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REACTION OF SINGLET OXYGEN WITH ALKENYLIDENECYCLOPROPANES: IMPLICATION FOR A PEROXYALLYL INTERMEDIATE[1]

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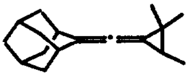
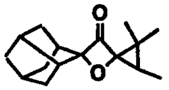
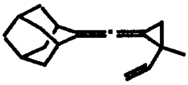
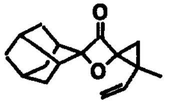
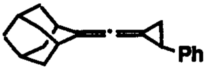
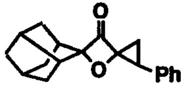
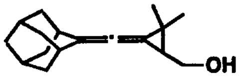
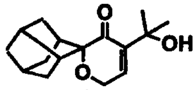
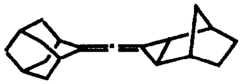
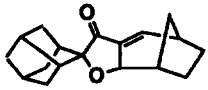
Summary: Photosensitized oxygenation of adamantenylidenecyclopropanes (1) gave either the corresponding oxetanones (2a-c) or the cyclic ketones (4 and 5) depending on the substituent on the cyclopropane ring in addition to adamantanone. The results are rationalized in terms of initial formation of a perepoxide followed by that of a peroxyallyl intermediate.

Despite the intense investigation,[2,3] there are only a few experimental evidences for zwitterionic intermediates in $^1O_2$ reaction of olefins that have been secured from trapping reaction with nucleophilic solvent such as alcohols,[4] a carbonyl function,[5] a silylcyanide[6] and the observation of rearrangement products.[7] Recently, we have reported that the $^1O_2$ reaction of alkylidenecyclopropanes affords either the corresponding 4-methylene-1,2-dioxolane,[8a,b] lactone[8b,c] or 1,2-dioxetane[9] via a zwitterionic intermediate, depending on the substituent on the cyclopropane ring. In this paper we would like to show an implication of a peroxyallyl intermediate derived from a perepoxide in photosensitized oxygenation of adamantenylidenecyclopropanes.[10]

In a typical experiment, photooxygenation of 1-adamantenylidene-2,2,3-trimethylcyclopropane[11] (**1a**, 3.0 x 10^{-2}M) was carried out at 15°C in methylene chloride with methylene blue as sensitizer with two 500W halogen lamps. When the reaction mixture was separated by preparative HPLC,[12] oxetanone **2a**[13] was isolated in 11% yield in addition to adamantanone (**3**, 66%) and polymeric products.[14] Their structures were readily assigned on the basis of spectroscopic data. That $^1O_2$ is the oxidizing species was shown by the fact that **1a** is stable under the reaction conditions in the absence of the sensitizer and light, and 1,4-diazabicyclo[2.2.2]octane,[15] a $^1O_2$ quencher, inhibited the reaction. Very similar results were obtained with adamantenylidenecyclopropanes, **1b-e**,[11] under the same conditions as shown in Table.[16]

One plausible rationale for these observations is that the oxidation seems to involve formation of ionic intermediates as the primary event. Electrophilic attack by $^1O_2$ on adamantenylidenecyclopropanes would take place preferentially at the more nucleophilic site to give the perepoxide **6**[10] followed by immediate ring-opening yielding peroxyallyl intermediate **7** as shown in Scheme. **7** as a key intermediate goes on ring-closure to give dioxetane **8**. Subsequent decomposition of the dioxetanes may produce adamantanone and the corresponding ketene **9**. Polymeric products might come from the oxidative decomposition of **9**.[14,17] In the case of **1a-c**, the O-O bond cleavage in 3-methylene-1,2-dioxetane **8** might also take place to give diradical intermediate **10** followed by rearrangement to **2**, similar to the case of $^1O_2$ reaction of 2,3-divinylidenebicyclo[2.2.1]heptane.[18] In the case of

Table. $^1O_2$ **Oxygenation of Alkenylidenecyclopropanes 1**

Substrates		Products and Yields(%)*	
	1a	 3 (66%)	 2a (11%)
	1b	3 (65%)	 2b (7%)
	1c	3 (68%)	 2c (12%)
	1d	3 (63%)	 4 (12%)
	1e	3 (33%)	 5 (38%)

