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Kinetics of Thermal Cis–Trans Isomerizations in Disilenes

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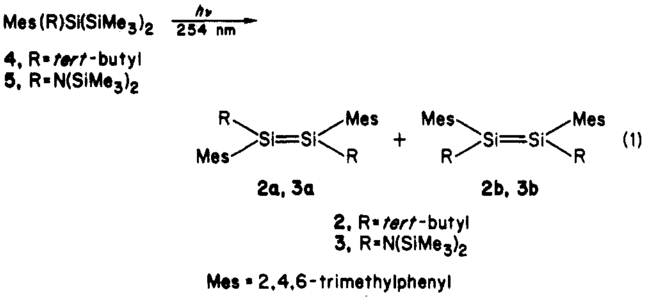
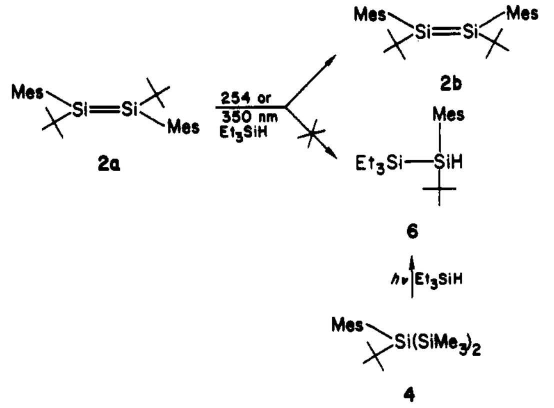
The synthesis of cis and trans isomers of 1,2-bis[(trimethylsilyl)amino]-1,2-dimesityldisilene, **3**, is reported. The trans isomer of this compound, **3a**, and *trans*-1,2-di-*tert*-butyl-1,2-dimesityldisilene, **2a**, both undergo photochemical isomerizations when irradiated at 254 or 350 nm giving mixtures enriched in the cis isomers **2b** and **3b**. These mixtures revert to equilibrium mixtures of trans and cis disilenes which at 25 °C in benzene are **2a**:**2b** = 98:2 and **3a**:**3b** = 94:6. Activation energies for thermal cis–trans isomerization in kcal mol^{-1} are 31.3 ± 3.7 for **2** and 25.4 ± 2.2 for **3**.

Disilenes, compounds which contain a silicon–silicon double bond, have been suggested for some time as intermediates formed in the pyrolysis or photolysis of certain organosilane precursors.[1] Following the synthesis in 1981 of tetramesityldisilene (**1**), the first stable disilene, considerable work has been done in the field of disilene chemistry.[2] X-ray crystallographic and NMR studies have verified the presence of a silicon–silicon double bond,[3] and disilene **1** has been shown to undergo a variety of reactions with organic substrates.[4]

Recently we have synthesized disilenes **2** and **3** by the route shown in eq 1.[5] Photolysis of 2-*tert*-butyl-2-mesitylhexamethyltrisilane (**4**) at −80 °C in pentane led to precipitation of disilene **2** as a pale yellow powder consisting of a 98:2 mixture of the trans isomer **2a** and the cis isomer **2b**.[3c] Pure **2a** was obtained by low temperature recrystallization from pentane. Similar photolysis of 2-mesityl-2-[bis(trimethylsilyl)amino]hexamethyltrisilane (**5**) at −60 °C provided a deep red solution of disilene **3**. Evaporation of the pentane and recrystallization at low temperature produced a mixture of trans (**3a**) and cis (**3b**) isomers in the ratio **3a**:**3b** = 3:97.[5] The preferential production of the less stable isomer **3b** is due to photolytic trans–cis isomerization which occurs at −60 °C while both isomers are in solution. Indeed photolysis of a 94:6 mixture of **3a**:**3b** at 25 °C in cyclohexane at 254 nm converts **3a** to **3b** producing a photostationary mixture of **3a**:**3b** = 14:86. Similar behavior is seen with **2a** which is converted to a photostationary mixture, **2a**:**2b** = 43:57, upon irradiation at 254 nm at 25 °C. No production of the corresponding 1,2-dihydrodisilanes was observed.[6]



