

of the surface in A resulting in Hammond movement toward the top of the figure and anti-Hammond movement toward the neutral sulfurane intermediate.⁸ Of these, the Hammond movement will dominate since the reaction coordinate has a larger vertical component.⁸ The resultant will be net movement toward the protonated sulfurane intermediate. This will lead to an increase in the Brønsted α value with a decrease in the pK_a of the leaving group. This prediction is consistent with the change in Brønsted α shown in Figure 3. In Figure 4B, lowering the pK_a of the leaving group will have the largest effect on the upper-left and lower-right corners of the diagram.⁸ The transition-state motion will be away from the dicationic sulfilimine and toward the nitrogen anion. The net resultant will be anti-Hammond movement toward the lower right with a decrease in the Brønsted α as the pK_a of the leaving group decreases. This prediction is contrary to the observed fact.

The second parameter to examine on the surfaces in Figure 4 is the effect of lowering the pK_a of the catalyzing acid. In A, this will result in the raising of the energy of the bottom edge. Coupled movements parallel and perpendicular to the reaction coordinate are predicted with parallel movement again dominating. The resultant is movement toward starting materials with a decrease in both β_{lg} and β_{nuc} as the acid strength is increased. Both of these are consistent with the observed data. In Figure 4B, the effect of acid strength will be greatest on the ionic intermediates in the upper-left and lower-right corners. This is because high-energy intermediates tend to dominate changes in potential energy surfaces for S_N2 reactions.¹⁴ This phenomena is most often observed as the dominant anti-Hammond movement in S_N2 and E2 reactions involving benzyl carbons.¹⁵ The effect of the anti-Hammond movement in B is to move the transition state toward the dicationic intermediate with a resulting increase in β_{lg} coupled to a decrease in β_{nuc} . The predicted increase in the leaving group effect is inconsistent with the observed facts.

The coupled structure-reactivity data given above are consistent with a reaction coordinate oriented largely across the front face

of the cube in the scheme. The overall reaction, however, cannot be stepwise with the protonated sulfurane as a distinct intermediate since the pK_a of this sulfurane is estimated to be about 2 ± 1 .¹⁶ With acetic acid as the general acid the pK_a change for the formation of the sulfurane intermediate is unfavorable, hence concerted catalysis of sulfurane formation by acetate is not expected.¹⁷ The first "intermediate", therefore, must be the final product, and the overall reaction is, indeed, an example of a general catalyzed S_N2 reaction. The dashed line in the scheme represents a suggested reaction coordinate, proceeding largely in the face of the cube, "missing" the intermediate, and then proceeding toward products. This somewhat circuitous route allows a minimum of coupled motions in the rate-limiting transition state, probably allowing the fully concerted transition state to be observed. There are other reports of general catalyzed S_N2 reactions¹⁸ although they seem to be most often associated with ring-closure reactions, and the Brønsted α values usually reflect a fairly early transition state. In his original study of the thiol reduction of dehydromethionine, the concerted reaction was favored by Lambeth,¹ although insufficient data were available to distinguish the stepwise and concerted reactions. The ability of sulfonium compounds to expand their valence states and exist as sulfuranes no doubt contributes to the relative ease of the concerted reaction, and the sulfonium oxidation state would seem to be a useful system for investigating transitions from stepwise to concerted addition reactions.

Acknowledgment. This work was supported by a grant from the National Science Foundation, CHE 80-00054.

Registry No. I-Cl⁻, 35357-68-7; II-Cl⁻, 97732-00-8; H₂PO₄, 14066-20-7; CH₃CO₂H, 64-19-7; HCO₂H, 64-18-6; ClCH₂CO₂H, 79-11-8; Cl₂CHCO₂H, 79-43-6; F₂CHCO₂H, 381-73-7; F₃CCO₂H, 76-05-1; codylic acid, 75-60-5; 3-nitro-5-mercaptobenzoic acid, 97732-46-2; 3-mercaptobenzoic acid, 4869-59-4.

(16) The pK_a s for N-protonation of sulfilimines and sulfuranes derived from them are estimated to be about 16 and 7 units, respectively, below the pK_a of the parent amine. See ref 3a.

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(18) Cromartie, T. H.; Swain, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 232-237. Knipe, J. O.; Vasquez, P. J.; Coward, J. K. *Ibid.* **1982**, *104*, 3202-3209 and references cited therein. Thibblin, A.; Jencks, W. P. *Ibid.* **1979**, *101*, 4963-4973.