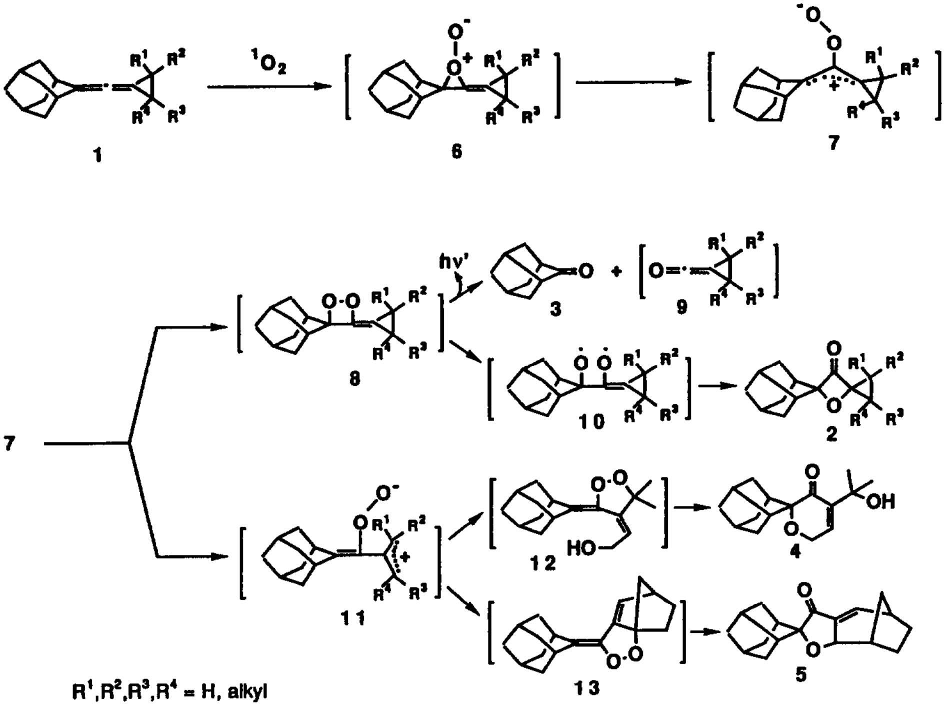
* In each experiment, polymeric product was obtained.

1d and 1e, the results are most easily rationalized by assuming the existence of intermediate 11 as is the case of 3-adamantylidenetricyclo[3.2.1.$0^{2,4}$]octane. A facile ring-opening of the cyclopropane ring in 7 might yield zwitterionic intermediate 10 which is stabilized by allylic conjugation. 10 goes on ring-closure to give the corresponding cyclic vinylperoxides 12 and 13, respectively.[18] Under the reaction conditions, these products evidently are unstable. Cleavage of the peroxide linkage in 12 and 13 homolytically gives the diradicals and intramolecular recombination of the radicals gives the observed products.

^{13}C-NMR monitoring of the reaction mixture at -40°C confirmed the presence of a thermally labile product, 3-methylene-1,2-dioxetane 8,[10] which exhibited ^{13}C resonances at δ 140.21, 86.25 and 106.0 ppm consistent with the chemical shifts of dioxetane ring carbons[18] and an olefinic carbon, respectively. Warming up to 30°C resulted in disappearance of the dioxetane peaks. Furthermore, when the reaction of 1d was carried out at -40°C with polymer-bound Rose Bengal[18] as sensitizer and then warmed up to room temperature, no direct chemiluminescence could be observed. However, the irradiated solution emitted a moderate light in the presence of a fluorescer such as 9,10-diphenylanthracene and 9,10-dibromoanthracene[9,10,21] by means of chemiluminescene analyzer. These experimental and spectroscopic results suggest that the dioxetane intermediate might be formed during the oxidation.

The extension of this mechanistic principle and the application for the synthesis of cyclic ketones are being in progress.

Scheme



R^1,R^2,R^3,R^4 = H, alkyl

References and Notes

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10) For $^1O_2$ oxygenation of allenes, see Akasaka, T.; Fukuoka, K.; Ando,W. *Bull. Chem. Soc. Japan*, **1989**, *62*, 1367, references cited therein.

