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FORMATION OF 1,2-DIOXOLANE IN THE SINGLET OXYGENATION OF A SILICON-SILICON σ-BOND: PEROXONIUM ION INTERMEDIATE

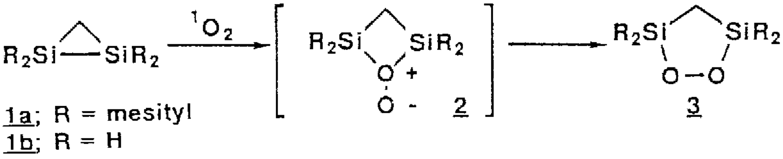
Wataru Ando*,[a], Masahiro Kako,[a] Takeshi Akasaka,[a]
Shigeru Nagase,[b] Takatoshi Kawai,[c] Yasushi Nagai,[c] and Tadashi Sato[c]
[a]*Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan*
[b]*Department of Chemistry, Faculty of Education, Yokohama National University, Yokohama 240, Japan*
[c]*Eisai Company Co., Ltd., Tokodai, Tsukuba, Ibaraki 305, Japan*

Abstract: Singlet oxygenation of 1,1,2,2-tetramesityl-1,2-disilirane **1a** afforded the corresponding cyclic peroxide **3a**. Trapping experiments and theoretical studies of the initially formed peroxidic intermediate were also carried out. Peroxonium ion type intermediate is required to rationalize the results.

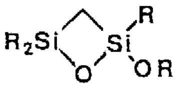
Much attention has been drawn to the reaction of organosilicon compounds with molecular oxygen. West et al. reported that the silicon-silicon π-bonds react readily with molecular oxygen to give 1,3-cyclodisiloxanes and oxadisiliranes with unusual structures.[1] It has been postulated that they arise from a primary intermediate such as perepoxide. Meanwhile, strained silicon-silicon σ-bonds are also known to be oxidized exothermically with molecular oxygen to afford disiloxanes as monooxygenated products.[2] In spite of significance of aerobic oxygenation of organosilicon compounds, few mechanistic investigations have been carried out.[3] Our interest in the reaction of singlet oxygen (${}^1O_2$)[4] has led us to initiate studies of the photooxygenation of organosilicon compounds. ${}^1O_2$ undergoes three classes 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.[5] However, C-C and C-H 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 by ${}^1O_2$.[6] We now report the results on the photooxygenation of 1,1,2,2-tetramesityl-1,2-disilirane **1a**[7] demonstrating the first example of efficient insertion of dioxygen into a silicon-silicon σ-bond. (Scheme 1.) Also described is the evidence for the intermediacy of peroxonium ion **2**.

Photooxygenation of **1a** (1.1×10^{-2}M) was carried out in dry benzene with tetraphenylporphine (TPP) (1.0×10^{-4}) as sensitizer. Irradiation of the solution with bubbling oxygen by use of two 500W halogen lamps at 15°C led to a rapid consumption of **1a**, monitored by HPLC. Recrystallization of the reaction residue from tetrahydrofuran gave cyclic peroxide **3a** in 52% yield (92% yield by HPLC).[8] Interestingly, treatment of **3a** with silica-gel afforded

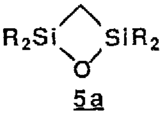
Scheme 1.



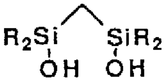
siloxane 4a[9] in 90% yield. The structures of 3a and 4a were assigned on the basis of spectroscopic data and also X-ray crystal analysis for 4a.[10] An ORTEP drawing for 4a is shown in Figure 1. The structure of 3a was further confirmed by chemical transformations as follows. 3a was reduced to 5a[11] with triphenylphosphine in 71% yield, and converted to 6a[12] with $LiAlH_4$ in 52% yield. 5a was also obtained by oxidation of 1a with mCPBA.[7]