A possible pathway for isomerization of disilenes would be through dissociation into silylenes followed by recombination. However, irradiation of pure **2a** in the presence of triethylsilane[7] at −60 °C produces only the usual trans–cis isomerization and none of the silylene trapping product **6**. Triethylsilane (Et_3SiH) is an efficient trap for silylenes; when trisilane **4** is irradiated either at 25 or −60 °C in the presence of Et_3SiH, the expected trapping product **6** is produced in high yield. Similar results are obtained with tetramesityldisilene, **1**. In pentane with Et_3SiH at 25 °C, **1** produces none of the products expected from dimesitylsilylene after 4 h exposure to 254-nm light in a Rayonet reactor. Only a small amount (<10%) of $Et_3Si-Si(Mes)_2H$ is seen after 7 h of irradiation with excess Et_3SiH at 25 °C.



The electronic absorption spectra of **2** and **3** have been previously reported[5] and show strong bands in the 350-nm region for both compounds. Irradiation of **2** and **3** with 350-nm light also induces trans–cis isomerization. Irradiation in benzene solution in a Rayonet reactor for 1.5 h at 25 °C produces photostationary mixtures, trans:cis 63:37 for **2** and 33:67 for **3**. Photodecomposition of **2** takes

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(1) (a) Peddle, G. J. D.; Roark, D. N.; Good, A. M.; McGenchin, S. G. *J. Am. Chem. Soc.* **1969**, *91*, 2807. (b) Roark, D. N.; Peddle, G. J. D. *Ibid.* **1972**, *94*, 5837. (c) Sakurai, H.; Nakadaira, Y.; Kobayashi, T. *Ibid.* **1979**, *101*, 487.

(2) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. (b) Masamune, S.; Hanazawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem.* Soc. **1982**, *104*, 1150. (c) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781. (d) Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 7776. (e) West, R. *Pure Appl. Chem.* **1984**, *56*, 163. (f) Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4992.

(3) (a) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1010. (b) Masamune, S.; Murakami, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Organometallics* **1984**, *3*, 333. (c) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Ibid.* **1984**, *3*, 793. (d) Zilm, K. W.; Fink, M. J.; Grant, D. M.; Michl, J.; West, R. *Ibid.* **1983**, *2*, 193.

(4) Fink, M. J.; De Young, D. J., West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

(5) Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 821.

(6) The 1,2-dihydrodisilanes seen in the preparation of 1 and 2 at 0 °C and above[4] are not observed when either pure 1 or 2 is irradiated at 25 °C. The dihydrodisilanes are now believed to arise by other routes than overphotolysis of disilenes.

(7) Skell, P. S.; Goldstein, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 1442. Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325. Steele, K. P.; Tzeng, D.; Weber, W. P. *Ibid.* **1982**, *231*, 291 and references therein.

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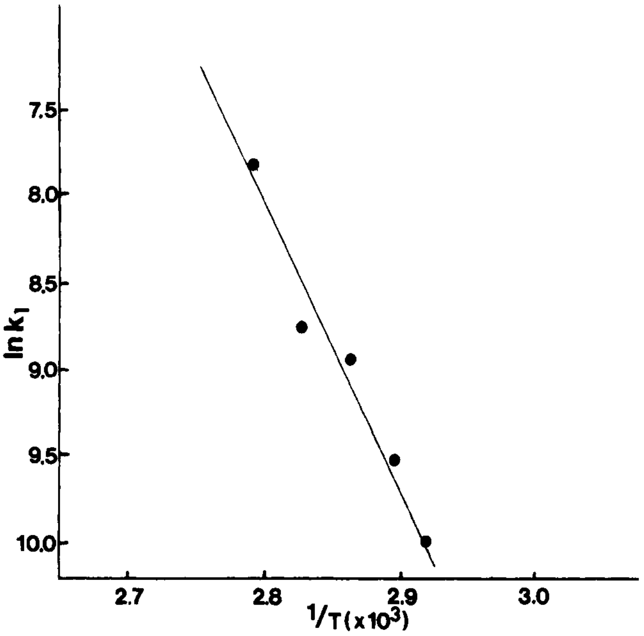
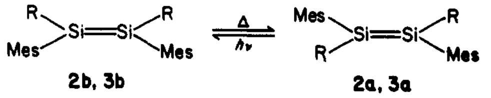


