Phosphorylated azahomo[60]fullerene: synthesis and electrochemical properties

I. P. Romanova,* G. G. Yusupova, A. A. Nafikova, D. G. Yakhvarov, O. A. Larionova, and O. G. Sinyashin

A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: romanova@iopc.knc.ru

A reaction of [60]fullerene with *O*,*O*-dibutyl azidophosphate affords a first representative of phosphorylated azahomo[60]fullerenes, which is easier to reduce electrochemically than the starting C_{60}.

Key words: [60]fullerene, *O*,*O*-dialkyl azidophosphates, phosphorylated azahomo[60]fullerene, electrochemistry.

The synthesis of stronger electron-withdrawing organofullerenes (compared to nonmodified fullerenes) is an important problem of the chemistry of fullerenes.[1] The most promising approach to the solution of this problem combines the formation of heterocyclic fragments ([6,6]-closed adducts) at the surface of the fullerene cage or extension of the fullerene sphere by inserting a heteroatomic bridge ([5,6]-opened adducts), with electron-withdrawing substituents in the heterocycles or bridges.[2] Using this approach, we obtained isocyanurato- and pyrimidinoazahomo[60]fullerenes[3,4] and fullerenoimidazopyrimidines[5], which are characterized by a higher electron affinity (EA) than the EA of the starting C_{60}. It was interesting to study the possibility of increasing the EA of the fullerene sphere in adducts through the use of phosphorylated fragments.

Phosphorylation of fullerenes has been investigated since the first steps in the study of their chemical properties were made.[6,7] The effect of phosphorylated fragments on the electronic state of the fullerene sphere was studied for a series of fullerene-containing tertiary phosphines, phosphinites, and alkyl phosphonates,[8] as well as for some phosphorylated methano[1,2][60]fullerenes.[9] All of these adducts were more difficult to reduce electrochemically than nonmodified C_{60}.

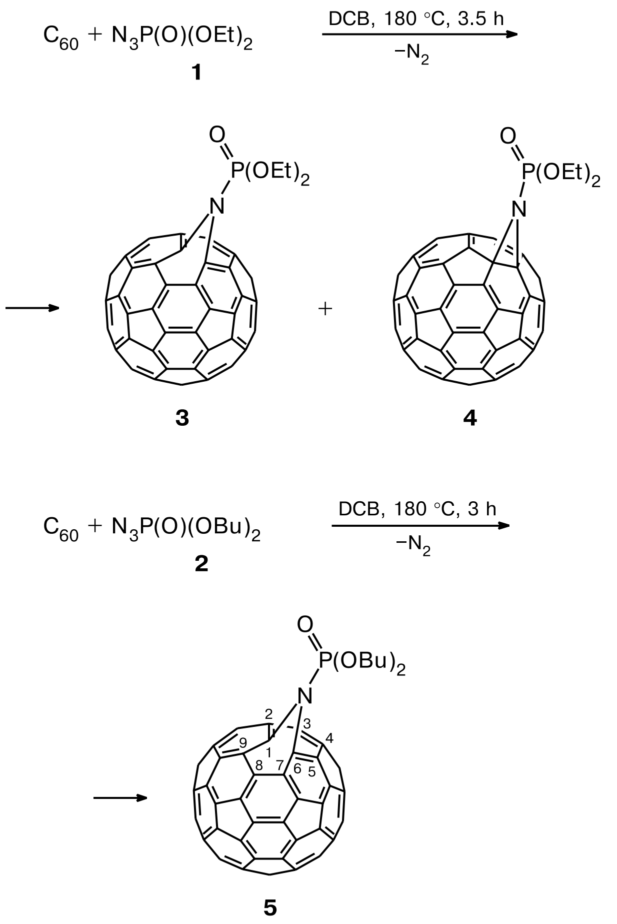
Unlike relevant studies dealing with known phosphorylated organofullerenes, the present work was aimed at synthesizing a compound in which a phosphorylated fragment would be connected to the fullerene sphere by an N heteroatom. First, we attempted to create such a structure by reacting C_{60} with azidodiphenylphosphinic acid.[10] However, the expected phosphorylated [60]fullereno[1,2-*c*]triazoline, [60]fullereno[1,2-*b*]aziridine, or azahomo[60]fullerene were not obtained. Instead, these reactions yielded acyclic adducts, namely, individual 2-[*N*-(diphenylphosphoryl)amino]-1-hydroxy[60]fullerene and a mixture of *N*-(diphenylphosphoryl)[60]fullereno[1,2-*b*]aziridine with a partially hydrolyzed bisadduct of phosphorylated azide and fullerene. Such an unusual result was theoretically important for discussing mechanisms of these reactions. However, the adducts obtained were poorly soluble, and the effect of the phosphorylated fragment on the electrochemical reduction of the fullerene sphere was not studied. In the present work, the adduct solubility was increased by attaching hydrophilic substituents to the P atom. For the first time, *O*,*O*-dialkyl azidophosphates were involved in the reaction with C_{60}.