4a



5a



6a

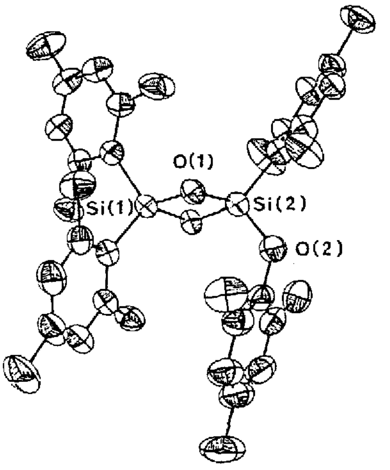
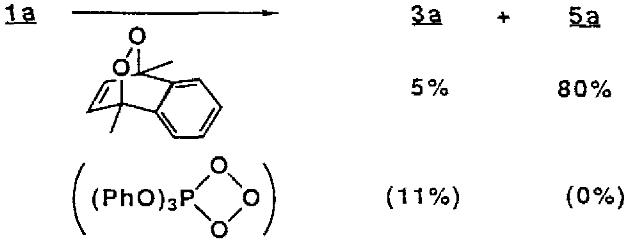


Figure 1. ORTEP drawing of 4a.

When the photolysis was carried out in the absence of a sensitizer or light, no reaction occurred. The reaction was inhibited by addition of 1,4-diazabicyclo[2.2.2]octane (DABCO),[13] a known $^1O_2$ quencher. Addition of triphenylmethane,[14] a free-radical scavenger or p-dimethoxybenzene,[15] an electron-transfer quencher did not have any influence. Reactions of 1a with $^1O_2$ chemically generated from 1,4-dimethylnaphthalene endoperoxide[16] and triphenylphosphite ozonide[17] were carried out at their decomposition temperature. 3a was obtained as illustrated in Scheme 2. 1a was also oxidized by the endoperoxide itself to afford 5a.

Scheme 2.



These results make it probable that $^1O_2$ is a primary oxidizing species and that the σ-π^* interaction[18] takes place between 1a and $^1O_2$ to give the adduct 2a followed by ring-closure yielding 3a. The following trapping experiments have been done to elucidate the proposed reaction mechanism. When 1a was photooxygenated in the presence of dimethyl and diphenyl sulfoxides, 5a was obtained with accompanying of 3a and the corresponding sulfones as shown in Scheme 3. 3a and 5a were confirmed to be stable under the photooxygenation condition in the presence of sulfoxides. Furthermore, addition of DABCO suppressed consumption of 1a and production of 3a and 5a completely. Since it is well documented that the sulfoxides are good trapping reagent for the nucleophilic peroxide intermediates such as perepoxide,[19] persulfoxide[20] and carbonyl oxide,[21] our results are fairly rationalized by assuming the existence of peroxonium ion[22] intermediate 2a and subsequent nucleophilic oxygen atom transfer from 2a to the sulfoxides. On the contrary, 5a was not formed at all when diphenyl sulfide was used as an electrophilic oxygen-atom acceptor. These findings on the reaction of $^1O_2$ with 1a are similar to those of Schaap,[19] who reported the trapping of a pereoxide with a sulfoxide.

Scheme 3.

$$\underline{1a} \xrightarrow[Me_2SO]{^1O_2} \underline{3a} + \underline{5a} + Me_2SO_2$$

Me_2SO	75%	25%	
(Ph_2SO)	(81%)	(11%)	(Ph_2SO_2)

Parallel theoretical studies of products of the reaction of 1b with $^1O_2$ offer a basis for the possible structure of the intermediate 2b.[23] The optimized structure of 2b at the HF/6-31G* level is shown in Figure 2. The most stable conformation has Cs symmetry with the pendant oxygen bending out of the molecular plane. The characteristic feature in 2b is the long O-O bond (1.582Å). The addition of $^1O_2$ to 1b was 75.7kcal/mol exothermic at the MP4SDTQ/6-31G*/HF/6-31G* level.[24] 3b was 56.6kcal/mol more stable than the intermediate 2b. We may therefore conclude that $^1O_2$ attacks on the center of the silicon-silicon bond to form 2b, which subsequently cyclizes to 3b. The extension of the mechanistic principle on this interesting system is in progress.

