Efficient Photooxygenation of Olefins by a C_{60} Derivative Bearing an Organofluorine Tail

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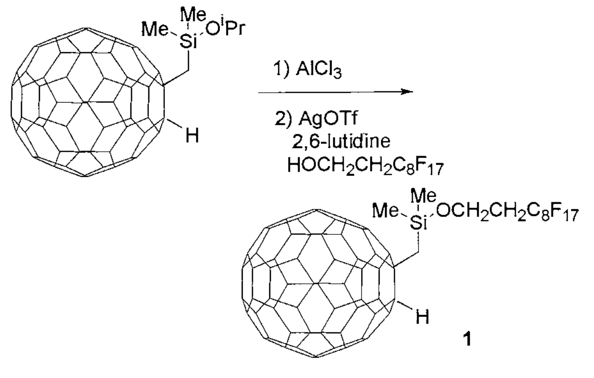
A C_{60} derivative bearing an organofluorine tail through the dimethylsilyl moiety (**1**) was proved to be an efficient photosensitizer in C_6F_6. Photooxygenation of olefins or dienes was accomplished by catalysis of **1** (0.5 – 1.5 mol%) at room temperature under an oxygen atmosphere.

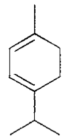
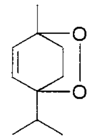
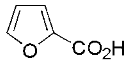
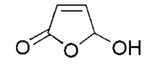
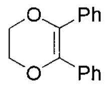
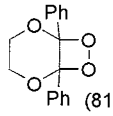
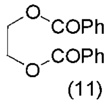
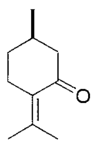
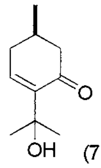
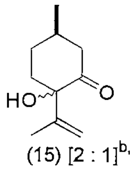
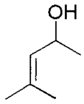
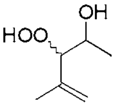
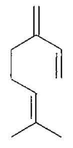
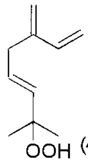
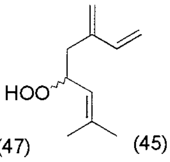
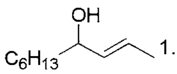
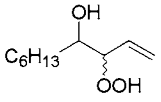
Photophysical properties of fullerenes and their derivatives have attracted attention since the dawn of fullerene research.[1] Pioneering work by Foote and coworkers revealed that C_{60} and its dihydroderivative were good singlet oxygen ($^1O_2$) producers when they were irradiated under an oxygen atmosphere.[1] Quantum yield of the $^1O_2$ production is as high as that with one of the most powerful conventional photosensitizers, Rose Bengal. Application of this property to photooxygenation of olefins was reported by Nakamura[2] and Orfanopoulos.[3] Although C_{60} itself is an efficient and relatively tough photosensitizer, conversion of C_{60} to $C_{60}O_n$ during the photooxygenation,[4] which is known to be a poor singlet oxygen producer, retards the reaction.[5] Thus, a less reactive substrate such as 2-decen-4-ol was hardly oxygenated by C_{60} as the photosensitizer (vide infra). In our study to develop an novel efficient photosensitizer based on C_{60}, we were interested in a paper reporting that 2-decen-4-ol underwent photooxygenation using fluorinated porphyrin in a fluorous biphasic system.[6] The effect of fluorous media was proposed to be attributable to the longer lifetime of $^1O_2$ and higher solubility of O_2 than those in other solvents, and to suppress degradation of the photosensitizer.[6] Use of the biphasic system emphasized the efficiency, because the formed hydroperoxide, which caused oxidative decomposition of porphyrins, could be removed from the phase containing the photosensitizer. These fascinating effects of fluorous media prompted us to investigate preparation of a C_{60} derivative dissolved in fluorous solvents and its property as the photosensitizer for the oxygenation of olefins. In this paper, we wish to report that a silylmethylated fullerene bearing an organofluorine tail, $C_{60}(H)CH_2SiMe_2(OCH_2CH_2C_8F_{17})$ (**1**), acted as a good photosensitizer in C_6F_6 leading to successful photooxygenation of even less reactive olefins.



Scheme 1.

