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FORMATION OF 1,2-DIOXOLANE IN THE SINGLET OXYGENATION OF CYCLOPROPANE[1]

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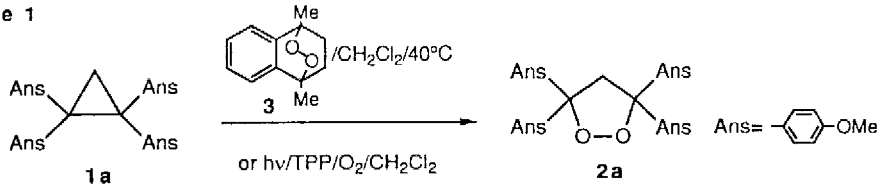
Abstract: Reaction of 1,1,2,2-tetraanisylcyclopropane (**1a**) with both thermally and photochemically generated singlet oxygen afforded the corresponding 1,2-dioxolane **2a** quantitatively. Singlet oxygenation of two stereoisomeric 1,2-dianisyl-1,2-ditolylcyclopropanes (**1b** and **1c**) gave a mixture of 1,2-dioxolanes **2b** and **2c** via a non-stereospecific addition in both cases.

Singlet oxygen ($^1O_2$) undergoes several types of reactions with various electron-rich olefins, namely [2+2]- and [2+4]-cycloaddition and the ene reaction, yielding 1,2-dioxetanes, endoperoxides and allylhydroperoxides, respectively.[2] However, carbon-carbon and carbon-hydrogen σ-bonds are usually inert toward $^1O_2$. To the best of our knowledge there are only a few examples indicating the cleavage of σ-bonds in the dye-sensitized oxygenation.[3] Recently, we have provided evidences for dioxygen insertion into a silicon-silicon σ-bond in the reaction of $^1O_2$ with disilirane[4] and oxadisilirane.[5] Our interest in the photooxygenation reaction has led us to initiate studies of singlet oxygenation of a cyclopropane ring,[6] which might be a superior candidate to gain an insight into the reactivity of $^1O_2$ with a carbon-carbon σ-bond. We now report here the results on the singlet oxygenation of 1,1,2,2-tetraarylcyclopropanes (**1**) to afford the corresponding 1,2-dioxolanes **2** as dioxygen insertion products into a carbon-carbon σ-bond.

In a typical experiment, oxidation of 1,1,2,2-tetraanisylcyclopropane[7] (**1a**) with excess of 1,4-dimethylnaphthalene endoperoxide[8] (**3**) which generates $^1O_2$ at 40°C under argon in methylene chloride gave 3,3,5,5-tetraanisyl-1,2-dioxolane (**2a**) in 20% yield[9] (conversion yield; 100%)(Scheme 1). **2a** was isolated by silica gel flash column chromatography and characterized by means of analytical and spectroscopic data.[10] The oxidation was suppressed by addition of 1,4-diazabicyclo[2.2.2]octane (DABCO),[11] a known $^1O_2$ quencher.

When **1a** (3.3×10^{-3}M) was photooxygenated with tetraphenylporphine (TPP, 3×10^{-5}M) as sensitizer at -40°C in methylene chloride, **2a** was obtained quantitatively, monitored by HPLC. Irradiation was carried out under oxygen with two 500-W tungsten-halogen lamps using a sodium nitrite filter solution (cutoff 400 nm).[12]