The reactions of C_{60} with *O*,*O*-diethyl (**1**) and *O*,*O*-dibutyl azidophosphate (**2**) were studied in *o*-dichlorobenzene (DCB) at 180 °C (Scheme 1). At lower temperatures, these reactions did not occur, and the starting fullerene was almost completely recovered from the reaction mixtures by column chromatography on silica gel.

After C_{60} was heated with azide **1** at 180 °C for 3.5 h, the mass spectrum of the reaction mixture contained peaks with m/z 720, 871, 1026, 1175 and 1326. The peaks with m/z 720 and 871 corresponded to the starting fullerene and monoadducts $C_{60}NP(O)(OEt)_2$, while the other peaks corresponded to bis-, tris-, and tetrakisadducts $C_{60}[NP(O)(OEt)_2]_n$ ($n = 2—4$). The reaction mixture was separated by column chromatography on silica gel into four fractions. Fraction 1 contains the unreacted fullerene, while fraction 4 is an unseparable mixture of polyadducts (HPLC and MS data). Two intermediate fractions 2 and 3 contain monoadducts $C_{64}H_{10}NO_3P$ (<70% purity) admixed with mono- and polyadducts. Major monoadducts of these fractions are different. Both intermediate fractions were purified by column chromatography on silica

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 140—143, January, 2004.

Scheme 1



gel to give individual monoadducts with retention times of 4.4 (R_f 0.27; Silufol, toluene—Et_2O, 10 : 2) and 5.1 min (R_f 0.37). The isolated fractions were evaporated to dryness, and UV spectra of the solid residues in CH_2Cl_2 were recorded. Monoadducts were assigned the structures of a [5,6]-adduct (most likely, azahomo[60]fullerene **3**) and a [6,6]-closed adduct ([60]fullereno[1,2-*b*]aziridine **4**). However, the yields of individual monoadducts **3** and **4** were very low (a few per cent), most probably because they are poorly soluble in such solvents as toluene, CH_2Cl_2, and $CHCl_3$. During the column chromatography, the main amount of the monoadducts were kept in the top part of the column. For the same reason, we failed to record NMR spectra of adducts **3** and **4**.

Thus, the presence of ethoxy groups at the P atom in azide **1** makes it possible to obtain new representatives of phosphorylated organofullerenes; however, they are difficult to purify and study because of their poor solubilities.

The reaction of C_{60} with azide **2** was carried out at 180 °C for 3 h (see Scheme 1). The HPLC profile of the reaction mixture contains a low-intensity peak of the unreacted fullerene and two peaks of reaction products. The starting fullerene, product **5**, and mixtures of bisadducts were isolated by column chromatography. According to the HPLC, TLC, and MS data, product **5** is an individual monoadduct ($C_{68}H_{18}NO_3P$). When dry, it is a dark brown powder. Its IR spectrum shows bands of the fullerene and phosphonate fragments. This adduct is well soluble in toluene, $CHCl_3$, and CH_2Cl_2, which allowed its spectroscopic studies.

The ^{31}P NMR spectrum of adduct **5** contains a single signal at δ –1.8; its chemical shift is the same as that of the P atom in the spectrum of the starting azide **2**. The ^1H NMR spectrum of adduct **5** is trivial for a dibutoxyphosphoryl fragment. The multiplets of the AA´XX´YY´ spin systems are degenerated into simple multiplet structures because the P—O—Alk chains are labile and, accordingly, the chemical shifts and vicinal spin-spin coupling constants are averaged. The central multiplet signals relating to the protons of the methyl and two next methylene groups appear at the same δ values as for analogous protons in the starting azide **2**. The signals for the protons of the methylene groups directly bound to the O atom were slightly shifted downfield.