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Experimental Search for the Silanone-to-Silylene Rearrangement

Thomas J. Barton* and Gregory P. Hussmann

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011.
 Received July 11, 1985

Abstract: Pyrolysis of 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(trimethylsilyl)cyclotetrasiloxane in the presence of 1,3-butadiene affords the silacyclopentene product from trapping of silylene, Me₃SiOSiMe. Although this result is consistent with isomerization reactions since 1952 when Adrianov² proposed their involvement in the thermal redistribution of poly(dimethylsiloxanes). Most evidence for the reverse reaction, isomerization of Me₃SiOSiMe to the silanone, could be found, although this silylene apparently decomposes to silanones.

Silanones, the silicon analogues of ketones, have frequently been postulated¹ as transient intermediates in a variety of organosilicon reactions since 1952 when Adrianov² proposed their involvement in the thermal redistribution of poly(dimethylsiloxanes). Most

recently, the silicon-oxygen double bond has been subjected to the scrutiny of theoretical studies³ which reveal moderate thermodynamic stability, with the C=O bond of formaldehyde being 20 kcal/mol stronger than the Si=O bond of H₂Si=O.⁴ How-

(1) For a general review of π -bonding silicon, see: Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

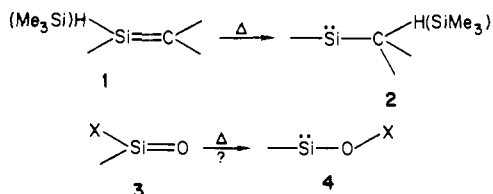
(2) Adrianov, K. A.; Sokolov, N. N. *Dokl. Akad. Nauk SSSR* **1952**, *82*, 909.

(3) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833 and references therein.

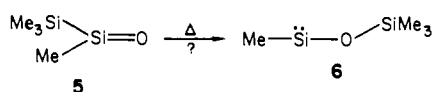
(4) Gordon, M. S.; George, C. *J. Am. Chem. Soc.* **1984**, *106*, 609. These authors report a difference of only about 10 kcal/mol.

ever, dimerization of $\text{H}_2\text{Si}=\text{O}$ has been investigated by ab initio molecular orbital calculations⁵ and found to proceed with no barrier. Thus, the only direct spectral observations have been performed by matrix isolation studies (Me_2SiO ,⁶ Cl_2SiO ,⁷ F_2SiO ,⁸ and H_2SiO ⁹).

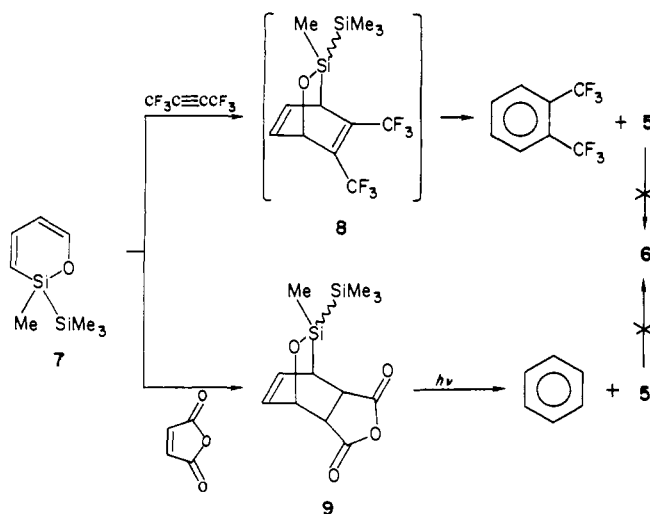
In view of the current theoretical¹⁰ and experimental¹¹ activity regarding the thermal isomerization of silenes **1** to silylenes **2**, via a 1,2-shift of either H or Me_3Si , it is of obvious interest to discover whether appropriately substituted silanones **3** would undergo an analogous rearrangement to oxysilylenes (**4**).



At the onset, we (naively) thought it not unlikely that if the migrating group were trimethylsilyl (as in silylsilanone, **5**), the formation of an additional silicon-oxygen single bond would provide sufficient driving force for the rearrangement to **6** to occur under relatively mild conditions.