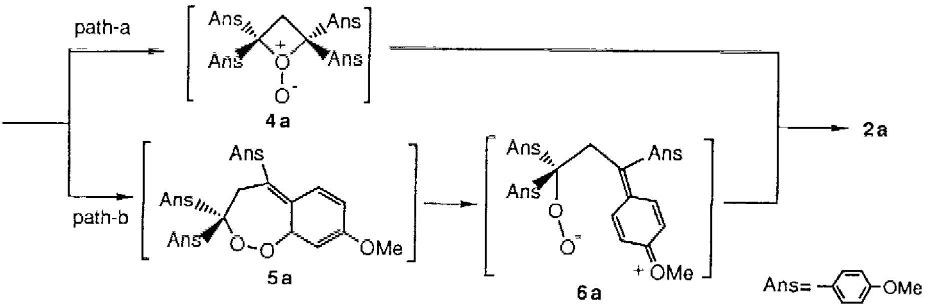
Scheme 1



When the photolysis of **1a** was carried out in the absence of a sensitizer or light, no reaction occurred. The photooxygenation was also inhibited by addition of DABCO. Addition of triphenylmethane,[13] a free-radical scavenger, or 1,2,4,5-tetramethoxybenzene,[14] an electron-transfer quencher, did not have any influence. The rate constant ($k_q = 8.2 \times 10^6 M^{-1}s^{-1}$ for **1a**) for the interaction of $^1O_2$ with **1a** was measured by quenching of $^1O_2$ emission at 1268 nm in methylene chloride.[15] These results make it probable that $^1O_2$ is a primary oxidizing species.

One plausible rationale for these observations is that the oxidation seems to involve electrophilic attack by $^1O_2$ at the edge of the cyclopropane[4,5,16] to give the adduct **4a** followed by ring-closure yielding **2a**[17] (path-a) or that $[\pi^2+\pi^2+\sigma^2]$-cycloaddition[18] affords the peroxide **5a** and then collapses to **2a** (path-b), similar to the case of formation of dioxetanes via rearrangement in the decomposition of endoperoxides[19] (Scheme 2).

Scheme 2



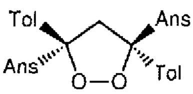
These results prompted us to examine the stereochemistry of the reaction of $^1O_2$ with cyclopropane in order to elucidate the reaction mechanism. The obvious candidates are two stereoisomeric 1,2-dianisyl-1,2-ditolylcyclopropanes[20] (**1b** and **1c**). The rate constants ($k_q = 1.1 \times 10^5 M^{-1}s^{-1}$ for **1b** and $1.4 \times 10^5 M^{-1}s^{-1}$ for **1c**) for the interaction of $^1O_2$ with **1b** and **1c** were obtained by the same procedure for **1a**.[15] Either **1b** or **1c** on treatment with thermochemically generated $^1O_2$ afforded the corresponding 1,2-dioxolanes[21] (**2b** and **2c**) in which the configurational integrity was lost; i.e., a 33:67 mixture[22] of **2b** and **2c** from **1b** or a 25:75 mixture[22] of **2b** and **2c** from **1c**. Very similar results were also obtained in the case of TPP-sensitized photooxygenation of **1b** and **1c**. Both **2b** (26% and 33%) and **2c** (53% and 55%) were isolated from **1b** and **1c**, respectively. The ^{1}H-NMR spectra of recovered cyclopropanes in the photooxygenation of **1b** and **1c** indicated that no isomerization occurred under the same conditions.

Judging from the results on the stereochemical investigation, non-stereospecific addition of $^1O_2$ to **1b** and **1c** might take place via path-b. The preferential formation of cis-product **2c** may be explained in terms of a charge-transfer interaction between two anisyl groups in **7**.[23,24]

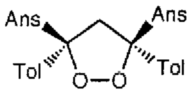
Studies are underway to provide firmer evidence for the reaction mechanism.

1b

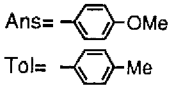
1c



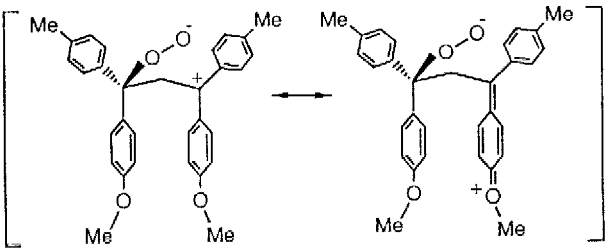
2b



2c



Acknowledgment: We thank the Inaba Biophoton Project, Research Corporation of Japan for the measurement of the rate constants (k_q).



