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Reactions of carbanions of bis(dialkoxyphosphoryl)bromomethane with fullerenes C_{60} and C_{70}

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The reactions of carbanions of bis(dialkoxyphosphoryl)bromomethanes with fullerenes C_{60} and C_{70} afforded new bis(dialkoxyphosphoryl)methanofullerenes C_{60} and C_{70}, respectively, whose structures were established by spectroscopic methods.

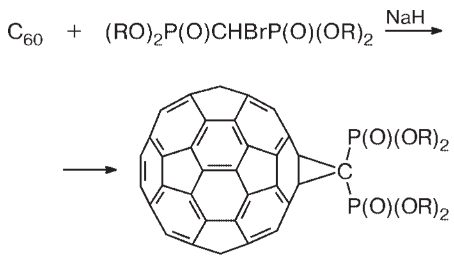
Key words: bis(dialkoxyphosphoryl)bromomethanes, fullerenes C_{60} and C_{70}, methanofullerenes, UV and IR spectra, ^{1}H, ^{13}C, and ^{31}P NMR spectra, the Bingel reaction, quantum-chemical calculations, PM3 method.

The chemistry of methanofullerenes have attracted growing interest[1—4] due to the fact that mild conditions of the synthesis allow one to insert various functional groups into the fullerene molecule thus preparing new organic derivatives of fullerene. It should be noted that malonic acid derivatives are generally used as the starting components in these reactions. Recently, we have described the use of phosphonoacetate derivatives for this purpose.[5—7] Previously,[8] methanofullerenes containing the P atom in the β position with respect to the 61st C atom have been prepared. In the present study, we report the results of the synthesis of bis(dialkoxyphosphoryl)methanofullerenes C_{60} and C_{70}. Such fullerene derivatives containing the bis(dialkoxyphosphoryl)methane fragment can be used for the preparation of new materials and biologically active compounds and also as ligands in new types of metal complex catalysts. Some results described in the present study have been reported previously.[6,7]

Results and Discussion

The reactions of bis(dialkoxyphosphoryl)bromomethanes with fullerene C_{60} in the presence of NaH in toluene afforded the corresponding bis(dialkoxyphosphoryl)methanofullerenes **1** and **2** (Scheme 1).

Scheme 1



1, 2

R = Et (**1**), Pr^i (**2**)

Bis(dialkoxyphosphoryl)bromomethanes are more reactive with respect to fullerene C_{60} as compared to the known bromo(dialkoxyphosphoryl)acetates.[5] At ~20 °C, the starting fullerene C_{60} was virtually completely consumed within 1 h after the beginning of the reaction to give monoadduct **1** in 71% yield. It should be noted that compound **1** has been synthesized previously[9] in 38% yield by the reaction of fullerene C_{60} with the product generated by iodination of bis(diethoxyphosphoryl)methane with iodine in the presence of NaH for 9 h.

Compound **2** was formed even faster (15—20 min) and also in high yield (~80%). The reaction conducted over a longer period of time gave rise to di- and polyadducts (HPLC data). Taking into account that adducts both at the 5,6- and 6,6-bonds of the fullerene core can be formed, we calculated the heats of formation of these compounds by the semiempirical PM3 method (the GAMESS program package). These calculations demonstrated that the addition at the 6,6-bond is energetically more favorable than the addition at the 5,6-bond (511.09 and 534.16 kcal mol^{-1}, respectively).

The structures of the resulting compounds were studied by spectroscopic methods. Thus the UV spectra of compounds **1** and **2** have absorption bands at 326, 427, 491, and 535 nm. The presence of a medium-intensity narrow absorption band at 427 nm is a simple and reliable criterion of the formation of cycloadducts at the closed

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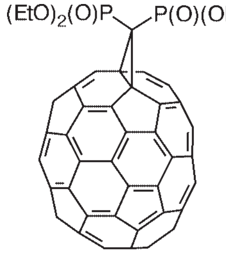
6,6-bond.[1—9] The IR spectra of compounds **1** and **2** have absorption bands at 526, 573, and 1428 cm^{-1} typical of many monoadducts of fullerene C_{60}. The ^{31}P NMR spectra of these compounds have singlets at δ ~14.

