Reaction of Singlet Oxygen with Disiliranes: Dioxygen Insertion into Si–Si σ Bonds

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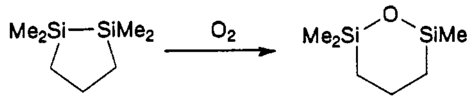
Singlet oxygen ($^1O_2$) oxidation of disiliranes **1a–g** has been investigated. Tetraphenylporphine-sensitized photooxygenation of **1a–g** afforded the corresponding 1,2,3,5-dioxadisilolanes **2a–g.** In the presence of sulfoxides, photooxygenation of disiliranes **1a,b** gave the corresponding 1,2,4-oxadisiletanes **3a,b** as monooxygenated products along with **2a,b**, respectively. $^1O_2$ oxidation of stereoisomeric oxadisiliranes, *cis*- and *trans*-**1g**, is stereospecific to yield the corresponding 1,2,4,3,5-trioxadisilolanes **2g**. These results are rationalized in terms of formation of peroxonium ion **6**, as a novel peroxidic intermediate. A parallel theoretical study of the reaction of the disilirane **1h** with $^1O_2$ was also carried out, and the results offer a basis for the proposed peroxonium ion mechanism.

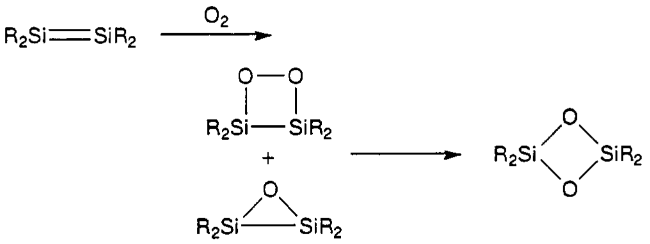
Introduction

The reaction of organosilicon compounds with molecular oxygen continues to attract much attention. Strained Si–Si σ bonds are reactive to atmospheric oxygen to afford the disiloxane compounds as monooxygenated products (Scheme I).[1] Kumada and co-workers proposed a radical mechanism involving formation of an intermediary bis(silyl)peroxide via the attack of molecular oxygen on the Si–Si bond.[1e] Meanwhile, West et al. reported that Si–Si π bonds react readily with molecular oxygen to give the 1,3-cyclodisiloxanes and the oxadisiliranes (Scheme II).[2] A perepoxide intermediate has been postulated at the initial stage of the oxygenation.[2g,i] No confirmative evidence, however, has been obtained.

Scheme I



Scheme II



To obtain insight into the mechanism of oxygenation of organosilicon compounds, we have investigated the dioxygen insertion reaction of Si–Si σ bonds by singlet oxygen ($^1O_2$).[3] Although there are four types of reactions of $^1O_2$ with various electron-rich olefins and sulfides, namely, [2 + 2] and [2 + 4] cycloaddition, ene reaction, and S-oxidation, yielding 1,2-dioxetanes, endoperoxides, allyl hydroperoxides, and sulfoxides, respectively,[4] there has so far been no example of $^1O_2$ oxidation of σ bonds. Recently, we have carried out spectroscopic observation of the azetidinium imide intermediate in [$_\pi 2$ + $_\sigma 2$] cycloaddition of disilirane with triazolinedione (Scheme III).[5] Similarity between the reactivity of triazolinedione and that of $^1O_2$[6] suggests that a peroxonium ion[7] operates as an intermediate in the reaction of $^1O_2$ with disiliranes.

In this paper we describe the complete details of our previous reports on the reaction of $^1O_2$ with disiliranes. Also presented is evidence for the intermediacy of a novel

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[7] (a) Mitchell, J. C. *Chem. Soc. Rev.* **1985,** *14,* 399. (b) Bloodworth, A. J.; Melvin, T.; Mitchell, J. C. *J. Org. Chem.* **1986,** *51,* 2613. (c) Bloodworth, A. J.; Melvin, T.; Mitchell, J. C. *Ibid.* **1988,** *53,* 1082.

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Scheme III

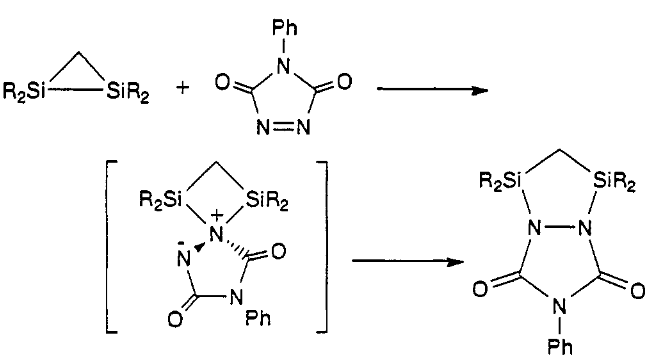


Chart I

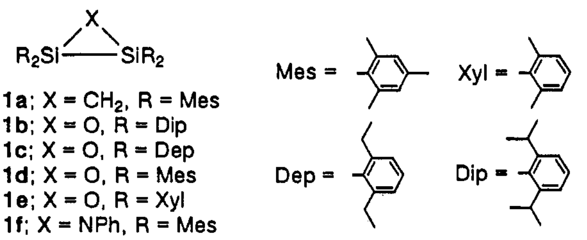


Table I. $^1O_2$ Oxidation of Disiliranes 1a–f

disilirane	E_{ox} (V) vs SCE[a]	$10^{-4}k_q$ ($M^{-1}\ s^{-1}$)[b]	products and yields (%) 2	3
1a	+0.81	6.4	92[c]	0
1b	+0.97	7.1	71[d]	0
1c	+0.97	8.4	60[d]	0
1d			40[d,e]	11[d,e]
1e			43[d,e]	9[d,e]
1f	+0.99		70[d]	0

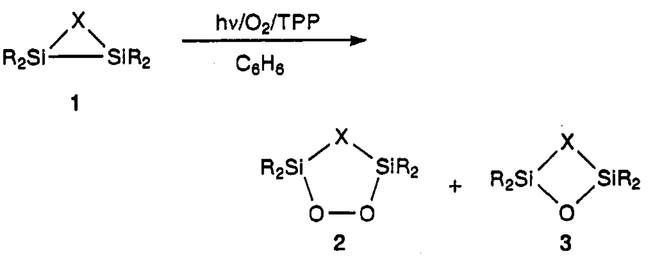
[a] Oxidation potentials (E_{ox}) of disiliranes measured by cyclic voltammetry at a platinum electrode in CH_2Cl_2 with 0.1 M Bu_4NClO_4 as a supporting electrolyte. [b] Quenching rate constants (k_q) of $^1O_2$ by disiliranes. [c] Determined by HPLC. [d] Isolated yield. [e] Based on cyclotrisilanes used as the disilene precursors.

peroxonium ion species on the basis of trapping and stereochemical studies and ab initio MO calculations.

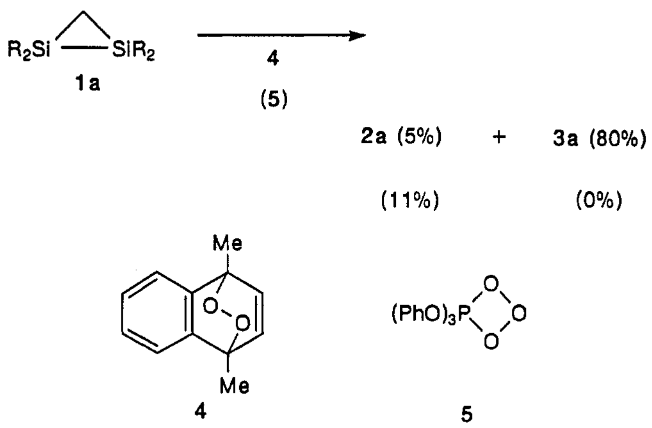
Results and Discussion

$^1O_2$ Oxidation of Disiliranes. Disiliranes **1a–f**[8,9] were prepared by the literature methods. Sterically less protected **1d** and **1e** were used without isolation for the oxygenation since they are labile to $^3O_2$, as reported by West et al.[2e] Table I lists the first anodic peak potentials (E_{ox}) of the disiliranes measured by cyclic voltammetry. The oxidation potentials fall in the range +0.8 to +1.0 V vs SCE in CH_2Cl_2. These values demonstrate the intensive electron-donating nature of disiliranes. It is known that Si–Si σ bonds are good electron donors to form easily a CT complex with tetracyanoethylene.[10] Thus facile interaction of disiliranes with $^1O_2$ as an electrophile would be expected to readily occur.

Scheme IV



Scheme V



Photooxygenation of disiliranes **1a–f** (1.1×10^{-2} M) was carried out in benzene with tetraphenylporphine (TPP) (1.0×10^{-4} M) as sensitizer (Scheme IV). Irradiation of the solution under an oxygen flow by use of two 500-W tungsten–halogen lamps passing through a sodium nitrite filter solution (cutoff < 400 nm) at 15 °C led to rapid consumption of **1a–f**, monitored by HPLC. Pure 1,2,4,3,5-trioxadisilolanes **2a–f** were separated by silica gel flash column chromatography and subsequent recrystallization in good yields, as summarized in Table I, and characterized by means of analytical and spectroscopic data. The structure of **2e** was further confirmed by X-ray analysis.[3b] In the case of **1d** and **1e**, small amounts of monooxygenated products **3d** and **3e**, respectively, were also produced by $^3O_2$ oxidation.[2e]

The following results provided proof for reagent $^1O_2$. When the oxygenation 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),[11] a known $^1O_2$ quencher. Addition of triphenylmethane, a free-radical scavenger, did not have any influence. Reactions of **1a** with $^1O_2$ chemically generated by thermolysis of 1,4-dimethylnaphthalene endoperoxide (**4**)[12] and triphenyl phosphite ozonide (**5**)[13] were also carried out. 1,2,3,5-Dioxadisilolane **2a** was obtained as illustrated in Scheme V. Oxadisiletane **3a** was obtained by oxidation of **1a** with endoperoxide **4** itself even below the decomposition temperature of **4**.