The ^{13}C NMR spectrum of adduct **5** shows two sets of lines at δ 13—68 and 134—148. The signals of the C atoms of the Bu groups were assigned from their multiplicity. In the ^{13}C NMR spectrum with proton decoupling, the butoxy groups are manifested by two doublets at δ 68.54 and 32.75 (the former relates to the C atom directly bound to the O atom) and two singlets of the methylene (δ 19.56) and methyl groups (δ 13.92). In the spectrum without proton decoupling, these signals are split into triplets or quartets of multiplets, respectively. It should be noted that these signals are shifted only slightly relative to the corresponding signals in the spectrum of the starting azide **2**.

The ^{13}C NMR spectrum of adduct **5** contains no signals at δ 70—110 for the sp^3-hybridized C atoms of the fullerene sphere. The latter was manifested by 30 signals at δ 134—148, the number and relative intensities of which suggest the azahomo[60]fullerene structure of adduct **5** with symmetry C_s about a plane perpendicular to the axis of the former [5,6]-bond. Five of the 30 signals were split as a result of the C—P spin-spin coupling, which allowed their identification. A signal at δ 143.81 (1 C, $J_{C,P}$ = 1.8 Hz) most likely belongs to the C(8) atom in the close vicinity of the P atom. The intensity of the other signals is 2 C. Among them, the signal at δ 138.80 characterized by the lowest spin-spin coupling constant ($J_{C,P}$ = 1.8 Hz) was assigned to the C(3) and C(4) atoms, which are most distant from the P atom. Because signals for the C(2), C(5), C(7), and C(9) atoms should not be very different in chemical shift, signals at δ 134.91 and 137.22 with $J_{C,P}$ = 3.7 Hz were assigned to these atoms. The signal at δ 146.77 ($J_{C,P}$ = 3.7 Hz) was assigned to the C(1) and C(6) atoms directly bound to the organic fragment.

Table 1. Reduction potentials (E_p^{Red}) and wave peak currents (I_p^{Red}) in the cyclic voltammograms of C_{60} and compound **5**

Compound	E_p^{Red}/V	I_p^{Red}/μA
C_{60}	−0.83	4.2
	−1.24	3.8
	−1.70	3.9
	−2.16	4.6
5	−0.72	3.3
	−1.17	6.0
	−1.66	3.4

Note. Cyclic voltammograms were recorded in DCB—MeCN (3 : 1) at 25 °C; the concentration of solutions is $1 \cdot 10^{-3}$ mol L^{-1}; the 0.1 *M* Bu_4NBF_4 as a supporting electrolyte; glassy carbon cathode; Ag/0.01 *M* $AgNO_3$ in MeCN as a reference electrode; linear scan rate 50 mV s^{-1}.

The UV spectrum of adduct **5** is typical[3,4] of azahomofullerenes, which agrees with the ^{13}C NMR data.

Thus, the reaction of C_{60} with azide **2** in boiling DCB for 3 h yields *O*,*O*-dibutyl (azahomo[60]fullereno)phosphate **5** as the major product and bisadducts of fullerene and azide **2** as by-products; the compounds obtained were characterized by different physicochemical methods.

To estimate the electron affinity of adduct **5**, its electrochemical reduction was studied by cyclic voltammetry (CV). The results obtained were compared with the CV data for the starting C_{60} (Table 1).

The cyclic voltammogram of adduct **5** shows three reduction peaks. The first peak is reversible and corresponds to the transfer of one electron to the fullerene sphere. The first reduction peak appears at a higher potential than the analogous peak of C_{60} ($\Delta E^{Red,1} = 110$ mV), which corresponds to EA = 2.76 eV. Thus, adduct **5** is a stronger electron acceptor than C_{60}. It is worth noting that this adduct is the first representative of phosphorylated azahomo[60]fullerenes.

Hence, the phosphonate fragment can be used to enhance the electron affinity of the fullerene sphere in organofullerenes.

