

**THE SYNTHESIS OF BISTRIETHYLAMMONIUM SALT OF
FULLERENE C₆₀ CYCLOPROPANE BISCARBOXYLIC ACID****FULLERĒNA C₆₀ CIKLOPROPĀNDIKARBONSKĀBES
BISTRIETILAMONIJA SĀLS SINTĒZE**

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Key words: fullerene, Bingel's cyclopropanation reaction, bistriethylammonium salt

Introduction

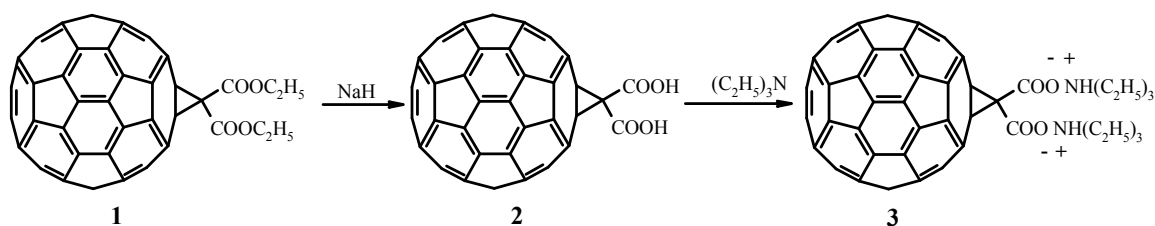
Since the discovery and large-scale production of fullerene C₆₀ the chemistry of fullerenes has become an exciting part of organic chemistry, especially taking into account recent developments in use of novel materials for biological, photophysical and electrochemical applications of these fascinating molecules. Thus, the investigations of fullerene reactivity and its covalent purposeful functionalization for the preparation of new compounds, as well as further side-chain transformations of known fullerene derivatives have been performed. However, the investigation of fullerene chemical properties and the development of practical application of fullerene derivatives can be preventing the some trivial factors, for example, reduced solubility in polar aprotic and protic solvents.

Results and discussion

Searching for new approaches to solve the reactivity and solubility problems of fullerene derivatives (especially in polar solvents, such as tetrahydrofuran, acetonitrile, methanol or water), the synthesis of bistriethylammonium salt of fullerene C₆₀ biscalboxylic acid (**3**) has been performed.

The product **1** was synthesized by cyclopropanation reaction of fullerene with diethylmalonate in the presence of iodine and 1,8-diazabicyclo[5.4.0]undecen-7-ene (DBU) as base adapting a literature procedure [1,2,3]. Cyclopropanation of fullerene, according to the original Bingel protocol, occurs by treating the fullerene with 2-bromomalonate esters in the presence of base (NaH) [2]. Modified procedures allowing *in situ* formation of the 2-bromo- or 2-iodomalonates have also been reported [1,3]. The reaction proceeds very uniformly and only the bonds common two six-member rings of fullerene are attached. The cyclopropane ring fused on the fullerene sphere has generally been found to be very stable [4]. Synthesized compound was hydrolyzed and

fullerenebiscarboxylic acid **2** obtained. Corresponding bistriethylammonium salt of fullerenebiscarboxylic acid **3** was produced after the treatment of C₆₀ derivative **2** with triethylamine.



Successful running of reaction was confirmed with the change of solubility of resulting product in the comparison with carboxylic acid **2** (product is soluble in polar solvents, for example, in methanol, acetonitrile) and IR spectra (for compound **2** C=O was detected at 1700 and 1675 cm⁻¹, and for **3** at 1660 and 1600 cm⁻¹). Presence of nitrogen was detected by element analysis (calculated N 2.74%, found 2.99%).

Synthesis of bis-, tris-, tetra-, penta- and hexaadducts of fullerene biscarboxylic acid triethylammonium salts are under progress.

Experimental

General: Reactions were carried out under dry argon. Solvents were distilled prior to use. Thin layer chromatography was performed on silica gel plates containing a fluorescent indicator (Merck Silica gel 60 F₂₅₄). The IR spectra were recorded in nujol on a „Specord M80” instrument and reported in wave numbers (cm⁻¹). Elemental analyses were determined with „Carbo Erba 1108”.

Diethyl 1,2-methano[60]fullerene-61,61-dicarboxylate 1 was synthesized adapting literature [1,2,3].

1,2-Methano[60]fullerene-61,61-dicarboxylic acid 2 resynthesized according to literature [3]: Diethyl 1,2-methano[60]fullerene-61,61-dicarboxylate **1** 130 mg (0,15 mM) was dissolved in 60 ml of dry toluene, 36 mg (0,15 mM) of suspension of 80 % NaH in mineral oil was added and reaction mixture was heated at 60⁰ C for 3 h. Then reaction mixture was cooled to room temperature and 60 ml of methanol was added. Precipitate was filtered off, washed with methanol, dried. Product was obtained as brown powder, yield of product 86 mg (72 %). IR: 1700; 1675 ((KBr): 1796; 1738 [3].)