It should be noted that the ^{13}C NMR spectra of methanofullerenes **1** and **2** are, as expected, simpler as compared to the spectra of non-symmetrical derivatives of fullerene C_{60}. Thus the ^{13}C NMR spectra of dimethoxyphosphoryl[61]methoxycarbonyl[61]methanofullerene[C_{60}] and its ethoxy and menthyloxycarbonyl analogs contain 25, 29, and 46 signals, respectively,[5] whereas the ^{13}C NMR spectra of compounds **1** and **2** contain only 17 signals of the fullerene core. Previously,[5] we have noted that the signal at δ 147 in the ^{13}C NMR spectra of phosphorylated methanofullerenes is split into a doublet. Analogously, the ^{13}C NMR spectra of bis(dialkoxyphosphoryl)methanofullerenes **1** and **2** show doublets at δ ~147—148 ($^3J_{P,C} \approx 5.0$ Hz). In the ^{13}C NMR spectra of compounds **1** and **2**, the signals for the alkoxy groups are observed at δ ~15 and 17 (Me groups) and at δ ~62 and 64 (CH_2O and CHO groups), respectively. The C(61) atom of compounds **1** and **2** gives a low-intensity triplet at δ 39.38 and 41.64 with $J_{P,C}$ = 151.6 Hz and $J_{P,C}$ = 150.0 Hz, respectively. The signals for the sp^3-hybridized C atoms of the fullerene core involved in the three-membered ring are observed as triplets at δ 67.46 and 69.71 with $^2J_{P,C}$ = 4.6 Hz and $^2J_{P,C}$ = 4.1 Hz, respectively.

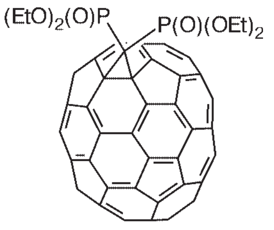
The ^{1}H NMR spectrum of compound **1** has signals for the methyl (δ 1.21) and methylene (δ 4.29) protons of the ethoxy groups bound to the P atom. The ^{1}H NMR spectrum of compound **2** shows two doublets for the protons of the Me groups (δ 1.32 and 1.41) and two multiplets for the protons of the CH—O groups (δ 5.01 and 5.07).

The question as to the difference in the reactivity of fullerenes C_{60} and C_{70} in cycloaddition was discussed in the literature,[10,11] in particular, in the studies with the use of calculation methods. It was demonstrated that the Diels—Alder reaction of fullerene C_{60} with cyclopentadiene in toluene proceeded seven times more rapidly than that with fullerene C_{70}.[11] However, calculations for the reactions of fullerenes with butadiene in the gas phase revealed that fullerene C_{70} is somewhat more favorable.[10] It was concluded that orbital interactions are of importance in these reactions, including the energies of the lowest unoccupied MO (LUMO and LUMO1) of fullerene and the highest occupied MO (HOMO and HOMO1) of the diene, and the medium (solvation effects) also makes a contribution to the course of the reactions of fullerenes with various reagents. Data on phosphorylated fullerene derivatives are virtually lacking in the literature. It should be noted that the adducts of phosphonyl radicals to fullerene C_{70} have been studied earlier by ESR spectroscopy without their isolation in the individual form.[12]

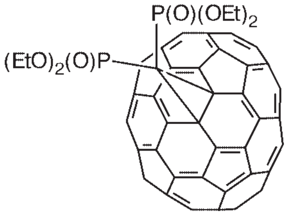
When considering the reactivities of fullerenes C_{60} and C_{70} in the reactions with carbanions of bis(dialkoxyphosphoryl)bromomethane, one must also take into consideration that the formation of the corresponding methanofullerene occurs at the 6,6-bond. This is evidenced[3,5] both by the spectroscopic data and the calculated heats of formation of methanofullerenes at the 6,6- and 5,6-bonds (see above). Note that the molecule of fullerene C_{70} has three types of nonequivalent 6,6-bonds (**a—b**, **c—c**, and **d—e**) due to which three products, *viz*., **A**, **B**, and **C**, can be formed. The **a—b** and **c—c** bonds in fullerene C_{70} are somewhat shorter (by ~0.03 Å) than the **d—e** bonds located closer to the equatorial region. The molecule of fullerene C_{60} contains 30 equivalent 6,6-bonds.