The rate constants (k_q) for $^1O_2$ quenching by disiliranes were obtained by $^1O_2$ emission (λ_{max} = 1270 nm) measurement.[14] The k_q values were calculated according to the Stern–Volmer equation (eq 1), where I_0/I, τ, [Q] are the ratio of the emission intensity of $^1O_2$ in the absence

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[9] For simplicity, we use the following short-hand notations in this paper: Dip = 2,6-diisopropylphenyl; Dep = 2,6-diethylphenyl; Mes = 2,4,6-trimethylphenyl; Xyl = 2,6-dimethylphenyl; Det = 4-*tert*-butyl-2,6-diethylphenyl.

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$$I_0/I = 1 + k_q\tau[Q] \qquad (1)$$

and presence of the quencher, the lifetime of $^1O_2$, and the concentration of the quencher, respectively, and given in Table I. These k_q values are fairly comparable to those of di- or trialkyl olefins which are reactive toward $^1O_2$.[15] These results present not only the first example of reaction of $^1O_2$ with σ bonds but also that of formation of bis(silyl) peroxides from Si–Si σ bonds.

Trapping of the Peroxonium Ion Intermediate by Sulfoxide. When disilirane **1a** was photooxygenated in the presence of dimethyl or diphenyl sulfoxide, 1,2,4-oxadisiletane **3a** was obtained together with 1,2,3,5-dioxadisilolane **2a** and the corresponding sulfone, as shown in Scheme VI and Table II. Although some Si–Si σ bonds are reported to be oxidized by sulfoxides,[16] **1a** does not react with them at all. Oxidation products **2a** and **3a** are also stable under the photooxygenation conditions in the presence of sulfoxides for prolonged irradiation. Furthermore, addition of DABCO[11] completely suppressed consumption of **1a** and production of **2a** and **3a**. In contrast, when diphenyl sulfide[17] was used as an electrophilic-oxygen acceptor, **3a** was not formed at all. Since it is well documented that sulfoxides are good trapping reagents for nucleophilic peroxide intermediates such as perepoxide (**7**),[17] persulfoxide (**8**),[18] and carbonyl oxide (**9**),[19] our results are rationalized by assuming the intermediacy of peroxonium ion **6**.[7] Subsequently, **6** cyclizes to **2** or transfers the terminal oxygen atom to sulfoxides affording **3** and sulfones. Alternative intermediate **10**, however, seems to be not responsible for the formation of **3** because none of open intermediates has been trapped by sulfoxides yet in the $^1O_2$ oxidation of alkenes.

Scheme VI

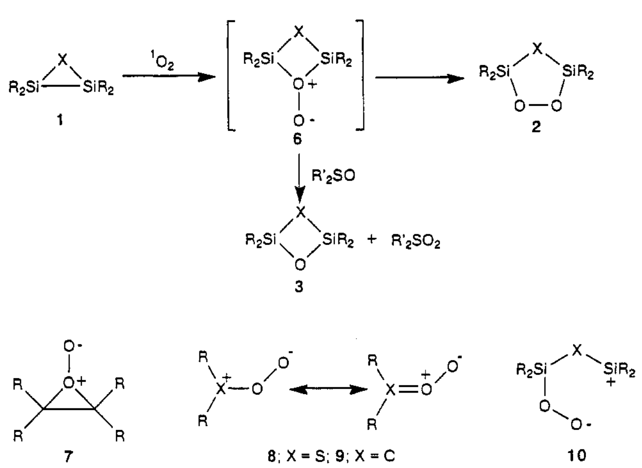

Table II. $^1O_2$ Oxidation of 1a and 1b in the Presence of Sulfoxides

entry	substrate	additive [amt (equiv)]	products and yields (%)[a] 3	2
1	**1a**	Me_2SO (10)	6	92
2	**1a**	Me_2SO (50)	15	85
3	**1a**	Me_2SO (100)	25	74
4	**1a**	Ph_2SO (10)	6	93
5	**1a**	Ph_2SO (30)	11	81
6	**1a**	Ph_2SO (100)	21	79
7	**1a**	Ph_2S (30)	0	90
8	**1b**	Me_2SO (100)	7[b]	80
9	**1b**	Ph_2SO (100)	3[b]	77
10	**1b**	Ph_2S (100)	0	85

[a] Conversion yields determined by HPLC. [b] By GLC.

When a 10-fold excess of sulfoxide was used, little of the presumed intermediate was trapped. This might be simply a matter of the relative rates of oxygen transfer and ring closure of **6**. Indeed, concentration dependence was observed; increasing sulfoxide caused more diversion of **6a** to **3a**. Therefore peroxonium ion **6a** is a fairly weak oxidant compared with biadamantylidene perepoxide.[17a] The sulfone yields are much higher than expected on the basis of the proposed mechanism. The net yields of sulfone are unknown at present since sulfoxides are also oxidized substantially by $^1O_2$ under the reaction condition. Similar results were also obtained in the case of oxadisilirane **1b**, as shown in Table II, except that the yields of sulfoxide trapping decreased substantially compared with the case of **1a**. The decrease is probably due to the considerable steric repulsion of 2,6-diisopropylphenyl groups on the silicon atoms, which blocks the approach of sulfoxides. Replacement of the methylene carbon atom of **1a** by an oxygen atom also might weaken the nucleophilicity of the peroxonium ion intermediate. Sterically less crowded oxadisiliranes **1c–e** could not be used for the trapping experiments since they react with sulfoxide to afford **3c–e**, respectively.[16]

Stereochemistry of the $^1O_2$ Oxidation of Oxadisiliranes. To verify the mechanism proposed above, stereochemical studies of the oxygenation were carried out as follows (Scheme VII). The two stereoisomers of **1g** were prepared as a mixture (ca. 1:1) by oxidation of the corresponding disilenes with nitrous oxide.[2e] Recrystallization of the reaction mixture from toluene afforded pure *trans*-**1g** as colorless crystals. Oxadisilirane *cis*-**1g** was obtained by a series of fractional recrystallizations of the reaction mixture. Structures of these isomers were verified by X-ray analysis of *trans*-**1g**. The ORTEP diagram of *trans*-**1g** is shown in Figure 1. The values of bond distances and angles are in good accordance with those of the known oxadisilirane **1d**[2e] (Table III). The purity of each isomer was easily determined by the ^{13}C NMR spectrum, in which a pair of methyl absorptions of ethyl groups (δ 15.31, 14.89 for *trans*-**1g**, δ 15.24, 15.05 for *cis*-**1g**) could be separately observed. TPP-sensitized photooxygenation of *trans*-**1g** gave *trans*-**2g** as a single product in 84% yield. The

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[15] Wilkinson, F.; Brummer, J. G. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809.

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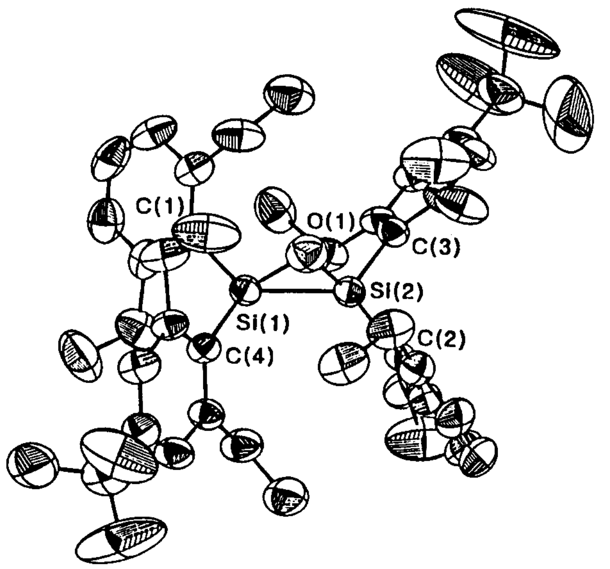


Figure 1. ORTEP diagram of *trans*-**1g**.

