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# Synthesis of phosphorylated methanofullerenes

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The reactions of fullerene $C_{60}$ with bromo(dimethoxyphosphoryl)acetates in the presence of NaH in toluene afforded alkoxycarbonyl(dimethoxyphosphoryl)methanofullerenes whose structures were established by UV, IR, and $^{1}H$, $^{13}C$, and $^{31}P$ NMR spectroscopy.

**Key words:** fullerene $C_{60}$, the Bingel reaction, 61-alkoxycarbonyl-61-(dimethoxyphosphoryl)methanofullerenes, UV and IR spectroscopy, $^{1}H$, $^{13}C$, and $^{31}P$ NMR spectroscopy.

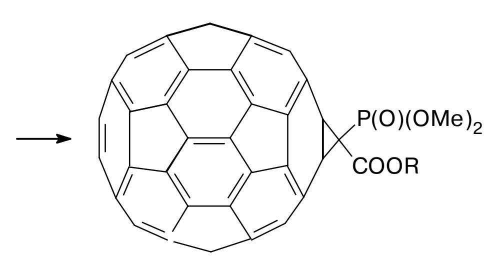
Methanofullerenes belong to the class of organic derivatives of fullerene $C_{60}$, which are successfully used for the preparation of new materials and biologically active compounds.[1—4] One of the most convenient procedures for the construction of this type of compounds involves cycloaddition of carbanions, which are generated from halogen-substituted compounds, to fullerene $C_{60}$. Bingel was the first to use this method for the functionalization of fullerenes.[5] The Bingel reaction has been most extensively studied for diesters of bromomalonic acid.[6—9]

It is known that the introduction of the phosphoryl group instead of the carboxy group into molecules of organic compounds may lead to a substantial change in their properties. In the present work, we report the synthesis of esters of (carboxy)phosphorylmethanofullerenes.

## Results and Discussion

We found that (bromo)phosphorylacetates react with fullerene $C_{60}$ in the presence of NaH under mild conditions to form 61-alkoxycarbonyl-61-(dimethoxyphosphoryl)methano[60]fullerenes (**1—3**) (Scheme 1).

**Scheme 1**



R = Me (**1**), Et (**2**), Menthyl (**3**)

The structures and compositions of the resulting compounds were confirmed by physicochemical methods and elemental analysis. It is known that the addition of carbanions generated from halogen-containing organic compounds, in particular, from derivatives of bromomalonic acid, to form [6,6]-cycloadducts of $C_{60}$ is the energetically most favorable process for fullerenes. According to the results of semiempirical quantum-chemical calculations by the PM3 method,[10] the difference in the energy of addition at the [6,6]- and [6,5]-bonds ranges up to 21 kcal $mol^{-1}$. The formation of [6,6]-adducts was confirmed by X-ray diffraction analysis of a number of methanofullerene derivatives.[11] We have performed semiempirical quantum-chemical calculations by the AM1 and PM3 methods (using the GAMESS program package) and demonstrated that the formation of the open and closed [5,6]-adducts (analogs of compounds **1—3**) is less favorable (by 22.5 and 9.6 kcal $mol^{-1}$, respectively) than the formation of the [6,6]-adduct,[12] which is in agreement with the results of the previous investigation.[10]

Studies of the structures of (alkoxycarbonyl)phosphorylmethanofullerenes **1—3** demonstrated that cycloaddition occurred at the [6,6]-bond of fullerene $C_{60}$. Thus, the UV spectra of all compounds under study have an absorption band at 430 nm, which is absent in the spectrum of the starting fullerene $C_{60}$ and which is characteristic of [6,6]-adducts of $C_{60}$, unlike [5,6]-open adducts of $C_{60}$ whose electronic spectra are virtually identical to the spectra of $C_{60}$.[8,13—15]

The IR spectra of compounds **1—3** have absorption bands at 528, 576, 1180, and 1430 $cm^{-1}$ characteristic of the fullerene core and bands at 1230 and 1730 $cm^{-1}$ corresponding to vibrations of the P=O and C=O groups, respectively. The $^{31}P$ NMR spectra of these compounds have one signal at $\delta$ 13—14. The $^{1}H$ NMR spectra show signals for the protons of the ester groups.

