ESR study of formation of allylic radicals in simultaneous photochemical generation of phosphoryl and carbon-centered radicals in the presence of C_{60} fullerene

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Allylic radicals resulting upon simultaneous photochemical generation of phosphoryl [$^{\cdot}P(O)(OPr^i)_2$] and carbon-centered [$^{\cdot}C(O)OMe$, $^{\cdot}CH_3$, $^{\cdot}CCl_3$] radicals in saturated toluene solutions of C_{60} have been studied by the ESR method. The donor-acceptor properties of carbon-centered radicals determine the positions of phosphoryl groups in the allylic system.

Key words: fullerene, ESR, allylic radical, phosphoryl.

The ability to add many free radicals is the characteristic feature of fullerenes.[1—3] The multiple addition of benzyl radicals to C_{60} fullerene results in the formation of allylic or cyclopentadienyl radicals.[2] The formation of allylic structures was also observed[3] in free-radical phosphorylation of C_{70}; however, no allylic radicals are formed upon multiple addition of phosphoryl radicals to C_{60}, probably due to steric hindrances.[4] The very fact of formation of allylic radicals testifies that the active radical situated in the solvent cage together with the substituted bis-adduct $C_{60}R_2$ fullerene adds not to any of the 29 remaining free double bonds, but finds the direction of the most thermodynamically favorable addition (Scheme 1).

Multiple addition of radicals of one type (benzyl, methyl, phosphoryl, *etc.*) to fullerenes has been studied up to the present time. Information about the formation of allylic structures could be obtained only in the case of radicals centered on atoms with magnetic nuclei. The characteristic feature of allylic radicals is the interaction of an unpaired electron with nuclei of two equivalent atoms arranged at the "termini" of the allylic system (2/3 of the spin density) and with the nucleus of a central atom (1/3 of the spin density). The purpose of this work was the ESR study of specific features of structures of allylic radicals formed upon multiple addition of radicals of various chemical natures, phosphoryl and carbon-centered that were simultaneously generated in a saturated toluene solution of C_{60}.

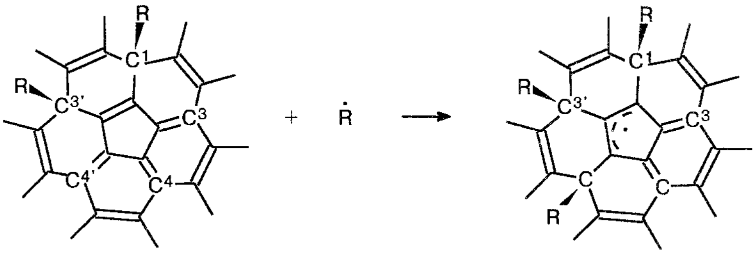
Experimental

Solutions were irradiated with nonfiltered light of a DRSh-1000 high-pressure mercury lamp. ESR spectra were recorded on a Varian E-12A spectrometer.

Results and Discussion

The $^{\cdot}C(O)OMe$, $^{\cdot}CH_3$, and $^{\cdot}CCl_3$ radicals were generated simultaneously with phosphoryl $^{\cdot}P(O)(OPr^i)_2$ radicals. A saturated toluene solution of C_{60} containing a threefold excess of radical sources, $Hg[P(O)(OPr^i)_2]_2$ and $ClHgC(O)OMe$, was prepared for studying adducts of the multiple addition of $^{\cdot}P(O)(OPr^i)_2$ and $^{\cdot}C(O)OMe$ radicals to C_{60}. UV irradiation of this solution in a

Scheme 1



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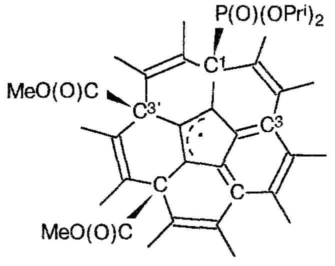
Scheme 2

$$Hg[P(O)(OPr^i)_2]_2 \xrightarrow{h\nu} {}^{\cdot}P(O)(OPr^i)_2 + {}^{\cdot}HgP(O)(OPr^i)_2$$

$$ClHgC(O)OMe \xrightarrow{h\nu} {}^{\cdot}C(O)OMe + {}^{\cdot}HgCl$$

$$C_{60} + {}^{\cdot}P(O)(OPr^i)_2 + 2\,{}^{\cdot}C(O)OMe \longrightarrow {}^{\cdot}C_{60}[C(O)OMe]_2P(O)(OPr^i)_2$$

1, 2



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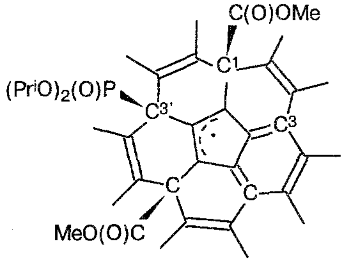


2

resonator of the ESR spectrometer results after 10—15 min in the formation of stable radicals of two types characterized by different constants of hyperfine coupling (HFC) between an unpaired electron and the nucleus of the phosphorus atom with the *g*-factors: a_P(1 P) = 43.0 G, g = 2.0027 and a_P = 6.25 G, g = 2.0028 for radicals **1** and **2**, respectively (Fig. 1). The value of the HFC constant for the nucleus of the P atom in radical **1** is close to the splitting value in allylic radical $^{\cdot}C_{70}[P(O)(OPr^i)_2]_3$ at terminal phosphorus atoms[3] (a_P = 44.5 G), and the HFC value in radical **2** is comparable to that for the central P atom (a_P = 5.25 G) of the allylic system. Thus, the simultaneous generation of phosphoryl and methoxycarbonyl radicals results in the formation of stable allylic radicals containing the phosphoryl group at various positions of the allylic system (Scheme 2).