Preparation of **1** was achieved by alcohol exchange reaction[7] of $C_{60}(H)CH_2SiMe_2(O^iPr)$[8] with $HOCH_2CH_2C_8F_{17}$ as shown in Scheme 1.[9] Although C_{60} is soluble in toluene but not in common fluorous solvents, **1** is soluble in both C_6F_6 and toluene. Photooxygenation of α-terpinene was carried out to examine the efficiency of the photosensitizer. Nakamura reported that photooxygenation of α-terpinene gave ascaridole in 90% yield in the presence of 1 mol% of C_{60} in toluene within 30 min.[2] The same reaction using 0.05 mol% of **1** in C_6F_6 at room temperature afforded ascaridole in 91% yield after 0.5 h. When the reaction in C_6F_6 was monitored by ^1H NMR, the conversion of α-terpinene after 10 min reached 45%, which was twice as much as that obtained when C_{60} (0.05 mmol) was

Table 1.

entry	substrate	cat.(%)	time	products (Yield%)^a
1		0.05	30 min	 (91)
2		0.5	30 min	 (95)
3		0.5	30 min	 (81)  (11)
4		0.5	1 h	 (70)  (15) [2 : 1]^{b,c}
5		0.5	40 min	 (94) [87 : 13]^b
6		0.5	30 min	 (47)  (45)
7		1.5	24 h	 (91)

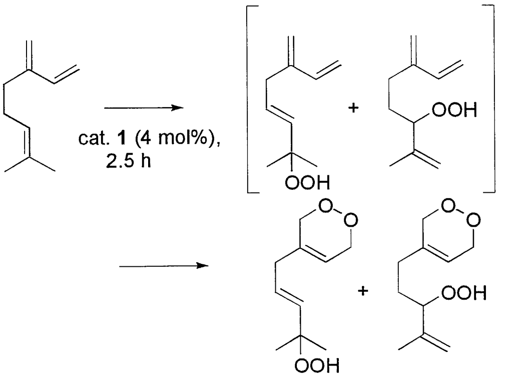
^{a}The yield was determined by ^1H NMR based on the integral values of internal standards. b. Diastereomer ratios. c. The alcohols were obtained after reduction of the fomed hydroperoxides by PPh_3.

used as the photosensitizer in toluene (21%). This apparently showed that use of **1** in C_6F_6 enhanced the efficiency of the photooxygenation. In Table 1 are summarized the results of photooxygenation of various dienes (entries 1-2) and a dioxene (entry 3), which led to the [4 + 2] cycloaddition and the [2 + 2] cycloaddition, respectively. The ene reactions of four olefinic compounds are listed in entries 4-7. All of the reactions except the oxygenation of 2-decen-4-ol were completed within 1 h at room temperature to afford the corresponding products in good yields.

As reported in the literature,[6] 2-decen-4-ol is an unreactive substrate for photooxygenation. Since the reaction is slow, degradation of the photosensitizer is a serious side reaction preventing the efficient oxygenation. Although C_{60} is one of the most efficient photosensitizers as reported by Foote,[1] we confirmed that attempted photooxygenation of 2-decen-4-ol in toluene with C_{60} (1.5 mol%) was terminated when the conversion of 2-decen-4-ol reached 10-20% (turnover = 7 – 13). HPLC analysis of the reaction mixture revealed that C_{60} disappeared at this point, suggesting that conversion of C_{60} to $C_{60}O_n$ retarded the catalytic activity. Use of **1** in C_6F_6 was effective for the photooxygenation of 2-decen-4-ol, though the reaction was much slower than those of the substrates shown in entries 1-6. In the presence of 1.5 mol% of **1** in C_6F_6, the yield of the hydroperoxide exceeded 90% after 24 h (turnover > 60).[10] The following two experiments suggested the importance of using both the fluorinated photosensitizer and the fluorinated solvent: **1** did not efficiently catalyze the photooxygenation of 2-decen-4-ol in toluene (using 1.5 mol% of **1**, the yield of the product was only 14% after 24 h), whereas use of C_{60} in C_6F_6 did not improve the efficiency compared with that in toluene.

The other result confirming the efficiency of **1** and C_6F_6 is photooxygenation of myrcene; this generally led to the ene reaction to afford the hydroperoxides shown in entry 6. Matsumoto et al. reported further but slow photooxygenation resulted in the [4 + 2] cycloaddition reaction.[11] The ene reaction catalyzed by **1** in C_6F_6 was completed within 1 h, and further reaction resulted in successful [4 + 2] cycloaddition reaction to form the 1,4-endoperoxides as shown in Scheme 2.

