on diamond and nondiamond substrates at (300 - 1600) ^{o}C and pressures (10^{-2} - 1) atm. The consideration of the general laws of kinetics of the diamond activated chemical crystallization indicates the priority of the reactions involving the radicals - at a low temperature and a combination of molecular and radical steps - at elevated temperatures[1]. Particular attention will be paid to the deposition of semiconductor DF with n-type conductivity and combined methods of activating the gaseous phase, allowing to increase markedly (by 2 or 3 times) the DF growth rate, while preserving their crystalline perfection. The examples of effective CVD diamond applications in the traditional and new technology will be given. The combination of new methods for chemical synthesis of diamond with the traditional ones permits to overpass significantly some diamond's properties, limited by Nature and to create a kind of "superdiamond"[1]. In conclusion, we consider a number of theoretical and experimental challenges on the roadmap towards to realizing the full potential of the chemical synthesis of diamond. The partial support from Presidium RAS Program №7P(2) highly appreciated.

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THE SYNTHESIS OF WATER SOLUBLE POLYQUANIDINES AND PH- SENSIBLE HYDROGELS BASED ON THEM

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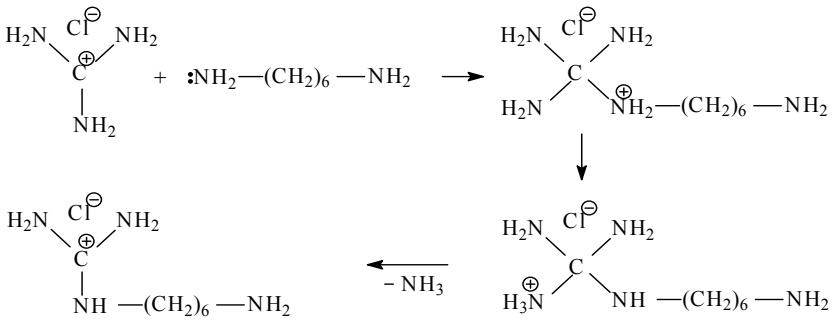
Polyguanidines is cationic polyelectrolytes spitted into polycation and low-molecular anion in water solutions.[1] The most prevalent polyguanidine is the water-soluble polyhexamethyleneguanidine hydrochloride (PHMQhc) which produces as the result of melt polycondensation of hexamethylenediamine (HMDA) and guanidine hydrochloride (QHC).

Polycondensation of HMDA and QHC represents transamination reaction and realizes as nucleophilic substitution mechanism.[2]



Since QHC is three-functional monomer the formation of cross-linked polymer (gel) swelling well in water is possible. Hydrogels based on PHMQhc was obtained by us and the susceptibility of such gels to hydrogen ion exponent was shown for the first time. The overall equilibrium swelling index observed in neutral and weak-acid medium. The most evident change of gels volume was observed in pH interval from 1 to 3. Full contraction observed in strong acid medium with pH-interval from -1 to 0. It is necessary to mark that process of swell/contraction is reversible process.

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ANISOMETRIC STRUCTURES IN LOW-DIMENTIONAL ORGANIC AND BIOORGANIC SOLUTIONS

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Solutions of many low-molecular organic substances (first of all chiral) such as fluoro-substituted aminoalcohols etc. gelate by concentration of 10^{-3} g/g in nonpolar solvent. This is three times less than the percolation threshold concentration, corresponding to formation of the 3D isotropic unlimited cluster of bounds providing the phase transition in the isometric phase.

We have found that gel-like substance is a solvent reinforced by strings – irregular system of significantly anisometric objects with thickness of less than microne and length of millimeters and even centimeters.

The matter in the strings phase is anisotropic, densely packed. The beginning point of the transformation into string phase is a concentration level at which the visible mist appears and rearranges the circular dichroism spectra. This stage is a process of growth of strings taking some seconds or minutes. Process is finished when the equilibrium between the two phases –phase of solution and phase of strings is set up.

Thermodynamic and kinetic calculations show that time of the thermal separation of solute molecules from the end of the string is of $\tau \sim 10^{-7}$ sec and from her side is of τ *> 10^{-2} sec. Hence we obtain the binding energy of the molecule at the end of U ~ (0.3-0.4) eV, and on the lateral surface of the string of U *> 0.6 eV. Molecules of many of the compounds can be regarded as fitting into stack, that forms spiral string. Binding energy on each side of such a molecule is estimated at (0.3-0.4) eV. that ensures stability of the phase of strings. We have shown the existence of such strings in the polar aqueous solutions of phenylalanine and other bioorganic compounds. We discuss the possible important role of such bio-evolutionary processes of anisometric structures in the formation of biological systems.

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THE THEORETICAL SUBSTANTITATION OF THE MOLAR RATIO OF THE SYSTEM OF POLYPROPYLENE CARBONATE-LITHIUM PERCHLORATE USING POLE SYSTEM

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For the development of the new solid lithium conducting electrolytes it is necessary to choose the ratio of polypropylene carbonate –lithium perchlorate, at which the maximum specific electrical conductivity is observed.

According to the theory of the pole systems, each ionized pole axis may split into several under- axis, those numbers is determined by the energy state of the system and the pole core elements involved in the formation of the system of polypropylene carbonate –lithium perchlorate [1].

The conductivity of pole models is determined by the ratio of polar and electrons conductivities.

With the ratio $[CO_3] : [Li^+] = 10:1$ we observe the contacts of all carbonate groups with the ten pole under-axis, which provides the maximum pole conductivity of the structure. A decrease in the number of carbonate groups the pole under-axis remains free, which reduces the conductivity. With increase of carbonate groups of more than ten the conductivity will also decrease.

These data are confirmed by the experimental studies, reported in the work [2].

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SURFACE PROPERTIES OF AQUEOUS SOLUTIONS BINARY MIXES SURFACTANTS OF THE VARIOUS NATURE

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Last decades the attention of many researchers is involved in studying colloid-chemical properties of water solutions of mixes of surfactants. Theoretical and practical interest to such systems is caused by that mixes of surfactants frequently possess the properties which are sharply distinct from properties of components making them. It allows using effectively them for management of the processes proceeding in disperse systems (adsorption, wetting, flotation, solubilization, etc.).

The present message is devoted to the description and a prediction of properties of solutions of mixes ionic peahens of different type with non-ionic peahens (dodecylsulfate sodium (DDSS) with the Twin - 40 (hydroxyethyl monopalmitate of sorbitan) and with the Twin - 60 (hydroxyethyl monostearate of sorbitan); dodecylpyridinium chloride (DDPC) with the Twin - 40 and with the Twin - 60) within the framework of model of pseudo-phase division. The known approach of the Ruby - Rosen leaning on the data of measurements of a superficial tension of individual peahens and their mixes is applied. The approach allows analyzing quantitatively structure and thermodynamic characteristics mixed адсорбционных layers on border of the unit of phases a solution - air in systems of binary mixes of peahens.

The researches of superficial properties of water solutions of binary mixes of Twins lead by us with cationic and anionic surfactants have shown that components of mixes basically show synergism a superficial tension on border of the unit of phases a solution - air. Thus the effect depends by nature ionic surfactants and is maximal for the diluted solutions of mixes DDPC - Tween 20. Calculation of structure aadsorption layers has shown that at the big maintenance ionic surfactants the mixed layers of the structure close to equimolar are formed. At all other parities of components in a solution are formed aadsorption layers enriched with Twins, having the big superficial activity. In mixed adsorption layers of value of parameter of intermolecular interaction are negative and depend by nature polar group of surfactants and length of a hydrocarbonic radical in a molecule of the Twin. It testifies to an attraction of molecules (ions) on border a solution - air which is more for a mix the DDSS-Tween. Dependences of parameter of interaction and free energy of the Gibbs of adsorption from mole shares ionic surfactants in a solution carry simbat character.

ELECTROSORPTION OF INORGANIC CATIONS ON ACTIVATED CARBONS

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The use of activated carbons in sorption processes is caused by their chemical resistance, low prices and possibility to obtain materials with wide spectrum of physicochemical (including adsorptive) properties. The high electroconductivity makes possible to introduce electric potential as additional factor for increasing sorption capacity and selectivity of carbon materials.

The use of polarized carbon materials for extraction important components from natural and waste waters offers the promise. The results of investigations done at Laboratory of the thermal waters physico-chemistry of Institute for Geothermal Problems of DSC RAS over a period of several years are presented in this work. These investigations are directed at the development of scientific fundamentals of electrosorption method of inorganic ions extraction from aqueous solution by activated carbons.

Activated carbons (KM-2. OKM-2, FKM-2. sulphocoal) having the different amounts of acidic surface functional groups were used as sorbents. Cations of alkali (Li^+, Rb^+, Cs^+) and alkali-earth (Ca^{2+}, Sr^{2+}, Ba^{2+}) metals has been the subject of investigation. The studies show that all cations (except for Li^+) are adsorbed by cathodic as well as anodic polarization.

The linkage between the sorption value of inorganic ions and carbon surface chemistry is established. The optimal conditions (solution pH, ion concentration, temperature, current density) of the studied ions electrosorption are determined. The kinetic regularities and mechanism of the alkali and alkali-earth metal ions electrosorption on different activated carbons are established. It is shown that polarization of activated carbons increases its sorption capacity with respect to the studied ions and makes possible the selective removal of solution individual compounds.

The study is supported by RFBR (grants 09-03-95506 r_yug_a, 09-03-96509 r_yug_a) and MON (Government Contract 14.740.11.0803).

Experiments are carried out by using the instrumentation of Analytical Centre for Collective Use of Daghestan Scientific Centre of Russian Academy of Science

PHOTOINITIATED CONTROLLED RADICAL POLYMERIZATION OF VINYL ACETATE IN THE PRESENCE OF COBALT (II, III) COMPLEXES

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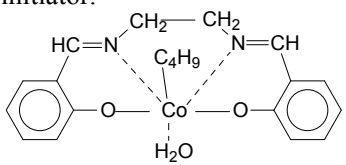
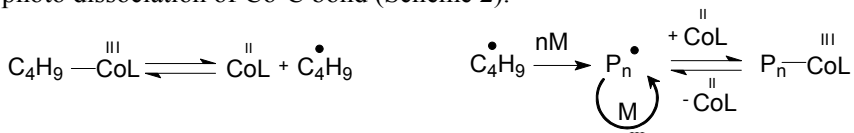
Organocobalt compounds are known to provide the controlled polymerization of vinyl acetate (VAc) (process CMRP - Cobalt Mediated Radical Polymerization)[1]. Commonly, the low-temperature azo-initiator is used as the source of free radicals. However, it is difficult to stock up and requires special storage conditions. This paper reports on the controlled radical polymerization of VAc photo initiated and mediated by complex C_4H_9-Co^{III}(salen)H_2O (salen – salicylidene ethylenediamine, Scheme 1), in order to exclude an external initiator.



Scheme 1. Complex C_4H_9-Co^{III}(salen)H_2O

Free radicals and mediator (compex CoII(salen)) are formed in a course of photo dissociation of Co-C bond (Scheme 2).



Scheme 2. L - salen; M - monomer; $P_n^{\bullet}$ - growing radical; P_n–$Co^{III}L$ - «dormant» chain.

The polymerization was carried out under irradiation of light with a wavelength of 320-500 nm. Special irradiation conditions were used to prevent side reactions. Typical symptoms of living/controlled polymerization were observed such as linear increase in molecular weight with monomer conversion. The process was investigated up to value of monomer conversion 15%. Molecular weight and polydispersity of polymer were found to be M_n=20000-60000 and M_w/M_n=1,2-1,3. «Dormant» chains were also obtained in a course of photo irradiation of VAc in the presence of complex Co^{II}(salen). This fact is in correspondence with the mechanism proposed.

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EXOTIC ORBITAL AND ATOMIC ORDERING IN SPINELS: EXAMPLE $MgTi_2O_4$

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It is theoretically shown that the structure of the tetragonal phase $MgTi_2O_4$ contains metal pico-and nanoclusters: two types of dimers Ti_2, two types of helices along the axis of the second and fourth-order of tetragonal cell and two types of one-dimensional infinite strands of titanium ions. Such unusual structural features of magnesium titanite arise due to atomic and d-orbital ordering.

A theory of structural phase transition in $MgTi_2O_4$ is presented: the symmetry of the order parameter, thermodynamics and mechanisms of formation of atomic and orbital structure of the low-symmetry phase $MgTi_2O_4$ are studied. The critical order parameter, which induces a phase transition, has been stated; it is shown that the calculated structure of the tetragonal phase $MgTi_2O_4$ is formed as a result of the displacements of magnesium, titanium and oxygen, the ordering of oxygen atoms, ordering d_{xy}, d_{xz}, d_{yz} – orbitals; it is proved that the contribution of non-critical representation in the ions displacements is insignificant. In the framework of the sixth degree of the components of the order parameter of the Landau theory the possible phase diagram is constructed and it is shown that the changes of phase states can be carried out as a result of phase transitions of second and first order: high-symmetry phase borders with two low-symmetry phases along the lines of transitions of second order, and the border between low-symmetry phases is the line of the phase transitions of first order.

A NEW EFFICIENT SYNTHESIS OF 2,3-BICHROMONE

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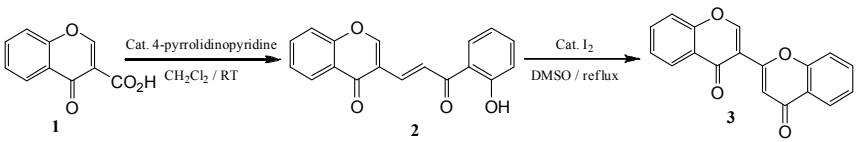
The first and the unique organic synthesis of the direct *C2—C3* bridged bichromone was achieved in 1988,[1] however, the reported synthetic strategy involves several steps and was obtained in low yield. Also, very poor data on bichromones are cited in literature.[2-4] Moreover, the biological spectra of the title compound and other synthetic bichromones is still being unknown, as a matter of fact, researches in both organic synthetic and biological activity issues should be encouraged.



An efficient "two steps" synthetic route is developed based on a one-pot decarboxylation and dimerisation of 3-chromone-carboxylic acid **1**, under basic catalysis with 4-pyrrolidinopyridine to afford (*E*)-3-(3-(2-hydroxyphenyl)-3-oxoprop-1-en-1-yl)-4*H*-chromen-4-one **2** (61%), which was then cyclised to 2,3-bichromone **3** by using the reagent system I_2(cat.) / DMSO (yield 57%). Structural characterization of all the products was established on the base of 1D and 2D NMR, MS and elemental analysis techniques.

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This work is realized within the Marie Curie ITN project, (European Community's) Seventh Framework Programme (FP7/2007-20139) under grant agreement nº 215009. The financial support from the Portuguese Foundation for Science and Technology FCT and FEDER and also from the University of Aveiro to the Organic Chemistry Research Unit is also acknowledged.

DEVELOPMENT OF THEORETICAL MODEL OF IONS MOBILITY AND ISOMORPHISM OF TRANSFER PROCESS IN ELECTROLYTE SOLUTIONS

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Dissociation of any electrolyte into ions and recombination in the neutral molecule (or in some cases - in associates) occur at a certain speed U_1 (straight) and U_2 (the reverse reaction):

$$KtA \leftrightarrow Kt_s^+ + A_s^- \qquad (a)$$

At a fixed concentration KtA, the average length of free run of solvated ions Kt_s^+ and A_s^- is finite, their movement is finite, it occurs in the vibrational mode, and has limit cycles with velocities U_1 and U_2.

Speed of motion of the solvated ions is given by

$$U = [(2/\mu_s)(C_v T - 2e\varphi)]^{1/2} \cdot \alpha \cdot f,$$

and the ion mobility is represented by the formula

$$b = U/F = U/eE = \frac{Z_{Kt} Z_{An} e^2}{4\varepsilon \Delta H^2} [\frac{2}{\mu_S}(C_V T - 2e\varphi)]^{1/2} \alpha \cdot \exp(-e\varphi / k_B T), \qquad (1)$$

where μ_s is reduced mass of the solvated ions; α is a degree of dissociation of the electrolyte; f is Maxwell distribution of velocities; ε is the dielectric constant of the solvent, ΔH *is* the energy of hydrogen bonds in the molecules of the solvent, E is the external field for the force acting on test charge from the self-consistent field the other ions; eφ is energy particle interactions.

Let's examine the dissipative processes (transfer processes) in solutions of electrolytes:

$$\lambda = Fb\,,\ \eta = 1/6\pi r_s b\,,\ D = k_B T b\,,\ \chi = C_V / 6\pi r_s M b \qquad (2)$$

It is obvious that all the equations of transfer processes (electrical conductivity λ, the viscosity η, the diffusion coefficient D, thermal conductivity χ) include mobility and they are isomorphic:

$$b = \lambda / F = D / k_B T = 1/6\pi r_s \eta = C_V / 6\pi r_s M \chi$$

Thus, the equation of the ion mobility in solutions of strong and weak electrolytes acceptable for transfer processes (viscosity, diffusion and electrical conductivity) is worked out. In view of equations (1), (2) and the Debye screening parameter transfer properties of electrolytes in the concentration range 0 ... 4-5 mol/l in a wide temperature range without introducing any corrective options are calculated.

EXPERIMENTAL DEFINITION OF ORIGIN AND GROWTH RATES OF CENTERS OF PHASE TRANSFORMATIONS AT CRYSTALLIZATION AND COOLING OF HIGH-TEMPERATURE MELTS OF INORGANIC SALTS

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Improvement of industrial technologies of hardening and granulation of inorganic substances melts (fertilizers, alkali, sulfur and etc.) can be possible on basis of reliable information about transport phenomenon and crystallization and polymorphic transitions kinetics.

Using introduced universal method of definition of origin and growth of crystallization centers and polymorphic transition rates these parameters were obtained experimentally for the cases of KNO_3, NaOH, KOH melt crystallization and $\beta \rightarrow \alpha$ polymorphic transitions in their crystal phase. These kinetic depends from supercooling on interface are defined experimentally in the comparable conditions at the formation and growth of single crystals (on the special framed for these aims experimental installation) and in polycrystalline layer.

In practice, in the calculation of process in crystallization (granulation) equipment it's necessary to use kinetic parameters which have been obtained for the restricted conditions of process. In the study of origin and growth mechanisms of crystallization centers and polymorphic transitions and in evaluating of difficult-defined physical and chemical parameters, such as surface energy on the phase boundary and interface activation energy, what has been done in the work for KOH, NaOH, KNO_3 it's necessary to use kinetic parameters, which have been resulted for single-crystals. The work is a stage of development of energy-efficient, ecologically safe technology of granulated inorganic compounds production (including such large-tonnage products as KOH, NaOH, and KNO_3) by crystallization of their high-temperature melts drops.

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SYNTHESIS OF POTENTIAL RECEPTOR SYSTEMS BASED ON 2,2',7,7'-TETRAHYDROXYDINAPHTHYLMETHANE

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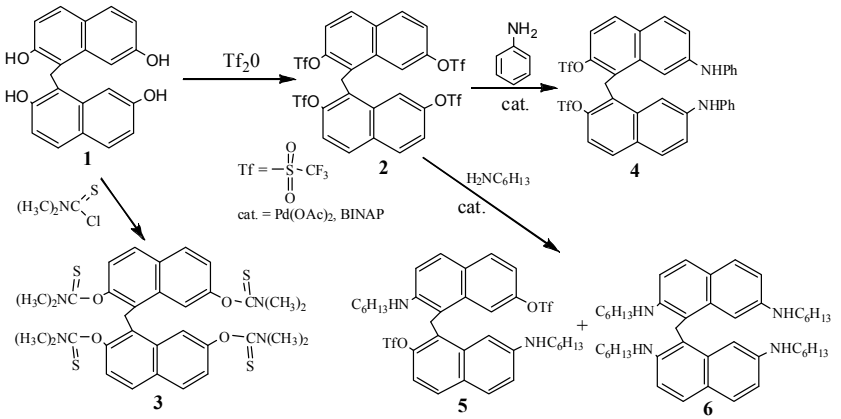
Functionalized derivatives of dynaphthalenes are widely used in fine organic synthesis and in the design of coordinated and supramolecular systems.

We carried out oligofunctionalization of 2,2',7,7'-tetrahydroxydynaphthylmethane **1**, using such reactions as triflation and thiocarbamoylation of **1**, and the catalytic amination of synthesized tetratriflate **2**.



The interaction of **1** with trifluoromethanesulfonic acid anhydride and $(CH_3)_2NC(S)Cl$ resulted in tetrafunctionalized derivatives. Tetratriflate-(**2**) and tetrathiocarbamate-(**3**) dynaphthylmethanes were isolated with 67 and 75% yields respectively. The results of the catalytic amination ($Pd(OAc)_2$, BINAP) **2** depended on the nature of the aminating reagent. The interaction of **2** with aniline occurred selectively with the formation of 2,2'-ditriflato-7,7'-bis(phenylamino)-dynaphthylmethane **4** with the yield 70%. Under reaction of **2** with hexylamine two major product, 2,7'-bis(hexylamino)-2',7-bis(trifluoromethanesulfonic)-(**5**) and tetra(hexylamino) -(**6**) dynaphthylmethanes, were isolated in 11 and 13% yields respectively.

The work was supported in part by the Russian Foundation for Basic Research (project no. 09-03-00201a).

PECULARITIES OF "GREEN TECHNOLOGIES" OF THE RADIATION-INDUCED SYNTHESIS OF THE PHOSPHOROUS-CONTAINING POLYMERS

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The organophosphorus chemistry ecologically oriented trends to switch from the use of elemental (white) phosphorus as the phosphorylating agent to less toxic polymeric phosphorus forms with controllable properties.

This work continues the studies of radiation chemical synthesis of phosphorus-containing polymers (PCP) in solutions and in heterogeneous dispersion systems in the presence of carbon-containing modifying agents of various types, including carbon nanotubes.

Phosphorus-containing polymers (PCP) obtained by radiation-induced polymerization in solution and heterogeneous dispersion polymerization in various reaction systems (table) are finely dispersed powders with color variation from orange (PCP0 and PCP1) and red (PCP4) to olive-black (PCP2) and black- brown (PCP3).

Table. **Some physicochemical properties of the resulting PCP samples**

№ Sample	Reaction system	*D*, kGy	PCP yield (P4/100 eV)*	PCP content, wt %.		
				P	C	H
PCP0	Benzene	117	6	81	8	1
PCP1	Benzene + Mg oleate	94	12	57	5	1
PCP2	Benzene +Taunit + Mg oleate	135	7	46	34	3
PCP3	H_3PO_4 + graphite	454	3	54	23	1
PCP4	H_3PO_4 + chitosan	398	5	65	6	2

It was shown that the structure and composition of phosphorus-containing polymers can be controlled by varying the absorbed dose of ionizing radiation and the type of modifying additive.

This work was supported by the RFBR project nos. 09–03–00493 and 08–03–00251.

STRUCTURE OF SECONDARY AND TERTIARY POLYDIALLYLAMINES AND THEIR ANTIMICROBIAL ACTIVITY

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Secondary and tertiary polydiallylamines (PDAAs) are novel promising polymers synthesized recently.[1,2] Their properties may be varied with pH of medium from polysalts to polybases, due to presence of $\sim NH_2^+/\sim NH^+$ groups. Difficulties are well known in preparation of polymers from monomers of the diallylamine (DAA) (or allylamine) series in non-quaternary form, which are related to degradative chain transfer to monomer. We validated theoretically a strategy for polymerization of the non-quaternary DAA monomers,[3] and elaborated the methods of synthesis to obtain PDAAs with MM up to ~65000.[1,2]

It has been revealed that the synthesized PDAAs polysalts exhibit, unlike the quaternary polymers of this series, a high biocidal efficiency of a broad spectrum that distinguishes them among known cationic biocides.[4-6] The secondary/tertiary structure of ammonium links was shown to play the crucial role in the PDAAs activity. Combination of a rather high hydrophobicity of the pyrrolidinium cycles with hydrophilic secondary/tertiary ammonium groups, which localize main charge of the links and are able to form hydrogen bonds (with oxygen atoms of phospholipids as well) are responsible for the high antimicrobial biocidal activity of the PDAAs polymers.[5,6]

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This work was supported by the Program for Basic Research of the Department of Chemistry and Material Science of RAS “Biomolecular and Medical Chemistry”.

FEATURES OF NUCLEOPHYLIC SUBSTITUTION OF HALOGEN IN ALKYL- AND ARALKYLHALOGENIDES BY S- AND O- ANIONS, PRODUCED FROM 6-METHYL-2-THIOURACIL AND ITS DERIVATIVES

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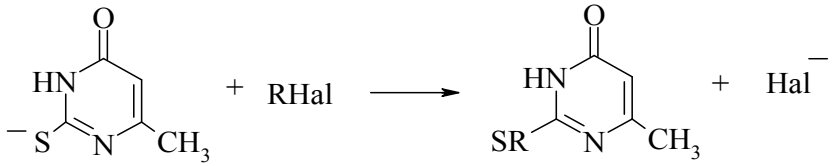
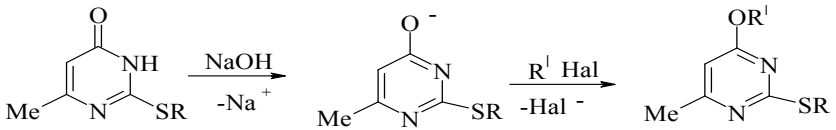
It is positioned, that formation S-and O-anions from sodium salts 6-methyl-2-thiouracil (I) and its S-alkyl(aralkyl)derivations occurs in water-dioxane mediums[1,2]. Nucleophilic substitution of halogen on specified anions is observed in these conditions. Feature of nucleophilic substitution is that in case of (I) reaction goes with participation S-anion:



S-alkyl(aralkyl)derivations (I) substitute halogen in the same halogenides with formation S-and O-diderivatives (I)[1,2]:



Hal=Cl, Br, I; R, R$^{/}$ = $CH_2C_6H_4$(*n*-Ad), Pr, All, Bn, $CH_2C_6H_4$(*м*-OPh), Et; $CH_2C_6H_4$(*м*-OPh), $CH_2C_6H_4$(*n*-Br)

Quantum chemical analysis of reaction coordinates with results on allocation of products of reaction and kinetic researches.

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COMPLEXATION OF IIIA-SUBGROUP METALS WITH IMINODISUCCINIC ASID

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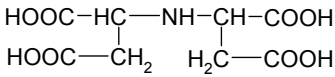
Iminodisuccinic asid (IDSA) is a complexone, a derivative of succinic acid.



Biological activity[1] and environmental safety of this complexone makes it an interesting object for comprehensive investigation. Complexes IDSA with alkaline earth metals, rare-earth metals, and a number of 3d-transition metals have been studied earlier. There is no information about the complexation with IIIA-subgroup metals.

The stability of the complexes IDSA with aluminum Al^{3+}, gallium Ga^{3+}, indium In^{3+} and thallium Tl^{3+}, Tl^{+} were determined by potentiometric titration. All measurements were spent at constant temperature 295 K and ionic strength of a solution equal 0,1 in the environment of KNO_3. The potentiometric results were processed under the computer simulation program[2]. The results are shown in the table.

Complex	Tl^{+}	Tl^{3+}	In^{3+}	Ga^{3+}	Al^{3+}
MeL	4.81 ± 0.07	31.5 ± 0.1	22.45 ± 0.1	16.77 ± 0.2	14.00 ± 0.03
MeHL	12.20 ± 0.09	33.7 ± 0.2	19.13 ± 0.2	20.11 ± 0.3	18.04 ± 0.04

Among IIIA-elements stability of averages and protonated complexes decreases $Tl^{3+} > In^{3+} > Ga^{3+} > Al^{3+}$, that may be associated with a decrease in ionic radii investigated metals.

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STABLE OZONIDES OF N-TRIFLUOROACETYL 3a,4,5,9b-TETRAHYDRO-3*H*-CYCLOPENTA[C]QUINOLINES: SYNTHESIS AND Δ-LACTONIZATION AT HYDRIDE REDUCTION

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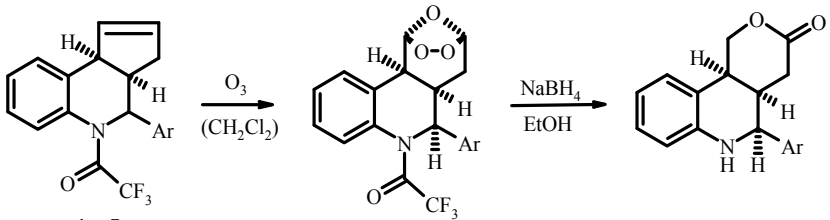
Detection of high anti-malarial activity of peroxide sesquiterpene lactones artemisinin stimulated increased interest to the synthesis of peroxides and ozonides, especially those containing heterocyclic fragments, as potential anti-parasitic agents. We investigated the ozonolysis of substituted 3a,4,5,9b-tetrahydro-3*H*-cyclopenta[c]quinolines **1-5** for the synthesis of ozonides of nitrogen-containing heterocyclic compounds. Structure and stereochemistry of ozonides **6-10** were proved by the 1D and 2D methods of ^{1}H and ^{13}C NMR spectroscopy and were confirmed by RSA. In the crystalline state, the aryl group at C(6) takes a pseudoaxial position in tetrahydropyridine cycle. It was found that the solution contains conformationally stable ozonides with pseudoequatorial C(6)-aryl group.

It was shown that the reduction of ozonides **6-8** by equimolar amount of $NaBH_4$ leads to the regiodirected formation of δ-lactones **11-13**. The reaction was accompanied by deprotection of the nitrogen atom protecting trifluoroacetyl group. The presence of N-trifluoroacetyl group is defining for such direction of reaction as at its replacement by N-acetyl group lactones aren't formed



Ar=Ph, *м*-ClC_6H_4, *p*-ClC_6H_4, *p*-$CF_3C_6H_4$, *p*-$CH_3C_6H_4$

Synthesized ozonides showed high in vitro activity against the intestinal Manson's schistosomiasis exciter

This work was supported by Fundamental Research Program of the Presidium of RAS "Fundamental Sciences – to Medicine"

1,2,3,4,5,6,7-HEPTA(METHOXYCARBONYL)CYCLOHEPTATRIENE: SYNTHESIS, PROPERTIES AND USE IN THE SYNTHESIS OF NOVEL CARBO AND HETEROCYCLIC COMPOUNDS

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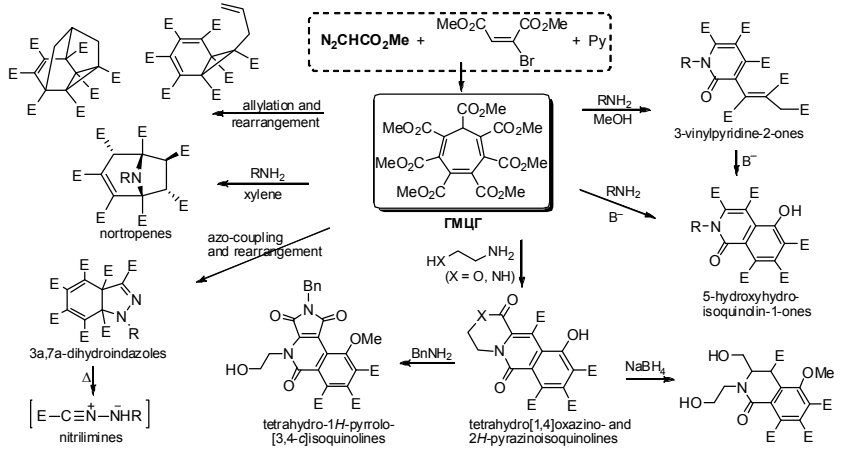
For the first time we have synthesized heptamethoxycarbonylcycloheptatriene (HMCH) on the basis of cascade reactions of methyl diazoacetate with dimethyl bromomaleate which can easily form a stable cycloheptatrienyl anion. We have shown that HMCH is highly effective in the reactions with electrophilic reagents (*C*- and *O*- alkylation, azocoupling etc.) as well as with primary amines to form *N*-substituted nortrop-2-enes and 3-propenylpyridin-2-ones. The latter ones undergo a selective cyclization under basic conditions to form 1,2-dihydroisoquinolin-1-ones. Being treated with either 2-aminoethanol or 1,2-diaminoethane HMCH transforms into condensed heterocyclic compounds such as tetrahydro[1,4]oxazino[4,3-b]- or 2H-pyrazino[1,2-b]isoquinolines. All the transformations observed were suggested a mechanism.



Thus, on the basis of HMCH we have developed methods for the directed synthesis of variable condensed carbo- and heterocycloc compounds with a big number of functional groups.

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SYNTHESIS AND INVESTIGATION OF SPECTRAL AND ELECTROCHEMICAL PROPERTIES OF FUNCTIONALLY SUBSTITUTED LANTHANIDE (III) BISPHTHALOCYANINES

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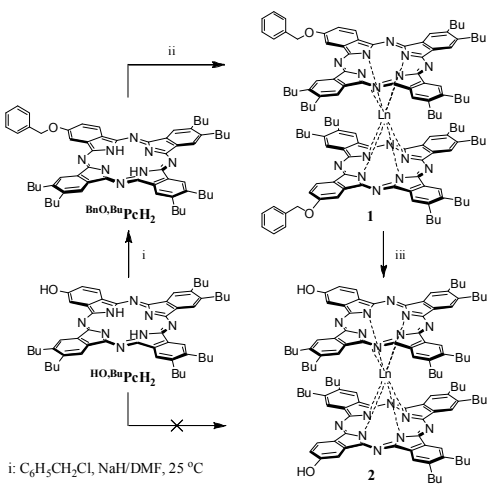
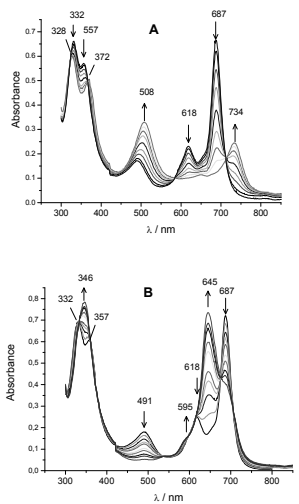
Since the first synthesis more than 40 years ago sandwichtype phthalocyanines of lanthanides (Ln) became an important class of tetrapyrrolic coordinating compounds including several different types of structures. Starting from 2-benzyloxy-9,10,16,17,23,24-hexabutyl-phthalocyanine we have firstly prepared a series of A_3B-type ligand based homoleptic Ln bisphthalocyanine complexes **1, 2** including hydroxy substituted derivatives which turned out to be inaccessible directly from corresponding 2-hydroxy-9,10,16,17,23,24-hexabutylphthalocyanine ligand.





UV/Vis spectral changes for **2a** during: (**A**) controlled potential oxidation (+0.15 V) and (**B**) reduction (–0.85 V) in DCB.

The phenolic hydroxy groups containing complexes **2** were found to be stable π-radicals as a conventional bisphthalocyanines which is unambiguously supported by spectral and electrochemical data.

The work was supported by the Russian Foundation for Basic Research, project 08-03-00753 and the Program for fundamental research of Presidium of the Russian Academy of Sciences "Development of methods for the synthesis of chemical compounds and creation of new materials".

ALKYLATION OF HYDROPHOSPHORYLIC COMPOUNDS UNDER CATALYTIC ACTION OF ONIUM SALTS

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Addition reaction of dialkyl phosphites to electrophilic double bond was discovered in 1946 by A.I. Pudowick[1]. Unfortunately there are very few publications devoted to performance of Pudowick reaction under "so-called phase-transfer catalysis". Makosza and Wojcitchowski implemented the addition of dialkylphosphites to acetonitrile, maleic ether and vinylacetate in the absence of solvent, in the presence of anhydrous potash and TBAB(tetrabutylammonium bromide)[2]. It's interesting to find out whether it's possible to carry out the addition of dialkyl phosphites and other hydrophosphorilic compounds in the environment of "PTC" to non-activated double and triple bonds such us isoprene, vinylacetylene, vinyl halids, dihalids and see the reaction. For comparison should also be investigated the reactions with unsaturated 1,4-dihalids such us 1,4-dichloro-2-butene and 1,4-dichloro-2-methyl-2-butene. Variously constructed acetylenes, dienes, amines, diines and variously constructed compounds with halogen atom by sp^2-hybridized carbon atom. Various transformations of derived compounds were studied.

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SYNTHESIS OF NEW SPIROAZAHETEROCYCLIC SYSTEMS

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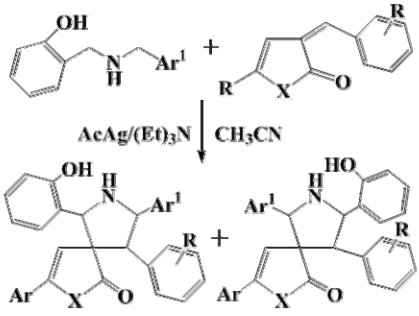
The most important direction of development of organic chemistry is developing methods of obtaining new biologically active heterocyclic systems.

Strictly spatially organized molecular spiroaza heterocycles are potentially promising in the study of biological activity.

Arilmetiliden-3H-furan-2-ones and N-heteroanalogs are dipolarophiles with fixed S-cis configuration and easy to interact with activated azomethines.

Formation of spiro heterocyclic systems is possible in the reaction conditions [3 +2]-dipolar cycloaddition of unsymmetrical Schiff bases, activated system CH3CN/CH3COOAg/Et3N.



X=O, NH. R=3-NO_2, 2-Cl, H. Ar= $CH_3C_6H_4$, Ph. Ar^1= Ph, Try.

Proposed methods of synthesis of spiro heterocycles include pyrrolidine with furan or pyrrolidine with pirrolonovym fragments.

The factors responsible for regionapravlenost [3 +2]-dipolar cycloaddition of unsymmetrical azometinilidov.

This work was supported by RF Presidential grant for state support of young Russian scientists № MK-635.2009.3. and RFBR (grant № 05-03-32196).

THE NON-TRANSITION METAL COMPLEXES WITH TRIDENTATE REDOX-ACTIVE LIGANDS

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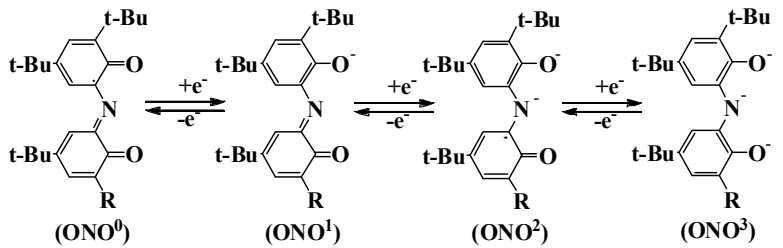
The chemistry of non-transition metal complexes with redox-active ligand develops intensively in recent times. The most important property of this type compounds is their ability to take part in different redox transformations, in which the ligands undergoes to oxidation or reduction.

Tridentate O,N,O-ligands are perspective building blocks for the preparation of these complexes. These ligands are able to be in four oxidation states in metal complexes.



R=H, t-Bu

Neutral(ONO^0) and dianion(ONO^2) forms of these ligands are radicals, and mono(ONO^1)- and trianion(ONO^3) are diamagnetic.

A number of complexes of non-transition metals of II and IV groups with tridentate O,N,O-ligands in different oxidation states was obtained. The new synthetic methods were developed. The paramagnetic compounds were investigated by EPR spectroscopy in solutions. The metal complexes with monoanion tridentate ligands were characterized by NMR spectroscopy.

We are grateful to the Russian Foundation for Basic Research (grant 10-03-00788-a, 11-03-97041-r_povolzh'e_a), Russian President Grant (grants NSh-7065.2010.3, MK - 614.2011.3) and FSP "Scientific and pedagogical cadres of innovation Russia" for 2009-2013 years (GK-P982 from 27.05.2010) for financial support of this work.

EFFECT OF MOLECULAR STRUCTURE ON GAS-PHASE DECOMPOSITION MECHANISMS OF NITROAROMATIC COMPOUNDS

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Formation enthalpies and reaction enthalpies of C-N homolytic bond cleavage for more than thirty derivatives of mono nitro benzene with donor and acceptor substituents together with 1,3,5-trinitrobenzene and hexanitrobenzene were calculated using modern methods of quantum chemistry. It was found that calculated data is in a good agreement with available experimental estimations. Better performance of formation enthalpies was achieved using composite multilevel techniques. Small deviation of predicted D(C-N) values for nitrobenzene, its halogen derivatives, *m*- and *p*-isomers of nitrotoluene, nitroaniline, nitrophenol as well as dinitrobenzenes from experimental activation energies allows to propose that decomposition of nitroaromatic compounds mainly proceeds via homolytic C-N bond breaking.

Moreover, significantly large values of Arrhenius parameter makes radical mechanism more favorable at 600-700 K in comparison than nitro-nitrite rearrangement for some compounds, though activation enthalpies for later pathway are by 15-30 kJ/mole lower than reaction enthalpies for former mechanism.

It was concluded, regarding decomposition of *o* isomer of nitrotoluene, nitroaniline and nitrophenol, that formation of aci-form takes place on the primary step of reaction.

THE INFLUENCE OF ALIFATIC AMINES ON POLYMERIZATION OF METYL METHACRYLATE IN THE PRESENCE OF SYSTEMS BASED ON RUTHENACARBORANES

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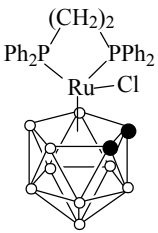
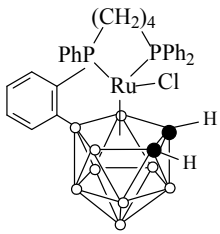
Ruthenium carborane complexes are known as effective catalysts for Controlled Radical Polymerization via the atom transfer mechanism (Atom Transfer Radical Polymerization, ATRP). One of disadvantages of such systems is low rate of the process. It was established that the specified disadvantage can be eliminated by addition of amines in system.

We chose the following ruthenacarboranes 1-3 for our work:



1



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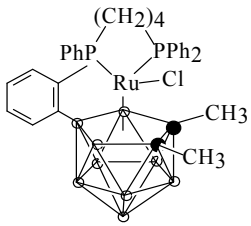

3

It was established that addition of aliphatic amines (diethylamine, triethylamine, tert-butylamine and iso-propylamine) can significantly increase the rate of polymerization of MMA drastically reducing time of the total monomer conversion. The polymerization remains controlled that is reflected in linear growth of MM of polymer with conversion, unimodal molecular-weight distributions and low polydispersity of the obtained samples (PDI = 1.35-1.6).

It is notable that use of amines allow to decrease concentration of complexes up 100 ppm that is very interesting aspect of this work.

Interestingly that addition of the amines to a complex **3** leads to full loss of control over polymerization. Apparently, it is connected with the steric demands created by methyl groups at carbon atoms in the carborane ligand.

Thus the use of ruthenacarboranes in combination with amines allows to increase the rate of polymerization, to decrease catalyst concentration and to obtain polyMMA with the desired molecular-weight characteristics.

The work was supported by RFFI (project № 11-03-00074)

STRUCTURE AND COMPLEXATION OF THE BORACYCLOPENTAN(EN)ES.

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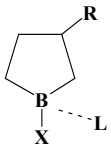
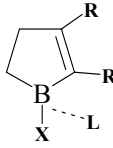
Recently, we reported the synthesis of 1-fluoro-3-alkyl—boracyclopentanes (1a-d) and 1-fluoro-2,3-dialkyl-boracyclopentenes (5, 7) *in situ* by transmetallation reactions of aluminiumcyclopentan(en)s with boronhalides[1,2].

By means of multinuclear NMR ^{1}H, ^{13}C, ^{11}B, ^{19}F spectroscopy and 1D, 2D experiments the new complexes 1-fluoro (chloro)-3-substituted boracyclopentan(en)es with $EtBX_2$ (X=F,Cl) and pyridine were established. The report discusses their spectral parameters in different solvents (Tol, THF, CD_2Cl_2). All the theoretically possible structures calculated by the quantum-chemical methods PBE/3z and MR_2/L1were shown.



1. R = Bu(a), Hex(b), Bn(c), Cyclohex-3-enyl(d), X= F, L=$EtBX_2$
2. R = Bu(a), Hex(b), Bn(c), X=Cl, L=$EtBX_2$
3. R = Bu(a), Hex(b), Bn(c), Cyclohex-3-enyl(d), X = F, L=Pyr
4. R = Bu(a), Hex(b), Bn(c), X=Cl, L=Pyr



5. R= R_1=Pr, X= F, L=$EtBX_2$
6. R = Bu, R_1=CH_2NMe_2, X=Cl, L=$EtBX_2$
7. R= R1=Pr, X= F, X = F, L=Pyr
8. R = Bu, R_1=CH_2NMe_2, X=Cl, L=Pyr

It was found that there are all cyclic boralanes under consideration in complexes with Pyr (or $EtBCl_2$(F)), but 1-fluoro-2-()3-buthyl-boracyclopentene can exist without chelating agent due to the intramolecular B···N bond. When pyridine is added to 1a-d, 2a-c, 5, 6 the new compounds 3a-d, 4a-c, 7, 8 is formed, because the process is thermodynamically possible ($\Delta Gr \approx$ -0.9 kcal/mol) and runs without barrier. As result we traced the chemical shifts changes in ^{1}H, ^{13}C, ^{11}B spectra depending on the cycle's structure, composition of the complexes, solvent effect and the nature of the heteroatom compared with aluminumorganic compounds.

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TO THE QUESTION OF SCALING IN WATER

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The chemical nature of sediments formation process remains overlooked, and development of more advanced methods of a scum elimination is in fundamental research of this phenomenon.

In sedimentation processes in water medium causes interest the high maintenance of the spin centers in samples of the scum, registered by an electronic spin resonance method. This experimental fact allows to estimate the spin mechanism of a deposit formation in water medium, however this question remains opened and gives ample opportunities for research.

To study the dynamics of scaling process in water systems the most perfect method is the photon correlation spectroscopy/dynamic light scattering/ (DLS). With the temperature growth for all samples of water the increase in the sizes of particles of a disperse phase is observed. For identical temperatures mean radiuses of particles in the unpurified water systems, appeared bigger than radiuses in the same samples after purifying.

Growth of mean radiuses of disperse phase particles shows the presence of the associative processes proceeding in system at heating which are directly connected with formation of an insoluble deposit of salts of hardness. The nature of deposits and the data of DLS experiment give the rise to believe that associates formation in the water medium occurs on the spin mechanism.

With the temperature growth the energy consumed by system, increases, and at the same time such conditions which promote formation of particles with uncompensated spin are created. The substances causing water hardness, are initially in the dissolved condition. It is obvious that at system heating dissociation on homolytic type occurs, and it is possible to present the dissolved molecules in the form of some dimers which in certain conditions dissociate, forming the spin centers. This process intensively proceeds with temperature increase that conducts to associates formation – because of exchange interaction forces. Gradually the sizes of particles increase, and there is sedimentation because in the water, representing spin compensated medium, similar combinations can exist only insignificant time for the reason coulomb's repulsion of external electron envelope.

THERMODYNAMICS OF POLYSACCHARIDES AND PROCESS OF THEIR PLASTICIZATION

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The role of polysaccharides (PS) in the life of modern man can hardly be overestimated. They are drugs, are included in cosmetics and dietary supplements. Determination of the thermodynamic properties of polysaccharides and their mixtures with low molecular weight substances (LMWS) is necessary both for studying the processes for their preparation, and transformations in living organisms. Polysaccharides have a complicated molecular and supramolecular structure. In this context, is of great theoretical and practical importance to establish patterns of influence of structure on their physical, chemical and, in particular, the thermodynamic properties. Given that the processes involving the PS occur in the presence of LMWS, it is important to examine the physical condition of LMWS in mixtures with polysaccharides, as well as the influence of LMWS on the temperature of their physical transitions. Valuable information about the diagrams of the physical states of systems PS–LMWS, development and analysis which the authors engaged in more than 35 years. They allow us to determine the temperature and concentration boundaries of a homogeneous mixture of education, as well as two-phase gels. For the construction and analysis of such diagrams are needed, in particular, data about temperatures vitrification mixtures of PS with LMWS, as well as the melting phase of excess LMWS over their solubility in the PS. Such data can be obtained by measuring the heat capacity of mixtures of biologically active substances from the LMWS and by differential thermal analysis.

Was investigated over 30 different polysaccharides, 15 of plasticizers and their mixtures with PC, built and analyzed the 19 diagrams of the physical states of systems of PS–LMWS. The interrelation between the thermodynamic characteristics of the structure of the PS, the type of vegetable and animal raw materials and the degree of substitution of OH groups of cellulose. Investigated the thermochemistry of enzymatic hydrolysis of starch and chitosan.

Complex precision thermodynamic characteristics of PS and their blends with LMWS is a fundamental basis for developing new and optimize existing processes allocation PS from natural raw materials and their processing.

SOLVENT AS A MEANS FOR CONTROLING THE PROCESS OF IONIC AND MOLECULAR COMPLEXES FORMATION OF CROWN ETHER 18-CROWN-6

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A solvent is not only an environment but also a means for controlling the processes in liquid-phase through various solvating ability of solvents for the participants of chemical reactions. The study of the reactions of amine and carboxylate complexes with d-metals in aqueous-organic solvents allowed us establish some general regularities in the influence of reagents solvation on the thermodynamics of reactions[1].

Investigation of reactions of ionic and molecular complexes formation of crown ether 18-crown-6 (18C6) revealed features of their thermodynamics due to the cyclic structure of the 18C6 and the different influence of non-aqueous solvent components in the solvation of ions and neutral molecules. Maximum stability and exothermicity of the complex formation of cationic complexes of 18C6 is observed at X_{H2O} = 0.7-0.8 mol. fraction in mixtures of water with aprotic solvents. The increase in concentrations of both aprotic and protolytic solution components leads to the monotonic increase in the stability of molecular complexes of 18C6 with amino acids. It is also the characteristic for the formation of ionic complexes of 18C6 in protolytic media.

Analysis of the enthalpy characteristics of the reagents showed that the energy of the processes is mainly determined by changes in the solvation state of 18C6. Calculation of enthalpy characteristics of the reactions on the basis of changes in the solvation state of 18C6 showed the applicability of established regularities[1] for predicting changes in the energy of complex formation reactions of 18C6 at their transfer from water to aqueous-organic mixtures.

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This work was supported by the AVP for Development of Scientific Potential of Higher School (2009-2011), N 2.1.1/5593, Federal Program "Research and scientific-pedagogical staff of Innovative Russia" for 2009-2013 (State contract № 02.740.11.0253).