Experimental

IR spectra were recorded on a Bruker IFS-113V FTIR spectrometer (KBr pellets). ^{31}P NMR spectra were recorded on a Bruker CXP-100 instrument (36.47 MHz) with 85% H_3PO_4 as the external standard. ^1H NMR spectra were recorded on a Bruker WM-250 instrument (250.13 MHz) with Me_4Si as the internal standard; ^{13}C NMR spectra were recorded on a Bruker MSL-400 instrument (ν_0 = 100.62 MHz). The δ values are referenced to a signal of $CDCl_3$. UV spectra were recorded on a Specord UV-VIS instrument. HPLC analysis was carried out on a Gilson chromatograph (UV detector, column with the reversed phase C_{18} (Partisil-5 ODS-3), toluene—MeCN (1 : 1 v/v) as the eluent, 0.3 mL min^{-1}). MS spectra were recorded on a MALDI TOF MS instrument (Dynamo) with the use of *p*-nitroaniline matrix. In CV studies, the working electrode was a fixed glassy carbon disk (working area 3.14 mm^2). Cyclic voltammograms were recorded in a three-electrode electrochemical cell on a PI-50-1 potentiostat equipped with a PR-8 programmer and plotted by an XY-recorder at a linear scan rate of 50 mV s^{-1}. Cyclic voltammograms were recorded in DCB—MeCN (3 : 1) with 0.1 *M* Bu_4NBF_4 as a supporting electrolyte. The reference electrode was Ag/0.01 *M* $AgNO_3$ in MeCN. A platinum wire served as an auxiliary electrode. Measurements were carried out in a temperature-controlled (25 °C) cell under argon. DCB was dried by distillation over P_2O_5. [60]Fullerene was synthesized at the G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences (Nizhnii Novgorod) by the electric arc method and purified by preparative chromatography.[11]

Processing of the CV data. The measurement error for E_p^{Red} was ≤10 mV. The electron affinity of the adduct **5** was calculated by the approximating formula $E_p^{Red} = 1.0EA_{exp}$ + const ($EA_{exp} = 3.48 + E_p^{Red}$, for the system Ag/0.01 *M* $AgNO_3$ in MeCN).

O,*O*-Diethyl (**1**) and *O*,*O*-dibutyl azidophosphates (**2**) were prepared according to a known procedure.[12]

Dibutyl azidophosphate (2). IR, ν/cm^{-1}: 1027 (P—O—C); 1270 (P=O); 2161 (N_3); 1466, 2875, 2936, 2963 (CH). ^{31}P NMR ($CDCl_3$), δ: −1.8. ^1H NMR ($CDCl_3$), δ: 0.95 (t, 6 H, 2 Me, $^3J_{H,H}$ = 7.3 Hz); 1.43 (sextet, 4 H, 2 CH_2, $^3J_{H,H}$ = 7.3 Hz); 1.70 (quintet, 4 H, 2 CH_2, $^3J_{H,H}$ = 7.5 Hz); 4.13 (q, 4 H, 2 CH_2, $^3J_{H,H}$ = 6.8 Hz, $^3J_{P,H}$ = 7.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.55 (qm, 2 Me, $^1J_{C,H}$ = 125.0 Hz); 18.72 (tm, 2 CH_2, $^1J_{C,H}$ = 126.0 Hz); 32.28 (tm, 2 CH_2, $^1J_{C,H}$ = 126.0 Hz, $^2J_{C,P}$ = 0 Hz); 68.64 (tm, 2 CH_2, $^1J_{C,H}$ = 150.0 Hz, $^2J_{C,P}$ = 3.8 Hz).

***O*,*O*-Dibutyl (azahomo[60]fullereno)phosphate (5).** Azide **2** (91.6 mg, 0.39 mmol) was added to a solution of C_{60} (93.6 mg, 0.13 mmol) in 25 mL of dry DCB, and the reaction mixture was stirred at 180 °C for 3 h. The HPLC profile of the reaction mixture contained three peaks with retention times of 3.5 (bisadduct), 4.6 (monoadduct), and 6.4 min (C_{60}). The solvent was removed *in vacuo*, and the residue was separated by column chromatography on silica gel with toluene as the eluent to give C_{60} (20 mg, 21%), compound **5** (24 mg, 20%), and a mixture of bisadducts. Compound 5. R_f 0.48 (TLC, Silufol plates, toluene—Et_2O (10 : 2)). Retention time: 4.6 min (HPLC). UV (CH_2Cl_2), λ_{max}/nm: 259, 326, 483, 537, 588. IR, ν/cm^{-1}: 525 ($C_{60}N$); 1024 (P—O—C); 1277 (P=O); 1449, 2845, 2922, 2955 (CH). ^{31}P NMR ($CDCl_3$), δ: −1.8. ^1H NMR ($CDCl_3$), δ: 0.96 (t, 6 H, 2 Me, $^3J_{H,H}$ = 7.2 Hz); 1.43 (sextet, 4 H, 2 CH_2, $^3J_{H,H}$ = 7.0 Hz); 1.70 (quintet, 4 H, 2 CH_2, $^3J_{H,H}$ = 7.0 Hz); 4.37 (q, 4 H, 2 CH_2, $^3J_{H,H}$ = 6.7 Hz, $^3J_{P,H}$ = 6.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.92 (qm, 2 Me, $^1J_{C,H}$ = 124.0 Hz); 19.56 (tm, 2 CH_2, $^1J_{C,H}$ = 131.0 Hz); 32.75 (tm, 2 CH_2, $^1J_{C,H}$ = 124.0 Hz, $^2J_{C,P}$ = 6.3 Hz); 68.54 (tm, 2 CH_2, $^1J_{C,H}$ = 150.0 Hz, $^2J_{C,P}$ = 6.4 Hz); 134.60, 134.91 ($J_{C,P}$ = 3.7 Hz), 137.22 ($J_{C,P}$ = 3.7 Hz), 138.02, 138.11, 138.80 ($J_{C,P}$ = 1.8 Hz), 139.41, 140.15, 141.71, 142.28, 143.16, 143.25, 143.34, 143.55, 143.58, 143.77, 144.02, 144.27, 144.56, 144.68, 144.82, 145.14, 146.77 ($J_{C,P}$ = 3.7 Hz), 147.80 (all 2 C, C_{60}); 144.29, 144.48 (both 4 C, C_{60}); 143.81 ($J_{C,P}$ =

