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REACTION OF SINGLET OXYGEN WITH METHYLENECYCLOPROPANES: FORMATION OF 4-METHYLENE-1,2-DIOXOLANES[1]

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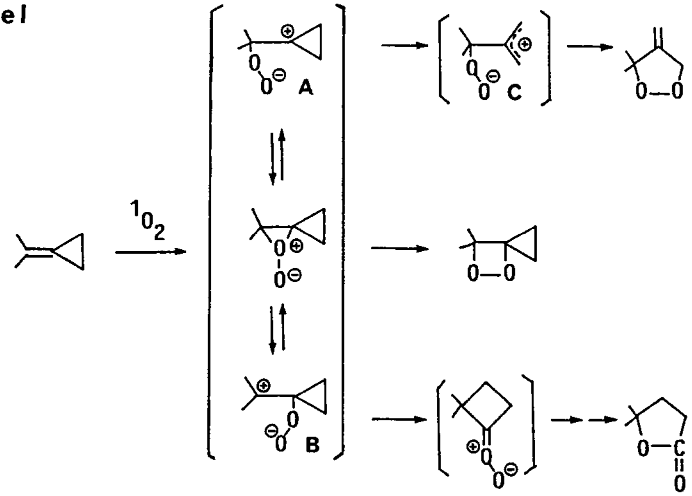
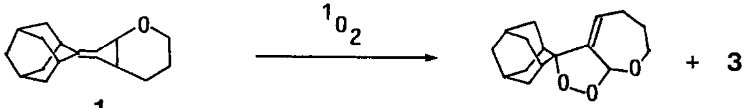
Summary: Photosensitized oxygenation of adamantylidenecyclopropanes gave either the corresponding 4-methylene-1,2-dioxolane or lactone and cyclic ketone depending on the substituent on the cyclopropane ring. The results are rationalized in terms of initial formation of a perepoxide intermediate followed by that of an allylic cation-type zwitterion or a carbonyl oxide, respectively.

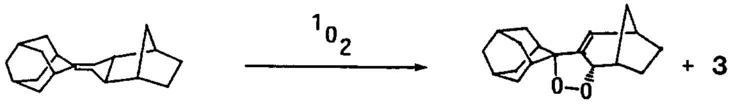
Singlet oxygen reaction of electron-rich olefins,[2] which are denied the opportunity of forming hydroperoxides, invariably forms 1,2-dioxetanes. As an alternative to [2 + 2] addition, two step mechanisms involving diradicals, zwitterions, charge-transfer complexes, and radical ion pairs have been proposed to account for the course of the reaction. Recently, experimental evidence for zwitterionic peroxides in singlet oxygen reaction of hetero atom-substituted olefins such as enol ethers has been secured from trapping reaction[3] with nucleophilic solvent such as alcohols[2] and a carbonyl function.[4] Despite this intensive investigation, there are only few evidences that are suggestive for the existence of perepoxides in singlet oxygen reaction of simple olefins.[5] Accordingly, the molecule that may serve as diagnostic test for a perepoxide intermediate is clearly desirable for mechanistic studies of oxidation reactions of olefins. Presently we report direct evidence for a zwitterionic peroxide derived from a perepoxide formed initially in photooxygenation of olefins. The candidates are methylenecyclopropanes[6] (Scheme I). Their particular advantages are that a cationic center generated by singlet oxygen reaction is stabillized by allylic conjugation (**C**) to form 4-methylene-1,2-dioxolane. This expection is realized.

Photooxygenation of 2-adamantylidenebicyclo[4.1.0]-4-oxaheptane (**1**)[7] with methylene blue as sensitizer with 500 W halogen lamps at 15°C in methylene chloride gave 4-methylene-1,2-dioxolane **2**[8] in a yield of 75%, together with trace of adamantanone (**3**)(eq.1). Dioxolane **2** was isolated by silica-gel column chromatography using benzene as an eluent and its structure was readily assigned on the basis of spectroscopic data.[8] Another substrate is 3-adamantylidenetricyclo [$3.2.1.0^{2,4}$]octane (**4**).[7] Reaction of **4** using tetraphenylporphine[9] as sensitizer in methylene chloride at 15°C provided the same result. Dioxolane **5**[10] was formed in 80% yield, together with recovered **4** (17%) and trace of **3** (eq.2). **5** was separated by preparative HPLC.[11]

Scheme I

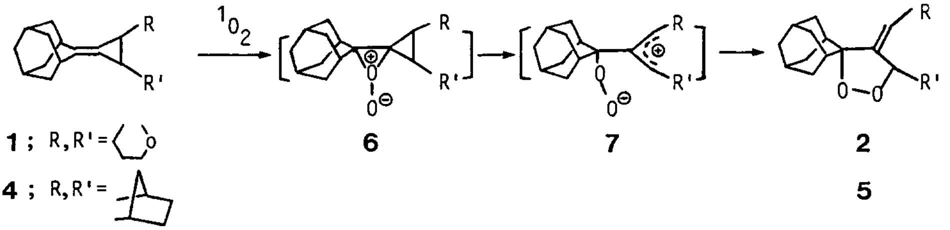



1 2 (eq.1)


4 5 (eq.2)

