

SINGLET OXYGENATION OF OXADISILIRANES. SYNTHESSES AND CRYSTAL STRUCTURE OF 1,2,4,3,5-TRIOXADISILOLANES

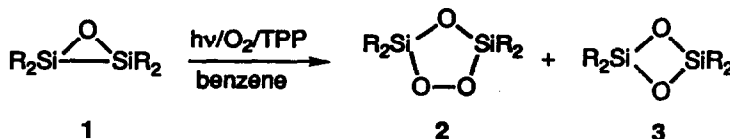
Wataru Ando,* Masahiro Kako, Takeshi Akasaka and Yoshio Kabe
Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan

Abstract: Singlet oxygenation of 2,2,3,3-tetraaryloxadisiliranes 1a-d gives the corresponding 1,2,4,3,5-trioxadisilolanes 2a-d, derivatives of a novel class of cyclic peroxides. The reaction mechanism is discussed in terms of possible peroxonium ion intermediate 6a as a nucleophilic oxidizing species.

A considerable interest has been devoted to the oxidation of organosilicon compounds. It is well known that strained organosilicon molecules are readily oxidized by molecular oxygen.¹ Disilenes are reported to afford oxadisiliranes, 1,2,3,4-dioxadisiletanes and 1,3,2,4-dioxadisiletanes in comparable amounts.² Oxadisiliranes slowly undergo further oxidation by atmospheric oxygen to 1,3,2,4-dioxadisiletanes. Despite the significance of these reactions, few mechanistic investigations were carried out. Recently, however, a considerable evidence has been provided for dioxygen insertion into a silicon-silicon σ -bond in the reaction of singlet oxygen ($^1\text{O}_2$)³ with tetramesityldisilirane.⁴ This paper reports a preliminary study on $^1\text{O}_2$ addition to oxadisiliranes 1a-d, which shed some light on these oxygenation reactions.

Photooxygenation of oxadisiliranes 1a-d⁵ was carried out in dry benzene with $2 \times 10^{-2}\text{M}$ of substrate and tetraphenylporphine (TPP, $1 \times 10^{-3}\text{M}$) as sensitizer. The solution was irradiated at room temperature under oxygen with two 500-W tungsten-halogen lamps using a sodium nitrite filter solution (cut off 400nm). Pure 1,2,4,3,5-trioxadisilolanes 2a-d⁷ were separated by silica gel flash column chromatography and characterized by means of analytical and spectroscopic data. The rate constants ($k_q = 7.1 \times 10^4 \text{M}^{-1}\text{s}^{-1}$ for 1a and $8.3 \times 10^4 \text{M}^{-1}\text{s}^{-1}$ for 1b) for the interaction of $^1\text{O}_2$ with 1a and 1b were measured by quenching of $^1\text{O}_2$ emission (1268nm) in benzene.⁸ When the photolysis of 1a and 1b was carried out under nitrogen or in the absence of sensitizer, no reaction occurred. The photooxygenation was inhibited by 1,4-diazabicyclo[2.2.2]octane (DABCO), a $^1\text{O}_2$

Scheme 1.



quencher. Addition of tri-*tert*-butylphenol, a radical trap, did not have any influence. Dioxadisiletanes **3c**⁹ and **3d** are produced by molecular oxygen without light or sensitizer, and in the presence of DABCO, consistently with West's results^{2d}. These control experiments show that ¹O₂ is surely responsible for the production of trioxadisilolanes **2a-d**, and triplet oxygen for **3c** and **3d**.

Table 1. Photooxygenation of Oxadisiliranes

Oxadisilirane 1	Additive	Products and Yields(%)	
		2	3
a; R = 2,6-diisopropylphenyl	————	71 ^{a,d}	0
	Me ₂ SO	80 ^{b,d}	7 ^{c,d}
	Ph ₂ SO	77 ^{b,d}	3 ^{c,d}
	Ph ₂ S	85 ^{b,d}	0
b; R = 2,6-diethylphenyl	————	60 ^a	0
c; R = mesityl	————	40 ^{a,e}	11 ^{a,e}
d; R = 2,6-dimethylphenyl	————	43 ^{a,e}	9 ^{a,e}

