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Fullerene C_{60} as an effective trap of acenaphthenone carbene generated in the reaction of acenaphthenequinone with hexaethyltriaminophosphine

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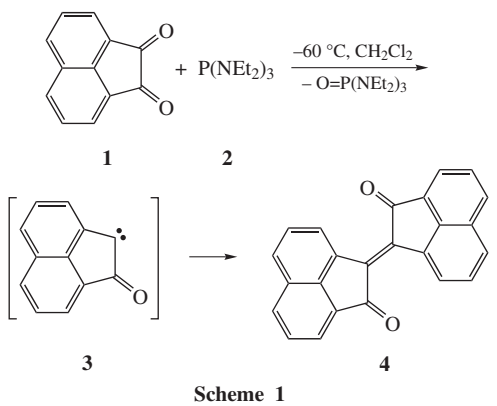
The three-component reaction of acenaphthenequinone, fullerene C_{60} and hexaethyltriaminophosphine leads to the formation of the new methanofullerene – 2-{3′-cyclopropa[1,9](C_{60}-I_h)[5,6]fulleren-3′-yl}-1-acenaphthenone.

Among the numerous fullerene derivatives, methanofullerenes are the most interesting ones due to their future trends in wide variety of practical applications. For example, there are projections directed to create efficient organic solar cells, photodetectors, transistors, *etc.*[1–7] The biological activity of those compounds is also of interest, and they are used for the preparation of new materials such as liquid crystals.[8,9] Methanofullerenes are traditionally synthesized *via* the Bingel-Hirsch reaction or its modifications, as well as *via* reactions of fullerenes with diazo compounds and carbenes.[10–14] There are also reports describing the synthesis of phosphorylated methanofullerenes by the reaction of fullerene C_{60} with a mixture of triphenylphosphine and dimethyl acetylenedicarboxylate.[15] All of the above reactions are carried out by long-time heating or by irradiation. In addition, as a rule, the reactions of fullerenes with diazo compounds lead to the formation of non-separable mixtures of methanofullerenes and homofullerenes.

Here we suggest a new synthetic route to methanofullerenes by the reaction in three-component system acenaphthenequinone–fullerene–hexaethyltriaminophosphine. The approach bases on the deoxygenation of quinone **1** with aminophosphine **2**, which proceeds[16] through the intermediate formation of α-ketocarbene **3**, which undergoes dimerization to 1,1′-bis(acenaphthen-1-ylidene)-2,2-dione **4** under the reaction conditions (Scheme 1).

Fullerene is an effective trap for postulated α-ketocarbene **3** and the formation of methanofullerene, 2-{3′-cyclopropa[1,9]-(C_{60}-I_h)[5,6]fulleren-3′-yl}-1-acenaphthenone **5**, can serve a direct proof of its intermediate origination in the reaction of quinone **1** with phosphine **2** (Scheme 2). The interaction proceeds in the temperature range of –10 to 25 °C and by the addition of phosphine **2** to the mixture of fullerene and quinone **1** in *o*-dichlorobenzene (*o*-DCB).† Molar ratio **1**:C_{60}:**2** was varied from 1:1:1 to 3:1:3 and 1:1:3. The best yield of compound **5** was achieved in the case of the 1:1:3 ratio.

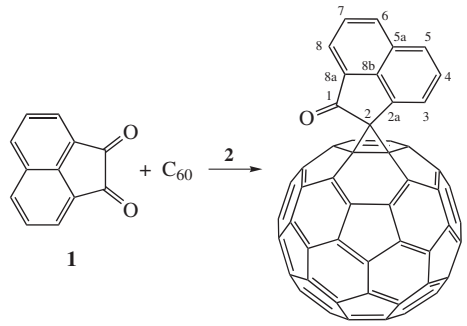


1 **2** **3** **4**

Scheme 1

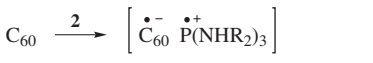
† NMR experiments were carried out with a Bruker AVANCE-600 spectrometer (14.1 T) equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the *z*-direction of 56 G cm^{-1}. All spectra were acquired in a 5 mm inverse probehead working at 600.0 MHz in ^{1}H and 150.9 MHz in ^{13}C NMR experiments. Chemical shifts are reported on the δ (ppm) scale and are relative to the residual ^{1}H and ^{13}C NMR signal of $CDCl_3$. IR spectra were recorded on the Bruker IFS-113V instrument in KBr pellets. UV spectra were recorded on Specord UV-VIS in CH_2Cl_2. Mass spectra were measured on a MALDI TOF MS (Dynamo) apparatus. Chemical shifts of **5** were determined within the DFT framework using a hybrid exchange-correlation functional, B3LYP, at the 6-31G(d) level as implemented in Gaussian 98.[22] Full geometry optimizations were done at the *ab initio* RHF/6-31G level. All data were referred to TMS (^{1}H and ^{13}C) chemical shifts that were calculated under the same conditions.