ACTIVITY OF MONO- AND BIDENTATE NICKEL COMPLEXES AND HALIDE INITIATORS IN POLYMERIZATION OF METHYL METHACRYLATE

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The phosphine complexes $NiBr_2(PPh_3)_2$ and $NiBr_2$dppe (dppe – 1,2-bis(diphenylphosphine)ethane) are capable of actively catalyzing the polymerization of methyl methacrylate (MMA) in the presence of zinc dust and iodobenzene.[1,2] It was established that nature of nitrogen ligands attached to a nickel atom exerts a considerable influence on the rate of MMA polymerization. So, the catalysis by $(Py)_4NiCl_2$ complex (Py – pyridine) together with zinc dust and initiator RX (C_6H_5I, $(CH_3)_2C(Br)C(O)OC_2H_5$, $CHCl_3$, $C_6H_5CH_2Cl$) results in higher yield of the polymer than that realized with 2,2'–bipy$NiBr_2$, but in lower yield than in the case of $NiBr_2(PPh_3)_2$ using.

In addition, structure of initiator in MMA polymerization also influences the polymer yield which grows in the row C_6H_5I<$(CH_3)_2C(Br)C(O)OC_2H_5$<$CHCl_3$<$C_6H_5CH_2Cl$ when used with the studied catalysts and zinc dust. It was shown that introduction of strong accepting moieties into para-position of benzene group of C_6H_5Br causes the increase in initiating activity of the latter and therefore allows growth of the yield of the polymer in $NiBr_2(PPh_3)_2$/Zn-mediated polymerization of MMA in comparison to the reaction initiated with bromobenzene under similar conditions. Thus, polyMMA was isolated in 11 h with 89 % yield of the polymer having number-average molecular weight M_n =10.1*10^3 and polydispersity index (M_w/M_n) =1.5 prepared with the action of p-bromobenzonitrile. MMA polymerization proceeded with C_6H_5Br reaches only the yield of 8 % in 5 h to give the polymer with M_n 5.0*10^3 and M_w/M_n 1.9.

Thus, monodenate nickel complexes $NiBr_2(PPh_3)_2$ or $(Py)_4NiCl_2$ together with benzyl chloride and zinc dust are found to be the most active components of the catalytic system that allow MMA polymerization to proceed up to limiting conversions (~ 100 %) for 5 hours at 65^0C.

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CHEMICAL MODIFICATION OF PROTEINS BY "SMART" POLYMERS

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The unique specificity of biological action is a characteristic feature of almost all biologically active natural compounds, including proteins. They are naturally adapted to function under specific conditions, which often differ from the conditions of the use of these proteins in applied biochemistry and medicine. These problems are usually solved by modifying the proteins with low molecular weight compounds. It can be supposed that a modification by the so-called "smart" polymers capable of reversible conformational changes induced by changes in the environment opens up much wider prospects; the modifying action of such polymers would also be reversible and dependent on the parameters of the environment.

The aim of the present work is to study the possibilities of manipulating protein activity by a chemical modification with smart polymers.

The modification of duck ovomucoid (the polyfunctional natural inhibitor of proteolytic enzymes used in therapy) by poly-*N,N*-diethylacrylamide possessing a low critical solution temperature (LCST) has been investigated. The free amino groups of the lysine residues and the *N*-terminal residue of the ovomucoid molecule were modified; as a result, the inhibitor activity towards trypsin decreased significantly and that towards chymotrypsin decreased slightly. The transformation of ovomucoid antitryptic centers into antichymotryptic centers was observed upon the heating of the solutions of the modified protein above the LCST. The hydrophobization of the lysine residues situated in the reactive centers of the inhibitor was shown to cause this phenomenon. The structure of the binding loop was not distorted and the modified lysine residues could be recognized by chymotrypsin molecules, similarly to the hydrophobic amino acid residues of the antichymotryptic center.

Financial support for the present work was provided by the program "Fundamental Sciences for Medicine" of the Presidium of the Russian Academy of Sciences and the Russian Foundation for Basic Research (project no. 10-03-00029).

REACTIVITY OF RHODIUM(III) COMPLEXES WITH PYRIDINE DERIVATIVES

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Continuous interest to the chemistry of rhodium(III) complexes *trans*-$[RhL_4X_2]^+$ with heterocyclic ligands (L) stems from the fact that chemical transformations of these compounds lead to derivatives manifesting pronounced photochemical and catalytic properties, as well as promising as medicines. However, despite of numerous studies devoted to this class of complexes, only few of them concern chemical transformations.

Present work is devoted to study of rhodium(III) complexes *trans*-$[RhL_4Cl_2]X$ with heterocyclic ligands of pyridine series (pyridine, γ- and β-picoline, 4-hydroxypiridine, isonicotinic acid) and different conterions X^- (Cl^-, SCN^-, ClO_4^- ,ReO_4^-, MnO_4^-, $AuCl_4^-$, $AuBr_4^-$, BPh_4^-, BF_4^-). Thermal transformations of compounds were studied by DTA and DSC methods. Due to high chemical stability of $[RhPic_4Cl_2]^+$ cations, they were used for examination of oxidation of coordinated picoline to isonicotinic acid, the coordination core being preserved. Complexes of rhodium with a general formula $[Rh(i\text{-}NicH)_n(i\text{-}Nic)_mCl_2]^{-m+1}$ (i-NicH - isonicotinic acid, i-Nic - isonicotinate anion) were studied as presynthesized synthon for construction bimetallic (Rh-Cu) coordination polymer. In addition reaction of complexes *trans*-$[RhL_4X_2]^+$ with bidentate O,O-ligands (EDTA, salicylic acid) was studied. Obtained compounds were characterized by elemental analysis, visible and UV-spectroscopy, IR and NMR spectroscopy, X-ray powder and single crystal analysis.

The work has been supported by RFBR grant 11-03-00668, Presidium SB RAS interdisciplinary project No 112 and RF state contract № P960 of Federal target program «Scientific, Research And Teaching Specialists In Russia» 2009–2013.

NOVEL APPROACH TO THE SYNTHESIS OF N-ARYL-1,5,3-DITHIAZEPINANES

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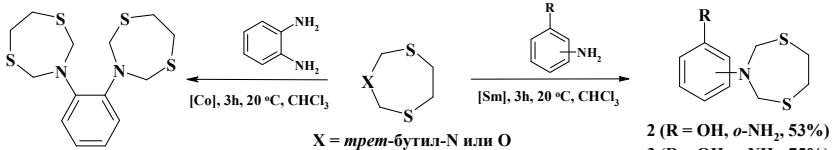
Sulfur- and nitrogen-containing heterocycles are of special interest as potential biocides and fungicides. They are also widely used as selective complexones and sorbents of noble metals. As recently shown,[1] catalytic transamination of *N*-methyl-1,3,5-dithiazinane with arylamines is an efficient method for synthesizing a variety of *N*-substituted 1,3,5-dithiazinanes.

In order to develop the novel approach to the selective synthesis of 5-substituted-1,5,3-dithiazepinanes, we have studied the catalytic reaction of aryl amines, namely, phenylenediamines, aminophenols and aminothiophenols with 3-*tert*-butyl-1,5,3-dithiazepinane or 1,3,6-oxadithiapinane.

Thus, *ortho*-phenylenediamine under optimized reaction conditions (5 mol % $CoCl_2 \cdot 6H_2O$, 20 °C, 3 h, CH_3Cl) enters into reaction with 3-*tert*-butyl-1,5,3-dithiazepinane or 1,3,6-oxadithiapinane giving 3,3′-(1,2-phenylene)bis-1,5,3-dithiazepinane **1** in 68% yield. The reaction of 3-*tert*-butyl-1,5,3-dithiazepinane or 1,3,6-oxadithiapinane with regioisomeric *ortho*-, *para*-aminophenols and *para*-aminothiophenol under optimized conditions (5 mol % $SmCl_3 \cdot 6H_2O$, 20 °C, 3 h, CH_3Cl) leads to 2-(**2**) and 4-(1,5,3-dithiazepinane-3-yl)phenols **3** and also 4-(1,5,3-dithiazepinane-3-yl)phenylhydrosulfide **4** respectively in 53–75% yield.



The structures of novel *N*-aryl-1,5,3-dithiazepinanes **1–4** were proved by means of 1D (^1H, ^{13}C) and 2D (COSY, NOESY, HSQC, HMBC) NMR spectroscopy, MALDI TOF-MS and confirmed by single-crystal X-ray diffraction.

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SYNTHESIS OF AZAHETEROCYCLIC COMPOUNDS WITH CARBAMATE FUNCTION

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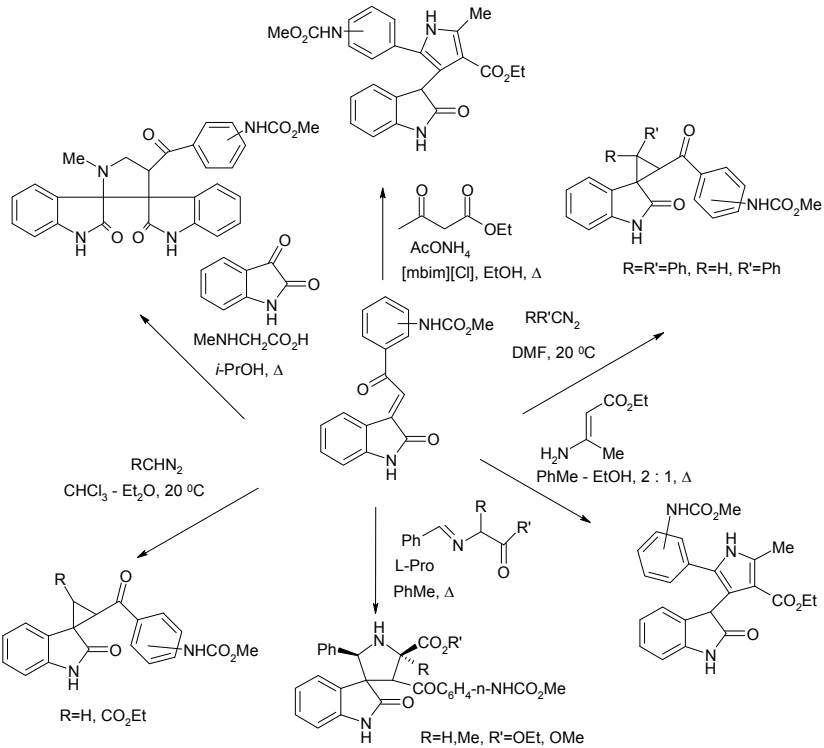
Functionalization of methyl {4(3)-[2-(2-oxo-2,3-dihydro-1*H*-indole-3-yliden)acetyl]phenyl}carbamates with obtaining of new bioactive azaheterocyclic compounds was carried out.



The structure of new compounds was confirmed by IR, ^{1}H, ^{13}C NMR spectroscopy and mass-spectrometry. Compounds with high antimicrobic and antifungal activity were found.

SYNTHESIS AND PROPERTIES OF N, O-POLYFLUORALKYL DERIVATIVES OF ACRYLAMIDE WITH SODIUM ACRYLATE

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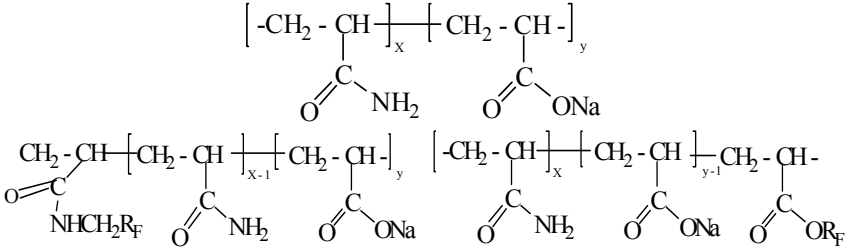
It was shown that polyfluoralkylchlorosulfites react with salts of carboxylic acids with formation of polyfluoralkyl esters[1,2].

It was found that copolymers of acrylamide and sodium acrylate react too. Conditions of introduction of polyfluoralkyl groups in copolymer were selected. We were studied properties of aqueous salts solutions for original copolymer and N, O-polyfluoralkyl derivatives (molecular mass of $1{,}2*10^6$, fluorine content of 2 to 4 percent):



In contrast from aqueous solutions of sodium acetate (freezing temperature of minus 10 °C) non-fluorinated copolymer has a freezing temperature of minus 18 °C, but fluorinated esters – minus 20 °C, N-polyfluoralkylamide – minus 21 °C.

We observed the effect of reducing the relative viscosity (from 59 to 10 sec) for 0,1% aqueous solutions of N-polyfluoralkylamide and O- polyfluoralkyl esters compared to the original copolymer.

Such an effect of polyfluoralkyl groups in copolymers on the properties of their aqueous solutions is due to the restructuration of water clusters. That phenomenon on the example of the interaction between sodium acetate and water was studied by the quantum-chemical method ab-initio in the 6-$31G^3$.

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FLUORINATED BENZOQUINOLONES AND 2-AMINO-4-NAPHTHYLPYRIMIDINES BASED ON CHEMICAL TRANSFORMATIONS OF 2,3-DIFLUORONAPHTHALENE

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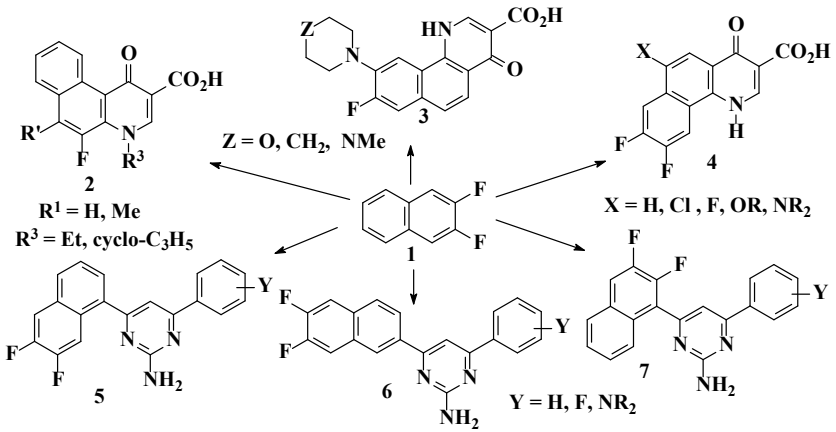
For the purpose of search new biologically active compounds methods for the synthesis of fluorinated benzoquionolones with different fusion type of naphthalene and pyridone fragments (compounds **2-4**) as new structural derivatives of fluoroquinolone antibacterial drugs were developed. Series of fluorine-containing 2-amino-4-naphtyl-6-arylpyrimidines (compounds **5-7**) as potential antibacterial and antifungal substances were prepared.



Developed synthetic ways are based on common starting compound 2,3-difluoronaphtalene **1**, prepared by copyrolysis of $CHCF_2$ and styrene [1,2], and subsequent efficient introduction of various functional groups (NO_2, NR_2, CO_2H, COR, CHO) in different positions of 2,3-difluoronaphtalene structure.

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SYNTHESIS AND X-RAY CRYSTALLOGRAPHIC STUDY OF DIFLUOROPOLYCHLOROTRICYCLO[5.1.0.0^{3,5}]OCTANES

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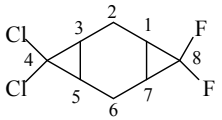
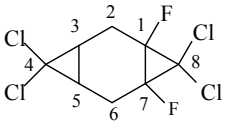
Introduction of halogen atoms into cyclopropane ring leads to considerable of the cycle deformation affecting on the reactivity of the halocyclopropanes. For the purpose of a quantitative estimation of the deformation effects of fluorine and chlorine atoms, two model compounds 4,4-dichloro-8,8-difluorotri-cyclo[5.1.0.0$^{3.5}$]octane **1** and 1,7-difluoro-4,4,8,8-tetrachlorotri-cyclo[5.1.0.0^{3,5}]octane **2** were synthesized and their structures determined via x-ray diffraction crystallographic techniques. It was established, that structures of compounds **1** and **2** represent a practically planar central six-memberd ring jointed with two anti-located cyclopropane fragments



1



2

3

C-C distances (A°)

C_3-C_5	1.533	C_1-C_7	1.558	C_3-C_5	1.533	C_1-C_7	1.514	C_1-C_3	1.514
C_3-C_4	1.496	C_1-C_8	1.465	C_3-C_4	1.495	C_1-C_8	1.518	C_1-C_2	1.514
C_4-C_5	1.498	C_7-C_8	1.463	C_4-C_5	1.497	C_7-C_8	1.518	C_2-C_3	1.514

Comparison of the observed bond lengths of cyclopropane fragments for compounds **1** with known similar characteristics of unsubstituted cyclopropane **3** indicates that *gem*-difluoro substitutients lead to dramatic deformation of cyclopropane skeleton shown in considerable lengthening of C-C bonds opposite to CF_2 group along with an impressive shortening of the adjacent bonds. Similar effects are observed also for *gem*-dichloro substitutients, however they are less expressed. In case of compound **2** two atoms of the fluorine in vicinal position (1 and 7) of difluorodichlorocyclopropane fragment compensate the deformation effects of *gem*-dichloro substitutients (position 8) equalizing the lengths of all three cyclopropane C-C bonds which become almost identical to bond lengths in unsubstituted cyclopropane.

ELECTROKINETIC CHARACTERISTICS OF THE VOLUME TITANIUM DIOXIDE IN PRESENCE OF SINGLY AND MULTICHARGED CATIONS

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Measurements of electrophoretic mobility U_{ef} of TiO_2 particles were carried out in NaCl, KCl, $BaCl_2$, $LaCl_3$ background solutions with concentration 10^{-3} M – 10^{-1} M in the pH range 3 – 9 on the Zetasizer Nano ZS (Malvern). The values of electrokinetic potential were calculated according to the Smoluchowski equation (ζ^S) and then were corrected within the framework of the Wiersema – Loeb – Overbeek model taking into account polarization of a double electric layer (DEL) (ζ^W).

It is established that in NaCl and KCl background solutions the isoelectric point (IET) lies at values of pH_{IET} = 6.2 and 6.3 correspondingly, and its position slightly depends on electrolyte concentration at constant ionic composition of a background solution. At the same removal from IEP, values of electrophoretic mobility (electrokinetic potential) coincide within an experiment error in both background electrolytes.

Only positive region of electrokinetic potential and complicated dependences of U_{ef} and ζ^W on concentration and pH of a background solution are observed in the presence of multicharged cations that is caused by superequivalent adsorption of these ions in the Stern layer.

Work is performed with financial support of the grant of Russian Foundation for Fundamental Research № 09-03-01089 and the grant of the Russian President for support of leading scientific schools № 6291.2010.3.

NON-COVALENT INTERACTIONS AND THEIR INFLUENCE ON SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE MATTER

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It is well-known that non-covalent interactions are important for some physical and chemical properties of compounds. Detailed analysis of such interactions allows to explain and in some cases to predict the properties of the compound being investigated.

In the present work we report on the non-covalent interactions in the structurally-related derivatives of uracyl and isocyanurate, isoindigo and mucochloric acid.

It was shown that the LP…π interactions in the crystals of uracyl and isocyanurate derivatives are the structure-forming ones. The similarities and the differences of these interactions have been analyzed depending on the heterocycle nature. The influence of the LP…π non-covalent interaction on the possibility of the Pummerer reaction occurrence has been shown on the example of the isocyanurate derivatives. The unusual molecular structure of the isoindigo derivatives has been analyzed and it was found that molecular structure in the crystals of this class is defined by the type of the intermolecular interactions, which form the crystal. The ability of the racemic mixtures to the spontaneous resolution into enantiomers upon crystallizations has been evaluated for the mucochloric acid derivatives. It was shown that the non-covalent interactions in the enantiopure and racemic crystals differ significantly, what, apparently, explains the differences in the crystallization type.

This study is financially supported by the Russian Foundation for Basic Research (Project 09-03-00696a), and the grant of the President of the Russian Federation for the state support of young Russian scientists (1670.2010.3)

THE DEPENDENCE OF THE STRUCTURE OF SILATRANES, GERMATRANES AND THEIR ANALOGS FROM THE NUMBER OF COORDINATION CYCLES

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The study of non-classical interatomic interactions that are, in particular, take place in organic derivatives of silicon, germanium and tin plays a special part in the solution of the issue of the nature of the chemical bond.. The most important representatives of this type are metalatranes and quazimetalatranes, viz., intercomplex tetra-, tri-, bi- and monocyclic complexes of elements of the 14-th group with tris-, bis- and mono-2-hydroxyethylamines $X_{4-n}M(OCH_2CH_2)_nNH_{3-n}$ (M=Si, Ge n=1-3) and salts of tetrakis-2-hydroxyethylammonium.

Depending on the nature of substituents X, atom M and the number of cycles n these compounds have a broad spectrum of the biological activity. A special feature of their composition is a trans-annular coordination bond N→M the length and firmness of the latter depend on the nature of atom M and number of cycles in a molecule (n).

We have carried out the quantum-chemical investigation of the equilibrium geometry of molecules $X_{4-n}M(OCH_2CH_2)_nNH_{3-n}$ and cations $[X_{3-n}M(OCH_2CH_2)_nNH_{3-n}]+$ (X=H, F; M=Si, Ge; n=1-3) to study the influence of the number of cycles on the length of the trans-annular bond in intercomplex cyclic compounds of silicon and germanium.

Here, it has been established that the firmness of the bond N→M in neutral compounds where X=H increases with the increase of cycles number (n), while, on the contrary, it decreases when X=F, as a positive charge of atom M (and consequently the firmness of N→M) increases with the increase of the total electronegativity of substituents surrounding it. At the same time, the firmness of N→M bond changes inconsiderably for appropriate cations.

In the course of this study, we have also proposed new methods of synthesis of silatranes, germatranes and their quazi-, hypo- and hyperanalogs containing a highly electronegative substituent at atom M. These methods are characterized by simplicity, high yields and ecological compatibility. These are suggested precursors of previously unknown compounds and cations. Their structure, physical-chemical properties, reactivity and biological activity are being studied at the present time.

SYNTHESES OF HYDROFURANONES BY PEROXIDE OXIDATION OF FURFURAL UNDER THE CONSTANT CURRENT INFLUENCE

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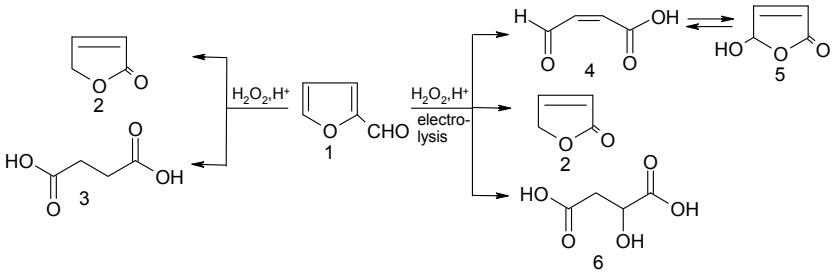
The process of furfural 1 oxidation with aqueous hydrogen peroxide under the conditions of acid autocatalysis was shown earlier to lead to formation of 2(5H)-furanone 2 and succinic acid 3 as main products[1]. We have established the constant current influence to accelerate the process and to change its purposefulness to principal formation of cis-β-formylacrylic acid removed from reaction mixture as cyclic tautomer – 5-hydroxy-2(5H)-furanone 5. Other main products of electrochemical oxidation of aldehyde 1 are furanone 2 and acid 6. Such typical non-electrochemical process products as acid 3 и 2(3H)-furanone 7 are not formed appreciably under the electrosynthesis conditions.



Dependence of aldehyde 1 electrochemical oxidation main products yields on the reaction conditions has been established. That made it possible to create a new method for furanones 2 and 5 synthesis in general preparative yield up to 70 %. The method has some advantages in comparison with known methods for these compounds synthesis.

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SELF-ORGANISING SUPRAMOLECULAR AND DISSIPATIVE POLYMER NANOSTRUCTURES

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In frameworks of the scaling theory of phase transitions and critical phenomena the direct quantitative dependence of macroscopic properties on nanostructural parameters in a polymeric material is revealed. The structure is characterized by the average thickness of amorphous layers in isotropic melt-crystallized linear polyethylene of high density chosen as an example. The square of the neck draw ratio is equal to the product of the square of the draw ratio at break and a probability of collision of the chain ends. This probability in its turn is proportional to the average thickness of amorphous layers in isotropic material. In solid state, polymers with flexible chains are solutions, and the ends of chain serve as a solvent. The transition from the solid isotropic or oriented state to the melt, or from the solid isotropic state to oriented one below a critical degree[1] of polymerization by means of the neck formation occurs at a nonzero external field on the combined line of phase transitions of the first and second order in semicrystalline polymers with flexible chains. The melt is a symmetric phase with a zero parameter of order. The lamellar and fibrillar partially crystalline phases are the phases with own parameters of order which are periodic functions of one co-ordinate, the neck draw ratio being another parameter of order. At the critical polymerization degree all these phases are identical. Problems of dynamic scaling and entanglements are considered.

Study of supramolecular (bicontinuous) structures of different symmetry and ordering degree in novel polymer-colloid complexes[2], dendrons and dendrimers based on gallic[3] and benzenesulfonic[4] acids is presented by the electron density distribution reconstruction method using SAXS data.

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This work is financially supported by RFBR, grants 11-03-00669a.

MACROTRICYCLIC COMPOUNDS BASED ON AZA- AND DIAZACROWN ETHERS

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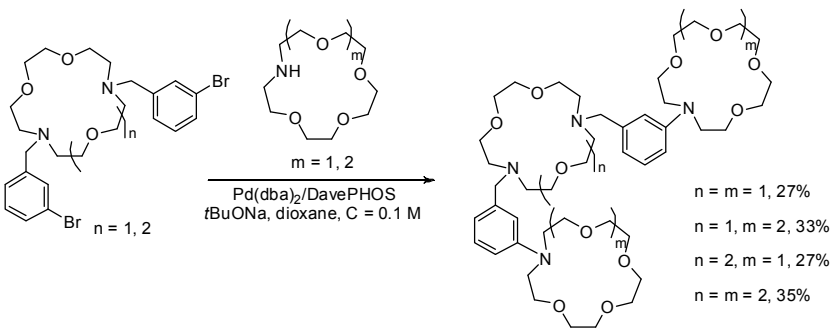
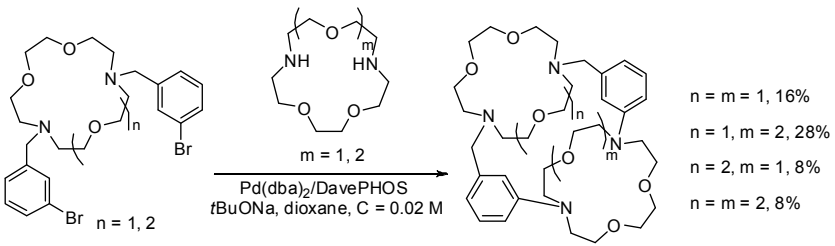
Macrotricyclic compounds were synthesized by the reaction of *N,N'*-di(bromobenzyl) substituted diazacrown ethers with 2 equiv. of azacrown ethers under the palladium catalysis conditions. We found out the dependence of the yields of macrotricycles and side macrobicycles on the nature of starting aza- and diazacrown ethers.



Macrotricycles of the cryptand type were synthesized in the reactions of the same compounds with 1 equiv. of diazacrown ethers. The second product in these reactions was found to be macrobicycles as a result of the side reduction reaction. The reaction proceeded better with *N,N'*-disubstituted 1,7-diaza-15-crown-5.



The work was supported by the RFBR grant N 09-03-00735.

APPLICATION OF LEWIS BASES IN NITROGEN HETEROCYCLES SYNTHESIS

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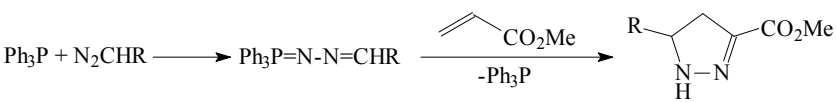
The main consistent patterns of the catalytic 1,3-dipolar cycloaddition of diazocompounds to C=C-bond in the presence of Lewis bases (nitrogen and phosphorus containing compounds) were studied to create new selective methods for building five-membered nitrogen heterocycles. We have found new effective catalysts (Lewis bases – tertiary amines, pyridine derivatives, phosphines and phosphites) of 1,3-dipolar cycloaddition of diazocompounds to C=C-bond; their application allows to synthesize the pyrazolines selectively and with high yields. Theoretical model for investigation of influence of Lewis bases on the 1,3-dipolar cycloaddition reaction of diazocompounds to unsaturated compounds was developed. It was determined that specific interaction of the reagents with Lewis bases is the key factor for acceleration of cycloaddition reaction of diazocompounds to C=C-bond, the scale of the effect is reaching four orders over that of non-catalytic reaction. To confirm the quantum-chemical calculations we have studied the interaction of pyridine with methyl acrylate and methyl diazoacetate by ^{13}C and ^{1}H NMR method. It was found that in $CDCl_3$ solution pyridine interacts with methyl diazoacetate.

Phospazines (adducts of diazocompounds with triphenyl phosphine) that are intermediates in pyrazolines synthesis were obtained; they are having good prospects for application in the carbo- and heterocyclic compounds synthesis.



R=H, $COCH_3$, CO_2CH_3

This study was financially supported by the Russian Academy of Sciences (Program OKh-01 of Basic Research "Theoretical and Experimental Studies of the Nature of Chemical Bonds and Mechanisms of Important Chemical Reactions and Processes")

QUANTUM- CHEMICAL MODELING OF LIGAND SUBSTITUTION IN PALLADIUM FLAT SQUARE COMPLEXES

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Kinetics and thermodynamics of formation of complexes of composition $[PdCl_n(H_2O)_{4-n}]^{2-n}$ have been investigated by density functional theory (DFT) methods of quantum chemistry, in system $Na_2PdCl_4 \times nH_2O$, where n varied from 8 to 12.

The initial system is a solvate - divided ion pair $Na^+ (H_2O)_4 * [PdCl_4]^{-2} * (H_2O)_4 Na^+$. System as a whole, excluding the hydrogen atoms of water molecules is symmetrical about the plane $[PdCl_4]^{-2}$ and represents both above and below the plane a distorted octahedron with a base of four oxygen atoms of water molecules (R_{O-O} = 3.2 Å -3.34 Å). Distance Na^+ - O_{H2O} is 2.38 Å– 2.40 Å, what is well agrees with the X-ray diffraction data.

When the number of water molecules increases to 12, additional water molecules on each side form a cyclic trimer $(H_2O)_3$, involving two water molecules of the first coordination sphere of the sodium atom, and increases the contribution of solvation energy component in the process.

The final state remains flat square structure of $[PdCl_3(H_2O)]^{-1}$. Na^+ ions are displaced along with its solvation shell in the direction of the outgoing atom Cl^-, surrounded by four water molecules. The results for the sodium ion and chlorine are consistent with the hydration number of ions. The most significant factor for the system is to reduce the charge of the complex ion - 2 to -1 for the replacement of the chlorine atom in the molecule of water $[PdCl_{4-n}(H_2O)_n]^{-2+n}$. In this case, water molecules are solvated mainly singly chargedions Na^+ и Cl^-.

Effect of charge state tested on the system cis-$[PdCl_2(H_2O)_2]^0$ * C_2H_4*$(H_2O)_4$, thus there is a substitution H_2O to C_2H_4. Molecule H_2O in the system form a cyclic n-mer of water with two water molecules of the complex ion, as in the initial and final systems. The absence of significant modifications of the solvation shell in the uncharged system leads to a decrease in ΔG^0 more than 10ccal/mol. Finaly, the thermodynamics of the process is largely influenced by the charge state of the complex ion and the destruction and formation of the solvation shell as a source of ions, and the resulting ionmonovalent ions.

ANALYSIS OF INTERMOLECULAR INTERACTIONS WITH IODINE PARTICIPATION IN BIOLOGICALLY ACTIVE STRUCTURES

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In biological systems iodine is a component of thyroid hormones and nonsteroidal anti-inflammatory drugs (iodoindometacin and iodosuprofen), it is also used as X-ray contrast and for specific detection of melanoma.[1] A variety of functions performed by iodine derivatives is achieved because of rich possibilities to intermolecular binding.

Intermolecular interactions analysis was based on calculated quantum-topological characteristics of electron density and extrapolation dependences of these quantities on the internuclear distances.[2] Such exponential functions were constructed according to calculations of the electronic characteristics of the model structures with known single-crystal geometries including C–I, N–I, S–I, I–I and I–H interactions.[3] Subsequently obtained data about bond characteristics in organic polyiodides, neutral iodine complexes and structures with iodine-alkyl fragments were compared.

A versatile analysis of intermolecular interactions with iodine participation in protein macromolecules, taken from protein data bank was made.[4] Iodine was located in I-tyrosine in proteins, in nucleotides or in drugs associated with proteins. All protein macromolecules or their complexes were divided into classes according to iodine participation in intermolecular interactions. A comparison concerning iodine-bond characteristics in the units of small molecules and complicated biological systems in crystal state was made.

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BF_2-COMPLEXES OF DIPYRROLYLMETHENES AND *BIS*(DIPYRROLYLMETHENE)S: SYNTHESIS, ABSORPTION AND EMISSION SPECTRA

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Bifluorineboride complexes of dipyrrolylmethenes (BODIPY) and *bis*(dipyrrolylmethene)s possess of practically useful properties, intense absorption and emission in a visible region of spectral range. The detection of correlation between "structure-property" and developing synthetic aimed procedures are the main problems of the chemistry of these compounds. In this connection, BF_2-complexes of 3,3′,5,5′-tetramethyl-4,4′-diethyldipyrrolyl-methene (**I**), *ms*-phenyl-3,3′,5,5′-tetramethyl-4,4′- diethyldipyrrolylmethene (**II**) and 1,2,3,7,13,17,18,19-octamethyl-8,12-diethyl-biladiene-*a,c* (**III**) were obtained. The structure of these compounds was confirmed by elemental analysis, NMR and IR spectroscopies. The absorption and emission spectra of **I**, **II** and **III** compounds were investigated in various organic solutions. It was established that the peaks of intense absorption bands of these compounds are in the range of 528-534, 523-527 and 559-568 nm, respectively. The values of Stokes shift for **II** and **III** compounds belongs in the range 11-15 nm, the less amounts (5-10 nm) being for **I** in studied solvent. The synthesized BODIPYs are characterized by considerably high fluorescence quantum yields (Φ_{fl}=0.99) and life time (τ_{fl}). It was shown that changing nonpolar for polar solvents results in reduction of fluorescence quantum yields by ~10-20% for **I** and **II** complexes and almost in 100 time for **III**.

Thus, the high selectivity of fluorescent properties in organic solvents of different origin makes it possible to recommend **III** as fluorescent probe on the environment polarity. It should be noted, because of the molecules aggregation of the synthesized BODIPYs absence in the range of working concentration in methanol, dipyrrolylmethene dyes have a considerable advantage of applying as limiters of hard laser emission as compared with rhodamine dyes.

This work was supported by the Analytical Departmental Target Programme "The Development of Research Potential of Higher School (2009–2011)", Federal Target Programme "Research and Research-Teaching Stuff of Innovative Russia" (2009–2013).

ABOUT THE ROLE OF CYCLIC PRODUCTS IN FORMATION OF LINEAR MACROMOLECULES AT POLYCONDENSATION

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At polycondensation studying dihaloarenes with Na_2S us formation enough high-molecular poly(arylene sulfide) at early steps of polycondensation is revealed at low values of conversion of functional groups when at reactionary weight there is a significant amount of initial monomers. As within the limits of traditional S_N2 the polycondensation mechanism the given phenomenon doesn't give in to an explanation prof. Heitz has assumed in due time participation of ions-radicals and, in particular, has considered possibility of the anionic-radical mechanism of the given reaction.

In our opinion, formation high-molecular polycondensation products at early steps of reaction can be quite logically explained participation is collateral formed macrocycles in formation polymer. So, us it is revealed that formation of macrocycles at polycondensation of dihaloarenes with Na_2S depends on an isomerism of an aromatic monomer, the nature in it bridge groups, concentration, an order of introduction of reagents in reactionary weight and, regulating these factors, the exit of macrocycles can make 70 % and more.

At the same time, owing to propensity Ph-S to sulfidolisis at interaction with Na_2S, arylene sulfide macrocycles easily enough are exposed anionic to polymerization under the influence of being in reactionary weight sulfide-anions, as leads to formation of high-molecular products at early stages of polycondensation.

It is interesting that linear macromolecules also are subject to sulfidolisis reaction under action sulfide-anions in the conditions of the synthesis, accompanied by formation of the same set of macrocycles. It follows from this that polycondensation has reversible, equilibrium character in spite of the fact that its low-molecular by-product (NaCl) is insoluble in the environment and is deduced from reaction sphere. Macrocycles – linear polymer promotes balance high flexibility and non intencity there of Ph-S communications in macrocycles. By method X- ray analysis it is established that macrocycles about 4 and more *p* - replaced Ph-S links and with 3 and more *m*- Ph-S fragments in a cycle because of distinctions in conformation cycles are not intense.

SOLID SOLUTIONS OF PLATINUM(II) AND PALLADIUM(II) COMPLEXES: SYNTHESIS AND THERMAL PROPERTIES

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At present time the more than a half of mined platinum and palladium are expended on production of automotive catalytic converters. In particular, bimetallic Pd-Pt superfine systems are used in diesel oxidation catalysts. One of the most effective routes for synthesis bimetallic nanoalloy is use single-source precursors, which contain both metals mixed on atomic level. Precursor compounds should match many requirements. They shouldn't contain sulfur, halogens or alkali metals and should decompose at relatively low temperatures.

We propose a study of a series of square planar Pt(II) and Pd(II)complex compounds. Due to an additional requirement of isostructurality these complexes can cocrystallize at any ratio in a single phase. Ligands should consist of light nonmetals (C, H, N, O) in order to yield gaseous thermolysis products, therefore ammonia and oxalate-ions suit for these purposes best of all. By means of joint crystallization or precipitation the next bimetallic solid solutions were obtained: $[M(NH_3)_4](NO_3)_2$, $[M(NH_3)_4](HCO_3)_2$, $[M(NH_3)_4]C_2O_4$ and $(NH_4)_2[M(C_2O_4)_2]\cdot 2H_2O$ ($M = Pt_xPd_{1-x}$, x=0.25, 0.5, 0.75). Individual salts and bimetallic phases have been characterized with IR-spectroscopy, elemental, XRD and thermal analysis.

Thermal properties of mixed complexes are closer to pure palladium analog but thermal stability grows with increase of platinum content. Decomposition of $[M(NH_3)_4](NO_3)_2$ and $[M(NH_3)_4]C_2O_4$ accompanies with thermal explosion. The most interesting is the fact that both metals in mixed complex salts reduce simultaneously at temperatures appreciably lower than the temperature of corresponding pure platinum compound reducing.

Bimetallic thermolysis products were characterized with XRD, EDS, SEM and TEM. It was shown that heating rate and annealing time have less influence than annealing temperature.

The work is supported by RFBR grant 11-03-00668, Presidium SB RAS interdisciplinary project No 112 and RF state contract № P960 of Federal target program «Scientific, Research And Teaching Specialists In Russia» 2009–2013.

MULTIFUNCTIONAL SUPRAMOLECULAR SYSTEMS AT THE INTERPHASE: PROPERTIES AND APPLICATIONS

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Design, study and application of multifunctional supramolecular systems (MSS) present a whole complex of the actual and important problems at the "cross-section" of colloid and polymer chemistry; physical-organic and biological chemistry; chemical and biotechnology. Such systems have fundamental importance for studying of the self-organization molecular recognition and diffusion phenomena, including the process of cell reception and membrane transport. The numerous types of the ultrathin films and membranes based on crow-ethers derivatives (CED), peptides-ionophores, synthetic and natural polymers and lipids have been studied in the frame of our scientific projects (RFBR; RFBR-DFG; Ministry of Education and Science).[1] Such MSS have a complex of desirable properties: special hydrophobic – hydrophic ratio; self-association at the interphases; selective binding of particular cations, anions and small biologically active compounds (BAC); photoreception and photoactivation; combination of order and mobility; 6. desirable changes in the nanodimentional structures by complex formation. The most pronounced example of such MSS is the CED monolayers of particular structure that can selectively bind alkali-earth or heavy metal cations, biogenic amino acids and other BAC.[1,2] The importance of such MSS is due to their fundamental importance and great potential for application in chemical and biological sensors; filters, membranes, electrodes, photochromic and photorefractive elements, materials recording, for processing and storage of optical information, atomic force and fluorescence confocal microscopy. [1]

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STEREOSPECIFIC POLYMERIZATION OF DIENES UNDER ULTRASONIC IMPACT

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The ultrasonic irradiation can be used as a method of influence on molecular weight of polymers, a way of generation of free radicals and influence on dispersity of heterogeneous catalysts. In connecting with that ultrasonic irradiation influences at the same time on a few characteristics of process can be considered as convenient instrument for disclosing peculiarities of polydienes synthesis on microheterogeneous Ziegler-Natta catalysts.

The ultrasonic irradiation at the stage of forming reaction mixture at the butadiene and isoprene polymerization with present catalytic system $TiCl_4$-$Al(i\text{-}C_4H_9)_3$ result in intensification of synthesis process due to the increase of the chain propagation constants rate. At polymerization of butadiene is observed increase of content of 1,4-trans-units and decrease in average molecular weights. The polyisoprene synthesis under ultrasonic impact is characterized high content 1,4-cis-units and increase of average molecular weights. Independently of monomer nature the short-term ultrasonic irradiation of reactionary mixture makes for synthesis polymer with more narrow MWD.

At the analysis of molecular characteristics of synthesized products the method of the decision of inverse problems MWD with identification of typical set of the active centers had used. In the process of synthesis of polyisoprene and polybutadiene multiplicity catalyst system is transformed into single-center catalyst system. However, for the butadiene and isoprene are dominating the different types of active centers: $\ln M = 11.3$ for butadiene and $\ln M = 13.1$ for isoprene. This corresponds differently selectivity of butadiene and isoprene for types of active centers. Variation of catalyst size particle distribution under ultrasonic irradiation and reduction of number types of the centers of butadiene polymerization determine of correlation between dispersion microheterogeneous titanium catalyst system and it's kinetic heterogeneity.

The study was support by grants of Russian President МД–3178.2011.8, МК-831.2011.3, Program of RAS № 7 and Federal Task Program № 02.740.11.0648.

SPECTROSCOPIC AND QUANTUM-CHEMICAL STUDY ON BINARY EXTRACTANTS BASED ON QUATERNARY AMMONIUM BASES

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For the isolation, separation, concentration and purification of a wide range of objects with using extraction methods binary extractants (salts of organic acids with organic bases)[1] are of great interest.

In this work, the systematic studies of the composition, structure and properties of binary extractants of various compositions using a set of spectroscopic and quantum-chemical methods are given. The binary extractants based on quaternary ammonium bases (QAB) and different organic acids (*p*-tert-butylphenol, caprylic, di(2-ethylhexyl)phosphoric, di(2-ethylhexyl)-dithiophosphoric, dinonylnaphtalene sulphoacid etc.) were obtained. Synthesis of these binary extractants was carried out on the previously developed method[2]:

$$R_4NCl_{(o)} + HA_{(o)} \longleftrightarrow R_4NA_{(o)} + H^+_{(aq)} + Cl^-_{(aq)}$$

The IR transmission spectra of initial organic acids, mixtures of acids with QAB chloride and synthesized binary extractants in CCl_4 were obtained.

A computer simulation of binary extractants structures of different compositions by semiempirical and nonempirical methods using freeware (noncommercial) software package PC CAMESS[3] was carried out. The geometric and energy characteristics of the calculated optimal structures were found.

The conducted spectroscopic and quantum chemical studies confirmed the composition and the ionic character of the formation of binary extractants based on QAB and organic acids.

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HETEROGENEOUS SOURCE OF HALOGENS IN THE TROPOSPHERE

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Heterogeneous processes are the component part of overall chemical reactions in the troposphere, which determine its chemical composition. The flux of marine aerosol into the troposphere is evaluated to be of 1,500 Tg / year and exceeds 50% of total aerosol flux. Because of mass transfer, increased concentration of sea-salt aerosol particles is detected at a distance far from coastal line. Reactions of nitrogen containing trace gases NO_x and NO_y at a gas-particle interface liberate halogens and their derivatives from the aerosol into the gas phase.

Using coated-insert flow tube reactor coupled to mass spectrometer with molecular beam sampling, a reactive uptake of NO_3 radicals as the "night-time oxidant" as well as NO_2 and $ClNO_3$ molecules on polycrystalline saline films was studied, the coverings being the main reactive constituents of natural sea salt. The studies were carried out for the uptake of NO_2 molecules on NaCl films, $ClNO_3$ molecules on NaCl, $MgCl_2 \cdot 6H_2O$ and NaCl doped with $MgCl_2 \cdot 6H_2O$ films, and NO_3 radicals on NaCl, NaBr, NaI, $MgCl_2 \cdot 6H_2O$, $MgBr_2 \cdot 6H_2O$ as well as on NaCl doped with NaBr, NaI, $MgCl_2 \cdot 6H_2O$, $MgBr_2 \cdot 6H_2O$ films under conditions of varying humidity up to 10^{16} molecules cm^{-3} and the reactant concentrations ranging between 10^{10} and 10^{14} molecules cm^{-3}. The temporal dependences of the uptake coefficient γ on (i) the reactant concentration at a fixed humidity; (ii) humidity at a fixed gas-phase reactant concentration; (iii) temperature; (iv) admixture of a doped salt in NaCl were measured. Under the same conditions, the reaction gas-phase products were detected and their branching ratio in the total uptake was determined.

On the basis of our experimental dependences and an analysis of literature data, a kinetic model of the uptake is proposed. The main outcome of the model is an analytical representation of γ in terms of some elementary parameters and the rate coefficients of elementary processes. By handling of experimental data with the proposed model, some elementary rate coefficients were evaluated, i.e., the desorption rate coefficients and the adsorption heats, the rate coefficients of elementary heterogeneous reactions and their activation energies. The model allows us to extrapolate the laboratory data to real tropospheric conditions and to elucidate which of the uptake coefficients, i.e., the initial or steady-state ones has to be used in the databases for chemical modeling of the troposphere.

TRIPLET NITROCOMPOUNDS ROLE IN PHOTOCHEMICAL OXIDATIONS OF HYDROCARBONES, OLEFINS AND NITROSOCOMPOUNDS

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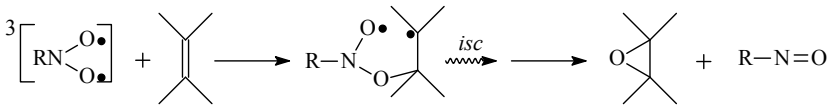
Aromatic nitrocompounds (RNO_2) being irradiated with u.v. light turns into the triplet state ($^3RNO_2$).[1]

$$RNO_2 \xrightarrow{h\nu} {}^1RNO_2^* \overset{isc}{\rightsquigarrow} {}^3RNO_2$$

$^3RNO_2$ are strong oxidizing agents and can take part in the hydrogen abstraction[2], addition to olefins double bonds, oxygen atom transfer reactions, interconvertion into nitroso oxides[3] or nitrites. Effectiveness of the reactions strongly dependent upon presence in the reaction system so called co-initiator being a substance that is able to react with $^3RNO_2$ effectively (mandelic acid, *iso*-propyl alcohol, N,N-dialkylamines , olefins).

$$^3RNO_2 + H\text{-}P \rightarrow {}^3\{P^{\bullet}\ldots RNO_2^{\bullet}H\} \rightarrow P^{\bullet} + RNO_2^{\bullet}H$$
$$RNO_2^{\bullet}H \leftrightarrow RNO + HO^{\bullet}$$



We performed quantum chemical calculations of the transition state geometries and obtained estimates of activation energies. Models with both $^1RNO_2^*$ and $^3RNO_2$ were studied, the latter activation energies being lower. The conclusion was arrived earlier on the base of the "heavy atoms effect" after addition of Br-containing compounds[2], metal oxides, or polyoxometalates.

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MASS-SPECTROMETRIC INVESTIGATION OF SUBLIMATION OF ABABAB-TYPE MACROHETEROCYCLE

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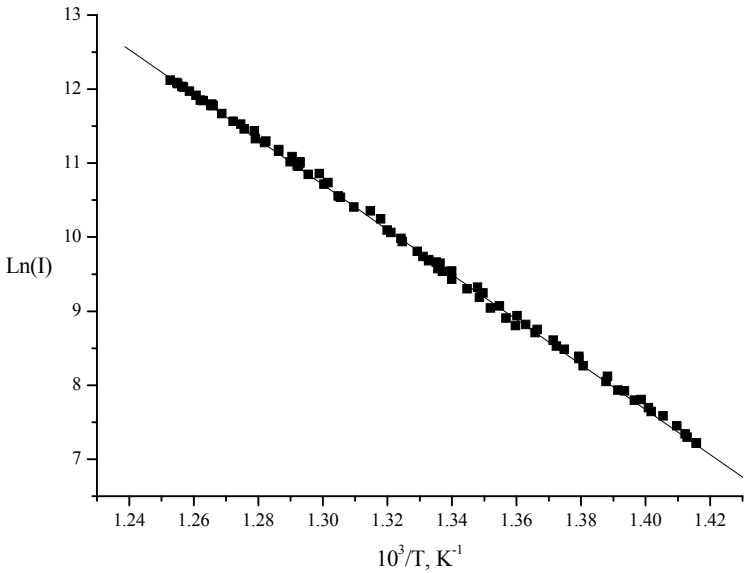
Recent years have witnessed an increased interest in modified-core analogues of porphyrazine and phthalocyanines in which one or two pyrrole or isoindole subunits are substituted by residues of aromatic diamines. In present work we investigated process of sublimation of expanded heteroazaporphyrinoid ($C_{30}H_{15}N_{15}S_3$) by the high temperature mass-spectrometric method. The mass spectrometric studies were carried out using the MI-1201 mass spectrometer modified for high-temperature studies. Investigated substance was evaporate from stainless cell by the Knudsen method.

At temperature T = 706 – 798 K, the molecular ion (m/z = 681) dominated, followed by several ions of weak (3–4%) intensity. No ions corresponding to the oligomeric species were detected. The enthalpy of sublimation calculated by the second law of thermodynamics is found to be 252(2) kJ/mol for the average temperature. The dependence of the logarithm of intensity of the molecular ion on temperature is shown in Figure.



