Photooxygenation of Olefins, Phenol, and Sulfide Using Fullerodendrimer as Catalyst

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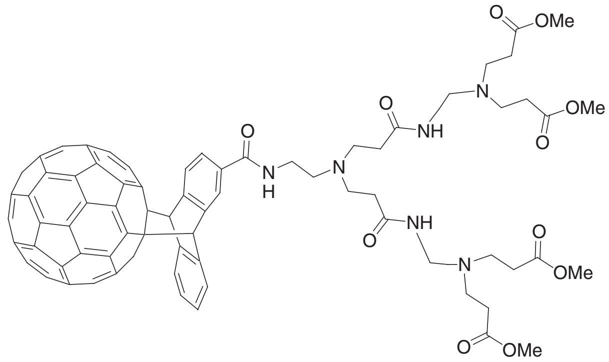
Fullerodendrimer acts as a new catalyst that uses oxygen and light to generate singlet oxygen ($^1O_2$). The dendrimer facilitates various types of singlet oxygenation reactions including ene reaction, the Diels–Alder reaction, and oxidation of phenol and sulfide.

Fullerene-based derivatives have received considerable attention because of a variety of interesting features in structural chemistry and material science.[1] In particular, photosensitizers made of fullerene have been attracting a great interest in the field of synthetic organic chemistry[2–6] and photodynamic therapy.[7] In terms of chemical applications, several reports are found in the literature on ene[3,5,6] and [4+2]cycloaddition[4–6] reactions of olefins with $^1O_2$ generated by photosensitization of ground-state oxygen with fullerenes or fullerene derivatives. Nakamura reported that C_{60}, C_{70}, and their derivatives are synthetically useful photosensitizers as assessed for the photooxygenation of olefins with singlet oxygen.[6] Lattassa et al. have reported a systematic study on the selective photooxidation of sulfides to sulfoxides by the use of a fullerene-based heterogeneous photosensitizer.[8] However, chemical uses of $^1O_2$ produced by fullerenes are often hampered by the limited solubility of the carbon cages in most solvents or the difficult recovery of soluble fullerene derivatives at the end of the reaction. Recently we have reported a facile synthesis of fullerodendrimer,[9] of which fullerene moiety is proved to be efficient photosensitizer to generate singlet oxygen.[9c] Despite the many studies focused on fullerodendrimer themselves,[9,10] very little has been determined about fullerodendrimer-mediated chemical transformations. Fullerodendrimer might be candidate molecule for photocatalyst because of versatile solubility introduced by dendritic substituent. This paper describes homogeneous photocatalytic activity of the fullerodendrimer to generate singlet oxygen.

In order to probe the scope of the fullerodendrimer sensitization and to investigate the nature of the reactive species so generated, we subjected a series of typical olefins to photooxygenation sensitized by fullerodendrimer (**1**), which was synthesized as described before.[9b] The Diels–Alder reaction and the ene reaction are two widely used applications of singlet oxygen with olefins.[11] Thus, we examined the Diels–Alder conversion of α-terpinene (**2**) to ascaridole (**3**) (Eq 1), and furan-2-carboxylic acid (**4**) to lactone (**5**) (Eq 2), as well as the ene reaction of 2,3-dimethyl-2-butene (**6**) (Eq 3) and 4-methylpent-3-en-2-ol (**8**) (Eq 4). Furthermore, oxidation of 1-naphthol (**11**) (Eq 5) and dibenzyl sulfide (**13**) (Eq 6) was also examined. All six reactions proved to be successfully catalyzed by fullerodendrimer **1** under the same reaction conditions as used by Nakamura et al.[6] The brown color of dendrimer **1** persisted until the end of the reaction.[12]