In summary, use of a silylmethylated fullerene bearing an organofluorine tail is proved to be an efficient photosensitizer in C_6F_6. Although the hydroperoxide, which caused the oxidation of photosensitizer to retard the reaction, was not removed by phase separation, serious degradation of **1** was not seen in this system even in the photooxygenation of a typical less reactive substrate, 2-decen-4-ol. Furthermore, the manipulation is easy; the reaction proceeded under an oxygen atmosphere, in which oxygen was supplied from a rubber balloon attached to the reaction flask. The efficiency of the reaction and the easy manipulation make this reaction useful for organic synthesis of oxygenates. Expansion of fullerene photosensitizer in fluorous phase to biphasic systems, which is desirable to remove the photosensitizer from the reaction mixture in a large-scale photooxygenation, is currently under investigation.



Scheme 2. 38% 23%

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9 A typical experimental procedure; $C_{60}(H)CH_2SiMe_2(O^iPr)$ (51 mg, 0.06 mmol) was treated with $AlCl_3$ (24 mg, 0.18 mmol) in CH_2Cl_2 (25 mL) at room temperature under an argon atmosphere. After 1 h, a dichloromethane solution of $C_8F_{17}CH_2CH_2OH$ (856 mg, 1.84 mmol, 0.06 M) was added to the mixture. The resulting solution was stirred at room temperature for 0.5 h, treated with a suspension of $AgOSO_2CF_3$ (15 mg, 0.06 mmol) and 2,6-lutidine (19 mg, 0.18 mmol) in CH_2Cl_2 (25 mL), and stirred at room temperature for 24 h. After the aqueous work-up, the crude product was extracted with a 5 : 2 mixture of toluene and methanol. Separation of a small amount of impurities was achieved by medium-pressure column chromatography (LOP ODS, toluene-methanol 55/45) to afford **1** (41 mg, 54% yield); Mp >300 °C. ^1H NMR ($CDCl_3$, 395 MHz) δ 0.67 (s, 6H, $SiMe_2$), 2.39 – 2.63 (m, 2H, CH_2), 2.98 (s, 2H, $SiCH_2$), 4.22 (t, J = 6.8 Hz, 2H, OCH_2), 6.64 (s, 1H, C_{60}-H). ^{13}C NMR ($CDCl_3$, 100 MHz, both ^1H and ^{19}F nuclei were irradiated) δ 29.7, 34.3, 37.9, 55.7, 61.5, 108.4, 110.3, 110.8 (2C), 111.0, 111.2, 117.2, 118.0, 135.1, 136.5, 140.2, 140.3, 141.7, 142.0 (2C), 142.1, 142.2, 142.6, 143.4, 144.7, 144.8, 145.4, 145.5 (3C), 145.7, 146.0, 146.3 (2C), 146.4, 146.5, 147.0, 147.4, 147.6, 154.3, 157.8. ^{19}F NMR ($CDCl_3$,376 MHz) δ 35.7 (2F), 38.2 (2F), 39.1 (2F), 39.9 (4F), 40.1 (2F), 48.3 (2F), 48.5 (quint, 2F, *J*= 15Hz), 81.0 (t, 3F, *J*= 10Hz). IR (KBr) 2920 (m), 1240 (m), 1210 (s), 1150 (s), 842 (s), 528 (m). Fab-mass (2-nitrophenyl octyl ether), 1257 (M+1). Anal. Found: .C, 68.93; H, 1.22%. Calcd. for $C_{73}H_{13}F_{17}OSi$: C, 69.75; H, 1.04%.

10 A typical example for the photooxygenation; In a flask connected to a rubber balloon filled with oxygen, **1** (1.9 mg, 1.5 μmol) and 2-(E)-decen-1-ol (15 mg, 0.1 mmol) were dissolved in C_6F_6 (3 mL). The solution was irradiated by a 400 W high pressure Hg lamp at 15 – 20°C for 24 h. After removal of the solvent, the corresponding hydroperoxide was obtained (diastereomer ratio = 55 : 45). ^1H NMR data of the product were identical with the reported data.[6] The yield was determined by ^1H NMR using anisole as the internal standard. Isolation of the hydroperoxide was possible by chromatographic purification of the crude sample.

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