Supported by RFBR (Grant 10-03-00884a).

UNUSUAL BROMINATION OF SUBSTITUTED 8-ALLYL-2-METHYL-1,2,3,4-TETRAHYDROQUINOLINES

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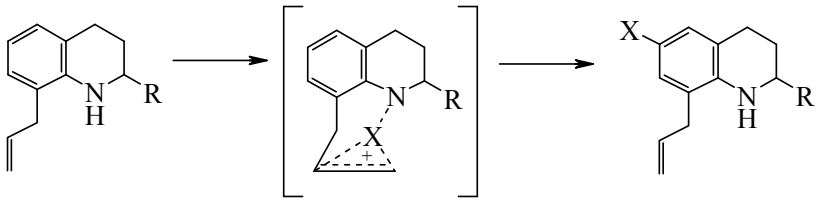
Halogencyclisation reactions of *o*-allylanilines are often used to synthesize indole[1] and tetrahydroquinoline[2] structures.

We have carried out the bromocyclisation of 8-allyl-2-methyl-1,2,3,4-tetrahydroquinoline-4-carboxylate acid. However only methyl 8-allyl-6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline-4-carboxylate was isolated instead of cyclic product.

The reactions of 2-substituted 8-allyl-1,2,3,4-tetrahydroquinolines with different halogens in various conditions (Br_2 and I_2 in CH_3CN, CCl_4, AcOH, MeOH) have been studied. 6-Halogensubstituted tetrahydroquinolines are formed almost in all cases. Only a small amount of 9-bromo-3-methyl-2,3-dihydro-1*H*-pyrido[3,2,1-ij]quinolinium bromide is formed when bromine in acetonitrile is used.



R=H, Me, Ph; X=Br, I

The unusual results of the bromination could be explained by the intermediate forming “bridge” bromonium ion which leads the reaction as the brominating agent.

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STRUCTURE AND PROPERTIES OF PARAMAGNETIC IONIC LIQUIDS

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In recent years, increased interest in class of compounds, such as ionic liquids (IL). Ionic liquids – are salts liquid at room temperature or near it. The composition of ionic liquids is bulk organic cation: 1,3-dialkilimidazoly, alkylammonium, alkilfosfony, N-alkylpyridinium, etc., and inorganic or organic anion. The main characteristics of the IL - high thermal stability, low vapor pressure, good solvent power, nontoxic, incombustibility.

We obtained chlorides of quaternary salts of pyridinium, imidazolium and ammonium different structure of the organic cation and on their basis the paramagnetic ionic liquids with the anion $[FeCl_4]^-$. For the first time a complex of complementary physical methods (IR, NMR, Raman spectroscopy, spectroscopy in the visible area and X-ray) described the structure of new compounds. It was demonstrated that the structure and nature of the organic cation in the paramagnetic IL has a significant influence on the structural organization of the crystal, which leads to a change in their physical and chemical properties.

The obtained results extend and deepen knowledge about the relationship of structural and physicochemical properties of paramagnetic IL for their use in specific purposes. We show that the new paramagnetic ionic liquids can be used as media for levitation and manipulation of various diamagnetic macro-and microscopic object. With its high thermal stability ($350\text{-}400^0$C), they can be used as a catalytic media in a fairly wide temperature range. New paramagnetic IL can be a source of nanoscale paramagnetic particles in nanocomposites. The obtained results and established patterns of influence of the structure paramagnetic IL on their properties may provide a basis for targeted controlled of IL properties and their use in new chemical nanotechnology.

This work was supported by the Foundation for Assistance to Small Innovative Enterprises in science and technology, project №8701r/13135

EFFECT OF MICROWAVE IRRADIATION ON ALUMINUM ORGANIC COMPOUNDS

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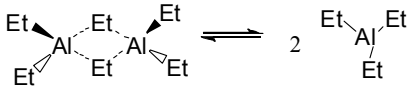
It was found that microwave irradiation of aluminum organic compounds (AOC) during preparation of ethylene trimerization catalyst can significantly increase its activity.[1]

We investigated the mechanism of the microwave irradiation effect using triethylaluminum (TEA) as an example. Real-time IR spectra of microwave-irradiated TEA in toluene showed that there are significant changes within first 5 minutes after the irradiation. There is an isosbestic point at 2975 cm^{-1}, which indicates presence of two interconverting species.

It is known that TEA at normal conditions is an equilibrium mixture of its monomer and dimer with predominance (>99%) of the dimer.[2]



Cryoscopic measurements of TEA in benzene after microwave irradiation showed that there is partial monomerization of TEA (degree of dissociation up to 0.4), followed by return to the dimer. This is in accordance both with the IR experiment and with relative activity of the catalysts prepared using irradiated AOC with different delay after the irradiation. The monomer is the kinetically active specie of TEA in many of its reactions[3]. We suppose that TEA is monomerized under microwave irradiation, and this facilitates formation of active ethylene trimerization catalyst species.

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The work has been done under corporate research program of Sibur Holding (2009).

REGIO- AND STERESELECTIVE FUNCTIONALIZATION OF THE SUBSTITUTED GEM-DICHLORCYCLOPROPANES.

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Substituted gem-dichlorcyclopropanes are formed by dichlorcycylopropanation of the linear and cyclic olefins and dienes, alkenylhalides, unsaturated alcohols, acids and others. It is of interest to develop the way of selective functionalisation of the substituted gem-dichlorcyclopropanes, which permit to retain carbocyclic fragment.

We have found the conditions of the selective halogenation and hydrohalogenation of the vinyl-, alkenyl-gem-dichlorcyclopropanes which occur without destruction of the cycle. As result of the soft oxidation of the vinyl- gem-dichlorcyclopropanes we have got appropriate alcohols, carbonyl compounds and acids.

O-alkylation of alcohols, phenols and chlormetylhemedichlorcyclopropanes depend on exo- and endocyclic chlorine atom which allowing to get appropriate ethers and ketals. When we used pyrocatechols we get appropriate benzo-1,3-dioxalanes.

Liquid-phase, radical oxidation of the alkyl- and phenyl-gem-dichlorcyclopropanes goes with intermediate formation of the tertiary hydro peroxides, decomposition of it is attended by opening of carbocycle.

We found the conditions of the selective reduction of the chlorine atom in the endocyclic CCl_2-group.

We receive the whole range of the polyfunctional gem-dichlorcyclopropanes among this compounds we found molecules with high biological activity.

COMPOSITION CATIONIC POLYELECTROLYTES AS REGULATOR PROPERTIES OF DISPERSIONS

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The high - molecular compounds aggregate capability study, having resulted in the disperse phase sedimentationly unstable state, is being presented the obviously scientific and the practically real interest at the dispersions destabilization processes examination. The individual flocculants use just in the compound multi-component dispersions is not being permitted to achieve the high level efficiency of the dispersions division in the majority of the cases. Therefore, the use bases development of the cationic polyelectrolytes composition is being presented the perspective direction just in this field of the researches.

The aggregate capability of the cationic polyelectrolytes compositions peculiarities finding, on the basis of the kinetic stability analysis of the model kaolin aqueous suspension and the activated sludge structure formation processes is the work's aim. As flocculants we used the polyelectrolytes: poly-1,2-dimethyl-5-vinylpyridine metal sulfat (A), poly-N,N-dimethyl-N,N-diallilammony chloride (B), poly-N,N,N-trimethylamineethylmethacrylate metalsulfat (C, E) copolymer of acrylamide with N,N,N-trimetilpropilakrilamidammony chloride (D).

The synergism effect has been discovered, in the result of the PE binary and the ternary mixtures aggregate capability investigation for the compositions' most part. For example, for 0,8% kaolin suspension at a total concentration of flocculants 1 mg/l:

$V_s \cdot 10^{-2}$, s^{-1}	1,0	10,5	4,7	12,0	16,0	15,9	17,0
PE	-	A	B	C	A+B	A+C	A+B+C

Finding synergies flocculation of mixtures of cationic polyelectrolytes can be explained by the fact that when using polymers of different chemical structure in the process of flocculation effect is manifested incompatibility of adsorbed chains of macromolecules, which results in their contraction and expulsion of water from the surface layer. This leads to an increase in surface hydrophobicity floccules, which makes them denser and increases the rate of their deposition.

NITROGEN- AND OXYGEN-CONTAINING MACROPOLYCYCLES ITH NAPHTHALENE AND BIPHENYL MOIETIES

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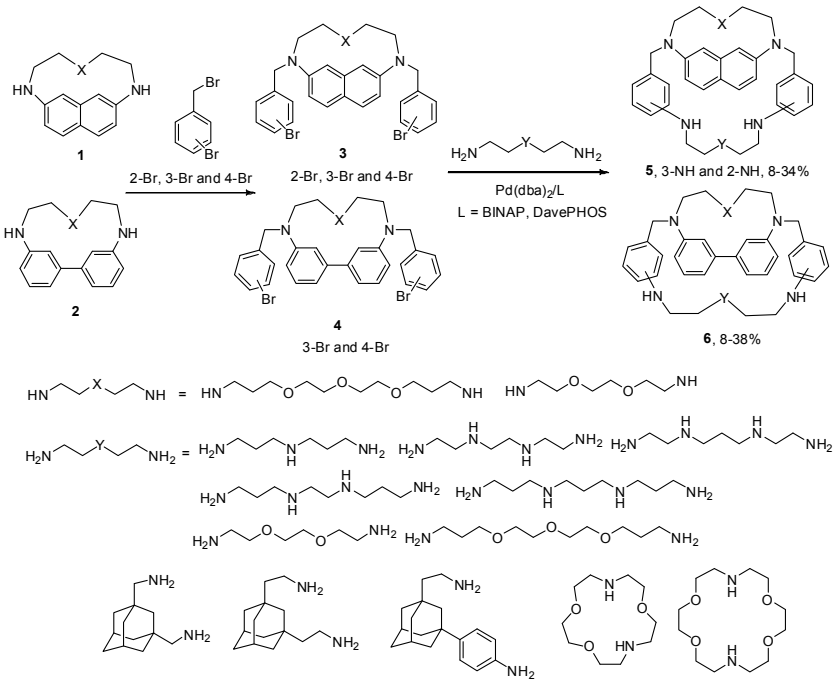
Macrocycles based on naphthalene **1** and biphenyl **2** were modified with bromobenzyl substituents in quantitative yields and resulted compounds **3** and **4** were introduced in the Pd-catalyzed amination reaction with various polyamines. Macropolycycles **5** and **6** were synthesized in these reactions in yields up to 34–38%. A strong dependence of the macrocyclization reaction results on the structure of the starting macrocycle, substitution pattern at bromobenzene and the nature of the second polyamine chain was established.



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Correspondent presentations

STRUCTURE OF ANILIDES

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According to the results of quantum-chemical studies (PM3 method) of molecules of formanilide, acetanilide, o-methylacetanilide, 4-aminoacetanilide, o-hydroxyacetanilide, nitroacetanilides almost all the compounds the nitrogen atom of the amide group is full or almost in the plane of the benzene ring. [1-2] Anilide molecules are in (E) - (formanilide, acetanilide and its O-methyl-, aminosubstituted forms) and a (Z)-conformation (hydroxyl and nitroacetanilides). One of the C-H bonds acyl methyl group obscures the C-N group.

Introduction of different substituents in the molecule of acetanilide controversial changes its geometry.

Length of C=O and C-N bonds in the molecules anilide lie in the range 1.21-1.23 Å and 1.39-1.42 Å respectively. Found that the introduction of substituents in acetanilide molecule does not affect the bond lengths.

Comparison of geometric parameters of acetanilide molecules in the gas phase with the results of XRD analysis of its crystals indicates a decrease in the length of C=O bond and increasing the length of C-N bond in the gas phase compared with the solid.

In the transition from molecules of amides to anilides (acetamide - acetanilide) the length of C=O bond becomes somewhat shorter (down to 1.21-1.23 Å), and bond C-N, on the contrary, longer (1.39-1.42 Å).

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MECHANISM OF THE HOUBEN-HOESCH REACTION: MOLECULAR STRUCTURE OF $[Pd(NHC(CH_3)C_6H_4)]_2(M\text{-}CH_3CO_2)_2$ COMPLEX

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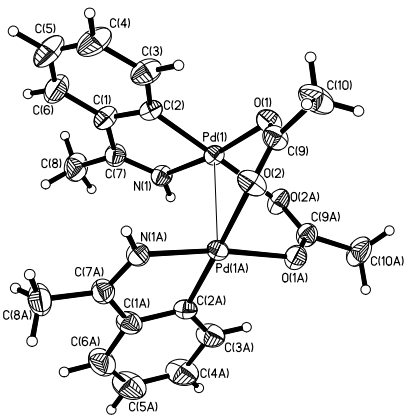
The Houben-Hoesch reaction is one of the general applied methods of the arenes acylation with nitriles in the presense of the Lewes and/or Brensted acids ($ZnCl_2$, HCl and etc.). The reaction products are aromatic imines, which hydrolyze to ketones hereafter. Larock and co-workers used for the reaction palladium(II) acetate and suitable additives (usually CF_3COOH). In spite of the extensive use of this reaction its mechanism isn't completely resolved and two possible catalytic cycles are discussed.



We have found out that boiling of palladium(II) acetate $Pd_3(OAc)_6$ in the mixture of benzene and acetonitrile without strong Brensted acids leads to formation $[Pd(NHC(CH_3)C_6H_4)]_2(\mu\text{-}CH_3CO_2)_2$ complex. This compound carries 1-phenylimine ligands which are C-C addition products of nitrile and benzene molecules. Moreover, free 1-phenylethanimine was detected in the solution. Hence, this complex can be considered as intermediate of the Houben-Hoesch reaction between benzene and acetonitrile.

Our data is allowed to correct hypothesis [2] about this reaction mechanism:

1. Electrophilic addition of acetonitrile to benzene proceeds between molecules coordinated on palladium.

2. The role of trifluoroacetic acid in the Pd-catalyzed system is acidolysis of intermediate palladium compounds for the formation of free imine.

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INVESTIGATION OF HIGH FERRIFERROUS SULPHIDE LEAD CONCENTRATES PROCESSING TECHNOLOGY

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The complex processing of hard enrichable ores contributes to involving the new raw materials sources in industry and extending of non-ferrous metallurgy ore basis. In 2007 comes into the force the agreement according to the division of production between Azerbaijan Republic and group to the British investers for study and prospecting with the following output of the non-ferrous and noble metals industrial reserves of the hard enrichable high pyritous polymetallic ores of Filizchay deposit[1]. Sulphide lead concentrates, used in our researchs, have been obtained by means of flotation of Filizchay ores.

In large-scale laboratory conditions we have obtained the qualitative high ferriferrous lead sinter[2]. Average composition of damp agglomeration charge, %: Pb = 33.8; Fe = 15.10; SiO_2 = 8.7; CaO = 6.6; S = 9.3; Cu = 1.08; Zn = 4.16. The calculated average chemical composition of ferriferrous slag is as follows, %: ZnO = 10; FeO = 38 ÷ 42; SiO_2 = 21; CaO = 16. The average chemical composition of the obtained lead sinter, %: Pb = 36.4; Fe = 16.3; Zn = 4.3; Cu = 1.1; Ag = 1200 g/t, Bi = 0.11; SiO_2 = 10.65; CaO = 5.2; S_{total} = 3.2; $S_{sulphiden}$ = 1.4. Reducing melting of the obtained lead sinter has been carried out in laboratory conditions by use of converted natural gas in the capacity of a reducer. Optimum conditions of reducing process: temperature – 1200^0C, consumption of the gas-reducer is amount 1.5÷1.8% of the sinter′s weight. In optimum conditions low lead losses in the the ferriterrous slag (1.67÷1.78%) can be achieved with a CaO/SiO_2 ration and FeO concentration in the slag in the ranges of 0.79÷0.84 and 37.7÷40.5 wt % respectively. Possibility of the effective processing of Filizchay lead concentrates according to proposed technology is confirmed by means of results of industrial trials of high ferriferrous sulphide lead concentrates processing by the blast furnace reducing melting method[3].

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CALCULATION OF RADIUS OF ATOMS IN DIFFERENT ENERGY STATES

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Known methods of calculating the radii of the chemical elements do not allow their quantification in the whole energy range. We have proposed a mathematical expression that allows to conduct such an assessment. In accordance with the concept of the presence of the photonic electromagnetic field around the electrically charged particles [1,2], it was assumed that the torque (Mì) electron motion along the orbit created by the emission of a photon and the photon energy is equal to:

$$\square_i = h\nu_i = M_i = \frac{dL}{dt} = \frac{mvr}{\tau} = \frac{mvrv}{2\pi r} = m\upsilon_i^2/2\pi = E_к/\pi \quad (1)$$

From the equality of the Coulomb and centrifugal forces in e^- atom

$$\xi e^2/4\pi\square_o r_i^2 = m\upsilon_i^2/r_i \quad (2)$$

that $m\upsilon_i^2/2\pi=\xi e^2/8\pi^2\square_o r_i=h\nu_i$ and then

$$r_i = \xi e^2/8\pi^2\square_o h\nu_i = \xi e^2\lambda_i/8\pi^2\square_o hc, \quad (3)$$

here τ – the rotation period of the e^- around the nucleus ($\tau = \frac{2\pi r}{v}$) ; L– momentum e^-; $E_к$– is the kinetic energy of translational motion of the e^-on orbit; λ_i - the wavelength of the emitted ì-th photon, c - is the speed of light; and e - is the charge electron; $\square_o$ about - the dielectric constant; υ_i - speed of an electron in an orbit with a radius r_i; m - electron mass; ν_i -frequency of the radiation ì-th photon; h - Planck's constant; ξ - the force of an atom ($F_{ион}$) to the force of Coulomb attraction ($F_к$) of the electron to the nucleus (at the rate of one proton in the nucleus, regardless of the nuclear charge). For most items in the calculation adopted parameter $\xi = 0.8$. According to the proposed formula (3) to calculate the radii for the many atoms in the whole energy range of the emitted photons. Calculated values of limiting radii ($r_{min} – r_{max}$) are in good agreement with published data on individual elements.

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GAS PHASE DEHYDROGENATİON OF İZOPROPYL AND İZOAMYL ALCOHOLS TO CARBONYL COMPOUNDS ON METALZEOLİTE CATALYSTS

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Mixed oxide catalysts show high catalytic activity in the reaction of oxidation of aliphatic alcohols [1].

It has been studied the gas phase oxidation of isopropyl and isoamyl alcohols to carbonyl compounds with taking part of molecular oxygen on the synthetic zeolites of types A, X, Y. And natural zeolites, clinoptilolite and mordenit modified by cations of transition metals.

Modified zeolite catalysts were prepared by the method of ion exchange describe in [2].

On the basis of the experimental ininvestigations the efficient modified zeolite catalyst, CuPd-mordenite prepared by ion exchange, has been selected for the reaction of oxidation of isopropyl alcohol into acetone.

CaA synthetic zeolite containing of Pd^{2+} and Cu^{2+} shows the highest activity in the reaction of oxidation of isoamyl alcohol into isovalerianic aldehyde. It has been studied the influence of nature and concentration of cations on the direction of the reactions.

It was chosen conditions of activation and regeneration of the catalyst. It was shown, that after regeneration and activation the catalyst completely regenerate its activity.

By treatment of a surface of the catalyst by pyridine it has been studied roles of the acidic centers of the catalyst in the reaction of the partial oxidation of the isoamyl alcohol.

By means of experimental data it is proved, that in the absence of oxygen dehydrogenation of alcohols does not proceed. For this reason process refers as oxidative dehydrogenation.

Thus, results of the carried out investigations show perceptivity of the using modified metalzeolite catalysts obtaining by a method of an ionic exchange, in reactions of oxidative dehydrogenation of aliphatic alcohols.

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SELECTIVE OXIDATION OF METHANOL OVER METALZEOLITS CATALYSTS

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Modified with cations of transitions metals zeolite catalysts are polyfunctional catalytic systems for the oxidative conversion of alkyl alcohol into corresponding aldehydes, carboxylic acids, and complex esters of carboxylic acids [1, 2]. With the purpose of developing a high efficiency catalysts for selective oxidative conversion of methanol into formaldehyde, formic acid and methylformiat by method of ion exchange the row of zeolite catalysts on basic synthetic (NaA, NaX, NaY) and natural (mordenite, klinoptilolite) zeolites modified by Pd and Cu, it has been synthesized. After incorporating of ions, all of the specimens of modified catalysts were activated by air at temperature, 350^0C and space velocity, 2400 h^{-1}, during 30 min. The test of the activity of the prepared catalysts was carried out in a flow apparatuses with reactor connected directly to the gas chromatograph. The analyses products of the reaction were performed by gas chromatography, using a column filled with polisorb-1 with program control of the temperature. The activities of the specimens of the catalysts were tested in range of temperature, 80-270^0C; space velocity, 900-3200 h^{-1} and mole ratios of $(CH_3OH:O_2:N_2) = 1:(0{,}33\div3):(1\div3)$.

It has been established that NaY zeolite, modified by Pd and Cu ions shows high catalytic activity in reaction of oxidative conversion of methanol into the formaldehyde; Pd-mordenit shows high activity in the reaction of direct oxidation of methanol into formic acid; PdCu-klinoptilolite is the active catalyst for multistage reaction of oxidative conversion of methanol into methylformiat.

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PHASE EQUILIBRIUM IN QUASI TERNARY SYSTEM CU_2S-PBS-SM_2S_3

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Quasi ternary system Cu_2S-PbS-Sm_2S_3 was studied by the following poly thermal section: $CuSmS_2$-PbS, $PbNd_2S_4$-$PbSmCuS_3$, Cu_2S-$PbSmCuS_3$ and Sm_2S_3-$PbSmCuS_3$. Quaternary alloys were obtained from batch containing 2PbS+Cu_2S+ 2Sm+3S at 1300-1400K by the method [1, 2]. After the synthesis alloys were homogenized at 1100K within a week. Obtained alloys were studied by methods of physical-chemical analysis. It was established, that in system Cu_2S-PbS-Sm_2S_3 there are the following conjugated phases in balance: $PbSmCuS_3$-$PbSm_2S_4$, $PbSmCuS_3$-PbS, $PbSmCuS_3$-$CuSmS_2$, Cu_2S-$PbSmCuS_3$. In the system Cu_2S-PbS-Sm_2S_3 five slave triangles were separated: PbS-$PbSm_2S_4$-$PbSmCuS_3$, PbS-$PbSmCuS_3$-Cu_2S, Cu_2S-$PbSmCuS_3$-$CuSmS_2$, $CuSmS_2$-$PbSmCuS_3$-Sm_2S_3 and Sm_2S-$PbSmCuS_3$-$PbSm_2S_4$.

It was established that in system $CuSmS_2$-PbS complex sulphosalt $PbSmCuS_3$ is formed at ratio of initial sulphides 1:1. Compound $PbSmCuS_3$ is formed by peritectic reaction L+PbS $PbSmCuS_3$ at 1285K. Eutectics is formed with coordinates 25 mol% $CuSmS_2$ and T=1120K between $PbCuSmS_3$ and PbS. The system $CuSmS_2$-PbS is partially quasibinary. Quasibinary is broken at higher temperature of incongruent melting of $CuSmS_2$. Lower than this temperature in equilibrium there are conjugated phases $CuSmS_2$ and $PbSmCuS_3$, $PbCuSmS_3$ and PbS.

On directed crystallization monocrystals of quaternary sulphide $PbSmCuS_3$ were grown. X-ray diffraction research showed that sulphosalt $PbSmCuS_3$ crystallizes in rhombic syngony with parameters of elementary cell: a=3.90, b=13.28, c=10.30Å and belong to structural type $KZrCuS_3$, z=4, pr.gr. Cmcm ρ=5.42 g/sm^3, H=3250 MPa.

Systems Cu_2S-$PbSmCuS_3$, Sm_2S_3-$PbCuSmS_3$ and $PbSm_2S_4$-$PbCuSmS_3$ belong to eutectic type and are partially quasi binary sections. Narrow regions of homogeneity are formed on the basis of Cu_2S, Sm_2S_3 and $PbSm_2S_4$, but on the basis of quaternary compound solubility regions are not observed.

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Aliyeva R.A., Bairamova S.T., Ragimova V.M., Aliev O.M. Neorgan. Mater., 2010, **46**, No7, 701.

SYNTHESIS OF DECAHYDRO-4H-BENZO[d]PYRROLO [1,2-a]IMIDAZOL-1-ONES BY REACTION OF 3H-FURAN-2-ONES WITH 1,2-DIAMINOCYCLOHEXANE

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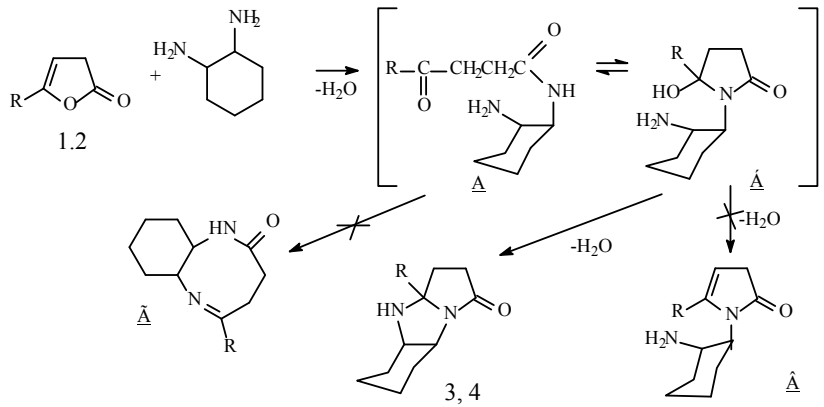
Earlier, the reactions of furan-2-ones with binucleophilic reagents of the aromatic and aliphatic series were studied. Synthesis conditions for 3a-R-decahydro-4H-benzo[d]pyrrolo[1,2-a]imidazol-1-ones (3,4) by the reaction of furanones (1,2) with 1,2-diaminocyclohexane (a binucleophil of the alicyclic series) were developed. The structure of the reaction products is noted to depend on the process conditions.

The recyclization of the heteroring of 5R-3H-furan-2-ones is shown to go through an intermediate amide of acid (А), whose cyclohydration results in decabenzopyrroloimidazolones.



1,3 R= C_6H_5; 2,4 R= 4-$CH_3C_6H_4$

One should not except possible formation of N-substituted 3H-pyrrol-2-ones Б. We have also considered possible formation of the product of attack of the second amino group of amide A at the carbon atom of the carbonyl group (bicyclic azepinone Г). Our NMR1H and 13C spectroscopy data confirm the formation of double heterocyclization products 3,4.

The work was supported by a grant of RFBR № 10-03-00640a.

SYNTHESIS OF ALIPHATIC DIAMIDODISULFOIMIDES

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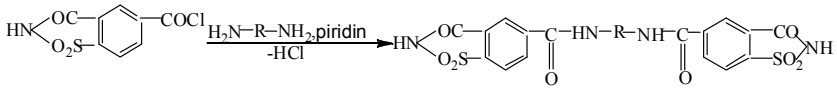
To obtain vysokotermostabilnyh geterotsiklotsepnyh polymers, as well as creating on their basis of new composite materials we synthesized diamidodisulfimidy on saccharin chloride-5-carboxylic acids with aliphatic diamines as follows:



where, R= $-(CH_2)-_{2,4,6}$

The resulting compounds are crystalline substances soluble in dioxane and aprotic solvents. The reaction was receiving diamidodisulfimidov performed at 40-45 ° C, gradually adding with stirring a solution of acid chloride to the diamine dissolved in DMAA in the presence of equimolar amount of pyridine as an acceptor of the liberated HCl [1].

As a result, were isolated in high yields bisimides containing molecule, amide and imide groups of interest as monomers for polyimides. The composition and structure of these compounds were confirmed by elemental analysis and infrared spectroscopy. The IR spectra bisimides pogdoscheniya bands in 1660-1600 The composition and structure of these compounds were confirmed by elemental analysis and infrared spectroscopy. The IR spectra bisimides pogdoscheniya bands in 1660-1600 cm-1 belong to groups C-N; 1380-1300 and 1200-1130 cm-1 characteristic of asymmetric stretching vibration of the group-SO2-saharinovogo cycle and 3350-3310 cm 1 refer to the N-H group.

Synthesized diamidodisulfimidy were used as curing agent modifier for epoxy resin ED-20, and polycondensation of these compounds with various diamines were obtained regularly alternating poliamidosulfimidy.

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SILVER(I) COMPLEXATION REACTIONS WITH THE *CLOSO*-DECABORATE ANION: THREE MODIFICATIONS OF $[AG_2B_{10}H_{10}]$

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The systematic study of Ag(I) complexation reactions with the $B_{10}H_{10}^{2-}$ anion as a ligand ked us to isolate and characterize complexes $[Ag_2B_{10}H_{10}]$ and $Cat[AgB_{10}H_{10}]$ [1]. Reactions were carried out in water and acetonitrile with *closo*-borates with organic cations $R_nNH_{4-n}^+$ (R = Me, Et, Pr, Bu; n = 0-4), GuH^+, $AguH^+$ (Gu = CN_3H_5, guanidine; Agu = CN_4H_6, aminoguanidine), Ph_4P^+, Ph_4As^+, (*Naph*CH_2)Ph_3P^+ (*Naph* - naphthyl) and alkali metals cations Li^+ - Cs^+. The structure of $[Ag_2B_{10}H_{10}]$ synthesized from water when salts of the $B_{10}H_{10}^{2-}$ anion were allowed to react with $AgNO_3$ and recrystallized from DMF was solved by X-ray diffraction [2], the monocrystals were found to have formulae $[Ag_2(DMF)(B_{10}H_{10})]$.

$$Cat_2B_{10}H_{10} + Ag^+ + H_2O \rightarrow [Ag_2B_{10}H_{10}] + DMF \rightarrow \rightarrow [Ag_2(DMF)(B_{10}H_{10})] \quad (1)$$

Ag(I) complexation reactions with the $B_{10}H_{10}^{2-}$ anion were studied when salts of the $B_{10}H_{11}^-$ anion was used as the initial reagent (2) or in conditions of protonation of the $B_{10}H_{10}^{2-}$ anion, in CH_3CN/CF_3COOH system (3).

$$CatB_{10}H_{11} + Ag^+ + CH_3CN \rightarrow [Ag_2B_{10}H_{10}]^{\#} \quad (2)$$

Complex formation reactions with onium *closo*-decaborates $(Cat)_2B_{10}H_{10}$ (Cat = RNH_3^+ (R = Me, Et, Pr, Bu)) in CH_3CN / anhydrous CF_3COOH mixture at 1 : 1 ratio of the initial reagents resulted in isolation of $[Ag_2B_{10}H_{10}]$* complex (3).

$$(Cat)_2B_{10}H_{10} + [Ag_2B_{10}H_{10}] + CH_3CN/CF_3COOH \rightarrow [Ag_2B_{10}H_{10}]^* \quad (3)$$

Notable differences in structures of the three $[Ag_2B_{10}H_{10}]$ complexes isolated from reactions 1-3 observed in IR-spectra in region of the stretching vibrations of BH-bonds. IR-spectroscopic data of three modifications of $[Ag_2B_{10}H_{10}]$ complex are presented in Table 1. Analysis of powder diffraction patterns of the three complexes $[Ag_2B_{10}H_{10}]$ isolated by reactions 1-3 revealed some structural differences in studied complexes, that confirm individuality of each modification. Differences in the structures of $[Ag_2B_{10}H_{10}]$ complexes are determined firstly by reaction conditions. Thus,

in reaction 2 complex formation reaction is accompanied by protonation of the $B_{10}H_{10}^{2-}$ anion, and in reaction 3 the initial $B_{10}H_{11}^{-}$ anion affected the path of the reaction.

Table 1. **Maxima of absorption bands in IR-spectra of three modifications of the $[Ag_2B_{10}H_{10}]$ complex, ν (cm^{-1}).**

Compound	ν(BH)	$\nu(BH)_{MHB}$	δ(BBH)
$[Ag_2B_{10}H_{10}]$	2556	2354	1070-930
$[Ag_2B_{10}H_{10}]$*	-	2365	1060-950
$[Ag_2B_{10}H_{10}]^{\#}$	2555, 2490	2365	1029, 999, 929

This work was supported by RFBR grant 10-03-00470 and NSh-3321.2010.3.

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PHARMACOCHEMICAL APPROACH TO THE MEDICAL USE OF HUMIC SUBSTANCES PELOIDS

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Recent years are characterized by an increasing use of natural humic compounds in various brances industries and agriculture.[2] The use of the humic substances is very important for the modern medicine as curative and preventive purposes.[1]

The object of our long-term research is the studying of the physicochemical and biochemical bases of the humic substances in order to get drugs to increase the efficiency of the pelotherapy, save dwindling resources of mud and maintain the ecological balance biogeocenoses zones.

The observation of the structural organization of the humic substances in therapeutic mud by amphiphilic chromatography confirmed their polydispersity. The research result of the humic acids by the capillary electrophoresis mathod makes it possible to place them to the natural polyelectrolytes with different intensity of the charged fragments.

Studying the biological activity of fulvic, hymatomelanic, humic and humus acids groups in a wide range of concentrations in model of acute carrageenan inflammation discovered a polymodal dependence of all the drugs on the dose. The dynamics of changes of the hematological and immunological parameters by injection of humic acid to animals with the development of adjuvant arthritis reflects a decrease in the inflammatory process with an autoimmune component, and at same time show us the increasing curative action by increasing of course dose.

Based on the totality of the experimental data established that humic peloids substances maintain internal homeostasis of biological systems at the organism, cellular and subcellular levels, contributing to the restoration of physiological functions in pathological conditions and in extreme situations.

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PROJECTION OF LIQUIDUS SURFACE OF TRIPLE SYSTEM Nd_2S_3-Ga_2S_3-EuS

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Search and formation of new materials with optical properties (luminophore, luminescence) are integral parts of modern scientific-technological progress. Considering this the study of systems with chalcogenides Nd_2S_3, Ga_2S_3 and EuS is scientifically and practically important. In the present article researches of complex methods of physical-chemical analysis of triple system Nd_2S_3-Ga_2S_3-EuS were given. For studying the triple system we researched internal quasi binary and non-quasi binary sections. The projection of liquidus surface of triple system was plotted. Initial crystallization region θ $[(Nd_2S_3)_{1-x}(EuNd_2S_7)_x]$; x=0÷1; EuS and α′$(Nd_6Ga_{10/3}\ S_{14})$ is the widest region in the projection of liquidus surface and is in high temperature part of crystallization field. Isotherms of this part were dotted. All isotherms were plotted by graphical interpolation every 200 hrs.

It must be stated that in the projection of liquidus surface of triple system Nd_2S_3-Ga_2S_3-EuS there are 10 fields of initial crystallization, which characterize initial components and new phases:

1 – γ (Ga_2S_3)	6 – α′$(Nd_6Ga_{10/3}\ S_{14})$
2 – β (Ga_2S_3)	7 – θ $[(Nd_2S_3)_{1-x}(EuNd_2S_7)_x]$; x=0÷1
3 – Nd Ga_2S_3	8 – γ $(EuGa_2S_4)$
4 – α $(EuNdGa_3S_7)$	9 – EuS
5 – β′ (Eu Ga_4S_7)	10 – θ $[(Nd_2S_3)_{1-x}(EuNd_2S_4)_{1-y}(EuNdGa_3S_7)_y]$

Crystallization fields are divided by monovariant curves. They are 16 in the system. Curves of monovariant equilibrium were plotted by crossing points of curves of initial crystallization phases in the systems. In the system there are 7 tetra-phase points of non-variant equilibrium. E_1, E_6 of them are points of triple eutectics, but P_1- triple peritectics. We studied the reaction in non-variant points and monovariant curves.

The character of chemical interaction in triple system was studied and for the first time the projection of liquidus surface was plotted.

We determined the character of chemical interaction, which proceeds by curves of monovariant and non-variant points.

PHYSICAL-CHEMICAL PROPERTIES OF GLASS FORMING MELTS OF SYSTEM La_2S_3 –Ga_2S_3–Nd_2S_3

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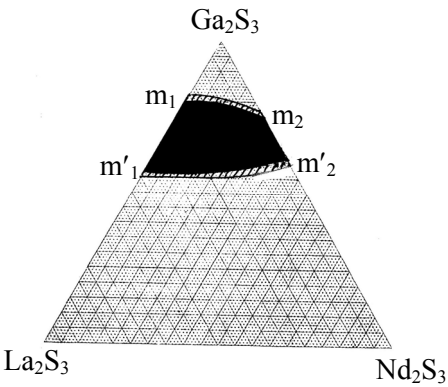
Glass-forming region in triple system La_2S_3–Ga_2S_3–Nd_2S_3 was determined and theise borders were defined by using methods of physical-chemical analysis (DTA, derivatography, X-ray diffraction) (Figure)



In the figure (m_1m_2 and $m'_1m'_2$) limits glass-forming region in system La_2S_3–Ga_2S_3–Nd_2S_3. Shaded bands in figure correspond to opaque glasses and are explained by crystallization centers in them which is confirmed by X-ray diffraction method. Shaded region conforms to transparent stable glasses. Derivatographic analysis shows, that when heating a glasses $(Ga_2S_3)_{0,60}(La_2S_3)_{0,10}(Nd_2S_3)_{0,30}$ on air at 880 K softening takes place, that coincides with shelly effect. Observed exoeffects at 915-1299 K and loss in weight shows staged oxidation of a glass. By coincidence of temperature of crystallization and decomposition of a glass, we didn't observer exoeffect of crystallization.

In IR-spectra of La_2S_3, Nd_2S_3 and Ga_2S_3 identical at 220-360 sm^{-1} region, there is an intensive band, which is valence vibrations of Me-S bond. However, this band in spectra Ga_2S_3 appears in more high frequency region of spectra (260-480 sm^{-1}). Besides, in spectra of sulfides there are number of weak bands at 540-759 sm^{-1} region, which are valence vibrations of Me-S. These bands in spectra of glasses of sulfides become more intensive which is explained by change of covalence of Me-S.

Accordingly we determined borders of glass-formation region in system La_2S_3–Ga_2S_3–Nd_2S_3, studied thermal decomposition and IR-spectra of produced glasses.

NEW METHOD FOR THE SYNTHESIS OF N-PHOSPHORYLATED UREAS CONTAINING NITROGEN HETEROCYCLES

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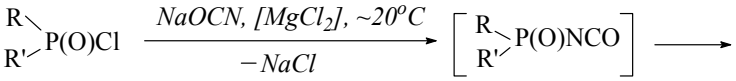
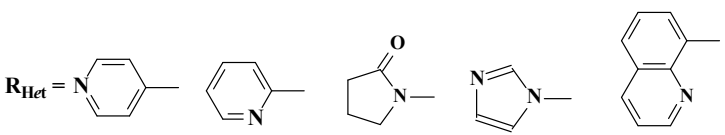
With the aim of designing new types of high-throughput and selective neutral organophosphorus extractants for removing actinides and lanthanides from acid liquid radioactive wastes, we have developed a one-pot method for the synthesis of a series of previously unknown N-phosphoryl-N'-(ω-heteroarylalkyl)ureas where the heterocyclic group can behave as a supplementary liganding fragment.

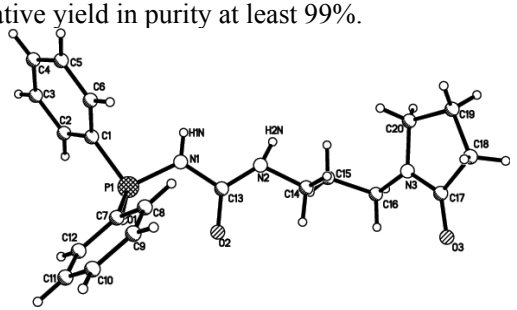


yields 91-99%

R, R' = Ph, Me, PhO, EtO; n = 2, 3



The developed one-pot method is simple and industrially feasible: both stages proceed at high rate at ambient temperature to give environmentally benign NaCl as a sole byproduct, all the target compounds are isolated in almost quantitative yield in purity at least 99%.



The structure of the obtained ureas was confirmed by the data of IR and ^{1}H and ^{31}P NMR spectra, X-ray diffraction study, and elemental analysis.

SYNTHESIS AND PROPERTIES OF 2-HYDRAZINO-3-HYDROXYKHINOZALIN-4(3H)-ONE

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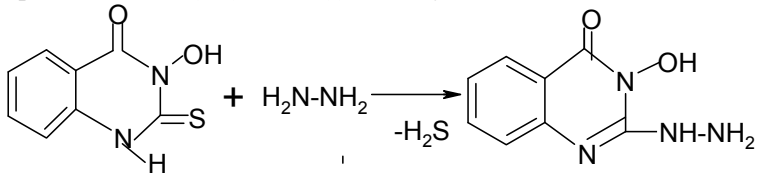
Derivatives of quinazoline-4-one are of great interest as biologically active compounds[1].

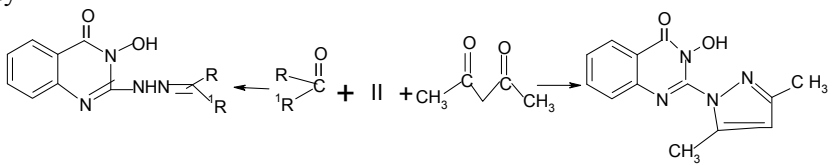
The synthesis of previously unknown 2-hydrazino-3-hidroksihinazolin-4 (3H)-one (II), which is a bifunctional quinazolinone and are of interest as synthons for the introduction of substituents on the hydrazine and hydroxyl groups.

Synthesis of compound (II) was carried out by reaction of 3-hydroxy-2-merkaptohinazolin-4 (3H)-one 1 (I). with hydrazine



I II

In studying the chemical properties of II revealed that with aldehydes and ketones, it forms hydrazones (III), and acetylacetone with 2-pyrazolyl-3-hydroxy quinazolinone (IV), which has antiviral and antimicrobial activity [2]



III IV

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THE PERSPECTIVES IN STUDY OF ELECTROCHEMICAL PROPERTIES OF PORPHYRIN COMPOUNDS

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Intensive studying of electrochemical properties of porphyrin compounds has the big scientific and practical value. It is caused by participation of representatives of this group of compounds in redox reaction proceeding in the alive world surrounding us, switching and the person. The understanding of physiological, enzymatic, biological and other functional activity of porphyrin and related compounds is impossible without thorough investigation of probable changes of redox condition both molecules of porphyrin, and the molecules entering with them in reactionary interaction.

In the report ordering of the data on electrochemical researches of oxidation-reduction behaviour of various derivatives of porphyrin is carried out. Methods and conditions of carrying out of electrochemical measurements are specified. On an example more than 50 connections and complexes are shown the basic laws on influence of the nature of the central ion of metal, a structure of porphyrin ligand and its possible modification on redox properties of molecules. The special attention is given to results of researches electrochemical and electrocatalytic properties of porphyrin synthesized in the Ivanovo State University of Chemistry and Technological. Advantages and possible problems are shown at studying of porphyrin compounds and their complexes in water solutions and in a firm phase.

New perspective directions in inverstigation of electrochemical, electrocatalytical, corrosion and other properties of this group of unique compounds are explained.

Work is executed with financial support by FTP «Scientific and scientific-pedagogical staff of innovative Russia» for 2009-2013 (the state contract № 02.740.11.0253). The analytical departmental target program "Development of scientific potential of the higher school 2009-2011" (a project code:2.1.1/14169)

CHEMISORPTION INTERACTION OF SUPEROXIDE ANION RADICAL WITH THE METAL SURFACE AS A MAJOR FACTOR IN THE BIOCORROSION INITIATION

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Very much metals in contact with microorganisms are exposed to deep degradation. At research the dynamics of corrosion of some metals at influence on them of microscopic fungi and organotrophic bacteria the earlier not described phenomena were revealed by us. The most important of them that at the initial stage after 3-5 days since the beginning of the exposure in some parts of the metal accumulates the transparent liquid phase containing hydroxyl ions (pH = 8 ... 11). Based on these data, we have made the assumption that the above features may be caused by participation in the corrosion process of superoxide anion radical $O_2^{-\bullet}$, produced by microorganisms during it lives [1-4]. Although the intracellular formation of $O_2^{-\bullet}$ characteristic of all forms of life, its role in biocorrosion of metals earlier wasn't discussed.

Using a test system consisting of a derivative of tetrazole and the enzyme superoxide dismutase, specifically interacts with the $O_2^{-\bullet}$, it is shown that the intracellular superoxide anion is indeed able to move into the environment and take part in reactions on metal surfaces. It is established the symbasis between the property of fungi to secrete $O_2^{-\bullet}$ to the environment and the degree of corrosion destruction.

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MACROHETEROCYCLIC COMPOUNDS WITH FRAGMENTS OF 2-FENILINDANDIONE

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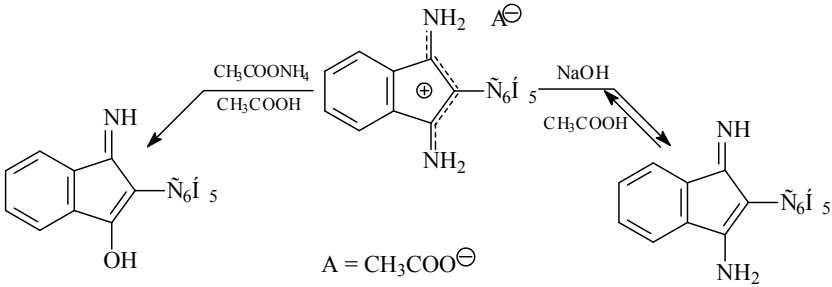
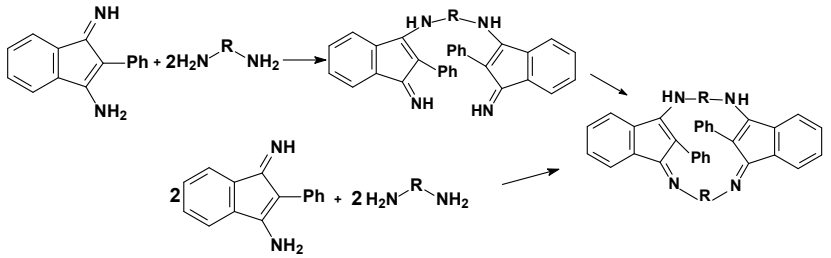
Synthesis of macroheterocyclic compounds with different structures due to the variety of their molecular structures and possible applications in science and technology.

Imines of indandionov can exist in three tautomeric forms. Intense color of iminoindonov indicates the presence of conjugated bonds of the molecule chains. Iminirovanie of imine 2-fenilindandiona proceeds in acetic acid in ammonium acetate.



Arylendiamines and macroheterocycles are synthesized by reaction of aminoimina 2 fenilindandiona-1,3 and n-diamines of diaryl series on the scheme.



R = *n*-C_6H_4-C_6H_4-*n*′, *n*-C_6H_4-S-S-C_6H_4-*n*′, *n*-C_6H_4-O-C_6H_4-*n*′.

Synthesized compounds are powdery substance with different reds, soluble in the majority of organic solvents. There are identified by elemental analysis, UV-Vis-spectra, IR- and NMR H^1 spectroscopy. The features of the behavior of these compounds in different solvents depending on the molecule structure are revealed.

SYNTHESIS AND ANTIPLATELET ACTIVITY OF ALKYLSALICYLATES SODIUM SALTS

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There are several pharmaceutical options for the prevention and treatment of thrombosis. While current anticoagulant drugs have been the mainstay of antithrombotic therapy for decades, acetylsalicylic acid, the active ingredient of Aspirin, is widely used. Aspirin exerts a maximal antithrombotic effect at low doses.[1] Because of its antiplatelet effects and its suppressive effects on gastric mucosal protection, gastrointestinal bleeding is the major side effect of aspirin use.[1] A chemical modification of salicylic acid can develop medications with reduced side effects. Sodium salts of alkylsalicylates have been synthesized by the reaction of alkylsalicylate with sodium phenolate in inert solvent at room temperature.[2,3] Acute toxicity (LD_{50}) and effect of synthesized salts and aspirin (as a control) on platelet aggregation have been studied. Aggregation of platelet-rich plasma was induced by ADP. The therapeutic index has been calculated.[4]

Table.

Substance	LD_{50}, mg/kg	therapeutic index
Sodium salt of amylsalicylate	4005,5	132,90
Aspirin	250,0	29,58

The leader among studied substances was amylsalicylate sodium salt which therapeutic index is in 4.49 times higher than that of aspirin. All surviving mice exhibited normal body weight gains during all observation period. Necropsy observations were not noted.

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METHODS FOR PREPARATOIN OF GLYCIDILIC ESTERS OF OXYBENZOIC ACIDS AND THEIR ACYLATED DERIVATIVES

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Oxybenzoic acids are widely used in medicine and the food-processing industry as bactericidal, anti-inflammatory and antipyretic. However, not looking at their efficiency, they have different side-effects, such as, infringement of function of kidneys, stomach ulcers (salicylates), allergic reactions (parabens).[1,2] Chemical modification of molecules with new functional groups allows to change biological activity and decreases the risk of side-effects.[3] Synthesis of the derivatives containing strained oxyrane cycle is the one of modification methods. Glycidilic ether of oxybenzoic acids has been synthesized in several ways [4,5,6] . The unsaturated part in allylic part has undergone epoxydation with excess of 30 % hydrogen peroxide in the alkaline medium. Using 3-chlorperoxybenzoic acid for the same purpose has not given satisfactory result. The reaction of acylated acids with excess of epychlorohydrine in presence of tetrabutylammoniabromide in chloroform at 100^0C has been the most effective.

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INVESTIGATION OF METHODS OF SYNTHESIS OF GLYCIDILIC ESTERS OF ANTHRANILIC ACIDS AND ITS DERIVATIVES

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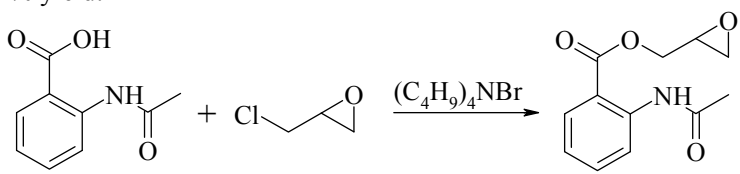
Many derivatives of anthranilic acids have biological activity. Some of them are anti-inflammatory remedies. We investigate an opportunity of preparation perspective intermediates which can be used for synthesized of biologically active substances. Presence in a molecule a part of anthranilic with epoxylic group allows to expand an opportunity of synthesized of potential medicines. Reactions of anthranilic acids derivatives with epychlorohydrine, *β*-dichlorohydrine, allylbromide[1-3] have been investigated. Epychlorohydrine is most efficient reagent for preparation of glycedilic esters. Reaction of *N*-acethylanthranilic acid with epychlorohydrine in presence of tetrabutylammoniabromide is given glycidil-*o*-acethamidobenzoate in 85 % yield.



