thereby depopulating the ligand π-HOMO. Inspection of Figure 7 shows that the effect of depopulating π is similar to that of populating π^*, at least as far as the bonds C1C1′ and C1C2 are concerned. Note, however, that *all* complexes with triple positive charge (except one) are found in a field which does not overlap with the field of M(II) complexes and is intermediate between the field of M(II) complexes and the point representing the Co(I) complex (Figure 2). In the field of complexes with triple positive charge both $d_\pi^5$and d_π^6 electronic configurations are found. This shows that $\pi \rightarrow d_\pi$ is an unlikely explanation for the observed structural patterns and indicates that charge may have a more important influence on the geometry of bpy in its metal complexes than partial ligand oxidation by an incomplete d_π-subshell. Note, that the only exception to the grouping by charge is the Cr(III) complex with three holes in its electronic configuration. The bpy and protonated bpy structures are distributed throughout the M(II) and M(III) complexes.

In summary, we feel that the usual backbonding model does not provide a consistent explanation of the relationships between charge, M–N distances, bpy geometry, and electronic structure in $[M(bpy)_3]^{n+}$ complexes. In part this may be due to the limited accuracy of the available data. The crystal structure analyses of $[Ni(bpy)_3]^{2+}$ have already been mentioned as an example of systematic error in the bond distances due to omission of hydrogen atoms from the model. The structure of $[Ir(bpy)_3]^{3+}$ is judged unreliable because it shows large displacement parameters and some unusual CCC and CCN bond angles. Further clarification of the relationship between electronic and geometric structure in $[M(bpy)_3]^{n+}$ complexes will therefore have to rely on a combination of improved structural data and more sophisticated theoretical investigations. However, there is little doubt in our minds, that the inconsistency mentioned above is real. It became apparent with the help of quantitative principal component analysis, which at present would seem the most reliable procedure to distinguish as well as is possible the electronic effects of interest from effects related to data collection and data treatment. At present, we are unable to give a consistent description of electronic effects on the M–N, N–C, and C–C distances in $M(bpy)_3^{n+}$ complexes. To the best of our knowledge the inconsistency has not been noted before.

Acknowledgment. We gratefully acknowledge financial help by the "Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung", Grant Nos. 20-5370.87, 20-29585.90, and 20-26448.89. We thank Johnson Matthey for a loan of $RuCl_3{\cdot}xH_2O$ and CIBA-GEIGY for the microanalyses.

Supplementary Material Available: Listings of crystal data, intensity collection and refinement parameters, atomic positional parameters, calculated hydrogen positional parameters, and anisotropic displacement parameters (7 pages); listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

1,2-Disiladioxetanes: Structure, Rearrangement, and Reactivity

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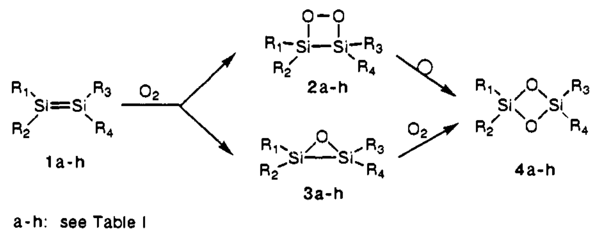
Abstract: The low-temperature reaction of (*E*)-1,2-dimesityl-1,2-di-*tert*-butyldisilene (**1a**) with dioxygen gives (*E*)-1,2-dimesityl-1,2-di-*tert*-butyldisiladioxetane (**2a**), the structure of which has been established by X-ray crystallographic analysis. This result establishes that both oxidation of **1a** and rearrangement of **2a** to 1,3-cyclodisiloxane **4a** take place with retention of configuration at silicon. Disiladioxetane **2a** forms monoclinic crystals, space group *C*2/*c*. Extra electron density found above and below the Si–Si bond was shown by ^1H and solid-state ^{29}Si NMR to be due to **4a**, arising from rearrangement of **2a** in the solid. X-ray crystal structures were determined for crystals that were 5.6%, 15.2%, and 20.3% rearranged. Cell dimensions for the 5.6% rearranged crystal are a = 12.549 (7) Å, b = 12.174 (7) Å, c = 17.133 (7) Å, b = 103.94 (4)°, V = 2529 (2) Å^3 (Z = 4). The rearrangement of **2a** in solution is first order with E_a = +21.7 ± 1.0 kcal mol^{-1}, ΔH^* = 21.1 ± 1.4 kcal mol^{-1}, and ΔS^* = −9.0 ± 4.5 cal K^{-1} mol^{-1}. Isotope labeling studies with ^{18}O showed the rearrangement to be intramolecular in the solid and in solution. In the presence of phosphines or sulfides, **2a** is partially deoxygenated to form disilaoxirane **3a**.

Introduction

Although alkenes react rapidly with singlet dioxygen,[1] reaction with triplet dioxygen is normally slow. Exceptions are very electron-rich alkenes such as tetraaminoethylenes,[2] alkenes with low-lying triplet states such as cyclobutadienes,[3] and ketenes.[4] For other alkenes, $^3O_2$ oxidation takes place only catalytically or at high temperatures.

Scheme I. Oxidation of Disilenes with $^3O_2$



Disilenes have much lower oxidation potentials than olefins,[5] and they are correspondingly much more reactive toward $^3O_2$. The

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[1] See: Bartlett, P. D.; Landis, M. E., Chapter 7; Schaap, A. P.; Zaklika, K. A., Chapter 6. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979.

[2] Urry, W. H.; Sheeto, J. *Photochem. Photobiol.* **1965**, *4*, 1067.

[3] Meijer, E. W.; Wynberg, H. *Tetrahedron Lett.* **1981**, *22*, 785. Maier, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425.

[4] Turro, N. J.; Chow, M.-F.; Ito, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5880.

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Table I. ^{29}Si NMR Chemical Shifts for **2** and **4**

system	substitution[a]	δ, ppm	
		2	**4**
a	$R_1 = R_4 = \text{Mes}$	+54.81	+13.22
	$R_2 = R_3 = t\text{-Bu}$		
b	$R_1 = R_2 = R_3 = R_4 = \text{Mes}$	+41.37	−3.35
c	$R_1 = R_2 = R_3 = R_4 = \text{Xyl}$	+40.96	−3.30
d	$R_1 = R_2 = R_3 = R_4 = \text{Dmt}$	+41.49	−2.46
e[b,c]	$R_1 = R_2 = \text{Mes}$	+41.66	−3.63
	$R_3 = R_4 = \text{Xyl}$	+40.67	−2.33
f[b,d]	$R_1 = R_2 = R_3 = \text{Xyl}$	+41.26	−3.49
	$R_4 = \text{Mes}$	+40.77	−2.75
g[b]	$R_1 = R_3 = \text{Mes}$	+41.16	
	$R_2 = R_4 = \text{Xyl}$	+41.15	
h[e]	$R_1 = R_3 = \text{Ad}$	+49.10	+8.1
	$R_2 = R_4 = \text{Mes}$		

[a] Mes = 2,4,6-trimethylphenyl, Xyl = 2,6-dimethylphenyl, Dmt = 2,6-dimethyl-4-(*tert*-butyl)phenyl, Ad = 1-adamantyl. [b] Not indicating assignment of Si signals to specific silicons. [c] $^1J_{\text{SiSi}} = 98$ for **2e**. [d] $^1J_{\text{SiSi}} = 94$ for **2f**. [e] Reference 15.

air oxidation of disilenes was one of the first reactions to be observed after these compounds were discovered.[6] The general course of this reaction has been described in earlier publications.[7] Typically disilenes **1** react in solution with triplet dioxygen to give 1,2-disiladioxetanes **2** as the major product, accompanied at room temperature by a smaller amount of disilaoxirane **3** (Scheme I).

