Synthesis and structures of new C_{60} fullerene derivatives containing carbonyl groups

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The reactions of fullerene C_{60} with substituted haloketones, including organophosphorus haloketones, in the presence of bases afforded new methanofullerenes containing carbonyl or carbonyl and acetal groups. The structures of the resulting compounds were established by spectroscopic methods. Their electrochemical reduction and oxidation were studied by cyclic voltammetry and ESR spectroscopy. The three-dimensional structures were calculated by the PM3 and DFT/PBE/TZ2P methods.

Key words: fullerene C_{60}, methanofullerenes, haloketones, Bingel reaction, high-performance liquid chromatography, ^{1}H and ^{13}C NMR spectroscopy, UV spectroscopy, IR spectroscopy, MALDI TOF mass spectrometry, cyclic voltammetry, ESR spectroscopy, quantum-chemical calculations, PM3 and DFT/PBE/TZ2P methods.

Fullerene derivatives containing reactive functional groups substantially extend the synthetic potential of this class of compounds and allow one to prepare new materials and promising biologically active compounds.[1—4]

The synthesis of fullerene derivatives containing carbonyl groups has been considered in several publications. The Diels—Alder reaction of various dienes containing the protected keto group with C_{60} was demonstrated to produce fullerene derivatives containing α-diketo or α-oxyketo groups.[5] It was also found that refluxing of enamines with C_{60} in the dark followed by acidification of the reaction mixture affords [6,6]-adducts of fullerene with bicyclooctanone or 1-(β-ketocyclopentynyl)-1,2-dihydro[60]fullerene depending on the enamine structure.[6—9] New methanofullerenes containing the aldehyde group were synthesized with the use of sulfonium salts.[10]

Bingel has demonstrated[11] that α-bromoacetophenone reacts with fullerene in the presence of bases to form the corresponding methanofullerene. However, the synthesis of functionalized methanofullerenes by the Bingel reaction has attracted little attention. We believe that an expansion of the range of readily accessible methanofullerene derivatives containing functionalized reactive groups will help in searching for new practically useful substances. However, it should be noted that the presence of certain groups adjacent to the cyclopropane fragment can complicate the preparation of various methanofullerene derivatives. For example, attempts to reduce the imino group bound to the cyclopropane fragment of methanofullerenes led to the three-membered ring opening rather than to the formation of the desired amino acid derivatives of methanofullerenes.[12]

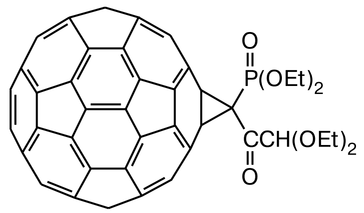
Results and Discussion

Earlier,[13—18] we have studied phosphorylated methanofullerenes with different structures. However, data on reactive organophosphorus derivatives of fullerene are scarce in the literature. Phosphorylated haloketone derivatives are convenient reagents for the synthesis of carbonyl derivatives of fullerene. These compounds can be useful in searching for new biologically active compounds and materials. In the present study, we examined the reactions of fullerene C_{60} with phosphonates $(EtO)_2P(O)CH_2C(O)CH(OEt)_2$ (**1**) and $(EtO)_2P(O)CH_2C(O)Me$ (**2**) in the presence of CBr_4 and DBU and with haloketones $(Pr^iO)_2P(O)CHBrC(O)Me$ (**3**), PhCHClC(O)COOMe (**4**), and $PhCHClC(O)C(O)CMe_3$ (**5**) in the presence of a base (NaH or DBU) under the conditions of the Bingel—Hirsch reaction.[11,19]

These reactions proceed under mild conditions to form previously unknown methanofullerenes **6—10** containing the keto and acetal groups at the *exo*-carbon atom.

Compounds **6—10** were isolated in pure form by column chromatography on SiO_2 using a 1 : 1 toluene—hexane mixture as the eluent in yield of 55.8, 55.4,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1424—1429, June, 2005.