The investigating compound are taken place screening on a spectrum of their biological activity.

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SYNTHESIS OF CROWN ETHERS-EXTRACTANTS OF METALS

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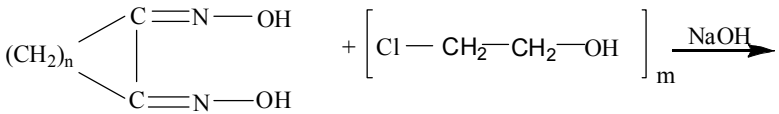
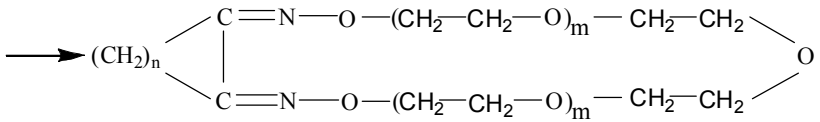
Crown-compounds are effective extractants of metals[1,2]. The method for producing new crown-ethers was developed by poly-condensation reaction of cyclic dioximes with ethylenechlorinehydrine by alkali[3].





where n= 4-5; m=4-8.

These nitrogen containing macrocyclic polyethers were used while defining Ni(II) and Pd(II) by extraction-photometric and gravimetrical method at pH 3-12.

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STUDY OF COORDINATION COMPOUNDS OF PD (II) WITH DIALKYLDITHIOPHOSPHOROUS ACIDS

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The development of chemistry of the platinum metals coordination compounds with P, S, O-containing organic ligands is caused by a wide spectrum their action as analytical reagents, extragents, the compounds used in the chemical industry and nonferrous metallurgy. The potassium salts of diethyl -, di-iso-propyl-, di-n-butyl - di-iso-butyl-, di-n-amyl -, di-izoamyldithiophosphorous acids were synthesised [1]. On the base of the combined results of PMR - , IR -, electronic spectroscopy, XRD, thermal analyses the structure, the general laws and features of a structure of the synthesized coordination compounds with general formula $[Pd((RO)_2PS_2)_2]$ are revealed. The energetic parameters characterizing changes of electronic spectra by electronic transitions and IR-spectra by the phosphorus-sulphur vibrations are estimated. The comparative analysis of spectra of metal complexes is carried out taking into account the factor of gradual replacement of an alkyl-radical at phosphorus atom.

According to IR-spectroscopy in all complexes of a palladium (II) with dialkyldithiophosphorous acids (DADTPA) the shift to lower frequencies of valent vibrations P=S and P-S- (to 600 cm^{-1} and 525 cm^{-1} accordingly), and the disappearance of a band of vibration SH in the field of 2800 cm^{-1} are observed. The DADTPAs act as bidentate ligands co-ordinating to metal by two atoms of sulphur with formation of four-membered chelate cycle.

According to electronic and PMR spectra of the Pd (II) complex it is established the square-planar environment of the Pd(II) ion in complexes. Study of thermal stability of the synthesized complexes by differential thermogravimetric analysis has shown the character of thermal destruction depends on structure of a complex and the metal nature.

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The work was supported by Coordination Center of Development of Science and Technics of Republic Uzbekistan, Grant № F-143.

INVESTIGATION OF THE REACTION OF ZINC WITH BENZYL CHLORIDE IN DIPOLAR APROTIC SOLVENTS

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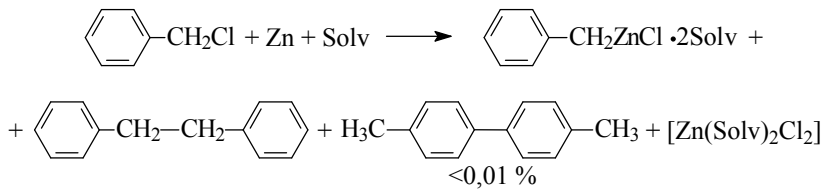
The reaction of zinc with benzyl chloride in dipolar aprotic solvents occurred with the formation of znc (II) complexes and organozinc reagents, in the oxygen-free argon:



Solv = THF, DMF, DMSO, DMAA, HMPA.

The formation of 1,2-diphenylethane and 4,4'-dimethylbiphenyl indicate that the reaction under research proceeds according to the radical mechanism forming benzyl radicals.

The investigation of the stereochemistry of the reaction of zinc with (+)-R-1-chloro-1-phenylethane in dipolar aprotic solvents (THF, DMF, DMSO, DMAA, HMPA) provides a possibility to conclude, that reaction occurs by radical mechanism forming 1-phenylethyl radicals. Their recombination and disproportionation takes place in solution.

Stable 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) was used as a spin trap at 298 K. TEMPO was added into ampoule with reaction mixture. The ESR spectra of TEMPO disappeared and the reaction mixture was treated by hydrogen peroxide in alkali media. The ESR-spectrum did not appear again. Thus the disappearance of ESR spectrum indicates the radical intermediates in solution.

As a chemical trap of radicals, we used dicyclohexyldeuterophosphine (DCPD). It is interested to note, that yield of organozinc reagent is decreases:

$$PhCH_2Cl + Zn + Solv \xrightarrow{DCPD} PhCH_2ZnCl \cdot 2Solv + PhCH_2D + [Zn(Solv)_2Cl_2]$$

Solv = THF, DMF, DMSO, DMAA, HMPA.

The results obtained indicate that reaction of zinc with benzyl chloride in dipolar aprotic solvents occurs by radical mechanism, forming benzyl radicals. Their recombination and isomerization takes place in solution. Organozinc compounds form at the metal surface by radical mechanism too.

SYNTHESIS AND OXIDATION OF MONOTERPENIC QUINAZOLINE-CONTAINING SULFIDES

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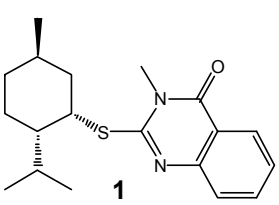
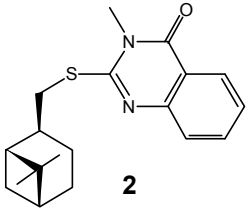
Quinazolines[1,2] and their derivatives[3,4] are important class of heterocyclic compounds, which are used as antagonists of some receptors, enzyme inhibitors, and possess antitumor, antibacterial and antiviral activity. Monoterpenes also have a wide spectrum of biological activity. Thus, terpenic quinazoline-containing sulfides and sulfoxides are of interest as potential biologically active compounds and their synthesis is an important task.



1



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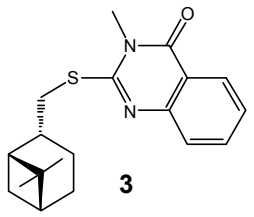

3

In this paper we synthesized 2-[(neomentyl)sulfanyl]-3-methylquinazoline-4- (*3H*)-one (**1**), 2-[(*cis*-myrtanyl)sulfanyl]-3-methylquinazoline-4-(*3H*)-one (**2**), 2-[(*trans*-myrtanyl)sulfanyl]-3-methylquinazoline-4-(*3H*)-one (**3**) with yields 63, 72 and 78% respectively. Further oxidation of sulfides leads to a mixture of diastereomeric quinazoline-containing monoterpenic sulfoxides with high diastereomeric excesses.

Structures of the compounds were confirmed by NMR, IR spectroscopy and by element analysis.

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CATALYTIC PROPERTIES OF INTERMETALLIDE COFE – THE PRODUCT OF REDUCTIVE THERMOLYSIS OF $[Co(NH_3)_6][Fe(CN)_6]$

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A search for approaches to effective catalysts preparation is a matter of extensive theoretical and applied investigations. Catalysts on the basis of the 1st-row transition metals (TMF) are used in general organic synthesis. Currently, attention is focused on preparing catalysts from compounds-precursors, including double complex compounds (DCC). The composition of these catalysts is assigned strictly with precursor stoichiometry, while the formed products are very homogeneous and dispersed. Usually the combinations of two noble metals or a noble and non-ferrous metal are used. In our experiments with bimetallic catalyst, we used only TMF-compounds. It has been found that the intermetallide CoFe, obtained by reductive thermolysis of $[Co(NH_3)_6][Fe(CN)_6]$ in hydrogen flow, can increase the olephine yield in Fischer-Tropsch synthesis.[1] In this work, its activity in the H_2O_2 decomposition reaction has been studied in comparison with a reference 1% Pt-catalyst on γ-Al_2O_3. This reaction is a model for activity studies of redox reaction catalysts. The table presents the data for two intermetallide samples with different carbon contents depending on preparation conditions.

Sample	C, mass.%	K, l /sxg, x10^4, by temperature, °C				Ea, kJ/mole	S_{spec}, m^2/g
		25	35	45	55		
CoFe	12.1	5.3	15.6	32.0	71.6	70.2	80
CoFe	5.3	11.0	17.8	34.9	85.2	55.2	41
Pt/Al_2O_3	-	5.6	4.9	8.7	14.6	23.2	135

It can be seen that the intermetallide is highly active in model reaction, its activity depending on residual C content, despite the decrease of specific surface area of the sample with decrease of C-percentage. The characteristics comparison of both CoFe and Pt/γ-Al_2O_3 catalysts has revealed that S_{spec} for the reaction of H_2O_2 decomposition is not significant.

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NEW CHROMOPHORIC SENSORS OF AMINES AND DOUBLE CHARGED CATIONS OF *d*-METALS NUMBER ON THE BASIS OF HYDROBROMIC SALTS OF 3,3'-*BIS*(DIPYRROLYLMETHENE)S

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The authors performed a number of researches in the area of synthesis and application of hydrobromic salts of alkylated 3,3'-*bis*(dipyrrolylmethene)s ($H_2L{\cdot}2HBr$) as high sensitive analytical agents for qualitative and quantitative spectrophotometric detection of trace amounts of amine and *d*-metals cations in the organic environments. As a result of complexation of 3,3'-*bis*(dipyrrolylmethene)s with cations Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} stable binuclear helicates [M_2L_2] with individual spectral characteristics are formed. Thermodynamic constants of complexation ($K°$) increase for ~5 order in a number of metal-complexations Cu(II) < Cd(II) < Hg(II) < Ni(II) < Co(II) < Zn(II). In complexation color of solutions (from orange to red-crimson), characteristics of electronic absorbtion spectra and, in case of coordination by zinc, fluorescence are changed.

On the example of $H_2L{\cdot}2HBr$ – triethylamine – organic solvent, it is shown that reaction of salt with a nucleorhylic reagent is accompanied by bright changes in colour (from bright orange to citreous) and evident transformations in electronic absorption spectra of a solution: transformation of a band of protonated form of chromophor $H_2L{\cdot}2HBr$ in a band of molecular ligand H_2L with significant hypsochromic (~20-60 nm) shift and hypochromic effect occur. Conditional sensitivity of analytical detection of nucleophyl in the organic environment is not lower 1×10^{-8} mole/l.

The listed features provide the perspectivity of using hydrobromic salts 3,3'-*bis*(dipyrrolylmethene)s as colorimetric ("naked-eye") and fluorescent hemosensors for spectrophotometric detection of trace amounts of amines and both ultraselective detection and the express-analysis of ions microamounts (up to 10^{-9} mole/l) Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} и Hg^{2+} in organic environments.

This work was supported by the Analytical Departmental Target Programme “The Development of Research Potential of Higher School” (2009–2011), Federal Target Programme “Research and Research-Teaching Stuff of Innovative Russia” (2009–2013).

Ti-CATALYZED CYCLOADDITION OF 1,2-DIENES AND 1,3,5-CYCLOHEPTATRIENE

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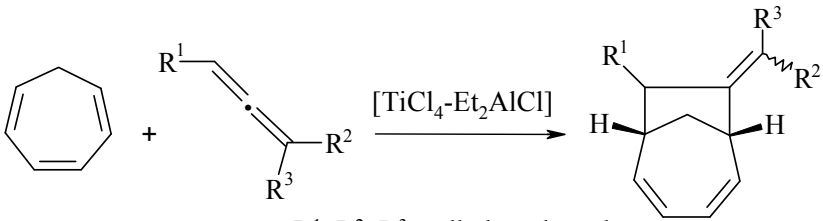
The catalytic [6π+2π] and [6π+4π] cycloaddition reactions of 1,3,5-cycloheptatriene (CHT) with unsaturated compounds, namely, 1,3-dienes, norborna-2,5-dienes, and acetylenes are well known being used for the synthesis of a wide range of ring systems,1,2and also practically important natural compounds.3

In continuation of our investigations on the synthesis of polycyclic compounds derived from homo- and codimers of CHT,3 for the first time cycloaddition of CHT and a series of substituted cyclic and also acyclic 1,2-dienes has been implemented in the presence of the two-component catalyst TiCl4–Et2AlCl, which shows the best catalytic activity and selectivity in the [6π+2π] and [6π+4π] cycloaddition reactions.3

Thus, the interaction between CHT and 1,2-dienes with different structures (1:1.1 molar ratio) affected by TiCl4-Et2AlCl catalyst (1 mol %) at 80 oC for 8 h in benzene was shown to afford endo-bicyclo[4.2.1]nona-2,4-dienes (60–81% yield) isolated by column chromatography (eluent: hexane/benzene, 10:1) as a Z and E isomeric mixture (Z:E = 10:1).



R^1, R^2, R^3 = alkyl, aryl, cyclo

In the report, the influence of the reaction parameters such as temperature, nature of solvent, ligand environment, and central atom of a catalyst on the yield and molar ratio of cyclodimers obtained are also discussed.

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CP_2TICL_2-CATALYZED SYNTHESIS OF NOVEL "NON-GRIGNARD" N,O-CONTAINING CYCLIC ORGANOMAGNESIUM REAGENTS

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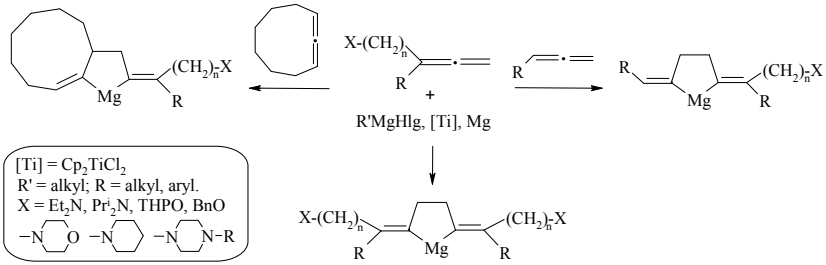
Cyclic organomagnesium compounds (OMC) are promising reagents in one-pot synthesis of carbocycles and heterocycles.1 We have shown previously,1,2 that cyclic and acyclic allenes undergo the cyclomagnesiation reaction mediated by Grignard reagents and Cp2TiCl2 as a catalyst giving rise to 2,5- dialkylidenemagnesacyclopentanes in high yields.

Our further investigations have shown that N- and O-containing 1,2-dienes, able to enter into the catalytic cyclomagnesiation reaction, are also involved in combined intermolecular cyclomagnesiation with cyclic and acyclic allenes using Grignard reagents in the presence of activated Mg (acceptor of halogenide ions) and 5 mol% Cp2TiCl2 catalyst (Et2O, 4 h, r.t.) to produce appropriate functionally substituted unsaturated OMC in 85% yield. These compounds appear to be promising reagents for developing efficient one-pot methods for the synthesis of previously inaccessible heterocyclic compounds, as well as cis,cis-1,5-dienes of a desired structure.



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The work was supported by Russian Foundation for Basic Research (grant 10-03-00046).

EFFICIENT METHOD FOR THE SYNTHESIS OF TETRASPIROCYCLOPROPANE-CONTAINING MACROCARBOCYCLES

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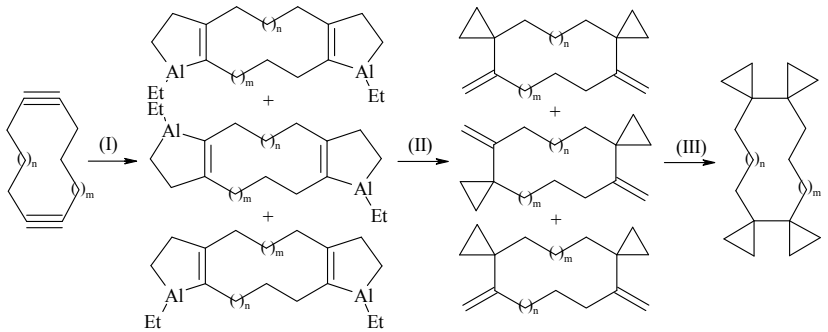
Recently,[1,2] we have developed an efficient method for the synthesis of unsaturated tricyclic dialuminum compounds via the catalytic cycloalumination reaction of symmetric and asymmetric cycloalkadiynes with Et_3Al mediated by Cp_2ZrCl_2.

Our previous studies on the transformation of aluminacyclopentenes to substituted cyclopropanes[3,4] allowed to develop the new efficient method to synthesize tetraspirocyclopropane-containing macrocarbocycles C_{12}–C_{18} in very high yields (85–92%). The procedure represents a sequence of chemical reactions involving cycloalumination of cyclic diynes with the formation of the above-mentioned tricyclic OAC, treatment of these compounds with $BrCH_2OMe$ providing formation of dispirocyclopropyldimethylidene macrocarbocycles, and cyclopropanation of the latters by Et_3Al–CH_2I_2 reagent.[1] The target macrocyclic spiranes are promising as building blocks in the synthesis of macrocyclic rotanes.[5]



n = 2, 3, 4; m = 3, 4, 5. (I): Et_3Al, [Zr]; (II): $BrCH_2OMe$; (III): Et_3Al, CH_2I_2; [Zr]=Cp_2ZrCl_2; n = m = 2, 3, 4; n = 2, m = 3; n = 3, m = 4; n = 3, m = 5.

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The work was financially supported by RFBR (grant 10-03-00046).

SOLVOPHOBIC EFFECTS IN SOLUTIONS WITH SPATIAL NETWORK OF HYDROGEN BONDS

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In this work, volumetric properties of liquid mixtures of *tret*-butyl alcohol with water, ethylene glycol and glycerol at atmospheric pressure were studied and reported. *tret*-Butanol was chosen as model compound for investigation of solvophobic (hydrophobic) effects in mixtures under consideration. It is known that aqueous solutions of *tret*-butanol are characterized by availability of extremes in the region with low alcohol content.[1] Such extremes displayed on the "property–composition" dependences are ascribed to occurrence of hydrophobic effects in solution.[2,3]

Structural organization of individual liquids as well as the processes taking place when *tret*-butanol is mixed with water, ethylene glycol and glycerol are discussed in this report. In spite of fact that all solvents are characterized by existence of spatial network of hydrogen bonds, H-bonds in each of them differ. If the hydrogen bond in three-dimensional structure of water is characterized in the space relative to the other H-bond by only a certain direction, then it is not observed in ethylene glycol and glycerol. Ethylene glycol molecule may be in the 27 different conformations, and the molecule of glycerol can form 126 possible conformers.

The observed solvophobic effects in water–*tret*-butanol mixture at low concentration of *tret*-butanol are related to the destruction of water packaging. It means that "free" water molecules located in the cavities of water structure and connected with water framework by weak hydrogen bonds are displaced by molecules of *tret*-butanol. Similar solvophobic effects were not revealed in the mixtures of ethylene glycol–*tret*-butanol and glycerol–*tret*-butanol.

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This work was supported by Russian Foundation for Basic Research (project 09-03-97501a)

SYNTHESIS OF 5-ARYLIDENE DERIVATIVES OF THIAZOLIDINE-2,4-DIONE UNDER MICROWAVE IRRADIATION

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Currently, the use of microwave activation in organic synthesis is one of the most studied and promising areas of organic chemistry, which allows significantly accelerate reactions and increase the purity of the final products. We have first studied the effect of microwave radiation on the reactivity of thiazolidine-2,4-dione (1) with various aromatic aldehydes obtaining 5-arylidene derivatives of thiazolidine-2,4-dione (2-5). For comparison, the synthesis of (2-5) was carried out in classical terms, and under the influence of microwave irradiation (irradiation power 50-750 watts) as follows:

(1) (2-5)

R = C_6H_5 (2), *n*-F–C_6H_4 (3), *n*-CH_3O–C_6H_4 (4), *o,n*-$(CH_3O)_2$–C_6H_3 (5)

We have found out that target products (2-5) can be synthesized within 2-3 minutes under microwave irradiation of reaction mixture consisting of 0.01 mol thiazolidine-2,4-dione (1), 0.01 mol of anhydrous sodium acetate and 0.0125 mol of the corresponding aromatic aldehyde in 10 ml AcOH, when the irradiation power 750 W. Outputs (2-5) after recrystallization from AcOH are similar to outputs in classical terms and constitute 67-80% depending on the nature of the radical in the original aldehyde. Synthesized 5-arylidene derivatives of thiazolidine-2,4-dione (2-5) are white crystalline substances, well soluble in polar organic solvents. Structure and composition of the obtained compounds (2-5) have been proved by IR-, NMR^1H- and ^{13}C-spectroscopy and elemental analysis.

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INTRAMOLECULAR CYCLIZATION OF 2,3-SECOTRITERPENOIDS

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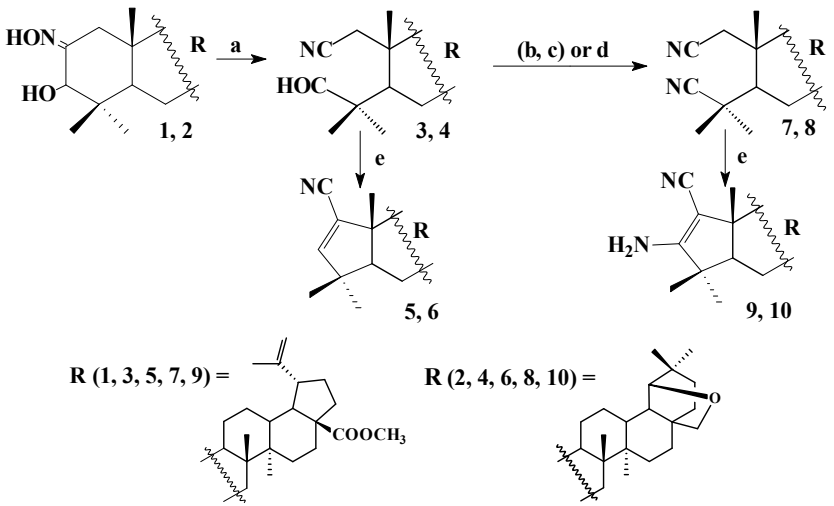
The triterpene 2,3-secoaldehydonitriles **3**, **4**, obtained by Beckmann splitting of α-hydroxy oximes[1] **1**, **2**, were subjected to catalytic recycling to a five-membered ring A formation with fragment of the ennitrile (**5**, **6**). Mild Thorpe cyclisation to the appropriate enaminonitriles **9**, **10** took place for the dinitriles **7**, **8**, which were synthesized from the **3**, **4**.



a)TsCl, C_6H_5N; b) NH_2OH HCl, C_2H_5OH, C_6H_5N; c) $(CH_3CO)_2O$, CH_3COON d)KF/Al_2O_3, DMFA; e) t-C_4H_9OH, t-C_4H_9OK

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The work was supported financially by the RAS Presidium program No. 09-П-3-1016.

THEORETICAL AND EXPERIMENTAL STUDY OF THE REACTIONS OF ESTERS OF P(IV) ACIDS WITH 1H- AND 2H-PERCHLOROPROPANES

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In this paper, we report on theoretical and experimental evidence of dehydrochlorinating reactivity of P(IV) esters. The study was mainly concerned with the reactions O-methyldimethyl and O-methyldiethylphoshinates (Ia-b) with 1H- and 2H-perchlorpropanes (IIa-b). Theoretical predictions were made using density functional method DFT/PBE/TZ2P according to the PRIRODA program[1].

The calculations show that the first step of the reaction starts with the formation of the prereaction H-complex (III), which is transformed via transition state TS1 into the intermediate complex (IV). The latter decomposes to give the phosphorane intermediate (V) and hexachloropropene (VII)

$$Me_2P(O)(OMe) + CCl_3CCl(X)C(Y)Cl_2 \longrightarrow [CCl_3CCl(X)C(Y)Cl_2]...O=P(OMe)Me_2 \longrightarrow$$
$$\text{Ia} \qquad \text{II, X=Cl,Y=H(a); X=H,Y=Cl(b)} \qquad \text{III}$$
$$\longrightarrow TS1 \longrightarrow Me_2PCl(OMe)OH \cdot CCl_3CCl{=}CCl_2 \longrightarrow Me_2PCl(OMe)OH + CCl_3CCl{=}CCl_2$$
$$\text{IV} \qquad \text{V} \qquad \text{VI}$$

At the second step of the reaction the intermediate (V) rearranges into complex (VII) via transition state TS2, which decomposes to give reaction products (VIII) and (IX)

$$Me_2PCl(OMe)OH \longrightarrow TS2 \longrightarrow Me_2P(O)(OH) \cdot MeCl \longrightarrow Me_2P(O)OH + MeCl$$
$$\text{VII} \qquad \text{VIII} \qquad \text{IX}$$

In compiliance with the calculations the reactions are endothermic and they proceed with 2H-perchloropropane (IIb) considerably faster than with 1H- perchloropropane (IIa). This theoretical prediction was confirmed experimentally: for completion of the reactions the 1:1 mixtures of the compounds (Ib, IIa) and (Ib, IIb) slould be heated for 14 h at 170 °C and 5 h at 100 °C, respectively.

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DIFFERENTIATING MIXTURE OF APROTIC SOLVENTS FOR THE INVESTIGATION OF PROTOLYTIC EQULIBRIA

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Studying of the protolytic equlibria in aprotic solvents is a non-trivial experimental problem due to complication by ion-molecular and ion-pair association. From the analytical chemistry point of view aprotic solvents are valuable because of strong differentiating ability in relation to acidity of organic acids of different types. Acetonitrile (MeCN) is typical example of this class of solvents.

The proton solvation is a main factor governing the acidity constant values (pK_a) of organic acids in polar solvents. That why small amount of water are drastically affects quantitative parameters of prototropic equilibria in aprotic solvents due to preferable solvation of proton by water molecules rather than by solvent[1]. On other hand addition protophilic solvent such as DMSO to protophobic in amounts up to 5 molar percent may result in resolvation of proton and formation the lyonium cation (Me_2SOH^+).

In the present work pK_a values of picric acid were experimentally determined in series of DMSO-MeCN mixtures with molar ratio from 0.1 to 3.24 molar percent. The dependence of obtained by spectrophotometric dilution technique pK_a values *vs*. molar DMSO content (x_{DMSO}) is presented at table.

Table. **The dependence of pK_a values for picric acid *vs*. molar DMSO content**

x(DMSO), molar %	0	0.097	0.26	0.53	1.06	1.6	2.14	2.69	3.24
pK_a (HPic)	11.0[2]	5.81	4.72	4.36	3.75	3.38	3.3	3.24	3.22

Based on the analysis of this dependence the optimal molar composition (97.9 : 2.1) of the MeCN–DMSO mixture was chosen (mass ratio 96 : 4). This medium retains the differentiating ability of MeCN, but the addition of small amounts of water (0.1 M) lowers the pK_a value of picric acid only by 0.07. At the same time the pK_a value of picric acid stills moderately high: $pK_a = 3.30$, compared to $pK_a(H_2O) = 0.3$ and $pK_a(DMSO) = -1$.

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CONFORMATIONAL ISOMERS OF PADDLE-WHEEL CARBOXYLATE COMPLEXES OF NICKEL(II): QUANTUM-CHEMICAL DFT STUDY

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The results of quantum chemical studies allow to explain the existence of different stable conformational isomers of binuclear paddle-wheel type carboxylate complexes of Ni(II). The data obtained allow to explain the existence of two types of structures differing in the geometry of the bridging carboxylate ligands in the core $Ni_2(\mu\text{-}O_2CR)_4$: symmetrical and asymmetrical.

Quantum-chemical calculations of electronic structure of the complex $[Ni_2(\mu\text{-}O_2CCH_3)_4(O\text{-}DMSO)_2]$[1] and the "model" fragment $Ni_2(\mu\text{-}O_2CCH_3)_4$ were done by DFT method in B3LYP at 6-31G(d,p) basis. They revealed the existence of two types of stable structures of high-spin binuclear carboxylate complexes of Ni(II) with various terminal ligands.

Coordination compounds of the symmetric (S) type genetically descended from the high-energy symmetrical $Ni_2(\mu\text{-}O_2CR)_4$ core. There are some differences in interatomic distances of diagonal bridged carboxylate ligands of oxygen atoms (S-type). They may be caused by the effect of terminal ligands, but in these cases they do not exceed 0.3Å. Another type of binuclear carboxylates of nickel is asymmetrical (AS) and it is genetically related to the low-energy distorted $Ni_2(\mu\text{-}O_2CR)_4$ core. One should include to the AS-type complexes where diagonally opposited atoms of oxygen of bridging carboxylate ligands have a considerable disparity of the distances.

First of all this distortion is caused by indication of the second order Jahn–Teller effect. The effect of terminal ligands can just increase this distortion.

The asymmetric structures is energetically more stable than the symmetrical structures about 100-130 kJ/mol taking into account the zero-point energy vibrational levels.

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BIOMIMETIC METALLOPORPHYRINS WITH 2,6-DI-*TERT*-BUTYLPHENOL PENDANTS

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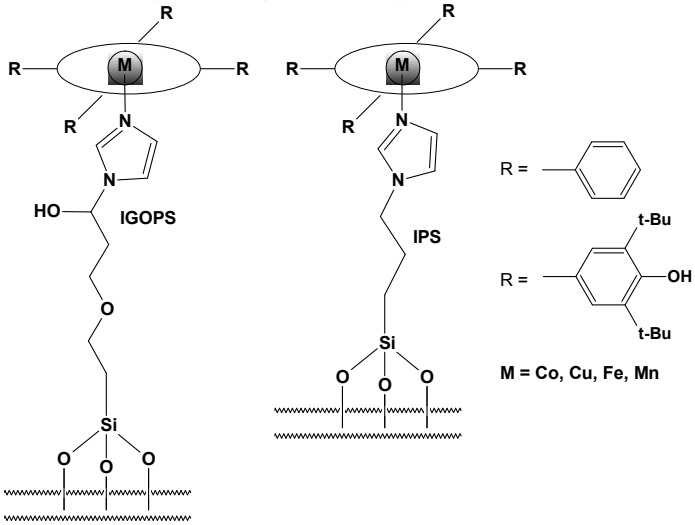
The catalytic activity of Mn^{III}, Fe^{III}, Co^{II} and Cu^{II} *meso*-tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrins and *meso*-tetraphenylporphyrins immobilized via coordination bond on the surface of modified silica IPS and IGOPS has been studied in oxidation of cyclooctane, cyclohexane, cyclooctene, cyclohexene, styrene, ethylbenzene by $NaIO_4$[1], H_2O_2[2], O_2.



The key role of 2,6-di-*tert*-butylphenol groups in the mechanism of catalytic activity in stabilization of $[R_4P^{+\cdot}Fe^{IV}=O]$ intermediate by intramolecular electron transfer (Fe) and in deactivation of catalytic Mn cite has been established.[1-2]

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COPOLYMERIZATION OF 2,2-DIALLYL-1,1,3,3-TETRAETHYLGUANIDINIUMCHLORIDE WITH N-ALLYLMALEIMIDE

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It is well known containing guanidine group compounds possess wide spectrum of antibacterial activity and use as medicine and fungicides[1]. That is why guanidine group introduction into high molecular compounds is undoubtedly of present interest.

Activity of 2,2-diallyl-1,1,3,3-tetraethylguanidiniumchloride (AGC) in reactions of radical copolymerization with N-allylmaleimide (AMI) has been studied. 2,2-Diallyl-1,1,3,3-tetraethylguanidiniumchloride was found to be copolymerized with N-allylmaleimide in the conditions of free-radical initiation, the copolymers being characterized by statistical distribution of monomer units with a high tendency of the comonomer units toward alternation.

AGC is less active if compared with AMI. The rate of copolymerization of AGC with AMI reduces with increasing molar fraction of diallyl monomer in initial monomer mixture.

As a result of kinetic investigations at initial conversions it was determined that a usual for radical polymerization reaction half order with respect to initiator is observed indicating bimolecular mechanism of the growing chain failure, as well as deficiency of degradative chain transfer to the monomer intrinsical to allyl monomers.

The structure of the polymers obtained was identified by NMR ^{13}C. Analysis of the values of chemical shifts of the signals and their multiplets shows AGC to copolymerize with N-allylmaleimide both double bonds participating.

The copolymers of AGC with maleic and fumaric acides are nontoxic, have a notable antibacterial activity and can be used for medicine aims.

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This study was suppoted by the Russian Fund for Basic Reseach (grant № 09-03-00220).

THE *IN VIVO* STUDY OF PORPHYRIN WITH 2,6-DI-*TERT*-BUTYLPHENOL GROUPS ACTIVITY IN THE DECREASE OF TRIMETHYLTIN CHLORIDE TOXIC EFFECT

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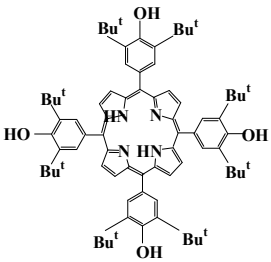
The novel protectors capable of restoring the natural defense system under the pathological conditions induced by toxic organometallic compounds have received considerable research attention in recent years. This study demonstrates the *in vivo* effect of porphyrin **1** on the enzymatic activity of *catalase*, *superoxide dismutase* (SOD), and on the total content of free SH-groups as the components of cellular antioxidative defense system in *Wistar* rat liver and kidney after the oral administration of Me_3SnCl. The dramatic decrease of the enzymes activity after 24 h in the rat liver and kidney has been observed when the animals have been exposed to Me_3SnCl.

Activities of *catalase*, *SOD* and the total content of *SH-groups* after the oral administration of Me_3SnCl, 1 and their mixture (1:1) in rat liver(kidney)



1

Additives	Enzymes activity, mmol•mg^{-1}•min^{-1}		SH- groups total content, mmol•mg^{-1}
	catalase	SOD	
control	241±11 (157,6±5,8)	12,8±0,5 (6,7±0,2)	155,4±6,4 (136,3±6,5)
1	224,8±8,4 (144,9±4,3)	10,8±0,4 (6,6±0,3)	139,1±6,9 (132,1±0,5)
Me_3SnCl	136,5±6,7 (102,1±3,8)	1,0±0,05 (0,5±0,01)	9,5±0,5 (32,8±0,8)
Me_3SnCl and **1**	164,8±6,4 (128,2±1,9)	3,8±0,06 (2,1±0,1)	99,4±3,8 (62,6±3,2)

It was shown that polyfunctional porphyrin **1** significantly suppresses Me_3SnCl inhibitory impact by mechanism of 2,6-di-*tert*-butylphenol groups antioxidative functioning and by Sn chelating effect of free base porphyrin.

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SYNTHESIS OF DERIVATIVES 2-AMINO-4-PHOSPHONOMETHILQUINOLINES

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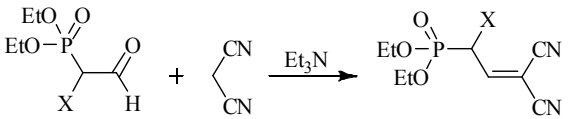
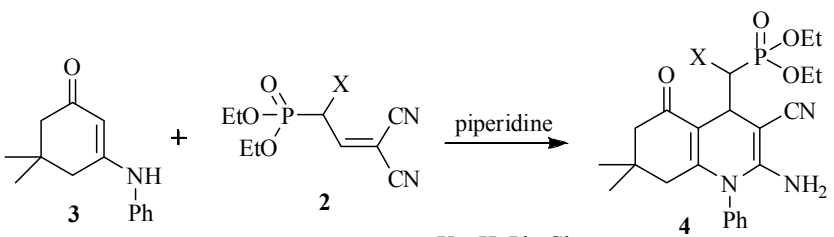
Last years chemists have the big interest to synthesis of phosphorilated derivative heterocycles. High interest to these compounds is caused by potential possibility of their application as biologically active substances.

It is known, that reaction of aldehydes and ketones with malononitrile give to ilides, which are applied in synthesis of various heterocycles. By analogous interaction of derivatives phosphonoacetaldehydes **1** with malononitrile in the presence of a catalytic amount of triethylamine are obtained corresponding 3,3-dicyanoallilphosphonates **2**.



1 **2**

Obtained 3,3-dicyanoallilphosphonates **2** have been used for synthesis of derivatives 2-amino-4-phosphonomethilquinolines **4** by interaction with cyclic enaminoketone **3**. Reaction carried out in ethanol in the presence of a catalytic amount of piperidine.



3 **2** **4**

X = H, Ph, Cl

Possibly the reaction mechanism includes initial addition of enaminoketone **3** to 3,3-dicyanoallilphosphonates **2**. Next heterocyclization of adducts Michael in the conditions of reaction give to final 2-amino-3-cyano-4-phosphonomethil-7,7-dimethyl-5-oxo-1-phenyl-1,4,5,6,7,8-hexahydroquinolines **4**.

The structure of obtained compounds was confirmed by IR- and mass-spectroscopy.

DISTRIBUTION OF CHEMICAL COMPONENTS IN PETROL

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Petrol is complex organic system. In is composition there are identified more than 900 individual compounds, 500 of which are hydrocarbon compounds. Consequently, study of petrol as energy bearer and understanding of its genesis are impossible without chemical researches. In the beginning of XX century great Russian chemists like D.I.Mendeleev, I.F.Zelinskiy, V.V.Morkovnikov and others were interested in chemistry of Azerbaijan petrol. Highly evaluating the petrol, D.I.Mendeleev in his period said: "Petrol is not a fuel, may be buried by assignments". Thereby, he wanted to emphasis limitation and non-regenerability of oil resources.

Unlike other natural minerals, petrol is studied in two directions: oil-chemists study it as energy bearer, but geochemists for the purpose of understanding genesis of oil hydrocarbons and for more rational development. Lack of comprehensible scientific result in geochemical research is explained with that they were not meant as research object. For avoiding such errors, we used the selection method of petrol samples from separate exploitation wells, but not from common oil-gathering reservoirs, which are used for experiments by oil-chemists.

As an experiment we studied oil, taken from Garachukhur and Surakhani field. As a result of chromatograph test we found out unknown facts, which haven't been explained to the present time. In chromatograph of petrol we observed n-(C_{10}-C_{30}) and alkanes of isoprenoid structure iso-(C_{11}-C_{23}). In oil of YII horizon of the same deposit with isoprenoid hydrocarbons we didn't observe n-(C_{10}-C_{30}). In oil of these horizons from Surakhani field we didn't observe n-(C_{10}-C_{30}) and iso-(C_{11}-C_{23}). Accordingly, we can state that secrets in formation of oil hydrocarbons haven't been found yet.

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AZANGULAR HETEROCYCLES SYNTHESIS OF HETERO CONDENSED AZEPINES AND DIAZEPINES BY THE BECKMANN REARRANGEMENTS OF THE ISOQUINO[2,1-*A*]QUINOLIN-1,13-DIONE OXIMES

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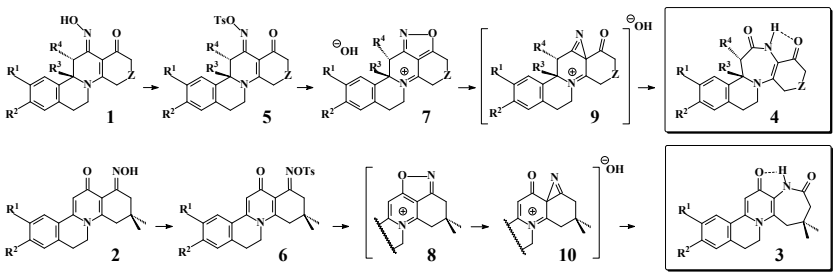
Interest manifested to the hetero condensed azepine and diazepine derivatives is caused by a wide spectrum of their biological activity, mainly their neuro- and psychopharmacological properties. In the network of researches on synthesis azangular heterocycles by the annelation of the Schiff's bases with β-di - β,β′-tricarbonyl compounds (β-di-, β,β′-триКС)[1,2] obtained oxime derivatives **1** and **2**. Besides their biological activity these derivatives are interesting and as synthetic precursors of the hetero condensed derivatives of azepines **3** and diazepines **4**.



Presented on the scheme transformations of oximino derivatives **1** and **2** reveals preparative and technological approaches to derivatives **3** and **4** through the tosylates **5** and **6**. Established that the Beckmann's rearrangements of the esters **5** and **6** are carried out under the influence of bases through the isoxazoles **7**, **8** and aziridines **9** and **10**. In consideration of the availability of oximes of type **1**, **2**[4] developed methods are of general significance for heterocyclic synthesis.

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ACETAL CONTAINING α-CHLOROXIRANES AND α-THIOCYANATOCARBONYL COMPOUNDS

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The new method of synthesis acetal containing α-chloroxiranes from available corresponding vinylchlorides derivatives, by their epoxidation using 3-chloroperoxybenzoic acid and hydrogen peroxide, was found.

It has been found that oxazolopyridine salts, synthesized by the reaction of chloroxiranes with pyridone-2, in the reactions, with secondary amines undergoes recyclization with the formation of acetylaxazalcarbaldehydes-5 derivatives.

It has been shown that intermediate products azides in the reactions between chloroxiranes with sodium azide undergoes unusual dimerization, leading to formation of 1,3-oxazole-3-ine derivative.

For the first time it was found that condensation of α-thiocyanatocarbonyle compounds with o-phenylenediamine can be convenient preparative method of synthesis of condensed heterocycles - 2-iminothiazolo-[3,4-a]- quinoxalines.

It has been found that the reactions of chloroxiranes and isomeric chlorketones with anionic nucleophiles such as potassium phtalimide and sodium ethoxyde – proceeds unnormally and form 2,5-bis(diacetales)-3,6-diphenyl-1,4-dioxine.

The reactions of phosphorylcontaining thiocyanatoaldehydes with Ph3P, Me2PhP and (EtO)2PHO proceeds with participation of thiocyanato- and aldehyde groups to form bisphosphorylated heterocycles.

This work was supported by the RFFI, grant № 10-03-00528-a.

THE SEARCH FOR PHARMACOLOGICALLY ACTIVE SUBSTANCTS AMONG N-ALKOXYALKYLPIPERIDINE DERIVATIVES

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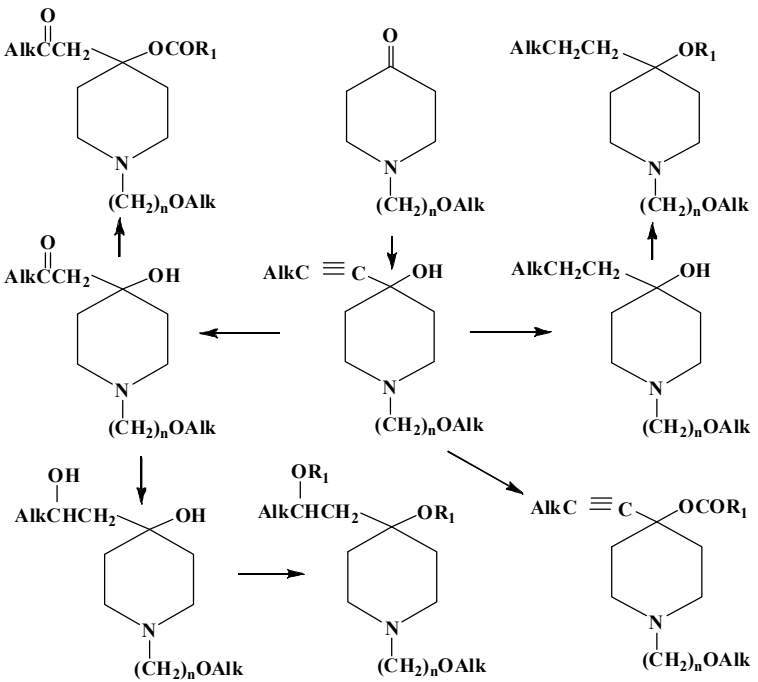
The generation of organic substances with given properties on the basis of 1-(2-ethoxyethyl)-4-oxopiperidine as the structural model has proved in practice its usefulness for the search and creation of compounds with defined pharmacologically activity.

The treatment N-alkoxyalkyl-4-oxopiperidines with some alkynes has been chosen as an instrument of potential drugs creation. The reactive centers of synthesized N-alkoxyalkyl-4-alkynyl-4-hydroxypiperidines and their derivatives have been exposed to chemical modification: hydrogenation and hydration of triple bond, reduction of carbonyl group and acylation of hydroxyl group:



THE INTERACTION OF 4-HYDROXY-3,5-DI-*TERT*-BUTYLBENZYLIDENE CHLORIDE WITH O-NUCLEOPHILIC REAGENTS

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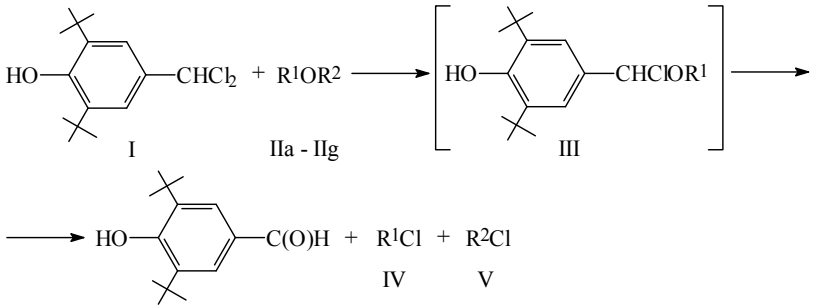
For the research progress of the chemical behavior of organic polyhalides[1-2] we investigated the interaction of 4-hydroxy-3,5-di-*tert*-butylbenzylidene chloride (I) with a number of oxygen containing nucleophilic reagents (II).

According to ^{1}H NMR spectroscopy data it was established that allowing to stand the solution of dichloride (I) in an excess of triethyl orthoformate (IIa) for a long time (36 days) at room temperature leads to the formation of its exhaustive dechloroetoxylation product (4-hydroxy-3,5-di-*tert*-butylbenzaldehyde diethyl acetal).

The reaction product of dichloride (I) with triethyl orthoformate (IIa), methyl- and ethyl(diphenylmethyl) esters (IIb, IIc), O-methyldiethylphosfinate (IId), acetic (IIe), phenylacetic (IIf) acids at heating and acetic anhydride (IIg) at ambient temperature was a 4-hydroxy-3,5-di-*tert*-butylbenzaldehyde, which was finally formed by dechloroalkylation of intermediate α-chloroether (III).



For compounds II-V: R^1 = Et, R^2 = $(EtO)_2CH$ (a); R^1 = Me, R^2 = Ph_2CH (b); R^1 = Et, R^2 = Ph_2CH (c); R^1 = Me, R^2 = $Et_2P(O)$ (d); R^1 = MeC(O), R^2 = H (e); R^1 = $PhCH_2C(O)$, R^2 = H (f); R^1 = MeC(O), R^2 = MeC(O) (g).

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This work was supported by the Federal target program "Research and scientific-pedagogical staff of innovation Russia in 2009-2013" (state contract no. P-1108).

PHOTOCHEMICAL REACTIONS 2,6-DIPHENYL-1,4-BENZOQUINONES IN TRI- AND TETRAETHOXYSILANES

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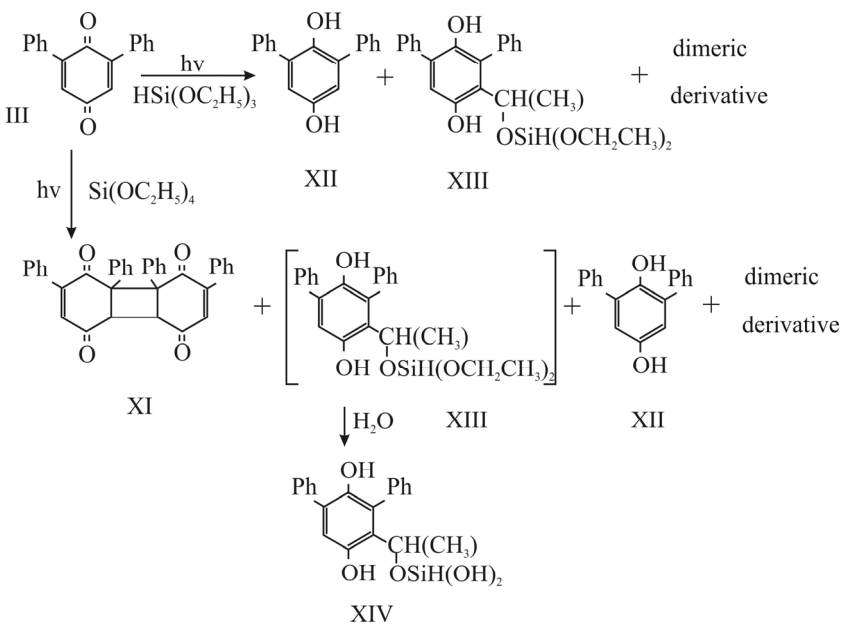
Photolysis 2,6-diphenyl-1,4-benzoquinones in three-and tetraethoxysilanes leads to identical products of reaction, but in different correlations (see the scheme). In both cases the output of silanohydrokinones (XIII) and (XIV) make 10 %. In triethoxysilanes,a strong reducer, the basic product of reaction is diphenylhydroquinone (XII), the output of photodimer (XI) is 10 %. In tetraethoxysilanes the basic product of reaction is photodimer (XI), and the output (XII) about 10 %.



The investigation was carried out with the help of mass-spectrometric method while implying the system of direct introduction of molecular distillation in vacuum.