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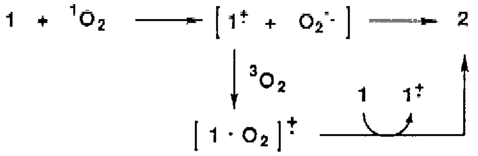
20. **1b** and **1c** were prepared according to the same procedure used for **1a**.[7] **1b**: m.p. 199-200°C; ^{1}H-NMR($CDCl_3$) δ 7.24-6.56(m,16H), 3.68(s,6H), 2.37(s,2H), 2.19(s,6H); ^{13}C-NMR($CDCl_3$) δ 157.30(s) 139.59(s), 134.82(s), 131.24(d), 130.05(d), 128.20(d), 112.91(d), 55.09(q), 42.94(s), 25.50(t), 20.92(q); MS m/e 434(M^+). Anal Calcd for $C_{31}H_{30}O_2$: C,85.68; H,6.96. Found: C, 85.82; H, 6.95. Eox=+0.94 V vs. SCE. **1c**: m.p. 195-196°C; ^{1}H-NMR($CDCl_3$) δ 6.97-6.59(m,16H), 3.67(s,6H), 2.37(dd,2H), 2.20(s,6H); ^{13}C-NMR($CDCl_3$) δ 157.35(s), 139.64(s), 134.84(s), 131.40(d), 129.96(d), 129.82(s), 128.22(d), 112.90(d), 55.11(q), 42.99(s), 25.49(t), 20.91(q); MS m/e 434(M^+). Anal Calcd for $C_{31}H_{30}O_2$: C, 85.68; H, 6.96. Found: C, 85.79; H, 6.95. Eox=+1.00 V vs. SCE.
21. **2b**: m.p. 158-159°C; ^{1}H-NMR(C_5D_5N) δ 7.57-6.88(m,16H), 4.32(s,2H), 3.59(s,6H), 2.19(s,6H); ^{13}C-NMR ($CDCl_3$) δ 158.87(s), 140.70(s), 137.01(s), 135.14(s), 128.90(d), 128.49(d), 128.20(d), 113.50(d), 92.48(s), 62.76(t), 55.24(q), 21.02(q); Exact Mass Calcd for $C_{31}H_{30}O_4$: 466.2145. Found: 466.2122. **2c**: m.p. 183-184°C; ^{1}H-NMR(C_5D_5N) δ 7.57-6.94(m,16H), 4.32(dd,2H), 3.61(s,6H), 2.17(s,6H); ^{13}C-NMR($CDCl_3$) δ 158.84(s), 140.48(s), 137.06(s), 135.38(s), 128.87(d), 128.41(d), 126.98(d), 113.55(d), 92.48(s), 62.81(t), 55.24(q), 21.02(q); Exact Mass Calcd for $C_{31}H_{30}O_4$. 466.2145. Found: 466.2182.
22. The product ratios were determined by means of ^{1}H-NMR(500MHz) measurement.
23. We acknowledge a reviewer who suggested this point.
24. An alternative mechanism which involves a singlet oxygen-initiated oxidation like the result on the photooxygenation of azine[25] may be conceivable. The resulting cation radical $\mathbf{1}^{+\bullet}$ and superoxide anion radical ($O_2^{-\bullet}$) can either collapse to **2** or $\mathbf{1}^{+\bullet}$ and triplet oxygen can give **2**. These process may be supported by the observations that electron-transfer oxygenation by using 9,10-dicyanoanthracene[26] and 2,4,6-triphenylpyrylium perchlorate[27] as photosensitizer and tris(*p*-bromophenyl)aminium hexachloroantimonate-catalyzed oxygenation[28] of **1a** also afforded **2a** quantitatively. Based on thermochemistry that an electron-transfer from **1** to $^1O_2$ is endothermic,[29,30] however, it may be unlikely that this pathway is involved.



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