A
(**a—b**)



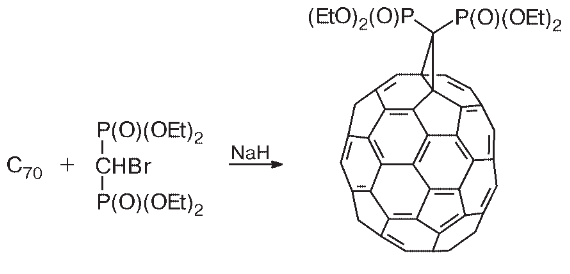
B
(**c—c**)



C
(**d—e**)

We studied the reaction of bis(diethoxyphosphoryl)bromomethane with fullerene C_{70} in toluene in the presence of NaH as a base (Scheme 2). The reaction proceeded at ~20 °C to produce primarily bis(diethoxyphosphoryl)methanofullerene C_{70} (**3**) along with several minor products (HPLC). Based on comparison of these results with the known data[13] on cycloaddition of *N*-methylazomethine to fullerene C_{70}, which gave rise to the addition products at the **a—b**, **c—c**, and **d—e** bonds, it can be concluded that the carbanion of bis(diethoxyphosphoryl)bromomethane is added to fullerene C_{70} at three types of 6,6-bonds to yield product **A**, **B**, and **C**. Judging from the results of calculations, the heats of formation of methanofullerenes **A** and **B** at the **a—b** and **c—c** bonds differ only slightly (582.89 and 583.96 kcal mol^{-1}, respectively). To the contrary, the formation of cycloadduct **C** at the **d—e** bond requires 600.6 kcal mol^{-1}, *i.e.*, the formation of the addition products to fullerene C_{70} at 6,6-bonds of the **a—b** and **c—c** types is energetically more preferable (calculations with the use of the GAMESS program package were carried out for bis(dimethoxyphosphoryl)methanofullerene C_{70} as the model compounds).

Scheme 2



3

We succeeded in chromatographic isolation of compound **3** in amounts sufficient for the study by spectroscopic methods. Based on comparison of the spectroscopic data with the results of calculations and the data available in the literature,[13] we assigned structure **A** to methanofullerene **3**. This structure corresponds to the addition at the **a—b** bond. Thus the ^{13}C NMR spectrum of compound **3** has two signals for the sp^3-hybridized C atoms of the fullerene core (δ 64.10 and 65.01 with $J_{P,C}$ = 5.0 Hz and $J_{P,C}$ = 4.7 Hz, respectively). In the case of the **c—c** adduct, these C atoms would, most likely, give identical signals because these atoms have the same environment. In addition, the signals for the sp^2-hybridized C atoms involved in spin-spin coupling with the ^{31}P nucleus are also different (δ 138.13, 138.17, and 144.46, 144.50; $J_{P,C}$ = 5.3 Hz in all cases).

The ^{31}P NMR spectrum of the compound obtained shows a singlet at δ 14. In the ^{13}C NMR spectrum, 38 signals belong to the C atoms of the fullerene core and the ethoxy groups each give two signals for the C atoms. It is known[14] that the ^{13}C NMR spectrum of unsubstituted fullerene C_{70} has five signals, which differ in intensity (1 : 2 : 1 : 2 : 1). After the attachment of the diphosphonomethane fragment to fullerene C_{70}, ten C atoms lying in its equatorial region give five signals with virtually equal intensities (δ 131.55, 131.62, 131.86, 133.95, and 134.23) instead of one signal (δ ~130) observed in the NMR spectrum of unsubstituted fullerene C_{70}. It should be noted that the ^{13}C NMR spectrum of compound **3**, like the spectra of compounds **1** and **2**, has doublet signals at δ 138.13, 138.17 and 144.46, 144.50 with $^3J_{P,C}$ = 4.7 Hz and $^3J_{P,C}$ = 5.0 Hz, respectively.