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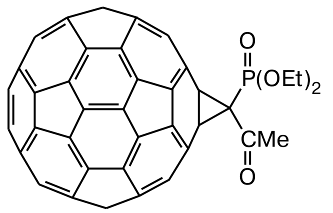

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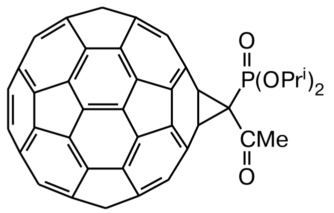

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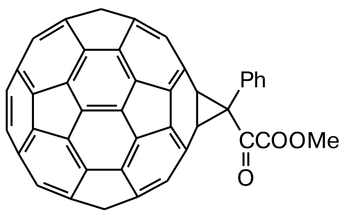

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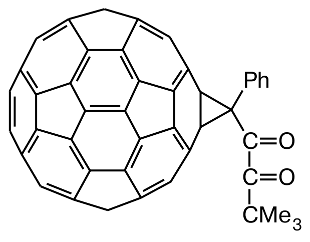

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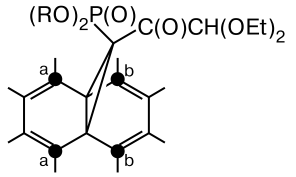
6.0, 34.9, and 39.4%, respectively, based on the consumed fullerene. The purity of compounds **6—10** was confirmed by HPLC. Study by HPLC using a C_{18} reversed-phase column and a 1 : 1 toluene—MeCN mixture as the eluent demonstrated that compounds **6—10** are chromatographically homogeneous. The compositions of the compounds were confirmed by MALDI TOF mass spectrometry. The mass spectra of compounds **6—10** have molecular ion peaks at *m/z* 1000.84, 912.83, 941.60, 896.38, and 923.10, respectively.

The structures of these compounds were completely confirmed by physicochemical methods (UV, IR, and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy).

The UV spectra of compounds **6—10** show absorption bands at 258, 326, 432, and 704 nm characteristic of fullerene derivatives.[9—11] The IR spectra have absorption bands at 526 and 1180 cm^{-1} belonging to stretching vibrations of the fullerene core, absorption bands of the phosphoryl group at 1256—1266 cm^{-1}, and absorption bands of the carbonyl group at 1713—1731 cm^{-1}.

The ^{31}P NMR spectra of compounds **6—8** have the only signal at δ 11—12.

The ^{13}C NMR spectra compounds **6—10** show signals for the carbon atoms of the addend and the fullerene core. The ^{13}C NMR spectrum of compound **6** is shown in Fig. 1. This spectrum has signals for the carbon atoms of the Me groups at δ 15.0—16.5 and signals for the carbon atoms of the CH_2 groups at δ 64.0—64.5. The doublet at δ 53.17 belongs to the methane *exo*-C(61) atom. The signals at δ 70.70 and 70.75 corresponds to the sp^3-hybridized C atoms of the fullerene core, and the signals at δ 138—148 are assigned to the sp^2-hybridized C atoms of the fullerene core. Two doublets at δ 146.09 and 148.17 occur due to spin-spin coupling through three bonds between the carbon nuclei of the fullerene core and the ^{31}P nuclei ($^3J_{C,P}$ = 5.37 Hz and $^3J_{C,P}$ = 4.04 Hz, respectively). Unlike diphosphonomethanofullerenes, in which the difference in shielding of these carbon atoms is insignificant,[15] carbonyl phosphorylated methanofullerenes synthesized in the present study are characterized by a pronounced difference in the chemical shifts of the carbon nuclei of the fullerene core involved in spin-spin coupling with the phosphorus atom. Based on the commonly accepted view of the spin-spin coupling between substituents at the double bond, which are in *cis* and *trans* positions with respect to each other, the signal at δ 148.17 ($^3J_{C,P}$ = 4.04 Hz) can be assigned to the C_a atoms of the fullerene core, which are in *cis* positions with respect to the phosphorus atom, and the signal at δ 146.09 ($^3J_{C,P}$ = 5.37 Hz) can be assigned to the C_b atoms of the fullerene core (*trans* positions with respect to the phosphorus atom).



These data provide additional evidence that phosphorylated fullerene derivatives are useful for labeling the carbon atoms of the fullerene core by NMR spectroscopy. Earlier,[18] we have demonstrated that the spectra of bismethanofullerenes containing four phosphoryl groups show signals associated with spin-spin coupling between the phosphorus nuclei and 24 different carbon nuclei of the fullerene core. The carbon atom of the CH group bound to the acetal fragment is characterized by a signal at δ 102.04 ($^1J_{C,P}$ = 160.5 Hz).

