DEVELOPMENT OF THE APPROACH TO THE SYNTHESIS OF INDIVIDUAL ISOMERS OF BIS(ORGANO)[60]FULLERENES. BIS(AZAHOMO)FULLERENES

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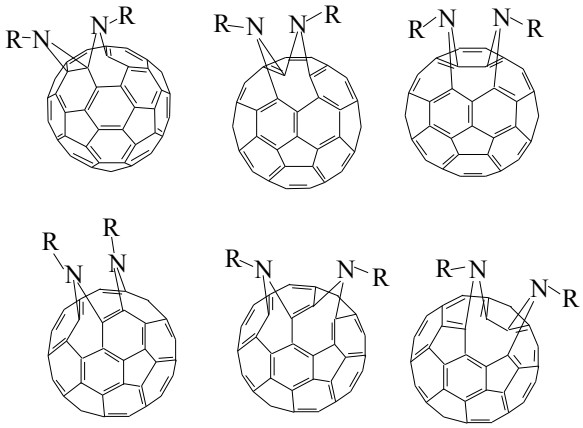
Introduction

As pristine fullerenes, the organofullerenes have unusual electronic, electrochemical, photochemical, optical and biological properties. [1]. The polyaddition to fullerene framework is attractive both for the creation of unique three-dimensional architectures, and the synthesis of compounds having better filming, amphiphilic and biological properties, than the pristine fullerenes or monoorganofullerenes. However the manufacture of individual isomers of the poly(organo)fullerenes is a complicated synthetic problem. As a rule the mixture of isomers form in the reactions, which is hardly separated by conventional methods of the column chromatography.

In this contribution it is proposed to obtain the individual bis(organo)fullerene isomers by the reactions, which pass via the formation of monoazahomofullerenes.

Scheme 1



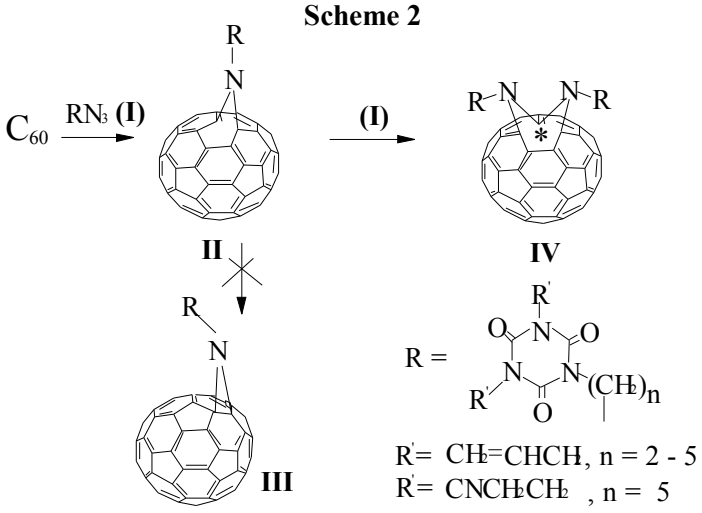
The reactions of monoazahomofullerenes are poorly studied. In spite of that one call assume, that the azide molecule will be bond most likely to the monoazahomofullerenes by the C=C-bonds, which are in immediate proximity to the nitrogen containing bridge Certainly, at that the six isomers (scheme 1) both with open and closed fullerene framework bonds may be formed.

However the analysis of literature and our data allow to suppose, that only one individual isomer will form instead of six isomers. This approach significant simplify the separation of this isomer. To confirmat this assumption we studied the reaction of fullerene C_{60} with isocyanurate substituted azides.

Results and discussion

The reactions of C_{60} with the fourfold excess of the azides **I** were carried out in *o*-dichlorobenzene. The temperature regime and the reaction time was selected, to provide the stability of intermediate monohomofullerenes **II**. In these conditions the compounds **II** not converted to the monofullereno[1,2-b]aziridines **III** (scheme 2) during the reaction, but added one more azide molecule, rezalting in the formation of the bis(organo)fullerenes.

Scheme 2



The unreacted fullerene and the reaction products were separated by the column chromatography. As a result both the individual monoazahomofullerenes **II** and individual isomers **IV** were separated from the reaction mixtures.

The yields of the isomers **IV** were about 10-15% of the amount of pristine fullerene involved in the reactions.

The structure of isomers **IV** was established by the IR, UV-VIS, ^{1}H and ^{13}C NMR spectroscopy, as well as elemental analysis. Most of monoorganofullerenes **II** were synthesized by us earlier [3].

It have been shown that the addition of one azide molecule to compounds **II** led to formation of the same bis(organo)fullerene isomer **IV**, in which two 5,6-bonds were open (bis(azahomo)-fullerenes)). This conclusion based on the ^{13}C NMR spectroscopy data, mainly. It was proved in case of R = COOEt [4] that the compounds of such structure should have the signals at 160 ppm in the ^{13}C NMR spectrum. These signals corresponded to carbon atom C*, bond to two nitrogen atoms. The presence both of such signals in the ^{13}C NMR spectra of compounds **IV** and the signals at 133 – 147 ppm, corresponding to carbon atoms of fullerene spheres, gave grounds to ascribe them the structure of this isomer.

^{1}H NMR spectra of bis(azahomo)fullerenes **IV** and monoazahomofullerenes **II** had no essential distinctions. At the same time in contrast to UV spectra of compounds **II** the absorption bands in the field from 400 to 800 nm were absent in the same spectra for compounds **IV**. Moreover the absorption bands at 527 cm^{-1} in the IR spectra of compounds **IV** had much more low intensity than that in the IR spectra of compounds **II**.

The literature analysis and our data suggest that the formation of one or another isomers of bis(azahomo)fullerenes in the reaction of fullerene C_{60} with organic azides as mainly stipulated by the volume of the organic addend. The smaller measure the more is the probability of the formation of the isomer **IV**.

In the case of reactions under study the plane isocyanurate cycle is separated from the fullerene sphere by the methylene groups, what removes the steric strain in the bis(azahomo)fullerenes molecules **IV**.

The data concerning the electrochemical properties of bis(azahomo)fullerenes are absent in literature. The study of the products **IV** obtained in this work by cyclic voltammetry demonstrated that similar to the pristine fullerene and monoazohomofullerenes **II,** compounds **IV** accepted several electrons step-by-step. The first reduction wave in the CVA- curves was reversible and corresponded to reduction of fullerene sphere of molecules **IV**. It is noted that the neareris the isocyanurate cycle to fullerene sphere the more is effects the electrochemical properties of sphere.

Conclusion

The approach to synthesis of individual isomers of bis(organo)fullerenes have been developed on the basis of the reactions of fullerene C_{60} with organic azides.

References

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