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LETTERS TO THE EDITOR

Fullerene C_{60} Derivatives as Efficient Sensitizers of Oxidation under the Mild Conditions of Atmospheric Air

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Abstract—The ability of fullerene C_{60} and of its derivatives to sensitize oxidation of triphenylphosphine with atmospheric oxygen under sunlight illumination at room temperature was found. Reuse of fullerene conjugates did not lead to reduction in their reactivity; the conjugates were recovered unchanged from the reaction mixture. The use of a xenon lamp significantly shortened the time of the process.

Keywords: fullerene C_{60}, oxidation, fullerene conjugate, triphenylphosphine, diadamantylidene, xenon lamp

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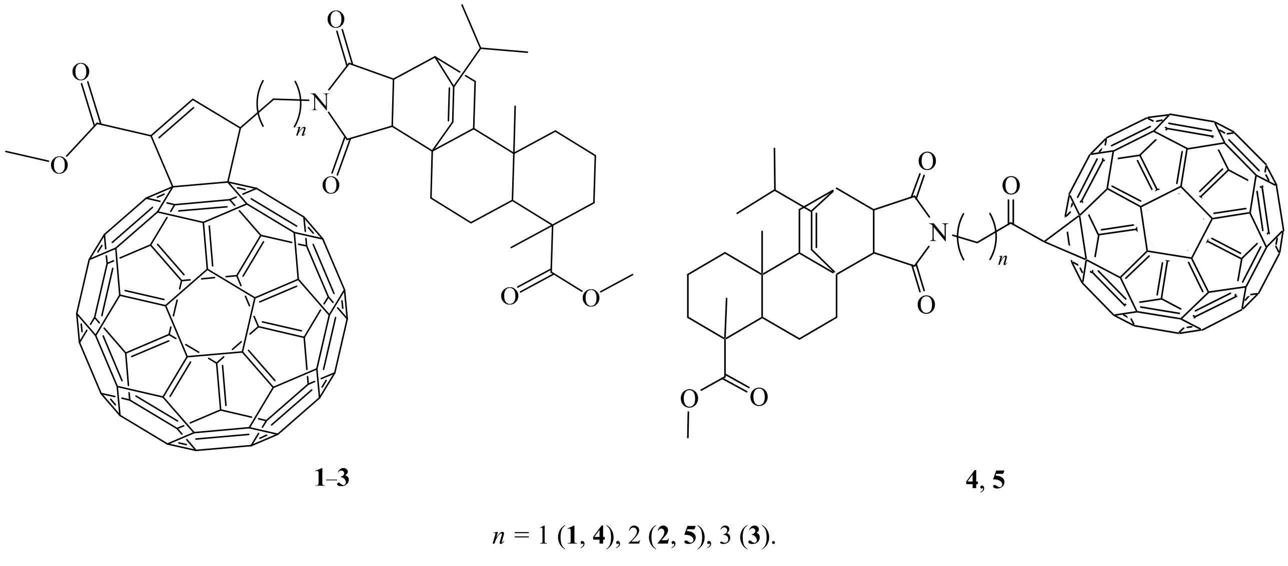
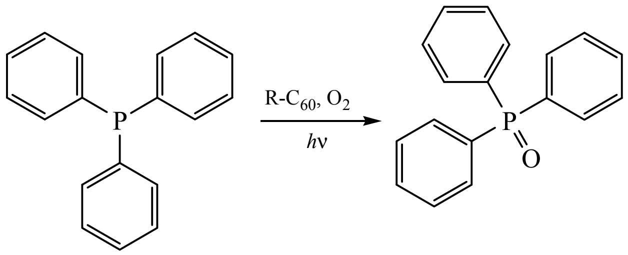
Fullerene C_{60} and many of its derivatives possess unusual photophysical properties. Absorption of ultraviolet and visible light by these compounds leads to a long-lived excited triplet state, and the energy transfer from the excited fullerene molecule to the oxygen molecule causes the formation of a highly reactive species, singlet oxygen [1–4]. This ability of fullerenes makes them suitable as efficient sensitizers of singlet oxygen production [5, 6] rendering possible the oxidation under mild conditions. The main obstacle to extensive use of fullerenes is their poor solubility in many solvents [7–10]. This problem can be addressed by functionalization of the fullerene core with solubilizing groups [11–15] (Scheme 1).

Scheme 1.



n = 1 (**1**, **4**), 2 (**2**, **5**), 3 (**3**).

Scheme 2.



Herein, we studied the oxidation of triphenylphosphine and diadamantylidene with atmospheric oxygen in the presence of fullerene conjugates R–C_{60}. As side substituents served derivatives of maleopimaric acid. The latter is an easily accessible compound which can be synthesized from renewable feedstock rosin, a wood chemical product, by a Diels–Alder reaction with maleic acid anhydride [16]. Maleopimaric acid is widely used in technology of paints, varnishes, and polymer materials [17] and is regarded as a promising starting compound whose derivatives are readily soluble in most organic solvents.