The spectroscopic characteristics of other compounds (**7—10**) also confirm the proposed structure and are described in detail in the Experimental section.

We studied selected properties of methanofullerenes **6—9** by cyclic voltammetry and ESR spectroscopy com-

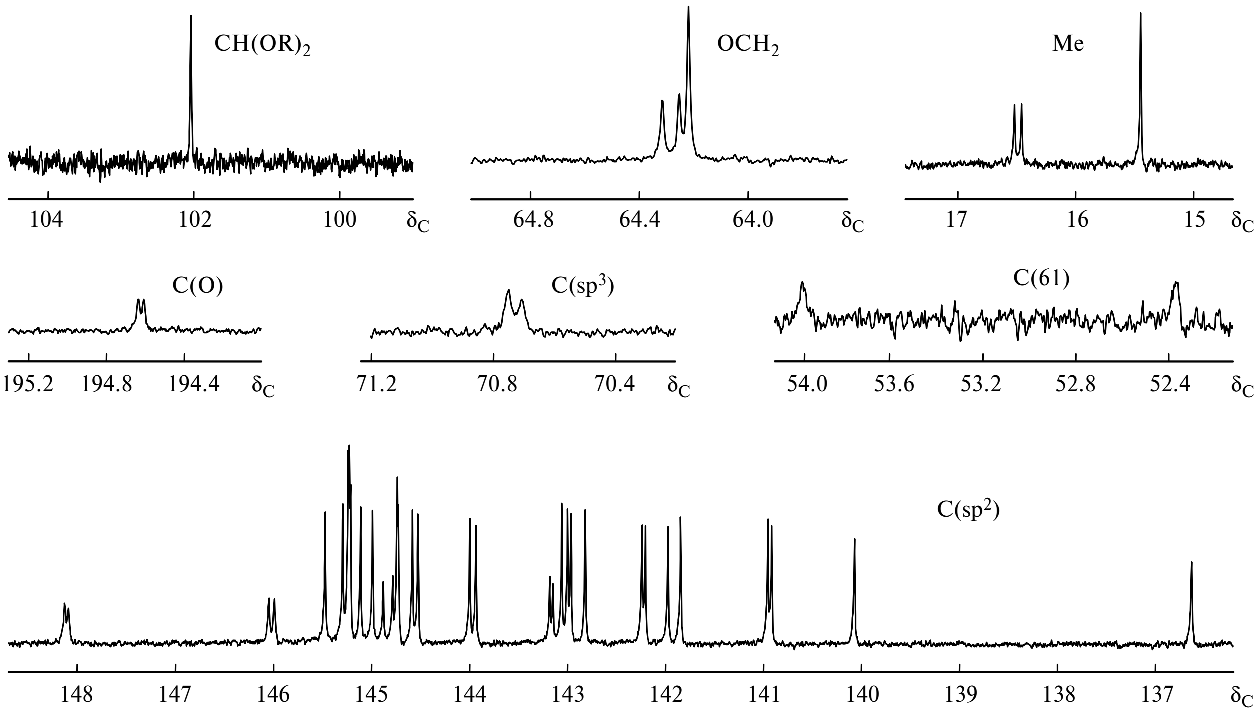


Fig. 1. Fragment of the ^{13}C NMR spectrum of compound **6**.

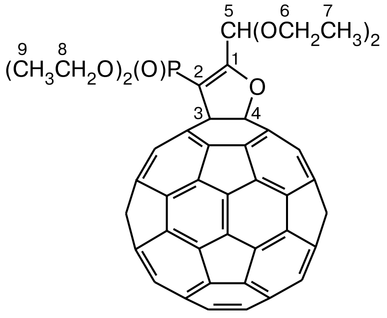
bined with *in situ* electrolysis, because the electrochemical properties of fullerene derivatives provide important evidence for the electron affinity of these compounds.[20] The electrochemical properties of compounds **6**—**9** differ from those of methanofullerenes studied earlier[13,16] (Table 1). Under the conditions of electrochemical reduction, compounds **6**—**9** do not undergo the retro-Bingel reaction. This was unexpected because, under analogous conditions, the three-membered ring in many methanofullerenes is eliminated giving rise to free fullerene.[13,20]