SPACIAL EVALUATION OF SOME DITHIOLS COMPLEXES WITH Cd(II), Hg(II),In(III),Tl(III),Sn(II) AND Pb(II) CHLORIDES AND NITRATES

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These days the study of molecule geometrical characteristics with quantum-chemical methods enables acquiring more comprehensive and precise idea of initial molecules structure and those variations within them that occur during their interaction with other molecules that is not always possible to do by means of chemical and physical-chemical research methods.

Geometrical structures of some dithiol complexes with Cd , Hg, In, Tl, Sn and Pb[1] salts have been calculated by means of PM3 quantum-chemical method included into MOPAC-7 program complex. It has been found out that the model complex bandings under research differ from each other by geometrical parameters, what is proved by the calculations of interatomic spacings of both valence and dithedral angles. It has been demonstrated that when forming a complex with sulfur-containing bidentate ligands in the cases of cadmium, mercury, tin and lead the bandings with coordination number 4 are formed while in the cases of indium and thallium the coordination number is 5. Meanwhile cadmium and mercury complex bandings have the structure resembling a flat square with valence angles equal to ~ 90^0. In tin and lead complexes a deformed tetrahedral structure is realized. For banding indium and thallium complexes a trigonous bipyramid structure are formed. Anion nature of initial salts doesn't influence the geometrical parameters of complex bandings significantly. It is worthwhile to say that the shortest M–S banding between a complex forming ion and sulfur-containing ligand is formed in Hg (II) complexes while the longest one is formed in Tl (III) complexes.

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DEVELOPMENT OF PHYSICAL - CHEMICAL THEORY OF LIQUID ELECTROLYTE SOLUTIONS AS A CHEMICAL SYSTEMS

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One of the main trends of modern development of the theory of electrolyte solutions is the investigation of solutions of both chemical systems and quantitative description of their thermodynamic, kinetic, structural, rheological, etc. properties depending on the physical and chemical properties of the components in the whole concentration range of existence of a homogeneous solution with the widest ranges of external parameters of state (temperature, pressure, etc.).

Liquid chemical systems are characterized by the presence of various subsystems - the chemical forms of different levels of organization: molecules, ions, associates, ion-molecular complexes, clusters, dynamic ordering of higher level. To construct a theory of any kind of solution you need to know, for the entire concentration range of existence of the solution, the dependence of properties on the concentration and chemical forms, affecting this property; regularities determining the presence and quantity in the solution of these chemical forms, the impact of physical and chemical properties of the solution components physical and chemical processes that determine this property, the dependence of properties on external parameters of state.

The solution of each of these questions requires the use of certain model representations, methods of research, organizing and interpreting the results. Systematic approach involves consideration of all aspects of existence and properties of specific chemical forms specific to their organization (size, charge, number of particles, their ordering, the effect of other particles).

Based on the idea that the formation of electrolyte solution is always the result of chemical interaction between molecules of different substances with the formation of ionic compounds (ionophores, geterolitov, salts) and / or interaction of identical molecules to form autoliths, avtosolvatov, autocomplexes, an equation of the electrical conductivity of liquid salt systems - solvent quantitatively describe dependence of the conductivity of dilute solutions to molten salts.

USING A PROBABILISTIC APPROACH TO DERIVE THE HETEROGENEOUS KINETIC EQUATIONS OF d-ELEMENTS OXIDES DISSOLUTION IN ACID SOLUTIONS

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To analyze the kinetic curves of dissolution in the coordinates of α (t) are encouraged to use the contracting volume equation for the probability that the formation of active centers (W (t)):

$$\partial\alpha/\partial t = W_i \cdot d \cdot (1-\alpha)^{(d-1)/d} \cdot W(t)$$

The proposed method allows us to derive the equations of the function of oxide dissolved from time at different probabilities, which are widely used in heterogeneous kinetics:

Probability	The probability density distribution of active centers $W(t)$	The equation of the function of oxide dissolved from time, or time on the fraction of oxide dissolved
Uniform distributio n	$W(t) = 1$	Equations of compressible volume to the fractal dimension: $\alpha = d \cdot \int_0^{\tau} (1-\xi)^{d-1} d\xi = 1-(1-\tau)^d$
Poisson distributio n	Delmon modification: $W(t) = 1 - \exp\left(-\int_0^t \gamma(t) \cdot S(t) dt\right)$ where γ (t) - the current number of active centers S (t) - the current area of active centers	The Delmon equation of a geometric model: $0 \le \tau \le 1$ $\alpha = 1-(1-\alpha)^d - -d \cdot \int_0^{\tau} (1-\xi)^{d-1} \cdot \exp\left[-A\frac{\left(\tau^2-\xi^2\right)^{(d-1)/2}}{(1-\xi)^{(d-1)/2}}\right] \cdot d\xi$
		The equation of the chain mechanism: $\alpha = 1-\exp\left(-A \cdot W^d \cdot \int_0^t ((1-\xi)\cdot(t-\xi))^{d-1} \cdot ch(W\cdot\xi) \cdot d\xi\right)$
Weibull distributio n	$kn \cdot \xi^{\beta-1} \cdot \exp\left(-k \cdot \xi^n\right)$ where k,n - constants	Erofeev-Avrami equation: $\alpha = d \cdot k \cdot n \cdot \int_0^t (1-\xi)^{d-1} \cdot \xi^{n-1} \cdot \exp\left(-k \cdot \xi^n\right) \cdot d\xi$
Beta distribution	$\frac{1}{B(x,y)} \cdot (a)^{y-1} \cdot (1-a)^{x-1}$ where B(x,y) – gamma function	The equation of the universal model: $t = \frac{1}{W} \cdot \frac{1}{B(x,y)} \cdot \int_0^{\alpha} \alpha^{y-1} \cdot (1-\alpha)^{x-1} \cdot d\alpha$

where $\tau = W \cdot t$ - given time; W- velocity constant; t-current time; ξ - instantaneous kinetic parameter A - the number of centers/cm2

STUDY OF BIOLOGICAL PROPERTIES OF COMPLEX COMPOUNDS OF HYDROXAMIC ACID AND AMINOBENZIMIDAZOLE DERIVATIVES

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Recently, the vivo insulin mimetic activity of vanadium compounds, extensive studies exploring vanadium chemistry, including the synthesis of novel complexes and their biological effects both in vitro and in vivo have been studied[1-2]. Such complexes can be considered as possible potential agents for diabetes therapy. Among the several existing compounds, diketone based vanadium complexes with aminobenzimidazole and hydroxamic acid have been chosen for the current study.

The 2-oxo-1-pyrrolidineacetohydroxamic, nicotinehydroxamic acids vanadium complexes, mixed ligand complex of acetylacetonate and 2-amino-1-methylbenzimidazole were synthesized and characterized by UV-visible, FT-IR and X-ray structural studies. The hydroxamic acids and acetylacetonate are coordinated to metal ion through the oxygen atoms with formation of 5-memberes chelate cycle, and the aminobenzimidazole ligand is coordinated via the endocyclic N-atom of benzimidazole cycle.

The antidiabetic activity and toxicity of the complexes was proved by animal study. During experiments the sugar level in blood of rats was decreased after 60 minites of on 32.7% after single oral inserting. The results show that the complexes have comparable antidiabetic potential with respect to the standard drug as well as with cis-acetylacetonatooxovanadium(IV). It is allows to recommend it for further more detailed researches on hypoglycemic and insuline mimetic activity and for design of new generation therapeutic agents for diabetes treatment.

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THE REACTION OF DIFLUOROCARBEN WITH THIOURACIL'S DERIVATIVES.

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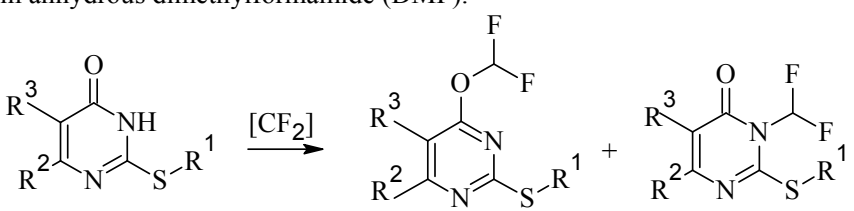
One of the most intensively developing trends in chemistry of biological activity heterocycliks is the synthesis of fluorinated analogues. Replacement of hydrogen atoms by fluorine and fluorine-containing group has a significant impact on physical, chemical and biological properties of these molecules. One of this substituent is difluoromethoxy group CHF_2O. The drug analogues containing difluoromethoxy groups have been synthesized. The introduction of CHF_2O groups increases the pharmacological and biochemical properties of drug substances.

The aim of the present work was the synthesis and study of properties of difluoromethoxical derivatives of thiouracil. We investigated the reaction of difluorometylation with singlet difluorocarben, formed *in situ* from clorodifluoromethan (Freon-22) with bases t-BuOK or KOH in anhydrous dimethylformamide (DMF).



R^1 = H, Me, Et, i-Pr, All, Bu, s-Bu, Bn R^2= Me,Et,Bn,i-Pr R^3=H,Me,Et, =Bn

In this work we have focused on the study the effect of substituents, mechanism of reaction, computational studies support the formation of carben - solvent complex between difluorocarben and dimethylformamide complex that leads to the formation of O-difluorometylcompaunds.

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FIELD IONIZATION OF WATER MOLECULES ON VANADIUM DIOXIDE SURFACE

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It has been earlier experimentally shown[1] that superficial conductivity of vanadium dioxide (T_c=338-340) is ionic, and also an assumption has come out that the products of irradiation-chemical transformations of the components of environment participate in the processes of charge transfer (in particular, water molecules).

The properties of isomeric clusters $16VO_2 \cdot 14H_2O$ (Fig. 1) modeling both surface (K1) and bulk (K2) phases of VO_2 have been studied by Hartree-Fock-Roothaan method by means of the PC GAMESS[2] program module. The energy values of the highest occupied and the lowest unoccupied orbitals (HOMO-LUMO) and their difference for the K1 and K2 clusters slightly differ. The HOMO for the cluster K2 has a structure paid by a rich set of valuable atomic orbitals unlike that for the K1 one.

K1 K2

Fig. 1. Isomeric clusters of $16VO_2 \cdot 14H_2O$; dark circles depict superficial vanadium atoms

Maps of electrostatic potential distribution near VO_2 surface have been calculated. When the number of coordination spheres in cluster increases, the optimum distance for interaction between the surface and a charged particle decreases. Over surface VO_2, the values of field intensity can reach about 10^7 V/cm. Therefore field ionization of water molecules is possible on vanadium dioxide surface. Obviously, ionic conductivity of VO_2 surface is caused by field ionization of H_2O molecules.

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CYCLOPROPANATION OF ARYLOLEFINES WITH $EtAlCl_2$ AND DICARBOXYLATES CATALYZED BY Cp_2ZrCl_2

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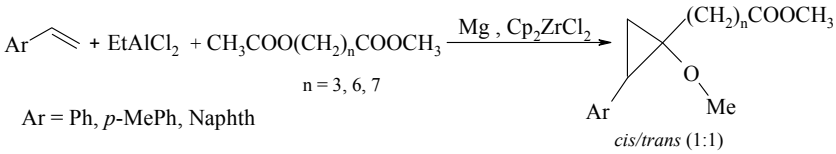
As it has been recently shown[1], the interaction between arylolefins and alkylhalogenalanes appear to be an efficient cyclopropanation method for the synthesis of aryl-substituted alkoxycyclopropanes.

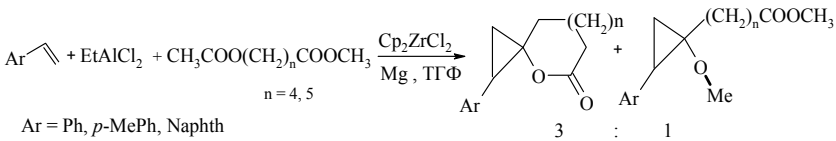
Now, we report our further investigations on the catalytic cyclopropanation reaction of arylolefins with $EtAlCl_2$ mediated by esters of dicarboxylic acids.

Dicarboxylates, in which the number of the CH_2 groups less than 3 and more than 7, were found to be inert in this reaction.

However, dimethyl esters of α,ω-dicarboxylic acids such as glutaric, suberic and azelaic ones can involve arylolefins in the reaction giving rise to appropriate substituted cyclopropanes.



Of interest is the reaction of arylolefins with EtAlCl2 aided by esters of adipic and pimelic acids resulting in the predominant formation of spirocyclopropane substituted lactones, while the cyclopropane derivative was detected as a minor product in 42 % total yield.



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SYNTHESIS OF BORACYCLOPENTANES VIA THE EXCHANGE REACTIONS BETWEEN ALUMINACYCLOPENTANES AND BORON HALOGENIDES

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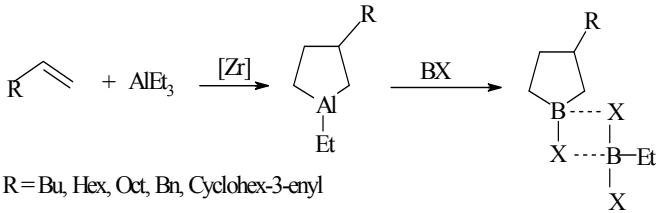
Zr-Promoted cycloalumination of olefins with Et_3Al leads to the formation of substituted aluminacyclopentanes in high yields.[1,2]

This report presents the results on further investigations of the exchange reaction between aluminacyclopentanes, generated *in situ*, and BX_3 (X = F, Cl). Thus, it was shown that 1-ethyl-3-alkyl(cycloalkyl, benzyl)-substituted aluminacyclopentanes enter into reaction with boron halogenides to produce corresponding 1-fluoro(chloro)-3-substituted boracyclopentanes as a complex with $EtBX_2$. Analysis of one-dimensional (^1H, ^{13}C, ^{11}B, ^{19}F) and two-dimensional (COSY, HMBS, HSQS) NMR spectra, and also the molecular mass determined by the cryoscopic method have confirmed the structure of this complex.



R = Bu, Hex, Oct, Bn, Cyclohex-3-enyl

X = F, Cl

The exchange reaction between 1-ethyl-3-substituted aluminacyclopentanes and boron halogenides successfully proceeds in different solvents such as THF, Et_2O, hexane, toluene, and CH_2Cl_2.

The results of the NMR-investigations carried out immediately in the cell of the NMR spectrometer to study successive transformations of aluminacyclopentanes to appropriate boracyclopentanes are also discussed.

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PHYSICAL PICTURE ELUATING OF MOBILE PHASES FLOW AND EFFECTIVENESS OF COLUMNS PREPARATION

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In present work nonuniformity eluating flow of mobile phases through stationary beds of chromatographical packed beds and their connection with effectiveness of preparation division is discussed.

By means of laser doppler anemometer method we carried out direct measure of distribution velocity of flow of mobile phases above bed of packed beds (different natures, shapes, sizes and dispersiveness) in preparation columns -50, 100 and 150 mm. Received data were worked up on computer with special worked out methods.

Revealed results in the flow of large - scale and small - scale (micro- and macro-) nonuniformity and in the structure of given packed bed micro- and macro- aggregates. Large scale nonuniformity of different types are approximated by polynom of the fourth degrees and small scale nonuniformity of flow and micro-, macro- aggregates packed bed are characterized by statistic moments. There is a line dependence between nonuniformity of flow and diameter of packed beds.

It is valued quantitative deposit of large and small scale forming in general size nonuniformity of flow by mobile phases. It is showed, that considerable deposit carries not only large scale as it is considered early, but and small scale nonuniformity, stipulated by micro- and macro- aggregate bed of packed bed. It is defined middle diameter of micro -and macro- aggregates, their distribution sizes and dispersion. It is established correlative dependence between indexes of nonuniformity bed packed beds and mobile flow phases and parameters of chromatograghical process. In dependence on diameter preparation columns, ways of filling and parameters of bed packed beds large and small scale nonuniformity may be formed 50-75 % and 25-50 % accordingly.

Received modification equation of Giddings for data of ВЭТТ, taking into consideration nonuniformity of bed sorbent and flow and it is showed, that the deposit of small scale nonuniformity in longitudinal dispersion concentrated zones may reach to 50%.

Results of the research showed us that large and small scale nonuniformity laying on each other forms general character of physical picture eluating of flow mobile phases and itself defines hydroairdinamics of mass - exchange processes in the packed bed.

ETHERS OF OXYMES AS A POTENTIAL BIOLOGICALLY ACTIVE SPASMOLITICS

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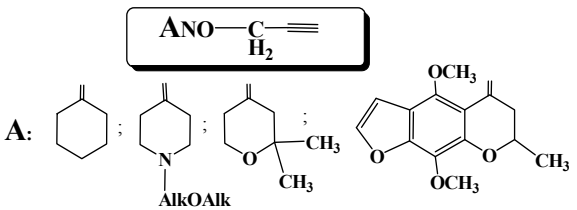
As it was previously shown, complex alkoxy- and phenoxyalkyl ethers of secondary and tertiary acetylenic and phenylacetylenic alcohols of 1-(2-etoxyethyl)piperidine provides an ability to eliminate pain, inhibit a growth of pathogenic bacteria, stimulate immune system, and relives spasm caused by the action of acetylcholine and/or histamine.[1,2]

Propargyl ether of 1-(2-ethoxyethyl)-4-ketoximpiperidine exhibits spasmolitic activity at the same level as no-spa with a lower-toxic effect. [3] In order to find a new antispasmodic a number of propargyl ethers of oxime were synthesized by known methodic of oximation of cyclohexanon, N-alkoxyalkyl-4-ketoximepiperidine, 2,2-dimethyltetrahydropyrane-4-one, and natural khellin.



Alkylation of oximes according to Williamson based on reaction between propargyl bromide and DMFA in a presence of KOH at room temperature for several days. Using of MW-radiation on the one hand causes significant reduction of reaction time; on the other hand it leads to a declining of a reaction yield by tarring processes.

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POLY(ARYLENE ETHER KETONE)S

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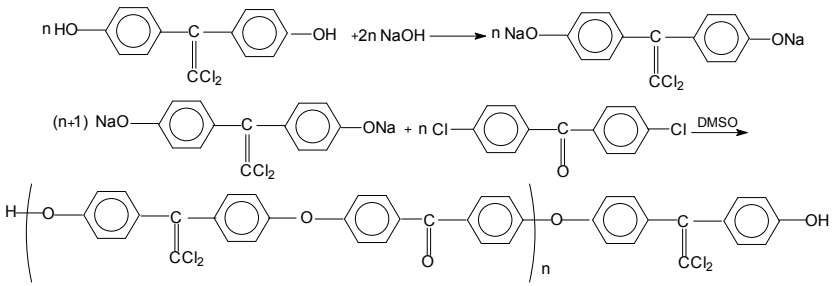
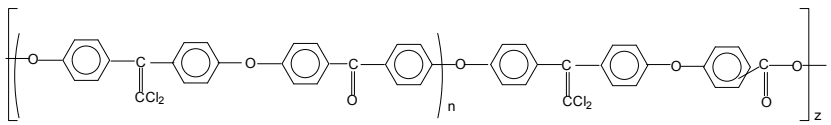
In the present paper poly(arylene ether ketone)s were synthesized in two steps on account of low activity of dichlorbenzophenon in polycondensation process and also having a desire to hold the process of synthesis under softer conditions. Poly(arylene ether ketone)s were synthesized by means of acceptor-catalytic polycondensation from olygoketones (OK) on the basis of 1,1-dichlore-2,2-(4-oxyphenyl)ethylene, containing two hydroxyl end groups and dichloranhydride phallic asides. Olygoketones with different condensation degrees were synthesized by means of interaction of disodium salt of 1,1-dichlore-2,2-(4-oxyphenyl)ethylene with 4,4'- dichlorbenzophenon in anhydrous dimethylesulphoxide (DMSO) according to schema[1]:



where n=l,5,10 and 20.

The poly(arylene ether ketone)s was obtained by the technique of acceptor-catalytic polycondensation in 1,2-dichloroethane for 1 hour at 20°C. Triethylamine was used as an acceptor-catalyser, and isopropanole - as a precipitator.



They are not flammable, they show high resistance to the diluted mineral acids.

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THE SYNTHESIS OF TRANSFORMATION AND COORDINATIVE ABILITY OF 1-ALLYL 4-PROPARGYLOXIBENZENE

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According to the growing demands for different multifunctional substituted allyl derivatives of benzene used as an initial monomers both for obtaining membraneous types of polymere materials and for obtaining ionic functional extragents as a more effective and selective extraction of ions from different metals, in the present work we introduce experimental results on the synthesis of 1-allyl 4-propargyloxibenzene $CH_2=CH–CH_2C_6H_4OCH_2–C\equiv CH$ (I), on investigation the reactional ability, as well as coordinative possibilities in some solvated $MX_2 (Solv)_n$ and non-solvated MX_2 by the dihalogen derivatives of transitive metals. Synthesis I have been obtained by the reaction between 1-allyl 4-hydroxibenzene and $BrCH_2C\equiv CH$ with the yield 55-80% and boiling temperature 98-100^{0}C, the temperature dependence and pH medium, as well as some other factors influencing the selectiveness of reaction. Thus, we have worked out a very comfortable unstated method of synthesis.

It has been established, that the reaction of transmetal interaction of I with AlkMgBr leads to formation of a more reactionable Grinyard derivative $CH_2=CH–CH_2C_6H_4OCH_2C\equiv CMgBr$ (II), which in its turn, reacting with CH_3CHO, leads to the high yields (up to 74%) 5-(n) of allylphenoxipentyl 2-ol,

$$CH_2=CH–CH_2C_6H_4OCH_2–C\equiv CH–CH_3 \quad \text{(III)}.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

With the boiling t^0 122-124^{0}C. The investigation of reactional abilities of I, for example, ethyl, butyl by the oxialkylhalogen derivatives $ROCH_2Cl$ has shown that these reactions only in average polar dissolvents lead to exclusively three ether groupings 6 methyl 3,5, 10 trioxi 12(n-) allyl phenoxipropine (or buthyne)

$$CH_2=CH\text{-}CH_2C_6H_4OCH_2C\equiv C\text{-}CH_3 \quad \text{(IV)}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OCH_2OR$$

with the yields R = C_2H_5 – 82%;
R = C_4H_9 – 87%.

While carrying these reactions out in such strong dissolvents as DMCO, DMFO and TGF, the reaction doesn't go selectively and it brings the creation of non-identifical subordinate products (up to 70%).

A special interest has the product of reaction I with the different substituted amines. They can be very effective extracting agents as they have in the molecule both several functional and chelating group complexes.

As an example of I with representatives of secondary amines, diethylamine $(C_2H_5)_2NH$ at the presence of CH_2O there has been obtained 1-diethylamine 4-(n-) allylphenoxi-2-buthyne, $CH_2=CH–CH_2–C_6H_4OCH_2C\equiv C–CH_2N(C_2H_5)_2$ (V)

with the yield 61% and with the boiling t^0 144-146^{0}C.

Complex V has in its molecule both chelatoforming (-CH_2-N(C_2H_5)$_2$ and two (–CH_2–C≡C–; –CH_2=CH–CH_2–) coordinative centers.

The structure of all newlyobtained complexes has been established by IR, NMR, H and C, mass - and ultra-violet spectroscopy. Being investigated in such, way, the I, II-V derivatives have been used further for display both structural peculiarities and coordinative possibilities at the interaction of solvate and non-solvate salts of some transitive metals.

At the example of hydratedichloride $MCl\cdot nH_2O$ and carbonoldichloride $MCl_2\cdot nROH$ of the solvate salts Fe, Co and Mn it has been established that independent on both nature and number of active centers in I, III-V derivatives and independent on reactional conditions we haven't found any interaction between the active centers in I, III–V with the atoms of transitive metals.

Besides, while using the solvateless dichloride MCl_2 for these interactions in the conditions of average polar medium (different alkylsubstituted aromatic hydrocarbons) according to IR-spectroscopy data there has been observed very light shifting of the valence waving $\nu_{CH=CH_2}$ 20–30 sm^{-1} in total, and $\nu_{C=C}$ – 18-25 sm^{-1} in total, as compared with the initial complexes, they are shifting to the high frequent field of spectrum, which in its turn proves though very poor, the fact of interaction of CH_2=CH and C=C-active centers with the atoms of transitive metals. Thus, it has been established that taking part in these interactions MCl_2 displays the properties of electrono-acceptors.

It has been found out that taking place of the mentioned above interactions in such strong-polar dissolvent as DMCO, DMFO, TGF we haven't observed any interactions of MCl_2 with the mentioned active centers. Besides, it has been determined, that in the conditions of high polar medium MCl_2 because of its high solvating ability with the polar dissolvent transfers into the corresponding solvate salt $MCl_2\cdot(Solv)_n$ (where Solv – DMCO, DMFO, TGF: n=2-4).

However, the obtained experimental result leads to an idea that exclusiveness of interaction of solvativated dichlorides of the transitive metals with the active centers in the derivatives I-V is first of all connected with coordinating saturation of the atom of a transitive metal.

On the base of joining V with MCl_2 in the conditions of weakpolar dissolvents (petroleum ether) in the temperature interval 36-38^{0}C (start boiling t=38^{0}C end boiling t=70^{0}C) it has been established that as compared with derivatives I, III, V the strongest interaction of MCl_2 with all CH_2 = CH, C ≡C and CH_2–N(C_2H_5)$_2$ active centers has taken place in derivatives V.

The obtained products VI a,b,c have been extracted from the homogenous solution in the individual type and have been characterized by the data of elemental analysis, by IR-and UV-spectral methods. The thermal stability of the obtained complexes has been determined. All of them have precise starts of the temperatures of decomposititon. For VIa – t^0 of start decomp. is >168^{0}C, VI/b – t^0 of start decomp. is >174^{0}C VI/c – t^0 of start decomp.is > 138^{0}C.

with the yield 61% and with the boiling t^0 144-146^{0}C.

Complex V has in its molecule both chelatoforming (-CH_2-$N(C_2H_5)_2$ and two (–CH_2–C≡C–; –CH_2=CH–CH_2–) coordinative centers.

The structure of all newlyobtained complexes has been established by IR, NMR, H and C, mass - and ultra-violet spectroscopy. Being investigated in such, way, the I, II-V derivatives have been used further for display both structural peculiarities and coordinative possibilities at the interaction of solvate and non-solvate salts of some transitive metals.

At the example of hydratedichloride $MCl{\cdot}nH_2O$ and carbonoldichloride $MCl_2{\cdot}nROH$ of the solvate salts Fe, Co and Mn it has been established that independent on both nature and number of active centers in I, III-V derivatives and independent on reactional conditions we haven't found any interaction between the active centers in I, III–V with the atoms of transitive metals.

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It has been found out that taking place of the mentioned above interactions in such strong-polar dissolvent as DMCO, DMFO, TGF we haven't observed any interactions of MCl_2 with the mentioned active centers. Besides, it has been determined, that in the conditions of high polar medium MCl_2 because of its high solvating ability with the polar dissolvent transfers into the corresponding solvate salt $MCl_2 \cdot (Solv)_n$ (where Solv – DMCO, DMFO, TGF: n=2-4).

However, the obtained experimental result leads to an idea that exclusiveness of interaction of solvativated dichlorides of the transitive metals with the active centers in the derivatives I-V is first of all connected with coordinating saturation of the atom of a transitive metal.

On the base of joining V with MCl_2 in the conditions of weakpolar dissolvents (petroleum ether) in the temperature interval 36-38^{0}C (start boiling t=38^{0}C end boiling t=70^{0}C) it has been established that as compared with derivatives I, III, V the strongest interaction of MCl_2 with all CH_2 = CH, C ≡C and CH_2–$N(C_2H_5)_2$ active centers has taken place in derivatives V.

The obtained products VI a,b,c have been extracted from the homogenous solution in the individual type and have been characterized by the data of elemental analysis, by IR-and UV-spectral methods. The thermal stability of the obtained complexes has been determined. All of them have precise starts of the temperatures of decomposititon. For VIa – t^0 of start decomp. is >168^{0}C, VI/b – t^0 of start decomp. is >174^{0}C VI/c – t^0 of start decomp.is > 138^{0}C.

THE ANALYSIS POROUS STRUCTURE OF A SURFACE OF COMPOSITE ADSORBENTS

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One of actual problems of a heterogeneous catalysis is working out new nanoporous materials – of the sorbents intended for the decision of many practical problems, including in nature protection activity of the person. It was investigated porous composite material, used as an adsorbent in a computer gas chromatography. The dominant role in adsorbtions processes belongs to micropores, therefore the big role in processes of a heterogeneous catalysis is played by substance carrying over to catalyst porous. At research of porous structure of a sorbent in it a mesotime in radius of 1- 3 nm are found out; micropores in radius 0,023nm and a macrotime 2,53 mkm. Experimental studing of a transport properties of polymeric composite electolits has shown that the factor of diffusion facing molecyl in a time is distinct from factor diffusion gas dimmers on a surface and proportional to diameter of a time is a consequence of a active role of a walls in process masstransfer. Dimers migrate on dislocations to tubes (fig.1).

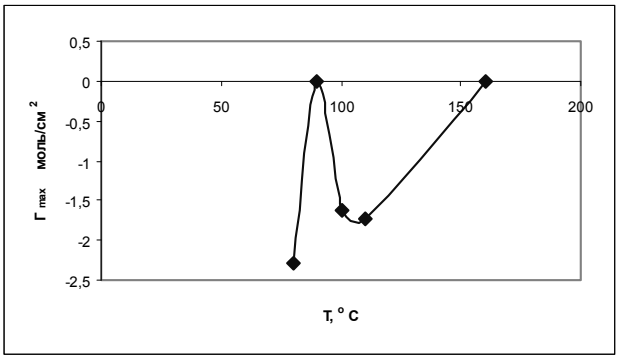

Fig.1. Dependence Γ_{max} dimmers benzene from sobent temperature.

In the table diffusion factors dimmers benzene in a time depending on sorbent temperature, and also diameter dimmers the benzene (d), calculated of the assumption are presented that in a time there is catalytic reaction of 1 order.

D_{mol}	$T_{col.}$, °C	D, m^2/s
0,78 нм	80	$1{,}08 \cdot 10^{-10}$
3,8 нм	90	$1{,}15 \cdot 10^{-8}$
0,36 нм	100	$1{,}1 \cdot 10^{-10}$
0,35 нм	110	$1{,}08 \cdot 10^{-10}$
$0{,}92 \cdot 10^{-7}$ м	160	$1{,}3 \cdot 10^{-5}$

CRYSTAL STRUCTURE OF TETRACOORDINATED PALLADIUM(0) COMPLEX WITH THE GERMYLENE BASED ON SUBSTITUTED DIALKANOLAMINE

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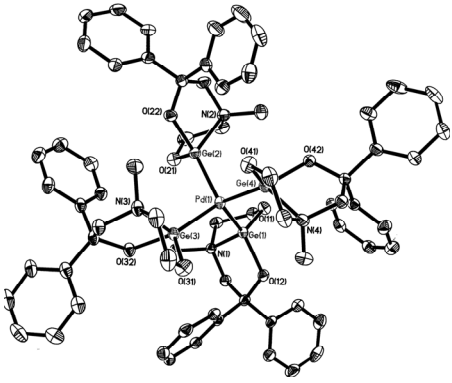
The modular design of ligands based on the modification and recombination of large structural subunits, is an effective strategy in the development of new molecular catalysts. Traditionally, phosphine ligands play a role in the chemistry of late transition metals. Nowadays, carbenes and their heavy analogs (germylenes and stannylenes) are regarded as a new family of ligands coordinating transition metals.[1] We have recently obtained a number of stable germylenes based on substituted diethanolamine. The compounds produced of interest to investigate them as ligands in palladium complexes. One of the possible schemes for the synthesis of similar complexes - the interaction of derivatives of Pd^{2+} with germylenes, during which germylene is both ligand and reductant.[2]

As a result of ligand exchange in the coordination sphere of transition metal, the complex of Pd^0 with four germylene molecules was obtained by the interaction of excess of the germylene $MeN(CH_2CH_2O)(CH_2CPh_2O)Ge$ with palladium(II) acetate. The crystal structure of this compound was studied by X-rays analysis.



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ABOUT THE PHENOMENON OF SYNERGISM IN CATALYTIC SYSTEMS Mo (VI) – HYDROXYL-CONTAINING LIGAND – $KClO_3$

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The influence of some oxy-acids (citric, glucaric acid) and hydroxyl-containing aromatic compounds (catechol, 2,3-dihydroxybenzaldehyde, thiosemicarbazone 2,3- dihydroxybenzaldehyde, mandelic acid) on the catalytic current in the system molybdenum (VI) – potassium chlorate has been studied. It has been shown, that the phenomenon of synergism at studying catalytic currents is associated with activating action of the hydroxyl-containing ligand (L). The activity of mixture of L and an oxidant (Ox) significantly exceeds the sum of effects for their separate influence. The growth of catalytic current is possible, if the catalyst (a metal ion M) possesses free or labile seats in the coordination area for formation of intermediate active compounds of the catalyst with Ox.

The hydroxyl-containing ligands, forming complexes with Mo, provide the possibility to increase the lability of catalyst coordination spheres as well as to facilitate the formation of intermediate active complexes of Mo with L and Ox, which in turn leads to a substantial growth of the analytical signal and an increase of sensitivity of the catalyst M determination. At presence of hydroxyl-containing ligands the catalytic wave in the form of a big maximum covers the area of potentials for the first and second waves of the Mo reduction (background of H_2SO_4, pH 1.0-2.5). However at the greatest display of catalytic effects at Mo(VI) concentrations $<5 \cdot 10^{-6}$ M, the potential of maximum corresponds to the first catalytic wave in the system Mo (VI) – ClO_3^-, i.e. its occurrence is related with formation of an active Mo (V) form while in the process of Mo (III) formation the current falls. Dependence of the current magnitude I_p on the concentration of oxidant ($KClO_3$) looks like a curve with a bend and a saturation section that testifies about the formation of a polarographically active complex Mo (V) with L and Ox.

The dependence of the catalytic current value on various concentration factors in Mo (VI) – L - ClO_3^- solutions has the same character, explicable by generality of the mechanism of catalytic processes in considered systems. The scheme of reactions occurring in the solution and on the electrode has been elaborated. The rate constants for the active intermediate complex reaction formation as well as the activation energies and activation entropies of reactions have been calculated. These characteristics testify about a high catalytic activity of such systems that allows significantly increasing the sensitivity of the metal – catalyst determination.

THE THEORETICAL STUDY OF MONO- AND DIPROTONATED DECAHYDRO-CLOSO-DECABORATE ANION

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One of the characteristics of boron cluster anions $B_nH_n^{2-}$ (n = 6-10) is their ability to attach a proton in the presence of strong organic acids to form the corresponding protonated anions $B_nH_{n+1}^-$.[1] In the 70 years of the XX century in the study of reactions of acid-catalyzed substitution of hydrogen atoms in the *closo*-decaborate anion $B_{10}H_{10}^{2-}$ first suggested the existence of protonated intermediates with high reactivity – undecahydrodecaborate anion $B_{10}H_{11}^-$.[2]

The report summarizes the results of a systematic quantum-chemical calculations of geometric and electronic structure, isomerism, stability, normal vibration frequencies and other molecular characteristics of boron clusters $B_{10}H_{11}^-$ and $B_{10}H_{12}$.

Analysis of the possible positions of the proton H* and its migration in $B_{10}H_{11}^-$, slackness of the core and the distribution of charges on the boron atoms can explain to a large extent the preferential formation of certain complex compounds in a series of chemical reactions, we have studied previously. Also, a comparison with the possible positions of two additional protons in $B_{10}H_{12}$ and their migration, the charges on the boron atoms in $B_{10}H_{12}$ etc.

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This work was supported by RFBR (grants 10-03-00470 and 11-03-01261), the Presidential Council on grants and financial support of leading scientific schools (grant NSH - 3321.2010.3).

SORPTION PROPERTIES OF MONOMOLECULAR FILMS DERIVATIVES OF B-CYCLODEXTRIN DEPOSITED ON GRAPHITE SUBSTRATE

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Presently, a variety of macrocyclic compounds have widespread occurrence. Because of their ability to form inclusion complexes, they are used in the design and simulation of molecular devices in a variety of sensory, biological, optical technologies and analytical chemistry. Most of the sorption and chromatographic technologies with similar compounds are based on their application in a dissolved state. The properties of monomolecular films of macrocyclic compounds deposited on a solid substrate were investigated to a lesser degree.

We have investigated the adsorption of steams of organic compounds with different polarity by the gas chromatography on the modified adsorbents, obtained by deposition of monomolecular layers of β-cyclodextrin and its derivatives on the carbon adsorbent Carbopack Y (CpY) (Supelco Inc., USA; $s_{уд} = 25$ *м*^{2}*/г*).

It was noted that the composition of the modifier monolayer deposited on a carbon substrate, is determined by the properties and position of substituents in the cyclodextrin molecule. It was established that the possibility of the formation of inclusion complexes with cyclodextrin molecules, and thermodynamic characteristics of adsorption of modified adsorbents are highly dependent on the molecular structure of adsorbates and the nature and size of the substituents in the macrocyclic molecule. The increase in the absolute values of entropy of adsorption as compared with the original CpY, observed for some of the modified adsorbents, due to the limited mobility of the adsorbed molecules, and is interpreted as the evidence of the formation of inclusion complexes of the type "guest - host".

The work was supported by project N 02.740.11.0650 Program "Research and scientific-pedagogical staff of Innovative Russia" 2009-2013.

PERSPECTIVES OF THE USE OF LUMINESCENCE OF LANTHANIDE COMPOUNDS IN THE NOVEL TECHNOLOGIES

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The search of high-luminescent complex compounds of lanthanides as active components of materials of new technique is actual scientific direction simultaneously of chemical, physical and biological investigations. Some of these materials already find application in different fields, in particular, in medicine (fluorescent diagnostics, immunofluorescent analysis), chemistry and biology as sensors and markers, in the systems of telecommunication, in materials science.

In the lecture the basic tendencies, in authors' opinion, in development of investigations in the field of lanthanide luminescence in the last few years are analyzed. The conclusion that nanocomposite hybrid organo-inorganic compounds on polymeric and/or inorganic carriers will attract the greater attention is one of key. First of all, it is related to that in hybrid materials on the base of lanthanide-containing complexes there is the principle possibility to improve substantially the characteristics of 4f-luminescence with the same concentration of radiative (i.e. lanthanides) centers as compared to known before.

The quickly increased amount of data about of luminescence of lanthanides (neodymium, ytterbium and erbium) in the near IR-spectral range also marked. Obviously, that development and obtainment of such IR-emitters will allow not only to make a valuable contribution to understanding of fundamental bases of the directed synthesis of new types of lanthanide-containing compounds but also effectively to utilize them in the different branches of science and modern technology.

The features of formation and structure of lanthanide complexes of different types are considered on concrete examples and spectral-luminescent effects, the result of which is appearance of new practically useful properties of these objects, also analyzed.

The work was supported by NAS of Ukraine (project № 6.22.7.43).

STANDARD ENTHALPIES OF COMBUSTION AND FORMATION 2,5-DIAMINO-1,3,4-THIADIAZOLES

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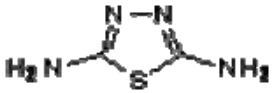
Currently, of particular interest are compounds having a structure of five-membered heterocycles with a sulfur atom. This is due to biological activity and a wide variety of other aspects of the application of synthesis macroheterocyclic compounds 2,5-diamino-1 ,3,4-thiadiazole precursors.



Heat of combustion was determined in a liquid calorimeter type B-08-MA according to the method described previously [1]. During processing data of thermo-chemical of the experiment the flow of the following reactions was taken into account:

$$C_2H_4N_4S_{(solid)} + 4O_{2(gas)} \rightarrow 2CO_{2(gas)} + 2H_2O_{(liquid)} + 2N_{2(gas)} + SO_{2(gas)}$$

$$SO_{2(gas)} + H_2O_{(liquid)} \rightarrow H_2SO_{3(solution)}$$

$$1/2N_{2(gas)} + 5/4O_{2(gas)} + 1/2H_2O_{(liquid)} \rightarrow HNO_{3(solution)}$$

Thus, the energy of combustion of studied substance ΔcU° =- 1907,62 ± 2,12 kJ/mol, the standard enthalpy of combustion ΔcH° =- 1905,14 ± 2,12 kJ/mol and a standard enthalpy of formation ΔfH° = 249,56 ± 2,12 kJ/mol were obtained from experimental data.

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MANAGEMENT BY REACTIONARY ABILITY AND SPEED OF DECOMPOSITION OF HEAVY METALS AZIDES

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Management problem actual reactionary ability of power materials which the objects of the real research (azides of heavy metals are a traditional model object of research of chemical reactions in a hard phase) behave to, both for a theory and for practice, in connection with importance of decision of questions of stability of explosives.

From the most widespread factors influencing to work of wares, where the azides of heavy metals (AHM) are used, all greater interest is presented by the electromagnetic fields. External power influence initiates the processes of decomposition in the crystals of AHM, flowing in reactionary areas a chain chemical reaction will be realized in which. Reactionary areas in these materials are formed by regional dislocations.

Management by reactionary ability and speed of decomposition of AHM possible of different ways: by the change of imperfect structure (quantitative contents of admixture and density of dislocations); by means of permanent noncontact electric and magnetic the fields (including ultralow, designing the real terms of storage and transporting of these materials). Possibility of the use of weak noncontact electric-field is shown as an inhibitor of solid-phase of chemical reaction in AHM, management instrument by their explosive sensitiveness. Hypothetical reason of influence of noncontact electric-field on speed of chemical reaction is displacement along the vector of tension of electric-field of electronic closeness of reactive particles, that results in diminishing of probability of ceiling of electronic clouds at formation of chemical connection.

Also there is an effective method of management by an imperfect structure and reactionary ability of these materials on the stage of height by growing in the weak electric and magnetic fields. Varying tension electric or magnetic the fields during crystallization, it is possible to get the crystals of different size, with minimum contents of defects (admixtures and distributions), with the improved workers by descriptions (stability to external influences - light, action of electric-field) during a certain expiration date.

3,1-BENZOXAZINE COPPER COMPLEX AS NEW ADDITION FOR CONTROLLED METHYL METHACRYLATE RADICAL POLYMERIZATION

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Searching a way for increasing efficiency and selectivity radical polymerization catalysts and control morphology polymers possibility is actual problem. The new complex in terms of 2-phenylspiro[3,1-benzoxazine-4,1`-cyclopentane] and cuprous chloride(II) was obtained for the first time.[1] IR and NMR spectroscopy data illustrated that copper ion coordinated with nitrogen atom and complexation passed without opening benzoxazine cycle.

Methyl methacrylate radical polymerization over a copper catalyst (1.0 mmol/l) and initiator AIBN (1.0 mmol/l) features were investigated (333 K). Reverse curves had induction period (200 min) and observed gel-effect moved larger conversion area as compared with check sample. Synthesized polymers had comparatively narrow chain-length distribution ($M_w/M_n \approx$ 1.9). Chain-length distribution curves were unimodal and with fractional conversion monomer increasing moved high-molecular area.

The mechanism of radical polymerization inhibition over complex $CuCl_2L_2$ we suppose according to scheme:

$$CuCl_2 \cdot 2L + \sim R^{\cdot} \rightarrow CuCl \cdot 2L + \sim RCl,$$

here central copper atom is deoxidized and chlorine atom is contained in structure of macromolecule. It was verified by elemental analysis results of all obtained PMMA samples.

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THE MECHANISM OF SILVER AZIDE PHOTODECOMPOSITION

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The main purpose of this work is to investigate the mechanisms of silver azid photo- and radiochemical decomposition. In terms of suggested mechanism crystal lattice defects and decomposition process products take part in the reaction stages and leads to the feedback appearance. The feedback leads to complicated system dynamical behavior. Suggested mechanism of the azid heavy metals decomposition is based on the next statements:

- Molecular nitrogen (the anion sublattice decomposition product) generation is a two-stepreaction. First step is the formation of N_6 complex as a result of localization of two holes on the cation vacancy. Second step is the N_6 complex decay. Second step limits the anion sublattice decomposition rate.

- Small silver clusters formed in the ionic and electron holes process stages are the electron and holes recombination center.

- Cation and anion sublattice decomposition reactions are interconnected by the common stages of defects formation and electron's transitions.

In terms of the mechanism it was shown that the whole of experimental data (spectral, lux-ampere characteristics, photocurrent kinetics in case of stationary and interrupted radiation, photo fatigue effect, photoconduction kinetics curve and radiation gas liberation form changing) are the result of the recombination center generation and growth. Recombination center growth depends on the electron holes generation velocity produced by the external irradiation.

Additional centers recombination formation and growth in the ion sublattice is a system response to the external action as a result of the Le Chatelier's – Braun principle realization. This mechanism is rather common because it considers the external irradiation only as an electron and hole generating agent, and products form as a result of electron and ionic stages alternation what is common for a lot of the compounds decomposition.

SYNTHESIS OF PHOSPHORUS DERIVATIVES OF ARABINOGALACTAN

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Natural polysaccharide arabinogalactan (AG) isolable from larch wood shows a wide spectrum of biological activity including anti-inflammatory, antiallergy, immune-stimulating effect, and others.

This work deals with the synthesis of phosphorus derivatives of AG that are of interest for preparing novel promising pharmaceuticals. We have used two phosphorylation methods to modify AG. Treatment of AG with tris(dimethylamino)phosphine in the presence of catalytic amount of Me_2NH_2Cl in dioxane at reflux followed by the oxidation of nascent amidophosphite with an excess of NO_2 gave modified AG containing $(Me_2N)_2P(O)$- groups.

An alternative phosphorylation method consisted in the reaction of diethyl phosphite with AG in boiling dioxane in the presence of triethylamine as a catalyst followed by the oxidation of resultant acid phosphite ester with NO_2 excess to produce a modified AG containing (EtO)(HO)P(O)- groups.

According to elemental analysis data, the content of phosphorus reaches 7.4–8.1% that corresponds to the phosphorylation of about a half of the monosaccharide units.

The obtained compounds are whity powders well soluble in water. High water solubility of the prepared phosphorylated arabinogalactans and low viscosity of resulting solutions facilitates the use of these derivatives in biological entities. Moreover, the presence of arabinogalactan chain in the molecule can favor the transport of the phosphorus-containing fragmnets through cell membrane.

THE THIOCARBAMIDE COMPLEXES OF OSMIUM

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The role of thiocarbamide complexes of platinum metals in evolution of coordination chemistry is widely known. The actual task is obtaining the information about chemical forms of existence of osmium, processes of their formation and transformation in various solutions at presence of thiocarbamide, that is physical and chemical base of technological processes and analysis techniques.

The interaction of practically important osmium compounds $K_2[OsX_6]$ (X=Cl, Br) and $K_2[OsO_2(OH)_4]$ (C_{Os}= 10^{-4}–10^{-3} mol/l) with thiocarbamide in water solutions of HX at various ratios Os:Thio (1:1 – 1:100) and concentration of acids (C_{HCl} = 0 – 10 mol/l, C_{HBr} = 0 – 7 mol/l) have been investigated by electronic absorption spectroscopy.

In the systems $K_2[OsO_2(OH)_4]$ – Thio – HX the halogenocomplexes of osmium(VI) – $[OsO_2X_4]^{2-}$, $[OsO_2(H_2O)X_3]^-$ and osmium(IV) – $[OsX_6]^{2-}$, $[OsX_5(H_2O)]^-$; the thiocarbamide complexes of osmium(III) – $OsThio_6]^{3+}$, $[OsXThio_5]^{2+}$ и $[OsX_2Thio_4]^+$ and osmium(IV) – $[OsX_3Thio_3]^+$, $[OsX_4Thio_2]^o$, $[OsX_5Thio]^-$ were identified. Existence of three last complexes was established for the first time. Their spectrophotometrical characteristics were received.

In the systems $K_2[OsX_6]$ – Thio – HX only three forms of osmium were determinated: $[OsX_6]^{2-}$, $[OsX_5(H_2O)]^-$, $[OsThio_6]^{3+}$. That can be explained by kinetic inertness of $[OsX_6]^{2-}$-ions. The replacement of the first X^-–ion by Thio is the limiting stage of the reactions.

Totally 11 new osmium compounds were synthesized and identified by different physical and chemical methods of analysis. They can be divided on four various classes: a) thiocarbamide complexes of osmium(III) – $[OsThio_6]Br_3\cdot H_2O$ and $[OsBrThio_5]Br_2$; b) hexahalogenocomplexes of osmium(IV) containing $ThioH^+$ or the product of its oxidation in external sphere – $(ThioH)_2[OsX_6]$ and $[(H_2N)_2CS\text{-}SC(NH_2)_2]_2[OsX_6]X_2\cdot 3H_2O$; c) bicomplexes, consisting of cationic thiocarbamide complexes of osmium(III) and anionic bromocomplexes of osmium(IV) – $[OsThio_6]_2[Os_2OBr_8(H_2O)_2]Br_4\cdot 17H_2O$, $[OsThio_6][OsBr_6]Br$ and $[OsBrThio_5][OsBr_6]$; d) thiocarbamide complexes of osmium(IV) – $[OsCl_4Thio_2]\cdot 2H_2O$ и $[OsBr_4Thio_2]$.

The molecular and crystal structures of complexes $[OsThio_6]Br_3\cdot H_2O$, $[(H_2N)_2CS\text{-}SC(NH_2)_2]_2[OsBr_6]Br_2\cdot 3H_2O$, $[OsThio_6]_2[Os_2OBr_8(H_2O)_2]Br_4\cdot 17H_2O$ and cis-$[OsCl_4Thio_2]\cdot 2H_2O$ were determinated.

SYNTHESIS OF (2-THIO-3,4-DIHYDRO-2-H-BENZO[e][1,3]OXAZYNE-4-YL)THIOUREAS

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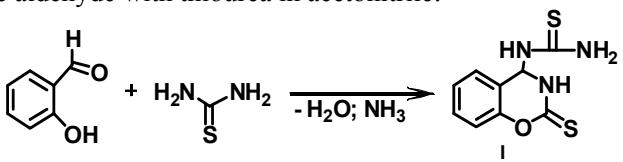
Synthesis of natural and biologically active heterocyclic compounds is one of the actual problems of organic and medicinal chemistry. Among the oxazines derivatives have been found effective medicines with high cytostatic, antibacterial, antiviral activity. The compounds with a pronounced fungicidal effect and hypotensive effect have been found.

All this has been encouraged the study of this interesting class of compounds, the development of effective methods of their preparation, as well as a comprehensive study of their structure and chemical transformations, which allowed the defining their role and placing in a number of other heterocycles oxo-derivatives.