$^{13}C$ NMR spectroscopy is most widely used for the structural studies of fullerene $C_{60}$ derivatives because the

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addition of particular reagents leads to distortion of the symmetry of the fullerene core and, consequently, to the difference in shielding of the carbon nuclei in $C_{60}$ derivatives.

The $^{13}C$ NMR spectra of compounds **1—3** have signals in the region of δ 54 belonging to the carbon atoms of the $CH_3OP$ and $\underline{C}H_3OCO$ groups. The spectrum of compound **2** has signals of the $MeCH_2O$ group at δ 14.14 and 63.43 belonging to the Me— and $—CH_2O—$ fragments, respectively. The spectrum of compound **3** shows signals of the menthyl residue in the region of δ 15—79. The signals in the region of δ 69 belong to the $sp^3$ hybridized carbon atoms of the fullerene core, whereas the doublet signals with $^1J_{P,C}$ = 170 Hz in the region of δ 48 are characteristic of the C(61) atom of the methanofullerene fragment of compounds **1** and **2**. We failed to detect the signal for this carbon atom in compound **3**. Previously,[9] it has been mentioned that the signal for the C(61) atom at δ 50 has a low intensity. In the case under consideration, the intensity of the signal for this carbon atom is halved due to the $J_{P,C}$ spin-spin coupling, which may also hinder its detection. The signals in the region of δ 136—147 belong to the $sp^2$ hybridized carbon atoms of the fullerene moiety and the signals in the region of δ 164 belong to the carbonyl carbon atom of the ester group. The portion of the $^{13}C$ NMR spectrum of the fullerene fragment of compound **2** is shown in Fig. 1. It should be noted that comparison of the $^{13}C$ NMR spectra of phosphorylated methanofullerenes synthesized by us with the spectra of the corresponding derivatives of malonic acid[5,6,9] demonstrated that the presence of the asymmetrical fragments bound to the fullerene core leads to large differences in shielding of its carbon atoms because the number of the signals in the spectra of compounds **1—3** is larger compared to those in the spectra of symmetrical derivatives of methanofullerenes based on malonates.

To summarize, we synthesized phosphorylated methanofullerenes whose structures were confirmed by spectral methods.

## Experimental

We used $C_{60}$ of 99.9% purity (according to the HPLC data). The organic solvents were dried and distilled before use. Bromo(phosphoryl)acetates were prepared from the corresponding phosphorylacetates. Their synthesis will be described elsewhere.

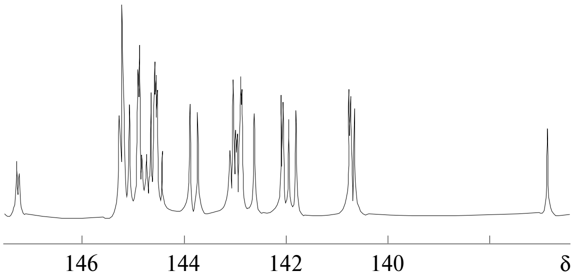

**Fig. 1.** $^{13}C$ NMR spectrum of compound **2** in the region of the $sp^2$ hybridized C atoms of the fullerene core.

The UV spectra were recorded on a Specord M-40 spectrophotometer in $CHCl_3$. The IR spectra were measured on a Vector (Bruker) spectrometer (KBr pellets). The $^1H$, $^{13}C$, and $^{31}P$ NMR spectra were recorded on a Bruker MSL-400 spectrometer (400, 100.57, and 161.92 MHz for $^1H$, $^{13}C$, and $^{31}P$, respectively) in $CDCl_3$; the chemical shifts were measured relative to $Me_4Si$ ($^1H$ and $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$). The course of the reaction was monitored on a Gilson liquid chromatograph equipped with an UV detector (λ = 328 nm) and a reversed-phase column ($C_{18}$; Partisil-5 ODS-3) with the use of a toluene—acetonitrile mixture (1 : 1, v/v) as the eluent.