Compounds **2** undergo a remarkably, quantitative rearrangement to 1,3-cyclodisiloxanes **4**, either thermally or photochemically.[8] In this the 1,2-disiladioxetanes behave very differently from either their germanium or carbon analogs. The 1,1,2,2-tetrakis(2,6-diethylphenyl)-1,2-digermadioxetane has been isolated, but it only rearranges to the 1,3-cyclodigermoxane photochemically.[9] The organic 1,2-dioxetanes do not rearrange, and in fact no carbon analog of the 1,3-cyclodisiloxane is known. Instead, these compounds undergo the well-known thermal photoluminescent cleavage into ketones.[10] In contrast, rearrangement of silicon compounds **2** does not involve the silanone as an intermediate, since the rearrangement proceeds unaltered in the presence of ethanol, an efficient silanone trap.[11]

Oxidation of disilenes by $^3O_2$ is known to take place stereospecifically. Pure samples of *E*-**1a** oxidize to give only one disiladioxetane isomer, as shown by ^{1}H and ^{29}Si NMR. X-ray crystal structure determinations have shown that (*E*)-1,2-dimesityl-1,2-di-*tert*-butyldisilene (**1a**) reacts with $^3O_2$ to give, after rearrangement, pure (*E*)-**4a**; *E–Z* mixtures of **1a** produce after oxidation **2a** and after rearrangement **4a** with the same *E–Z* ratio.[11] However, since the configuration of **2a** remained undetermined, it was not known whether formation of **4a** from **1a** took place via two inversion or two retention steps. The structures of compounds **3b** and **4a**,**b** have been determined;[12,13] both classes of compounds show unexpectedly short Si–Si bond distances, which have been interpreted in terms of unusual bonding between the silicon atoms.[14]

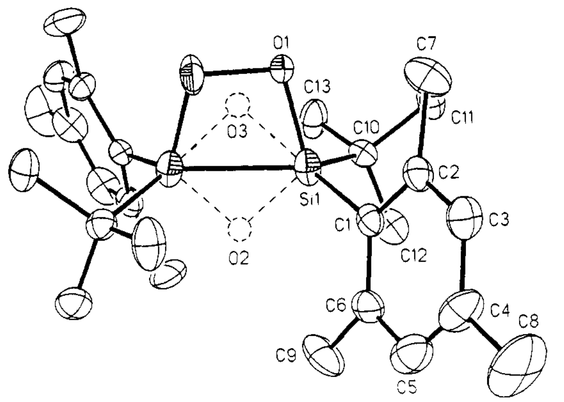

Figure 1. Thermal ellipsoid drawing of 1,2-dimesityl-1,2-di-*tert*-butyldisiladioxetane (**2a**) with hydrogen atoms omitted for clarity. Dotted lines indicate the 5.6% **4a** present. Selected bond distances (pm) and angles (deg) are as follows: Si(1)–Si(1A), 233.1 (2); O(1)–O(1A), 148.2 (5); Si(1)–O(1), 173.2 (3); Si(1)–C(10), 189.4 (3); Si(1)–C(1), 188.7 (4); Si(1)–O(3), 170.2 (2); Si(1)–O(2), 170.2 (2); Si(1A)–Si(1)–O(1), 75.5 (1); Si(1)–O(1)–O(1A) 103.7 (1); Si(1)–O(3)–Si(1A), 86.5 (1); Si(1)–O(2)–Si(1A), 86.4 (1); O(3)–Si(1)–O(2), 93.6 (1); C(10)–Si(1)–Si(1A); 123.0 (1); C(1)–Si(1)–C(10), 112.9 (2); C(1)–Si(1)–Si(1A), 119.5 (1).

Table II. Cell Dimensions of **2a** as a Function of the Percent Rearrangement to **4a**

% **4a**	*a*, Å	*b*, Å	*c*, Å	*β*, deg	*V*, Å^3
5.6	12.549 (7)	12.174 (9)	17.133 (7)	103.94 (4)	2529 (2)
15.2	12.526 (5)	12.255 (7)	17.226 (6)	104.23 (3)	2563 (3)
20.3	12.526 (7)	12.272 (7)	17.263 (7)	104.33 (4)	2571 (2)

In this paper, we report on the structure and chemistry of the 1,2-disiladioxetanes **2a–h**, focusing especially on the novel rearrangement of these compounds.

Results and Discussion

Synthesis of 1,2-Disiladioxetanes. Air oxidation of disilene **1a** or **1b** at low temperature in hexane afforded the corresponding 1,2-disiladioxetanes **2a** and **2b** as the sole products. The 1,2-disiladioxetanes are easily distinguished from the other oxidation products by proton NMR or by their ^{29}Si NMR chemical shifts, as shown for a variety of substituted compounds in Table I. The ^{29}Si resonances for the 1,2-disiladioxetanes are strongly deshielded, approaching the range of chemical shifts for multiply bonded silicon.[6] A downfield shift of the ^{29}Si NMR signal is common for both silyl peroxides[16a] and for other silicon-containing four-membered-ring compounds.[16b,c] In the 1,2-disiladioxetanes these two features are combined, leading to very deshielded ^{29}Si NMR signals.

Structure of 1,2-Disiladioxetane 2a. X-ray quality crystals of the single isomer of **2a** produced from the oxidation of **2a** were grown from toluene at −24 °C and then stored at −78 °C to minimize thermal rearrangement. As shown in Figure 1, the molecular structure of **2a** produced by oxidation of (*E*)-**1a** also has the *E* configuration. Both the oxidation of **1a** to **2a** and the

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(6) (a) For reviews on disilenes, see: West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201–1211. (b) Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Chapter 17, pp 1015–1043.

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(8) Tetrakis(2,4,6-triisopropylphenyl)disilene oxidizes similarly to the 1,2-disiladioxetane but then rearranges in a more complicated manner: (a) Watanabe, H.; Takeuchi, K.; Nakajima, K.; Nagai, Y.; Goto, M. *Chem. Lett.* **1988**, 1343. (b) Millevolte, A. J.; Powell, D. R.; Johnson, S. G.; West, R. *Organometallics*, in press.