Figure 1. Arrhenius activation energy plot for the thermal isomerization of 2.

place upon prolonged exposure to 350-nm radiation; no such decomposition is seen with 3 even after 12-h irradiation. Photolysis of **2a** in the presence of Et_3SiH at 350 nm again produces only trans–cis isomerization, and no 6. Thus it seems that the excited states reached with 254- and 350-nm light involve mostly silicon–silicon bond rotation and not reversion to silylenes.[8]

Thermal Isomerizations. Disilenes 2 and 3 both undergo thermal transformation to the equilibrium isomeric mixtures by rotation about the silicon–silicon bond.[5,9] The equilibrium trans:cis ratios at 25 °C in C_6D_6 are 98:2 for 2 and 94:6 for 3. Equilibrium constants were nearly constant over the range 69.5–80.5 °C for 2 and 42.5–65.8 °C for 3, from which it follows that entropy differences between cis and trans isomers are small.



At 25 °C the half-lives for isomerization are 3220 ± 200 h[10] for 2 and 42 ± 2 h for 3. The kinetics of this facile cis–trans isomerization were studied by using variable-temperature NMR. The cis–trans interconversion is a first-order process which follows the rate expression shown in eq 2, where the starting concentrations, $[\text{cis}]_0$ and $[\text{trans}]_0$, are nonzero and K is the equilibrium constant, $[\text{trans}]_\infty/[\text{cis}]_\infty$.[11] Rate constants k_1 and k_{-1} (eq 3) are for the forward and back isomerizations respectively. Values of k_1 and k_{-1} were calculated at different temperatures (Tables I and II) and the Arrhenius activation energy, E_a, was obtained from the plots shown in Figures 1 and 2. The activation energies for cis to trans conversion in kilocalories per mole are 31.3 ± 3.7 for 2 and 25.4 ± 2.2 for 3; for the reverse process, trans to cis, E_a is 34.0 ± 3.7 for 2 and 27.2 ± 2.2 for 3.[12]

$$\ln \frac{K[\text{cis}]_t - [\text{trans}]_t}{K[\text{cis}]_0 - [\text{trans}]_0} = -(k_1 + k_{-1})t \qquad (2)$$

$$\text{cis} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{trans} \qquad (3)$$

Table I. Rate Constants, Temperatures, and Free Energies of Activation for the Cis to Trans Isomerization of 2

T, °C	k_1, s^{-1}	k_{-1}, s^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}	ΔG_0, kcal mol^{-1}
69.5[a]	4.6×10^{-5}	8.3×10^{-7}	27.0 ± 0.6	−2.7 ± 0 1
72.0[a]	7.3×10^{-5}	1.3×10^{-6}	26.8 ± 0.6	−2.8 ± 0.1
76.0[a]	1.3×10^{-4}	2.4×10^{-6}	26.8 ± 0.6	−2.8 ± 0.1
80.5[a]	1.6×10^{-4}	2.9×10^{-6}	27.0 ± 0.6	−2.8 ± 0.1
85.0[a]	4.0×10^{-4}	7.3×10^{-6}	26.7 ± 0.6	−2.8 ± 0.1
71.5[b]	1.1×10^{-4}	4.6×10^{-6}	26.5 ± 0.6	−2.2 ± 0.1

[a] In C_6D_6. [b] In THF-d_8.

