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A 3-Methylene-1,2-dioxetane as a Possible Chemiluminescent Intermediate in Singlet Oxygenation of Allene

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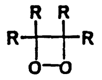
Synopsis. Photosensitized oxygenation of bis(adamantylidene)methane and vinylideneadamantane at −78 °C afforded adamantanone and the former also emitted light when warmed up to room temperature in the presence of a fluorescer. A 3-methylene-1,2-dioxetane as a possible chemiluminescent intermediate is proposed.

The chemistry of 1,2-dioxetanes (**1**) has been extensively studied and utilized for the synthetic and mechanistic exploration of chemienergized electronic excitation in connection with chemiluminescence and bioluminescence systems.[1–3] The thermal stability of 1,2-dioxetanes is affected by a substituent on the dioxetane ring.[4] Work on the synthesis and characterization of dioxetanones[1,2] (**2**) and dioxetanimines[5] (**3**) through the singlet oxygenation of ketenes and ketene imines has recently been reported. Greibrokk[6] and Gollnick et al.[7] reported that the photosensitized oxygenation of allenes yields the corresponding ketones and CO_2, in which singlet oxygen ($^1O_2$) cycloaddition is considered to give the bi(dioxetane) and methylene-1,2-dioxetane (**4**). Recently, Sander and Patyk reported the matrix isolation of a ter(dioxetane) at 10 K in photooxidation of 2,5-dimethyl-2,3,4-hexatriene, in which a methylene-substituted dioxetane intermediate is proposed.[8] As a part of our continuing research for new chemiluminescence systems,[9] we report here our results on the photosensitized oxygenation of bis(adamantylidene)methane[10] (**5a**) and vinylideneadamantane[11] (**5b**) and the chemiluminescence of the product (**4a**) in the presence of a fluorescer.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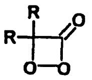
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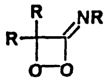
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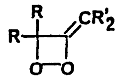
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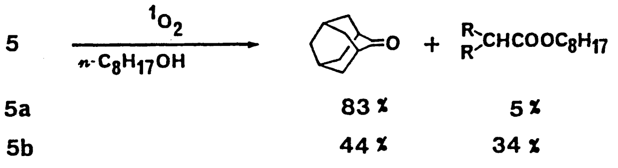
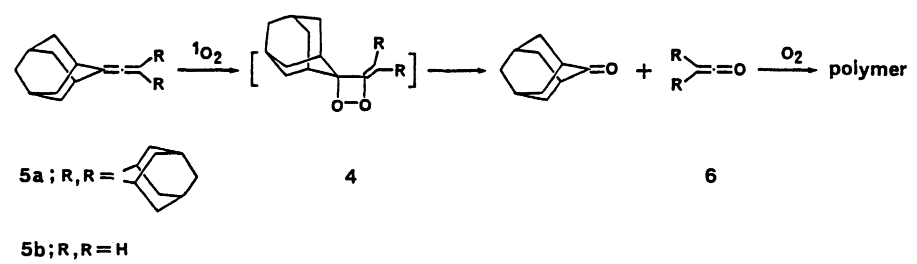
Results and Discussion

Photosensitized oxygenation of **5a** in dichloromethane at 15 °C with Methylene Blue (MB) as sensitizer led to formation of adamantanone in 87% yield as an isolable product accompanied by polymeric products.[12] Very similar results were obtained with allene **5b** (adamantanone; 56% yield). **5** is stable under the reaction conditions in the absence of the sensitizer and light, and 1,4-diazabicyclo[2.2.2]octane, a $^1O_2$ quencher,[13] inhibits the reaction. Moreover addition of triphenylmethane as free radical scavenger[14] and *p*-dimetoxybenzene as an electron-transfer quencher[15] left the photooxygenation unaffected. These results reveal that $^1O_2$ is an actual oxidizing species.