Based on the results of voltammetric studies and ESR spectroscopy, it was hypothesized that electrochemical reduction leads to the rearrangement of methanofullerenes into compounds having a dihydrofuran structure of a previously unknown type. To confirm this hypothesis, we performed preparative reduction of compound **6**. We chose this compound because its reaction would be expected to give the target product in the highest yield taking into account that the rearrangement of compound **6**, unlike other compounds, occurs in the first reduction step and is complicated by the formation of by-products to a lesser extent. Methanofullerene **6** was demonstrated to be quantitatively transformed into dihydrofullerenofuran **11** already in the first reduction step.[21,22] Compound **11** was isolated from the reaction mixture by flash chromatography on SiO$_2$.

Table 1. Cyclic voltammetric data (potentials of reduction peaks ($E_{\rm p,red}$) and oxidation peaks ($E_{\rm p,ox}$)) for electrochemical reduction of methano[60]fullerenes **6**—**9** and fullerene C$_{60}$ in an *o*-dichlorobenzene—DMF (3 : 1, v/v)/0.1 *M* Bu$_4$NBF$_4$ solution at a glassy-carbon electrode*

Compound	$-E_{\rm p,red}{}^1$	$-E_{\rm p,ox}{}^1$	$-E_{\rm p,red}{}^2$	$-E_{\rm p,ox}{}^2$	$-E_{\rm p,red}{}^3$	$-E_{\rm p,ox}{}^3$	$-E_{\rm p,red}{}^4$	$E_{\rm p,ox}{}^4$	$-E_{\rm p,red}{}^5$	$-E_{\rm p,red}{}^6$
	V									
C$_{60}$	0.96	0.90	1.40	1.33	1.90	1.84	2.39	−2.32	—	—
6	1.02	0.96	1.45	1.39	1.97	1.91	2.16	—	2.30	2.43
7	1.03	0.97	1.46	1.40	1.99	1.84	2.16	—	2.30	—
8	1.03	0.97	1.46	—	1.86	—	1.97	—	2.16	2.33
9	1.02	0.96	1.43	—	1.72	—	1.86	—	2.24	2.46

* The potentials were measured relative to the standard potential of the Fc/Fc$^+$ redox system using an Ag/0.01 *M* AgNO$_3$ solution in MeCN as the reference electrode at a potential scan rate υ = 100 mV s^{-1}.



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All spectroscopic characteristics of the pure product are in complete agreement with the structure of the expected dihydrofullerenofuran **11** and are consistent with the spectra of other dihydrofullerenofurans prepared by the reactions of [60]fullerene with β-dicarbonyl compounds.[23] The IR spectra show intense absorption bands of the fullerene core and the phosphoryl group at 526 and 1251 cm^{-1}, respectively. The absorption band of the carbonyl group, which is observed in the spectrum of the starting methanofullerene **6** at 1731 cm^{-1}, is absent. The UV spectrum of compound **11** has absorption maxima at 429 and 686 nm, which is indicative of the formation of a monocycloadduct at the closed [6,6]-bond. The $^{31}P\{^1H\}$ NMR spectrum measured with proton decoupling has one signal at δ 11.97, whereas the spectrum measured without proton decoupling shows a multiplet due to spin-spin coupling between the phosphorus nuclei and the protons at the C(8) atom. The ^1H NMR spectra have two triplets of two Me groups at δ 1.2—1.5, two multiplets of the methylene protons at δ 4.0—4.3, and a signal for the proton at the C(5) atom at δ 6.62.

The ^{13}C NMR spectrum shows two signals for the sp^3-hybridized carbon atoms at δ 73.4 and 103.3 (C(3) and C(4), respectively) and 28 signals for the sp^2-hybridized carbon atoms of the fullerene core at δ 135.1—148.6. The signals for the carbon atoms of the dihydrofuran ring appear at δ 101.7 (C(2)) and 167.7 (C(1)). In addition, there are signals for the carbon atoms of the substituents at δ 15.49 (C(7)), 16.09 (C(9)), 62.29 (C(8)), 63.96 (C(6)), and 95.69 (C(5)). Some carbon atoms are involved in spin-spin coupling with the phosphorus nucleus: C(1), $^2J_{C,C,P}$ = 29 Hz; C(2), $^1J_{C,P}$ = 209 Hz; C(3), $^2J_{C,C,P}$ = 9 Hz; C(8), $^1J_{C,P}$ = 5 Hz; C(9), $^2J_{C,C,P}$ = 7 Hz.