Table II. Rate Constants, Temperatures, and Free Energies of Activation for Cis–Trans Isomerization of 3 in C_6D_6

T, °C	k_1, s^{-1}	k_{-1}, s^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}	ΔG_0, kcal mol^{-1}
42.5[a]	4.7×10^{-5}	2.7×10^{-6}	24.8 ± 0.6	−1.8 ± 0.1
44.5[a]	6.2×10^{-5}	3.6×10^{-6}	24.8 ± 0.6	−1.8 ± 0.1
47.2[a]	7.4×10^{-5}	4.3×10^{-6}	24.9 ± 0.6	−1.8 ± 0.1
49.5[a]	1.4×10^{-4}	8.1×10^{-6}	24.6 ± 0.6	−1.8 ± 0.1
53.0[a]	1.9×10^{-4}	1.1×10^{-5}	24.7 ± 0.6	−1.8 ± 0.1
65.8[a]	7.3×10^{-4}	4.2×10^{-5}	24.8 ± 0.6	−1.9 ± 0.1
45.0[b]	1.1×10^{-4}	4.5×10^{-6}	24.4 ± 0.6	−2.0 ± 0.1

[a] In C_6D_6. [b] In THF-d_8.

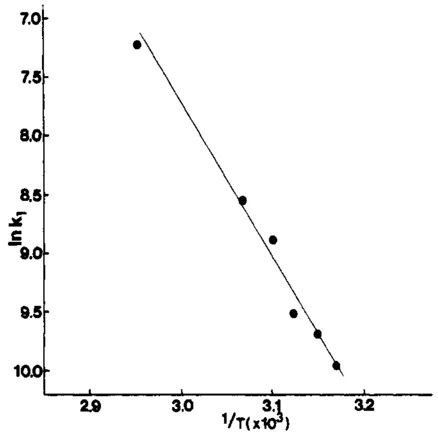


Figure 2. Arrhenius activation energy plot for the thermal isomerization of 3.

Discussion

The strength of the silicon–silicon π bond in the parent molecule disilene, $H_2Si{=}SiH_2$, has been the subject of several calculations.[13] An early report estimated a value of 20 kcal mol^{-1};[13a] more recent ab initio MO calculations predict energies of 25[13f] and 30[13c] kcal mol^{-1} for the π bond strength. Our energies of activation are in good agreement with these calculations. This is in accordance with the

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(8) Other workers have irradiated the closely related compound tetrakis(2,6-dimethylphenyl)disilene at 254 nm in the presence of 2,3-dimethylbutadiene and isolated a silacyclopentene product; this was interpreted as indicating that the major photochemical pathway at 254 nm was reversion of the disilene to silylene, the silylene then being trapped by the diene.[2d] However, from our results it seems unlikely that the silylene is formed in this reaction, unless the two disilenes behave in totally different ways upon photolysis.

(9) An independent study of the thermal isomerization of 2 has recently been reported: Murakami, S.; Collins, S.; Masamune, S. *Tetrahedron Lett.* **1984**, 2131.

(10) Our earlier values of 570 ± 5 h[5] was in error.

(11) Drenth, W.; Swart, H. "Kinetics Applied to Organic Reactions"; Marcel Dekker: New York, 1980; p 17.

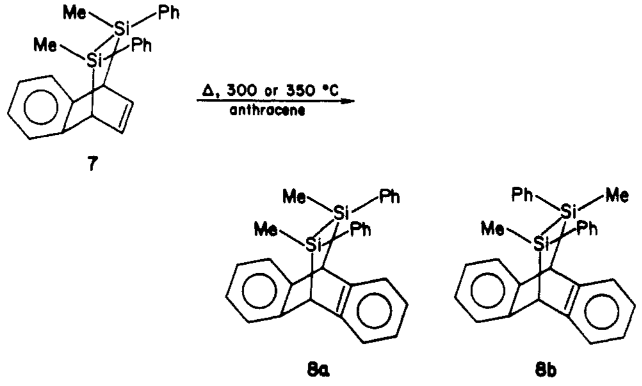
limited ability of silyl radical centers to conjugate with an attached π system in the 90° rotated state. Although disilenes evidently have a strong π-bonding component,[3c,d] it is distinctly weaker than the C=C π bond in alkenes. For example the E_a values for interconversion of 1,2-dideuterioethylene and stilbene are 65[14] and 42.8 kcal mol^{-1},[15] respectively. With increasing steric bulk of substituted groups on the olefin, the activation energy usually decreases.[16]