Scheme VII

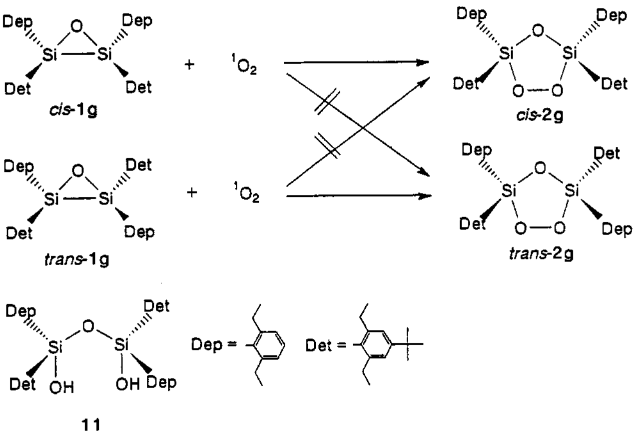


Table III. Selected Bond Distances (Å) and Angles (deg) in *trans*-1g (Esd's in Parentheses)

Si(1)–Si(2)	2.214(2)	Si(1)–O(1)	1.726(4)	Si(1)–C(1)	1.891(8)
SI(1)–C(4)	1.885(6)	Si(2)–O(1)	1.748(4)	Si(2)–C(2)	1.877(8)
Si(2)–C(3)	1.884(6)				

Si(2)–Si(1)–O(1)	50.9(1)	Si(2)–Si(1)–C(1)	122.2(1)
Si(2)–Si(1)–C(4)	122.8(3)	O(1)–Si(1)–C(1)	113.3(3)
O(1)–Si(1)–C(4)	109.2(2)	C(1)–Si(1)–C(4)	114.8(3)
Si(1)–Si(2)–O(1)	50.0(1)	Si(1)–Si(2)–C(2)	121.7(2)
Si(1)–Si(2)–C(3)	124.5(2)	O(1)–Si(2)–C(2)	114.4(2)
O(1)–Si(2)–C(3)	109.6(2)	C(2)–Si(2)–C(3)	113.6(2)
Si(1)–O(1)–Si(2)	79.2(2)		

stereochemistry was assigned by means of the X-ray crystal analysis of disiloxanediol **11** obtained by $LiAlH_4$ reduction of *trans*-**2g**. The ORTEP diagram of **11** is shown in Figure 2. The bond distances and angles of **11** are all in the range of normal values, as shown in Table IV. Similarly, photooxygenation of *cis*-**1g** afforded a single peroxide *cis*-**2g** in 79% yield. Each isomer of **2g** is easily distinguished from the other by means of the ^{13}C NMR spectrum, in which methyl absorptions of ethyl groups appear at δ 15.80 and 15.34 for *trans*-**2g** and at δ 15.66 and 15.46 for *cis*-**2g**. Thus, the photooxygenation of each pure isomer yielded its own peroxide **2g** unaccompanied by the other. Clearly, the TPP-sensitized photooxygenation of *cis*-**1g** and *trans*-**1g** is stereospecific, consistent with the peroxonium ion mechanism, similar to the case of the 1,2-dioxetane formation by $^1O_2$.[20] Intermediacy of the open structure **10**, however, cannot be excluded if rotation is slower than closure. Therefore we investigated the potential energy surface of the reaction by means of ab initio MO calculations.[21]

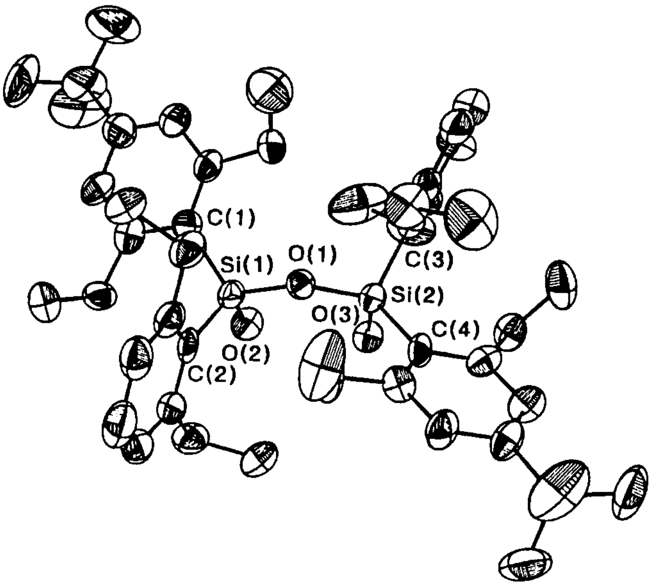


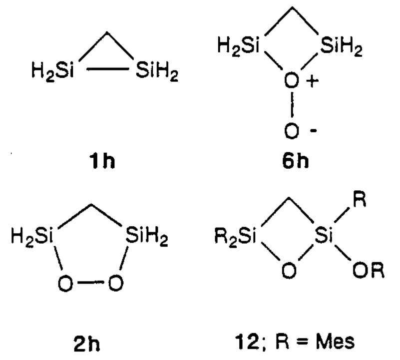
Figure 2. ORTEP diagram of **11**.

Table IV. Selected Bond Distances (Å) and Angles (deg) in 11 (Esd's in Parentheses)

Si(1)–O(1)	1.640(5)	Si(1)–O(2)	1.633(5)	Si(1)–C(1)	1.890(8)
Si(1)–C(2)	1.887(7)	Si(2)–O(1)	1.637(6)	SI(2)–O(3)	1.638(4)
Si(2)–C(3)	1.879(6)	Si(2)–C(4)	1.896(8)		

O(1)–Si(1)–O(2)	103.0(3)	O(1)–Si(1)–C(1)	116.3(2)
O(1)–Si(1)–C(2)	105.2(3)	O(2)–Si(1)–C(1)	106.2(3)
O(2)–Si(1)–C(2)	115.6(2)	C(1)–Si(1)–C(2)	110.8(4)
O(1)–Si(2)–O(3)	105.6(2)	O(1)–Si(2)–C(3)	106.0(3)
O(1)–Si(2)–C(4)	116.7(3)	O(3)–Si(2)–C(3)	115.0(3)
O(3)–Si(2)–C(4)	103.6(3)	C(3)–Si(2)–C(4)	110.3(3)
Si(1)–O(1)–Si(2)	140.2(2)		

Chart II



Theoretical Investigation. Disilirane (**1h**) was chosen as a model for the reactant (see Chart II). The optimized geometries of the calculated compounds at the HF/6-31G* level[22] are shown in Figure 3. This basis set gives the geometry of **1h** in good agreement with experimental data

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(20) (a) Bartlett, P. D.; Schaap, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 3223. (b) Ando, W.; Kabe, Y.; Takata, T. *Ibid.* **1982**, *104*, 7314. (c) Kabe, Y.; Takata, T.; Ueno, K.; Ando, W. *Ibid.* **1984**, *106*, 8174.

(21) The program used is GAUSSIAN 82 developed by Binkley et al.: Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Rahgavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.

(22) 6-31G*: Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. MP4SDTQ: Krishnan, R.; Frish, M. J.; Pople, M. J. *Ibid.* **1980**, *72*, 4244.

