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Synthetic Chemistry with Fullerenes. Photooxygenation of Olefins

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Under irradiation with visible or UV (>290 nm) light in the presence of molecular oxygen and a minute amount of fullerenes, olefins and dienes undergo ene and Diels–Alder reactions with singlet oxygen to give photooxygenation products. The regio- and stereoselectivities of the photooxygenation of β-myrcene, (+)-pulegone, 4-methylpent-3-en-2-ol, and (+)-limonene were very similar to those observed in known singlet oxygen reactions, indicating that the fullerene-sensitized reaction generates free singlet oxygen. The efficiency of fullerenes and conventional sensitizers was qualitatively examined by using the Diels–Alder reaction between $^1O_2$ and furan-2-carboxylic acid as a probe. Among those examined, C_{70} was found to be the most effective. The reaction was the fastest and completed with as little as 0.0001 equiv of C_{70}. C_{60} and hematoporphyrin were found to be of similar efficiency. The methanofullerene **13**, which lacks one olefinic conjugation in the C_{60} core, was as good as C_{60} itself, but the aminofullerene **14**, lacking six double bonds, was quite inferior. The fullerene carboxylic acid **15**, which was previously shown to show considerable biochemical activity, was found to be capable of generating singlet oxygen in aqueous DMSO.

Following the initial structural proposal,[1] spectroscopic characterization,[2] and development of large-scale preparations,[3] intense studies of the physical and chemical properties of buckminsterfullerenes have been carried out.[4] Despite the many studies focused on fullerenes themselves, very little has been determined about fullerene-mediated chemical transformations.[5] Among the numerous synthetic applications, the exploration of fullerenes as photosensitizers held potential, given the existing body of physical and physicochemical measurements[6] and our recent report of the photoinduced biochemical activity of a water-miscible fullerene.[7] In this article, we report that C_{60}, C_{70}, and their derivatives are synthetically useful photosensitizers, on a preparative scale, as assessed for the photooxygenation of olefins with single oxygen. We have found, for instance, that as little as 0.0001 equiv of C_{70} effects photolytic conversion of an olefin to an oxygenated product in high yield.

Results and Discussion

Despite the known ability of C_{60} and C_{70} to convert molecular oxygen to singlet oxygen,[6,8] several questions needed to be addressed to establish them as practical and useful sensitizers. First, the interactions of C_{60} with oxygen under photolytic conditions,[9] and the actual isolation of oxidized products[10] under such conditions, suggested that the efficiency of catalytic turnover might be low in the sensitized oxygenation under preparative conditions. Second, it was of interest to examine whether or not the chemical reactivity of singlet oxygen is affected by the fullerene sensitizer. Third, there is the question of whether fullerene derivatives bearing functional groups and lacking some olefinic conjugation are good sensitizers.[11] In addition, we wished to determine any difference in the reactivities of C_{60} and C_{70}.

The Diels–Alder reaction and the ene reaction are two widely used applications of singlet oxygen with olefins.[12] In order to probe the scope of the fullerene sensitization and to investigate the nature of the reactive species so generated, we subjected a series of typical olefins to C_{60}-sensitized photooxygenation. Thus, we examined the Diels–Alder conversion of α-terpinene (**1**) to ascaridole (**2**) (eq 1),[13] as well as the ene reaction of β-myrcerne (**3**) (eq 2),[14] (+)-pulegone (**5**) (eq 3),[15] and 4-methylpent-3-en-2-ol (**7**) (eq 4).[16] In these reactions, irradiation (with a 100-W tungsten lamp in eq 3, and a 400-W high pressure mercury lamp with Pyrex filter in the others) of a 0.1 M toluene solution of a substrate containing 0.5–1 mol % of C_{60} at room temperature generated the expected products in high yield. The purple color of C_{60} persisted until the

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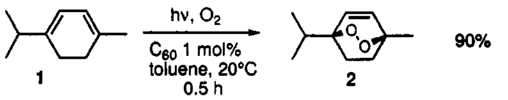