Lowering of the rotation barier with increased steric bulk may be in part responsible for the difference of 5.5 kcal mol^{-1} in the activation energies for isomerization of **2** and **3**. However, it is likely that electronic effects of the nitrogen substituents also play a part. Interactions of nitrogen lone pairs with the silicon π system either could weaken the Si–Si π bond in **3** or could decrease the energy of the (~90° rotated) transition state.[17] The electronic spectra of **2b** and **3b** provide an indication that N–Si interaction takes place. The absorption bands for **3b** (361, 468 nm) are lower in energy than the corresponding bands for **2b** (~332, 385 nm).[5]

The presence of a low-lying triplet state might also lower rotation barriers. Triplet involvement will lower not only E_a but also the transmission coefficient, k, in the Eyring equation[16] resulting in abnormally low log A values, where A is the preexponential term in the Arrhenius equation. We find A values of $10^{15.7}$ s^{-1} for **2** and $10^{13.2}$ s^{-1} for **3**, compared to "normal" preexponential factors, log A = 12–13,[16] supporting the conclusion that the triplet state is not involved.

As shown in Tables I and II, the free energy of activation for cis to trans conversion for **2** and **3**, $\Delta G^\ddagger$, 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_1h/k_BT vs. $1/T$. For **2**, $\Delta H^\ddagger = 30.6 \pm 3.7$ kcal mol^{-1} and $\Delta S^\ddagger = {}^+11 \pm 3$ cal K^{-1} mol^{-1},[18] and for **3** $\Delta H^\ddagger = 24.7 \pm 2.2$ kcal mol^{-1} and $\Delta S^\ddagger = -0.3 \pm 0.1$ cal K^{-1} mol^{-1}.[12] The small negative entropy seen with **3** along with the lack of solvent effect on $\Delta G^\ddagger$ suggests that the transition state is as polar as the ground state. Therefore the lower barrier of **3** vs. **2** is not due to a greater ionic character in the transition state of the type observed for "push–pull" substituted ethylenes.[19]

One earlier report may bear on the question of cis–trans isomerization in disilenes.[1c] When cis disilabicyclooctadiene **7** is pyrolyzed at 300 °C in the presence of anthracene, the disilene moiety is transferred to give the cis and trans products, **8a** and **8b**, in a 94:6 ratio. Similar pyrolysis at 350 °C decreased the ratio to 90:10. These results were interpreted in terms of intermediacy of the free disilene, which maintained its configuration until trapped by anthracene.



The proposed disilene in this pyrolysis is very different from **2** or **3**. Nevertheless it is interesting to calculate the expected lifetimes of our disilenes at these temperatures using the Arrhenius equation and the activation energy values for **2**. We estimate k_1 to be 5.3×10^3 s^{-1} at 300 °C and 4.8×10^4 s^{-1} at 350 °C; the corresponding half-lives are 1.3×10^{-4} and 1.4×10^{-5} s, respectively. If the kinetics of isomerization of 1,2-diphenyl-1,2-dimethyldisilene were similar to those of **2**, it could maintain stereochemistry only if the rates of reaction with anthracene were rapid compared to these isomerization rates. Such high rates of trapping are conceivable under the conditions of the experiments, which were sealed-tube pyrolyses.

Note Added in Proof. An estimate of the π bond energy of 1,2-diphenyl-1,2-dimethyldisilene, based on the pyrolysis data for **7**, has recently appeared;[19b] the value of ≥ 26 kcal mol^{-1} is close to our values for the more hindered disilenes.

