

## SYNTHESIS AND CHARACTERISATION OF NEW PHOSPHORILATED BIS-METHANOFULLERENES

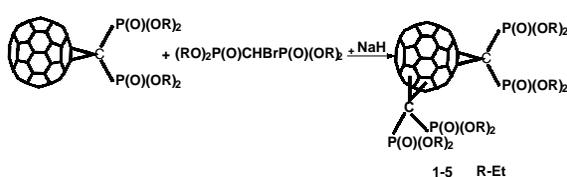
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Organophosphorus derivatives of fullerene C<sub>60</sub> and C<sub>70</sub> is poorly known. At the same time derivants of phosphonic acid and also pyrophosphoric acid there is an important value for biology.

Here we report the result of study of the methods of the synthesis bis-methanofullerenes, containing dialkoxyphosphoryl group.

We synthesized these compounds by the interaction of carbanion of esters di(alkoxyphosphoryl)bromomethanes with di(alkoxyphosphoryl)methanofullerene.



The products of these reactions were isolated by column chromatography on SiO<sub>2</sub> using three-component eluent (toluene-hexane-acetonitrile) with continuous monitoring by HPLC.

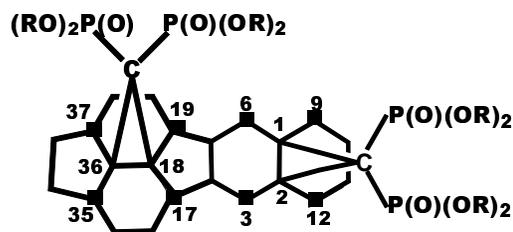
We are separated 5 regioisomeres bis-methanofullerenes (*tr1*, *tr2*, *tr3*, *tr4* and *e*).

The structure and purity of the obtaining bis-methanofullerenes 1-5 is proved by spectrums NMR, IR, UV, mass-spectrums and HPLC. The spectral data confirm formation of the 6,6 adducts.

UV spectrums of regioisomeres shows almost complete coincidence of spectral pattern for malonic acid bis-methanofullerene [1, 2]. Thus the obtained data confirm the "fingerprint" rule proposed in [1,2]. In the mass-spectrums of EI of regioisomeres is peak of molecular ion and some fragmentation ions, generated at disintegration of a molecular ion.

The NMR spectrums bis-methanofullerenes 1-5 clearly indicate the influence of spatial structure on the shielding of <sup>31</sup>P nuclei. The presence of one signal in the <sup>31</sup>P NMR spectrum of *tr3* and *tr1* may indicate that the arrangement of phosphorus atoms in these compounds is similar. This is possible if the cyclopropane fragment in these molecule are in the same plane. Four signals of <sup>31</sup>P are observed for *tr2* and *tr4* isomeres, whereas two signals of phosphorus nuclei are detected for *e* isomer. The scission of signals from phosphorus is caused by a spin-spin interaction non-equivalent of nucleus of phosphorus. (~ J<sub>pp</sub> = 6Hz).

The <sup>13</sup>C NMR spectra of isolated regioisomeres 1-5 show strong dependence of the substituent position on fullerene cage. It is interesting to note a spin-spin coupling of phosphorus and carbon nuclei within fullerene scaffold. The <sup>13</sup>C NMR spectrum of initial monomethanofullerene shows a triplet from the carbon of fullerene cage in the region of 147 ppm. The spectra of compounds 2-5 show 4 triplets in different spectral regions (<sup>3</sup>J<sub>PC</sub> ~ 5 Hz). In spectrum of *tr1* all 4 triplets gives one signal. On the Scheme shows what atoms of carbon and the phosphorus participate in a spin-spin interaction in case of an equatorial isomer *e*.



As it is visible from this Scheme, the atoms 3,6,9,12 interact with two atoms of phosphorus, and atoms 17, 19, 35 and 37 - with two other atoms of phosphorus. Thus there are triplets in various ranges of a spectrum. The analysis of spectrums NMR discharged 1-5 allows to make a deduction about an opportunity to "label" particular of carbon atoms of fullerenes shell.

We carried out the quantum-chemical calculations of new bis-methanofullerenes containing phosphonate group at various level of the theory with use of the software packages GAMESS (AM1, PM3, MNDO), density functional theory-PRIRODA(PBE/TZ2P).

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### References

1. Q. Lu, D.L. Schuster, S.R. Wilson J. Org. Chem., 1996, **61**, 4764
2. F. Djojo, A. Herzog, I. Lampart, F. Hampel, A. Hirsch, Chem. Eur. J. 1996, **12**, 1537