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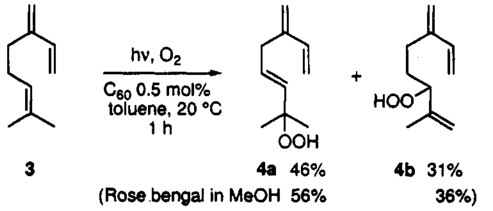

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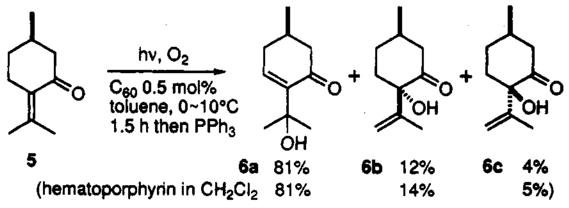

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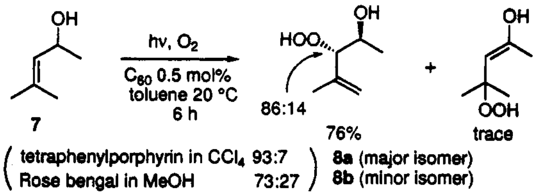
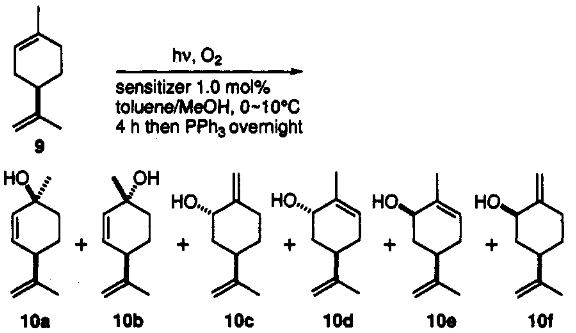


(4)

end of the reaction. The observed regioselectivity for myrcene and pulegone and the stereoselectivity for the oxidation of the allylic alcohol conform to the known selectivity of singlet oxygen reactions, as shown in parentheses.

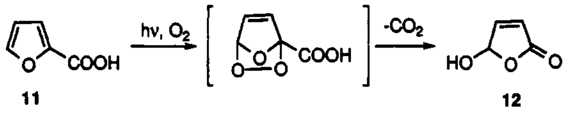
A more rigorous comparison of the fingerprint of the reactive species was carried out for a limonene (**9**) oxidation sensitized with C_{60} (eq 5).[12a,17] The ratio of six products (**10a–f**) observed for the fullerene sensitization was virtually identical with the values obtained by the established singlet oxygen reaction as shown in eq 5.[12a] It was thus concluded from the reactivity analyses that free singlet oxygen, rather than some kind of a $C_{60}/{}^1O_2$ complex, takes part in the C_{60}-sensitized photooxygenation reaction.



(5)

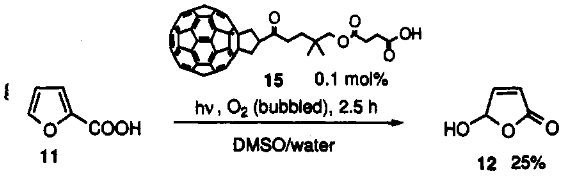
sensitizer	10a	10b	10c	10d	10e	10f
C_{60}	43%	9%	20%	6%	1%	22%
Rose bengal	41%	9%	20%	8%	1%	21%