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(13) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531.

(14) (a) Yokelson, H. B.; Millevolte, A. J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 4116. (b) Grev, R. S.; Schaefer, J. F., III *J. Am. Chem. Soc.* **1987**, *109*, 6577. (c) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 7863.

(15) (a) Shepherd, B. D.; Powell, D. R.; West, R. *Organometallics* **1989**, *8*, 2664.

(16) (a) Deshielded ^{29}Si NMR chemical shifts have been reported for $Me_3SiOOCF_3$ (δ +34.3 ppm) and $Me_3SiOOMe$ (δ +22.0 ppm): Marsmann, H. C.; Horn, H. G. *Z. Naturforsch., B* **1972**, *72*, 1448. (b) ^{29}Si for carbonyl adducts to silenes, +42 to +65 ppm: Brook, A. G.; Chatterton, W. J.; Sawyer, J. G.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246. (c) ^{29}Si for carbonyl adducts to disilenes, +14 to +35 ppm: Fanta, A. D.; DeYoung, D. J.; Belzner, J.; West, R. *Organometallics*, in press.

rearrangement of **2a** to **4a** therefore take place with retention of configuration.

The molecule possesses a C_2 rotation axis which bisects both the Si–Si and the O–O bonds. The most striking feature of the crystal structure of **2a** is the additional electron density found along the C_2 axis, above, and below the Si–Si bond, which we assign to oxygen atoms. The original crystals had 5.6% occupancy in the atypical positions; a crystal from the same preparation stored for 3.5 h at 25 °C then showed 15.2%, and a third crystal stored at −24 °C for 3 weeks had 20.3% occupancy of the unusual positions. (In each case the total occupancy at the typical and atypical oxygen positions sums to 100%.) Apparently, even with the greatest care, the **2a** rearranges to a small extent in the crystal under the conditions employed for crystal growth, although if solid **2a** is stored at −78 °C, no additional rearrangement takes place. The lattice of the crystal can support the **4a** "impurity" up to about 20%, at which point the solubility limit of the intermediate structure in the **2a** lattice is apparently exceeded and the sample no longer diffracts X-rays. As the rearrangement proceeds, the unit cell dimensions change somewhat as shown by the data in Table II. The *a* values decrease slightly and the values of *b*, *c*, and *V* increase significantly. The entire system appears to expand along the *b* and *c* axes, and it is probably this process that leads to breakdown of the lattice.

The structure of the 1,3-cyclodisiloxane within the host crystal was modeled as closely as possible to that of the previously reported structure for **4a**.[13] Constraints were placed on the Si–O bond to keep them both equal and near 170 pm. The Si–Si bond length is dependent on the amount of the rearranged structure in the crystal, since the silicons in the final structure are a weighted average of both **2a** and **4a**. As the rearrangement progresses, more of the molecules in the unit cell will have a silicon–silicon bond length of 239.6 (11) pm, that of free **4a**, and fewer will have the bond length of **2a**, 233.1 (2) pm. The **2a** structure with the least rearrangement (5.6%) is the nearest to unaltered 1,2-disiladioxetane and is used in the following discussion of the structural details of **2a**.

The four-membered ring in **2a** is nearly planar, with a torsional angle of only 8.9 (6)° between the Si–Si and O–O vectors. Theoretical calculations on the parent 1,2-disiladioxetane predict the ring to be planar.[17] In 1,1,2,2-tetrakis(2,6-diethylphenyl)-1,2-digermadioxetane this angle is 19.5°.[9] Structural studies of various substituted organic 1,2-dioxetanes gave a torsional angle range of 0–21.3°; the size of the angle was not found to be related to the degree of the stability of the dioxetane.[18] The puckering in all these dioxetane systems, whether carbon, silicon, or germanium, can be attributed to lone pair–lone pair repulsion of the peroxide oxygens.

The arrangement of carbon and silicon atoms around each silicon is also nearly planar; the sum of bond angles C(1)–Si(1)–C(10), C(1)–Si(1)–Si(1A), and C(10)–Si(1)–Si(1A) at silicon is 355.4 (5)°. The Si–Si distance of 233.1 (2) pm is slightly shorter than the usual Si–Si single bond length of 235 pm,[19] and also shorter than the Si–Si bonds in other four-membered rings.[20a–c] The Si–O bond distance of 173.2 (3) pm is greater than the Si–O distance in **4a** (167.7 pm),[12,21] consistent with molecular orbital

Scheme II. Rearrangement of a Mixture of ^{18}O Labeled and Unlabeled **2a**

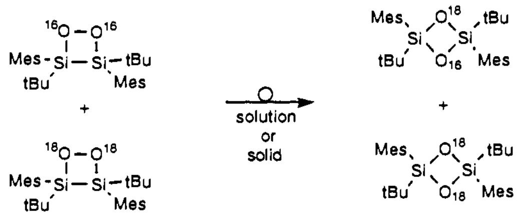

Table III. Temperatures, Rate Constants, and Free Energies of Activation for Rearrangement of **2** to **4**[a]

system	*T*, °C	10^5k, s^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}
2a[b]	40.0	12.7 ± 0.4	23.9 ± 0.1
2a[b]	35.0	8.2 ± 0.2	23.8 ± 0.1
2a[b]	30.0	3.9 ± 0.2	23.9 ± 0.1
2a[b]	24.0	1.9 ± 0.1	23.8 ± 0.1
2a[b]	19.0	1.1 ± 0.1	23.7 ± 0.1
2a[c]	35.0	9.6 ± 0.4	23.7 ± 0.1
2b[b]	35.0	26.9 ± 0.4	23.0 ± 0.1
2a-^{18}*O*[b]	35.0	7.3 ± 0.3	23.9 ± 0.1

[a] Values are from single runs except for **2a**, 35 °C, which is the average from three runs, and **2a**-^{18}*O*, which is the average of two runs. [b] In toluene. [c] In THF.

calculations on the hydrogen-substituted parent molecules, $H_2SiO_2SiH_2$.[17]

These bond lengths and angles for **2a** are in excellent agreement with the predicted structural parameters for the parent compound.[16] The longer Si–O bond, shortened Si–Si distance, and planarity of groups about silicon are consistent with some p-type bonding between the silicons, due to decreased back-donation from the oxygens to the antibonding Si–Si p* orbital, of the type invoked to explain the structural properties of the disiladioxiranes **3** and other three-membered-ring structures.[14] As would be expected from such a p bond, calculations show preferential charge accumulation in the plane perpendicular to the ring.[17]

The O–O bond length of **2a** is 148.2 (5) pm. This is almost the same as the bond distance in the 1,2-digermadioxetane, 147 (1) pm,[9] and is within the range (144–151 pm) found for organic 1,2-dioxetanes,[19] although usually this bond length increases slightly as carbon is replaced by silicon in linear peroxides.[22]