11) Adamantenylidenecyclopropanes used were prepared by the literature method; Eguchi, S.; Arasaki, M. *J. Chem. Soc., Perkin Trans.* 1, **1988**, 1047. **1a**; mp 60-63°C; IR(KBr) ν 2900, 2830, 2000, 1440, 1350, 1240, 1120, 1080 cm^{-1}; ^1H NMR($CDCl_3$)δ 2.40-2.60(m,2H), 1.81-2.11(m,12H), 1.35-1.6(m,1H), 1.21

(s,3H), 1.1(d,3H,J=5.9Hz), 1.14(s,3H) ppm; ^{13}C NMR($CDCl_3$) δ 177.8(s), 112.5(s), 93.9(s), 39.2(t), 39.0 (t), 37.5(t), 36.3(d), 35.8(d), 28.5(d), 26.4(q), 26.0(d), 23.8(s), 19.1(q), 13.3(q) ppm; MS(EI) 228 (M$^+$). Cacld for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.37; H, 10.77.

12) Gel permeation chromatography was performed on a series of JAIGEL 1H and 2H columns with a flow of 3.5 ml m^{-1} of chloroform on a LC-08 liquid chromatograph of Japan Analytical Industry Co. Ltd.

13) **2a**: The isomeric mixture (1.2:1) was separated by preparative TLC; major component; mp 60-62°C; IR (KBr) ν 2940, 2920, 2860, 1780, 1455, 1385, 1270, 1190 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.38-2.39(m,15H), 1.25(s,3H),1.12(d,3H,J=6.3Hz), 1.11(s,3H) ppm; ^{13}C NMR($CDCl_3$) δ 210.8(s), 104.9(s), 87.4(s), 36.7(t), 34.1 (d), 34.0 (t), 33.9(t), 33.7(t), 33.3(d), 32.6(t), 31.3(s), 26.7(d), 26.4(d), 21.6(q), 14.5(q), 8.1(q) ppm; MS (EI) 260(M+). Exact Mass(FAB) Calcd for $C_{17}H_{25}O_2$: 261.1855. Found: 261.1840. minor component IR(CCl_4) ν 2900, 2860, 1780, 1450 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 1.22-2.32(m,15H), 1.16(s,3H), 1.11(s, 3H),1.08(d,3H, J=5.9Hz)ppm; ^{13}C NMR($CDCl_3$) δ 212.4(s), 104.7(s), 86.3(s), 36.7(t), 33.9(t), 33.6(d), 33.3 (d), 32.6(t), 30.9(d), 29(s), 26.7(d), 26.5(d), 21.8(q), 14.2(q), 7.2(q) ppm; MS(EI) 260(M$^+$). Exact Mass (FAB) Calcd for $C_{17}H_{25}O_2$: 261.1855. Found: 261.1835.

14) IR analysis of the polymeric product indicates the presence of a carbonyl function at 1700 cm^{-1}.

15) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* 1980, *102*, 6083.