At the same time, some representatives of this class of heterocyclic compounds remain virtually unexplored, particularly this concerns to (2-thio-3,4-dihydro-2H-benzo[e][1,3]oxazine-4-yl)thiourea and their derivatives.

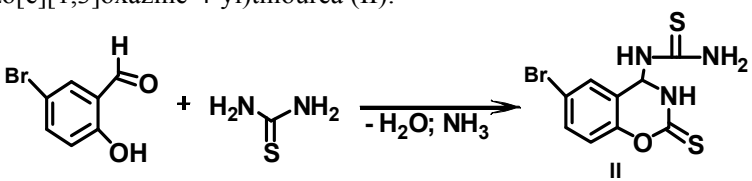
Thus, (2-thio-3,4-dihydro-2H-benzo[e][1,3]oxazine-4-yl)thioureas and their derivatives, are interesting objects as with standpoint of synthetic and theoretical organic chemistry, so and with standpoint of searching for of new efficient medicinal substances.

Take into account the above, we synthesized the(2-thio-3,4-dihydro-2H-benzo[e][1,3]oxazine-4-yl)thiourea (I) on the basis of the condensation of salicylic aldehyde with thiourea in acetonitrile:



I

Similarly, there has been synthesized (6-btomo-2-thio-3,4-dihydro-2H-benzo[e][1,3]oxazine-4-yl)thiourea (II):



II

The structures of synthesized compounds have been proved by IR- and NMR-spectroscopy, and also by X-ray structure analysis.

SYNTHESIS OF α-CHLORALKYL POLYFLUOROALKYL ETHERS AND MONOMERS ON THEM BASED

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The presence of polyfluoroalkyl fragments in organic compounds uses for production of materials with new specific properties, such as high thermo-, chemical stability and hydrofobic properties .[1]

We obtained α-chloroalkyl polyflyoroalkyl ethers and monomers on them based.[2]

$$H(CF_2CF_2)_nCH_2OCH(R)Cl \text{ and } H(CF_2CF_2)_nCH_2OCH(R)R_1,$$

here R–H, CH_3, C_2H_5, C_3H_7; n–1-3,

R_1–CH_2=CHC(O)O, CH_2=$C(CH_3)$C(O)O, CH_2=$CHCH_2$–

It is that yield of α-chloroethers (reaction between aldehides, alcohols and HCl led in dry chloroform at $-5 \div +5^oC$) decreases with increase carbon atoms in polyfluoroalcohol from 71 % to 61 %. α-Chloroethers are easy boiling (Boiling point 35-68^{o}C /12-27 mm).

Density of ethers is equal 1,22-1,59 g/cm^3 (20^{o}C) and it is increases with length of perfluorinated chain.

α-Chloropolyfluoroalkylic ethers are high reactivity in nucleophilic reaction substitution.

Fluorinated monomers (yield 65-70 %) are colorless, easily polymerizated liquids.

Polyfluoropolymers was obtained by block polymerization of fluoromonomers. Polyfluoropolymers have high hydrofobic properties.

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THE CALCULATION METHOD FOR INTERACTION ENERGY OF THE ORGANIC MOLECULE WITH NON-IONIC SOLVENT

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Estimation of the interaction energy between organic molecules and condensed phase is necessary to construct a quantitative model of solvation process. In the present paper, the solvation of neutral molecules in non-ionic solvents is examined. Thus, it is possible to take into account only nonspecific interaction, which is calculated based on the atom-atomic assumption.

Organic solute and solvent molecules are described as a space combination of atoms with Van der Waals radii. The surface of a solvating molecule is represented as a smooth layer, it envelops its atoms and bounds volume, inaccessible to other molecules.[1] The calculation of interaction energy of a solute with solvent molecule, which is regularly moved on its surface, allows to take into account their various mutual orientation, to construct the potential maps and to simulate dynamics of solvent molecules.[2] The physical meaning of the calculated values is most adequate to experimental solvation parameters.

The energy of solute-solvent molecular interaction was estimated for the series of normal and iso-alkanes, and for molecules containing various heteroatoms. The close linear correlations are established between numerical values and the enthalpy of solvation in cyclohexane and gas chromatographic retention indices on nonpolar liquid phases.[3]

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THE REACTIONS OF 1-NITRO-2-FUNCTIONALIZED ALKENES WITH SOME N,S-BINUCLEOPHILES

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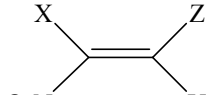
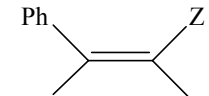
The presence of the nucleofugal substituent Z in the β-position to the conjugated nitro group of the alkenes like (**1**-**3**) make them more active substrates in the reactions with the nucleophiles and results into the formation of the new substitution products.



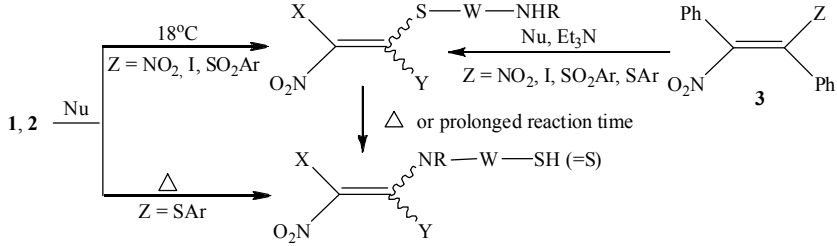
1, 2



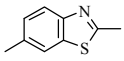
3

1: X = H, Y = Ph;
2: X = Ph, Y = H;
Z = NO_2, I, SO_2Ar, SAr;

The interaction of the nitrostyrene derivatives (**1**, **2**) with N,S-binucleophiles at room temperature leads to the formations of the substitution products through the S-reaction center. The prolonged time of the reaction or heating cause the conversion of the S-adducts into the thermodynamically more stable aminoderivatives. The less active nitrostilbene derivatives (**3**) demand more violent conditions: the prolonged reaction time or the presence of the base and form only S- adducts.



Nu = $(RNH)_2C{=}S$: R = H (a), Ph (b); NH_2WSH: W = *o*-C_6H_4 (c),



(d)

The results of the investigation according to the electrofilicity and nucleogaticity made it possible to arrange the β-substituents in the row by the influence on the reactivity of the nitroalkenes: NO_2 > I > SO_2Ar > SAr.

ANALYSIS OF AMPLITUDE-FREQUENCY CHARACTERISTICS OF SYSTEM «PERFECT-MIXING CONTINUOUS REACTOR + CONSECUTIVE REACTION $A_1 \to \alpha_2 A_2 \to \alpha_3 A_3$»

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The account of small perturbations and the calculation of local effects are one of the main problems of development of mathematical (numerical) modeling[1].

Previously, we[2] had calculated the relations $\zeta_j = E_j / E$ of the amplitudes of output signals $|\varepsilon_j| = |\Delta c_i| / c_{0i} = E_i |\sin(\bar{\omega}\bar{\tau} + \varphi_i)| << 1$ and of input signal $\varepsilon_1^{ex} = \Delta c_1^{ex} = E \sin \bar{\omega}\bar{\tau}$ of concentrations $c_i = \alpha_i \eta_i$: the conversion coefficients, the system sensitivity to changes in concentration c_1^{ex} at the entry of a reactor

$$\zeta_1 = 1/(c_0 \varpi_1),\ \zeta_2 = a_1/(\eta_{02}\varpi_1\varpi_2),\ \zeta_3 = a_1 a_2/(\eta_{03}\varpi_\circ\varpi_1\varpi_2), \qquad (1)$$

where $x_0 = 1 - c_0$ – the nominal $(E = 0)$ degree of transformation A_1; $\eta_{02} = x_0 - \eta_{03}$ – the yield A_2; $a_i = \partial \bar{w}_{0i} / \partial c_{0i} \equiv n_i \tilde{a}_i$ – the sensitivity of reaction rates $\bar{w}_{0i} = \bar{k}_{0i} c_{0i}^{n_i}$: $\tilde{a}_1 = x_0 / c_0$, $\tilde{a}_2 = \eta_{03} / \eta_{02}$; $\varpi_\circ = (1 + \bar{\omega}^2)^{1/2}$, $\varpi_i = [(1 + a_i)^2 + \bar{\omega}^2]^{1/2}$ – the modules of full sensitivity; $\bar{\omega} = \omega\tau_0$ – the complex of frequency (τ_0 – the mean time of stay of reagents in a reactor); $i = 1, 2$; $j = 1, 2, 3$.

In an implicit point $x_{0\bullet} \Leftarrow \partial\eta_{02} / \partial\tau_0 = 0$, the maximal yield of product is equal

$$\eta_{02}^{\max} = a_{1\bullet}\eta_{03\bullet} = n_1 x_{0\bullet}^2 / (n_1 x_{0\bullet} + c_{0\bullet}) = [\gamma_0 c_{0\bullet}^{n_1+1} \alpha_2^{1-n_2} / (n_1 x_{0\bullet} + c_{0\bullet})]^{1/n_2}, \quad (2)$$

where $a_{1\bullet} = n_1 x_{0\bullet} / c_{0\bullet} = n_2 / a_{2\bullet}$, $\gamma_0 = \bar{k}_{01} / \bar{k}_{02}$ – the simplex of rate constants.

Then, for the relation of the maximal absolute deviations the "universal" amplitude-frequency characteristic $\xi_2(\bar{\omega}) = \eta_{02}\zeta_2 = \Delta\eta_{2\max} / \Delta c_{1\max}^{ex}$ has the form

$$\xi_{2\bullet} = a_{1\bullet}\{[(1 + a_{1\bullet})^2 + \bar{\omega}^2][(1 + a_{2\bullet})^2 + \bar{\omega}^2]\}^{-1/2} \Rightarrow$$

$$\xi_{2\bullet}^{\max}(\bar{\omega} << 1) \approx n_2[(1 + a_{2\bullet})(n_2 + a_{2\bullet})]^{-1},\ \xi_{2\bullet}(\bar{\omega} >> 1) \approx n_1 x_{0\bullet} c_{0\bullet}^{-1} / \bar{\omega}^2 << 1.$$

It follows from (3) and is proved in[3,2], at high frequencies $\omega >> 1/\tau_0$ (rad/s) the stationarity of operating mode of system practically is not being disturbed.

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THE THERMODYNAMIC CHARACTERISTICS OF THE PROCESSES OF cd(II) COMPLEXFORMATION WITH IMINODISUCCINIC AND ETHYLENEDIAMINE-N,N-DISUCCINIC ACIDS IN AQUEOUS SOLUTION

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Such complexones as EDDSA and IDSA are of interest as ligand that form fairly strong water-soluble complexes with metal ions, possess high biological activite and cant connected of cadmium in nontoxic compaunds for people and environment.

The enthalpies of complex formation between Cd(II) and ethylenediamine-N,N-disuccinic(H_4A) and iminodisuccinic acid (H_4L) were determined calorimetrically at 298,15 K and ionic strength of 0.5, 1.0 and 1.5 (KNO_3). The heats of dilution of $Cd(NO_3)_2$ in solutions of the background electrolyte were also measured experimentally. The experimental data were treated taking into account acid-base interactions, complex formation between Cd^{2+} and acid dissociation products, and hydrolysis of Cd(II). The thermodynamic characteristics of the processes complexformations at fixed and zero values ionic strength are calculated.

A sharp decrease in the exothermic effect value in the formation of protonated complexes (and even a change of sign of the heat effect for complex formation) shows that the protonation of complexes weakens metal-nitrogen bonds. Protonation occurs at the carboxyl ligand fragment, and the addition of a proton to the complexonate molecule results in glycinate ring opening with a decrease in the number of bonds formed by the ligand. The protonated acetate group in then replaced by water molecules in the coordination sphere of the metal.

Thermodynamic characteristics of formation of metal complexonates Cd^{2+} with iminodisuccinic and ethylenediamine-N,N-disuccinic asids at 298,15 K

Reaction	ΔH^0	$-\Delta G^0$	ΔS^0, J/mol·K
	kJ/mol		
$Cd^{2+}+L^{4-}=CdL^{2-}$	-16,75±0,91	57,9±0,2	138±3
$Cd^{2+}+HL^{3-}=CdHL^{-}$	15,06±0,60	25,6±0,2	136±2
$Cd^{2+} + A^{4-} = CdA^{2-}$	-16,51±1,08	68,8±0,3	176±4
$Cd^{2+} + HA^{3-} = CdHA^{-}$	7,84±0,52	33,6±0,6	139±3

MICROWAVE IRRADIATION ASSISTED SYNTHESIS OF 1,8-DIOXOOCTAHYDROXANTHENE DERIVATIVES

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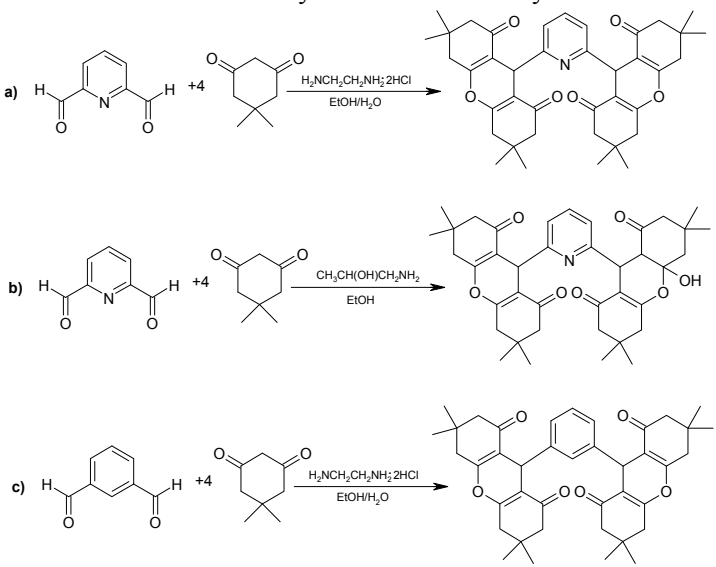
1,8-Dioxooctahydroxanthene derivatives exhibit broad spectrum of biological and pharmaceutical properties such as antibacterial, antiviral and anti-inflammatory activities as well as photo toxicity and antagonist activity[1-2].

Synthesis of a series of 1,8-dioxooctahydroxanthene derivative has been achieved under microwave irradiation. The products were obtained in excellant yields within few minutes during the reaction of aromatic aldehydes or aromatic bisaldehyde with dimedone in ethanol in presence of aminoalcohol or diaminoethan hydrochloride as catalyst.



The structure of synthesized compounds have been confirmed by IR, NMR spectroscopy and x-ray crystallography.

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NEW COMPREHENSIVE SYSTEM OF CHEMICAL ELEMENTS PERIODIZATION, OR "MAKHOV'S TREE"

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The new approach to arrangement of the Periodical system–"Symmetrical Quantum Periodic System of Neutral Atoms" [1]–is based on the most up-to-date achievements in investigation of line optical and X-ray spectra and related Pauli exclusion principle, Academician V.M.Klechkovsky's rules, D.N.Trifonov's (Doctor of Chemical Sciences) rule, and achievements in atom models [2].

The essence of the suggested system can be defined as follows: the chemical elements sequence–the Mendeleev-Moseley row–has been maintained, but new division into periods has been introduced (so that all of them are paired and form dyads) on the basis of well-defined and unambiguous parameters (quantum numbers). The System includes all of the elements up to $Z \leq 120$.

- The place of each element (its coordinates) is determined by its own unique combination of invariable by time four quantum numbers which determine the quantum equilibrium state of the atom in toto; that's why the whole system is called "Quantum System". All the previous vertical columns are maintained.

- The boundaries of horizontal rows, periods and dyads are formed by elements with ^1S_o spectral term. Each row starts with the same element which finishes the previous row. In each row the combination of quantum *n* and *l* and their sum $(n + l)$ and difference $(n - l)$ are constant [3].

- All the periods are paired, the period number is equal to the sum of quantum numbers $(n + l)$.

- All the periods comprise the progressive number of "superstructed" horizontal rows which is equal to the number of dyad M (in the first dyad – by one row –

s-elements, in the second dyad – by two– *p*-elements and *s*-elements, and so on in the order of ***f-d-p-s***). Outwardly the System looks like a tree.

The new Periodic System is quite important for further refinement of chemical bond theory, atom physics and development of nanotechnologies, in-depth understanding of the problems of the Earth and the Universe.

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NEW PHYSICAL AND CHEMICAL CONSTANT AND PROSPECTS OF ITS USE FOR OBVIOUS EXPRESSION OF THERMODYNAMIC FUNCTIONS

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Earlier authors on the basis of the analysis of Boltsman's distribution in the field infinite high temperature taking into account relativistic effects it was degeneration of thermodynamic system in purely information one with isolation of each particle at the power level is established, on it their full discernability and possibility of calculation of the maximum entropy by Boltsman's formula is provided

$$S_\infty = -kN_A \sum_{i=1}^{N_A} \frac{1}{N_A} \ln \frac{1}{N_A} = kN_A \ln N_A = R \ln N_A = 455,251 \text{ J/(mol·K)}. \quad (1)$$

This value, being expressed through fundamental constants, itself is a physical and chemical constant and for mol of one-nuclear ideal gas it appears unsurpassed in any investigated interval of temperatures. For complex substances this limit increases in direct ratio their quantaty of atoms.

Existence of two limits of change of entropy – bottom, equal to zero agrees the third low of thermodynamics, and top, equal S_∞, causes possibility of obvious expression of temperature dependence entropy in a kind exponent

$$S = S_\infty \exp\left[-\frac{5030,31}{M^{3/5}T} p^{2/5} \right]^{\frac{5}{2}R\frac{e}{S_\infty}}, \quad (2)$$

but not of in the form of logarithmic infinite dependence by the approached Sakura-Tetrode's formula with which dependence (2) practically coincides in the investigated interval of temperatures (100-10000), but without absurd negative values of entropy at extrapolation of Sakura-Tetrode's formula in area of absolute zero and the more so in area $T \to \infty$ where it turns out $S \to \infty$.

The thermal capacity with use of new dependence (2) is expressed as

$$C_p = T\frac{\partial S}{\partial T} = \frac{5e}{2} R \left(\frac{5030,31}{M^{3/5}T} \right)^{\frac{5}{2}R\frac{e}{S_\infty}} \exp\left[-\left(\frac{5030,31}{M^{3/5}T} \right)^{\frac{5}{2}R\frac{e}{S_\infty}} \right] \quad (3)$$

also it is characterized by increase from $C_p = 0$ at T = 0 K with passage through the extended smoothed maximum in a interval 100-10000 K at level

of C_p= (5/2)R and further slowed down, but steady aspiration $C_p \to 0$ at T $\to \infty$ that is a consequence of the valid existence of the top limit of entropy.

Enthalpy and Gibbs energy expressed through (3), remain in usual limits, accordingly from 0 to ∞ and from 0 to $-\infty$. Taking into account of quantaty of atoms at substance and the new form of temperature dependences the prospect of more strict expression in the obvious form of thermodynamic functions individual substances and chemical processes is opens.

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OBTAINING OF NEW FERROCENE (FERROCENE-DERIVATIVE)-POLYMER DOUBLE-PHASE COMPOSITION MATERIALS AND EFFECT OF NEGATIVE PHOTO CONDUCTIVITY

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Development of new light sensitive polymer composites and synthesis of their separate components (in particular coordinative, metal organic compounds, heteropolynuclear metal complexes of transition and rare earth elements) are the pressing problems. The mentioned above compounds together with polymers form composition materials with different optical and electric properties. The composites polymer-ferrocene (and its OH, NH_2 functional substituted derivatives), which show an effect of negative photo conductivity, are of special interest.

It turned out that dependence of an electric resistance of both polymer-ferrocene and polymer ferrocene-derivative composites on volume content (F, % vol.) of photo conductive phase of ferrocene has a great value. In the prepared samples the changes of R_+/R_0 take place depending on volume content of both ferrocene and ferrocene derivative phases at constant value of pressure (U=100 V) and with intensiveness of visible light (E=4000 W/m^2).

The results of experiments show that researched photo electric materials not depending on nature of polymer bearer show effect of negative photo conductivity-photo extinguishing of electro conductivity.

R_+/R_0 composites both in polymer-ferrocene and polymer-derivative ferrocene depending on volume of ferrocene grows faster than by linear law. Effect of photo extinguishing of electro conductivity is more clearly expressed in composite, based on non-polar polymer-polyethylene of high density-ferrocene.

THE MECHANISM OF HYDROCHEMICAL SYNTHESIS OF METAL CHALCOGENIDE FILMS

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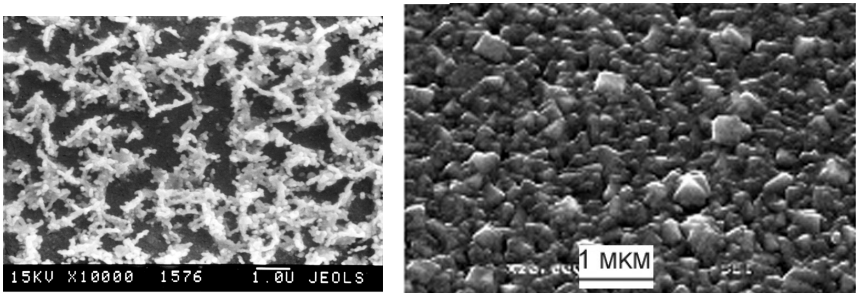
Progress in area of micro- and nanoelectronics is determined by creation of new semiconductor materials and development of methods of purposeful management by their functional properties. Process of metal sulfide films growth during hydrochemical synthesis is in most cases considered on the basis of molecular-ionic mechanisms. However, operating by consideration of crystal growth mechanism by separate atoms and molecules is justified for initial stages in low supersaturation conditions on formed phase.

In our opinion, fractal formalism is perspective in disclosing of a new phase formation mechanism in far from thermodynamic balance conditions. From positions of fractal-claster approach the processes of formation of chemically deposited metal chalcogenide film can be presented as the form of evolution of consequent structural forms, having scale-structural hierarchy: critical germs, colloidal particles in the form of fractal clusters, spheroids, grains and microcrystals.

Values of radiuses of formed PbS and CdS critical germs calculated by us on the basis of kinetic researches depending on supersaturation degrees, created in system are for PbS − 3.1-3.8 nm and for CdS − 3.4 nm.

Process of hydrochemical synthesis of films is accompanied by formation of colloidal sulfide forms and metal hydroxides, adsorbing on substrate in the form of fractal clusters (*a*) and further formation of microcrystals (*b*).



a *b*

Fig. 4.a. Electron-microscopic image of PbS film in a stage of fractal clusters growth (*a*) and microcrystals (*b*)

CIRCUMAMBULATORY REARRANGEMENTS OF CYCLOPOLYENES WITH ELEMENT-CENTERED MIGRANTS

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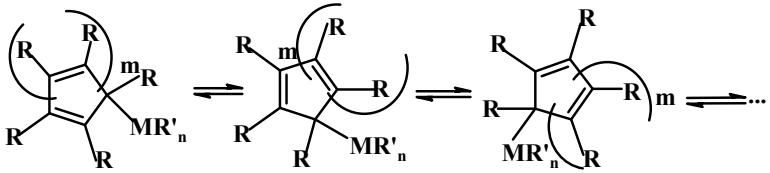
Circumambulatory rearrangements of cyclopolyenes are simple and highly versatile models for a number of important chemical processes relating to group-transfer reactions. This is why proper understanding their mechanisms, driving forces and factors controlling energy barriers to displacement of migrants over the rings helps to gain a better insight into mechanisms and stereoelectronic requirements of more complex reactions. Circumambulatory rearrangements of cyclopolyenes are not confined by migrations of mobile organometallic groups and comprise also the whole range of main-group element centred groups.



M = 0 (CYCLOPROPENE), 1 (CYCLOPENTADIENE), 2 (CYCLOHEPTATRIENE)

Rates of the circumambulatory rearrangements cover a wide range of frequencies for the intramolecular migration: from 10^6 to 10^{-8} s^{-1} at room temperature, which corresponds to energy barriers within the range 5 to 40 kcal mol^{-1}. Depending on the size of the ring, origin of the migrating group, substituents in the ring and medium, the cyclopolyenyl compounds can show very high structural flexibility or, oppositely, a high degree of rigidity, i.e. vary in their properties between fast fluxional and slow rearranged compounds. The same structural factors affect selection of an energy favourable mechanism for a circumambulatory rearrangement. There exists a multitude of reaction pathways that can govern circumambulatory rearrangements: diverse sigmatropic shifts of a migrating group, haptotropic rearrangements and ionisation pathways. In many cases rather subtle structural variations may effect switching between the possible pathways leading to topomerization or isomerization of cyclopolyenyl derivatives.

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SYNTHESIS OF ISONICOTINIC ACID BY VAPOUR-PHASE CATALYTIC OXIDATION OF 4-METHYLPYRIDINE

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Isonicotinic acid is one of the main semiproducts in the production of anti-tuberculosis medical products.

Nowadays it is not made in Kazakhstan and in CIS countries. Industrial ways of preparation of isonicotinic acids by liquid-phase oxidation of 4-methylpyridine and its methylol derivatives of nitric acid have several disadvantages: insufficiently high coming out of target product, expensive corrosion-resistant equipment is required, the process of preparation is accompanied by the formation of significant amounts of nitrocompounds and polluted sewage.

In connection with this, creation of one-stage catalytic process of preparation of isonicotinic acid is an actual problem.

Vapour-phase catalytice oxidation of 4-methylpyridine by atmospheric oxygen is one of the most perspective ways of preparation of isonicotinic acid. During the last years extensive researches directed on the creation of the effective catalyst of oxidation of 4-methylpyridine are carried out in the JSC «A.B.Bekturov ICS». The significant importance has the activity of the used catalyst which determines the temperature of the process, and the contact, which directs oxidation aside of the primary formation of isonicotinic acid, is necessary for a selective realization of the process.

It is shown, that among tested modified vanadium-oxide catalysts, the high selectivity was showed by V-Ti-Sn-O-catalyst. This catalyst passed tests on the laboratory pilot facility. Optimum conditions of the reaction are determined. It is shown, that it is necessary to carry out it at the temperature of 320 ^{o}C, submission of 14 moles of atmospheric oxygen and 200 moles of water in relation to 1 mole of raw materials. Technical characteristics of the reactor which allow to carry out the process of synthesis with the parameters representing commercial interest: conversion of 4-methylpyridine 97%, coming out of isonicotinic acid of 75% are found.

The way and catalyst of synthesis of isonicotinic acid developed in the JSC «A.B. Bekturov Institute of Chemical Science» are perspective in the sphere of oxidizing catalysis by scientific and technical development which represents the interest for practical use.

The Work is carried out with the financial support of the JSC «Science Foundation».

THE RESEARCH OF FLOW PROCESSES AT MIXING AND FORMING STAGES FOR CHARGES OF HIGHLY VISCOUS ENERGETIC COMPOSITE CONDENSED SYSTEMS BY MEANS OF PHYSICAL AND MATHEMATICAL MODELLING

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This paper presents the results of physical and mathematical modelling of flows in the production of charges made of highly viscous composite energetic condensed systems (ECS). Mixing and molding stages were explored.

Features of modern ECS were briefly discussed. The main issues of technology development for ECS charges manufacturing were stated.

A mixing process of ECS components in barrel mixers without mixing devices with horizontal and inclined rotor was examined. When adhesion is high the flow in the rotor space is divided into two zones: a circulating zone (mixing zone) and a wall boundary layer. The power versus rotational velocity is presented by a curve with a peak. The position and value of the peak depend on rheological nonlinearity of the composition and mixer load. Rotational velocity corresponding to power maximum is optimal from the point of view of intensity and quality of mixing.

We carried out an experimental investigation of ECS batch interface shape for multibatch forming by free casting technology. The height of batch interface deflection (on which item band of performance depends) at non-axis-symmetrical filling is higher than at axis-symmetrical filling. The height also depends upon correlation of viscoplastic resistance of mixture batch. The results of this research show the methods of characteristic adjustment of ECS charges forming procedure.

MOLECULAR DESIGN OF THE PHOSPHOROUS-CONTAINING PODANDS ORIENTATED TO COMPLEXATION WITH EUROPIUM

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Metal-containing complexes with podands are a special type of coordination compounds possessing a number of unique properties and imitating the properties of natural substances[1]. Podands containing phosphorilic[2] and amino[3] donor groups reveal the best complexating abilities toward Eu^{3+} ion.

The molecular design of the complexing agents makes possible to carry out a purposeful research of ligands optimized to binding the specific metal ions. The works in which the software product (SP) HostDesigner[4] was used showed successful results.

The selection of bridges between pointed functional groups in order to construct the ligand oriented to complexation with Eu^{3+} ion was the main object of this study. The facilities of the SP HostDesigner and HyperChem were applied for achieving this goal.

The bridges having an optimum geometry for each couple of the functional groups were determined with the use of SP HostDesigner. The bridge selection was accompanied by calculating through the instrumentality of molecular mechanics method and semiempirical method PM3 to adjust their conformation. The pre-organization energy selection of structures was also carried out.

After calculating six structures optimized to complexation Eu^{3+} ion were obtained, their pre-organization energies and complexation energies were calculated.

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SYNTHESIS, CHEMICAL PROPERTIES AND BIOLOGICAL ACTIVITY OF SCHIFF'S BASES OF THE ADAMANTANE SERIES

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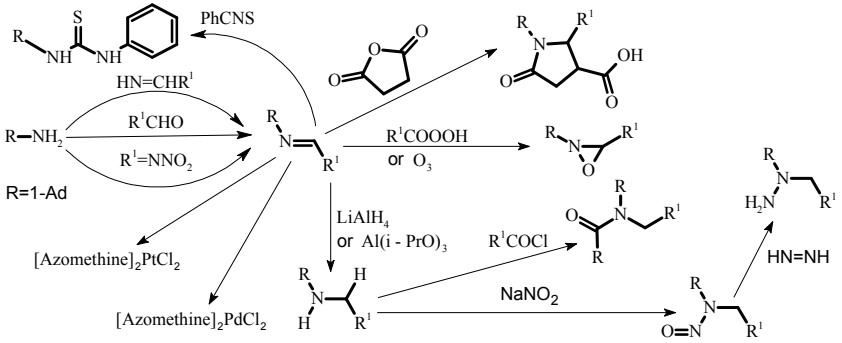
It is known many of amines with freme fragments are highly effective drugs.[1]As known azomethines of adamantine series including both substituted benzylidenadamantylamine show high antiviral potency.[2-3] As they can be widely used as starting materials in the synthesis of new biologically active substances. We have developed a new method of preparing of Schiff's bases of substituted aminoadamantanes and aldehydes under the influence of adsorbent. In this same conversion according to GC was 95-99%, which was not possible to reach by classical methods. Synthesized from imines obtained a wide range of new compounds, such as secondary amines, oxaziridines, oxopyrrolidine acid and complexes with c Pt^{2+} и Pd^{2+}.



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POSSIBILITY OF USING PARAMETERS OF THE METHOD OF SOLUTIONS STRUCTURE-GROUP CONTRIBUTION FOR EVALUATION OF CHROMATOGRAPHIC SEPARATION PROCESSES

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Role of the chromatography as a method of separation and analysis of the mixtures of different nature and composition in the determination of physical-chemical parameters of sorption processes increases from year to year. Fully automated chromatographic processes have led to the creation of various systems for effective control of production processes. The major achievements in this area are based on experimental data. In this connection, development of the methods to estimate the impact of various parameters on chromatographic separation and optimization of the separation process, taking into account the structure-group contribution of solutions is actual.

Purpose of the investigation is to study the possibility of using the energy parameters and parameters of the size of structure-group contribution of the solutions in the evaluation of chromatographic retention values and separation processes.

Subjects and methods of the investigation. Different classes of organic compounds, stationary phases, ion exchangers, various synthetic, natural and medical facilities. All of the studies on gas-liquid chromatography were carried out on chromatograph "Tsvet-100, model 165" with flame ionization detector, and on ion chromatography by liquid chromatograph Tsvet 3000" with conductometric detector.

Obtained results and their discussion. To estimate activity coefficients the UNIFV model was used, which is described as follows:

$$\ln \gamma_i = \ln \gamma_i^G + \ln \gamma_i^R + \ln \gamma_i^{FV},$$

where, γ_i^{FV} - activity coefficient due to the interaction energy; γ_i^{FV} - activity coefficient due to the size of the molecule; γ_i^{FV} - activity coefficient due to free volume of the molecule.

Calculation error is up to 9 units of index.

In ion chromatography evaluation of ions retention and optimization of their separation have been carried out on the basis of UNIFAC parameters. The thermodynamic parameters and sizes of the group contributors of the system "ionyte-ionate-eluent" were used in it.

On the basis of findings proved the possibility of using the solutions structure-group contribution method to describe the parameters of retention in thermodynamic terms and separation processes in the systems "sorbent-sorbate" and "ionyte-ionate". It was found that the difference in calculated and experimental data does not exceed 6 -8%.

Thus, evaluation and optimization of the separation of complex composition mixtures by gas and ion chromatography using semi-empirical approach, based on the use of size and thermodynamic parameters of the group-contribution of the system "sorbent-sorbate" and "ionyte-ionate-eluent" is perspective and has several advantages over empirical methods.

INFLUENCE OF FUNCTIONAL GROUP ON KINETICS, THE MECHANISM AND REACTIVE OF CH-BONDS AT OXIDATION OF METHYLHEXANOAT

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Oxidizing transformations of esters occur at liquid-phase oxidation of organic compounds by molecular oxygen, at thermooxidizing destruction lubricant oils, softeners and solvents on the basis of esters, at burning biodiesel fuel from vegetable oils.

The recombination peroxyl radicals at initiated by a cumene peroxide oxidation methylhexanoat at 373 K occurs both with chain termination and without chain termination. The relation of constants of speed of these two reactions is 3.31[1](at 373 K). It is connected with feature of oxidation carbonyl-containing compounds on β-CH-bonds, proceeding under the scheme:

$$C_3H_7CH_2CH_2COOCH_3 \xrightarrow{+RO_2^{\bullet},O_2} C_3H_7CH(OO^{\bullet})CH_2COOCH_3\ (\mathbf{I});$$

$$\mathbf{I} \longrightarrow C_3H_7CH(OOH)\dot{C}HCOOCH_3\ (\mathbf{II});$$

$$\mathbf{II} \longrightarrow C_3H_7CH{=}CHCOOCH_3 + HO_2^{\bullet};$$

$$\mathbf{II} \longrightarrow C_3H_7CH\text{-}CHCOOCH_3 + HO^{\bullet};$$

$$\mathbf{II} \xrightarrow{+O_2,RH} C_3H_7CH(OOH)CH(OOH)COOCH_3.$$

By Howard-Ingold method was defines total rate constant of reactions of interaction *tret*-butylperoxyl radikals with CH-bonds of methylhexanoat at 373 K (1.18 l/mol·s). From it and kinetics formation of products of reaction partial constants (position, l/mol·s): 2, 0.083; 3, 0.114; 4, 0.138; 5, 0.140; 6, 0.012; alkoxyl, 0.066.

Decrease in reactive methylen CH-bonds in positions 2 and 3 in comparison with position 5 is explained from positions of deactivating influence electron-acceptor groups on reactive of CH-bonds to attack electrophil peroxyl radicals and its stabilizing influence on stability intermediate carbon-centered radical.

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CHIRAL DITHIOPHOSPHORIC ACIDS AND THEIR DERIVATIVES

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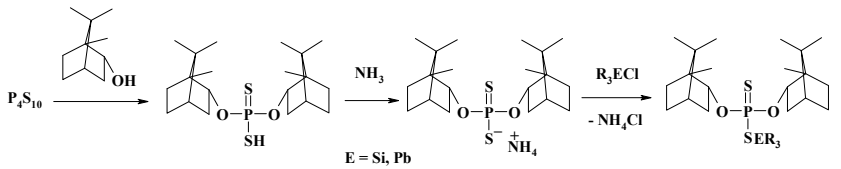
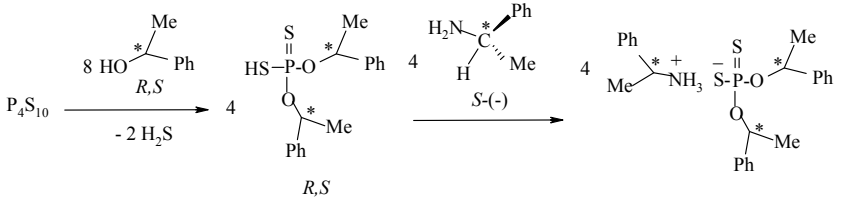
The interest in dithiophosphoric acids and their derivatives is due to their potential biological activity. We deemed it to be necessary to prepare novel dithiophosphoric acids containing asymmetric centers in organic substituents. For this purpose, we have synthesized dithiophosphoric acids by the reactions of tetraphosphorus decasulfide with chiral terpen alcohols and *R,S*-α-phenylethanol. We have used chiral terpenols such as (1*S*)-*endo*-(-)-borneol, (1*R*)-*endo*-(+)-fenchyl alcohol, (1*R*,2*S*,3*S*,5*R*)-(+)-isopinocampheol and (1*R*)-(-)-nopol. Optically active O,O-diterpenyl dithiophosphoric acids were prepared when these chiral terpenols were involved in reactions with tetraphosphorus decasulfide. These acids were transformed into the corresponding ammonium salts, silyl and plumbyl derivatives.



The tetraphosphorus decasulfide has brought about to react with *R,S*-α-phenylethanol with the formation of the racemic O,O-di(α-phenylethyl) dithiophosphoric acid transformed into the corresponding ammonium salt in the reaction with (*S*)-(-)-(α-phenylethyl) amine.



The reaction of O,O-diethyl dithiophosphoric acid with *R,S*-α-phenylethylamine yields to ammonium salt those structure was established by single crystal X-ray analysis.

STUDY OF INTERACTION OF ALIPHATIC NITRO COMPOUNDS WITH ADAMANTANONOM AND ITS DERIVATIVES

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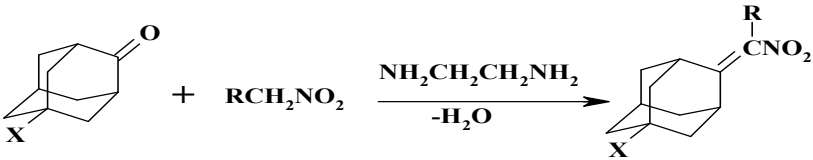
Nitroolefiny are valuable intermediates in organic synthesis. They are the starting compound for many classes of organic compounds. We studied the interaction of 2-adamantanon and 1-hydroxide-2-adamantanon (kemantan) with nitromethane, nitroethane and nitropropane in the presence of ethylene diamine as a catalyst. Synthesis was carried out by the scheme below:



1: X= H; R= -CH_3. 2: X= H; R= -C_2H_5. 3: X= OH; R=-H.

4: X= OH; R= -CH_3. 5: X= OH; R= -C_2H_5.

Investigation of the influence of synthesis conditions on the yield of 2-nitrometilenadamantan compounds showed that the molar ratio adamantanon: catalyst should not exceed 1: 0,05 0,1. In the case of increasing this ratio we observed decreasing of the yield of the desired product as a result of side-reactions. The synthesis was conducted in an appropriate aliphatic nitro compounds under boiling. The time of the synthesis, depending on the structure of the adamantyl derivative and aliphatic nitro compounds varies from 24 to 48 hours. The yield of 2-nitrometilenadamantan compounds - from 43 to 76%. The structure of the compounds was confirmed by IR and NMR^1H spectroscopy and mass spectroscopy.

OXIDATION MEDIATORS IN SULFURORGANIC COMPOUNDS SYNTHESES

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Nitrogen-containing electromediators series of hydrogen sulfide and polysulfanes was studied in the thiols reactions with aromatic substrates. The research was studied purposely to study the one-step thio- and alkyl-thio-substituents introduction into aromatic ring.

The following mediators were studied: triphenylamine, tri-*p*-bromphenylamine, tri-*p*-toluenelamine, N,N,N`N`-tetramethyl-1,4-phenylenediamine, phenoxazine. All of the referred mediators are oxidized up to stable radical cation forms at low electrochemical potentials in anhydrous conditions that allow to decrease the electrolysis potential in 0.4-1.25V range in the mediator's nature dependence.

Electromediator system works by the following mechanism: mediator – sulfur regent – aromatic substrate. Only neutral molecules of mediators oxidizes on the platinum anode up to radical cations respectively. Electron transfer occurs in the solution from thermodynamically stable hydrogen sulfide, thiols and polysulfanes to the generated radical ion mediator's form. After that mediator recovers and reacts in the oxidation of sulfur reagents providing the catalytic process cyclicity.

It is shown that *p*-iminobenzoquinone form of 2,2`,4,4`– tetramethoxyphenylamine as secondary oxidizing product is active to sulfur reagents.

Thus thio-group direct insertion into aromatic ring was occurred yielding thiophenol, thiosalicylic acid, thiocresols, thionitrobenzene. Introduced approach allows to change the sequential process aromatic thio- derivatives reception by the green one-pot syntheses processing without intermediate extraction.

This study was financially supported by the Russian Foundation for Basic Research (Project №09-03-00677a).

ALLOCATION OF ALIFATIC AMINO ACIDS ON SUBACID IONEXCHANGERS

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Now the great value has manufacture of medical products and the foodstuff containing in the structure of amino acid. Sewage treatment of such manufactures means removal from their structure of biologically active substances. It is interfaced with difficulties, the caused difficult processes accompanying sorption of amino acids.

In work processes of sorption of glycine and methionine by carboxyl cationexchangers in copper, protonic and deprotonic forms are studied. As acidity of industrial sewage can have various values, researches spent in an interval pH from 2 to 12. To definition of characteristics of sorption and the structure of sorption centers in researches applied IR-spectroscopic, spectrofotometric and titrimetric methods.

It is established that on sorption of amino acids from water solutions various factors influence: the ionic form and sorbent mark, acidity of a solution. The most significant influence is rendered, in our opinion, by the ionic form, and the most thin effects are created by mark carboxyl cationexchanger, influence of acidity of environment is intermediate. For allocation of a glycine from water solutions it is expedient to use copper form КБ-4. It is established that high enough of sorption capacity on a glycine carboxyl cationexchangers have in protonic form at sorption from alkaline solutions. КБ-4 can be used for selective extraction of amino acid from a solution, methionine in a greater degree is sorbin on КБ-2. At joint presence of amino acids methionine optimum to take from alkaline solutions on copper form КБ-2 and КБ-4.

The thermodynamic characteristics of sorption processes received in work, occurring at interaction carboxyl cationexchangers with solutions of amino acids, can be used for working out of technological processes of allocation and division of amino acids. Acidity influence can be used for effective realization laboratory and productions ionexchanger allocation that will allow to lower economic and power costs.

Work is executed with financial support FCP «Scientific and scientific and pedagogical shots of innovative Russia» on 2009 – 2013, the state contract № P1041.

FEATURES OF FRAME STRUCTURES WITH M-RELATIONS WITH THE UNITED METALS (+ I) WITH CYCLIC β,β'-TRICARBONYL LIGANDS

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We have studied the structure of a number of complex metal compounds (M = Li^I, Na^I, K^I, Rb^I, Cs^I, Ag^I) with 2-(diphenylacetyl)indandione-1,3 (HL), they are cyclic *β,β'*-tricarbonyl derivatives. It was discovered that the formation of channel structures occurs simultaneously with alternating layers of carbon-hydrogen atoms (sub L) and metal-oxygen fragments.

The study of crystal structures of substances shows delicate layers of complex architecture. They consist of di-, tri-and tetrameric complex of subunits, which are connected to each other. This is done by the donor oxygen atoms of L. The implementation of different sets of directed C–H…π и π–π– stacking interactions between conjugated and aromatic systems, as well as the IHB between the layers leads to the formation of skeletal structures.

The emergence of channels for RbL and AgL, partly due to the presence of additional links M - C between the aromatic fragments of L, their education is established for the derivatives of Rb (η^6-coordination), Ag (η^2-) and Cs (η^3-, η^6-). Shortest distances are: 3.45, 2.50 and 3.47Å, respectively. The formation of sandwich complexes and strong IHB (for Cs-substances), apparently prevented the formation of channels in karkase.[1]

Channels have an oblong cross section. Channels for RbL and AgL differ markedly. This is the result of a significant difference in the size of the covalent radii of Rb^I and Ag^I (2.48 and 1.44Å, respectively), and large differences in the nature of the clearing house. Greater dimers Rb_2O_6 fits neatly along the seam than across. Therefore, layers of RbL smoother than AgL (zigzag). This leads to a strong increase in channel diameter.

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SPECTROSCOPIC METHODS IN CHEMISTRY OF LANTHANIDE COMPLEXES

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The combination spectroscopic methods (UV, IR, NMR, EPR, fluorescence spectroscopy, etc.), as well as quantum chemical calculations to study the structure and properties of lanthanide complexes.

Since the description of the line NMR and ESR is performed using the formalism of spin density matrix, which was first proposed by us in 1980.

For the reaction complexation

$$M + L \rightleftharpoons ML,$$

we can write:

$$\rho \rightleftharpoons \rho_m,$$

where ρ and ρ_m - spin density matrix of states of M and ML, respectively.

Then the line shape of the EPR spectrum is described as

$$Y(H) = pI_m[Sp(\rho S^*) + p_L I_m(Sp\ \rho_L)],$$

where p and pL - the populations of M and ML.

For more multiple reactions complexation:

$$M + nL \rightleftharpoons ML + (n-1)L \rightleftharpoons ML_2 + (n-2)L \rightleftharpoons \ldots \rightleftharpoons ML_n,$$

line shape of the EPR spectrum is defined as:

$$Y(H) = \sum_{k=0}^{n} P_k I_m(S_p(P_k S^*))$$

where P - the mole fraction of *k*-component in the system.

When studying the dynamic processes of complexation by NMR calculation of the line was carried out as

$$S(\nu) = I_m \sum_i P_i n_i S_p(P_i \hat{I}^-)$$

where n_i - amount of molecules, which give a signal in the NMR spectrum, belonging to the *i*-component, P_i - the occupation of the states in proportion to their average lifetimes.

Use by formalism of spin density matrix in the analysis of line shapes of NMR and EPR, as well as data from other methods that allow you to define the structural and other parameters of complexation reactions.

SELF-ASSOCIATION OF SULFONATOMETHYLATED CALIX[4]RESORCINARENE

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It is known that depending on the type of functionalization and the concentration calix[4]resorcinarenes are capable of forming nanostructures of various types in solution (micelles, vesicles, bilayers), which are used in practice as systems for drug delivery, sensor devices, catalysts and membranes.

In this work, we study the aggregation behaviors of water-soluble sulfonatomethylated calix[4]resorcinarene (CR) with hydrophobic moieties containing the double bonds at the lower rim.

The tensiometry method shows that the CR, similar to classical surfactants, reduces the surface tension at the air-water interface. Critical association concentration (CAC) for the CR is 6.2 mm (method tensiometry). We have observed the two CAC values for the CR (CAC_1 of 1 mM and CAC_2 of 6.1 mM) obtained by conductometry. The analysis by dynamic light scattering revealed that a bimodal distribution of particles takes place for the CR aqueous solution regardless of its concentration. Particle sizes are in the range from 7 to 10 nm and from 50 to 100 nm depending on the CR concentration. The particle size distribution in terms of number of particles indicates that particles with the size 7÷10 nm (Figure) predominate in the solution.

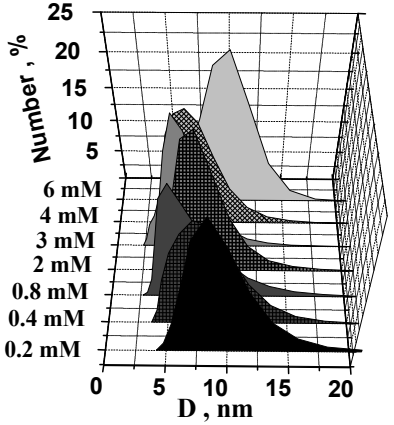

Figure. The particle size distribution (in terms of number of particles) for the CR at its various concentrations in water of 25 °C.

This work was supported by RFFI grant no10-03-90-Ukr_a, 09-03-00581-a.

PHYSIOLOGICAL ACTIVITY OF NEW DIPICOLYLAMINE COMPLEXES OF METALS

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It is important to obtain polyfunctional physiologically active substances including heterometallic complexes. Ferrocenylmethilbis(2-piridylmethyl)amine[1] $FcCH_2N(CH_2Py)_2$ (**1**) and a number of its metal complexes (Mn (**2**), Fe (**3**), Co (**4**), Ni (**5**), Cu (**6**), Zn (**7**)) have been synthesized and characterized by NMR and IR spectroscopy, mass-spectrometry MALDI-TOF, monocrystal X-Ray diffraction and elemental analysis.

Inhibition of Cyt P450 enzymes (CYP 1A2, CYP 2C19, CYP 2C9, CYP 2D6, CYP 3A4) by **1-7** have been investigated. Ligand **1** substantially inhibites all the analyzed enzymes, except CYP 1A2, while activity of complexes differs for various enzymes.

The distribution coefficient between *n*-octanol and PBS (pH 7.4) - log D - have been determined for **1-7**. All of them especially **1** and **2** appear to be lipophilic.

Compounds **1-7** have been tested by PAMPA and PAMPA-BBB assays which allow to predict blood-brain barrier penetration. According to PAMPA **1** and **2** can penetrate into the brain more efficiently, while according to PAMPA-BBB **2**, **4** and **7** are the most active.

The survivability of cortical neurons of Wistar line rats after incubation with substances obtained have been determined. Compounds **1, 2, 4-7** have shown low toxicity, while **3** is nontoxic at all.

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Acknowledgements: This work was supported by Russian Foundation for Basic research (11-03-01134, 11-03-01137, 11-03-01165) and Program №9 “Medicinal chemistry” of RAS.

THE EFFECT OF THE NATURE OF OXYHYDROXIDE SORBENT PRECURSOR ON OXALATE-ION SORPTION

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Systematical investigation (2007-2011) of oxalate-ion sorption regularities from aqueous NaCl and Na_2SO_4 solutions on freshly precipitated gelatinous oxyhydroxides (OH) of Fe, Zr and Al, has allowed to generalize about the effect of the sorbent and ionic background nature on these ions' sorption. The sorbent performance is affected by the nature of initial salt – an OH-precursor, and the pH precipitation value (pH_{prec}), because OH were obtained by the alkali hydrolysis method. As OH-precursors, the iron(III) chloride and perchlorate, two different samples of zirconium nitrate and aluminium nitrate were used. The range of pH_{prec} values was 4-11 for Fe(III) and Zr(IV) and 6-9 for Al. The ionic strength of sorbate solutions was 0.5 for NaCl and Na_2SO_4; the amount of sorbents was 0.01 mole per 0.25 liter.