The electronic and three-dimensional structures and the electron affinities of the model compounds, *viz*., $(MeO)_2CHC(O)C_{61}P(O)(OMe)_2$ (**12**) and $MeC(O)C_{61}P(O)(OMe)_2$ (**13**), and compounds **9** and **10** were studied by the density functional theory method DFT/PBE/TZ2P with the use of the PBE exchange-correlation potential[24] and the triple-zeta basis set using the PRIRODA 2.10 program package.[24—28] After geometry optimization, the total energies of compounds **12**, **13**, **9**, and **10** are −3350.88977, −3122.02700, 2895.33870, and −2937.96058 atomic units, respectively. The electron affinities, which were determined from the energies of the lowest unoccupied level and scaled against the experimental electron affinity of fullerene C_{60} (2.65 eV), are 2.58, 2.58, 2.62, and 2.64 eV for compounds **12**, **13**, **9**, and **10**, respectively. The electron affinities estimated from the differences between the total energies of the molecule and the radical anion are 2.62, 2.64, 2.58, and 2.58 eV, respectively.

To summarize, we synthesized new methanofullerenes containing reactive keto and ketoacetal groups and studied their structures and properties. The formation of dihydrofullerenofuran **11** by electrochemical reduction of methanofullerene **6** was confirmed by preparative electrolysis.

Experimental

Studies by HPLC were carried out on a Gilson chromatograph equipped with an UV detector (C_{18} reversed-phase column (Partisil-5 ODS-3); toluene—MeCN, 1 : 1 v/v, as the eluent). The organic solvents were dried and distilled before use. Fullerene C_{60} of 99.9% purity (produced by the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences, Nizhny Novgorod) and commercial DBU (Lancaster) were used. Phosphorylated ketones were prepared according to known procedures.[29] All chemical operations were carried out under 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-transform spectrometer (KBr pellets). The ^1H and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz for ^1H) and Bruker MSL-400 (100.57 MHz for ^{13}C, 162.00 MHz for ^{31}P, and 400.00 MHz for ^1H) spectrometers in $CDCl_3$ using Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P) as the standards. The mass spectra were obtained on a MALDI-TOF MS instrument (DynamoThermo-BioANALYSIS, Germany) using trihydroxyanthracene as the matrix. The high-resolution mass spectrum of compound **11** was recorded on a Finnigan MAT-212 spectrometer at V_i = 60 eV, the electron emission current was 0.1 mA, and the evaporator temperature was ~573 K.

Electrochemical studies were carried out on a PI-50-1 potentiostat equipped with an H 307/2 X-Y recorder in the *o*-dichlorobenzene—DMF (3 : 1)/Bu_4NBF_4 (0.1 mol L^{-1}) system. A glassy-carbon disk electrode (*d* = 2 mm) pressed into Fluoroplast and a platinum disk electrode (*d* = 0.5 mm) pressed into glass served as working electrodes. Before each measurement, the electrodes were subjected to mechanical polishing. The potentials were measured relative to the standard potential of the ferrocene—ferrocenium ion redox system (Fc/Fc$^+$) using an Ag/$AgNO_3$ silver reference electrode (0.01 mol L^{-1}) in MeCN. Dissolved oxygen was removed by bubbling nitrogen through the solution at 295 K.

Quantum-chemical calculations were carried out by the density functional theory method DFT/PBE/TZ2P with the use of the PBE exchange-correlation potential and the triple-zeta basis set using the PRIRODA 2.10 program package.[24—28]

Diethoxymethyl carbonylmethano(diethoxyphosphonate) (1) was prepared according to a known procedure,[29] b.p. 100—105 °C (5 Torr), n_D^{20} 1.4350, d_4^{20} 1.1026. ^{31}P NMR, δ: 20.