**61-Alkoxycarbonyl-61-(dimethoxyphosphoryl)methano[60]fullerenes (1—3).** Methyl bromo(dimethoxyphosphoryl)acetate (0.234 g, 0.9 mmol) and NaH (0.72 g, 0.3 mmol) were added to a solution of fullerene $C_{60}$ (0.216 g, 0.3 mmol) in toluene (200 mL) and the reaction mixture was stirred at ~20 °C for 7 h. Then 6—7 drops of 1 *M* $H_2SO_4$ were added. The solution was washed with water (2×30 mL) and concentrated. The residue was chromatographed on a column with $SiO_2$. Unconsumed fullerene $C_{60}$ was washed out with hexane. Product **1** was washed out with hexane—toluene mixtures (10 : 1 → 1 : 10). According to the HPLC data, the purity of **1** was 99.8%; the yield was 120 mg (45% with respect to consumed $C_{60}$); a dark-brown powder; m.p. > 300 °C. Found (%): P, 3.27. $C_{65}H_9O_5P$. Calculated (%): P, 3.44. UV, $\lambda_{max}$/nm (ε): 328.7 (14285), 469.9 (1189.7), 489.2 (1044.5), 695.0 (110.5). IR (KBr), ν/cm$^{-1}$: 529, 573, 1030, 1180, 1235, 1270, 1430, 1732, 2810, 2950. $^{31}P$ NMR, δ: 13.19. $^1H$ NMR ($CDCl_3$), δ: 4.09 (s, 3 H); 4.16 (d, 6 H, *J* = 9.38 Hz). $^{13}C$ NMR ($CDCl_3$ + 2 mg of $Cr(AcAc)_3$), δ: 47.79 (d, C(61), $J_{P,C}$ = 82 Hz); 54.12 (Me—O—P); 54.55 (Me—O—P); 54.61 (Me—O—C); 69.87 (1 C); 69.91 (1 C); 136.82 (2 C); 140.62 (2 C); 140.78 (4 C); 141.78 (2 C); 142.00 (2 C); 142.05 (2 C); 142.09 (2 C); 142.64 (2 C); 142.89 (4 C); 142.99 (2 C); 143.05 (2 C); 143.09 (2 C); 143.74 (2 C); 143.88 (2 C); 144.38 (2 C); 144.55 (2 C); 144.57 (2 C); 144.64 (2 C); 144.71 (2 C); 144.76 (2 C); 144.87 (4 C); 145.08 (2 C); 145.21 (4 C); 147.19 (2 C); 147.22 (2 C); 164.46 (d, C=O, $J_{P,C,C}$ = 2.7 Hz).

Under analogous conditions, compound **2** was obtained in a yield of 100 mg (40% with respect to consumed $C_{60}$), m.p. > 300 °C. Found (%): P, 3.25. $C_{66}H_{11}O_5P$. Calculated (%): P, 3.39. UV ($CHCl_3$), $\lambda_{max}$/nm (ε): 326.6 (15572), 427.9 (1219.8), 489.5 (1160), 695.4 (223.9). IR (KBr), ν/cm$^{-1}$: 530, 577, 590, 1030, 1182, 1230, 1275, 1430, 1730, 2810, 2950. $^{31}P$ NMR, δ: 13.44. $^1H$ NMR, δ: 1.46 (t, 3 H); 4.57 (d, 6 H, *J* = 10.7 Hz); 4.56 (br.m, 2 H). $^{13}C$ NMR ($CDCl_3$ + 2 mg of $Cr(AcAc)_3$), δ: 14.14 (Me—C); 48.15 (d, C(61), $J_{P,C,C}$ = 170 Hz); 54.48 (Me—O—P); 54.54 (Me—O—P); 63.43 ($CH_2$—O—P); 63.43 ($CH_2$—O); 69.92 (1 C); 69.96 (1 C); 136.88 (2 C); 140.65 (2 C); 140.74 (2 C); 140.76 (2 C); 141.80 (2 C); 141.94 (2 C); 142.05 (2 C); 142.09 (2 C); 142.62 (2 C); 142.88 (4 C); 142.97 (2 C); 142.99 (2 C); 143.04 (2 C); 143.11 (2 C); 143.73 (2 C); 143.88 (2 C); 144.42 (1 C); 144.52 (3 C); 144.56 (2 C); 144.64 (2 C); 144.72 (1 C); 144.81 (1 C); 144.86 (3 C); 145.06 (2 C); 145.17 (2 C); 145.20 (3 C); 145.26 (2 C); 147.24 (1 C); 147.27 (1 C); 163.8 (d, C=O, $J_{P,C,C}$ = 2.8 Hz).