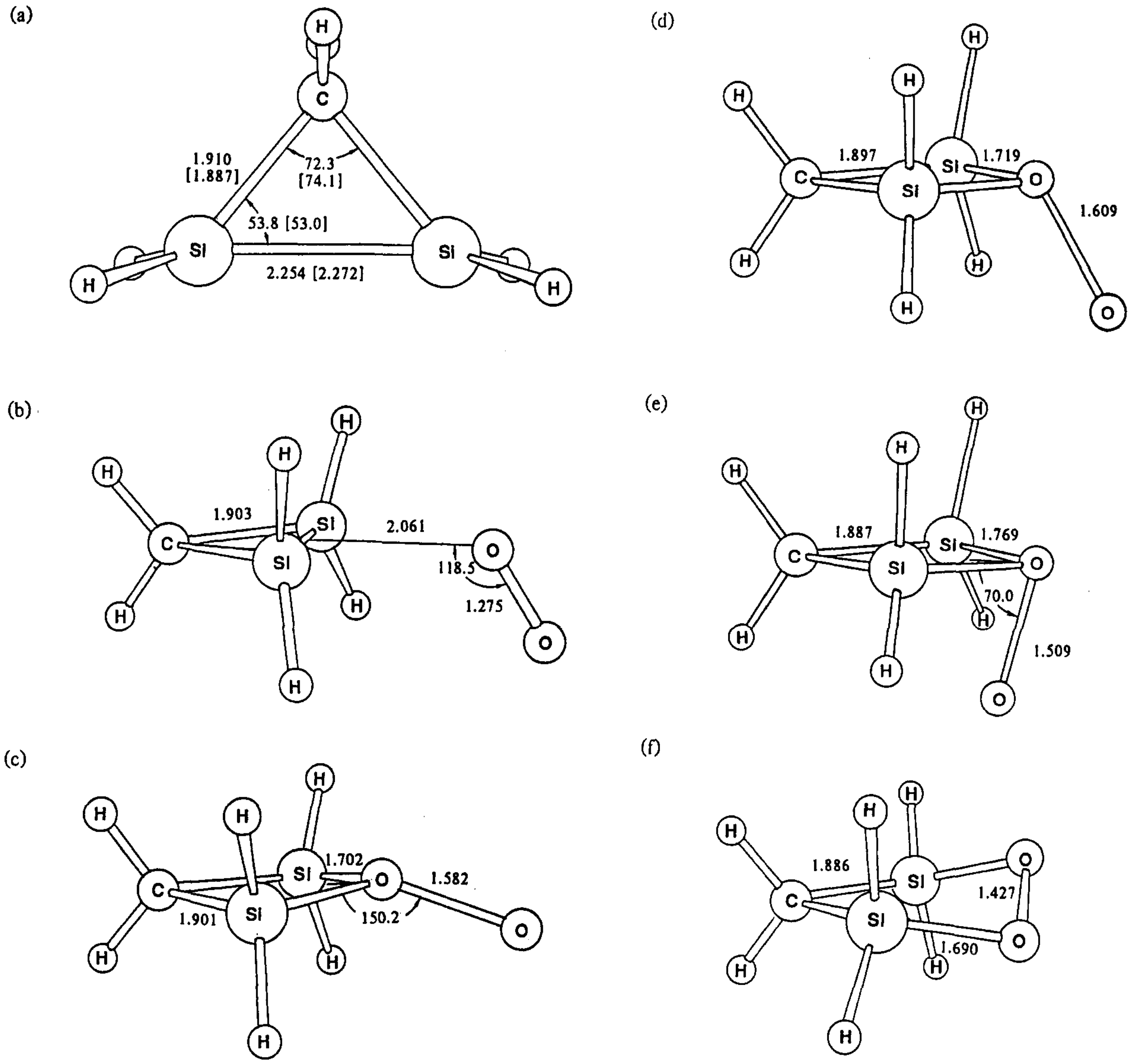

Figure 3. ORTEP diagram of the $^1O_2$ addition to disilirane (**1h**) in angstroms and degrees, obtained at the HF/6-31G* level: (a) disilirane (**1h**) (experimental values are in brackets); (b) transition-state TS1 (Si–C–Si 75.5, Si–Si 2.329); (c) peroxonium ion **6h** (Si-C-Si 86.0, Si-O-Si 99.3, Si-Si 2.594); (d) TS2 (Si-C-Si 85.7, C-Si-O 88.5, Si-O-Si 97.3); (e) TS3 (Si-C-Si 86.0, C-Si-O 90.3, Si-O-Si 93.4); (f) 1,2,3,5-dioxadisilolane (**2h**) (Si-C-Si 98.3, C-Si-O 99.9, Si-O-O 106.0, Si-Si 2.857).

for the structure of 1,1,2,2-tetrakis(2,6-dimethylphenyl)disilirane, which has been determined by X-ray crystal analysis (Figure 3a).[8a] The 6-31G* basis was also used in the search for stable intermediates on the potential energy surface. The reaction path involves an end-on approach of $^1O_2$ to the Si–Si bond. The transition structure (TS1) leading to peroxonium ion **6h** has C_s symmetry with a distance of 2.06 Å from the terminal oxygen to the midpoint of the Si–Si bond (Figure 3b). Bond distances of O–O and Si–Si of TS1 are substantially elongated. A structure corresponding to the proposed peroxonium ion **6h** was found as shown in Figure 3c. The most stable conformation has C_s symmetry with the pendant oxygen (O_p) bending out of the 1,2,4-oxadisiletane plane by 150.2°. The characteristic feature in **6h** is the long O–O bond (1.58 Å). Interestingly, the calculated structure of **6h** (Figure 3c) as a 1,2,4-oxadisiletane derivative is very similar to that of the related compound **12** obtained by thermolysis of 1,2,3,5-dioxadisilolane **2a**.[3a] The O_p atom in **6h** bends decreasing the C–O–O angle to give two transition states, TS2 (Figure 3d) and TS3 (Figure 3e), while the structure of the oxadisiletane ring scarcely changes. The O–O bond then twists so as to develop a new bond between one of the Si atoms and the O_p atom, which leads to 1,2,3,5-dioxodisilolane (**2h**). The product **2h** has C_2 symmetry with the O–O bond of 1.43 Å and the Si–O–O angle of 106.0° as normal values compared to the related organic peroxides (Figure 3f).[23] In contrast, no significant minimum corresponding to **10** (R = H) was located on the singlet potential energy surface, indicating that the addition goes through **6h** without ring-opening.

Table V. Relative Energies (kcal/mol)

reaction	HF/ 6-31G*	MP2/ 6-31G*	MP3/ 6-31G*	MP4SDTQ/ 6-31G*
1h + $^1O_2 \rightarrow$ TS1	24.0	−7.5	2.4	−5.5
1h + $^1O_2 \rightarrow$ **6h**	−89.8	−75.8	−76.9	−75.7
1h + $^1O_2 \rightarrow$ **2h**	−136.6	−137.2	−134.9	−132.3

The calculated reaction energies at different levels of theory are shown in Table V. At the HF/6-31G* level, formation of peroxonium ion **6h** was calculated to be exothermic by 89.8 kcal/mol and to have a barrier of 24.0

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[23] Patai, S., Ed. *The Chemistry of Peroxides*; Wiley: New York, 1983.

kcal/mol. When electron correlation is included, the activation energy is lowered while peroxonium ion **6h** is raised in energy. At the MP4SDTQ/6-31G*//HF/6-31G* level,[24] TS1, 6h, TS2, and TS3 are more stable than the reactants **1h** and $^1O_2$ by 5.5, 75.7, 74.9, and 80.4 kcal/mol, respectively. The final product **2h** is located 132.3 kcal/mol lower in energy than the reactants. Theoretical studies also indicate that there is no appreciable barrier (<1 kcal/mol) from **6h** to **2h** in the reaction pathway. It is therefore concluded that $^1O_2$ approaches perpendicularly onto the Si–Si σ bond to afford the peroxonium ion intermediate, which subsequently cyclizes to produce the 1,2,3,5-dioxadisilolane.

Conclusion

Reaction of $^1O_2$ with disiliranes **1** afforded dioxadisilolanes **2**, as dioxygen insertion products. In the presence of sulfoxides, oxadisiletanes **3** were obtained together with **2** and sulfones. Meanwhile, $^1O_2$ oxidation of *cis*- and *trans*-**1g** proceeds stereospecifically to afford the corresponding trioxadisilolanes **2g**. These results are fairly rationalized by assuming the intermediacy of peroxonium ion **6**. The structure of the peroxonium ion has been investigated by ab initio MO calculation. The calculated energetics suggest that the formation of **2** goes through **6** with no appreciable barrier.

Experimental Section

All melting points are uncorrected. IR spectra were recorded with a Hitachi 260-50 and a JASCO FT/IR-5000 spectrometer. ^1H, ^{13}C, and ^{29}Si NMR spectra were obtained with a JEOL EX-90 and a Bruker AM-500 spectrometer. UV–visible spectra were obtained with a JASCO Ubest 50 spectrometer. Mass spectral data were obtained on Hitachi RMU-6M and Shimadzu GC-MS QP-200A mass spectrometers, and exact mass data, on a JEOL LMS-D300 mass spectrometer. Gas chromatography was done on a Hitachi 163 and a Shimadzu R-14A gas chromatograph equipped with a FID detector. HPLC analyses were carried out on a JASCO TRIROTAR-VI instrument. A Finepak SIL $C_{18}S$ reversed-phase column (250 mm × 4.6 mm; acetonitrile as eluent) was used for HPLC. Gel permeation chromatography (preparative HPLC) was performed on a series of Jaigel 1H and 2H columns with a flow of toluene on an LC 908 liquid chromatograph of Japan Analytical Industry Co. Ltd. A cyclic voltammogram of substrates was obtained in 0.1 M n-Bu_4NClO_4/CH_3CN solution (vs SCE; Hokuto Denko Ltd., potentiostat/galvanostat Model HZ-301). The light sources for photosensitized oxygenation were two 500-W halogen lamps with a Pyrex filter. Irradiation was carried out in a water bath while oxygen was passed through it. A spiral 125-W low-pressure mercury-arc lamp was used for photolysis of the trisilane.

Preparative column chromatography was performed with Kieselgel 60 (Merck) and Wakogel C-300 (Wako Pure Chemical). Reagent grade solvents were used for the experiments. Hexane, benzene, methylene chloride and hexamethylphosphoramide (HMPA) were dried over calcium hydride and distilled before use. Tetrahydrofuran (THF) was refluxed on benzophenone ketyl and distilled before use. TPP (Tokyo Kasei) and methylene blue (Wako Pure Chemical) were used as received. Diazabicyclo[2.2.2]octane was used after purification of sublimation. Triphenylphosphine was used after purification by recrystallization. Triphenyl phosphite was washed with aqueous NaOH and distilled before use.

Preparation of Diaryldichlorosilane. The procedures were represented by the case of dichlorodimesitylsilane (Mes_2SiCl_2).[25a] A hexane solution of 104 mL of 2.4 M n-butyllithium in hexane (0.25 mol) was added to a solution of 50 g of MesBr (0.25 mol) in 200 mL of dry THF over a period of 1 h at −78 °C. Monitoring by gas chromatography (GLC) showed complete disappearance of MesBr, providing the formation of MesLi. To this solution was added 14 mL of $SiCl_4$ (0.12 mol) dropwise over a period of 30 min, and the solution was allowed to stand for 5 h with stirring at −78 °C. The resulting solution was then warmed to room temperature. At this point it was confirmed by means of GLC that the reaction was completely finished. THF was removed by distillation and replaced by 200 mL of dry benzene. The lithium salts were filtered off, and the filtrate was concentrated in vacuo, yielding a white crystalline solid. Subsequent recrystallization from hexane gave 19.9 g (48%) of Mes_2SiCl_2: mp 118–122 °C; ^1H NMR ($CDCl_3$) δ 6.65 (s, 4H), 2.26 (s, 9H), 2.10 (s, 9H), 0.28 (s, 18H); MS m/e 412 (M^+), 339 ($M^+ - SiMe_3$). Other dichlorosilanes were prepared from aryllithium and $SiCl_4$ by analogous procedures and characterized by their typical ^1H NMR spectra. Dip_2SiCl_2: ^1H NMR (CCl_4) δ 7.47–6.93 (m, 6H), 3.70 (sept, 4H, J = 6.4 Hz), 1.06 (d, 24H, J = 6.4 Hz). Dep_2SiCl_2:[25b] ^1H NMR (CCl_4) δ 7.47–6.88 (m, 6H), 2.87 (q, 8H, J = 7.0 Hz), 1.06 (t, 12H, J = 7.0 Hz). Xyl_2SiCl_2:[25c] ^1H NMR ($CDCl_3$) δ 7.43–6.83 (m, 6H), 2.47 (s, 12H).