***O,O*-Diisopropyl (2-oxo-1-bromoprop-1-yl)phosphonate (3).** A toluene solution of diisopropyl acetonylphosphonate[29] (0.5 g, 2.0 mmol) and NaH (0.05 g, 2.0 mmol) was stirred for 30 min. Then a solution of Br_2 in CH_2Cl_2 (0.36 g, 2.0 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 2 h, washed with water (2×50 mL), and dried over anhydrous $MgSO_4$. After vacuum distillation, bromoketophosphonate **3** was obtained in a yield of 0.5 g (73.7%), b.p. 100 °C (2 Torr), n_D^{20} 1.4608, d_4^{20} 1.2937. Found (%): C, 35.34; H, 5.98; Br, 26.54; P, 10.31. $C_9H_{18}BrO_4P$. Calculated (%): C, 35.89; H, 6.25; Br, 26.54; P, 10.28.

61-(Diethoxymethylcarbonyl)-61-(diethoxyphosphoryl)methano[60]fullerene (6). A solution of ketophosphonate **1** (0.1269 g, 0.45 mmol) in toluene (5 mL), a solution of CBr_4 (0.1494 g, 0.45 mmol) in toluene (5 mL), and a solution of DBU (0.0685 g, 0.45 mmol) in toluene (5 mL) were successively added to a solution of fullerene C_{60} (0.216 g, 0.3 mmol) in toluene (200 mL). The reaction mixture was stirred at 28—30 °C for 18 h and acidified with three drops of 1 *M* H_2SO_4. The resulting solution was washed with water (2×30 mL). The organic layer was concentrated *in vacuo* and the residue was applied onto a column with SiO_2. Elution with hexane afforded unconsumed C_{60} (76 mg), and elution with a 1 : 1 toluene—hexane mixture gave compound **6** in a yield of 108.6 mg (55.8% based on consumed fullerene) and a mixture of bis-adducts. MALDI TOF MS, found: *m/z* 1000.84 $[M]^+$, 1023.60 $[M + Na]^+$, 1040.10 $[M + K]^+$, 956.30 $[M - OEt]^+$. $C_{71}H_{21}O_6P$. Calculated: M = 1000.95. UV, λ_{max}/nm (ε): 329 (15975), 431 (3946), 491 (2208), 696 (142). IR, ν/cm^{-1}: 525, 574, 590, 668, 732, 806, 986, 1041, 1161, 1266 (P=O), 1389, 1423, 1534, 1731 (C=O), 2924, 2971. ^{1}H NMR, δ: 1.37 (t, 6 H, *J* = 6.8 Hz); 1.51 (t, 6 H, *J* = 7.2 Hz); 3.92 and 4.51 (both m, 4 H each); 5.53 (s, 1 H). ^{31}P{^{1}H} NMR, δ: 12.4. ^{13}C NMR, δ: 15.45, 16.46, 16.52, 52.37, 53.98, 64.21, 64.25, 64.31, 70.70, 70.75, 102.04 (d, $J_{C,H}$ = 160.8 Hz), 136.68, 140.10, 140.94, 140.98, 141.88, 142.01, 142.24, 142.27, 142.85, 142.99, 143.03, 143.09, 143.18, 143.21, 143.97, 144.03, 144.53, 144.61, 144.76, 144.77, 144.82, 144.92, 145.01, 145.15, 145.24, 145.25, 145.27, 145.32, 145.51, 146.02 ($^3J_{C,P}$ = 5.37 Hz), 148.10 (*J* = 4.04 Hz), 194.6 (d, $^2J_{C,P}$ = 2.65 Hz).