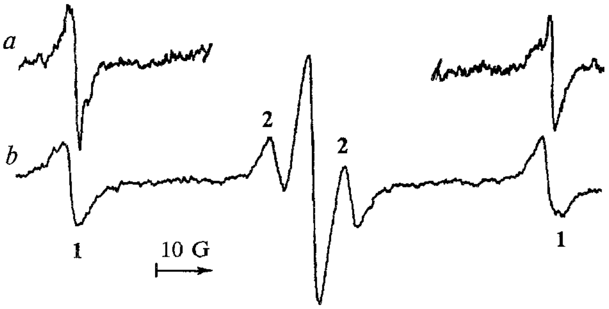


Fig. 1. ESR spectrum of type **1** radicals at 20 °C after 5 min of photolysis (*a*) and stable allylic radicals of types **1** and **2** after 15 min of photolysis (*b*). The central signal corresponds to the $^{\cdot}C_{60}[C(O)OMe]_n$ radical, where n = 3 or 5.

As seen from Fig. 1, at the initial stage of photolysis (~5 min), the lines in the recorded ESR spectrum are the superposition of two signals, a narrow signal ($\Delta H \approx$ 1.2 G), whose width is comparable to that of the signal of $^{\cdot}C_{60}P(O)(OPr^i)_2$, and a broad signal ($\Delta H \approx$ 2.0 G). We attribute the narrow line to radical **1**, and the broad line is related to the addition of an additional even number of free radicals $^{\cdot}C_{60}[C(O)OMe]_2P(O)(OPr^i)_2R_n$, where n = 2, 4, 6, *etc.*, to fullerene.

The addition of methyl iodide to a saturated toluene solution of C_{60} containing a threefold excess $Hg[P(O)(OPr^i)_2]_2$ results in the generation of methyl radicals due to the detachment of the iodine atom by the phosphoryl or mercury-centered radicals formed upon photolysis of the diphosphorylmercury compound[5] (Scheme 3).

Scheme 3

$$CH_3I + {}^{\cdot}P(O)(OPr^i)_2 \longrightarrow {}^{\cdot}CH_3 + IP(O)(OPr^i)_2$$

$$CH_3I + {}^{\cdot}HgP(O)(OPr^i)_2 \longrightarrow {}^{\cdot}CH_3 + IHgP(O)(OPr^i)_2$$

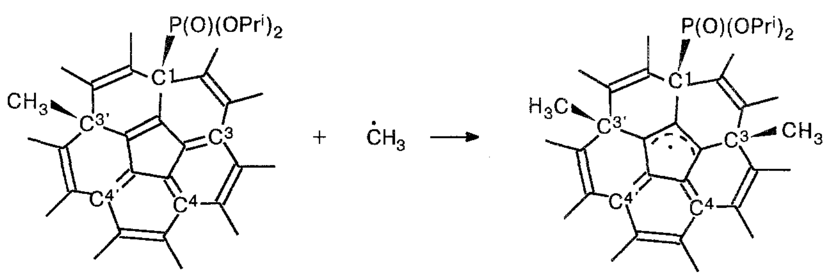
$$C_{60} + {}^{\cdot}P(O)(OPr^i)_2 + 2\,{}^{\cdot}CH_3 \longrightarrow$$

$$\longrightarrow {}^{\cdot}C_{60}(CH_3)_2P(O)(OPr^i)_2$$

3

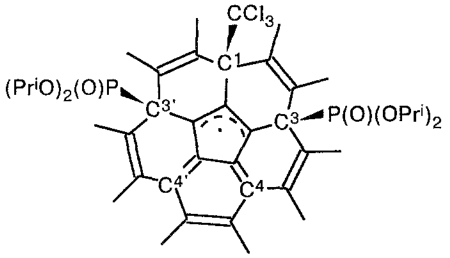
Unlike the previous example, the simultaneous addition of phosphoryl and methyl radicals results in the formation of an allylic radical of only one type determined by the ESR method. This radical contains the

Scheme 4



phosphoryl group in the center of the allylic system with the HFC constant on the nucleus of the P atom equal to 6.75 G. Thus, the nucleophilic methyl radical adds to $C_{60}(CH_3)P(O)(OPr^i)_2$ only from the side of the phosphoryl substituent (Scheme 4).

A considerable effect of chemical properties of carbon-centered radicals on the composition of allylic radicals is confirmed by the data obtained from the simultaneous generation of phosphoryl and electrophilic trichloromethyl radicals, which have formed from CCl_4 similarly to the formation of $^\cdot CH_3$ radicals from MeI. In this case, stable allylic $^\cdot C_{60}[P(O)OPr^i)_2]_2CCl_3$ radicals containing two phosphoryl groups arranged at the termini of the allylic system are detected.



The HFC constant with two equivalent nuclei of P atoms corresponds to this radical [$a_P(2\ P) = 41.25$ G].

Thus, the formation of allylic radicals upon simultaneous generation of phosphoryl and carbon-centered radicals in saturated toluene solutions of C_{60} is observed for the first time, and the effect of donor-acceptor properties of carbon-centered radicals on the structure and composition of allylic radicals is established.

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