(2,6-Diethylphenyl)trichlorosilane ($DepSiCl_3$). A hexane solution of 104 mL of n-butyllithium in hexane (2.0 M, 116 mL, 0.23 mol) was added to solution of 43 g of DepBr (0.20 mol) in 200 mL of dry THF over a period of 1 h at −78 °C. Analysis by gas chromatography (GLC) showed the formation of DepLi to be complete. The slurry of DepLi·THF was transferred portionwise to the stirred solution of 60 mL of $SiCl_4$ (0.122 mol) in 200 mL of THF over a period of 2 h, and the mixture was stirred for 3 h at −78 °C. The resulting solution was then warmed to room temperature. At this point the reaction was complete, as seen by GLC, and the excess $SiCl_4$ and THF were removed by distillation and replaced by 200 mL of dry benzene. The lithium salts were filtered, and the filtrate was concentrated in vacuo. The crude product was distilled under reduced pressure, yielding 41.7 g (78%) of $DepSiCl_3$: bp 116–120 °C/6 mmHg; ^1H NMR ($CDCl_3$) δ 7.52–6.87 (m, 3H), 3.03 (q, 4H, J = 7.0 Hz), 1.27 (t, 6H, J = 7.0 Hz); GC–MS m/e 266 (M^+).

4-*tert*-Butyl-2,6-diethylaniline ($DetNH_2$). 2,6-Diethylaniline (44.7 g, 0.30 mol), $ZnCl_4$ (51 g, 0.39 mol), and *tert*-butanol (36 mL, 0.33 mol) were mixed under nitrogen atmosphere in a glovebox. The mixture was heated at 150 °C in a sealed tube for 3 days. After being cooled to room temperature, the reaction mixture was dissolved in methylene chloride. Distillation in vacuo gave 35.8 g (58%) of $DetNH_2$: bp 117–119 °C/6 mmHg; ^1H NMR ($CDCl_3$) δ 6.83 (s, 2H), 3.83 (brs, 2H), 2.52 (q, 4H, J = 7.0 Hz), 1.27 (s, 9H), 1.23 (t, 6H, J = 7.0 Hz). Exact mass calcd for $C_{14}H_{23}N$: 205.1831. Found: 205.1814.

1-Bromo-4-*tert*-butyl-2,6-diethylbenzene (DetBr). A solution of 36 g (0.2 mol) of $DetNH_2$ in 102 mL (0.70 mol) of 40% aqueous HBr was cooled to 0 °C and diazotized with a solution of 13.5 g (0.20 mol) of sodium nitrite in H_2O (32 mL) with the temperature kept below 5 °C. After diazotization was complete, 1.8 g of copper powder was added, and the flask was attached to a reflux condenser and heated very cautiously. As soon as nitrogen began to evolve, the flask was cooled with ice. When the reaction subsided, the mixture was heated for 1.5 h at 90 °C. After cooling to room temperature, 300 mL of hexane was added and the organic layer was separated and washed with concentrated sulfuric acid and then twice with water. It was dried over calcium chloride, filtered, and distilled under reduced pressure to yield 20.6 (44%) of DetBr: bp 113 °C/4 mmHg; ^1H NMR ($CDCl_3$) δ 7.03 (s, 2H), 2.78 (q, 4H, J = 7.0 Hz), 1.30 (s, 9H), 1.22 (t, 6H, J = 7.0 Hz). Exact mass calcd for $C_{14}H_{21}{}^{79}Br$: 268.0827. Found: 268.0813.

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[24] (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1976**, *10*, 1.

[25] (a) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793. (b) Masamune, S.; Murakami, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Ibid.* **1984**, *3*, 333. (c) Yokelson, H. B.; Siegel, D. A.; Millevolte, A. J.; West, R. *Ibid.* **1990**, *9*, 1005.

Dichloro(4-*tert*-butyl-2,6-diethylphenyl)(2,6-diethylphenyl)silane [Dep(Det)SiCl$_2$]. A slurry of DetLi·THF was prepared from 50 mL of 1.67 M *n*-butyllithium in hexane and a solution of 20.6 g (76.6 mmol) of DetBr in 200 mL of dry THF at −78 °C. To this stirred slurry was added a solution of DepSiCl$_3$ (20.5 g, 76.6 mmol) in 100 mL of THF with stirring over 1 h, and then the mixture was warmed to room temperature. The solvent was distilled and replaced by 200 mL of dry benzene. Filtration of the reaction mixture and the removal of the solvent gave 30.5 g of crude Dep(Det)SiCl$_2$, which was used for the next step without purification. ^{1}H NMR (CDCl$_3$): δ 7.41–7.06 (m, 5H), 2.88 (q, 8H, J = 7.1 Hz), 1.28 (s, 9H), 1.03 (t, 6H, J = 7.1 Hz), 1.01 (t, 6H, J = 7.1 Hz). Exact mass calcd for $C_{24}H_{35}{}^{35}Cl_2Si$: 420.1807. Found: 420.1814.

Preparation of 2,2-Diarylhexamethyltrisilane. The procedures were represented by the case of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (Mes$_2$Si(SiMe$_3$)$_2$).[25a] A solution consisting of 23 mL (0.18 mol) of Me$_3$SiCl and 6.8 g (0.28 mol) of Mg turnings in 98 mL of dry HMPA (0.558 mol) was heated to 90 °C. To this solution was added dropwise Mes$_2$SiCl$_2$ (15 g, 0.04 mol) dissolved in 50 mL of dry THF. The colorless reaction mixture immediately turned to yellow and finally to deep orange after 9 h of heating. After addition of hexane, the solution was filtered to remove excess Mg. The resulting mixture was carefully hydrolyzed with 10% HCl, and the hexane layers were washed with distilled water to remove HMPA and then dried over MgSO$_4$. Concentration of the solution in vacuo yielded 15.6 g of white powder. Subsequent recrystallization from hexane and ethanol gave 14.0 g of pure Mes$_2$Si(SiMe$_3$)$_2$: mp 169–171 °C; ^{1}H NMR (CDCl$_3$) δ 6.65 (s, 4H), 2.26 (s, 9H), 2.10 (s, 9H), 0.28 (s, 18H); MS *m/e* 412 (M$^+$), 339 (M$^+$ − SiMe$_3$). Other 2,2-diarylhexamethyltrisilanes were also prepared by the same procedure in 50–70% yields.

2,2-Bis(2,6-diethylphenyl)-1,1,1,3,3,3-hexamethyltrisilane [Dep$_2$Si(SiMe$_3$)$_2$]: mp 260–300 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.17–6.95 (m, 6H), 2.78 (q, 18H, J = 7.5 Hz), 1.00 (t, 12H, J = 7.5 Hz), 0.20 (s, 18H); ^{13}C NMR (CDCl$_3$) δ 150.17 (s), 138.56 (s), 127.99 (d), 124.95 (d), 31.47 (t), 14.49 (q), 1.04 (q); ^{29}Si NMR (CDCl$_3$) δ −11.11, −50.40; MS *m/e* 798 (M$^+$). Anal. Calcd for $C_{26}H_{44}Si_3$: C, 70.83; H, 10.06. Found: C, 70.85; H, 10.20.

2,2-Bis(2,6-dimethylphenyl)-1,1,1,3,3,3-hexamethyltrisilane [Xyl$_2$Si(SiMe$_2$)$_2$]:[25c] mp 210–214 °C; ^{1}H NMR (CDCl$_3$) δ 7.20–6.90 (m, 6H), 2.21 (brs, 12H), 0.13 (s, 18H); ^{13}C NMR (CDCl$_3$) δ 143.01 (s), 138.23 (s), 127.67 (d), 127.50 (d), 25.85 (q), 1.32 (q).

2-(2,6-Diethylphenyl)-2-(4-*tert*-butyl-2,6-diethylphenyl)-1,1,1,3,3,3-hexamethyltrisilane [Dep(Det)Si(SiMe$_3$)$_2$]: mp 103–105 °C; ^{1}H NMR (CDCl$_3$) δ 7.22–6.90 (m, 5H), 2.64 (q, 4H, J = 7.3 Hz), 2.10 (s, 9H), 0.28 (s, 18H); ^{13}C NMR (CDCl$_3$, 60 °C) δ 148.84 (s), 148.65 (s), 138.93 (s), 134.71 (s), 129.31 (s), 127.97 (d), 125.04 (d), 122.05 (d), 34.45 (s), 31.65 (t), 31.55 (t), 31.33 (q), 14.68 (q), 14.41 (q), 1.47 (q). MS *m/e* 496 (M$^+$), 423 (M$^+$ − SiMe$_3$). Anal. Calcd for $C_{30}H_{52}Si_3$: C, 72.50; H, 10.54. Found: C, 72.20; H, 10.61.