Solid-State NMR of 2a and 4a. Solution ^1H NMR was used to verify the amount of rearrangement to **4a** in the crystals which were found by X-ray to be 5.6 and 15.2% rearranged. Integration of the *tert*-butyl regions in the spectra showed 5% and 16% of **4a**, respectively. However, to verify *by another solid-state method* that **2a** and **4a** were present and were all that was present during the rearrangement in the solid, ^{29}Si CP-MAS solid-state NMR spectroscopy was used to follow the rearrangement in the solid. This is the first report of solid-state NMR spectra for the oxidized compounds. At −87° C, **2a** has a signal at +55.7 ppm vs. 54.8 ppm (C_6D_6) in solution.[23] An independent sample of **4a** gave, at both room temperature and −87 °C, a signal at +11.3 ppm vs +13.2 ppm (C_6D_6) in solution. Finally a sample of **2a** was allowed to stand at room temperature for 3.5 h, and after cooling back to −87 °C, the spectra showed only the two peaks corresponding to **2a** and **4a**. Since integration is not accurate in the CP-MAS experiment due to variation in the efficiency of polarization transfer, the final *ratio* was determined by an independent solution ^1H NMR study of the CP-MAS sample and showed a **2a**:**4a** ratio of 10.6:1 (8.6% **4a**). The solid-state NMR experiment shows that

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(17) Gordon, M. S.; Packwood, T. J.; Carroll, M. T.; Boatz, J. A, in press.

(18) Adam, W.; Arias, L. A.; Zahn, A.; Zinner, K.; Peters, K.; Peters, E.; Von Schnering, H. G. *Tetrahedron Lett.* **1982**, *23*, 3251.

(19) A similarly bulky disilane, 1,1-di-*tert*-butyl-2,2-dimesityldisilane, has two independent Si–Si bond distances which are much longer, 239.5 (2) and 240.0 (2) pm: Weidenbruch, M.; Kramer, K.; Peters, K.; von Schnering, H. G. *Z. Naturforsch. B* **1985**, *40*, 601.

(20) Si–Si bond lengths (pm) available for other bulky four-membered-ring silicon compounds follow. (a) Nitrile adducts of tetra-*tert*-butyldisilene with tri-*tert*-butylsilyl cyanide: 243.5 (1) [Weidenbruch, M.; Flintjer, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 95]. (b) Dimethylketene adduct of 1,1,2,2-tetramesityldisilene: 237.3 (2) [Fanta, A. D.; Belzner, J.; Powell, D. R.; West, R. *Organometallics* **1991**, *10*, 3466]. (c) Thiobenzophenone adduct of tetramesityldisilene: 244.3 (2) [Kabeta, K.; Powell, D. R.; Hanson, J.; West, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *31*, 4177].

(21) (a) The dimethylketene adduct of disilene has a Si–O bond length of 169.3 (4) pm.[20b] (b) The 1,2,4,3,5-trioxadisilolanes have a 1,2-dioxetane type Si–O bond length of 171.1 pm: Ando, W.; Kako, M.; Akasaka, T.; Kabe, Y. *Tetrahedron Lett.* **1990**, *31*, 4177.

(22) The bond length of the O–O bond does not seem to be greatly affected by whether it is in a ring or a linear system. Hydrogen peroxide (147.5 (5) pm) and linear organic peroxides (148 pm): Shklover, V. E.; Ad'yaasuren, P.; Tsinker, I.; Yablokov, V. A.; Ganyushkin, A. V.; Struchkov, Y. T. *J. Struct. Chem.* **1980**, *21*, 342. Linear silylperoxides (148–150 pm): Shklover, V. E.; Timofeeva, T. V.; Struchkov, Y. T.; Ganyushkin, A. V.; Yablokov, V. A. *J. Struct. Chem.* **1981**, *22*, 366.

(23) Small changes in chemical shift between solid and solution are normal, due to interaction of the molecule with the solvent.

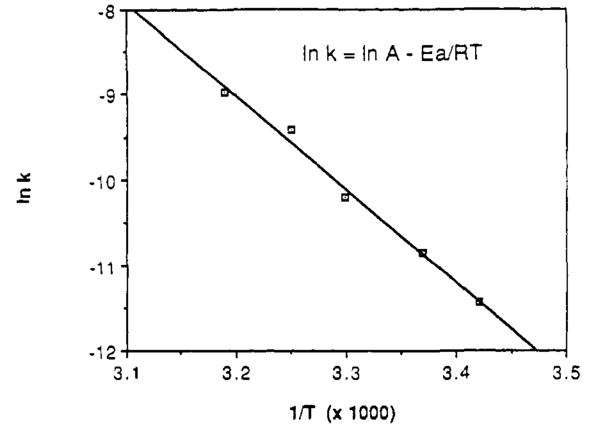


Figure 2. Arrhenius activation energy plot for the thermal rearrangement of **2a**.

2a rearranges to **4a** in the solid without a detectable intermediate.

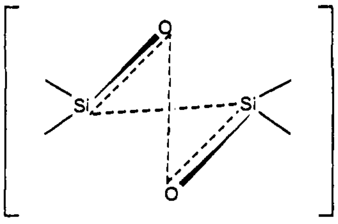
Isotope Labeling Studies. To gain additional information about the molecularity of the rearrangement, **2a** was obtained from $^{18}O_2$ and disilene. Equimolar mixtures of the labeled and unlabeled compounds were allowed to rearrange at room temperature, both in solution and as a homogeneous solid. Final HR/MS of the isolated solid following complete rearrangement showed no evidence of the crossover product [M^+ 442 or (M^+ - *t*-Bu) 385], only equal amounts of completely labeled **3a** [M^+ 440 or (M^+ - *t*-Bu) 383] and completely unlabeled **3a** [M^+ 444 or (M^+ - *t*-Bu) 387] (Scheme II). The isotope labeling studies therefore indicate that the rearrangement is *intramolecular both in the solid and in solution.*

Kinetics of Rearrangement of 2a. The kinetics of the rearrangement of **2a** to **4a** were studied using ^{1}H NMR spectroscopy. The rearrangement is a first-order process which follows the simple rate expression $\ln (c/c_0) = -kt$ and is not reversible; $t_{1/2}$ in solution at 25 °C = 4.5 h. Values of k were calculated at different temperatures (Table III), and the Arrhenius activation energy (E_a) was determined from the plot in Figure 2 to be 21.7 ± 1.0 kcal mol^{-1}.[24] The activation energies for the thermal decomposition of various organic 1,2-dioxetanes range from 21.7 to 33.8 kcal mol^{-1}.[10] Therefore, **2a** is about as stable as the most unstable organic dioxetane studied, the parent compound 1,2-dioxetane, itself. A single experiment using **2b** at 35 °C gave $\Delta G^{\ddagger} = 23.0 \pm 0.1$ kcal mol^{-1}, indicating that the rearrangement is more facile for the tetraaryl compound.