61-Acetyl-61-(diethoxyphosphoryl)methano[60]fullerene (7). A solution of phosphonate **2** [29] (0.0873 g, 0.45 mmol) in toluene (5 mL) and a solution of CBr_4 (0.1494 g, 0.45 mmol) in toluene (5 mL) were successively added to a solution of C_{60} (0.216 g, 0.3 mmol) in toluene (200 mL). After stirring, a solution of DBU (0.0685 g, 0.45 mmol) in toluene (5 mL) was added. The reaction mixture was stirred at ~25 °C for 4.5 h. The progress of the reaction was monitored by HPLC. The reaction mixture was worked up as described in the synthesis of compound **6**. Column chromatography on SiO_2 afforded unconsumed C_{60} in a yield of 58.6 mg and compound **7** in a yield of 110.5 mg (55.4% based on consumed C_{60}). MALDI TOF MS, found: *m/z* 913.83 $[M + H]^+$. $C_{67}H_{13}O_4P$. Calculated: M = 912.84. UV, λ_{max}/nm (ε): 327.9 (16146), 431.2 (4214), 492.3 (2168), 695 (112). IR, ν/cm^{-1}: 524, 571, 669, 696, 820, 1011, 1091, 1158, 1207, 1256 (P=O), 1313, 1420, 1457, 1553, 1713 (C=O), 2856, 2926. ^{1}H NMR, δ: 1.55 (t, 6 H, *J* = 6.95 Hz); 2.93 (s, 3 H); 4.53 (m, 4 H). ^{31}P{^{1}H} NMR, δ: 12.2. ^{13}C NMR, δ: 17.35, 29.84, 39.65, 64.43, 69.18, 70.34, 137.13, 140.76, 140.97, 141.05, 141.91, 141.94, 142.28, 142.31, 142.86, 143.10, 143.21, 143.24, 143.27, 143.91, 144.04, 144.63, 144.69, 144.81, 144.84, 144.98, 145.12 (d, $^3J_{P,C}$ = 5.9 Hz), 145.27, 145.32, 145.34, 145.38, 145.47, 147.14 (d, $^3J_{P,C}$ = 4.24 Hz), 195.88.

61-Acetyl-61-(diisopropyloxyphosphoryl)methano[60]fullerene (8). A solution of phosphonate **3** (0.18 g, 0.6 mmol) in toluene (5 mL) and NaH (0.072 g, 3.0 mmol) were added dropwise to a solution of C_{60} (0.216 g, 0.3 mmol) in toluene (200 mL). The reaction mixture was stirred at 30—50 °C for 3 days, filtered, and washed with water. The organic layer was concentrated *in vacuo*. The residue was chromatographed on a column with SiO_2 (toluene—hexane, 1 : 1, as the eluent). Unconsumed C_{60} and compound **8** were isolated in amounts of 84 and 15.6 mg (6% based on unconsumed C_{60}), respectively. MALDI TOF MS, found: *m/z* 941.60 $[M]^+$. $C_{69}H_{17}O_4P$. Calculated: M = 940.89. UV, λ_{max}/nm (ε): 327 (14528), 431 (4721), 492 (2346), 696 (132). IR, ν/cm^{-1}: 527, 573, 603, 668, 798, 998, 1038, 1099, 1167, 1263 (P=O), 1381, 1427, 1528, 1720 (C=O), 2923, 2971. ^{1}H NMR, δ: 1.54 (m, 12 H); 2.90 (s, 3 H); 5.10 (m, 2 H). ^{31}P{^{1}H} NMR, δ: 11.0. ^{13}C NMR, δ: 17.30, 30.66, 39.75, 63.19, 137.91, 141.54, 141.75, 141.84, 142.69, 142.72, 143.06, 143.09, 143.64, 143.88, 143.99, 144.02, 144.69, 144.82, 145.41, 145.47, 145.59, 145.62, 145.76, 145.92, 146.05, 146.10, 146.12, 146.15, 146.25, 147.99 (d, $^3J_{P,C}$ = 4.25 Hz), 188.95.

61-Phenyl-61-(methoxyoxalyl)methano[60]fullerene (9). A solution of methyl 3-chloro-2-oxo-3-phenylpropionate[30] (**4**) (0.0637 g, 0.3 mmol) in toluene (5 mL) and a solution of DBU (0.0456 g, 0.3 mmol) in toluene (5 mL) were successively added to a solution of C_{60} (0.216 g, 0.3 mmol) in toluene (200 mL). The reaction mixture was stirred at 30 °C for 5 days and then worked up as described for the synthesis of compound **6**. Column chromatography on SiO_2 afforded unconsumed C_{60} and compound **9** in amounts of 78.2 and 59.9 mg (34.9% based on consumed fullerene), respectively. MALDI TOF MS, found: *m/z* 896.38 $[M]^+$, 919.59 $[M + Na]^+$, 936.06 $[M + K]^+$. $C_{70}H_8O_3$. Calculated: M = 896.83. UV, λ_{max}/nm (ε): 326 (14528), 431 (4721), 494 (2346), 696 (132). IR, ν/cm^{-1}: 525, 553, 576, 705, 735, 806, 1030, 1123, 1182, 1208, 1380, 1425, 1490, 1652 (C=O), 1703 (C=O), 2855, 2924. ^{1}H NMR, δ: 3.92 (s, 3 H); 7.48—7.95 (m, 5 H, H arom.). ^{13}C NMR, δ: 39.78, 51.77, 65.35, 68.83, 128.31, 128.35, 128.59, 129.02, 130.20, 140.02, 140.31, 141.60, 141.94, 142.15, 142.35, 142.41, 142.49, 142.75, 142.89, 144.31, 144.37, 144.42, 144.93, 145.17, 145.22, 145.45, 145.57, 145.82, 145.98, 146.03, 146.23, 146.32, 147.36, 202.32, 212.87.