^aIsolated yield. ^bBy HPLC. ^cBy GLC. ^dConversion yield. ^eBased on cyclotrisilanes used as the disilene precursors.^{5a}

X-ray crystallographic study of **2d** established the structure of the new ring system unambiguously as shown in Figure 1, together with selected bond distances and angles.¹⁰ The molecule possesses a two fold rotation axis which passes through the O(1) atom and bisects O(2)-O(2)' bond. The central ring system adopts C₂ half-chair conformation. The aryl

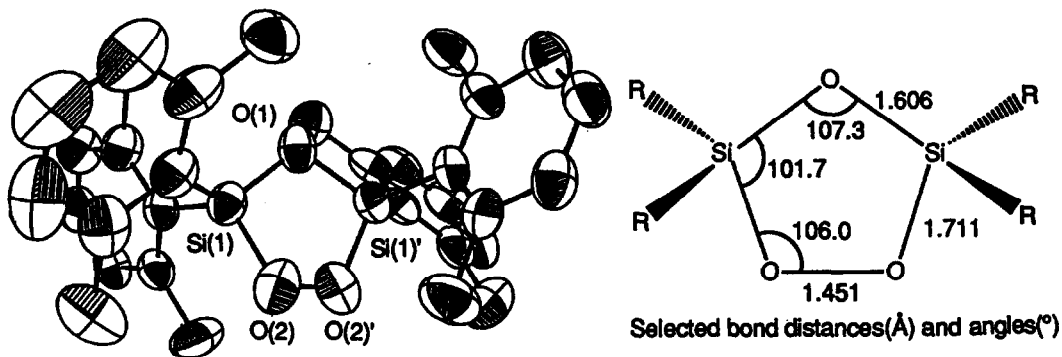
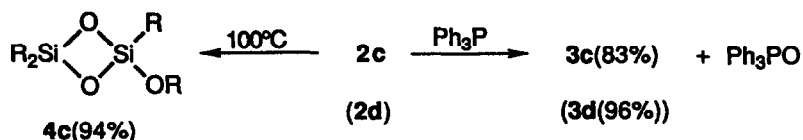


Figure 1. ORTEP diagram of **2d**

groups occupy helical arrangement about each silicon atom. The bond lengths around the 1,2,4,3,5-trioxadisilolane ring are generally within expected ranges and the structure may be regarded roughly as a "similar figure" of that of secondary ozonides in the carbon series.^{11b} The C-Si-C angle (113.5°) is slightly larger and the O-Si-O one is correspondingly smaller than that expected for a tetrahedrally coordinated silicon. The Si-O-Si angle is less constrained compared to that of **3c** (86°).¹²

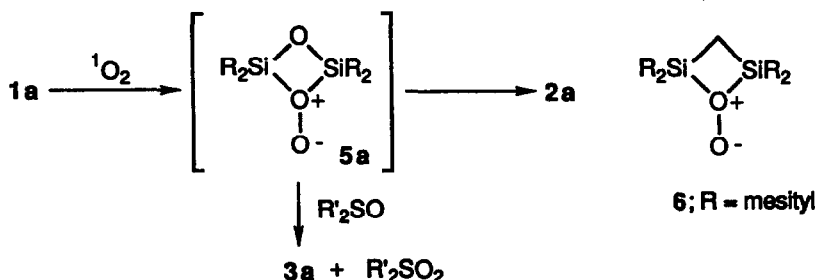
1,2,4,3,5-Trioxadisilolanes have some different chemical properties in contrast to secondary ozonides.¹³ Thermolysis of 2c in toluene at 100°C afforded 4c via Criegee type rearrangement.¹⁴ Reduction of 2c and 2d with triphenylphosphine took place very rapidly at room temperature yielding 3c and 3d, respectively, as shown in Scheme 2.

Scheme 2.