As shown in Table III, the free energy of activation for the rearrangement, $\Delta G^{\ddagger}$, is not affected by changing the solvent from benzene to THF. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be calculated from an Eyring plot of $\ln k_h/k_b T$ vs $1/T$. $\Delta H^{\ddagger} = 21.1 \pm 1.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9.0 \pm 4.5$ cal K^{-1} mol^{-1}.[24] The small negative entropy and lack of solvent effect of $\Delta G^{\ddagger}$ suggest that the transition state is about as polar as the ground state, and is fairly ordered. The entropy values, $\Delta S^{\ddagger}$, for the carbon analogs range from +2.9 to -5 K^{-1} mol^{-1},[25] indicating that the transition state for the thermal rearrangement of **2a** has fewer degrees of freedom or is more rigid than for the organic dioxetanes. This is consistent with the fact that the 1,2-disiladioxetanes rearrange to a single molecule of 1,3-cyclodisiloxane, while the organic 1,2-dioxetanes decompose into two carbonyl fragments.

The experimental data are consistent with a concerted retrocyclic path for the rearrangement of **2a**, similar to the mechanism suggested by Turro for the decomposition of organic dioxetanes.[26] The possible transition state **6** shown in Figure 3 would account for the small solvent effect, because the dipole moment of the transition state should be similar to that of 1,2-disiladoxetane. The least-motion pathway for the rearrangement seems to be one in which the oxygen atoms in **2a** stay above the silicon–silicon axis during the rearrangement (Scheme III). However, this seems very improbable in the solid state since the crystallographic data show that **4a** is formed from **2a** in *the same plane*. Therefore, without inverting the configuration at silicon, one oxygen atom must move from its position in **2a** all the way below the silicon–silicon bond to form **4a**.

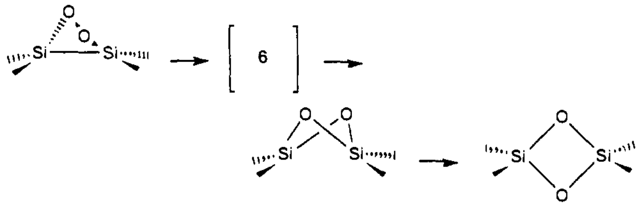
Reactivity of 2a. Although the most intensively studied area of the chemistry of the 1,2-dioxetanes is their thermally induced chemiluminescence, they also exhibit interesting nonluminescent reactivity at the O–O bond.[10] In particular, they are reduced to epoxides by phosphines and sulfides.[27] Similar reactions were



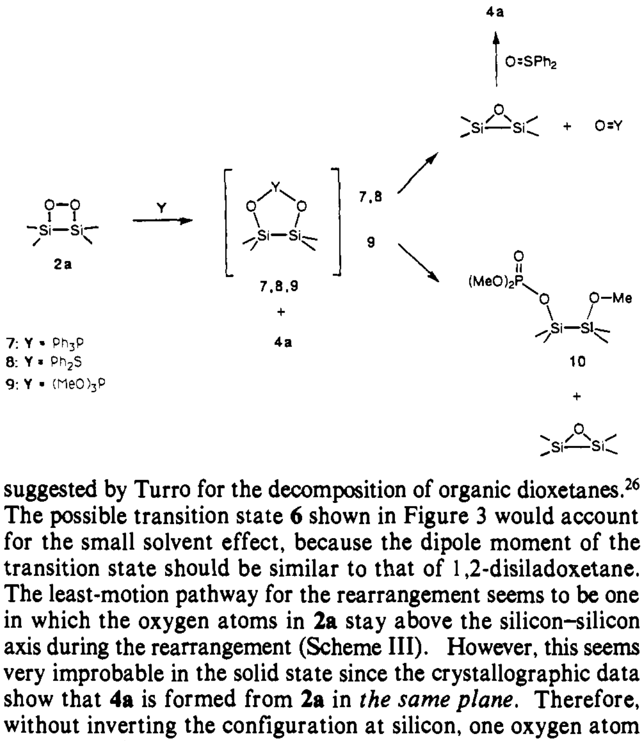
6

Figure 3. Possible transition state for rearrangement of 1,2-disiladioxetanes.

Scheme III. Possible Pathway for Rearrangement



Scheme IV. Reactions of **2a** with Phosphines and Diphenyl Sulfide



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(24) Errors of c and c_0 were calculated by assuming a 5% error in NMR integration. The errors in k and E_a were obtained by the use of the expression error(slope) = $[m/mSx_i^2 - (Sx_i^2)]^{1/2}$[error($y$)] where m is the number of data points in the least-squares analysis. The error in k_i was determined to be ±10% for all values. See also: Showemaker, K. P.; Garland, C. W.; Steinfeld, J. L. *Experiments in Physical Chemistry*; McGraw-Hill: New York, 1974; pp 55–57. Gordus, A. A. *Schaums Outline of Analytical Chemistry*; McGraw-Hill: New York, 1987; Chapter 2.

(25) Adam, W. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1977; p 465.

(26) (a) Steinmetzer, H.-C.; Yekta, A.; Turro, N. J. *J. Am. Chem. Soc.* **1974**, *96*, 282. (b) Turro, N. J.; Lechtken, P.; Schore, N. E.; Schuster, G.; Steinmetzer, H.-C.; Yetka, A. *Acc. Chem. Res.* **1974**, *7*, 97.

(27) For other examples of reduction of other cyclic silyl peroxides see: Ando, W.; Kako, M.; Akasaka, T.; Nagase, S.; Kawai, T.; Nagai, Y.; Sato, T. *Tetrahedron Lett.* **1989**, *30*, 6705 and ref 21b.

(28) No rearrangement of **2a** is seen at this temperature, even after 24 h.

(29) (a) 1,2-Di-*tert*-butyl-1,2-dimesityldisilene: Gillette, G. R.; Yokelson, H. B.; West, R. *Organomet. Synth.* **1988**, *4*, 518. (b) 1,1,2,2-Tetramesityldisilene: Yokelson, H. B.; Gillette, G. R.; Tan, R. T.; Millevolte, A. J.; West, R. *Inorg. Synth.* In press. (c) 1,1,2,2-Tetrakis(2,6-dimethyl-4-*tert*-butylphenyl)disilene: Yokelson, H. B.; Siegel, D. A.; Millevolte, A. J.; Maxka, J.; West, R. *Organometallics* **1990**, *9*, 1005.

observed for dioxetane **2a** (Scheme IV).