Compound **3** was prepared analogously to compound **1** in a yield of 150 mg (60% with respect to consumed $C_{60}$) as a high-melting dark-brown powder (m.p. > 300 °C). Found (%): P, 2.83. $C_{74}H_{25}O_5P$. Calculated (%): P, 3.03. UV, $\lambda_{max}$/nm (ε): 327.6 (13175), 427.9 (1138.7), 489.2 (11288), 695.1 (160.3). IR (KBr), ν/cm$^{-1}$: 530, 576, 591, 1030, 1185, 1232, 1273, 1432, 1731, 2812, 2954. $^{31}P$ NMR, δ: 13.39. $^1H$ NMR, δ: 0.82 (d, 3 H, Me, $J$ = 7 Hz); 0.92 (d, 3 H, Me, $J$ = 7 Hz); 0.96 (d, 3 H, Me, $J$ = 6.5 Hz); 1.15 (m, 1 H, $\mathrm{C\underline{H}H}$); 1.22 (m, 1 H, $\mathrm{CH\underline{H}}$); 1.60 (m, 2 H, CH); 1.75 (m, 2 H, $\mathrm{C\underline{H}H}$); 2.17 (m, 1 H, CH); 2.35 (m, 1 H, $\mathrm{CH\underline{H}}$); 4.13 and 4.17 (both d, 3 H each, MeOP, $J$ = 11.4 Hz); 5.01 (m, 1 H, CHO). $^{13}$C NMR, δ: 15.58 (Me); 20.92 (Me); 21.96 (Me); 22.79 ($CH_2$); 25.56 (CH); 31.47 (CH); 34.07 ($CH_2$); 40.33 ($CH_2$); 47.03 (CH); 79.53 (CHO); 54.41 (COP); 69.99 (1 C); 70.01 (1 C); 137.07 (1 C); 137.15 (1 C); 140.72 (1 C); 140.78 (3 C); 140.80 (3 C); 141.79 (1 C); 141.81 (2 C); 141.85 (1 C); 142.08 (1 C); 142.10 (1 C); 142.13 (1 C); 142.15 (1 C); 142.68 (1 C); 142.69 (1 C); 142.87 (1 C); 142.89 (1 C); 142.91 (1 C); 142.92 (1 C); 143.00 (1 C); 143.04 (1 C); 143.07 (2 C); 143.79 (2 C); 143.90 (1 C); 143.91 (1 C); 144.52 (2 C); 144.54 (2 C); 144.59 (1 C); 144.60 (1 C); 144.62 (1 C); 144.67 (2 C); 144.79 (1 C); 144.82 (1 C); 144.88 (1 C); 144.89 (1 C); 144.98 (1 C); 145.06 (1 C); 145.09 (1 C); 145.18 (1 C); 145.19 (1 C); 145.22 (3 C); 145.25 (1 C); 145.32 (1 C); 145.34 (1 C); 147.24 (1 C); 147.26 (1 C); 147.44 (1 C); 163.75 (d, C=O, $J_{P,C,C}$ = 2.7 Hz).

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