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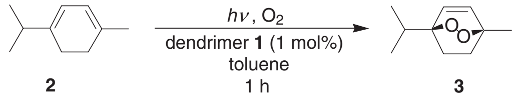
In typical run, a toluene solution (7 mL) of α-terpinene **2** (83 mg, 0.61 mmol) in the presence of fullerodendrimer **1** (1 mol %, 9.0 mg, 0.0059 mmol) was irradiated with a 500-W high-pressure mercury lamp through a Pyrex filter at room temperature. During irradiation, oxygen was passed through the reaction mixture. After a 1 h irradiation, the mixture was concentrated to afford the crude product as colorless oil. Purification by silica gel column chromatography (10% EtOAc/hexane) gave ascaridole **3** (99 mg, 0.059 mmol) in 93% yield.[13] On the other hand, photooxygenation of furan-2-carboxylic acid **4** proceeded employing only 0.1 mol % of dendrimer **1** to give the lactone **5** in 99% yield after 80 min (Eq 2). Furthermore, we confirmed the reactivity of the fullerodendrimer **1** as the sensitizer by the use of the ene reaction with 2,3-dimethyl-2-butene **6** as a model reaction. Compound **6** was easily converted to 3-hydroperoxy-2,3-dimethyl-1-butene (**7**) in 97% yield by the use of fullerodendrimer **1** (1 mol %) as photocatalyst (Eq 3). Ene reaction of 4-methylpent-3-en-2-ol **8** with singlet oxygen generated by photosensitization of fullerodendrimer **1** gave compounds **9** and **10** in 98% and 1.9% yields, respectively (Eq 4). The observed regioselectivity and the stereoselectivity of the products conform to the known selectivity of singlet oxygen reactions,[6] indicating that the fullerodendrimer-sensitized reaction generates free singlet oxygen. Meanwhile, oxidation reactions of phenol and sulfoxide were also examined. Photooxidation of 1-naphthol **11** in the presence of dendrimer **1** (1 mol %) gave 70% conversion to only 1,4-naphthoquinone (**12**) after 50 min (Eq 5). The performance of the fullerodendrimer **1** in the photooxidation of sulfides to sulfoxides was tested on benzyl sulfide (**13**). Photooxygenation of dibenzyl sulfide **13** sensitized by **1** (1 mol %) afforded the corresponding sulfoxide (**14**) in 90% yield (Eq 6). In this case, a mixture of chloroform and methanol was used as the solvent of choice according to the observation of Foote and Peters that protic solvents, minimizing the physical quenching of singlet oxygen, afforded better yields of sulfoxides than aprotic ones.[14] Hence, when we used pure chloroform as a solvent of the photooxidation reaction, sulfoxide **14** was obtained in only 59% yield. It is remarkable that no side or cleavage reactions were observed with the benzylic substrates, in particular the Pummerer rearrangement which is often descried in this context. As opposed to C_{60} and many of its derivatives, the fullerodendrimer can be readily soluble and used in protic solvents such as methanol which makes the photooxygenation highly selective, affording good yield of sulfoxides with benzylic sulfide.



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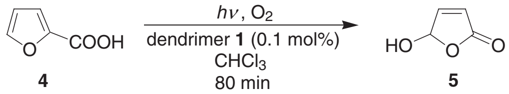

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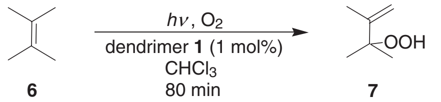

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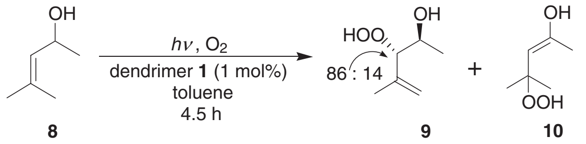

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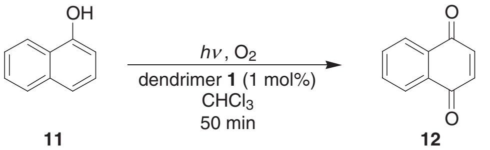

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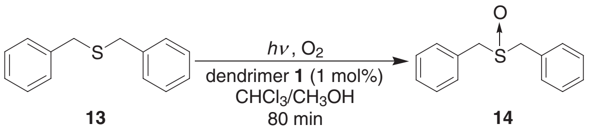

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In summary, we have shown that fullerodendrimer-sensitized photoreactions generate free singlet oxygen in synthetically useful amounts. One simple illustrative advantage is that fullerodendrimer is soluble in a wide variety of solvents while maintaining the chemical properties of the crucial C_{60} core. In particular, formation of singlet oxygen in protic solvent is quite useful. Further work is in progress to explore the applications and advantages of the fullerodendrimer as a photosensitizer.

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12 Decomposition of fullerodendron **1** was observed by GPC analysis and NMR experiment after the reaction.

13 When we used pristine C_{60} as photosensitizer under completely the same reaction conditions, we obtained ascaridole **3** in 75% yield.

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