The ^1H NMR spectrum of compound **3** shows signals for the protons of the ethoxy groups bound to the P atom. The protons of the Me groups give two triplets with equal intensities whose chemical shifts differ by 0.14 ppm. The signals for the protons of the methylene groups are observed as two doublets of quartets with equal intensities whose chemical shifts differ also by 0.14 ppm. We assumed that the difference in shielding of the protons of the ethoxy groups in bis(diethoxyphosphoryl)methanofullerene C_{70} results from the effect of the fullerene core. Analysis of the charges on the atoms of the methoxy groups in bis(dimethoxyphosphoryl)methanofullerene[C_{70}] (which was used as the model compound in quantum-chemical calculations) both at the **a—b** and **c—c** bonds showed that the charges on these groups bound to the same P atom are different. Apparently, this is the reason for the difference in shielding of the protons of the ethoxy groups bound to the P atom in compound **3**. An analogous nonequivalence of the protons of the ethoxy groups has been observed previously[15] for 2-diethoxyphosphoryl-5-phenyl-3,4-fullero[60]pyrrolidine.

To reveal the differences in the reactivity of fullerenes C_{60} and C_{70} in cycloaddition to the carbanion of bis(diethoxyphosphoryl)bromomethane, we examined the reaction of the latter with a mixture of fullerenes C_{70}—C_{60} (3 : 1). The course of the reaction was monitored by HPLC, which allowed us to establish that fullerene C_{60} was consumed more rapidly than fullerene C_{70}. Thus fullerene C_{60} was not detected in the reaction mixture even 40 min after the beginning of the reaction, whereas fullerene C_{70} remained unconsumed after 3 h.

Experimental

Fullerenes C_{60} (99.5% purity) and C_{70} (98% and 75% purities) were prepared according to procedures described previously.[16] The purities were checked by HPLC on a Gilson chromatograph (UV detector, column with the reversed phase C_{18} (Partisil-5 ODS-3), a 1 : 1 (v/v) toluene—MeCN mixture as the eluent). The organic solvents were dried and distilled.

All chemical operations were carried out in an atmosphere of dry argon. The UV spectra were recorded on a Specord M-40 spectrophotometer in CH_2Cl_2. The IR spectra were measured on a Bruker Vector-22 Fourier spectrometer (in KBr pellets). The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker WM-250 (250 (^1H) and 101.2 MHz (^{31}P)) and Bruker MSL-400 (100.57 (^{13}C), 400.00 (^1H), and 161.92 MHz (^{31}P)) spectrometers in $CDCl_3$ using Me_4Si and 85% H_3PO_4, respectively, as the standards.

Bis(diisopropoxyphosphoryl)bromomethane. A solution of bis(diisopropoxyphosphoryl)methane (2.9 g, 8.4 mmol) in toluene (10 mL) was added dropwise to a suspension of NaH (0.2 g, 8.3 mmol) in anhydrous toluene at ~20 °C. The reaction mixture was stirred for 1.5 h and cooled to 0—5 °C. Then a solution of Br_2 (1.35 g, 8.4 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The mixture was stirred for 3.5 h and washed with distilled water (2×20 mL). The organic layer was dried with $MgSO_4$, the solvent was distilled off *in vacuo*, and the residue was distilled. Bis(diisopropoxyphosphoryl)bromomethane was obtained in a yield of 1.05 g (29.4%), b.p. 116 °C (0.2 Torr), n_D^{20} 1.4551 (*cf.* lit. data[17]: n_D^{25} 1.4528), d_4^{20} 1.2470. Found (%): C, 36.66; H, 6.63; Br, 18.53; P, 14.49. $C_{13}H_{29}BrO_6P_2$. Calculated (%): C, 36.97; H, 6.87; Br, 18.72; P, 14.69. ^{31}P NMR, δ: 15.0.

Bis(diethoxyphosphoryl)bromomethane was prepared analogously in 31.9% yield, b.p. 114 °C (0.15 Torr), n_D^{20} 1.4660 (*cf.* lit. data[17]: n_D^{25} 1.4682), d_4^{20} 1.3585. Found (%): C, 29.31; H, 5.44; Br, 21.43; P, 16.69. $C_9H_{21}BrO_6P_2$. Calculated (%): C, 29.51; H, 5.74; Br, 21.58; P, 16.94. ^{31}P NMR, δ: 16.0.