61-Phenyl-61-(1,2-dioxo-3,3-dimethylbutyl)methano[60]fullerene (10). Compound **10** was synthesized under analogous conditions from fullerene C_{60} (0.216 g, 0.3 mmol), 5-chloro-2,2-dimethyl-3,4-dioxo-5-phenylpentane[31] (0.0715 g, 0.3 mmol) (**5**), and DBU (0.0456 g, 0.3 mmol) in a yield of 0.0718 g (39.4% based on consumed fullerene). MALDI TOF MS, found: *m/z* 923.10 $[M]^+$. $C_{73}H_{14}O_2$. Calculated: M = 922.91. UV, λ_{max}/nm (ε): 327 (16084), 431 (4268), 491 (2118), 696 (128). IR, ν/cm^{-1}: 526, 549, 700, 874, 1036, 1426, 1545, 1651 (C=O), 1707 (C=O), 2921. ^{1}H NMR, δ: 1.11 (s, 9 H); 7.50—7.99 (m, 5 H, H arom.). ^{13}C NMR, δ: 26.16, 26.48, 30.12, 43.01, 66.37, 68.45, 128.77, 129.21, 129.92, 133.19, 138.02, 138.69, 141.28, 141.34, 142.28, 142.29, 142.39, 142.49, 143.13, 143.18, 143.24, 143.35, 143.99, 144.23, 144.65, 144.72, 144.96, 144.99, 145.04, 145.46, 145.52, 145.68, 145.71, 146.44, 146.48, 147.73, 200.21, 204.28.

2-(Diethoxymethyl)-3-(diethoxyphosphoryl)-3a,61a-dihydrofullereno[1,2]furan (11). High-resolution mass spectrum, found: m/z 1000.1080 $[M]^+$. $C_{71}H_{21}O_6P$. Calculated: M = 1000.1075. UV, λ_{max}/nm (ε): 326 (15120), 429 (4205), 452 (2015), 686 (108). IR, ν/cm^{-1}: 526, 554, 562, 588, 612, 700, 728, 782, 947, 971, 1019, 1049, 1098, 1156, 1254 (P=O), 1274, 1292, 1368, 1438, 2362, 2922, 2972. ^{1}H NMR, δ: 1.27 and 1.47 (both t, 6 H each, $^3J_{H,C,C,H}$ = 7 Hz); 3.98—4.13 and 4.15—4.29 (both m, 4 H each); 6.60 (s, 1 H). ^{31}P{^{1}H} NMR, δ: 11.97. ^{13}C NMR, δ: 15.49, 16.09 ($^2J_{C,C,P}$ = 7 Hz); 62.29 ($^1J_{C,P}$ = 5 Hz); 63.96, 73.45 ($^2J_{C,C,P}$ = 9 Hz); 95.69, 101.70 ($^1J_{C,P}$ = 209 Hz); 103.25, 135.10, 137.29, 139.58, 139.85, 141.54, 141.68, 142.34, 142.36, 142.48, 142.73, 142.83, 143.94, 144.26, 144.38, 145.09, 145.17, 145.24, 145.29, 145.61, 146.04, 146.06, 146.13, 146.24, 146.31, 146.39, 147.47, 148.06, 148.55, 167.69 ($^2J_{C,C,P}$ = 29 Hz).

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 02-03-32900, 03-03-96248rTatarstan, 04-03-32287, and 05-03-32633) and the Academy of Sciences of the Republic of Tatarstan.

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Received July 28, 2004;
in revised form April 21, 2005