10TH PAUL WALDEN SYMPOSIUM ON ORGANIC CHEMISTRY

Programm and Abstracts

Riga
June 15-16, 2017

Friday, June 16

9.00-10.00 **Professor Olafs Daugulis** (University of Houston, Houston, USA)
New methods for carbon-hydrogen bond functionalization

10.00-10.30 **Dr. Vilnis Liepiņš** (JSC Olainfarm, Olaine, Latvia)
The use of DoE in chemical process optimization

10.30-11.00 **Dr. Ronalds Zemribo** (Latvian Institute of Organic Synthesis, Riga, Latvia)
Discovery of Remeglurant, a potent and selective mGluR5 receptor negative allosteric modulator

11.00-11.30 Coffee break

11.30-12.30 Poster Session II

12.30-13.45 Lunch break

13.45-14.45 **Professor Roger Strömberg** (Karolinska Institute, Department of Biosciences and Nutrition, Huddinge, Sweden)
Modification and conjugation of oligonucleotides for development of oligonucleotide therapeutics

14.45-15.10 Coffee break

15.10-15.30 **Doctoral student Jevgeņija Luginina** (RTU)
Aziridine ring opening and other reactions in liquid sulfur dioxide

15.30-15.50 **Doctoral student Mārtiņš Otikovs** (Latvian Institute of Organic Synthesis, Riga, Latvia)
Towards spinning of artificial spider silk

15.50-16.30 **Dr. Helmārs Šmits** (Syngenta Crop Protection, Basel, Switzerland)
Agrochemical process research: synthesis of aryl 1,3-diones and stereoselective cyclopropanation

16.30-16.45 Closing remarks, Award ceremony for poster prizes

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Aziridine Ring Opening and Other Reactions in Liquid Sulfur Dioxide

Jevgeņija Luginina

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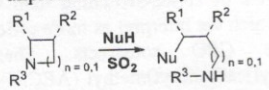
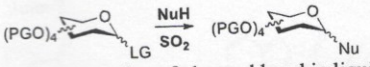
In recent years, many applications of SO_2 and its surrogates in organic synthesis have been reported [1]. Due to high polarity and Lewis acid properties sulfur dioxide can be used as strongly ionizing solvent. Furthermore, it has a high dipole moment (1.61 D), therefore it readily dissolves both organic and inorganic compounds. On the other hand, SO_2 has been reported as a reaction medium for processes involving carbenium ions. Surprisingly, despite all these facts sulfur dioxide has not entered the "classic toolbox" of synthetic organic chemist as an everyday-solvent. This has prompted us to search for organic reactions that would profit from their running in liquid SO_2 as a reaction medium.

We have discovered that different aziridines and azetidines undergo efficient ring-opening reactions in liquid SO_2 with metal halides and thiols as nuchleophiles (Scheme 1) [2,3]. Transformations proceed stereoselectively without racemization of chiral center in the case of enantiomerically pure protected or unprotected heterocycles.



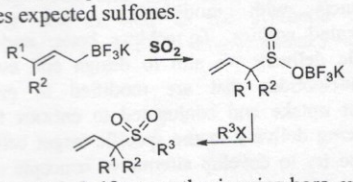
Scheme 1. Nucleophilic ring opening of small heterocycles in liquid SO_2.

We investigated glycosylation reaction with a wide range of *O*-, and *S*-nucleophiles of different monosaccharides in liquid SO_2 (Scheme 2). Employing SO_2 as a reaction media and glycosyl fluorides (LG = F) as glycosyl donors we performed nucleophilic displacement without any additional promoter or Lewis acid additive.



Scheme 2. Formation of glycosyl bond in liquid SO_2.

A novel method for the synthesis of sulfones also has been elaborated. The first step in this sequence is bora-*ene* reaction of sulfur dioxide and substituted potassium trifluoroborate giving a sulfinate moiety complexed to borate center (Scheme 3). It was observed that crotyl and prenyl systems react at their γ-position with SO_2. This serves as evidence for the *ene*-type regioselectivity. In the second step the alkylation of sulfinate moiety provides expected sulfones.



Scheme 3. Sulfone synthesis using bora-*ene* reaction as a key step.

Supervisor: Dr. chem. M. Turks

ACKNOWLEDGEMENTS

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REFERENCES

[1] Luginina, J. *Synlett*, **2014**, *25*, 2962.
[2] Luginina, J.; Uzuleņa, J.: Posevins, D.; Turks, M. *Eur. J. Org. Chem.* **2016**, 1760.
[3] Luginina, J.; Turks, M. *Synlett* **2017**, *28*, 939.