Photooxygenation of 1a in the presence of 100 eq of sulfoxides as a nucleophilic oxygen-atom acceptor⁴ gave 3a with accompanying 2a and the corresponding sulfones. On the contrary, 3a was not produced at all in the presence of 100 eq of diphenyl sulfide as an electrophilic oxygen-atom acceptor (Table 1). Compound 1a is inert toward sulfoxides, and 2a and 3a are thoroughly stable under the reaction condition. In the presence of DABCO, the consumption of 1a and the formation of 2a and 3a were completely inhibited. The results might be explained by the mechanism involving the peroxonium ion intermediate 5a as shown in Scheme 3. Nucleophilic oxygen-atom transfer from 5a to sulfoxides is less efficient compared to the case of 6⁴ with relative abilities of 1:3.6 probably due to the decrease of nucleophilicity of the exocyclic oxygen by the electronegative γ -oxygen, and also the steric repulsion of 2,6-diisopropylphenyl groups. The sterically less hindered oxadisilirane 1b might be a superior substrate for the oxygen-atom transfer of the peroxonium ion. Unfortunately, however, 1b is rapidly converted to 3b by sulfoxides.¹⁵ The reaction of ¹O₂ is less sensitive to the steric hindrance around the silicon atom than those of ³O₂ and sulfoxides. Our preliminary observation suggests that ¹O₂ may approach perpendicularly to the Si-Si bond to afford peroxonium ion 5, whereas both ³O₂ and sulfoxides may directly attack on the silicon atom.¹⁶

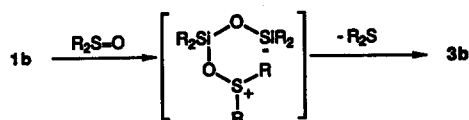
Scheme 3.



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References and Note

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- (4) Ando, W.; Kako, M.; Akasaka, T.; Nagase, S.; Kawai, T.; Nagai, Y.; Sato, T. *Tetrahedron Lett.* 1989, 30, 6705.
- (5) Oxadisiliranes 1a-d were prepared by oxidation of the corresponding disilenes⁶ with dinitrogen oxide^{2d} or mCPBA. Compounds 1c and 1d were used without isolation.
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- (7) All new compounds gave consistent spectroscopic and analytical data.
- (8) The rate constants (k_p) were obtained by means of Stern-Volmer Method; Mashiko, S.; Ashino, T.; Mizumoto, I.; Suzuki, N.; Goto, T.; Inaba, H. *Photomedicine and Photobiology*, 1989, 11, 191.
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- (10) Compound 2d crystallizes in the tetragonal space group ($p4_2/n$) with $a=13.936(2)\text{\AA}$ and $c=15.002(5)\text{\AA}$, $D_{\text{calcd}}=1.20\text{g/cm}^3$, and $Z=4$. Data were collected at $23\pm 1\text{C}^\circ$ with Mo $K\alpha$ radiation (graphite monochromator $\lambda=0.70930\text{\AA}$) on an Enraf-Nonius CAD-4. A total of 2684 reflections within $2\theta=50^\circ$ were measured by the $2\theta-\omega$ scan method with a scan rate of $1-7^\circ/\text{min}$. The structure was solved by direct methods and refined by full-matrix least-square refinement. Convergence on 1251 reflections [$F_0^2 > 3.0\sigma(F_0^2)$] and 167 parameters resulted in $R=0.091$ and $R_w=0.099$ ($p=0.03$).
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- (13) Secondary ozonides usually decompose to carbonyl compounds by thermolysis and reduction with triphenylphosphine. See ref. 11a.
- (14) Alexandrov, Y. A. *J. Organometal. Chem.* 1982, 238, 1.
- (15) It has been reported that small ring silicon compounds are oxidized by sulfoxides; a) Seyferth, D.; Lim, T. F. O.; Duncan, D. P. *J. Am. Chem. Soc.* 1981, 103, 3832; b) Weidenbruch, M.; Schafer, A. *J. Organometal. Chem.* 1984, 269, 231; c) Saso, S.; Yoshida, H.; Ando, W. *Tetrahedron Lett.* 1988, 29, 4747: The oxidation mechanism of 1b may be illustrated as follows.



- (16) Although the mechanism of the formation of 1,3,2,4-dioxadisilicetanes 3c and 3d by 3O_2 is still unclear, one possible explanation may involve peroxidic intermediates similar to the case of free radical oxidation of alkenes; Plesnicar, B. ref. 11b, chapter 16, p486.