Having established the identity of the reactive species, we next examined the structural effects of fullerene sensitizer by using the Diels–Alder reaction with furan-2-carboxylic acid (**11**) as a model reaction (eq 6, Table 1).[18] Photolysis of a 0.1 M 9:1 toluene/MeOH solution of the acid **11** in the presence of 1.0 mol % of C_{60}, with a 100-W tungsten lamp, gave the lactone **12** in 100% yield after 8 h (entry 1). Irradiation with a 400-W high pressure mercury lamp through a Pyrex filter completed the reaction in 2.5 h in the presence of only 0.10 mol % of sensitizer (entry 2), and further comparative studies were carried out under the same conditions. The efficiencies of C_{60}, C_{70}, and hematoporphyrin were compared (entries 3, 4, and 8). With 0.10 mol % sensitizer for 0.5 h, C_{70} brought the reaction nearly to completion (entry 4), while C_{60} and hematoporphyrin induced only 50–60% conversion (entries 3 and 8). It was found that a crude soot mixture consisting of 85% C_{60} and 15% C_{70} was of practical value, bringing the reaction to 92% conversion in 0.5 h (entry 6) and completion within 3.5 h with 0.07 mol % sensitizer (entry 7).[19] It is notable that the amount of the C_{70} sensitizer can be reduced to as little as 0.0001 equiv (entry 5). Further reduction to 0.00001, however, resulted in incomplete conversion and the eventual disappearance of the red color of C_{70}. The methanofullerene **13**[20] in which one double bond in the C_{60} core has been converted into a cyclopropane C–C bond was also found to be as good a sensitizer as C_{60} itself. Unlike the parent C_{60}, **13** is reasonably soluble in various solvents, including acetonitrile. The aminofullerene **14**, which is freely soluble in water, was also found to be capable of generating singlet oxygen.



(6)

The propanofullerene carboxylic acid **15** is capable of cutting DNA and inhibiting cell growth and enzyme activity under photolytic conditions. The biochemical behavior suggested that singlet oxygen is responsible for these observations.[7] We found that this fullerene acid indeed generates singlet oxygen in aqueous DMSO, under conditions similar to those employed for the biochemical studies. The efficiency of photooxygenation was much lower in an aqueous solution than in hydrocarbons, perhaps due to the much shorter lifetime of singlet oxygen in the former than in the latter.[21] The present finding strongly suggests that the biochemical activity reported earlier[7] is largely due to singlet oxygen, generated photolytically from the oxygen dissolved in the medium.



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In summary, we have shown that fullerene-sensitized photoreactions generates free singlet oxygen in synthet-

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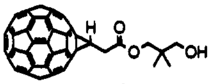
Table 1. Diels–Alder Reaction with Furan-2-carboxylic Acid

entry	sensitizer	equiv (mol %)	time (h)	% yield[a] 12	11
1[b]	C_{60}	1.0	8	100	-
2	C_{60}	0.10	2.5	100	-
3	C_{60}	0.10	0.5	52[c]	46
4	C_{70}[d]	0.10	0.5	92[c]	7
5[e]	C_{70}[d]	0.01	3.5	100	-
6	C_{60}/C_{70}[f]	0.10	0.5	92	8
7[e]	C_{60}/C_{70}[f]	0.07	3.5	100	-
8	HP[g]	0.10	0.5	64	31
9	13[h]	0.10	0.5	66	33
10	13[h]	0.10	2.5	97	-
11	14[i]	0.10	0.5	26	71

[a] Reactions were carried out with a 400-W-high-pressure Hg lamp with Pyrex filter except in entry 1. NMR yield based on an internal standard. [b] A 100-W tungsten lamp was used. [c] Average of three reactions for entry 3 and two runs for entry 4. [d] A >9:1 C_{70}/C_{60} mixture was used. [e] A gram-scale reaction. [f] A crude toluene extract of carbon arc soot consisting of 85% of C_{60} and 15% of C_{70}. [g] Hematoporphyrin. [h] See below for the structure of 13. [i] The value n in 14 was estimated to be 6 (see Experimental Section).