The sorption isotherms of $C_2O_4^{2-}$ in all cases are described by the Langmuir equation. The values of equation constants A_∞ and K decrease consistently with pH_{prec} increase, but the $C_2O_4^{2-}$ sorption occurs not only at $pH<pH_{PZC}$, but also at $pH >> pH_{PZC}$, which suggests the formation of inner-sphere sorption complexes. Comparative data about the sorption of $C_2O_4^{2-}$ on different OH at $pH_{prec} = 8$ in the NaCl medium are presented in the Table.

Precursor	$FeCl_3$	$Fe(ClO_4)_3$	$Zr(OH)_2(NO_3)_2$ x1.7H_2O	$Zr(OH)_2(NO_3)_2$ x1.5H_2OxHNO_3	$Al(NO_3)_3$
A_∞, mole/g, $x10^3$	0.55	0.40	1.24	0.50	1.20
K, l/mole, $x10^{-3}$	0.51	0.65	0.99	0.61	0.27

All the data available confirm that: 1) the Al-gel has a maximal sorption capacity to oxalate ions; 2) the sorption characteristics of Zr-gels are very unstable, diverging even for the same precursors from different commercial lots; 3) the anion nature of salt precursor influences the ferrogel sorption characteristics but slightly. It has been found that the chloride background promotes the oxalate sorption, while the sulphate background does not suppress it. Since the interest in oxalate ion sorption by mineral sorbents is due to the possibility of treating nuclear fuel waste water from chromate ions[1], present in these solutions together with oxalate ions, the results of this work are of practical importance.

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REACTIONS OF HYDROGEN SULFIDE WITH UNSATURATED HYDROCARBONS IN THE PRESENCE OF *O*-BENZOQUINONES

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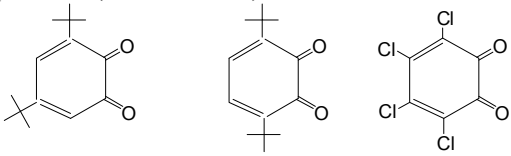
The reactions of hydrogen sulfide oxidized form with alkynes and alkadienes in the presence of 3,5-di-*tert*-butyl-*o*-benzoquinone (Q_1), 3,6-di-*tert*-butyl-*o*-benzoquinone (Q_2), *o*-chloranil (Q_3) (1 M) were researched at the different temperature (23, 50, 72 °C).



Q_1 Q_2 Q_3

The thyil radical ($HS^{\bullet}$) is generated in the oxidation process of hydrogen sulfide with quinone. The addition sour radicals with unsaturated hydrocarbons leads to vinylthiols which oxidize to radicals which participated in dimerization.

Mainly $(C_6H_{13}S)_2$ accumulates in the reactions of hexyne-1 and H_2S with Q_1 (E_{pa}=1,6 V) because the alkyl radicals dimerization rate is higher than the rate of addition to the multiple bonds. The presence of $(C_6H_{13})_2S$ in product mixture is explained by interaction of the RS- radicals and substratum. Q_2 is activated only with temperature increase to 71-72°C. With the participations of Q_3 $C_6H_{13}SH$ is the main product (E_{pa}=1,8 V) as result of interaction H_2S and RS^+ и $RS^{\bullet}$ which were obtained in the unsaturated disulphide oxidation.

The kinetic researching of hydrogen sulfide and alkynes reactions with quinone showed that rate constants had the same order for Q_1 и Q_2 in MeCN (k=0,06÷0,07 sec^{-1}) and substratum (k=0,02÷0,03 c^{-1}).

o- и *m*-Xylenes are obtained in the end of butadiene-1,3 and H_2S reaction with Q_1 (0,1 M, CH_2Cl_2). It can be explained by 1,2-, 1,4- addition of butadiene and subsequent isomerization.

Isoprene interaction with H_2S in the presence of Q_3 leads to sour 1,2-, 1,4-polymers.

This work was supported by the FCP (GK № 16.740.11.0441) and the RFBR (Grant № 06-03-00677).

CATIONIC ALKYL-ACYL GLYCEROLIPIDS WITH POTENTIAL ANTITUMOR PROPERTIES

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Alkyl glycerolipids are promising compounds for cancer therapy, but their use is limited by high hemolytic activity. This limitation can be circumvented by incorporating antitumor lipid into liposomes. In recent years, increasing attention is paid to enzymatically activated liposomes. These liposomal structures contain nontoxic alkyl-acyl glycerolipid ('prolipid'), evolving under the action of enzymes of neoplastic cells in active lysoglycerolipid - analogue of the well-known anticancer lipid edelfosine (ET-18-OCH_3, 1-O-octadecyl-2-O-methyl-*rac*-glycero-3-phosphocholine). We obtained new cationic glycerolipids containing polyunsaturated fatty acids (PUFA) in the hydrophobic domain. Because enzymatically hydrolysis of the ester bond two active agents appear into the cancer cell. These agents are cationic lysoglycerolipid and free PUFA, which also have antitumor properties.

One step was the acylation of the initial *rac*-1-O-octadecyl-3-O-(*tret*-butyldiphenilsilyl)glycerol whith 9Z,12Z-octadecadienoic (linoleic) and 11Z,14Z-heptadecadienoic acids in the presence of *N,N'*-dicyclohexylcarbodiimide and a catalytic amount of *N,N*-dimethylaminopyridine. The subsequent removal of the protective group by 0.2 M solution of *tetra*-butylammonium fluoride resulted in diglycerides containing polyunsaturated fatty acids at the position C(2) of glycerol. The introduction of spacer group in the lipid molecule was carried out by the acylation of synthesized diglycerides whith 5-bromovaleryl chloride in the presence of pyridine. The cationic 'head' was introduced by quaternization of *N,N*-dimethylethanolamine with bromides in the presence of NaI. Thus, we obtained new cationic glycerolipids containing linoleic and 11Z,14Z-heptadecadienoic acids in the hydrophobic domain.

^{1}H NMR spectroscopic and mass spectroscopic data agree with the structures of the compounds obtained.

Work is supported by Federal Program «Scientific and pedagogical human resources for innovative Russia 2009-2013» (the state contract № P1340) and the Russian Foundation for Basic Research (№ 10-03-00995-a).

ELEMENTARY PHOTOCHEMICAL PROCESSES BENZOQUINONES WITH CYCLIC ETHERS

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Spectra NMR 2,6-diphenyl-1,4-benzoquinones (I) with tetrahydrofuran in solutions C_6F_6, CCl_4 have not shown presence of complex. In case of 1,4-dioxan and 12-K-4 correlation of chemical shift of quinine meta-protons from donor concentration and temperature is observed. At pulse photolysis quinone in not polar solvent through time 10^{-5} s, it was registered semi-quinone radical $QH^{\cdot}$ [1].

Pulse photolysis (I) in 1,4-dioxan and a crown-ether 12-K-4 finds out shortly and the long-living products having absorption in the field of 620 nanometers - radical $QH^{\cdot}$, and in the field of 480 nanometers a radical - Q^{-}. Triplet- eximer (exiplex) are predecessors of radical intermediate products Q^{-} and QH^{+} which are in balance with each other. Constants of speed and energy of activation of complexes (I) with 1,4-dioxan - $k=1.1\cdot10^5$ cm c^{-1}, E=6.2 Kcal/ M; at reaction with a crown-ether - $k=3.2\cdot10^5$ cm c^{-1}, E=8.48 Kcal/M. Energy of activation of complex increases in line 1,4-dioxan <12-K-4 <15-K-5 <18-K-6, and speed reaction constants of complexes accordingly decrease.

The mechanism photolysis quinone (I) in ethers includes following elementary acts for two reactions proceeding simultaneously, but with different efficiency.

$$QQ \longrightarrow \text{eximer} \longrightarrow Q^{-} \ldots Q^{+} \underset{H^{+}}{\rightleftharpoons} QH^{\cdot} \ldots Q \longrightarrow \text{product}$$

$$QD \longrightarrow \text{exiplex} \longrightarrow Q^{-} \ldots D^{+} \underset{}{\rightleftharpoons} QH^{\cdot} \ldots D^{\cdot} \longrightarrow \text{product}$$

D - donor $\quad \lambda = 630$ nm $\quad \lambda = 480$ nm

The end-product is formed as result of H- atom tear away from carbon atom in crown-ether cation-radical with recombination radicals in radical pair.

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A NEW METHOD OF GRAPHIC REPRESENTATION OF CHEMICAL EQUILIBRIA IN HETEROGENEOUS SYSTEMS "SATURATED AQUEOUS SOLUTION – COMPLEXING AGENT - SOLID PHASE"

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A new type of diagram for graphic representation of complex chemical equilibria in the heterogeneous two-phase system "sparingly soluble compound $M_mA_{n(S)}$ (where M^{n+} is the metal ion and A^{m-} is the anion) – complexing agent L – saturated aqueous solution" has been developed. These diagrams are based on the thermodynamic determination of the solid phase stability area and original mass balance (MB) equations, which expose evidently the contribution of solid and dissolved species in heterogeneous systems. In their appearance, such diagrams resemble the distribution diagrams for homogeneous (single-phase) system; however, their construction principles fundamentally differ from that of homogeneous systems. The latter are usually constructed in the pH (or pL=-log[L]) – molar fractions α_i coordinates, since, in the absence of polymeric complexes M_iL_j, the molar fractions of species α_i in aqueous solution, are function of only pH or pL and do not depend on the initial concentrations of the components. In heterogeneous equilibria, the molar fractions α_i depend also on the initial composition of the mixture and, hence, are function of four variables: $\alpha_i = f(C_M^0, C_A^0, C_L, \text{pH})$. Therefore, it is expedient to construct the diagrams in the coordinates pH - α_i, C_M^0 - α_i, or C_A^0 - α_i at fixed values of all the other variables. The procedure for constructing the heterogeneous chemical equilibrium diagrams includes the following steps: (a) thermodynamic calculation of the stability area of the solid phase (sparingly soluble salt); (b) computing the molar fractions α_i of all the chemical species containing the given component of the solid phase; (c) for a complete description of the pattern outside this area, i.e., for a homogeneous aqueous solution, the molar fractions are calculated by the usual equations for constructing the distribution diagrams.

The Gibbs energy changes of a number of the studied systems under various conditions have been analyzed. The developed diagrams can be used for quantitative estimations in the synthesis and analysis of sparingly soluble compounds. Example diagrams are given for a series of real systems in the coordinates "partial molar fraction of the solid (or soluble complex species) – the initial concentration of the components (or the pH value of saturated solution).

DESIGN OF NEW PHARMOCOGICALLY ACTIVE AMINOPROPARGYLES

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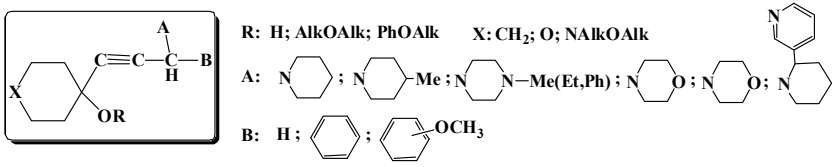
Mannich reaction provides a convenient way to construct complex molecules with potential biological activity – starting from psychotropic to cancer. Traditional carbo- and heterocyclohexane containing acetylenes on which series of active and low-toxic biologically active substances were synthesized, have become object of aminomethylation with paraform, benzaldehyde and its various metoxy- derivatives; as amine fragment there were used cyclic amines (piperidine, morpholine, thiomorpholine, substituted piperazines, anabazine) [1,2]



Aminomethylation with paraform and cyclic substances in dioxane in the presence of Cu_2Cl_2 at 100-110^oC for 10-15 min led to the target products with satisfactory yield. However, aromatic aldehydes are not active enough under the above conditions, to activate the process microwave radiation was applied. In addition to improved yield of aminomethylation reaction reducing of reaction time was achieved.

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NONRADIATIVE RESONANCE ENERGY TRANSFER BETWEEN CYANINE DYE MOLECULES NONCOVALENTLY BOUND TO DNA

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Forster resonance energy transfer (FRET) between molecules of polymethine (carbocyanine) dyes noncovalently bound to ds-DNA was studied. Carbocyanine dyes are capable of forming noncovalent complexes with DNA; the dye ligands in such a system are located close to one another; and the complexation of cyanine dyes is accompanied by a steep (tenfold) rise in the fluorescence quantum yield (Φ_f). All these features are favorable for detection of FRET. In the present work, two cyanine dyes, 3,3',9-triethyl-5,5'-dimethyloxacarbocyanine iodide and 3,3'-dimethyl-9-ethyloxacarbocyanine iodide, were used as excitation energy donors, and 3,3'-diethylthiacarbocyanine iodide served as an acceptor dye.

The fluorescence decay kinetics of the donors and its quenching by the acceptor in the presence of DNA were measured. The microphase model [1, 2] was used for interpretation of the experimental data, with allowance for concentrating dye molecules in the vicinity of DNA molecules [3]. As a result of the interaction of the dyes with DNA, the actual concentration of quencher A in the vicinity of molecules of donor fluorophores turns out to be higher than that averaged over the whole solution. It was shown that upon quenching of fluorescence of the donor dyes by the acceptor dye, the dynamic (diffusion) quenching does not play a significant role, and the quenching occurs mainly by the static mechanism, which causes an upward deviation and concavity of the experimental Stern–Volmer plots.

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STATE DIAGRAM OF SYSTEM SMTE-PBTE AND PROPERTY OF PHASES $(PbTe)_{1-X}(SmTe)_X$

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State diagram of system SmTe-PbTe was studied and plotted by methods of physical-chemical analysis. It was established that the system is characterized by formation of wide homogeneity region based on lead telluride and ternary phase of $SmPbTe_2$. Compound $SmPbTe_2$ melts with decomposition at 1030 K and forms eutectics with lead telluride. Coordinates of eutectic point: 30 mol % SmTe and 1000 K.

Solubility of SmTe to PbTe at eutectic temperature (1000K) makes 20 mol %, but at 300K it is 15 mol % SmTe. In homogeneity region parameter of cubic lattice firstly decreases till a=6.42Å (in alloy containing 5 mol % SmTe), but then increases, that is doesn't obey to Vegard's law.

Technological regime (T_1=920, T_2=850K, C_{J2}=4mg/sm^3) was developed and by chemical transportation reaction the monocrystals of ternary telluride $SmPbTe_2$ were grown with sizes $2\times0.5\times1nm^3$ useful for X-ray structural analysis. Bigger monocrystals $SmPbTe_2$ were grown by methods of oriented crystallization (by Bridgman-Stockbarger method) and regional treatment. X-ray structural research of monocrystals showed that compound $SmPbTe_2$ crystallize in rhombic syngony with periods of elementary cell: a=5.06, b=9.94, c=11,62 Å. Density equals to 7.01 g/sm^3, but micro hardness 150 kg/mm^2.

In wide temperature interval (300-850K) we studied electrophysical properties of solid solutions $(PbTe)_{1-x}(SmTe)_x$ and ternary compound $SmPbTe_2$. The research showed that they are semiconductors with p-type conductivity. Width of forbidden band ΔE for $SmPbTe_2$ calculated from region of its conductivity makes 0.45 ev. Temperature dependency of mobility of indications of charge $SmPbTe_2$ was studied and it was established that till 400K mobility of bearers increases and settled by law $T^{2.5-3.0}$. This shows that up to 400K scattering by ionized impurity centers plays great role, but higher than 400K heat hesitations of crystalline lattice have number of advantages in scattering.

THE INFLUENCE OF QUATERNARY AMMONIUM SALT CATION STRUCTURE ON THE EXCHANGE OF SINGLE-CHARGED ANIONS TO CHLORIDE

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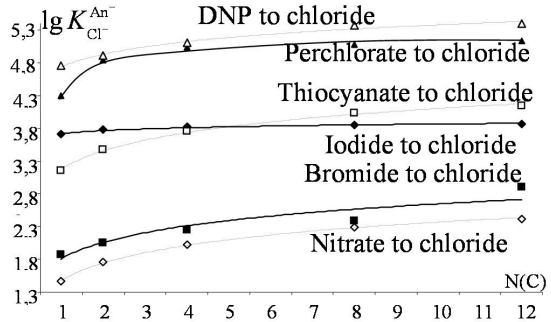
The introduction of methyl substituents to the nitrogen atom of the quaternary ammonium salt cation increases affinity of the double-charged to small single-charged anions in the presence of larger single-charged ones [1-3].

The research of the quaternary ammonium salt cation structure effect on the single-charged anions to chloride exchange was carried out.



The highest values of $K_{Cl^-}^{An^-}$ at $An^- - Cl^-$ exchanges are observed for the longest alkyl substituents.

The dependence of $\lg K_{An^-}^{Cl^-}$ from the number of carbon atoms in QAS cation substituents is nonlinear and it is the most effectively described by a logarithmic function[4].

The approximation of $K_{Cl^-}^{An^-}$ values to the asymptote was established. Further increase of $\lg K_{An^-}^{Cl^-}$ is expected while carbon atoms number in substituents increase up to 16 - 20 or more.

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HYDROXY- AND AMINOSUBSTITUTED DERIVATIVES OF CLUSTER BORON ANIONS – STARTING COMPOUNDS FOR CREATING NEW ORGANOSILICON POLYMERS

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High-molecular compounds based on cluster boron anions have good opportunities in solving ^{10}B-NCT tasks and in creating thermostable polymeric materials [1].

Hydroxy- and aminosubstituted derivatives of closo-borate anions can be used as a convenient molecular platfrom for creating elementorganic polymers and oligomers due to their ability to undergo condensation reactions with different linking agents.

To investigate processes of condensation of hydroxy- and aminosubstituted derivatives of closo-borate anions, reaction with trimethylchlorosilane was chosen as a model reaction. The reaction progress can be easily tracked via the changes in ^{11}B-NMR spectra. In the ^{1}H-NMR spectra of the products, new signals appear near 0 ppm from the protons of the methyl groups in trimethylsilyl fragment of the substitute. The compounds were also analyzed via ESI mass spectrometry and elemental analysis.

Thus, a method was developed that allows modification of hydroxy- and aminosubstituted closo-borates resulting in formation of exopolyhedric functional groups containing B-NH_2-Si$(CH_3)_3$ and B-O-Si$(CH_3)_3$ bonds.

The method can be extended to disubstituted closo-borates; this would allow to obtain compounds with cluster boron anions in the main polymer chain.

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ANTIPYRINE COMPLEXES OF RARE EARTH IODIDES: STRUCTURE AND PROPERTIES

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The present work is devoted to elucidation of the structure- and properties regularities for antipyrine complexes of rare earth iodides $[Ln(AP)_6]I_3$ (AP– antipyrine, $C_{11}H_{12}N_2O$, Ln = Sc, Y, La–Lu). It was demonstrated that the complexes prepared are the isostructural ones (sp.gr. *R*–3) except $[Sc(AP)_6]I_3$ (sp.gr. *P*–3)[1,2] having two types of different symmetry (–3 и 3) but of the same configuration complex cations in the unit cell. The distinction of the scandium complex structure from that of the lanthanide ones is connected with the changes of the ligand position due to intracomplex π–π stacking interactions. On the basis of the single crystal XRD and IR spectra studies it was found that the central atom coordinates antipyrine molecules via the carbonyl group oxygen atom, the iodide-ions being in the outer sphere.

Cytotoxic activity was studied with respect to cells of 60 different human tumors for both complexes and pure ligand (NCI, USA). It was demonstrated that $[Ln(AP)_6]I_3$ complexes reveal boundary cytotoxic activity with respect to CNS Cancer (SNB-75 cell line), the surviving percent being as follows: 69.12% for Ln = La, 64.94% for Ln = Gd, and 77.84 % for Ln = Lu in the presence of 10^{-5} M of these substances. At the same time antipyrine was ineffective and demonstrated practically uninhibiting effect (surviving percent: 95.3%) thus confirming the conclusion[3] about interrelation of bioactivity for ligands and complexes.

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TARGET SEARCH OF POTENTIAL ANTI-INFECTIOUS PREPARATIONS

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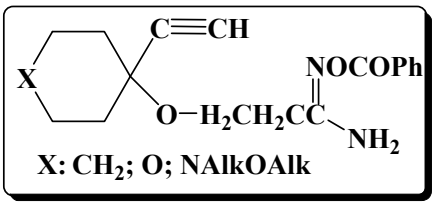
O-Aroylpropioamidoximes are well-known class of chemicals possess anti-TB activity.[1,2] Synthetic obtaining of new anti-infectious preparations bases on the design of molecules that contain O-benzoylpropioamidoxime fragment combination of saturated carbo-, aza- or oxa- cycle carrying its own potential biological activity and ethynyl group, often reduces the toxicity of the substance.



Cyanoethylation in Michael reaction conditions of acetylenic alcohols proceeds with a quantitative yield in presence of catalytic amounts of KOH without solvent.

The preparing cyanoethyl ether is easily converted into the corresponding amidoxime by interaction of ether with hydroxylamine hydrochloride in presence of freshly prepared sodium methoxide in methanol.

By interaction of benzoyl chloride with amidoxime the target benzoyl derivative with potential anti-infectious activity is prepared.

REACTIVITY OF β-ACRYLOYLOXYPROPIONIC ACID WITH AMINES

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The lacks of ethers and nitrile of acrylic acid as more reactive compounds in Michael's reaction are low solubility in water and high fugacity. It does not allow carrying out this reaction at the increased temperature. Necessity of a combination of high reactivity, hydrophility and low fugacity requires use of a new reagent, for example, β-acryloyloxypropionic acid. The reactivity of β-acryloyloxypropionic acid is not investigated nearly.

The nonylamine, aniline and 2-aminoethanol were used as nucleophylic reagents. The analytical studies carried out on a gas chromatograph/mass-spectrometer Agilent GC 7890A MS 5975C Inert XL and column HP-5MS. Mass-spectra were registered in electron ionization mode. The analysis of the reaction mixture has shown, that conversion of nonylamine was 27%; the main product was N-nonyl-3-aminopropionic acid (89%). In case of aniline conversion has made 97 %, the sole product of the reaction was adduct of aniline to β-acryloyloxypropionic acid. Formation of one product was additionally proved based on the ^{1}H NMR spectrum of crude reaction mixture.

The analysis of reaction of β-acryloyloxypropionic acid with 2-aminoethanol has shown absence of products of Michael's reaction, that, probably, is caused by heterogeneous character of the reaction mixture.

Thus, it has shown that β-acryloyloxypropionic acid is reactive reagent in Michael's reaction with amines. The course of the reaction depends considerably on amines nature.

The work was financially supported by Ural Branches of the Russian Academy of Sciences (project 10-3-NP-285).

THE VAPOUR PHASE COMPOSITION AND THERMODYNAMIC MIXING FUNCTIONS FOR MELTS OF GALLIUM – LEAD SYSTEM

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The analysis of the nature of phase equilibriums in the metallic gallium – lead system, the initial components of which are so essentially differentiated among themselves on many physicochemical properties, introduces the special concern from the point of view of the fundamentals of general chemistry. It is possible to explain the absence of the interest to the investigation of the vaporization processes in Ga – Pb system only the fact that these metals rather essentially differ on values of a saturated vapour pressure at fixed temperature. For example, at T = 1000 K the relation of the equilibrium values of vapour phase pressure above melts of pure individual Pb and Ga amounts to 4700.

The main purpose of this work is to evaluate of the quantitative composition of vapour phase above $Ga_{1-x}Pb_x$ melts (x = 0.05 – 0.95) by high-temperature mass-spectroscopy in an interval T = 800 – 1150 K with the subsequent calculation of thermodynamic mixing functions in gallium - lead system on the basis of the obtained experimental data.

It has been established that the presence of Ga atoms in a vapour phase over $Ga_{1-x}Pb_x$ melts can not be neglected[1]. Depending upon the temperature and the composition of $Ga_{1-x}Pb_x$ melts the concentration of Ga atoms in saturated vapour phase can change in enough broad limits and to run up to the value ~ 0.021 mole fraction for the $Ga_{0.95}Pb_{0.05}$ alloys at T = 1203 ± 3 K. Despite of some quantitative disagreements, the calculations of thermodynamic mixing functions performed with usage of the standard condition, the graphic integrations on the Gibbs – Duhem equation, and also Margules polynomials, testify that the process of $Ga_{1-x}Pb_x$ melts formation is endothermic ($\Delta H^M > 0$), and their thermodynamic stability is provided extremely by the entropic factor ($T\Delta S > 0$).

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ABOUT POSSIBILITY OF APPLICATION CARBONATE OF BREEDS AS SORBENTS OF WASTE WATERS

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Prevention of a problem of environmental contamination depends on the successful decision of a problem of clearing waste waters from ions of heavy metals. The way sorption impurity carbonate breeds is applied and is perspective.

Efficiency of clearing of waste waters depends on conditions of preliminary processing of a sorbent. Updating carbonate breeds was spent by chemical way (processing of 20 % by a solution of sulfuric acid) and thermal (calcinating at 800ºC to constant weight within 2 hours).

At studying of clearing of modeling solutions from iron ions (II, III) the method one-stage static sorption was used. The maintenance of ions of iron (II, III) defined photometric a method at length of a wave λ =420 nanometers (the dark blue filter).

Kinetic process of clearing of iron ions (II, III) by the raw, calcinated and chemically modified sorbent it was studied at a parity of phases: m=0,1 g, C=450,2 mg/l, V=20 ml. A raw sorbent in the given conditions for 30 minutes sorption 90,23 %. Full clearing by a raw sorbent is reached at increase in weight of a hinge plate to m=0,5 g . The modified sorbents allow to carry out for too time 100 % clearing of modeling solutions. In process sorption raw carbonate breed increases value pH environments with 2,03 to 7,02; chemically modified - to 6,79; thermally processed - to 10,78. It is connected with maintenance increase oxide calcium in a sorbent.

Thermally modified sorbent is most effective for sorption ions that it is possible to explain occurrence mesa porous structure and formation free oxides calcium and magnesium which in water solutions form oxygen containing the active centers. The obtained data is necessary for using at the further researches of process of sewage treatment from ions of heavy metals.

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COMPETITIVE SORPTION OF CHROMATE-, OXALATE- AND CARBONATE-ION ON OXYHYDROXIDE SORBENTS

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The current interest in CrO_4^{2-}-ion sorption by mineral sorbents is due to the possibility of treating nuclear fuel waste (NFW) water[1] and electrochemical enterprises. There are few works published on competitive sorption, although the sorption processes, both in nature and technology, are competitive because the CO_3^{2-} -ions are always present. $C_2O_4^{2-}$-ions are present in NFW water as well. We have studied the competitive sorption of CrO_4^{2-}, $C_2O_4^{2-}$ and CO_3^{2-}-ions from NaCl and Na_2SO_4 and without background solutions, in air by freshly precipitated oxyhydroxide (OH-hydrogels) of Zr(IV) and Fe(III) in pH precipi-tation (pH_{pres}) range 4-11 and CrO_4^{2-} initial concentration (C_{init}) 1-20 mmole/l.

Separately, CrO_4^{2-}, $C_2O_4^{2-}$ and CO_3^{2-} are readily sorbed by OH of Fe(III) and Zr(IV). Cl^- promotes their sorption, while SO_4^{2-} suppresses the sorption but slightly. The A∞ values decrease with pH_{pres} increase. The sorption isotherms are described by Langmuir equation. Some examples are given below.

Sorbent precursor	pH_{pres}	Sorbate	A∞, mole per g	K, liter per mole x g
$Zr(OH)_2(NO_3)_2x2.7H_2O$	5.5	CrO_4^{2-}	0.00069	8700
		$C_2O_4^{2-}$	0.00208	1690
		CO_3^{2-}	0.00264	404
$FeCl_3$	5.0	$C_2O_4^{2-}$	0.00155	750
		CrO_4^{2-}	0.00153	1800

$C_2O_4^{2-}$ and CO_3^{2-} greatly suppress the CrO_4^{2-} sorption, and CO_3^{2-} suppresses the $C_2O_4^{2-}$sorption. If C_{init} of $C_2O_4^{2-}$ and $CO_3^{2-}$is constant and that of the CrO_4^{2-} varies, the CrO_4^{2-}sorption isotherm, as well as the summary isotherm (Σ), are both described by Langmuir equation. Probably that both kinds of anions form sorption complexes of the same type. The examples are presented below.

System	sorbent	A∞, mole/g	K, l/mole·g	A∞,mole/g(Σ)	K, l/mole·g (Σ)
$C_2O_4^{2-}$+CrO_4^{2-}	Zr-gel	0.00059(CrO_4^{2-})	1823	0.00076	1260
CO_3^{2-} + CrO_4^{2-}		0.00060(CrO_4^{2-})	1102	0.00096	802
CO_3^{2-} + $C_2O_4^{2-}$		0.00114($C_2O_4^{2-}$)	2917	0.00178	363
$C_2O_4^{2-}$+CrO_4^{2-}	Fe-gel	0.00068(CrO_4^{2-})	1000	0.00122	400
CO_3^{2-} + CrO_4^{2-}		0.00031(CrO_4^{2-})	-	0.00050	-

The competition of $C_2O_4^{2-}$ and CO_3^{2-} relatively CrO_4^{2-} is more pronounced for ferrogels than for zirconogels.

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ACYIVATION OF MELTS IN THE SYSTEM $MgCl_2$-KCl AND THEIR RELAXATION IT NONQUILIBRIUM STATE

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The melts in MgCl2-KCl system are strongly associated. The ionic association in the molten electrolytes significantly alters their behavior, cause the mechanisms and kinetic pathways that may decrease current and voltage efficiency in magnesium production cells [1].The investigation of the Raman spectra indicates that these melts involve equilibrium between variety structural units-complex ions, epystructure factor shows the signs of the intermediate-range order presence in ionic structure [2].

Here we report the results of studying high-voltage behavior of these melts containing 0,0; 0,2; 0,4; 0,6; 0,8 and 1,0 mole factions of the components. First, we investigated the dependence of the conductivity of the melts on the electric field strength (EFS) in the regime of microsecond pulses by analyzing the features of the high-voltage discharge oscillographs. The conductivities of the melts increase with the EFS and, in the fields of about 1 MV/m reach the limiting values which surpass the usual low- voltage conductivities, $\chi(0)$, by up to 440% (Wien effect). The conductivities of the crystals increase with the EFS and, in the fields of about 1 MV/m reach the limiting values. After pulses exposure having been completed, the conductivity of the melts became increased by up to 40%. Fig. 1 presents, as a samples, some curves of quotient $\Delta\chi/\chi(0)$ as function of time after the pulses action.

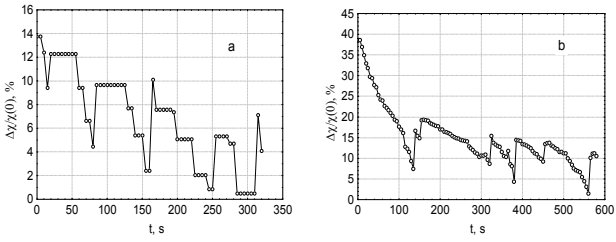

Fig.1. Change of relative values $\Delta\chi/\chi(0)$ in the time of mixture $MgCl_2$(0,2)-KCl activated by single pulse of voltage amplitude 2,2kV(a) and activated by 3 pulses of amplitude 10kV(b)

The curves show that the relaxation time has the order of 103 s and manifest the stepwise-oscillatory pattern indicating the variety of equilibrium structural species.

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ACTIVATION OF SUPERIONICS KAg_4I_5, $RbAg_4I_5$ AND THEIR PROLONGED RELAXATION IN NONEQUILIBRIUM STATE

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The ternary derivatives of the silver iodides $RbAg_4I_5$, KAg_4I_5 are the very promising representatives of the family rubidium silver iodide called "advanced superionic conductors (ASICs)" The ASICs are of greatest interest because of their exceptionally high ionic conductivities and the lower values of superionic transition temperatures ($RbAg_4I_5$: χ ~0.3/Ω cm, T~300 K). The possibility for creation of the efficient energy and power devices of nanosystems on the base of ASICs (sensors and supercapacitors) has been recognized [1]. Here we report the results of studying high-voltage behavior of α-$RbAg_4I_5$, and α-KAg_4I_5.

First, we investigated the dependence of the conductivity of the superioncs on the electric field strength (EFS) in the regime of microsecond pulses. The conductivities of the crystals increase with the EFS and, in the fields of about 1 MV/m, reach the limiting values. The limiting high-voltage conductivities, χ^0, of α-KAg_4I_5 surpass the usual conductivities, $\chi(0)$, by up to 53 % at 165^0C, and conductivity of α-$RbAg_4I_5$- by 35% at 165^0C. After pulses exposure having been completed, the conductivity became even more increased by up to 20-30%. Fig. 1 presents, as a samples, some curves of quotient $\Delta\chi/\chi(0)$ as function of time after the pulses action.

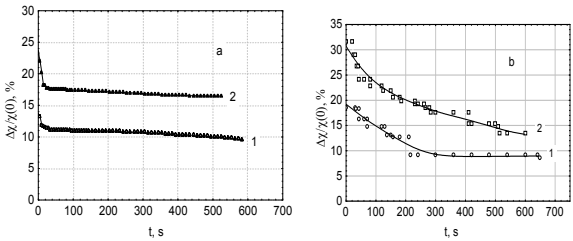

Fig.1. Change of relative rise in conductivity in the time for the superconductors activated by single pulse: a) α-$RbAg_4I_5$, voltage: 5.6 (curve 1) and 4.9 kV (curve 2); $T=105^0$C; b) α-KAg_4I_5 voltage: 5.1 (curve 1) and 6 kV (curve 2); $T=100^0$C.

As it shown from fig.1, the conductivities of the superioncs were even more heightened and increased by 20 and 30% indicating the rise in the fast ions density and conduction channels. The activated state and relaxation process were prolonged for more than ten minutes.

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EPOXY ETHERS OF AROMATIC ACIDS

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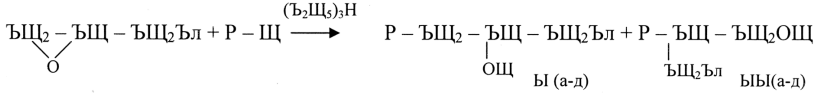
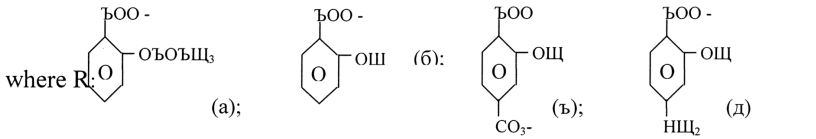
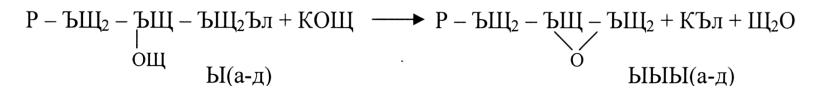
We have researched the reaction of epychlorohydrine with acetosalicylic, salicylic, para-sulfosalicylic and para-aminosalicylic acids in toluene solution at 100-110^{0}C with the presence of basic catalyst triethylamine and molar ratio of components 1:1, which proceeds with the formation of monochlorohydrine ethers of acids[1] according to the following scheme:





Dichlorohydrine ethers of salicylic, para-sulfosalicylic and para-aminosalicylic acids are formed correspondingly at molar ratio of components 2:1, but at 3:1 ratio trichlorohydrine ethers of para-sulfosalicylic and para-aminosalicylic acids are formed.

Monoepoxy thers of acids III (a-d) were obtained by dehydrochlorination of chlorohydrine ethers of equimolar quantity of KOH within 4 hrs. at media of sulphuric ether at 30-32^{0}C by the scheme:



Di- and triepoxy ethers of acids were synthesized similarly by interaction of di- and trichlorohydrine ethers with KOH at molar ratio of components 1:2 and 1:3 correspondingly.

Physical-chemical constants of synthesized compounds were determined.

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NOVEL PYRIDINE COMPLEXES WITH PHENOL GROUPS AS POTENT NEUPROTECTORS

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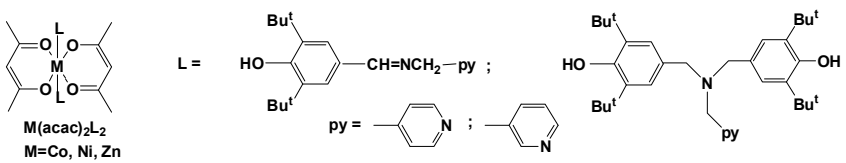
Oxidative stress plays an important role in neurodegeneration pathogenesis, therefore the use of antioxidants and chelators for d-elements is quite actual for treatment these deseases. 2,6-Di-alkylphenol derivatives are wide used as antioxidants.

The goal of this work was the synthesis of compounds which poses both phenol and N-donor ligand functional groups and the study of the complex formation with a series of biometals. Novel pyridines with 2,6-di-*tert*-butyl pendants and Co, Ni and Zn acetylacetonates were synthesized and characterized by IR, NMR, MALDI-TOF mass-spectrometry and elemental analysis.



The antioxidative activity of compounds as radical scavengers was evaluated in DPPH-test. The influence of test compounds in peroxidation of lipid of Wistar rat brain homogenates was studied. The number of phenol groups and the nature of metal in complex were found to be the main factors that influence the antioxidative properties. The data of Cyt P450 enzymes inxibition, LogD, n-octanol/PBS and high blood-brain barrier transport ability were obtained. The low toxicity of a series of compounds for rat brain neurons was emphasized. The results of this work let us to suggest that such derivatives might be used as potent neuroprotectors.

Acknowledgement: The financial support of RFBR (11-03-01165, 11-03-01134, 10-03-01137) is gratefully acknowledged.

MICROPHASE LIQUID—CRYSTAL SEPARATION IN THE POLYACRYLAMIDE—WATER SYSTEM

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By the literature data, there is hitherto no unambiguous opinion on the nature of phase separation in the PAA–water system. Judging on the nature of the temperature dependence of the second virial coefficient A_2 and the viscosity number η_{sp}/c [1], this system has an UCST. The positive sign of the temperature coefficient of $[\eta]$ [2] confirms this conclusion.

A different result [3] was obtained with the usage of classical light scattering. The obtained dependence $A_2=A_2(T)$ speaks for a high value of A_2, and its temperature coefficient is negative and has a minimum. Such a character of $A_2=A_2(T)$ correlates well with the literature data[4] on amorphous phase separation in the PVA-water system, which classifies among systems with a degenerated closed range of amorphous separation

Therefore, at to liquid–liquid phase separation, the PAA–water system is one with a degenerated closed separation range, i.e. it possesses no amorphous separation range. The temperature dependence of the thermodynamic quality of water is of extremal character with a minimum around 80^0C. The degree of degeneration is rather high, so water serves a good solvent for PAA in usual conditions ($T \approx 20^0$C). The data of X-ray and calorimetric analyses give evidence of PAA being an amorphous non-crystallizable polymer.

By exploring PAA solutions[5], we have found that supramolecular nanoparticles are formed in them.

We propose the term “microphase (nanophase) liquid–crystal separation” for the PAA–water system.

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THE REASONS OF MODIFYING EFFECT OF PHOSPHORUS-CONTAINING COMPOUNDS ON PROPERTIES OF PALLADIUM HYDROGENATION CATALYSTS

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The most important fundamental problem of catalytic chemistry is to establish the nature and regularities of formation, operation and deactivation of the catalytically active species. The report presents the results of research on the nature of the modifying action of different phosphorus-containing compounds (PR_3, PHR_2, PH_2R, PH_3, including white phosphorus) on the properties of nanosized palladium catalysts for hydrogenation.

The basic stages determining the composition, structure and catalytic properties of formed nanoparticles are experimentally proved. The key reactions are the reduction of the compounds Pd (II) to Pd(0), the oxidation of Pd(0) as a result of phosphines destruction in the coordination sphere of Pd(0) or the interaction of Pd (0) with white phosphorus yielding palladium phosphides of different composition, as well as clustering Pd(0)[1]. Depending on the rates ratio of elementary stages, and the molar ratio P/Pd can be formed palladium nanoclusters and nanophosphides, nanoparticles of the core-shell structure (core - phosphides or associates of palladium polynuclear complexes with μ-PR_2, μ-PR-ligands, the shell - Pd(0)), trinuclear palladium clusters with μ-PR_2-ligands.

On an example of interaction of complex $Pd(dba)_2$ with elemental phosphorus the formation mechanism of palladium phosphides in soft conditions, which represents a number of consecutive stages: $Pd(0) \rightarrow PdP_2 \rightarrow Pd_5P_2 \rightarrow Pd_3P$ is established. Opposite action of white phosphorus on the properties of palladium catalysts depending on the nature acido ligands in a precursor and a reducing agent is proved. The concept of modifying action of phosphines and element phosphorus on the properties of palladium hydrogenation catalysts is offered. Significant promoting effect of white phosphorus at low ratios P/Pd is due to the increased dispersion of the catalyst, the inhibitory effect at $P/Pd > 0.7$ is associated with an almost complete transfer Pd(0) to inactive in the hydrogenation palladium phosphides.

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This work was supported in part by the Federal Target Program "Research and Training Specialists in Innovative Russia, 2009-2013", Contract No P1344.

SYNTHESIS OF PHOSPHORCONTAINING SULPHONILAMIDOAZOBENZOLIUM

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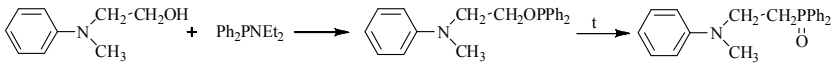
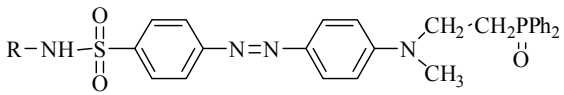
Generally known biological activity and antipiren properties of phosphororganic compounds, what explain interest to obtaining phosphorcontaining intermediate products stains and new drugs. In continue works [1] we realized synthesis of new azokomponent 2-(N-methyl-N-phenylamino)-ethylphenylphosphinoxyde **1** in scheme:

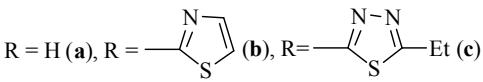


1

In purpose to modificate sulphanilamid preparations we studied diazotizated forms of sulphonilamid preparation combinations with azocomponent **1,** leaded to formation of azostains similar red streptocide:



2 (a-c)



The structure of the synthesized azocompounds is confirmed by a complex of spectral researches. Presence sulphonilamidazostains **2 (a-c)** diphenylphosphinyl groups allows to suppose implication sinergistic effect of the biological activity by them, similar phosphobenzid.

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REDOX PROPERTIES AND ANTIOXIDANT ACTIVITY OF ANTIMONY(V) COMPLEXES, CONTAINING O,N,O-DONOR LIGAND

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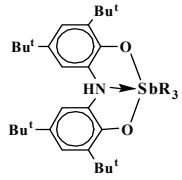
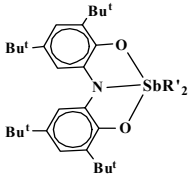
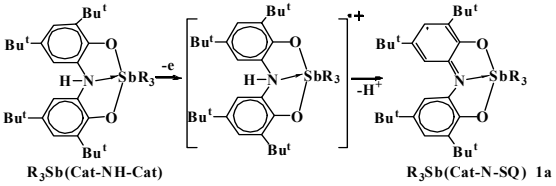
The electrochemical transformations of five-, sixcoordinated antimony(V) complexes containing tridentate O,N,O-donor ligand (**1-6**) were investigated.





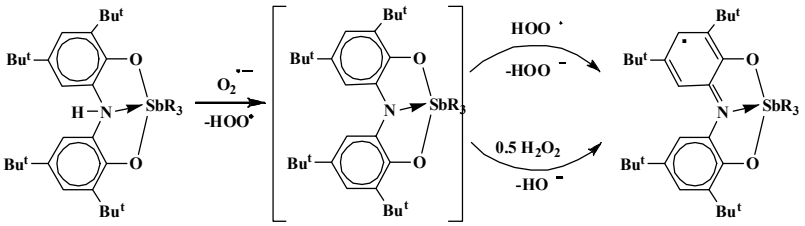
1) R = Ph; **2)** R = p-Tol; **5)** R' = Et; **6)** R' = C_6H_{11}
3) R = p-F-Ph; **4)** R = Et



$R_3Sb(Cat\text{-}NH\text{-}Cat)$ $R_3Sb(Cat\text{-}N\text{-}SQ)$ **1a**

It was shown, that the sequence stages EC during the electrochemical oxidation of complexes of **1-3** leads to the formation of neutral paramagnetic derivatives (**1a-3a**). The electrochemical oxidation of complexes **5** and **6** occurs as two successive reversible one-electron processes with the formation of mono- and dication complexes.

The set of electrochemical and spectral data indicates the formation of complexes **1a-3a** in the reaction of compounds **1-3** with the superoxide radical anion



The initial stage of reaction is the deprotonation, leading to a monoanion complex which is oxidized directly HOO-radical or a product of its disproportionation – H_2O_2 to form in both cases, **1a-3a**.

The work was financially supported by FCP (GK № 16.740.11.0441), RFBR (№ 11-03-00389-a, 10-03-00921-a), grants of the President of the Russian Federation (MK-1156.2011.3, MK-614.2011.3).

THEORETICAL STUDY OF THE MIXED LIGAND COMPLEXES OF COBALT DIKETONATES WITH O-BENZOQUINONE AND ITS DERIVATIVES

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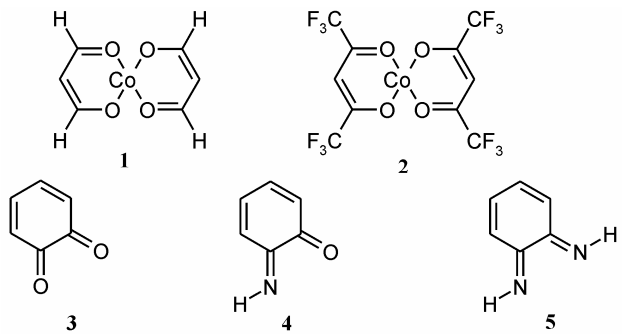
An actual problem of modern coordination chemistry is the search for bistable structures, the magnetic characteristics of which can be controlled by external stimuli and can be switched by variation of temperature, pressure or by irradiation. One of the mechanisms, which can lead to such molecule properties, is valence tautomerism.



For the purpose of search for the complexes, which are able to intramolecular electron transfer, the structure of diketonates Co(II) **1** and **2** with *o*-benzoquinone **3**, *o*-iminobenzoquinone **4** and *o*-diiminobenzoquinone **5** was studied by the method of density functional theory [B3LYP/6-311++G(d,p)]. According to results of the calculations all examined associates are more stable than isolated molecules of bis-chelate and corresponding redox-active ligand, which point to the possibility of their synthesis. The comparison of relative energies of high- and low-spin forms of complexes and the study of their intramolecular spin-forbidden rearrangements showed that the interaction of trifluoroacetylacetonate Co(II) with ligands of types **3** and **4** and also bis-chelate Co(II) **1** with diimine **5** leads to the formatoion of valence tautomeric systems.

This work has been supported by Russian Foundation for Basic Research (projects 09-03-00684a), and by the federal target program "Scientific and scientific-pedagogical personnel of innovative Russia in 2009-2013" (Contract 02.740.11.0456).

SYNTHESIS OF AMPHIPHILIC COPOLYMERS: COMPUTER SIMULATION

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A new approach to synthesis of copolymers with long-range correlations is proposed. Using Monte Carlo simulations and the lattice bond-fluctuation model, we perform the computer-aided sequence design of a two-letter (AB) copolymer with quenched primary structure near a chemically homogeneous impenetrable surface. We simulate an irreversible radical copolymerization of selectively adsorbed A and B monomers with different affinity to the surface, allowing for a strong short-range monomer(A)-surface attraction. To describe the chain growth analytically, we introduce and investigate a simple theoretical model based on stochastic processes and probabilistic statistics. We find that this model provides a close approximation to the simulation data and explains a number of statistical properties of copolymer sequences. It is shown that under certain conditions, the chain propagation near the adsorbing surface proceeds as a randomly alternating growth, leading to a copolymer with a specific quasi-gradient primary structure and power-law long-range correlations in distribution of different monomer units along the chain. The gradient extends along the entire chain for any chain length. We find that the statistical properties of the copolymer sequences correspond to those of a one-dimensional fractal object with scale-invariant correlations. Thus, just by radical copolymerization of two monomers with different affinity to a certain plane surface it is possible to obtain copolymers with a gradient primary structure.

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THE OXIDATION OF THIOLATE GROUPS OF GLUTATHIONE AND ACETYLCYSTEINE, CATALYZED BY PALLADIUM AND COPPER COMPLEXES: RELATIVE CATALYTIC EFFICIENCY AND PRESUMED REACTION MECHANISMS

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One of the most important properties of the thiol groups of sulfur-containing proteins and peptides is their oxidation to form disulfide crosslinks. In this case, the imbalance between the reduced (-SH) and oxidized (-SS-) forms in the cysteines of evolutionarily conserved domains of proteins in biological fluids in mammals (so-called "thiol-disulfide status") is associated with various severe and chronic diseases. One of the regulators of this process is: γ-GluCysGly - glutathione (GSH), contained in a cell at a concentration of about 5 mM. However, reactions with its participation is relatively slow and are catalyzed by enzymes, including metal, models which can serve as coordination compounds.

In this research is reported about the catalytic effect of bi- and polynuclear tiolatebridged complexes of palladium(II)[1] and copper(I)[2], formed in solutions of GSH and N-acetyl-L-cysteine, and their combined effect on the reaction of selective homogenous oxidation thiolate groups. Evaluate the effectiveness of the catalytic action of palladium and copper in the oxidation process established by the rate of accumulation of disulfide forms, when compared with cis-$[Pt(NH_3)_2Cl_2]$, whose activity was taken as a relative zero. The relative catalytic efficiency of complexes increases in the order: Pd ≤ (Pd-Cu) << Cu.

The possible reaction mechanisms for complexes of copper and palladium, and for the mixed Cu-Pd catalyst, on the basis of quantum chemical calculations performed by the DFT method at B3LYP 6-31G ** - basis.