Hexaethyltriaminophosphine **2** (128 mg, 0.375 mmol) was added dropwise to a mixture of acenaphthenequinone **1** (23 mg, 0.125 mmol) and C_{60} (90 mg, 0.125 mmol) in anhydrous *o*-dichlorobenzene (40 ml) at –10 °C. Reaction mixture was stirred for 8 h. Then the temperature was allowed to rise to 25 °C. The solvent was removed under reduced pressure and the residue was purified by column chromatography using silica gel (Acros organics, 0.060–0.200 mm, 60 Å) (eluent, toluene–light petroleum, 85:15) to give unreacted C_{60} (27 mg, 30%) and fraction containing **5** and a mixture of polyproducts. Repeated column chromatography gave pure compound **5**. Yield 0.044 g (40%). ^{1}H NMR (CS_2 + $CDCl_3$) δ: 7.81 [dd, 1H, C(4)H, $^3J_{H,H}$ 7.4 Hz, $^3J_{H,H}$ 7.8 Hz], 7.93 [dd, 1H, C(7)H, $^3J_{H,H}$ 7.4 Hz, $^3J_{H,H}$ 7.0 Hz], 8.07 [d, 1H, C(5)H, $^3J_{H,H}$ 8.15 Hz], 8.23 [d, 1H, C(8)H, $^3J_{H,H}$ 7.0 Hz], 8.28 [d, 1H, C(6)H, $^3J_{H,H}$ 8.15 Hz], 8.56 [d, 1H, C(3)H, $^3J_{H,H}$ 7.0 Hz]. ^{13}C NMR (CS_2 + $CDCl_3$) δ: 47.73 [s, C(2)], 121.54 [dd, C(3), $^1J_{C,H}$ 161.0 Hz, $^3J_{C,H}$ 7.2 Hz], 122.30 [dd, C(8), $^1J_{C,H}$ 165.2 Hz, $^3J_{C,H}$ 8.4 Hz], 125.78 [dm, C(5), $^1J_{C,H}$ 161.6 Hz], 128.20 [dm, C(7), $^1J_{C,H}$ 161.6 Hz], 128.60 [dm, C(4), $^1J_{C,H}$ 161.0 Hz], 130.41 [m, C(5a)], 131.79 [dm, C(6), $^1J_{C,H}$ 160.4 Hz], 131.92 [d, C(8a), $^3J_{C,H}$ 8.4 Hz], 135.21 [d, C(2a), $^3J_{C,H}$ 9.0 Hz], 141.27 [s, C(8b)], 193.15 [s, C(1)]; fullerene moiety: 76.48 (2C), 138.52 (2C), 140.74 (2C), 141.11 (2C), 141.25 (2C), 141.42 (2C), 141.83 (2C), 141.94 (2C), 142.02 (2C), 142.58 (2C), 142.75 (2C), 142.81 (2C), 142.83 (1C), 142.94 (1C), 143.37 (2C), 143.51 (2C), 143.91 (2C), 144.04 (1C), 144.15 (2C), 144.29 (2C), 144.43 (4C), 144.45 (2C), 144.50 (2C), 144.66 (4C), 144.77 (1C), 144.91 (2C), 144.96 (4C), 145.25 (2C), 146.17 (2C). UV-VIS (CH_2Cl_2, λ_{max}/nm): 258, 329, 438 (weak), 504, 690. IR (KBr, ν/cm^{-1}): 1723, 1625 (C=O), 1420, 1229, 1026, 774, 713 (acenaphthene moiety), 526 (fullerene moiety). MS (MALDI), *m/z*: found 886, 858, 720; calc. 886 ($C_{72}H_6O$), 858 ($C_{71}H_6$), 720 (C_{60}).



Scheme 2

The result of the reaction is sensitive to the manner of reagents mixing. The initial mixing of aminophosphine **2** and quinone **1** with the following addition of fullerene leads to the formation of compound **4** only; fullerene does not take part in the reaction in this case. An initial addition of fullerene C_{60} to phosphine **2** under the same conditions gives ion-radical pair **6** (Scheme 3), which does not react with quinone **1**, as we have found.[17]



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Scheme 3

Compound **5** was separated by column chromatography as a dark-brown powder. Its mass spectrum contains the molecular ion peak *m*/*z* 886, corresponding to the monoadduct of the fullerene and ketocarbene **3**. At the same time, an absorption band at λ_{max} 438 nm, which is characteristic of the 6,6-closed monoadducts, is observed in the UV spectrum. The complete structure elucidation of compound **5** was carried out by a variety of correlation NMR methods (COSY ^{1}H–^{1}H, HSQC ^{1}H–^{13}C, HMBC ^{1}H–^{13}C)[18] (related 1D and 2D NMR spectra are given in Online Supplementary Materials). First, from 2D COSY spectrum two spin systems of protons can be easily assigned in ketocarbene moiety. Then, all hydrogenated carbons can be determined from 2D HSQC spectrum. Finally, HMBC correlations from ketocarbene H^3 proton (8.56 ppm) to fullerene sphere carbon (76.48 ppm) allow us to link these structural fragments into whole molecular. Almost perfect correlation of calculated [GIAO B3LYP/6-31G(d)//HF/6-31G] for simpler model (model **5** ketocarbene moiety on the top of half fullerene sphere, see Online Supplementary Materials for details)[19] *vs.* experimental ^{13}C chemical shifts (R^2 = 0.998) provides an additional support for validity of above derived conclusion on the structure.†