13

$C_{60}H_n(HN\!\!\diagup\!\!\diagdown\!\!\diagup NMe_2)_n$

14

ically useful amounts. The reaction is rapid and the turnover of the sensitizer can be over 10000. It is notable that the raw soot containing C_{60} and C_{70}, which is reasonably priced at the present time and will rapidly become cheaper in the near future, is also a very effective sensitizer. Fullerenes differ from conventional sensitizers in two important respects. First, fullerene is readily amenable to the addition of functional appendages.[11,22] One simple illustrative result is that derivatization makes C_{60} soluble in a wide variety of solvents while maintaining the chemical properties of the crucial C_{60} core. Second, unlike conventional sensitizers which are usually compounds with conjugated structures and flat shapes, the unusual nature of their olefinic conjugation makes fullerenes a uniquely compact and spherical reagent. Hence, functionalized fullerene derivatives have been incorporated into a membrane structure[23] and into an enzyme cavity,[24] which will undoubtedly lead to further development in the construction of photosensitive molecular architectures.

Experimental Section

General. All ^1H NMR spectra taken at 200, 270, or 500 MHz and ^{13}C NMR spectra at 50, 67.5, or 125 MHz were measured on JEOL FX-200, GSX-270, or GSX-500 machines, respectively. ^1H NMR spectra were reported in parts per million from internal tetramethylsilane, and ^{13}C NMR from $CDCl_3$ (77.0 ppm). IR spectra were recorded on a JASCO IR-800 machine; absorptions are reported in cm^{-1}. Recycling preparative HPLC was performed on a Japan Analytical Industry LC-908 machine equipped with GPC columns (JAIGEL 1H and 2H) using $CHCl_3$ as eluant. Gas chromatographic (GC) analyses were performed on Shimazu 8A or 14A machines equipped with glass capillary columns (0.25 mm i.d. × 25 m) coated with HR-1 or HR-1701. Photoirradiation was carried out with a 100-W tungsten lamp (Toshiba) or 400-W high pressure mercury lamp (Riko Kagaku Sangyo Co., Ltd.).

Materials. Fullerenes were synthesized as described by Kräschmer et al.[3] Purification of the crude fullerene extract was achieved as described in the literature.[25] Separation of C_{70} from the crude fullerene extract was carried out by recycling preparative HPLC. The compounds **13** and **15** were prepared as reported previously.[7,20] Toluene was distilled from calcium hydride and stored over 4-Å molecular sieves, and methanol was distilled from Mg and stored over 4-Å molecular sieves.

Diels–Alder Reaction of α-Terpinene. A toluene solution (7 mL) of α-terpinene 1 (0.11 mL, 0.70 mmol) in the presence of C_{60} (5.0 mg, 0.0070 mmol, 1.0 mol %) was irradiated with a 100-W tungsten lamp from a distance of 5 cm at 20 °C. During irradiation, oxygen was passed through the reaction mixture via a 0.8 mm i.d. Teflon tube. After a 1-h irradiation, the mixture was concentrated to afford the crude product (167 mg) as a colorless oil. Purification by silica gel column chromatography (10% EtOAc/hexane) gave ascaridole **2** (106 mg, 90%): IR (neat) 2970, 2940, 2830, 1470, 150, 1380, 880, 700; ^1H NMR (200 MHz, $CDCl_3$) δ 1.00 (d, $J = 7.1$ Hz, 6 H, two methyl groups), 1.38 (s, 3 H, methyl), 1.50–1.63 (m, 2 H), 1.93 (sep, $J = 6.8$ Hz, isopropyl CH), 2.00–2.10 (m, 2 H), 6.41 (d, $J = 8.5$ Hz, 1 H, olefinic CH), 6.50 (d, $J = 8.5$ Hz, 1 H, olefinic CH). Spectral data were identical with those reported.[13]

Ene Reaction of β-Myrcene. A solution of β-myrcene **3** (0.17 mL, 1.0 mmol) and C_{60} (3.6 mg, 0.0050 mmol) in toluene (10 mL) was irradiated with a 100-W tungsten lamp at 20 °C for 1 h. During the irradiation, oxygen was passed through the reaction mixture via a 0.8 mm i.d. Teflon tube. The ratio of the regioisomer **4a**/**4b** was determined for the crude product mixture, by ^1H NMR integration of the olefinic proton signals, to be 60:40 (46 and 31% yield based on an internal standard, respectively). Purification on silica gel (9.4 g, 10% EtOAc/hexane) gave a mixture of **4a** and **4b** (109.2 mg, 65%), which showed complete agreement with the spectral data of an authentic mixture prepared by the reported method.[14]