Experimental Section

Proton NMR spectra were recorded on a Bruker WP-270 FT spectrometer equipped with a heated probe. ^{29}Si spectra were recorded on a JEOL FX-200 FT spectrometer. All reactions and manipulations were carried out under a dry atmosphere of nitrogen or argon, and all solvents were dried and distilled prior to use. MesSiCl$_3$ and disilene **2a** were synthesized by methods previously reported.[3c]

Photolyses were carried in a Rayonet Model RPR-100 photoreactor equipped with either 254- or 350-nm lamps. Low temperatures were maintained by the use of a cooling system previously described.[3c]

Mes[(Me$_3$Si)$_2$N]SiCl$_2$. Hexamethyldisilazane (1.9 g, 0.012 mol) in 10 mL of THF at 0 °C was converted to LiN(SiMe$_3$)$_2$ by addition of *n*-butyllithium (7.48 mL, 1.56 M in hexane, 0.012 mol). After the mixture was stirred overnight, the lithium reagent was added to 3.10 g (0.012 mol) of MesSiCl$_3$ in 10 mL of refluxing THF. The mixture turned cloudy during the addition and was refluxed overnight. After the solution was cooled 20 mL of hexane was added, and the solution was filtered under nitrogen and concentrated in vacuo, yielding 2.98 g (96%) of the dichloride as a viscous yellow oil: ^{1}H NMR (CDCl$_3$) δ 0.32 (s, 18 H), 2.28 (s, 3 H), 2.66 (s, 6 H), 6.85 (s, 2 H). The product was not purified and

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(12) Errors of (cis)$_t$, (trans)$_t$, and K were calculated by assuming a 5% error in NMR integration. The errors in k_1 and E_a were obtained by the use of the expression error (slope) = $[m/m\sum x_i^2 - (\sum x_i^2)]^{1/2}$[error ($y$)] where m is the number of data points in the least-squares analysis. The error in k_1 was determined to be ±10% for all values. See also: Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. L. "Experiments in Physical Chemistry"; McGraw-Hill: New York, 1974; pp 55–57.

(13) (a) Curtis, M. D. *J. Organomet. Chem.* **1973**, *60*, 63. (b) Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1311. (c) Daudel, R.; Kari, R. E.; Poirier, R. A.; Goddard, J. D.; Csizmadia, J. G. *J. Mol. Struct.* **1978**, *50*, 115. (d) Roelandt, R. F.; Van De Vondel, D. F.; Van Der Kelen, G. P. *J. Organomet. Chem.* **1979**, *165*, 151. (e) Snyder, L. C.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1979**, *101*, 5222. (f) Poirier, R. A.; Goddard, J. D. *Chem. Phys. Lett.* **1981**, *80*, 37. (g) Lischka, H.; Köhler, H. J. *Chem. Phys. Lett.* **1982**, *85*, 467. (h) Köhler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5884. (i) Lischka, H.; Köhler, H.-J. *Chem. Phys. Lett.* **1982**, *85*, 467. (j) Krogh-Jesperson, K. *J. Chem. Phys.* **1982**, *86*, 1492.

(14) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, 23, 315.

(15) Kistiakowsky, G. B.; Smith, W. R. *J. Am. Chem. Soc.* **1934**, *56*, 638; **1936**, *58*, 766.

(16) Kalinowski, H.-O.; Kessler, H. *Top. Stereochem.*, Allinger, N. L.; Eliel, E. L., Eds. Wiley: New York, **1973**, *7*, 300–308.

(17) Sandström, J. *Top. Stereochem.* **1983**, *14*, 138.

(18) A recent study[9] of the thermal isomerization of **2** reported values of $\Delta H^\ddagger = 23.4 \pm 0.9$ kcal mol^{-1} and $\Delta S^\ddagger = -9.4 \pm 2.7$ cal mol^{-1} K^{-1}, which disagree with our results. We find one of the two k_1's reported [k_1(60.3 °C) = 3.03×10^{-5} s^{-1}] falls far from the least-squares line of Figure 1 while the other value [k_1(79.3 °C) = 2.18×10^{-4} s^{-1}] lies near our line. Thus calculation of $\Delta H^\ddagger$ with these two points will lead to a lower value. We cannot account for the discrepancy seen in k_1(60.3 °C).

(19) (a) Reference 17, p 156. (b) Olbrich, G.; Potzinger, P.; Reimann, B.; Walsh, R. *Organometallics* **1984**, *3*, 1267.

was used immediately in the next step.