The electrochemical reduction of compound **5** was studied by cyclic voltammetry (CV). The obtained electrochemical data for methanofullerene **5** (the potentials of cathodic peaks and currents), as well as the comparative data for C_{60} and starting acenaphthenequinone **1** obtained under the same conditions, are shown in Table 1. Four classical reversible one-electron peaks of reduction are observed on the CV curve of fullerene C_{60}. The first peak of fullerene sphere electroreduction is realized at –0.83 V (*vs.* Ag/$AgNO_3$ 0.01 M in MeCN). At the same time, the first electron transfer step for quinone **1** is observed at more negative potentials (–1.22 V *vs.* Ag/$AgNO_3$ 0.01 M in MeCN) in comparison with the first peak of free fullerene moiety. The electrochemical reduction of methanofullerene **5** is also a reversible four-electron process (Figure 1, Table 1). The morphology of the CV curve is analogous to that obtained for free fullerene C_{60}. However, the potential of the first peak of reduction is shifted by 70 mV to the cathodic values. That could be a result of the fullerene sphere electrophilicity decreasing due to the opening of one C=C double bond in the fullerene molecule.[19] At the same time, the peaks C_3–C_4 are moved to the anodic values.

Table 1 Reduction peak potentials (E_p^{red}) and currents (I_p^{red}) on the CV curve of fullerene C_{60} and compounds **1** and **5**.[a]

Compound	E_p^{red}/V (I_p^{red}/μA)			
	C_1	C_2	C_3	C_4
C_{60}	–0.83 (4.2)	–1.24 (3.8)	–1.70 (3.9)	–2.16 (3.9)
1	–1.22 (11.25)	–1.51 (7.6)		
5	–0.90 (3.0)	–1.22 (2.3)	–1.41 (1.8)	–1.84 (1.8)

[a]Solution concentration, 1×10^{-3} mol dm^{-3}; supporting electrolyte, 0.1 M Bu_4NBF_4; cathode, glassy carbon (GC) (S_{work} = 3.14 mm^2); reference electrode, Ag/$AgNO_3$ 0.01 M in MeCN; scan rate, V_{pot} = 50 mV s^{-1}.

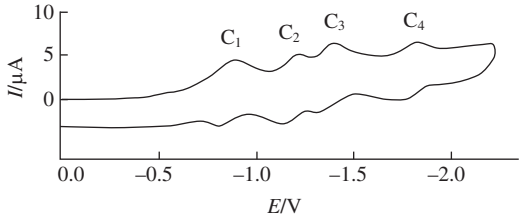

Figure 1 CV curve of methanofullerene **5** [recorded from 0.00 V to –2.30 V and back to 0.00 V; solution concentration 1×10^{-3} mol dm^{-3} in *o*-DCB:MeCN (3:1); supporting electrolyte, 0.1 M Bu_4NBF_4; cathode, glassy carbon (GC) (S_{work} = 3.14 mm^2); reference electrode, Ag/$AgNO_3$ 0.01 M in MeCN; scan rate, V_{pot} = 50 mV s^{-1}].

Comparative data on electrochemical properties of fullerene C_{60}, initial acenaphthenequinone **1** and methanofullerene **5** (Table 1) allow us to conclude that the first stage of methanofullerene **5** electroreduction (C_1) corresponds to the transfer of one electron onto the fullerene sphere. The other peaks (C_2, C_3) appeared on the CV curve of methanofullerene **5** (Figure 1) display the following reversible one-electron transfer processes. Obviously, this reduction involves both the fullerene sphere and attached polycyclic group.

Thus, the reaction in three-component system acenaphthenequinone–fullerene C_{60}–hexaethyltriaminophosphine leads to the formation of methanofullerene **5** and proceeds only if phosphine is added to the mixture of acenaphthenequinone and fullerene. The formation of methanofullerene **5** in three-component system, in our opinion, is the strong evidence of acenaphthenone carbene **3** generation. To the best of our knowledge, there are no reports dealing with the carbenes generation in the synthesis of methanofullerenes. Therefore, this three-component reaction is a new route to the synthesis of methanofullerenes.

The investigation of the interaction in the three-component system of α-dicarbonyl–fullerene–hexaalkyltriaminophosphine will be continued to study the properties of methanofullerenes with polycyclic addends, which can be of interest, for example, as electron acceptors in bulk heterojunction polymer–fullerene solar cells or as biologically active compounds.[9,21]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.11.003.

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