1,2-Methano[60]fullerene-61,61-dicarboxylic acid bistriethylammonium salt 3: 1,2-Methano[60]fullerene-61,61-dicarboxylic acid **2** was suspended into 70 ml of absolute methanol, 1,40 ml (1,00 g, 1,00 mM) of triethylamine was added and reaction mixture was stirred at room temperature. During 2 h all starting acid was dissolved and reaction mixture became to dark brown. Then solvent was evaporated, residue was dried in vacuum (3 mm Hg) for 3 h. Yield of product 45 mg (33 %). Melting point > 260⁰ C. IR: 1660; 1600. Element analysis C₇₅H₃₂N₂O₄: calc. C 88.04; H 2.96; N 2.27; found C 76.46; H 3.55; N 2.99. Analysis data for C and H can be incorrect due to incomplete combustion of fullerene derivative.

Acknowledgments

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M. Plotniece, J. Gulbis, V. Kampars. Fullerēna C₆₀ ciklopropāndikarbonskābes bistrietilamonija sāls sintēze. Meklējot jaunus risinājumus fullerēna C₆₀ atvasinājumu reaģētspējas un šķīdītības (īpaši jau polārajos šķīdinātājos, piemēram, tetrahidrofurānā, acetonitrilā, metanolā un ūdenī) palielināšanai, sekmīgi realizēta fullerēna C₆₀ ciklopropāndikarbonskābes bistrietilamonija sāls sintēze. Savienojums iegūts veicot fullerēna C₆₀ ciklopropanēšanas reakciju ar malonskābes dietilesteri joda un 1,8-diazabicyclo[5.4.0]undecēna-7 klātbūtnē. Reakcija norit ātri un ļoti selektīvi, jo tajā piedalās tikai ogleklis-ogleklis saites starp diviem blakusesošajiem sešlocekļu cikliem. Ir zināms, ka fullerēna ciklopropānatvasinājumi ir stabili; tādējādi var realizēt tālākas reakcijas sānu ķēdē. Iegūtais fullerēnciklopropāndikarbonskābes dietilesteris tiek hidrolizēts un veidojās attiecīgā fullerēnciklopropāndikarbonskābe, ko, apstrādājot ar trietilamīnu, iegūst fullerēnciklopropāndikarbonskābes bistrietilamonija sāli.

Plotniece M., Gulbis J., Kampars V. The synthesis of bistriethylammonium salt of fullerene C₆₀ cyclopropane biscalboxylic acid. Searching for new approaches to solve the reactivity and the solubility problems of fullerene derivatives (especially in polar solvents, such as tetrahydrofuran, acetonitrile, methanol or water) the synthesis of 1,2-methano[60]fullerene-61,61-dicarboxylic acid bistriethylammonium salt has been performed. The product was synthesized by cyclopropanation of fullerene with diethylmalonate in the presence of iodine and 1,8-diazabicyclo[5.4.0]undecene-7-ene. The reaction proceeds very uniformly and only the bonds common two six-member rings of fullerene are attached. The cyclopropane ring fused on the fullerene sphere has generally been found to be very stable; therefore it was possible to realize further side-chain reaction. Synthesized diethyl 1,2-methano[60]fullerene-61,61-dicarboxylate was hydrolyzed and 1,2-methano[60]fullerene-61,61-dicarboxylic acid obtained. 1,2-Methano[60]fullerene-61,61-dicarboxylic acid bistriethylammonium salt was produced by treatment of 1,2-methano[60]fullerene-61,61-dicarboxylate with triethylamine.

Плотниче М., Гулбис Ю., Кампарс В. Синтез бистриэтиламмониевой соли циклопропандикарбоновой кислоты фуллерена C₆₀. С целью повышения реакционной способности и растворимости производных фуллерена C₆₀ (особенно в полярных растворителях, таких как, тетрагидрофуран, ацетонитрил, метанол и вода) успешно осуществлен синтез бистриэтиламмониевой соли циклопропандикарбоновой кислоты фуллерена C₆₀. В результате реакции циклопропилирования фуллерена C₆₀ с диэтиловым эфиром малоновой кислоты в присутствии йода и 1,8-дiazобicyclo[5.4.0]ундецена-7. Упомянутая реакция проходит быстро и селективно, в реакции участвуют только связи углерод - углерод между двумя соседними шестичленными циклами. Известно, что циклопропилпроизводные фуллерена стабильные соединения, это позволяет легко осуществлять дальнейшие реакции в боковой цепи. Гидролизуя полученный диэтиловый эфир циклопропандикарбоновой кислоты фуллерена, получают соответствующую циклопропандикарбоновую кислоту, после обработки которой триэтиламино, получают бистриэтиламмониевую соль циклопропандикарбоновой кислоты фуллерена.