Preparation of Hexamesitylcyclotrisilane.[26] To a stirred solution of Mes$_2$SiCl$_2$ (10 g, 30 mmol) in THF (60 mL) was slowly added dropwise at −78 °C a solution of lithium naphthalenide prepared from finely cut lithium (0.9 g, 0.14 g-atom) and naphthalene (8.9 g) in THF (60 mL). After addition, the solution was allowed to stand with stirring for 3 h at −78 °C and then slowly warmed to room temperature. After removal of THF by evaporation under reduced pressure, benzene was added to the residue, precipitated LiCl was filtered off, naphthalene was sublimed from the filtrate in vacuo. Silica gel flash column chromatography of the crude product using hexane as eluent afforded 1.8 g (22%) of hexamesitylcyclotrisilane: mp 274–276 °C; ^{1}H NMR (CDCl$_3$) δ 6.56 (s, 12H), 2.15 (s, 18H), 2.06 (s, 36H); ^{13}C NMR (CDCl$_3$) δ 156.94 (s), 144.43 (s), 137.39 (s), 128.23 (d), 25.95 (q), 20.80 (q); MS *m/e* 798 (M$^+$). Anal. Calcd for $C_{54}H_{66}Si_3$: C, 81.14; H, 8.32. Found: C, 81.09; H, 8.50.

Preparation of a Disilene Solution from Trisilanes. A solution of 10 mmol of RR′Si(SiMe$_3$)$_2$ (R = R′ = Dep, Xyl, Mes) in toluene (30 mL) in a quartz tube was degassed by four cycles of freeze–evacuate–thaw. The magnetically stirred solution was cooled by a fan and photolyzed with a 125-W low-pressure mercury-arc lamp. The color of the reaction mixture immediately turned yellow, and precipitation of disilene began after 1 day. Aliquots were withdrawn at periodic intervals and analyzed by GLC. After 4 days the trisilane was completely consumed and the disilene in benzene solution was used for the preparation of disiliranes without isolation.

Preparation of a Disilene Solution from Cyclotrisilane. A suspension of hexamesitylcyclotrisilane (532 mg, 0.67 mmol) in cyclohexane (30 mL) in a quartz tube was irradiated at room temperature with a 125-W low-pressure mercury-arc lamp for 6 h. After hexamesitylcyclotrisilane was completely dissolved, a pale-yellow solution of the disilene was used for the preparation of disiliranes without isolation as in the case of linear trisilane.

Preparation of 1,1,2,2-Tetramesityldisilirane (1a).[8a] The disilene solution obtained by photolysis was added dropwise to a degassed ethereal solution of diazomethane (ca. 50 equiv) at −78 °C and the resulting mixture was allowed to warm to and stand at room temperature. During the reaction, nitrogen gas evolved, and the solution was decolorized. Silica gel flash column chromatography of the crude mixture using hexane as eluent provided **1a** as colorless crystals. When 2,2-diarylhexamethyltrisilane and cyclotrisilane were used as the disilene precursor, yields were 10% and 25%, respectively. Mp: 246–249 °C. ^{1}H NMR (CDCl$_3$): δ 6.69 (s, 8H), 2.29 (s, 24H), 2.20 (s, 12H), 1.12 (s, 2H). ^{13}C NMR (CDCl$_3$): δ 145.03 (s), 138.47 (s), 131.21 (s), 128.34 (d), 23.84 (q), 21.02 (q), 5.15 (t). ^{29}Si NMR (CDCl$_3$): δ −65.97. MS: *m/e* 546 (M$^+$). Anal. Calcd for $C_{37}H_{46}Si_2$: C, 81.25; H, 8.48. Found: C, 81.43; H, 8.59.

Preparation of 2,2,3,3-Tetrakis(2,6-diisopropylphenyl)oxadisilirane (1b).[8b,27] A solution of lithium naphthalenide prepared from lithium (55 mg, 8.0 mg-atom) and naphthalene (0.51 g, 4.0 mmol) in THF (20 mL) was added dropwise with stirring over 30 min to a solution of Dip$_2$SiCl$_2$ (1.0 g, 2.0 mmol) in THF (20 mL) at −78 °C. The mixture was stirred for 3 h at this temperature and then allowed to warm to room temperature. After stirring for another 1 h, the mixture was passed through a short silica gel column using benzene as eluent under an Ar flow. To the resulting solution was added dropwise a degassed benzene solution of mCPBA until the bright yellow color of disilene completely disappeared. After removal of solvent and naphthalene in vacuo, **1b** was obtained and purified by silica gel flash column chromatography. **1b**: (35% yield) mp >300 °C; ^{1}H NMR (CDCl$_3$) δ 7.29–6.95 (m, 12H), 4.46 (sept, 2H, J = 6.7 Hz), 3.95 (sept, 2H, J = 6.7 Hz), 3.57 (sept, 2H, J = 6.7 Hz), 3.17 (sept, 2H, J = 6.7 Hz), 1.32 (d, 12H, J = 6.7 Hz), 1.189 (d, 6H, J = 6.7 Hz), 1.187 (d, 6H, J = 6.7 Hz), 0.63 (d, 6H, J = 6.7 Hz), 0.41 (d, 6H, J = 6.7 Hz), 0.40 (d, 6H, J = 6.7 Hz), 0.19 (d, 6H, J = 6.7 Hz); ^{13}C NMR (CDCl$_3$) δ 156.52 (s), 155.57 (s), 153.85 (s), 153.80 (s), 135.42 (s), 133.29 (s), 130.45 (d), 130.20 (d), 125.11 (d), 124.61 (d), 123.02 (d), 122.53 (d), 36.63 (s), 35.38 (s), 33.65 (s), 28.51 (s), 25.04 (q), 24.68 (q), 24.56 (q), 23.94 (q), 23.90 (q), 23.09 (q); ^{29}Si NMR (CDCl$_3$) δ −31.48; IR (KBr) 1075, 1030 cm^{-1}; MS *m/e* 716 (M$^+$, 4%), 587 (M$^+$ − Dip, 43%), 426 (M$^+$ − 2Dip, 100%). Anal. Calcd for $C_{48}H_{68}OSi_2$: C, 80.38; H, 9.56. Found: C, 80.11; H, 9.51.

Preparation of Oxadisiliranes 1c–e and 1g.[8c] The disilene was prepared from photolysis of the corresponding linear trisilane as described above. When a stream of nitrous oxide was bubbled through a bright yellow solution of the disilene in toluene at 100 °C, decoloration of the solution completely finished within 1 h. Silica gel flash column chromatography of the crude product using hexane/CH$_2$Cl$_2$ as eluent afforded **2,2,3,3-tetrakis(2,6-diethylphenyl)oxadisilirane (1c)** as colorless cubes in 40% yield. **2,2,3,3-Tetramesityloxadisilirane (1d)** and **2,2,3,3-**

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tetrakis(2,6-dimethylphenyl)oxadisilirane (1e) were also obtained by this method at 80 °C but used for $^1O_2$ oxidation without isolation. **1c**: mp 192–195 °C; ^{1}H NMR (CDCl$_3$) δ 7.29–6.88 (m, 12H), 2.88 (q, 16H, J = 7.5 Hz), 0.78 (t, 24H, J = 7.5 Hz); ^{13}C NMR (CDCl$_3$) δ 150.20 (s), 134.44 (s), 129.97 (d), 125.52 (d), 28.92 (t), 15.11 (q); IR (KBr) 1075, 1063 cm^{-1}; MS m/e 604 (M$^+$, 0.6%), 575 (M$^+$ – Et, 100%), 471 (M$^+$ – 2Dep, 51%). Anal. Calcd for C$_{40}$H$_{52}$OSi$_2$: C, 79.41; H, 8.66. Found: C, 79.23; H, 8.76. The two stereoisomers of **2,3-bis(4-*tert*-butyl-2,6-diethylphenyl)-2,3-bis(2,6-diethylphenyl)oxadisilirane (1g)** were prepared in 35% yield as a mixture (ca. 1:1) by the same procedure. Recrystallization of the reaction mixture from toluene afforded pure *trans*-**1g** as colorless crystals. A series of fractional recrystallizations of the residue from acetone gave pure *cis*-**1g**. These isomers could also be separated by preparative HPLC. *trans*-**1g**: mp 188–185 °C; ^{1}H NMR (CDCl$_3$) δ 7.20–6.88 (m, 12H), 2.92 (q, 16H, J = 7.7 Hz), 1.24 (s, 18H), 0.81 (t, 12H, J = 7.7 Hz), 0.79 (t, 12H, J = 7.7 Hz); ^{13}C NMR (22.4 MHz, CDCl$_3$, 60 °C) δ 152.81 (s), 150.30 (s), 149.90 (s), 135.23 (s), 131.26 (s), 129.84 (d), 125.40 (d), 122.71 (d), 34.54 (s), 31.17 (q), 29.15 (t), 29.00 (t), 15.31 (q), 14.89 (q); IR (KBr) 1070 cm^{-1}; MS m/e 716 (M$^+$). *cis*-**1g**: mp 118–120 °C; ^{1}H NMR (CDCl$_3$) δ 7.20–6.88 (m, 12H), 2.92 (q, 16H, J = 7.7 Hz), 1.24 (s, 18H), 0.81 (t, 12H, J = 7.7 Hz), 0.79 (t, 12H, J = 7.7 Hz); ^{13}C NMR (22.4 MHz, CDCl$_3$, 60 °C) δ 152.81 (s), 150.30 (s), 149.90 (s), 135.23 (s), 131.26 (s), 129.84 (d), 125.40 (d), 122.87 (d), 34.33 (s), 31.21 (q), 29.23 (t), 29.00 (t), 15.24 (q), 15.05 (q); IR (KBr) 1070 cm^{-1}. Exact mass calcd for C$_{48}$H$_{68}$OSi$_2$: 716.4809. Found: 716.4766.