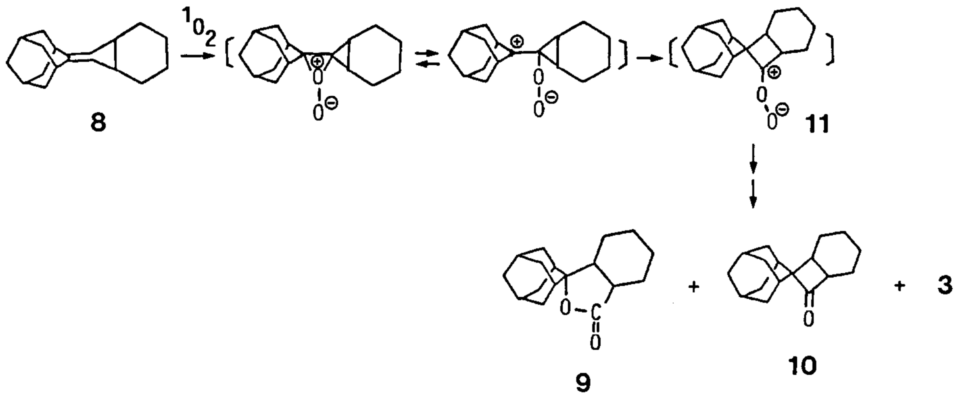
These results are convincingly rationalized in terms of formation of ionic intermediates as the primary event. Electrophilic attack by singlet oxygen on adamantylidenecyclopropanes would take place preferentially at the less hindered endo-face of the molecule to give the perepoxide **6**[12] followed by immediate ring-opening yielding **7**[13] as illustrated in Scheme II. Subsequently, **7** as a key intermediate goes on ring-closure to give **2** and **5**.

Scheme II



Lastly, **8**[7] was photooxygenated in a solution of methylene chloride at 15°C with methylene blue as sensitizer to give two major products, together with **4** (19%). The first product was the lactone **9**[14] in 16% yield after separation by HPLC.[11] The other was cyclic ketone **10** in 53% yield. The results are most easily rationalized by assuming the existence of intermediary carbonyl oxide **11**,[16] as is the case of unsubstituted adamantylidenecyclopropane[6d] (Scheme III).

Scheme III



Adamantylidenecyclopropanes, **1**, **4** and **8**, were found to be inert when submitted to irradiation in the presence of oxygen, but without sensitizer. The usual tests confirmed the intermediacy of singlet oxygen as reagent.[17] Moreover, addition of triphenylmethane as a free-radical scavenger[19] and p-dimethoxybenzene as an electron-transfer quencher[20] unaffected the oxidation. These results demonstrate that the perepoxide can be initially formed. Ring-opening of the cyclopropane ring may occur in two ways. Sterically hindered methylenecyclopropanes with a electron-donating group (**1** and **4**) prefer the formation of zwitterion **A** to give 4-methylene-1,2-dioxolane as shown in Scheme I. In another way, zwitterion **B** rearranges to the carbonyl oxide, which finally gives the lactone and cyclic ketone.[16]

The present results show first example of formation of 4-methylene-1,2-dioxolane by singlet oxygen reaction of methylenecyclopropanes.[6] The extension of the mechanistic principle and the application for the synthesis of 4-methylene-1,2-dioxolane in progress.

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8) **2**: mp 92-94°C; IR(KBr)ν2915,2855, 1450, 1070 cm^{-1} ^{1}H NMR($CDCl_3$)δ 6.22(brs,1H), 4.94(s,1H), 3.93-4.30(m,2H), 3.56-3.93(m,2H), 0.72-2.60(m,16H); ^{13}C NMR($CDCl_3$)δ132.2(s), 125.1(d), 97.9(d), 81.6(s), 66.9(t), 39.2, 37.8, 34.6, 33.9, 33.8, 32.8, 32.2, 31.3, 28.3, 27.5, 26.7; MS 262(M^+). Exact mass calcd for $C_{16}H_{22}O_3$ 262.1570, found 262.1598.
9) In the case of methylene blue- and rose bengal-sensitization, the exo-derivative **12** was also formed as a minor product. We have proposed that **12** is not a product from singlet oxygen reaction but from electron-transfer oxygenation. Akasaka, T.; Ando, W.; The detail is submitted in a separate paper.
10) **5** has been obtained by the reaction of **4** with chemically generated singlet oxygen. The structure was confirmed by means of X-ray crystal analysis.[9]
11) Gel permeation chromatography was performed on a series of JAIGEL 1H and 2H columns with a flow of 3.5 ml min^{-1} of chloroform on an LC-08 liquid chromatograph of Japan Analytical Industry Co. Ltd.
12) Methyl phenyl sulfoxide was not oxidized to the sulfone in the oxidation of 4.[5b]
13) Existence of intermediary zwitterionic peroxide **7** was confirmed by a trapping experiment with alcohol.[9]
14) **9**: mp 166-167°C; IR(KBr)ν1760, 1190 cm^{-1}; ^{1}H NMR($CDCl_3$)δ2.80-3.07(m,1H), 2.37-2.66(m,1H), 0.80-2.37(m,22H); ^{13}C NMR($CDCl_3$)δ177.6(s), 89.6(s), 39.7(d), 37.3, 35.9, 34.2, 33.6, 33.1, 32.0, 26.8, 26.5, 24.0, 23.3, 23.1, 22.7; MS 260(M^+). Calcd for $C_{17}H_{24}O_2$: C,78.41; H,9.29. Found: C,78.17; H,9.34.
15) **10**: mp 60-61°C; IR(KBr)ν1740 cm^{-1}; ^{1}H NMR($CDCl_3$)δ3.21-3.50(m,1H), 0.95-2.30(m,23H); ^{13}C NMR($CDCl_3$)δ215.2(s), 72.9(s), 51.4(d), 37.1, 36.8, 35.5, 34.9, 34.4, 34.1, 32.9, 30.0, 27.5, 27.0, 23.1, 22.5, 22.3, 20.4; MS 244(M^+). Exact mass calcd for $C_{17}H_{24}O_1$ 244.1828, found 244.1850.
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17) Proof for reagent singlet oxygen was obtained by testing oxygenation in the absence of light, oxygen, and by adding Dabco.[18]
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