1.8 Hz), 144.21, 142.15, 143.48 (all 1 C, C_{60}). MS, *m/z*: 929 (calculated: 927.65).

The authors are grateful to V. P. Gubskaya for discussing the HPLC data.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 02-03-32932 and 02-03-06076 (MAS)), The Ministry of Industry, Science, and Engineering of the Russian Federation (Contract No. 14/2002 within the scope of Contract Nos. 41.002.1.1.405 and MK-749.2003.03).

References

1. D. V. Konarev and R. N. Lyubovskaya, *Usp. Khim.*, 1999, **68**, 23 [*Russ. Chem. Rev.*, 1999, **68** (Engl. Transl.)].
2. B. M. Illesca and N. Martin, *J. Org. Chem.*, 2000, **65**, 5986.
3. O. G. Sinyashin, I. P. Romanova, G. G. Yusupova, A. A. Nafikova, V. I. Kovalenko, N. M. Azancheev, V. V. Yanilkin, and Y. G. Budnikova, *Mendeleev Commun.*, 2000, 61.
4. I. P. Romanova, V. V. Kalinin, D. G. Yakhvarov, A. A. Nafikova, V. I. Kovalenko, P. V. Plehanov, G. L. Rusinov, and O. G. Sinyashin, *Mendeleev Commun.*, 2002, 51.
5. I. P. Romanova, V. V. Kalinin, A. A. Nafikova, D. G. Yakhvarov, V. V. Zverev, V. I. Kovalenko, G. L. Rusinov, P. V. Plekhanov, V. N. Charushin, and O. G. Sinyashin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 163 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 173].
6. F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157.
7. I. A. Nuretdinov, V. P. Gubskaya, N. I. Shishikina, G. M. Fazleeva, L. Sh. Berezhnaya, I. P. Karaseva, F. G. Sibgatullina, and V. V. Zverev, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 317 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 320].
8. S. Yamago, M. Yanagawa, N. Mukai, and E. Nakamura, *Tetrahedron*, 1996, **52**, 5091.
9. V. V. Yanilkin, N. V. Nastapova, V. P. Gubskaya, V. I. Morozov, L. Sh. Berezhnaya, and I. A. Nuretdinov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 70 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 72].
10. I. P. Romanova, O. G. Sinyashin, G. G. Yusupova, V. I. Kovalenko, Yu. Ya. Efremov, Yu. V. Badeev, I. I. Vandyukova, and I. A. Arakelyan, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 2168 [*Russ. Chem. Bull.*, 1999, **48**, 2144 (Engl. Transl.)].
11. V. L. Karnatsevich, M. A. Lopatin, A. I. Kirillov, and B. S. Kaverin, *The VIII Int. Conf. ICHMS´2003 "Hydrogen Materials Science and Chemistry of Carbon Nanomaterials" (Sudak (Crimea, Ukraine), 14—20 September, 2003), Abstrs.*, Kiev, 2003, 486.
12. F. Scott, R. Riordan, and P. D. Morton, *J. Org. Chem.*, 1962, **27**, 4255.

Received December 27, 2002;
in revised form October 20, 2003