2-Mesityl-2-[bis(trimethylsilyl)amino]hexamethyltrisilane, 5. A mixture containing 3.0 mL (0.023 mol) of Me_3SiCl and 0.76 g (0.031 mol) of Mg turnings in 7.0 mL (0.040 mol) of dry hexamethylphosphoramide (HMPA) was heated to 90 °C. To this mixture was added the $Mes[(Me_3Si)_2N]SiCl_2$ made in the preparation reported above along with 3.0 mL (0.023 mol) of Me_3SiCl, producing a brown color. After 16 h the solution was cooled and transferred to a N_2 purged separatory funnel and extracted with two 5-mL portions of hexane. Only one product was seen by GLC. The organic layer was concentrated in vacuo, and the residue was recrystallized from hexane, yielding 2.8 g (65%) of trisilane 5 as a slightly water-sensitive white solid: ^1H NMR ($CDCl_3$) δ -0.02 (s, 9 H), 0.18 (s, 18 H), 0.28 (s, 9 H), 2.22 (s, 3 H), 2.42 (s, 6 H), 6.70 (s, 2 H); ^{29}Si NMR ($CDCl_3$) δ +5.81 (Me_3SiN), +3.64 (Me_3SiN), −15.91 (Me_3Si-*Si*), −19.20 (Me_3*Si*-Si); MS (70 eV), *m/e* 453 (M^+), 438 (M^+ - CH_3); exact mass for $C_{21}H_{47}NSi_5$ calcd *m/e* 453.2542, found *m/e* 453.2556. Anal. Calcd for $C_{21}H_{47}NSi_5$: N, 3.08; Si, 30.92. Found: N, 2.89; Si, 29.62.

1,2-Dimesityl-1,2-bis[bis(trimethylsilyl)amino]disilene, 3. A solution of 0.5 g (0.011 mol) of 5 in 15 mL of pentane was photolyzed in a quartz photolysis tube equipped with a recrystallization chamber attached as a side arm.[3c] The solution immediately turned dark orange-red, but no precipitation of disilene occurred during the photolysis. The reaction was monitored by GLC on samples removed and exposed to air. Disappearance of 5 was accompanied by the growth of a peak due to the 1,3-cyclodisiloxane, the sole oxidation product of 3. After 15 h the reaction was complete by GLC, and pentane and $(Me_3Si)_2$ were removed under vacuum. Fresh degassed pentane was vacuum transferred in to dissolve crude 3, and the solution was then transferred through a frit into the side arm where 3 was recrystallized at −78 °C. After filtration and drying pure 3 (~100 mg, 30%) was obtained as a 97:3 cis/trans mixture. **3a**: ^1H NMR (C_6D_6) δ 0.20 (s, 36 H), 2.10 (s, 6 H), 2.80–3.05 (br, 12 H), 6.90–6.95 (br, 4 H); ^{29}Si NMR (C_6D_6) δ +61.9 (sp^2Si), +6.8 (Me_3Si); UV–vis (C_6H_6) λ_{max} 351 (ϵ 5230), 8483 nm (ϵ 5510). **3b**: ^1H NMR (C_6D_6) δ 0.39 (s, 36 H), 1.91 (s, 6 H), 2.58 (s, 12 H), 6.62 (s, 4 H); ^{29}Si NMR (C_6D_6) δ +49.4 (sp^2Si), +6.2 (Me_3Si); UV–vis (C_6H_6) λ_{max} 372 (ϵ 8170), 468 nm (ϵ 3440); MS (**3b**) *m/e* 614 (M^+, 21%), 599 (M^+ – CH_3, 0.7%), 526 (M^+ – $(CH_3)_4Si$, 1.2%); exact mass for $C_{30}H_{58}N_2Si_6$ calcd *m/e* 614.3200, found *m/e* 614.3214.