Bis(diethoxyphosphoryl)methanofullerene C_{60} (1). A solution of bis(diethoxyphosphoryl)bromomethane (0.220 g, 0.6 mmol) in toluene (10 mL) was added to a solution of fullerene C_{60} (0.216 g, 0.3 mmol) in toluene (200 mL). The reaction mixture was stirred for 10 min and then a suspension of NaH (0.072 g, 3 mmol) in toluene (10 mL) was added. Fullerene C_{60} was virtually completely consumed after stirring during 1 h (HPLC). The reaction solution was concentrated to ~10 mL and then chromatographed on SiO_2 (a 9 : 1 toluene—hexane mixture as the eluent) after which the starting C_{60} was isolated in a yield of 0.002 g and compound **1** was obtained in a yield of 0.213 g (71.2%) as a brown powder, m.p. >300 °C. Found (%): P, 5.81. $C_{69}H_{20}O_6P_2$. Calculated (%): P, 6.16. UV, λ_{max}/nm (ε): 326.5 (16870), 426.7 (3420), 491.3 (2193), 692.7 (110). IR, ν/cm^{-1}: 525, 567, 604, 978, 1019, 1096, 1157, 1200, 1256, 1428, 1527, 1635, 2894, 2926, 2977. ^{31}P NMR, δ: 14.2. ^{1}H NMR, δ: 1.21 (t, 12 H, 4 Me, $^3J_{H,H}$ = 7.3 Hz); 4.29 (m, 8 H, 4 CH_2O, $^3J_{H,H}$ = 7.3 Hz, $^3J_{P,H}$ = 8.7 Hz). ^{13}C NMR, δ: 15.01 (q, 4 Me, $J_{C,H}$ = 127.6 Hz); 39.38 (t, C(61), $^1J_{P,C}$ = 151.6 Hz); 62.15 (t, 4 CH_2O, $J_{C,H}$ = 148 Hz); 67.46 (t, 2 C_{sp3}, $^2J_{P,C}$ = 4.6 Hz); 141.44; 142.00; 143.29; 143.96; 144.11; 144.17; 144.20; 145.13; 145.71; 145.76; 145.94; 146.00; 146.08; 146.34; 146.39; 147.55 (d, 2 C, $^3J_{P,C}$ = 5.0 Hz); 147.59 (d, 2 C, $^3J_{P,C}$ = 5.0 Hz).

Bis(diisopropoxyphosphoryl)methanofullerene C_{60} (2) was prepared analogously from a solution of fullerene C_{60} (0.216 g, 0.3 mmol), bis(diisopropoxyphosphoryl)bromomethane (0.254 g, 0.6 mmol), and NaH (0.072 g, 3 mmol) in toluene. After 15 min, the reaction was virtually completed (HPLC). After chromatography on SiO_2 (hexane as the eluent), unconsumed C_{60} was isolated in a yield of 0.002 g and bis(diisopropoxyphosphoryl)methanofullerene (**2**) was obtained in a yield of 0.245 g (79.2% with respect to consumed C_{60}) as a brown powder, m.p. >300 °C. Found (%): P, 5.56. $C_{73}H_{28}O_6P_2$. Calculated (%): P, 5.89. UV, λ_{max}/nm (ε): 326 (15300), 426.7 (3100), 491.3 (1980), 692.7 (100). IR, ν/cm^{-1}: 526, 568, 608, 996, 1021, 1103, 1147, 1175, 1200, 1265, 1384, 1427, 1531, 1635, 2890, 2926, 2974. ^{31}P NMR, δ: 14.3. ^{1}H NMR, δ: 1.32 (d, 12 H, ^3J = 6.0 Hz); 1.41 (d, 12 H, ^3J = 6.0 Hz); 5.01 (m, 2 H); 5.07 (m, 2 H). ^{13}C NMR, δ: 17.29 (q, 8 Me, $^1J_{C,H}$ = 127.1 Hz); 41.64 (t, C(61), $^1J_{P,C}$ = 150.1 Hz); 64.38 (dd, 4 CHO, $^1J_{C,H}$ = 149 Hz, $^2J_{P,O,C}$ = 4.6 Hz); 69.71 (t, 2 C_{sp3}, $^2J_{P,C}$ = 4.1 Hz); 141.39; 141.92; 143.27; 143.91; 144.09; 144.18; 144.30; 145.61; 145.68; 145.84; 145.99; 146.04; 146.31; 146.32; 146.33; 147.72 (d, 2 C, $^3J_{P,C}$ = 5.0 Hz); 147.87 (d, 2 C, $^3J_{P,C}$ = 5.0 Hz).