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STRUCTURE AND ELECTRICAL CONDUCTIVITY OF MOLTEN $MgCl_2$ IN EQUILIBRIUM AND NONEQUILIBRIUM STATES

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The structure and electrical conductivity of molten $MgCl_2$ in equilibrium and nonequilibrium state in the field of 1 kV have been studied by molecular dynamics simulation.

The modeling was based on a pair potential of the Born-Mayer-Higgins form including the polarization effects [1]. The main particularities of modeling nonequilibrium state by molecular dynamics method are to estimate the system temperature, velocities of particles movement and electrical conductivity arising in the high voltage fields. The obtained structural results for the equilibrium and nonequilibrium melts are compared with the experimental data for the equilibrium molten $MgCl_2$ [2] in Table 1, where the calculated and experimental electrical conductivity the equilibrium melt, $\lambda(0)$, and limiting high-voltage conductivity, λ^0, [3] of none-equilibrium melt are also presented.

Table 1. Properties of equilibrium and nonequilibrium melt $MgCl_2$

	r^0_{+-}, Å	n_{+-}	r^0_{++}, Å	n_{++}	$\lambda, 10^{-3}$ Ohm^{-1}m^2/mol
MD equilibrium	2.45	5.1	4.00	7	3.51
MD nonequilibrium	2.36	3.5	4.35	5	14.36
Experimental values	2.42 ± 0.03	4.3 ± 0.3	3.81 ± 0.05	5 ± 1	$\lambda(0)$=2.95 λ^0=10.78

The structural results and the conductivity of the equilibrium melt obtained by simulation are in satisfactory agreement with the experimental values. These results confirm the presence in molten magnesium chloride of tetrahedral and of other nature autocomplexes. The calculated conductivity of nonequilibrium melt is close to the experimental limiting high-voltage value. The results are interpreted on the base of the dissociation of structural complex ionic units on the elementary ions and destruction of the equilibrium intermediate-range order in ionic structure in the melt subjected to the strong pulsed electric fields.

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This work was supported by Russian Foundation for Basic Research, Project № 09-08-00141-a and by National Contract no 14.740.11.0803

ANTI-CORROSION EFFECTIVENESS OF THE COMPOSITIONS PREPARED ON THE BASE OF FERROCENE AND SOME OF ITS FUNCTIONALLY SUBSTITUTED DERIVATIVES

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At present time the demand for inhibitors of combined action with the high anti-corrosional indicators is very large and the most actual problem for today is creation of more profitable economically and ecologically pure methods of obtaining the new generations of anti-corrosional inhibitors.

With the aim of searching more effective, easy-obtained and distinguishing for their universal action inhibitors of corrosion, as an object of investigation we have chosen some unusual according to its structure (superaromatic) and activity on its coordinating ability ferrocene (I) and some of its (OH and NH_2) functionally substituted (II-V) derivatives: $C_5H_5FeC_5H_4C(CH_3)_2OH$ (II)…..

Being in the minimal degree of oxidation (just 0,6 part) the atom of Fe in ferrocene molecule very easily engages into different links: coordinative and donor-acceptable links because of its high resemblance (relationship) with the metal surfaces.

With the aim of revealation the structural and characteristic changes in the samples obtained on the base of I-V ferrocene complexes and petropolymers resins (PPR), there has been used the IR-spectral method. The investigation has shown that, at putting into the content of PPR ferrocene and its functionally substituted derivatives in the limits of 20 ÷50% (mass), especially OH and NH_2 groups of derivatives the valence fluctuation both ν_{OH} and ν_{NH_2} V are reacting very sensitively to the degree of these groups interaction with PPR. The IR-spectral data obtained by this way have shown that where OH and NH_2 groups are spontaneously tied with cyclopentadienyle ring (III, V) the interaction with PPR becomes weaker, and removal of these groups from the cyclopentadienyle ring (II, IV) on the contrary, makes these ties much stronger. It has been established that the compositions prepared on the base of derivatives II, IV with PPR OH and NH_2 groups will take an active part in the different coordinative linkformations with the metal surfaces, which provides in its turn much higher anti-corrosional effectiveness of the prepared compositions.

The anti-corrosional effectiveness of the compositions prepared on the

base of I-V with PPR has been tested on steel structural reinforcing bars of AT-500-brand. Besides, it must be mentioned that the reinforcing bars constituent elements make a high alkali medium. Therefore, one of the most important reasons of destruction the reinforcing bars in ferro-concrete hardware is formation of rust with complicated structure, with mixture of hydrating oxides of iron as a result of corrosional processes.

The anti-corrosional effectiveness of the prepared samples has been determined both by gravimetrical and potentiostatical methods. The samples with mentioned above complexes I-V have been tested in NaCl 3% at the temperature 25^0C in dynamic rejime in the period of 10 days and nights.

Besides, it has been established, that the investigated samples in NaCl 3 conditions are coordinated with very low rate, and the degrees of all samples protection are very close and they make 98,43 ÷ 99,30%.

While covering these steel samples it's necessary to save their glossy states after testing without any distractions or cracks with an aggressive electrolyte.

Thus, the obtained experimental data make it possible to think that the ferrocene and its derivatives are perspective complexes in order to protect the steels from corrosion in the aggressive spheres.

INVESTIGATION OF COMPOSITION AND STABILITY OF SUPRAMOLECULAR COMPLEXES OF 5-FLUOROURACIL TAUTOMERS WITH β-CYCLODEXTRINE USING FLUORESCENCE METHOD

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Many works are devoted to the study of the keto-enol tautomerism of 5-fluorouracil (FU) and its natural analog thymine, which defines DNA genetic information.

The study of spectral-luminescence properties, keto-enol tautomerism of FU, as well as the composition and the stability of its supramolecular complexes with β-cyclodextrine (CD) is the aim of the given work. The analysis of the spectra of the excitation and radiation of fluorescence (FL) of 5-fluorouracil allows to reveal experimentally all the four its most possible tautomeric forms.

To estimate the possibilities of the express analysis of an antitumor preparation FU quenching FL of blood and tryptophan was studied using FU ($K=15\times10^3$ $l\times mol^{-1}$). The results obtained reveal the outlooks for FL titration of multicomponent solutions of biological liquids.

It was found, that FU forms fluorescent complexes with CD of the equimolar compositions, which stability decreases in a series: diketo-, keto-enol and dienol tautomers of 5-fluorouracil. An equilibrium constant of complexing diketo-form of 5-fluorouracil with CD ($K=140$ $l\times mol^{-1}$) and a quantum yield of FL of the complexes [FU•CD] ($\varphi_K=37\times10^{-4}$) was determined. The FL quantum yield of uncomplexed FU is $\varphi_0=1.3\times10^{-4}$. The obtained results show that in the supramolecular complexes of CD with FU, which model the properties of FU in biological objects of «guest-host», 5-fluorouracil is in diketo-form and the content of toxical anionic tautomers in the biological systems is extremely small.

ACKNOWLEDGEMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 11-04-97042-p-povolzhje-a.

SELF-ASSOCIATION THERMODYNAMIC PARAMETERS OF SECONDARY HYDROPEROXIDS IN SOLUTIONS

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The self-association of secondary ethylbenzene (EBHP), sec-butyl (SBHP) and diphenylmethyl (DPMHP) hydroperoxides in solutions of the n-decan, carbon tetrachloride (CCl_4), chlorbenzene was investigated by IR-spectroscopy (3100 - 3700 cm^{-1}, 20-80^{0}C) It is established, that in solutions at concentration <0,6 mol/l hydroperoxids exist as a mix of monomers and hydrogen-bonded dimers and trimers. Processing of a package of IR-spectra of hydroperoxids solutions with various concentration determines concentrations of monomers and self-associats, then dimerisation and trimerisation equilibrium constants. On temperature dependence of equilibrium constants (Vannt-Goff equation) the thermodynamic parameters of self-association are calculated.

Table. **Equilibrium constants and thermodynamic parameters of hydrogen bond formation in SBHP, EBHP, DPMHP solutions**

HP	Solvent	K_D^{20}, l/mol	K_T^{20}, (l/mol)^2	$-\Delta H_D$, kJ/mol	$-\Delta S_D$, J/(mol·K)	$-\Delta H_T$, kJ/mol	$-\Delta S_T$, J/(mol·K)
SBHP	н-$C_{10}H_{22}$	2.7	5.4	22.5	67.0	31.6	91.8
	CCl_4	1.0	2.2	14.3	47.9	19.6	59.3
	C_6H_5Cl	0.8	1.6	13.3	46.9	18.5	58.1
EBHP	н-$C_{10}H_{22}$	3.2	21.9	19.6	56.0	26.8	63.5
	CCl_4	2.4	4.4	12.9	36.1	18.4	49.7
	C_6H_5Cl	1.1	2.1	11.0	36.2	15.9	47.1
DPMHP	н-$C_{10}H_{22}$	1.2	-	21.7	71.1	-	-
	CCl_4	1.0	4.1	16.2	54.2	20.3	56.5
	C_6H_5Cl	0.7	1.4	11.6	41.6	16.7	53.5

Apparently from the table, the maximal values of thermodynamic parameters di- and trimerisation are observed in n-decan solutions who for this reason should be counted the inert solvent which is in any way not influence on the self-association process. Decreasing of enthalpy in CCl_4 and chlorbenzene is caused solvation of monomers by solvents.

ON MECHANISM OF THE FORMATION OF GOSSYPOL BIS-SCHIFF BASE WITH 4-AMINOANTIPYRINE

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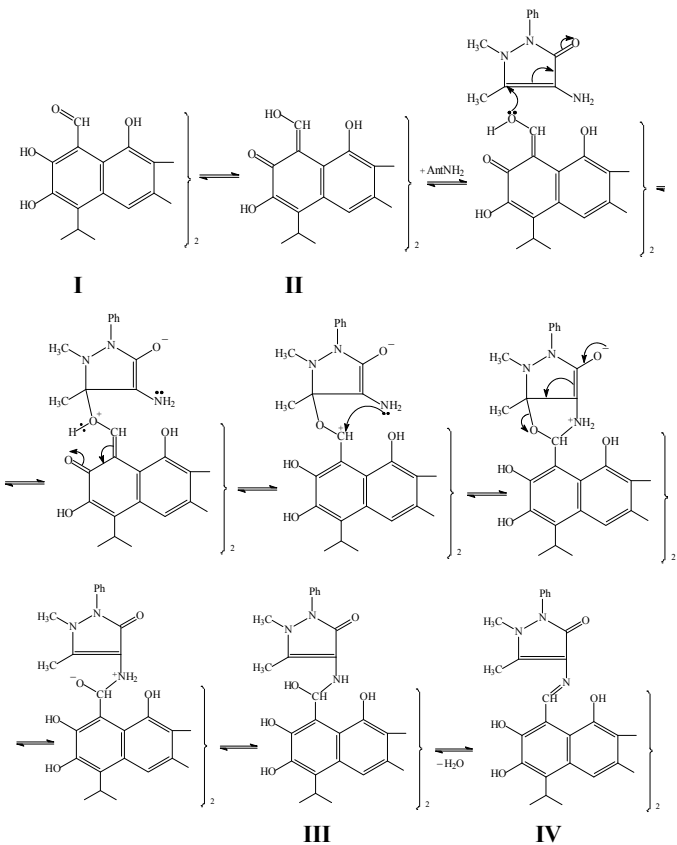
The investigation of dynamics of reaction between gossypol (Gp, **I**) and 4-aminoantipyrine ($AntNH_2$) in $CDCl_3$ by ^1H NMR- spectroscopy method allowed us to suggest a new scheme of their interaction based on vinylogy[1] of $AntNH_2$ and nucleophilic addition of naphthalone-carbinol tautomer of Gp (**II**) to $AntNH_2$ with the following attack of positively charged carbon atom by nucleophilic nitrogen atom of NH_2-group, intermediate cyclization, transition to "classical" aminal (**III**) and Schiff base formation (**IV**).



I **II** **III** **IV**

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INVESTIGATION OF TOXIC PROPERTIES ORGANIC COMPOUNDS BY APPROACHES QSAR BASED ON SIMPLEX REPRESENTATION OF MOLECULAR STRUCTURE

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Nowadays the pollution of the environment is a global problem. The main factor of pollution our planet is a different chemical compounds[1].

The data base «Toxic v.1.1.5.» for toxic properties and chemical structure organic substances has been prepared. It's contain the information about 2030 chemical compounds. The samples for different conditions with help of data base «Toxic v.1.1.5.» has been generated.

The investigation of influence of the molecular structure of different organic compounds on their toxic activity has been carried out by 2D simplex representation of molecular structure[2] with help of approaches PLS[3] and "Random Forest" (RF)[4]. The quite satisfactory QSAR models has been obtained.

Table 1. **The statistic characteristics for some QSAR models on base approach RF**

№	Test Type	Organism	Route	Quantity compounds in set (ws/ts)	R2oob	R2 test
1	Ld50	rat	oral	940(752/188)	0,510	0,560
2	Ld50	mouse	intravenous	302(241/61)	0,404	0,603

Table 2. **The statistic characteristics for QSAR model on base approach PLS**

№	Test Type	Organism	Route	Quantity compounds in set (ws/ts)	R2	Q2	R2 test
1	Ld50	rat	intravenous	127(101/26)	0.875	0.797	0.697

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THE ROLE OF Ni(0), Ni(I), Ni(II) COMPLEXES IN DI- AND OLIGOMERIZATION OF ALKENS

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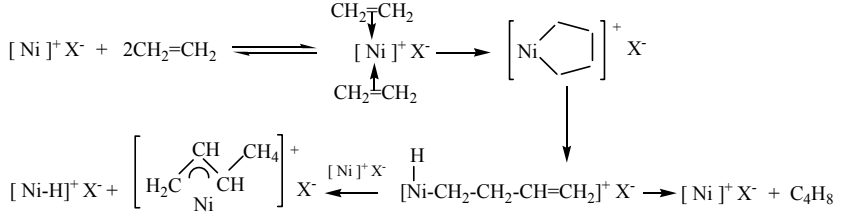
Nickel catalysts of alkene di- and oligomerization can be classified by the oxidation state of nickel in precursor. The systems based on zero-valent nickel complexes NiL_n (L= PR_3, $P(OR)_3$, COD, etc.) are of the special place. These catalysts are active in combination with Bronsted or Lewis acids and maximal catalytic effect is achieved whith their joint use. The key reactions in the active complex formation are as follows: the oxidation of Ni(0) to Ni(I) and Ni(II); contradisproportionation Ni(I) and transmetallation.[1] The interaction of cationic complexes $[Ni(PPh_3)_n]]^+BF_4^-$ (n = 1, 2) with alkenes:

$$2[L_nNi]^+BF_4^- + 2CH_2=CH_2 \rightarrow [L_{n-1}Ni-CH_2-(CH_2)_2-CH_2NiL_{n-1}]^{2+}(BF_4^-)_2$$

and further that complex transformations leads to the formation of catalytically active hydride $[L_{n-1}Ni–H]^+BF_4^-$ and π-butenyl $[L_{n-1}Ni–CH(CH_2)–CH_2–CH_3]^+BF_4^-$ nickel complexes.[1] The mechanism of the active complex formation using Ni(I) cationic complexes as a precursor can be represented by the schemes, including electrophilic addition of Bronsted acid to the alkene π-complexes of Ni(I); oxidative doubling of two alkene molecules:



The formation of π-allyl nickel complexes in such systems has earlier been noted.2 Thus Ni(I) complexes play a key role in the regeneration of catalytically active Ni(II) complexes regardless of the nature and oxidation state of the metal in the precursor.

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THE SURFACTANT ADSORPTION BY THE NATURAL POLYMERS

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The modern technologies of the adsorption processes of searching of the new, ecologically friendly adsorbents as natural polymers - chitin and chitosan. The chitin and chitosan adsorbents have high adsorption ability in relation to mineral oils, dyes, alcohols, phenols and heavy metals. The basic natural sources of chitin are the shells of crustacean and the biomass of fungus` mycelium. Chitin provides the mechanical strength of the structure without rigid bonds between microfibrilles, that allows to keep the certain elasticity of a cellular wall.

The submitted researches are devoted to studying adsorption activity of the chitin received from the shells of crustacean in relation to representatives of cationic and anionic surfactants. The studying of peculiar behavior features of systems containing surfactants and natural polymers can give the indispensable information for comprehension of intermolecular association process, establishment of disperse systems stabilizing mechanism, interpretation of colloidal-chemical processes proceeding on the interface etc.

The crushing of the adsorbent are made using a planetary mono-mill " Pulverisette 6 ". The subsequent dispersion into fractions are made with the help of the vibrating sifting machine " Analysette 3 ". The fraction with the size of particles $(0,5\text{-}1,0)\cdot10^{-3}$ m has been selected for researches. The equations of Langmuir, Hill – De Boer, BET have been used for the description of surfactant adsorption process. The calculation of constants of the equations is made by the graphic method using the equations to the linear form. It was used the computer program for calculation of constants of Langmuir. The analysis of the received isotherms has shown, that isotherms of anionic surfactants adsorption concern to L - type, the isotherms of cationic surfactants adsorption - to S - type according to Gilles classification. . Processing of experimental data with the help of the computer program gives satisfactory conformity of the parameters of the adsorption calculated by the various methods. The plateau and excesses in the field of concentration before critical micelle concentration are on the isotherms of adsorption of the researched surfactants. In some cases, the association of molecules of adsorbate at small degrees of filling of adsorbent surface long before critical micelle concentration is observed.

The researches have shown that in all cases the surfactant adsorption has the physical mechanism.

THE REACTION TRIPHENYLCARBINOL WITH ALKYNYL- AND ALLYLSILANES CATALYZED BY LEWIS ACID

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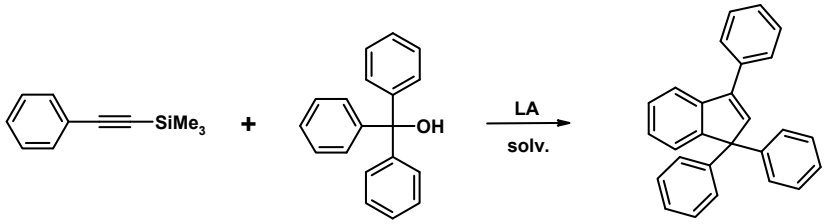
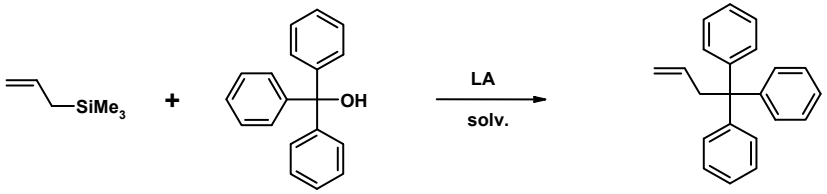
At the present time a lot of researchers pay attention to the study of classical reactions of C-C-bond formation with using new effective Lewis acid catalysts by reaction of nucleophilic substitution S_N1.[1]

The reaction of triphenylcarbinol with trimethylsilylphenylacetylene and allyltrimethylsilane were investigated in toluene and nitromethane in the presence of $Sc(OTf)_3$ or $FeCl_3$ (5 mol %) as Lewis acids. It was established that the reaction takes place in nitromethane with quantitative yield (95%) by using $Sc(OTf)_3$ as a catalyst and heating of 100 ^oC for 1 hour. The formation of by-products wasn't observed as in toluene as in nitromethane with using $FeCl_3$ as a catalyst.



In the similar conditions the allylation product was obtained with yield of 72%:



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ANTIOXIDATIVE ACTIVITY ASSAY OF CHROMOPHORES USING ELECTROCHEMICAL DPPH-TEST

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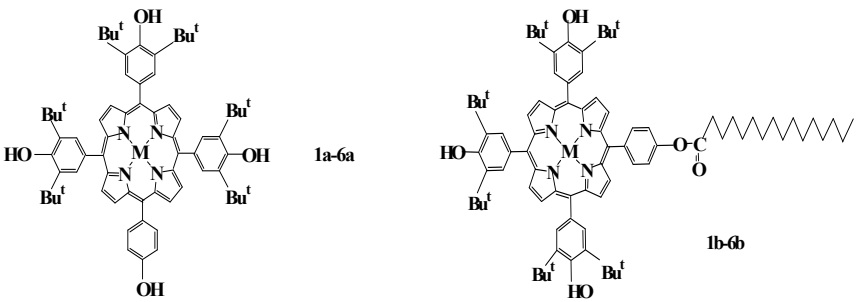
New methods of antioxidative activity evaluation are of importance. The reduction of a stable radical 2,2-diphenyl-2-picrylhydrazyl (DPPH) monitored spectrophotometrically is widely used as antioxidative activity assay [1]. But this method has certain limitations. For example, it is inapplicable for chromophores that have an adsorption band close to the band of DPPH (512 nm). We proposed to use in this case CVA method [2]. By means of electrochemically monitored DPPH-test ahtioxidative activity of ferrocene derivatives **Fc(L)R** (**R** – 2,6-di-*tert*-butylphenol or phenyl groups, **L** – spacer) and metalloporphyrins **1a-6a, 1b -6b**, bearing 2,6-di-*tert*-butylphenol moieties, were studied.



M= HH (1a, 1b), Zn (2a, 2b), Cu (3a, 3b), Co (4a, 4b), Fe (5a, 5b), Mn (6a, 6b)

It was shown that the compounds bearing 2,6-di-*tert*-butylphenol groups are effecient antioxidants which have higher activity than a known antioxidant ionol. The results of electrochemical DPPH-test correlate well with the data obtained in chemical study [3].

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S_N^H REACTIONS OF CYCLOPENTADIENYL COMPLEXES OF THE TRANSITION METALS

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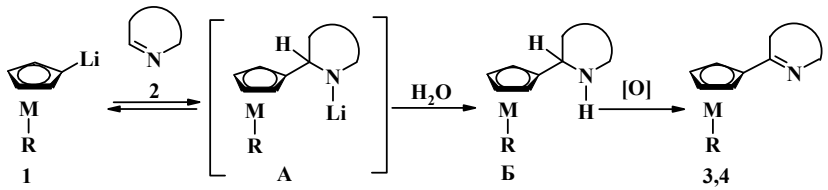
The methodology of nucleophilic substitution of hydrogen is a widely used synthetic tool for different C-X bonds formation (X = C, N, O, P, S and others) in the synthesis and modification of *N*-heterocycles. This may be considered as a type of cross-coupling reactions. The approach can effectively be applied for the introduction of metalocenes into the π-deficient heterocycles.

The S_N^H methodology has successfully been used in the synthesis of ferrocenyl- and cymantrenylhetarens. The reaction has been found to proceed in two stages in both cases. The first step is the addition of lithiometallocenes **1** to azine with formation σ^H-adducts, followed by the aromatization of dihydroazines **3**. It should be mentioned that the reactions proceed in good yields (50-90%) in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). This approach does not require any additional activation of heterocycles and the use of catalysts.



3: MR = FeCp, 4: MR = Mn(CO)$_3$

The structures of the metallocenylazines were confirmed by NMR and IR spectroscopy, mass spectrometry, and X-ray.

The work was supported by the Council on Grants of the President of the Russian Federation (NSh-65261.2010.3, MK-1901.2011.3) and the Russian Foundation for Basic Research (10-03-00756-a).

NICKEL-CATALYZED CROSS-COUPLING REACTION OF ARYL HALIDES WITH AROMATIC ALDEHYDES

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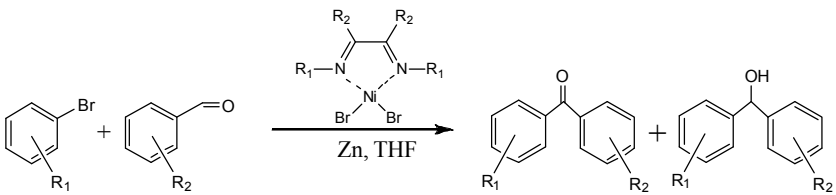
Synthesis of biaryl ketones is an important problem of modern preparative chemistry, since many pharmaceutical drugs include the functionalized benzophenone fragments.

Though few methods of synthesis of the functionalized benzophenones are described in literature, all of them have some limitations and drawbacks.

Recently, we have discovered efficient catalysts for homocoupling of aryl halides in the presence of zinc dust and Et_4NI. Here, we have found that these nickel catalysts bearing bis-imino (or 1,4-diazabutadiene) ligands can effectively perform cross-coupling reactions of aryl halides with aryl aldehydes to give the respective substituted benzophenones in high yield.



These systems based on inexpensive nickel salt and non-toxic 1,4-diazabutadiene ligands can catalyze the described cross-coupling reactions even at room temperature. Additionally, the developed protocol is tolerant to various functionalized substrates including the molecules bearing reactive functional groups. Scope of this cross-coupling reaction has been studied in detail particularly using nickel pre-catalysts bearing different 1,4-diazabutadiene ligands.

SYNTHESIS AND RELATIVE CATALYTIC ACTIVITY OF COPPER(II) TRIFLUOROACETATE COMPLEXES

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Nowadays, compounds based on copper carboxylates are active researched because of high interest to producing model copper-containing enzyme complexes, for example, dopamine hydroxylase need for epinephrine synthesis in view of it magnetic and catalytic properties.

In this article synthesis and roentgenium-structure analysis (RSA), IR-spectroscopy data for new mononuclear $[Cu(phen)_2(CF_3COO)](CF_3COO) \cdot CF_3COOH$ **(I)**

(phen – 1,10-phenanthroline) and polymeric cateno-$[Cu(phen)(CF_3COO)_2]_\infty$ **(II)** copper(II) complexes with trifluoroacetate ligands and it relative catalytic activity in the reaction of tripeptide glutathione oxidation by hydrogen peroxide are shown.

Complexes **I** and **II** were synthesized accordingly by interaction of $Cu(phen)_2Cl_2$ and $Cu(phen)Cl_2$ with CF_3COOAg in the aqueous solution of CH3COOH (pH ~3).

According to RSA complex **I** crystallized in monoclinic syngony with space group P2 1/c (a 9.05, b 15.45, c 22.28 Å, β 95.31°, V 3100.5 $Å^3$, Z 4, R 9.82%), complex **II** – in monoclinic syngony with space group C 2/c (a 19.38, b 11.36, c 7.68 Å, β 104.46°, V 1638.3 $Å^3$, Z 4, R 3.71%).

Relative catalytic activity of complexes **I** and **II**, $Cu(phen)_3Cl_2$ and $CuCl_2$ was quantified by the speed of accumulation of hexapeptide GSSG, which was defined by method of HELC (high-efficiency liquid chromatography) in the process of correlation with cys-$[Pt(NH_3)_2Cl_2]$, which activity was fixed as a nominal null. Relative catalytic activity of complexes increases in the rank:

$Cu(phen)_3Cl_2$ (63%) < **I** (74%) ≈ $CuCl_2$ (75%) < **II** (88%).

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STRUCTURE OF 6,6-DIMETHYL-1,5-DIAZABICYCLO[3.1.0]HEXANE AS DETERMINED BY GAS-PHASE ELECTRON DIFFRACTION

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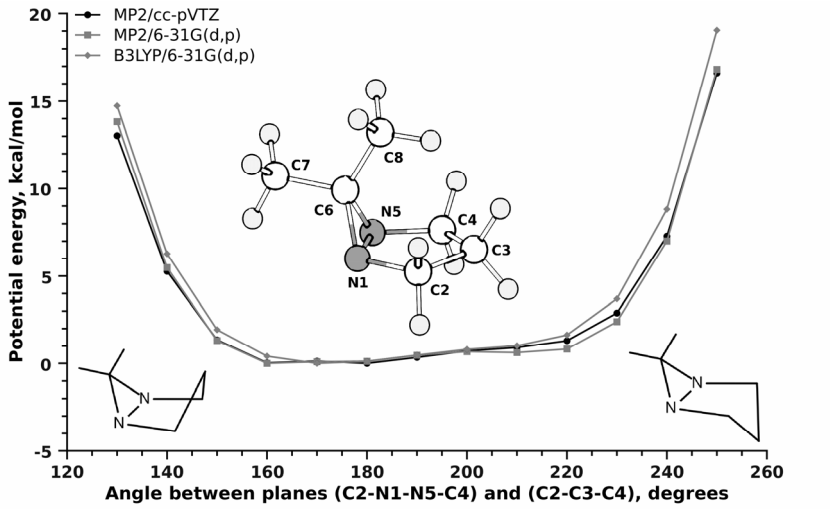
Derivatives of 1,5-diazabicyclo[3.1.0]hexane (DABH) are interesting objects in fundamental studies of structure and conformations of molecules. Recently we have experimentally investigated the structure of free DABH molecules by gas electron diffraction method.[1] In continuation of this work we have studied the molecular structure of 6,6-dimethyl-DABH. We have shown that the molecules of this compound in gas phase possess the only one stable non-rigid conformation, which corresponds to the planar five-membered ring.



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This work has been supported by RFBR (08-03-00507-a) and Alexander von Humboldt Foundation (Germany).

SORPTION OF PLATINUM AND NON- FERROUS METALS SILICAS, MODIFIED CROWN THIOETHER GROUPS

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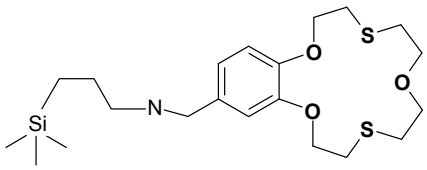
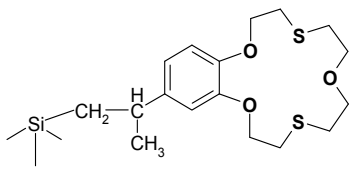
Mesoporous silicas were are a convenient carrier for immobilization of bulk organic chemicals, capable of selective binding of ions of metals (the so-called molecular recognition). We developed a new approach to fixing on the surface of silica crown-ether compounds, in particular derivative benzyldithia-18-crown-6 ether, which consists in the synthesis of the modifier contains reactive silicone group $(C_2H_2O)_3Si(CH_2)_3NH_2$, in the solution with the subsequent drawing of it, bypassing the stage ofon the surface of the silica. The ratio of the modifier and silica is calculated so that to assure the on the surface of SiO_2 ~2 molecules/nm^2, that of the "Silochrome S-120" (S_{sp} 120 m^2/g, d_{pores} 40 nm) is equivalent to 0.4 mmol/g.

The report presents the results of study of sorption extraction of Pt(IV), Rh(III), Ni(II), Cu(II), Pb(II) of hydrochloric acid in static conditions on chemically modified silicas:



Sorbent **1**



Sorbent **2**

Constant values of static exchange capacity (SEC) in relation to ions of Rh(III) are achieved in 30 min. For sorbent **2** Rh(III) is 0.36 - 0.38 mmol/$g_{sorbent}$. Although sorbents **1** and **2** contain the same thiacrown-essential fragments, they show various sorption capacity with respect to ions of Pt(IV). So, Pt(IV) is not sorbed by the sorbent **2** at room temperature, as, apparently, testifies to the participation in the complexation of nitrogen atoms spejsera sorbent **1**. Sorbent **2** does not remove from hydrochloric solutions and ions of non- ferrous metals. The data obtained demonstrate that the use of selected sorbents to separate the pairs Pt - Rh and separation of ions of platinum metals from non- ferrous.

REGIOSELECTIVE CYCLOCONDENSATION OF α-AMINO HYDROXAMIC ACIDS WITH ACETONE

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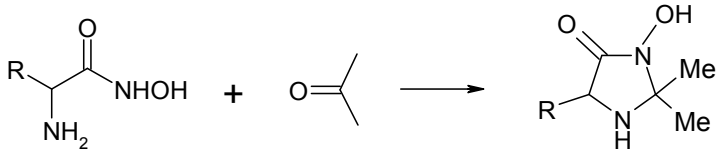
We found that the mode of N,N'-cyclocondensation regioselectivity occurs in the reactions of racemic aliphatic and aromatic α-amino hydroxamic acids (derived from glycine, α-alanine, valine, leucine, α-phenylglycine, β-phenylalanine and tyrosine) with acetone leading to the corresponding 5-substituted 2,2-dimethyl-3-hydroxyimidazolidin-4-ones **1**-**7** formation.[1]



R = H, Me, Pr^i, Bu^i, Ph, Bn, BnOH-*p* (±)-(**1**-**7**)

The reactions are self-catalytic and proceed with an excess of ketone leading to moderate product yields (~50-80%). The structure of cyclic hydroxamic acids **1**-**4** was confirmed by X-ray diffraction analysis. The comparison of crystal structures of homologues **1**-**4** shows that parent achiral acid **1** (R = H) crystallizes as a conglomerate (space group $P2_12_12_1$, Z=4). On the other hand, acids **2** (R = Me; $P2_1/c$, 8), **3** (R = *i*-Pr; $P2_1/n$, 4), and **4** (R = *i*-Bu; $C2/c$, 16) form racemic crystals. Moreover, asymmetric units of **2** and **4** contain two crystallographically independent molecules. The crystal structures of acids **1**-**4** exhibit the same pattern of intermolecular hydrogen bonding, namely, strong O-H…NH and weak N-H…O=C bonds are formed. The rings in crystalline **1**-**4** adopt a quite narrow range of forms closed to an envelope $_{C(2)}E$. According to the results of NMR spectroscopy, acids **1**-**7** in solution exist as a strongly predominant hydroxyamide tautomer.

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OBTAINING ALCOHOLATES OF ALKALI METALS

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Monohydroxypropylated aromatic amines can be used as a tension - active substances, anti-corrosion additives, fuel additives and in other areas of the economy, and their alcoholates can be used as individual starting compounds and additives for polymerization processes.

In this paper we consider the process of polymerization of alkali metals alcoholate, as well as the structure of the products formed.

In this paper, the proton nuclear magnetic resonance and electron spin resonance methods were used to study the structure of amine, hydroxyl and potassium - alcoholate groups, as well as the conditions for the reaction.

The process of obtaining consists of three stages: the first stage deals with the process of aniline β-oxyalkylation with propylene oxide, which effectively runs under the following conditions - temperature 70°C, molar ratio of alkylating agent : an aromatic amine is 1:1. When the amount of alkylating agent increases the reaction rate accelerates, but process selectivity decreases.

The second stage - the rectification of the resulting monohydroxypropylated amine. This stage is removal of unwanted materials at a temperature of about 200°S.

The third stage is the provision of alkali metal alcoholate. Metal is added to the to monohydroxypropylated aromatic amine in an amount of 1:1 molar.

The resulting products are starting compounds for the synthesis of rubber and high-performance rubber ingredients.

CRYSTAL VANADOMOLYBDATES

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In water solutions between ions there are the difficult equilibrium conditions including the asid-base transitions, including hydrolysis and polymerization pro- cesses.Thereupon use organic cations it is new for the purpose of stabilization of certain ions, astable in a water solution, shows rather perspective.

Vanadomolybdates solutions at the atomic V:Mo=1:3, 1:5 in the range pH 5,5-3 was investigated by NMR and IR spectroscopic methods.[1] The sediment of the composition $(Mo_{3-x}V_xO_{10}^{(2+x)-})_\infty$ deposited in the solutions and on standing crystals α – oktamolybdates $Na_6V_2Mo_6O_{26}\cdot 13H_2O$ were isolated. From solutions

over deposits with diethyl amine transparent crystals of green color, in the form of the truncated pyramid are allocated. By results of the element analysis com- pound has the formula:

$$[(C_2H_5)_2NH_2]_3Na_2VMo_7O_{26} \qquad (1)$$

It was spent rentgeno - structural analysis. On PSA anion has structure to β - $Mo_8O_{26}^{4-}$. The disubstituted β-oktamolibdat is synthesized.[2] Monosubstituted β-oktamolibdat earlier it is not received. The ^{51}V NMR spectrum of a water solu- tion of compound shows three resonant lines (δ =-494, - 502 and-533 m. d.). For stabilization anion $VMo_7O_{26}^{5-}$ organic solvent – dimethyl formamide in which reduction of processes the hydrolysis is supposed was used.The spectrum in dimethyl formamide shows a unique line with δ – 485 m.d., which testifies to individuality of the received compound. Crystals of the compound (1) it is allocated and from water solution $Na_6V_2MoO_6O_{26}$, in the presence of diethyl amine hydrochloride. In this case we observe transformation vanadiumsubstited α-oktamolybdate in vanadiumsubstituted β-oktamolybdate. In the literature it is known about interconversions α-, β- $Mo_8O_{26}^{4-}$,[3] similar process for vanadomo- lybdates is observed for the first time.

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OLIGOGERMANES WITH INCREASED COORDINATION NUMBER OF GERMANIUM ATOMS: SYNTHESIS, STRUCTURE, PROPERTIES

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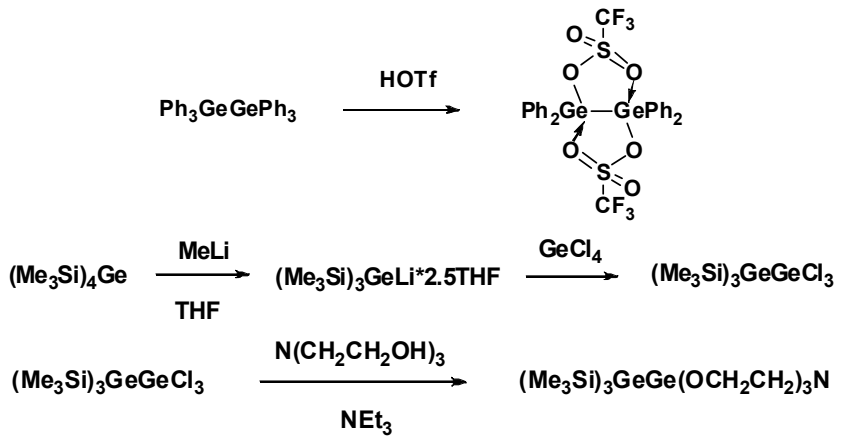
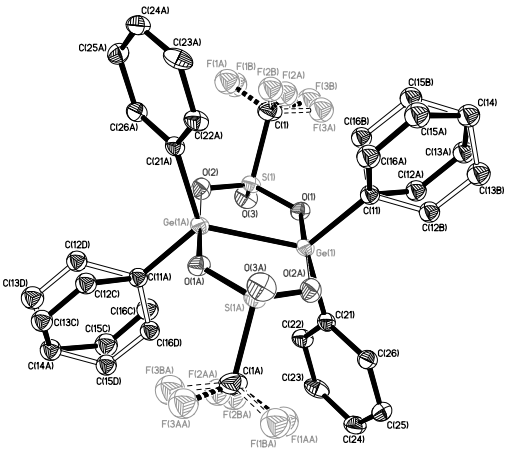
It is known that electrons of the element-element bonds don't localized on two central atoms, but delocalized on the whole chain of element atoms (σ-delocalization) [1]. This fact leads to unusual optic properties of these substances, and also makes them useful because of their other physical characteristics (conductivity, thermochromism). Special interest including probable practical application is concerned to investigation of germanium compounds. It may be supposed that introduction of additional electron donor in a molecule of oligogermane changes principally the properties of these substances, and control of force of such additional interaction allows finding correlations "structure – useful property". Analysis of literature data indicates that such germanium compounds are not investigated as opposed to similar silicon analogs that were recently synthesized.

In the course of this investigation the representatives of two types of digermanes with additional donation of electron density on Ge atom were synthesized.



The composition of the compounds obtained was established on the basis of elemental analysis data, and structure was investigated in solution by NMR spectroscopy and in solid state in several cases by X-ray analysis.



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AB INITIO INVESTIGATION OF INTERCALATION BY METHANE OF GRAPHITE-LIKE SYSTEMS.

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The possibility of introduction of molecules of methane between graphene-like planes has been investigated. As model of two graphene layers used ovalene dimer ($C_{32}H_{14}$) (fig.).

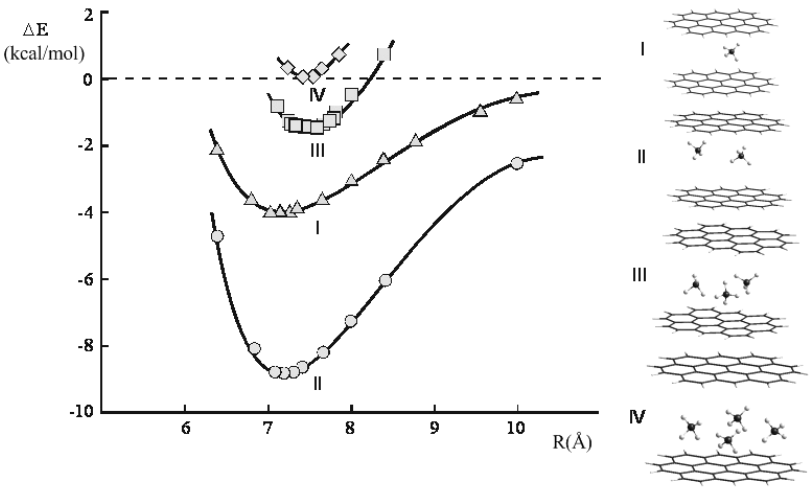

Fig. Dependence of relative electronic energy of clathrate (I - IV) from interplane distance

Ab initio - calculations were carried out in basis 6-31G, energy of electronic correlation was considered within the limits of the Möller-Plesset perturbation theory (MP2).

The obtained results testify that inclusion compound of one, two and three molecules CH_4 in graphite-like systems there can be, however, such compounds are endothermic, i.e. are unstable. The structure with four molecules of methane does not form any stable supra-molecular system. The most stable system is clathrate with methane in the dimeric form.

ADAPTIVE INFORMATION SYSTEM FOR MATERIAL CHEMISTRY

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Information support for implementation of 'science – manufacture – application' chain in modern conditions of almost unlimited access to free and paid worldwide scientific-technical information resources is limited ultimately by confined human specialist possibilities as to processing of potentially relevant sources, that determine the necessary focusing – filtration of information resources on tasks context to be solved.

The developed program-technological tools on relational DB platform are the extension of chemical information-analytical system [1], they address to the end user – expert-specialist and support the following functions:

- worldwide information resources monitoring, recognition – revealing, indexing and accumulation of relevant documental and factographic information;
- maintaining of the operational – technological resources, providing the substantial informational revision and secondary informational product development (background information, scientific reviews, reports, predictive estimates etc);
- meaningful information processing and maintaining of registration of formalized entities (information objects) and inventories of their links;
- integration of informational and program-technological tools for search, analyses, and predictive classification, allowing corporative user to acquire and employ efficiently huge documental and factographic information content;
- organization of electronic catalogues and index inventories to facilitate data mining and data classification;
- design and maintenance of particular scientific tasks, fast challenge-focused contextual adjustment of classifiers and links inventories for informational objects in the developed program – informational environment (databases and knowledge bases).

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HYBRID STRUCTURES WITH BOTH MICROTUBULE DEPOLYMERIZING AND TUBULIN CLUSTERING ACTIVITIES

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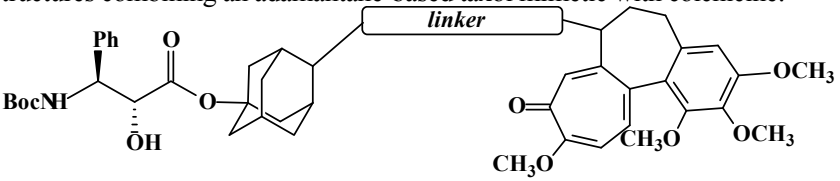
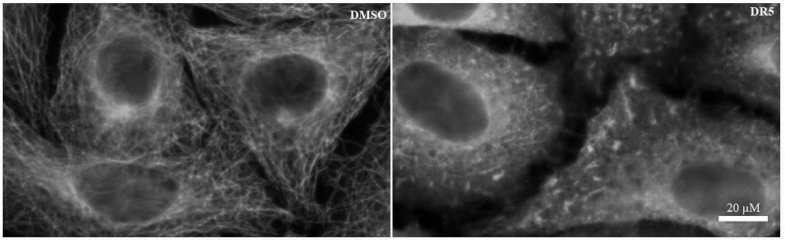
In the frame of the study on the bridgehead moieties application in the design of compounds with antitumor activity we synthesized unusual hybrid structures combining an adamantane-based taxol mimetic with colchicine:[1]



Some of these compounds possess very high cytotoxicity (in nanomolar range) against A549 human lung carcinoma cells.



The most active compounds were found to interfere with the microtubule dynamics in an unusual manner. Treatment of the cells with these compounds promoted disassembly of microtubules followed by the formation of stable tubulin clusters. Structural requirements for optimal activity have been established based on the SAR studies.

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THE RELATIVE ACIDITY SCALE METHOD

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The relative acidity scale method belongs to the class of unbuffered methods for determination of the strength of organic acid and bases[1]. The method is based on the electrolytic dissociation model of Brønsted-Lowry and operates with dimensionless constants of protolytic equilibria. In the case of water it can be written as:

$$K_a = \frac{\alpha[H_3O^{(+)}]}{(1-\alpha)[H_2O]} \quad K_{BH+} = \frac{(1-\alpha)[H_3O^{(+)}]}{\alpha[H_2O]} \quad K_S = \frac{[OH^{(-)}][H_3O^{(+)}]}{[H_2O]^2},$$

where $[H_3O^{(+)}]$, $[OH^{(-)}]$, $[H_2O]$ – quantities of the corresponding species, α – extent of ionization for compound under study.

The measurement of concentration dependence for extent of ionization by spectrophotometric or conductometric techniques allows one to determine protolytic equilibrium constant from the following equations

$$K_a = \frac{a\alpha^2}{2(1-\alpha)(1-a\alpha)}\left(1+\sqrt{1+4K_S\frac{1-(a\alpha)^2}{(a\alpha)^2}}\right) \quad K_{BH+} = \frac{a(1-\alpha)}{2(1+a\alpha)}\left(\sqrt{1+4K_S\frac{1-(a\alpha)^2}{(a\alpha)^2}}-1\right),$$

where a – relative molar fraction of compound in solution:

$$a = \frac{M_S C_A}{\rho - M_A C_A}.$$

M_S и M_A – molar masses of solvent and substance correspondingly , ρ – density of the solution with molar concentration C_A. The traditional equilibrium constant K_a^* (with dimension mole/l) related to dimensionless K_a as:

$$pK_a^* = -\log K_a - 1,744.$$

Thus determined K_a is not connected to the density of the buffer solution but to the density of pure solvent. The presented approach is methodologically more correct as it avoids taking in account the ionic strength of buffer solutions and calculation of ion activities due to measurements are performed at C_A below 0.1 M. In practice application of the method is hindered by the impurities in solvents and the existence of the lower limit for determination of α.

For the aqueous solutions calculations ware made taking in account presence of the carbonic acid in solution ($1{,}35\cdot10^{-5}$ M) and the lower limit for determination of extent of ionization (α = 0,001). With the above limitations the method allows one to determine the pK_a values up to 8.7 and pK_{BH+} above 4.0 in traditional pH scale.

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THE SYNTHESIS OF PHTHALONITRILES WITH HETEROAROMATIC SUBUNITS

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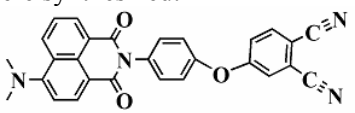
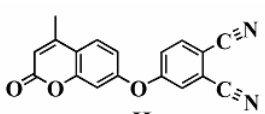
A study of processes of transfer of energy in the multichromophoric systems based on the phthalocyanines is an actual task, in connection with possible practical application of such systems in optoelectronic. [1,2] The synthesis of phthalocyanines comes true of tetramerisation corresponding substituted phthalonitriles [3], where a subunits acts part "antenna-effect", taking in light in a UV or visible range of spectrum and carrying energy on a central core.

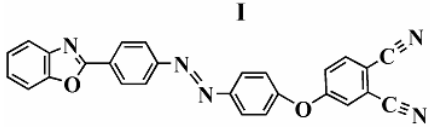
In this paper the series of phthalonitriles with heteroaromatic subunits (I-IV) were synthesized:



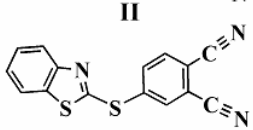
I



II



III



IV

Compounds were prepared by nucleophilic substitution of nitro-groups in 4-nitrophthalonitrile corresponds O- and S-nucleophilic reagents in DMF in presence K_2CO_3. Control of reaction was carried out by spectrophotometric and from data of TLC. Yields were 45-60 %. Structure of these compounds was determined by ^1H NMR, IR and UV-Vis spectroscopy and elemental analysis. The synthesis of tetrasubstituted phthalocyanines was beginning from the synthesized compounds.

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ORGANOCUPRATES FOR THE SYNTHESIS OF SYMMETRICAL DICARBAZOLOBIPHENYLS, AS PROMISING PHOLED MATERIALS

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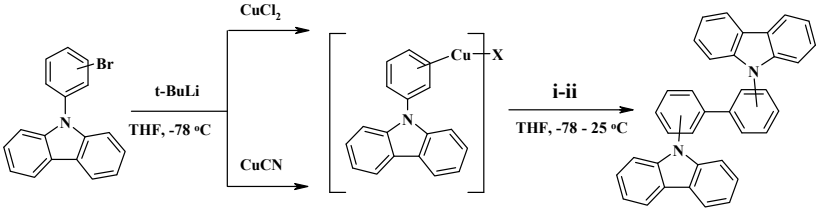
The efficiencies of organic light-emitting devices (OLEDs) have advanced rapidly in recent years because of the development of efficient phosphorescent guest molecules containing transition metals that can harvest both electrogenerated singlet and triplet excitons for emission.[1] 4,4'-Dicarbazol-1,1'-diphenyls 4,4'-(CBP) are common host materials for phosphorescent OLEDs (PHOLEDs) due to high triplet energy and carriertransport ability.[2] The application of 2,2'- and 3,3'-CBPs, which are more promising due to higher triplet energy levels, is limited due to luck of methods for their synthesis.



i: 1) CuCN, 2) p-Benzoquinone; ii: 1) $CuCl_2$, 2) N-(bromophenyl)-carbazole.

We found a convenient method for the synthesis of symmetrical CBPs *via* organocuprates. Thus, the reaction of N-(bromophenyl)-carbazoles with *t*-BuLi and $CuCl_2$ or CuCN/p-benzoquinone in dry THF affords smoothly symmetrical CBPs in moderate to high yields. The preliminary experiments demonstrate 2,2'- and 3,3'-CBPs to have a big promise for PHOLED application.

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