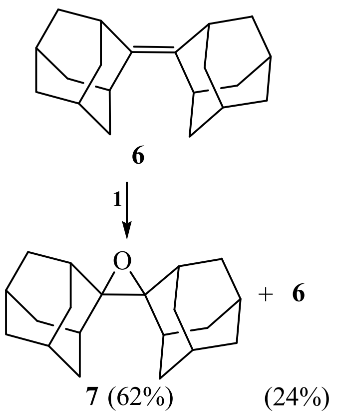
For fullerene conjugates **1–5** synthesized the solubility in toluene (~0.4 g/mL) proved to be two orders of magnitude higher than that of fullerene C_{60} (~0.0026 g/mL). However, to maintain the experimental integrity we used the same amounts of the reagents and of the solvent (see table).

The reaction was carried out in an open vial made of medical glass in toluene at room temperature using a 10-fold excess of PPh_3 relative to C_{60} and R–C_{60} (Scheme 2). The oxidation of triphenylphosphine proceeds under daylight illumination, otherwise the reaction stops.

Oxidation of triphenylphosphine with atmospheric oxygen in a toluene solution

Catalyst	*t*, °C	*h*ν	Time, h	Yield of PPh_3=O, %
–	20	+	64	2
C_{60}	20	–	64	2
C_{60}	20	+	32	91
C_{60}–H_2O	20	+	32	24
C_{60}	110	–	32	5
C_{60}	20	–	32	2
1	20	+	5	100
1	20	Xenon lamp	0.5	100
2	20	+	13	100
3	20	+	17	100
4	20	+	14	100
5	20	+	16	100

Scheme 3.



Triphenylphosphine oxidation for 32 h in the presence of fullerene C_{60} gave triphenylphosphine oxide in a 91% yield. The calculation took into account solely the daylight time, since with no exposure to light only trace amounts of PPh_3=O were formed both at room temperature and under reflux in toluene. In the presence of moisture in the reaction mixture the process was inhibited, in which case PPh_3=O was obtained in a 24% yield.

Our experiments with fullerene conjugates revealed a stronger sensitizing effect for cyclopentenofullerene derivatives compared to methanofullerenes. The best results were obtained for compound **1** with the shortest carbon bridge between the cyclopentenofullerene and the maleopimarimide moiety. In this case, already after 5 h PPh_3 was completely converted to triphenylphosphine oxide (see table).

Xenon lamps are known to produce bright white light that closely mimics natural *daylight* [18]. Through the use of a xenon lamp with a 35 W ignition block the time of the triphenylphosphine oxidation catalyzed by leader-compound **1** was substantially reduced to 30 min. Under the same conditions, diadamantylidene **6** was oxidized to diadamantylidene epoxide **7** (Scheme 3). The reaction was carried out for 8 h and gave compound **7** in a 62% yield.

Formation of **7** was proven by NMR spectroscopy, specifically, by disappearance in the ^{13}C NMR spectrum of the 133.17 ppm signal from the carbon of the multiple bond of **6** and by appearance of the 73.66 ppm signal characteristic of the carbon atoms of the oxirane ring.

It was shown in [19] that, during oxidation of diadamantylidene **6** in the presence of fullerene C_{60}, nearly half of the catalyst was converted to $C_{60}O$ and $C_{60}O_2$ oxides. In our experiments the C_{60} conjugates were recovered unchanged from the reaction mixture, which enabled their reuse. To this end, upon completion of the reaction these substances were isolated by column chromatography using 3 : 1 petroleum ether–ethyl acetate as eluent.

Thus, with triphenylphosphine taken as an example we demonstrated the capability of fullerene C_{60} and of its readily soluble derivatives to sensitize an oxidation process under mild conditions of atmospheric oxygen. The time of the process was significantly reduced through the use of a xenon lamp.

General procedure for the oxidation of triphenylphosphine and diadamantylidene with atmospheric oxygen in the presence of fullerene C_{60} or of its conjugates. A mixture of 1.4 mmol of triphenylphosphine (or diadamantylidene) with 0.14 mmol of fullerene C_{60} or of its conjugates **1–5** in 35 mL of toluene was stirred in an open glass vial under daylight (or under illumination with a xenon lamp placed at a distance of 20 cm from the reactor) until triphenylphosphine completely disappeared. The progress of the reaction was monitored by thin layer chromatography. Diadamantylidene epoxide was isolated by column chromatography using CH_2Cl_2 as eluent.

2-(Tricyclo[3.3.1.1]dec-2-ylidene)tricyclo[3.3.1.1]-decane 2,2'-epoxide (7). Yield 0.25 g (62%), colorless crystals, mp 182°C. ^{13}C NMR spectrum, δ_C, ppm: 27.22 (4CH), 31.71 (4CH), 35.16 ($4CH_2$), 36.83 ($2CH_2$), 37.41 ($4CH_2$), 73.66 ($2CH_2$). Found, %: C 84.39; H 9.90. $C_{20}H_{28}O$. Calculated, %: C 84.45; H 9.92; O 5.62.

The reaction was run in an FO-1 vial made of NS-3 medical glass. A ClearLight 5000K xenon lamp with a 35 W ignition block was used in the experiments.

The NMR spectra were recorded on a Bruker-AM 500 spectrometer operating at 125.76 MHz (^{13}C), with tetramethylsilane as internal reference. Elemental analysis was performed using a EURO EA-3000 CHN instrument. The melting point was determined on a Böetius micro-heating apparatus.

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