16) **2b**: The isomeric mixture (1.3:1) was separated by preparative TLC; major component; mp 64-67°C; IR(KBr) ν 2920,1790 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 4.89-5.10(m,2H), 1.48-2.39 (m,18H), 1.40(d,1H,J=6.4Hz), 1.2 (s,3H) ppm; ^{13}C NMR($CDCl_3$) δ 210.6(s), 144.0(s), 114.2(t), 106.5(s), 84.1(s), 36.8(s), 36.6(t), 34.1(t), 33.6(d), 32.5(t), 32.4(d), 26.6(d), 26.4(d), 26.1(t), 20.6(q), 18.3(q) ppm; MS(EI) 272(M$^+$). Exact Mass (FAB) Calcd for $C_{18}H_{24}O_2$: 272.1775. Found: 272.1780; minor component; mp 64-67°C; IR(KBr) ν 2950, 1795 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 4.74-4.99(m,2H), 1.51-2.42(m,18H), 1.37(d,1H,J=12.7Hz), 1.36(s,3H) ppm; ^{13}C NMR($CDCl_3$) δ 209.1(s), 143.0(s), 112.9(t), 106.2(s), 84.5(s), 37.0(s), 36.6(t), 34.1(t), 33.9(d), 33.6(d), 32.6(t),26.7(d), 26.4(d), 26.2(t), 20.4(q), 18.3(q): MS(EI) 272(M$^+$). Exact Mass(FAB) Calcd for $C_{18}H_{24}O_2$: 272.1776. Found: 272.1780. **2C**; The isomeric mixture (1:1) was not separated; IR($CDCl_3$) ν 2920, 2850,1760,1180 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 7.03-7.42(m,10H), 2.84(dd,1H, J=8.8, 10.4Hz), 2.66 (dd,1H,J=8.8,10.4 Hz), 1.40-2.40(m,16H) ppm; ^{13}C NMR($CDCl_3$) δ 210.3(s), 207.9 (s), 136.9(s), 128.2 (d), 127.2 (d) 126.7(d), 126.5(d), 107.8(s), 106.9(s), 81.8(s), 81.6(s), 36.61(t), 33.9(d), 33.6(t), 33.1(d), 32.6(d), 30.0(t) 29.7(d), 26.7(d), 26.3(d), 20.5(t), 19.4(t) ppm; MS(EI) 294(M$^+$) Exact Mass(FAB) Calcd for $C_{20}H_{22}O_2$: 294.1619. Found: 294.1622. **4**: ($CDCl_3$) ν 3475, 2920, 2850,1670, 1310, 1225, 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.67 (t,1H,J=2.5Hz), 4.4 (d,2H,J=2.5Hz),2.28-1.56(m,15H), 1.41(s,6H) ppm; ^{13}C NMR($CDCl_3$) δ 201.7(s), 139.8(s), 137.4(d), 79.9(s), 71.5(s), 59.9(t), 37.7(t), 33.9(t), 33.7(t), 32.1(d), 28.9(q), 27.2(d), 27.0(d); MS(EI) 259(M$^+$-OH). Exact Mass(FAB) Calcd for $C_{17}H_{23}O_3$: 275.1647. Found: 275.1643. **5**: The major component of isomeric mixture (2:1) was separated by preparative TLC; mp 47-49°C; IR(KBr) ν 2950, 2900, 1720, 1650, 1450, 1345, 1200 cm^{-1}; ^{1}H NMR($CDCl_3$) , δ 7.15(dd, 1H, J=1.4, 7.8Hz), 4.1(brs,1H), 1.03-2.94(m,22H); ^{13}C NMR ($CDCl_3$) δ 205.2(S), 142.8(d), 137.0(s), 85.2(s), 78.2(d), 37.9(t), 36.6(d), 35.1(d), 34.8(d), 33.5(t), 32.9 (t), 32.6(t), 31.8(t), 30.7(t), 30.1(d), 28.6(t), 27.1 (d), 26.9(d); Mass(EI) 284(M$^+$). Exact Mass(FAB) Calcd for $C_{19}H_{23}O_2$: 283.1698. Found: 283.1680. The following spectral data were obtained for the mixture; ^{1}H NMR($CDCl_3$) δ 7.14(dd,2/3H,J=1.4, 7.8Hz), 6.65-6.77(m,1/3H), 4.72-4.77(m,1/3H), 4.18 (brs, 2/3H) 1.26-2.80(m,22H); IR(KBr) ν 2950, 2900, 1720, 1650, 1450, 1345, 1205 cm^{-1}; ^{13}C NMR(CDCl3) δ 205.2(s), 204.6(s), 142.8(d), 138.4(d), 136.9(s), 134.6(s), 85.8(s), 85.2(s), 78.2(d), 75.4(d), 37.9(t), 37.4(d), 37.0(d), 36.6(d), 35.5(t), 35.1(d), 34.8(t), 34.1(t), 33.8(t), 33.5(t), 32.9(t), 32.8(t), 32.6 (t), 32.0(t), 31.8(t), 30.7(t), 30,4(d), 30.1(d), 28.6(t), 27.0(d), 26.9 (d), 20.5(t); Mass(EI) 284(M$^+$). Exact Mass(FAB) Calcd for $C_{19}H_{23}O_2$: 283.1698. Found: 283.1702.

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