When the reaction of **5a** was carried out at −78 °C with polymer-bound Rose Bengal[16] as sensitizer and then warmed up to room temperature, no direct chemiluminescence could be observed with the naked eye. However, the irradiated solution emitted a strong pale-blue light in the presence of 9,10-diphenylanthracene (DPA) as a fluorescer. The experimental and spectroscopic results suggest that the dioxetane intermediate might be formed during the oxidation. One plausible rationale for these observations is that the oxidation seems to involve [2+2]cycloaddition to yield 3-methylene-1,2-dioxetane **4**. Subsequent decomposition of these dioxetanes may produce adamantanone and the corresponding ketenes **6** as shown in Scheme 1 (with light emission in the presence of a fluorescer in the case of **5a**). To test these possibilities of the formation of ketenes, the following experiments were done. In order to trap the ketene intermediate, the photooxygenations were carried out in the presence of alcohols which were demonstrated ketene acceptors.[17] The formation of the corresponding ester was observed together with that of adamantanone (Scheme 2).[18] Ketene **6a** may react with $^1O_2$ to afford the correspond-



Scheme 2.



Scheme 1.

ing dioxetanone followed by decomposition to give adamantanone and CO_2.[19] This possibility may be ruled out by the following fact that the adamantanone formation was unaffected in the presence of 1-octanol. Since the reaction enthalpy (ΔH)[20] for the conversion **4a** → adamantanone + **6a** was estimated to be ca. 100 kcal mol^{-1}, both singlet (E_S=85 kcal mol^{-1} for acetone, 84 kcal mol^{-1} for adamantanone) and triplet (E_T=78 kcal mol^{-1} for acetone, 87 kcal mol^{-1} for ketene **5b**[25]) excited states of adamantanone and ketene **5a** are energetically accessible from the transition state. The relative intensities of chemiluminescence from the thermolysis of 3-methylene-1,2-dioxetane **4a** were approximately 1, 1, 3, and 22 for no additive, perylene, 9,10-dibromoanthracene and DPA as fluorescers, respectively (see Experimental) (Fig. 1). This result indicates that the role of CIEEL (chemically initiated electron-exchange luminescence) path in the light production from dioxetane **4a** is unimportant,[3,5a] similar to the case of the dioxetanimine[5] and 2-azaspiro[cyclopropane-1,3′-[1,2]dioxetane][9a] and in contrast to that of the dioxetanone.[3] This difference is presumably due to the general property of carbonyl compounds which can undergo one-electron reduction more easily than olefins. Direct ^{13}C NMR observation of **4a** was unsuccessful because of low solubility of **5a** in NMR solvent at low temperature.

It thus appears that singlet oxygen is able to undergo [2+2]cycloaddition with electron-rich allenes[26] to give methylene-substituted dioxetanes which decompose with light emission in the presence of a fluorescer.

Experimental

The light source was two 500-W tungsten-halogen lamps. Irradiations were carried out in Pyrex tubes in a water bath while oxygen passed through them.

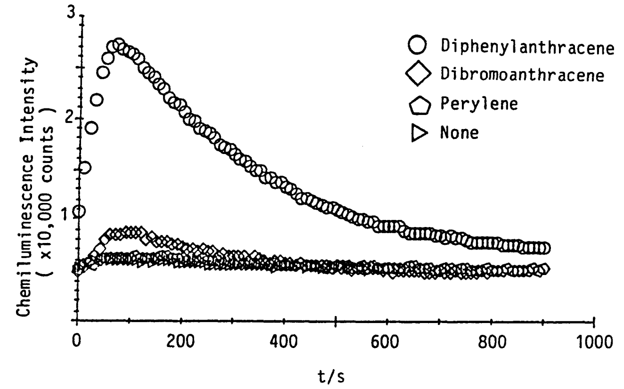


Fig. 1. Chemiluminescence from decomposition of dioxetane **4a**.