A solution of **2a** containing diphenyl sulfide, allowed to stand at 10 °C for 10 h,[28] produced a 1:6:1 mixture of **2a**:**4a**:**3a** by ^{29}Si NMR spectroscopy. Therefore, although **2a** reacts with Ph_2S to give **3a**, the predominant reaction is still the rearrangement. After 24 h, only **4a** remained, and as has been shown by an independent reaction of DMSO with **3b**, sulfoxides react further with disilaoxiranes to give sulfide and additional 1,3-cyclodisiloxane.[21b] No evidence of the sulfurane intermediate **8** was found by ^{29}Si NMR when the reaction was repeated, at temperatures ranging from −50 to +30 °C.

When the reaction of **2a** with Ph_3P was followed by ^{29}Si NMR spectroscopy, a doublet at $\delta = +2.61$ ($^2J_{SiP} = 7$ Hz) appeared which was assigned to the phosphorane species, **7** (Scheme IV). The ^{31}P NMR of this compound was −47.7 ppm vs −48.4 ppm for the carbon phosphorane.[10] As in the reduction of the organic dioxetane, this intermediate is only transient, and decomposes even at −25 °C to give the phosphine oxide and the epoxide. The final ratio of **4a** to **3a** was 2:1.

The reaction of organic 1,2-dioxetanes with phosphites yields phosphoranes which are stable up to 150 °C. In an effort to prepare a stable silicon analog, **2a** was treated with $(MeO)_3P$. This gave, in addition to **4a** and **3a**, not the phosphorane but a product which had two signals in the ^{29}Si NMR region, a doublet at +13.52 ppm ($^2J_{SiP} = 14$ Hz) and a singlet at +7.42 ppm. These results indicate that a ring-opened compound is formed, which we identify as **10**. The ^{31}P NMR spectra of this compound, at −5.0 ppm, is also much different than the chemical shift of −54.3 ppm for the phosphorane in the carbon system.[10] The final ratio of **10** to **4a** to **3a** was 6:1:1. Apparently, the phosphorane from the reaction of **2a** with trimethyl phosphite decomposes to both the epoxide and the ring-opened compound (Scheme IV). In the hopes of sterically stabilizing the 5-membered ring the reaction was tried with $(PhO)_3P$, but no reaction took place.

Conclusion

Elucidation of the structure of *E*-**2a** enables us to say that both the oxidation of disilenes and the rearrangement of disiladioxetanes take place with retention of configuration at silicon. This rearrangement has been shown to take place in the solid and in solution by means of a simple unimolecular mechanism. A mechanism is suggested which is possible in solution but is not consistent with the crystallographic data for the solid-state rearrangement. In fact we have not found a mechanism that can suitably account for all the experimental facts. It is the authors' hope that this work will stimulate other, possibly theoretical studies which will help answer this fascinating question more clearly.

Experimental Section

Proton NMR spectra were recorded on a Bruker WP-200 FT spectrometer; ^{29}Si, and ^{31}P NMR spectra were obtained on a Bruker AM-300 instrument. Solid-state ^{29}Si CP-MAS NMR spectra were recorded on a Varian UNITY 300 (solids/liquids) spectrometer, on samples packed into a sapphire tube. All reactions were carried out under an atmosphere of argon unless otherwise specified. Solids, especially disilene, were manipulated under nitrogen in a glovebox.

All solvents were dried, distilled, and degassed and all glassware was baked at 120 °C for several hours prior to use. Oxygen was dried by passing through a column of Drierite/Aquasorb. Doubly-labeled $^{18}O_2$ (97.6 atom % ^{18}O) was purchased from MSD Isotopes and used as received. Triphenylphosphine and triphenyl phosphite were purchased from Aldrich Chemical Co. and used as received. Diphenyl sulfide was purchased from Aldrich and was dried first over $CaCl_2$ and then sodium and finally distilled under vacuum. Trimethyl phosphite, purchased from Aldrich, was dried over sodium and distilled.

1,2-Di-*tert*-butyl-1,2-dimesityldisilene (**1a**), 1,1,2,2-tetramesityldisilene (**1b**), 1,1,2,2-tetrakis(2,6-dimethyl-4-*tert*-butylphenyl)disilene (**1c**), and 1,1,2,2-tetrakis(2,6-dimethylphenyl)disilene (**1d**) were prepared as previously reported.[29]

Synthesis of 1,2-Di-*tert*-butyl-1,2-dimesityl-1,2-disiladioxetane (2a). Disilene **1a** (50 mg, 0.12 mmol) was placed in a 50-mL sidearm flask with a magnetic stirbar. The flask was charged with 25 mL of hexane and fitted with a septum. The pale yellow solution was cooled to −65 °C in a dry ice/EtOH bath and O_2 gas was bubbled through a needle into the solution. After 45 min, the solution was almost colorless with the product present as a fine white precipitate. Half of the solvent was removed in vacuo with care taken to keep the flask cooled. Vacuum filtration through a cooled enclosed D-frit gave a white powder (45 mg, 91%) identified as **2a** which was stored at −78 °C to avoid rearrangement (rearrangement to **4a** is likely for melting point and mass spectra): mp 180–182 °C; ^{1}H NMR (toluene-d_8) δ 1.02 (s, 9 H), 2.00 (s, 3 H), 2.40 (s, 6 H), 6.61 (s, 2 H); ^{29}Si NMR (toluene-d_8) δ +54.8 ppm; HRMS 440.2566 (4.3, 440.2556 calcd for $C_{26}H_{40}Si_2O_2$), 383 ($M^+ - t$-Bu, 100), 263 [($M^+ - t$-Bu) − C_9H_{12}, 12.3].

Synthesis of 1,1,2,2-Tetramesityl-1,2-disiladioxetane (2b). The same procedure was followed as above beginning with tetramesityldisilene (50 mg, 0.09 mmol) and yielding a white solid (46 mg, 91%) identified as **2b** (rearrangement to **4b** probable for melting point and mass spectra): mp 214 °C; ^{1}H NMR (toluene-d_8) δ 2.01 (s, 3 H), 2.47 (s, 6 H), 6.60 (s, 2 H); ^{29}Si NMR (C_6D_6) δ +41.4 ppm; HRMS 564.2878 (5.3; 564.2868 calcd for $C_{36}H_{44}Si_2O_2$), 444 ($M^+ - C_9H_{12}$, 100), 325 [($M^+ - C_9H_{12}$) − C_9H_{11}, 94].

1,1,2,2-Tetrakis(2,6-dimethylphenyl)-1,2-disiladioxetane (2c). When a stream of air was bubbled through a deep yellow solution of 50 mg (0.1 mmol) of disilene **1c** in 0.5 mL of benzene at 25 °C, the solution decolorized over several minutes to pale yellow. Compound **2c** was obtained initially as the major component (>80%) of a binary mixture with oxirane **3c**: ^{1}H NMR (200 MHz, C_6D_6) δ 2.40 (s, 6 H), 6.73 (A*B*$_2$, 2 H), 6.98 (*A*B$_2$, 1 H); ^{29}Si NMR (C_6D_6) δ +40.96; exact mass for $C_{32}H_{36}Si_2O_2$ calcd *m*/*e* 508.2254, found *m*/*e* 508.2258. Isomerization to the 1,3-cyclodisiloxane in the heated MS probe (150 °C) is extremely likely.