Preparation of 1-Phenyl-2,2,3,3-tetramesitylazadisiliridine (1f).[8d,e] A yellow solution of tetramesityldisilene (5 mmol) in benzene was added slowly to a solution of 20% phenyl azide in hexane at –78 °C, and then the resulting solution was warmed to room temperature. Vigorous gas evolution took place, and the color of reaction mixture slowly became purple. The solvent was removed in vacuo, the residue was subjected to silica gel flash column chromatography and the colorless solid **1f** was isolated in 24% yield: mp >300 °C; ^{1}H NMR (CDCl$_3$) δ 7.36–6.60 (m, 13H), 2.22 (s, 12H), 2.09 (s, 24H); ^{13}C NMR (CDCl$_3$) δ 150.23 (s), 143.94 (s), 143.51 (d), 138.63 (s), 128.34 (d), 125.14 (d), 121.73 (d), 23.84 (q), 21.07 (q); ^{29}Si NMR (CDCl$_3$) δ –54.45; MS m/e 623 (M$^+$).

Measurements of the Oxidation Potentials of Disiliranes. Measurements of the oxidation potentials of disiliranes were performed in a specially devised cell equipped with a working electrode center electrode (Pt wire) and a saturated calomel electrode as a reference in anhydrous CH$_2$Cl$_2$ solution containing n-Bu$_4$NClO$_4$ (0.1 M) as a supporting electrolyte. All runs were made at room temperature after a 15 min of purging with nitrogen.

Measurement of Rate Constants for Quenching of $^1O_2$ with Disiliranes. The measurements were carried out by the literature method.[14] The microfeeder poured the solution to the flow cell (2 × 2 cm) directly from a syringe. The flow rate of 1.5 mL/min was used for $^1O_2$-quenching experiments. All solutions were saturated with air at room temperature and concentrations of TPP used for the quenching experiments were 0.2 μM. The near-infrared emission from the flow cell with Ar laser (Spectra Physics, Model 2016) light excitation was detected by a liquid nitrogen cooled germanium detector (transimpedance amplifier; Applied Detector, Model 403L) through collecting lenses, a light chopper, and a monochromator (JASCO, Model CT-10N). The appropriate electronic signals were isolated by a lock-in amplifier (Princeton Applied Research: Model 124A) from the output signals of the detector.

Photosensitized Oxygenation of 1a. In a typical experiment, photooxygenation of **1a** (1.1 × 10^{-2} M) was carried out in dry benzene (5 mL) with tetraphenylporphine (TPP; 1.0 × 10^{-4} M) as sensitizer. The solution was irradiated at 15 °C under oxygen flow with two 500-W tungsten–halogen lamps, and the reaction was monitored by HPLC. After consumption of **1a**, removal of the solvent and then recrystallization of the residue from THF gave 86% **3,3,5,5-tetramesityl-1,2,3,5-dioxadisilolane (2a)** (92% yield by HPLC): mp 133–135 °C; ^{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$_2$Si$_2$: C, 76.76; H, 8.01. Found: C, 76.75; H, 8.06.

Oxidation of 1a with 1,4-Dimethylnaphthalene Endoperoxide. A cold solution of **1a** (3.6 × 10^{-3} M) in CH$_2$Cl$_2$ (5 mL) was refluxed under Ar atmosphere for 1 h in the dark with 500 mg of 1,4-dimethylnaphthalene endoperoxide, prepared by methylene blue-sensitized photooxygenation of 1,4-dimethylnaphthalene according to the procedure given in the literature.[12] The yields of **2a** and **2,2,4,4-tetramesityl-1,2,4-oxadisiletane (3a)** were determined by HPLC. **3a** was also prepared by mCPBA oxidation of **1a**. **3a**: mp 158–161 °C; ^{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), 132.56 (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.

Oxidation of 1a with Triphenyl Phosphite Ozonide. A solution of triphenyl phosphite (3.7 × 10^{-3} M) in CH$_2$Cl$_2$ (10 mL) was ozonized at –78 °C and purged with nitrogen to exclude excess ozone.[13] A cold solution of **1a** (3.7 × 10^{-3} M) in CH$_2$Cl$_2$ (2 mL) was added to an ozonide solution, and then the cooling bath was removed. An evolution of gas was observed when the solution was warmed to –30 °C. The yield of **2a** (11%) was determined by HPLC.

Photooxygenation of 1b–f. A typical experiment is as follows. Photooxygenation of **1c** (1.1 × 10^{-2} M) was carried out in dry benzene (5 mL) with tetraphenylporphine (TPP; 1.0 × 10^{-3} M) as sensitizer. The solution was irradiated at 15 °C under an oxygen flow with two 500-W tungsten–halogen lamps through an aqueous NaNO$_2$ solution filter, and the reaction was monitored by HPLC. After consumption of **1c**, removal of the solvent and then silica gel flash column chromatography gave **3,3,5,5-tetrakis(2,6-diethylphenyl)-1,2,4,3,5-trioxadisilolane (2c)** in 71% isolated yield. The results are summarized in Table I.

2c: mp 118–119 °C; ^{1}H NMR (CDCl$_3$) δ 7.24–6.93 (m, 12H), 2.85 (q, 16 H, J = 7.4 Hz), 0.80 (t, 24H, J = 7.4 Hz); ^{13}C NMR (CDCl$_3$) δ 150.27 (s), 131.11 (s), 130.60 (d), 126.01 (d), 28.54 (t), 15.55 (q); ^{29}Si NMR (CDCl$_3$) δ –12.62; IR (KBr) 1070 cm^{-1}; MS m/e 638 (M$^+$, 3%), 504 (M$^+$ – Dep, 100%), 372 (M$^+$ – Depx2, 51%). Anal. Calcd for C$_{40}$H$_{52}$O$_3$Si$_2$: C, 75.42; H, 8.23. Found: C, 75.34; H, 8.27.

3,3,5,5-Tetrakis(2,6-diisopropylphenyl)-1,2,4,3,5-trioxadisilolane (2b): mp 170 °C dec; ^{1}H NMR (CDCl$_3$) δ 7.31–6.98 (m, 12H), 4.24 (sept, 2H, J = 6.7 Hz), 3.85 (sept, 2H, J = 6.7 Hz), 3.20 (sept, 4H, J = 6.7 Hz), 1.32 (d, 6H, J = 6.7 Hz), 1.28 (d, 6H, J = 6.7 Hz), 1.23 (d, 6H, J = 6.7 Hz), 1.13 (d, 6H, J = 6.7 Hz), 0.96 (d, 6H, J = 6.7 Hz), 0.53 (d, 6H, J = 6.7 Hz), 0.39 (d, 6H, J = 6.7 Hz), 0.20 (d, 6H, J = 6.7 Hz); ^{13}C NMR (CDCl$_3$) δ 155.16 (s), 154.98 (s), 154.69 (s), 153.90 (s), 131.40 (s), 130.78 (d), 130.66 (d), 129.63 (s), 124.52 (d), 124.39 (d), 123.09 (d), 122.86 (d), 35.49 (d), 35.39 (d), 30.66 (d), 30.11 (d), 26.99 (q), 25.39 (q), 24.15 (q), 24.07 (q), 23.80 (q), 23.68 (q), 23.46 (q), 23.25 (q); ^{29}Si NMR (CDCl$_3$) δ –13.65; IR (KBr) 1075, 1031 cm^{-1}; MS m/e 748 (M$^+$, 4%), 587 (M$^+$ – Dip, 43%), 426 (M$^+$ – 2Dip, 100%). Anal. Calcd for C$_{48}$H$_{68}$O$_3$Si$_2$: C, 76.95; H, 9.15. Found: C, 76.61; H, 9.13.

3,3,5,5-Tetramesityl-1,2,4,3,5-trioxadisilolane (2d): mp 146–148 °C; ^{1}H NMR (CDCl$_3$) δ 6.71 (s, 8H), 2.37 (s, 24H), 2.20 (s, 12H); ^{13}C NMR (CDCl$_3$) δ 144.46 (s), 140.24 (s), 130.48 (s), 128.79 (d), 22.60 (q), 21.16 (q); ^{29}Si NMR (CDCl$_3$) δ –12.14; IR (KBr) 1065, 1024 cm^{-1}; MS m/e 580 (M$^+$, 24%), 461 (M$^+$ – Mes, 100%), 342 (M$^+$ – 2Mes, 73%). Anal. Calcd for C$_{36}$H$_{44}$O$_3$Si$_2$: C, 74.43; H, 7.63. Found: C, 74.50; H, 7.74.