Ene Reaction of (+)-Pulegone. A mixture of (+)-pulegone **5** (0.16 mL, 1.0 mmol) and C_{60} (3.6 mg, 0.50 mol %) in toluene (10 mL) was irradiated for 1.5 h with a water-cooled 400-W high pressure mercury lamp through a Pyrex filter at 0–10 °C, while oxygen was passed through the reaction mixture via a 0.8 mm i.d. Teflon tube. Triphenylphosphine (314 mg, 1.20 mmol) was added, and the reaction mixture was allowed to stand overnight. Concentration gave a crude product as a mixture of isomers. The ratio of isomers **6a**, **6b**, and **6c** was determined by ^1H NMR integration of the olefinic signals to be 81:11:5. Purification on silica gel (ca. 15 g, 10–25% EtOAc/hexane) afforded the enone **6a** (137 mg, 81%) and the diastereomeric mixture of **6b** and **6c** (27 mg, 16%). **6a**: IR (neat) 3200–3600,2950, 2920, 850, 1660, 1350; ^1H NMR (270 MHz, $CDCl_3$) δ 1.05 (d, $J = 6.0$ Hz, 3 H, methyl), 1.39 (s, 6 H, two methyl group), 1.82–2.57 (m, 5 H), 4.43 (s, 1 H, OH), 6.89 (dd, $J = 2.4, 5.8$ Hz, 1 H, olefinic CH). The mixture of **6b** and **6c**: IR (neat) 3200–3600, 2950, 2920, 2850, 1720, 1670, 1650, 1460; ^1H NMR (270 MHz, $CDCl_3$) δ 0.97 (d, $J = 6.0$ Hz, 2.1 H), 1.02 (d, $J = 5.0$ Hz, 1.9 H), 1.2–2.2 (m, 7 H), 1.71 (s, 3 H), 4.06 (s, 0.7 H), 4.14 (s, 0.3 H), 5.02–5.12 (m, 1.4 H), 5.09 (s, 0.6 H). These data of ^1H NMR and IR spectra of the three isomers were identical with those reported.[15]

Ene Reaction of 4-Methylpent-3-en-2-ol. A mixture of 4-methylpent-3-en-2-ol (**7**) (70 mg, 0.70 mmol) and C_{60} (2.5 mg, 0.50 mol %) in toluene (7 mL) was irradiated with a 100-W tungsten lamp from a distance of 5 cm at 20 °C, while oxygen was passed through the mixture via a 0.8 mm i.d. Teflon tube. After a 6-h irradiation, the reaction mixture was concentrated. The ^1H NMR spectra of the crude product was identical with the reported ones[16] and the yield determined by ^1H NMR using an

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internal standard was 76%. The ratio of the diastereomers **8a**/**8b** was determined by integration of the C*H*OOH signals to be 86:14.

Major isomer 8a: ^1H NMR (270 MHz, $CDCl_3$) δ 1.12 (d, *J* = 6.4 Hz, 2.6 H), 1.72 (br s, 2.6 H), 3.48 (br s, 0.9 H), 3.86 (dq, *J* = 6.4, 8.4 Hz, 0.9 H), 4.14 (d, *J* = 8.4 Hz, 0.9 H), 5.00–5.08 (m, 1.6 H), 9.78 (br s, 0.9 H).

Minor isomer 8b: ^1H NMR (270 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.4 Hz, 0.4 H), 1.80 (br s, 0.4 H), 2.72 (br s, 0.1 H), 3.99 (dq, *J* = 4.6, 6.4 Hz, 0.1 H), 4.32 (d, *J* = 4.6 H, 0.1 H), 5.05–5.16 (m, 0.4 H), 9.50 (br s, 0.1 H).