Photolytic Trans–Cis Interconversion. Sealed NMR samples of 2 and 3 were made up by using either C_6D_6 or THF-d_8 (350 nm) or C_6D_{12} (254 nm) as the solvent. A quartz tube was used instead of Pyrex when irradiation was carried out at 254 nm. The NMR tube was suspended in a Rayonet photoreactor and photolyzed at 25 °C. NMR spectra were taken approximately every 10–20 min until the photostationary state was reached; usually 1–2 h was necessary for equilibration. Care must be taken with 2 since photodecomposition will occur upon overirradiation.

After photolysis, the samples for kinetic measurements were immediately frozen and used as described below.

Kinetic Measurements. Measurements were performed on a Bruker WP-270 NMR spectrometer equipped with a heated probe. The temperature (±0.1 °C) inside the probe was calibrated by measuring the difference (in hertz) between the chemical shifts of the CH_2 and OH protons in a neat sample of ethylene glycol.[20] When the chemical shift difference was constant for at least 15 min, the ethylene glycol sample was removed. The disilene sample was then inserted and allowed to equilibrate for 15 min. Proton spectra were taken approximately every 5 min until the sample contained mostly the trans isomer. The percentage concentrations of cis and trans at various times were obtained by using the integration of the *tert*-butyl, ortho-methyl, and Me_3Si resonances. Rate constants were calculated from the expression given in eq 2 by the use of a least-squares analysis. Errors were calculated by using standard methods and are at the 95% confidence limits.[12]

Photolysis of 1 with Et_3SiH. A solution containing 0.150 mL (9.4×10^{-4} mol) of Et_3SiH in 3.0 mL of pentane was degassed to remove traces of oxygen and added to 15 mg (2.8×10^{-5} mol) of 1 under Ar. Photolysis of the yellow solution at 254 nm in the Rayonet for 3.5 h produced no disappearance of the color. The irradiation was stopped and exposure to air quickly decolorized the solution. The solvent and Et_3SiH were removed in vacuo, yielding an off-white solid. ^1H NMR analysis ($CDCl_3$) showed only tetramesitylcyclodisiloxane, the oxidation product of 1 (78%) plus other products (22%) presumably associated with overphotolysis of 1. No $Et_3Si–Si(Mes)_2H$ was seen.

The above experiment was repeated by using 10 mg (1.9×10^{-5} mol) of 1 and 0.3 mL (1.9×10^{-3} mol) of Et_3SiH in 3.8 ml of pentane. Irradiation for 7 h at 25 °C, followed by air quenching of the products showed a decrease in the cyclodisiloxane yield (39%) accompanied by an increase in the over-photolysis products (50%) plus a small amount of $Et_3Si–Si(Mes)_2H$ (10%) identified by comparison to an authentic sample.

Photolysis of 2a with Et_3SiH. A solution consising of 0.30 mL (1.9×10^{-3} mol) of Et_3SiH in 5.0 mL of pentane was degassed and placed under Ar. This was added to 20 mg (4.9×10^{-5} mol) of **2a** under Ar, and the resulting yellow solution was cooled to −60 °C and photolyzed at 254 nm. After 4-h irradiation, the yellow mixture was quenched by exposure to air, and the pentane and Et_3SiH were removed in vacuo, yielding an off-white oil. ^1H NMR analysis (C_6D_6) showed products corresponding to oxidation of **2a** (71%) and **2b** (29%). No trace of trapped product 6 was seen by comparison with an authentic sample. Similar results were obtained when irradiation was carried out at 350 nm.

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Registry No. 1, 80785-72-4; **2a**, 88526-23-2; **2b**, 88526-24-3; **3a**, 88526-25-4; **3b**, 88526-26-5; 4, 88526-27-6; 5, 88526-28-7; 6, 89486-29-3; Et_3SiH, 617-86-7; $Et_3Si–Si(Mes)_2H$, 88957-30-6; $Mes[(Me_3Si)_2N]SiCl_2$, 95217-07-5; $LiN(SiMe_3)_2$, 4039-32-1; $MesSiCl_3$, 17902-75-9; Me_3SiCl, 75-77-4; tetramesitylcyclodisiloxane, 84537-22-4.

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