1,1,2,2-Tetrakis(2,6-dimethyl-4-*tert*-butylphenyl)-1,2-disiladioxetane (2d). The synthesis was analogous to that for **2c**; the product was examined as a mixture with about 20% **3d**: ^{1}H NMR (C_6D_6) δ 1.16 (s, 9 H), 2.56 (s, 6 H), 6.94 (s, 2 H); ^{29}Si NMR (C_6D_6) δ +41.49.

X-ray Structure Determination. Single crystals of **2a** for X-ray diffraction experiments were grown from a cooled solution of toluene. Very small pale yellow equidimensional prisms grew over 2 weeks at −25 °C. A single crystal was selected, mounted on a thin glass fiber with epoxy cement, and cooled to −150 °C. These crystals contained 20.3% **4a**.

Next, crystals were grown over about 2 days at −25 °C, isolated, and stored at −78 °C to avoid rearrangement. A single crystal was selected, coated with paratone-N, mounted on a thin glass fiber for X-ray analysis, and cooled to −165 °C immediately. These crystals were 5.6% **4a**.

Finally, crystals from the batch that contained 5.6% **4a** were allowed to stand at room temperature for 3.5 h. Next a suitable crystal was selected, coated with paratone-N, mounted on a thin glass fiber for X-ray analysis, and cooled to −165 °C immediately. These crystals showed 15.2% **4a**.

Initial anisotropic refinement of **2a** led to two peaks with densities of about 0.8 e/Å^3 in a difference electron density map. These peaks were located on the molecular 2-fold axis running through the silicons. The peak away from the **2a** oxygens was located about 1.7 Å from the silicons, a typical Si–O distance. These peaks were attributed to the rearranged **4a**. The refinement model was then changed to include a mix of **2a** and **4a** sitting on the same site with the relative amounts of the two compounds linked by a single variable. Since the oxygens in **2a** are greatest in proportion, these atoms most strongly influenced the occupancy variable. The refined anisotropic thermal parameters for the oxygens of **2a** were found to be comparable to thermal parameters of the silicons and carbons. The final refinement cycles included slack constraints on the bond distances between the silicons and the **4a** oxygens.

The X-ray crystallographic experiments were performed on a Siemens P3f diffractometer equipped with a graphite-monochromated Cu Ka X-radiation source (l = 1.54184 Å) for the 5.6% and 15.2% crystals and Mo Ka X-radiation source (l = 0.71072 Å) for the 20.3% crystal. All measurements were made using a nitrogen gas low-temperature device.

Unit cell parameters were determined by least-squares refinements based on 25 centered reflections. Three standard reflections were measured after every 50 reflections during the data collection. No significant decreases in the intensity of the standard reflections were observed during the data collection.

The structures were solved by direct methods using the SHELXTL PLUS program on a Microvax II and refined by the full-matrix least-squares refinement method on F using the reflections with $F_o > 4.0s(F)$. In the final refinement cycles the non-hydrogen atoms were assumed to vibrate anisotropically while the hydrogen atoms were included as idealized isotropic fixed contributors. The refinement converged to unweighted and weighted agreement factors of R = 4.94% and wR = 7.23%, R = 4.69% and wR = 6.65%, and R = 9.87% and wR = 9.66% for the crystals with 5.6%, 15.2%, and 20.3% rearrangement, respectively.

Solid-State NMR of 2a,4a and Partially Rearranged Sample. A sample of **2a**, cooled to −87 °C, showed a ^{29}Si NMR signal at +55.71 ppm; **4a** showed only a signal at +11.26 ppm. The sample of **2a**, still in the sample tube, was allowed to warm to room temperature for 3.5 h and then cooled back to −84 °C. The ^{29}Si NMR spectrum then showed peaks for both **2a** and **4a**. Solution ^{1}H NMR (C_6D_6) was taken of the partially rearranged sample and integration of *t*-Bu regions afforded a ratio 10.6:1 of **2a**:**4a** (8.5% **4a**).

Kinetic Measurements. Sealed NMR samples of 20 mg of **2a** in 0.5 mL of toluene or THF (0.09 M), containing 3 mg of $Me_{12}Si_6$ as an internal standard, were heated in a constant-temperature bath. Samples were removed at periodic intervals and the progress of the rearrangement monitored by ^{1}H NMR at least past 1 half-life. The rearrangement was repeated at 35 °C three times and gave similar rate constants in all cases. To test the influence of concentration on the rate, samples of 15 and 10 mg of **2a** in 0.5 mL of toluene were allowed to rearrange at 35 °C. The results showed that the rate of the rearrangement is independent of the concentration of **2a**. The ^{18}O isotope effect was determined on two independent samples of 0.05 mg of labeled **2a** in 0.5 mL of toluene at 35 °C. The rate of the rearrangement of a sample of **2b** was determined at 35 °C (23 mg, 0.09 M).

Synthesis of Doubly-^{18}O-Labeled 2a. A 50-mL sidearm flask was charged with 1,2-dimesityl-1,2-di-*tert*-butyldisilane (70 mg, 0.17 mmol), 25 mL of hexane, and a stirbar. This was stoppered, attached to one side of a small stopcock-sealed glass transfer line on a high vacuum line, and put through 3 freeze–pump–thaw degassing cycles. A 250-mL bulb of $^{18}O_2$ was attached with an O-ring seal to the other end of the transfer line, and the entire line was evacuated. The apparatus was left under a static vacuum and the flask with the hexane solution was cooled to −65 °C. The bulb of $^{18}O_2$ was opened to the flask allowing the oxygen to be taken up, aided by vigorous stirring, over a period of 4.5 h at which point the original pale yellow solution had become almost completely colorless. The labeled **2a** was isolated in the same manner as the unlabeled compound and was free of epoxide by ^{1}H NMR spectroscopy. HR/MS of the white powder gave a ratio of labeled to unlabeled species similar to that of the original gas (97.6 atom % ^{18}O).

Crossover Experiments in Solution. A 25-mL flask was charged with **2a** (30.5 mg, 0.07 mmol) and $^{18}O_2$-**2a** (30.5 mg, 0.07 mmol) and 6 mL of toluene. The homogeneous solution was allowed to stand at room temperature for 3 days to ensure complete rearrangement. The mixture was concentrated in vacuo to afford colorless crystals. HR/MS based on the (M^+ − *t*-Bu) peak showed masses at 383 and 387 in equal amounts without the enriched 385 mass expected for the crossover product.