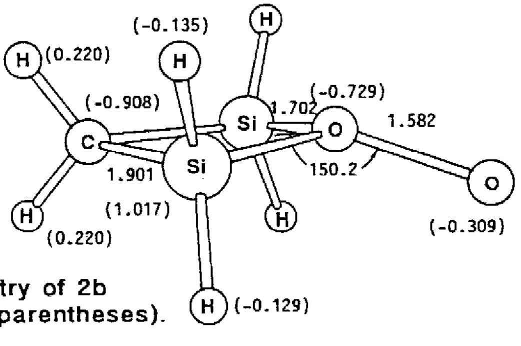


Figure 2. HF/6-31G* optimized geometry of 2b in Å and degrees (net charges are in parentheses).

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7. **1a** was prepared by the literature method.; S. Masamune, S. Murakami, H. Tobita, *J. Am. Chem. Soc.* ***105,*** 7776 (1983).
8. 3a: mp 133-135°; ^{1}H-NMR($CDCl_3$) δ 6.68(s, 8H), 2.28(s,24H), 2.18(s,12H), 1.84(s,2H); ^{13}C-NMR($CDCl_3$) δ 144.05(s), 139.45(s), 131.00(s), 129.10(d), 23.40(q), 21.02(q), 14.30(t); ^{29}Si-NMR($CDCl_3$) δ 9.60; IR (KBr) 1070, 1030 cm^{-1}; MS m/e 578(M^{+}). Anal. Calcd for $C_{37}H_{46}O_2Si_2$; C, 76.76; H, 8.01. Found: C, 76.75; H, 8.06.
9. **4a**: mp 155-156°C; ^{1}H-NMR ($CDCl_3$) δ 6.80(s, 2H), 6.66(s, 2H), 6.60(s, 2H), 6.53(s, 2H), 2.60(s, 6H), 2.30(s, 6H), 2.26(s, 3H), 2.24(s, 3H), 2.182(s, 3H), 2.179(s,3H), 2.16(s, 6H), 2.05(s, 6H), 1.61(dd, 2H, J=16Hz); ^{13}C-NMR($CDCl_3$) δ 148.37(s), 144.15(s), 143.90(s), 143.83(s), 140.15(s), 139.33(s), 139.07(s), 132.00(s), 131.01(s), 130.93(s), 129.14(s), 128.70 (d), 128.53(d), 128.52(d), 128.49(s), 128.48(d), 23.29 (q), 22.75(q), 22.70(q), 21.22(q), 21.06(q), 20.97(q), 20.49(q), 17.50(t), 17.32(q); ^{29}Si-NMR($CDCl_3$) δ 4.05, -15.50; IR(KBr) 1075, 1025 cm^{-1}; MS m/e 578 (M^{+}). Anal. Calcd for $C_{37}H_{46}O_2Si_2$: C, 76.76; H, 8.01. Found: C, 76.68; H, 8.10.
10. Full details of the X-ray analysis will be published elsewhere.
11. 5a: mp 158-161°; ^{1}H-NMR($CDCl_3$) δ 6.69(s, 8H), 2.29(s, 24H), 2.22(s, 12H), 1.95(s, 2H); ^{13}C-NMR ($CDCl_3$) δ 143.72(s), 139.01(s), 132.36(s), 128.77(d), 22.86(q), 21.40(t), 21.07(q); ^{29}Si-NMR($CDCl_3$) δ 4.05; IR(CCl_4) 1060, 1020 cm^{-1}; MS m/e 562(M^{+}). Anal. Calcd for $C_{37}H_{46}OSi_2$: C, 78.94; H, 8.24. Found: C, 78.69; H, 8.39.
12. **6a**: mp 195-197°; ^{1}H-NMR($CDCl_3$) δ 6.60(s, 8H), 2.63(s, 2H), 2.28(s, 24H), 2.21(s, 12H), 1.51(s, 2H); ^{13}C-NMR($CDCl_3$) δ 143.45(s), 138.85(s), 138.08(s), 129.59(s), 23.89(q), 20.91(q), 13.98(t); ^{29}Si-NMR ($CDCl_3$) δ -2.74; IR(CCl_4) 3500, 1030 cm^{-1}; MS m/e 580(M^{+}). Anal. Calcd for $C_{37}H_{48}O_2Si_2$: C, 76.50; H, 8.33. Found: C, 76.27; H, 8.42.
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