3,3,5,5-Tetrakis(2,6-dimethylphenyl)-1,2,4,3,5-trioxadisilolane (2e): mp 167–169 °C; ^{1}H NMR (CDCl$_3$) δ 7.23–6.80 (m, 12H), 2.40 (s, 24H); ^{13}C NMR (CDCl$_3$) δ 144.32 (s), 131.26 (s), 130.51 (d), 127.91 (d), 22.59 (q); ^{29}Si NMR (CDCl$_3$) δ –12.89; IR (KBr) 1060, 1020 cm^{-1}; MS m/e 524 (M$^+$, 21%), 419 (M$^+$ – Xyl, 71%), 314 (M$^+$ – 2Xyl, 100%). Anal. Calcd for C$_{32}$H$_{36}$O$_3$Si$_2$: C, 73.24; H, 6.91. Found: C, 73.34; H, 6.93. ***trans*-3,5-Bis(4-*tert*-**

butyl-2,6-diethylphenyl)-3,5-bis(2,6-diethylphenyl)-1,2,4,3,5-trioxadisilolane (*trans*-2g): mp 130–132 °C; ^{1}H NMR ($CDCl_3$) δ 7.25–6.90 (m, 10H), 2.88 (q, 16H, J = 7.3 Hz), 1.24 (s, 18H), 0.81 (t, 12H, J = 7.3 Hz), 0.77 (t, 12H, J = 7.3 Hz); ^{13}C NMR (22.4 MHz, $CDCl_3$, 60 °C) δ 153.26 (s), 150.28 (s), 149.94 (s), 131.46 (s), 130.36 (d), 127.75 (s), 125.82 (d), 123.01 (d), 34.45 (s), 31.04 (q), 28.74 (t), 28.50 (t), 15.80 (q), 15.34 (q); ^{29}Si NMR (17.6 MHz, $CDCl_3$) δ −12.15. Exact mass calcd for $C_{48}H_{68}O_3Si_2$: 748.4709. Found: 748.4753.

***cis*-2g**: mp 137–138 °C; ^{1}H NMR ($CDCl_3$) δ 7.25–6.90 (m, 10H), 2.88 (q, 16H, J = 7.3 Hz), 1.24 (s, 18H), 0.81 (t, 12H, J = 7.3 Hz), 0.77 (t, 12H, J = 7.3 Hz); ^{13}C NMR (22.4 MHz, $CDCl_3$, 60 °C) δ 153.26 (s), 150.28 (s), 149.94 (s), 131.46 (s), 130.36 (d), 127.75 (s), 125.89 (d), 123.08 (d), 34.50 (s), 31.06 (q), 28.77 (t), 28.52 (t), 15.66 (q), 15.46 (q); ^{29}Si NMR (17.6 MHz, $CDCl_3$) δ −12.15. Exact mass calcd for $C_{48}H_{68}O_3Si_2$: 748.4709. Found: 748.4642.

4-Phenyl-3,3,5,5-tetramesityl-1,2,4,3,5-dioxazadisilolidine (2f): mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 7.05–6.65 (m, 13H), 2.26 (s, 12H), 2.13 (s, 24H); ^{13}C NMR ($CDCl_3$) δ 144.21 (s), 139.88 (s), 131.91 (s), 129.26 (d), 128.83 (s), 128.12 (d), 127.53 (d), 123.03 (d), 24.38 (q), 21.13 (q). Exact mass calcd for $C_{42}H_{49}NO_2Si_2$: 655.3302. Found: 655.3323.

Photooxygenation of 1a–b in the Presence of Sulfoxide and Sulfide. A typical experimental procedure was described as follows. A solution of **1a** (3.6 × 10^{-3} M) and sulfoxide (3.6 × 10^{-1} M) in benzene (5 mL) was irradiated with two 500-W halogen lamps at 15 °C under oxygen with TPP as sensitizer. Aliquots were withdrawn at periodic intervals and analyzed by HPLC. The yields of **2a**, **3a**, and **2b** were determined by means of HPLC. The yields of **2,2,4,4-tetrakis(2,6-diisopropyl)-1,3,2,4-dioxadisiletane (3b)** and diphenyl sulfone were determined by means of GLC. **3b** was also prepared by mCPBA oxidation of **1b**. **3b**: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 7.31–6.95 (m, 12H), 4.26 (sept, 4H, J = 6.7 Hz), 3.30 (sept, 4H, J = 6.7 Hz), 1.31 (d, 12H, J = 6.7 Hz), 1.14 (d, 12H, J = 6.7 Hz), 0.63 (d, 12H, J = 6.7 Hz), 0.32 (d, 12H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 155.29 (s), 154.31 (s), 132.77 (s), 130.70 (d), 124.59 (d), 122.70 (d), 34.91 (d), 29.62 (d), 24.61 (q), 24.19 (d), 23.97 (d), 23.86 (q); ^{29}Si NMR ($CDCl_3$) δ −7.47; IR (KBr) 1075, 1030 cm^{-1}; MS *m/e* 732 (M$^+$, 4%), 571 (M$^+$ − Dip, 43%), 410 (M$^+$ − 2Dip, 100%). Anal. Calcd for $C_{48}H_{68}O_2Si_2$: C, 78.63; H, 9.35. Found: C, 78.47; H, 9.44.

Reduction of *trans*-1g with $LiAlH_4$. To a stirred suspension of 20 mg of $LiAlH_4$ in 5 mL of Et_2O was added a solution of 100 mg of *trans*-**1g** in Et_2O. The resulting mixture was stirred for 10 min and then hydrolyzed. The organic layer was extracted with Et_2O, washed with water and dried over anhydrous $MgSO_4$. Recrystallization of the reaction mixture from ethanol afforded ***dl*-1,3-bis(4-*tert*-butyl-2,6-diethylphenyl)-3,5-bis(2,6-diethylphenyl)-1,3-disiloxanediol (11)** in 60% yield. **11**: mp 129–130 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (t, 2H, J = 7.4 Hz), 6.97 (s, 4H), 6.96 (d, J = 7.4 Hz), 3.46 (s, 2H), 2.74 (q, 8H, J = 7.6 Hz), 2.71 (q, 8H, J = 7.6 Hz), 1.25 (s, 18H), 0.76 (t, 12H, J = 7.6 Hz), 0.74 (t, 12H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 152.33 (s), 149.55 (s), 149.19 (s), 135.40 (s), 131.77 (s), 129.60 (d), 125.94 (d), 123.12 (d), 34.43 (s), 31.09 (q), 28.77 (t), 28.65 (t), 15.44 (q), 15.07 (q); IR (KBr) 3425, 1076, 988 cm^{-1}. Exact mass calcd for $C_{34}H_{49}O_3Si_2$ (M$^+$ − Det): 561.3220. Found: 561.3224. Calcd for $C_{38}H_{57}O_3Si_2$ (M$^+$ − Dep): 617.3846. Found: 617.3851.

X-ray Crystal Analyses. Crystals of *trans*-**1g** and **11** suitable for X-ray diffraction experiment were obtained from toluene and from a mixed solvent of hexane–ethanol, respectively, by slow evaporation at room temperature. Those of **11** contained one molecule of ethanol per molecule of disiloxanediol. Intensity data for both compounds were collected with Mo Kα radiation (λ = 0.710 73 cm^{-1}) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator. The ω–θ scan technique was applied with variable scan speeds. Data were corrected for Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically by full-matrix least squares. All calculations were performed on a VAX computer using SDP/VAX.[28] For compound *trans*-**1g**, hydrogen atoms were located and their positions were refined in least squares; their isotropic thermal parameters were fixed at 4.0 Å^3. For compound **11**, hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. Crystal data, data collection, and least-squares parameters are listed in Table VI. ORTEP diagrams of the structures of *trans*-**1g** and **11** are shown in Figures 1 and 2, respectively.

Table VI. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters for *trans*-1g and 11

	trans-**1g**	**11**
emperical formula	$C_{48}H_{68}OSi_2$	$C_{48}H_{70}O_3Si_2{\cdot}C_2H_6O$
fw	717.25	797.32
cryst size, mm	0.20 × 0.20 × 0.20	0.10 × 0.20 × 0.27
cryst class	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	13.917(1)	13.391(7)
b (Å)	15.497(1)	13.389(6)
c (Å)	12.667(1)	16.347(7)
α (deg)	109.96(3)	107.50(2)
β (deg)	109.16(1)	96.00(3)
γ (deg)	63.50(1)	113.30(2)
V (Å^3)	2247.1	2482.3
Z	2	2
D_{calc} (g cm^{-3})	1.06	1.01
F(000)	784	820
ω scan width (deg)	0.9 + 0.350 tan θ	0.4 + 0.350 tan θ
max 2θ (deg)	50.0	50.0
total no. of reflns	8489	9089
no. of unique reflns	7914	8750
no. of obsd data [$I > 3\sigma(I)$]	3845	2830
R	0.073	0.060
R_w	0.074	0.065
goodness of fit	1.71	1.94
convergence, largest shift	0.91σ	0.06σ
no. of params refined	664	505
max density of ΔF map (e/Å^3)	1.55(6)	0.30(5)

Computational Details. Calculations were carried out at the Computer Center of the Institute of Molecular Science. Geometries were fully optimized at the Hartree–Fock (HF) level with the split valence d-polarized 6-31G* basis set.[22] The relative energies were calculated by means of the Møller–Plesset (MP) perturbation theory up to a full fourth order (MP4SDTQ).[24] In this paper, notations like MP2/6-31G*//6-31G* denote a single-point calculation at the MP2/6-341G* level on the HF/6-31G* optimized geometry.

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Supplementary Material Available: Detailed information on the X-ray crystal analysis of *trans*-**1g** and **11** including textual descriptions of experimental procedures, ORTEP diagrams, and tables of experimental details, positional and thermal parameters, temperature factor expressions, refined displacement parameter expressions, root-mean-square amplitudes, bond distances and angles, and torsion angles (55 pages). Ordering information is given on any current masthead page.

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