Materials. MB (Kanto Chemical) was used as received. Polymer-bound Rose Bengal (Ⓟ-RB) was prepared by the procedure given in the literature,[16] and this was also true of allene **5b**.[11] Oxidation potential (E_{ox} vs. SCE) of **5b** is +1.95 V.

Synthesis of Allene 5a. Triene **7**[27] (4.3 mmol) was treated with potassium peroxomonosulfate (8.8 mmol) by the modified method of Edwards et al.[28] in dichloromethane (70 mL), acetone (17 mL), buffered water (pH 7.5, phosphate buffer, 65 mL) and 18-crown-6 (0.75 mmol), and kept at 10 °C. During the addition of potassium peroxomonosulfate the pH was monitored with a pH-stat and kept at 7.5 by addition of 0.5 M (1 M=1 mol dm^{-3}) NaOH solution. The mixture was stirred at 10 °C. After consumption of **7** monitored by GLC, photolysis of the reaction mixture containing **8** (C=O; 1790 cm^{-1}) with a 400-W high-pressure mercury arc lamp was carried out.[29] (Scheme 3) The mixture was dried over $MgSO_4$ and then removed in vacuo. The residue was chromatographed on silica gel using hexane as an eluent. **5a** was isolated in 60% yield. **5a**: mp 245—247 °C (lit,[10] 224—226 °C); IR (KBr) 1960 cm^{-1} (C=C=C); ^{1}H NMR ($CDCl_3$) δ=1.67—2.08 (24H, m), 2.26—2.51 (4H, m); ^{13}C NMR ($CDCl_3$) δ=28.4 (d), 36.2 (d), 39.3 (t), 108.5 (s), 184.0 (s); MS (20 eV) m/z 280 (M^+). Anal. ($C_{21}H_{28}$) C,H. E_{ox}=+1.51 V vs. SCE.

Photosensitized Oxygenation of Allene 5. In a typical experiment, **5a** (0.11 mmol) was dissolved in dichloromethane with MB as sensitizer, and this solution was photooxygenated for 7.5 h at 15 °C. After separation by preparative gel permeation chromatography (Japan Analytical Industry Co.), adamantanone was obtained in 87% yield accompanied by polymeric products.

Photosensitized Oxygenation of Allene 5 in the Presence of Alcohol. A typical experiment was as follows: **5a** (0.1 mmol) was dissolved in 4 mL of dichloromethane containing 1 mL of 1-octanol with MB as sensitizer and the resulting solution was photooxygenated. Formation of adamantanone (83%) and 2-adamantanecarboxylic acid octyl ester (5%) was confirmed by comparison of their retention times on GLC (4 mm×1.5 m, 2% OV-1 on Uniport HP) with those of the authentic samples and GC-Mass analysis.

Chemiluminescence Analysis. Chemiluminescence was detected through a quartz window by a photomultiplier (Hamamatsu TV Ind., Model R878) with a chemiluminescence analyzer Model OX-70 (Tohoku Denshi Co.). For quantitative chemiluminescence measurement, a sample solution of **4a** was prepared by photooxygenation of **5a** in dichloromethane using Ⓟ-RB as sensitizer, followed by filtration at −78 °C. To the solution of **4a** thus prepared was added an equal volume of the stock solution of each fluorescer in dichloromethane, and the chemiluminescence was measured at −26 °C.

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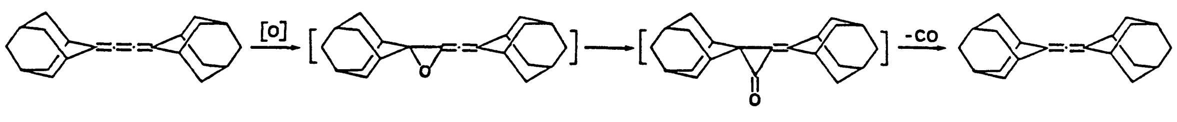

7 **8** **5a**

Scheme 3.

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