Crossover Experiment in the Solid. **2a** (30 mg, 0.07 mmol) and $^{18}O_2$-**2a** (30 mg, 0.07 mmol) were added to a cooled flask (−78 °C) and dissolved in 2 mL of toluene. The mixture was maintained at −78 °C and concentrated until solid began to precipitate. Two milliliters of hexane were added and the solution was concentrated until precipitation again occurred. The flask was held at −78 °C for 20 min and then the solid was isolated on a cooled D-frit. The homogeneous solid was allowed to stand at room temperature for 3 days to ensure complete rearrangement. HR/MS based on the parent ion showed masses at 440 and 444 in equal amounts without the enriched 442 mass expected for the crossover product.

Reaction of 2a with Ph_2S. A sample of **2a** (20 mg, 0.05 mmol), diphenyl sulfide (9 mg, 0.05 mmol), and 0.5 mL of benzene was sealed in an NMR tube and the reaction was followed by ^{29}Si NMR. After 17 h at 10 °C, the spectra showed signals at δ = +13.2 (**4a**) and −7.8 (**3a**) in a 7:1 ratio. After 2 days, only the +13.2-ppm signal remained. The experiment was repeated and spectra recorded every 10 °C from −50 to +35 °C, but no additional signal was seen which could be attributed to an intermediate five-membered-ring structure.

Reaction of 1,1,2,2-Tetramesityl-1,2-disilaoxirane (3b) with DMSO. A sealed NMR sample of dried, degassed DMSO (0.01 mL, 0.1 mmol) and **3b** (20 mg, 0.04 mmol) with 0.5 mL of toluene was monitored by ^{29}Si NMR. Initially only a signal for **3b** at δ −27 ppm was present, but this slowly disappeared and was replaced by δ +2.6 ppm (**4b**). After 2 days only **4b** was present.

Reaction of Ph_3P with 2a. An NMR sample of **2a** (20 mg, 0.05 mmol), triphenylphosphine (12 mg, 0.05 mmol), and 0.5 mL of toluene was sealed. Initially at room temperature the ^{29}Si NMR spectra showed only δ = +54.8 ppm (**2a**). After 1 h both **2a**, δ + 54.8 ppm, and **4a**, δ +13.2 ppm, were present in a 6:1 ratio. As the reaction continued signals grew in δ +2.61 ppm (d, $^2J_{SiP}$ = 7 Hz) and δ −7.8 ppm (**3a**). The doublet, about 10% of the reaction mixture, was attributed to the phosphorane **7**: ^{1}H NMR (C_6D_6) δ 1.04 (s, 9 H), 2.42 (s, 3 H), 2.67 (s, 3 H), 2.78 (s, 3 H), 6.98 (s, 2 H); ^{31}P NMR (C_6D_6) δ −47.7 ppm. At room temperature, **7** slowly fragments to give Ph_3PO [^{1}H NMR (200 MHz, C_6D_6) δ 7.6–7.8 (m, 2 H), 6.98–7.03 (m, 3 H); ^{31}P NMR (145.8 MHz, C_6D_6) δ +24.7 ppm (s)] and **3a** [^{29}Si NMR (71.548 MHz, C_6D_6) δ −7.8 ppm]. The fragmentation occurs even at −25 °C.

Reaction of 2a with $(MeO)_3P$. A 25-mL sidearm flask was charged with **2a** (97 mg, 0.22 mmol), $(MeO)_3P$ (90 mg, 0.66 mmol), and 10 mL of toluene. The reaction was stirred for 7 days at 10 °C to minimize rearrangement of unreacted **2a**. The solvent was removed slowly in vacuo and cooled to −25 °C to afford crystals. These were removed by filtration through an enclosed filter and identified as mostly **4a** [^{29}Si NMR (C_6D_6) δ +13.2 ppm] and some **3a** [^{29}Si NMR (C_6D_6) δ −7.8 ppm]. This procedure was repeated until all **4a** and **3a** were removed (3 times) and cloudy crystals were left that were identified as opened ring insertion product **10**: mp 160 °C dec; ^{1}H NMR (C_6D_6) δ 1.37 (s, 9 H), 1.41 (s, 9 H), 1.92 (s, 3 H, ortho), 1.96 (s, 3 H, ortho), 2.24 (s, 3 H, ortho), 2.30 (s, 3 H, ortho), 2.51 (s, 3 H, para), 2.89 (s, 3 H, para), 3.485 (d, $^3J_{HP}$ = 20 Hz, 3 H), 3.545 (d, $^3J_{HP}$ = 20 Hz, 3 H), 3.61 (s, 3 H, OMe), 6.36 (s, 1 H), 6.38 (s, 1 H), 6.75 (br s, 2 H); ^{29}Si NMR (C_6D_6) δ +13.51 (d, $^2J_{SiP}$ = 14 Hz), +7.43 ppm; ^{31}P NMR (C_6D_6) δ −5.02 ppm; HRMS 564.2981 (7.1, 564.2856 calcd for $C_{29}H_{49}Si_2O_2P$), 507 (M^+ − *t*-Bu, 63.8), 437 (44.3), 383 [(M^+ − *t*-Bu − $P(OMe)_3$, 41)], 119 (74.6), 89 (100).

Reaction of 2a with $(PhO)_3P$. An NMR sample of **2a** (20 mg, 0.05 mmol), $(PhO)_3P$ (14 mg, 0.05 mmol), and 0.5 mL of benzene was sealed. The ^{29}Si NMR spectrum showed only δ +54.8 (**2a**) initially which completely rearranged to **4a**, δ +13.2, with no evidence of epoxide formation.

Acknowledgment. This work was supported by the National Science Foundation and Dow Corning Corporation. We thank Dr. Howard Yokelson for assistance with synthesis and NMR spectroscopy.

Registry No. **1a**, 88526-23-2; **1b**, 80785-72-4; **1c**, 80593-68-6; **1d**, 110698-82-3; **1e**, 102780-91-6; **1f**, 108693-63-6; **1g**, 102780-92-7; **1h**, 122899-18-7; **2a**, 95206-58-9; $^{18}O_2$-**2a**, 141396-69-2; **2b**, 80785-74-6; **2c**, 141396-70-5; **2d**, 141396-71-6; **2e**, 141396-72-7; **2f**, 141396-73-8; **2g**, 141396-74-9; **2h**, 122923-85-7; **3a**, 95206-57-8; **3b**, 110698-83-4; **3c**, 110698-84-5; **3d**, 110698-85-6; **4a**, 89486-30-6; **4b**, 84537-22-4; **4c**, 108693-67-0; **4d**, 141396-75-0; **4e**, 108693-65-8; **4f**, 108693-66-9; **4h**, 122899-16-5; **7**, 141396-76-1; **10**, 141396-77-2; DMSO, 67-68-5; Ph_2S, 139-66-2; Ph_3P, 603-35-0; $(MeO)_3P$, 121-45-9; $(PhO)_3P$, 101-02-0.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates, isotopic displacement coefficients and occupancies, bond lengths, bond angles, H-atom coordinates, and isotropic displacement coefficients and occupancies (9 pages); listing of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.