Reaction of fullerene C_{70} with bis(diethoxyphosphoryl)bromomethane in the presence of NaH. Bis(diethoxyphosphoryl)bromomethane (0.041 g, 0.12 mmol) was added to a solution of fullerene C_{70} (0.062 g, 0.073 mmol) (98% purity) in toluene (100 mL). The reaction mixture was stirred for ~10 min and then a suspension of NaH (0.018 g, 0.75 mmol) in toluene (10 mL) was added. After 3 h, fullerene C_{70} was almost completely consumed (HPLC). An excess of NaH was filtered off and the solution was washed with water (2×30 mL) and concentrated to ~8 mL. HPLC analysis of the reaction mixture revealed the starting fullerene C_{70} (2.4%), a compound with retention time of 5.8 min (76%), and several minor products. Chromatography on a column with SiO_2 (a 35 : 4 : 1 toluene—MeCN—hexane mixture as the eluent) afforded bis(diethoxyphosphoryl)methano[70]fullerene (**3**) in a yield of 39.6 mg (49.4%), m.p. >300 °C. Found (%): P, 5.24. $C_{79}H_{20}O_6P_2$. Calculated (%): P, 5.51. UV, λ_{max}/nm (ε): 351 (14200), 365 (8900), 406 (110), 459 (320), 620 (230). IR, ν/cm^{-1}: 456, 530, 578, 595, 643, 662, 727, 794, 904, 948, 978, 1005, 1019, 1056, 1093, 1128, 1160, 1257, 1429, 1636, 1728, 2857, 2923. ^{31}P NMR, δ: 14.6. ^{1}H NMR, δ: 1.46 (t, 6 H, $^3J_{H,H}$ = 7.3 Hz); 1.60 (t, 6 H, $^3J_{H,H}$ = 7.3 Hz); 4.39 (dq, 4 H, $^3J_{H,H}$ = 7.3 Hz, $^3J_{P,H}$ = 8.4 Hz); 4.53 (dq, 4 H, $^3J_{H,H}$ = 7.3 Hz, $^3J_{P,H}$ = 8.4 Hz). ^{13}C NMR, δ: 17.28 (2 Me, $^1J_{C,H}$ = 127.3 Hz); 17.42 (2 Me, $^1J_{C,H}$ = 127.3 Hz); 25.11 (t, C(61), $^1J_{P,C}$ = 154.3 Hz); 64.10 (t, C_{sp3}, $^2J_{P,C}$ = 5.0 Hz); 64.82 (4 CH_2O, $^1J_{C,H}$ = 143.6 Hz); 65.01 (t, C_{sp3}, $^2J_{P,C}$ = 4.7 Hz); 131.55; 131.62; 131.86; 133.95; 134.23; 135.08; 138.13 (d, 2 C, $^3J_{P,C}$ = 5.3 Hz); 138.17 (d, 2 C, $^3J_{P,C}$ = 5.3 Hz); 141.73; 143.50; 143.57; 144.11; 144.46 (d, 2 C, $^3J_{P,C}$ = 5.3 Hz); 144.50 (d, 2 C, $^3J_{P,C}$ = 5.3 Hz); 144.61; 144.66; 145.22; 146.26; 146.75; 146.88; 147.35; 147.55; 147.68; 147.91; 148.41; 149.19; 149.31; 149.49; 149.81; 149.86; 150.01; 150.13; 151.38; 151.42; 151.56; 151.95; 152.06; 156.19.

The quantum-chemical calculations were carried out using the GAMESS program package.[18]

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