Ene Reaction of (+)-Limonene. A mixture of (+)-limonene (**5**) (0.59 mL, 4.0 mmol) and C_{60} (10 mg, 1.0 mol %) in toluene/methanol mixture (8.0 mL, 9/1) was cooled in an ice–water bath and irradiated externally with a water-cooled 400-W high-pressure mercury lamp for 4 h. Triphenylphosphine (1.1 g, 4.0 mmol) was added and the mixture was allowed to stand overnight. The crude mixture was subjected to GC analysis (HR-1701, 85 °C). The ratio of the ene products **10a**, **10b**, **10c**, **10d**, **10e**, and **10f** was determined to be 43:9:20:6:1:22 (retention times; 13.9, 15.7, 22.8, 29.5, 32.3, and 33.6 min, respectively). A control experiment using Rose bengal[17] in toluene/methanol solution was carried out and showed the ratio of **10a**, **10b**, **10c**, **10d**, **10e**, and **10f** to be 41:9:20:8:1:21.

General Procedure of Diels–Alder Reaction between Singlet Oxygen and Furan-2-Carboxylic Acid. Preparation of 5-Hydroxy-2(5*H*)-furanone. The experiments in Table 1 were carried out as described below. A mixture of furan-2-carboxylic acid (**11**) (157 mg, 1.40 mmol) and C_{60} (1.0 mg, 0.1 mol %) in a toluene/methanol mixture (14 mL, 9/1) was irradiated with a water-cooled 400-W high-pressure mercury lamp through a Pyrex filter from a distance of 5 cm, while oxygen was passed through the reaction mixture (30 mL/min) via a 0.8 mm i.d. Teflon tube for 0.5 h. The internal temperature was 40–50 °C. Concentration in vacuo afforded a crude product as semicrystalline white solid (153 mg). The yield of the lactone **12** (52%)[18] and the recovery of the carboxylic acid **11** (46%) were determined by ^1H NMR using an internal standard.

Gram-Scale Preparation. Furan-2-carboxylic acid (**11**) (1.34 g, 12.0 mmol) and C_{70} (>90:10 C_{70} and C_{60} mixture by HPLC analysis) were dissolved in a toluene/methanol mixture (60 mL, 9/1). The red-brown solution was irradiated externally at room temperature with a water-cooled 400-W high-pressure mercury lamp through a Pyrex filter from a distance of 5 cm, while oxygen was passed through the reaction mixture (30 mL/min.) via a 0.8 mm i.d. Teflon tube. After a 3.5-h irradiation, the reaction mixture was concentrated in vacuo to afford a furanone as a semicrystalline solid pure by ^1H NMR and TLC (1.20 g, 100%): IR ($CHCl_3$) 3000–3600, 3020, 1760, 1340, 1130; ^1H NMR (200 MHz, $CDCl_3$) δ 4.30 (br s, 1 H, OH), 6.18 (m, 1 H), 6.26 (br s, 1 H), 7.32 (dd, 1 H, *J* = 1.2, 5.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 98.97, 124.58, 152.06, 171.49. These data were identical with those of reported.[18]

Preparation of the C_{60}/*N*,*N*-Dimethylethylenediamine Adduct (14). The experiment was carried out as described briefly in the literature.[26] To a toluene (30 mL) solution of C_{60} (30 mg) was added 2 mL of *N*,*N*-dimethylethylenediamine and the mixture was stirred at 25 °C for 3 days. The solvent was removed in vacuo to afford a brown solid (ca. 60 mg). Purification was achieved by precipitation from $CHCl_3$ solution of the crude product by addition of hexane. Elemental analysis of this material (found C, 67.70%; H, 5.03%; N, 13.54%) was difficult to reconcile with a rational formula, but the ratios of H/C and H/N, indicated that the average number of *N*,*N*-dimethylethylenediamine added was six: IR (CCl_4) 3300, 2950, 2850, 2800, 2760, 1460, 1120, 1040, 650, 540; ^1H NMR δ 1.9-2.4 (br, 6 H, CH_3), 2.4-3.0 (br, 4 H, CH_2), 3.2–3.7 (br, 1 H, NH).

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