Our initial efforts¹² utilized the Diels-Alder adducts of 1-methyl-1-(trimethylsilyl)sila- α -pyran (**7**) for the production of silanone **5**. While this approach proved successful for the apparent production of **5**, it was not particularly amenable to the goal of demonstration of the rearrangement to silylene **6**. Diels-Alder

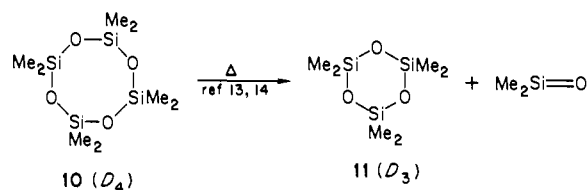


adduct **8** could never be isolated or observed, and thus it was not possible to subject it to thermal conditions likely to be required for the desired isomerization. The most severe conditions employed involved copyrolysis of **7** and excess $\text{CF}_3\text{C}\equiv\text{CCF}_3$ at ca. 460 °C in a flow system. Although apparent chemical trapping of **5** was observed, no evidence for the formation of **6** was obtained. Even though adduct **9** was isolable, thermolysis was limited to the solution phase due to lack of volatility, and photolysis of **9** could

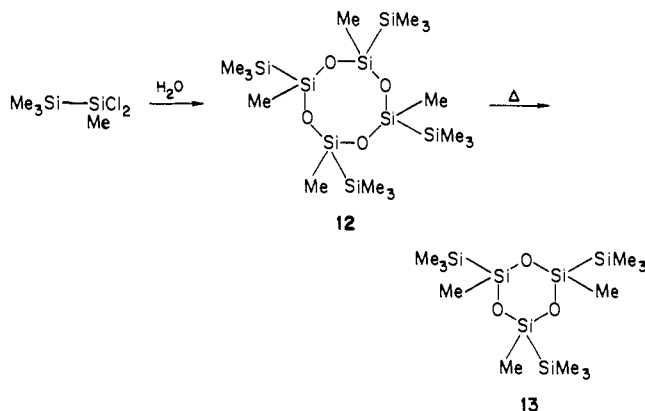
not be performed under severe thermal conditions.

Our inability to gain experimental evidence for the isomerization of silanone to silylene is in keeping with theoretical studies³ which have subsequently appeared. Indeed, Kudo and Nagase³ have calculated that the barrier for isomerization of $\text{H}_2\text{Si}=\text{O}$ to $\text{H}-\text{Si}-\text{OH}$ via 1,2-hydrogen shift is 60.8 kcal/mol even though the reaction is slightly (2.4 kcal) exothermic.

However, undaunted by this extreme theoretical barrier, we have continued to seek appropriate precursors to silanone **5** and look for its isomerization to silylene **6**. The thermal gas-phase decomposition of cyclic siloxanes appeared particularly attractive since Davidson^{13,14} had convincingly demonstrated by kinetic means that octamethylcyclotetrasiloxane (**10**) produced hexamethylcyclotrisiloxane (**11**) by way of a unimolecular extrusion of dimethylsilanone.¹⁵



Thus, 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(trimethylsilyl)cyclotetrasiloxane (**12**) was prepared in 44% yield by slow hydrolysis of 1,1-dichlorotetramethyldisilane. Pyrolysis of **12** was performed both by flash vacuum (780 °C, ca. 10^{-4} torr) and by N_2 flow (610 °C) to produce a complex product mixture from which cyclotrisiloxane **13** was identified by GCMS comparison with an authentic sample. Also identified by GCMS as major products were several isomers of **12** and **13**.



The observance of **13** was suggestive of extrusion of **5** from **12** and allowed a search for the isomerization of **5** to **6**. This was done by using butadiene as a chemical trap since it is an excellent trap for silylenes¹⁶ but has never been observed to react with silanones. A benzene solution of **12** was pyrolyzed at 610 °C by dropwise addition to a flow-pyrolysis system using butadiene as the carrier gas. Surprisingly, analysis of the pyrolysate by GCMS revealed only three major silicon-containing components: unreacted **12** (67% completion), **13** (11%), and 1-methyl-1-(trimethylsilyloxy)-1-silacyclopent-3-ene (**14**, 72% based on reacted **12**). The low yield of **13** is due to its instability under the reaction conditions. Indeed, it was found that an identical copyrolysis of **13** (610 °C, butadiene flow, 91% completion) afforded **14** in 11% yield.

The formation of silacyclopentene **14** from the copyrolysis of **12** and butadiene demands the intermediacy of methyl(tri-

(5) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.

(6) Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176.

(7) Schnöckel, H. Z. *Anorg. Allg. Chem.* **1980**, *460*, 37.

(8) Schnöckel, H. *J. Mol. Struct.* **1980**, *65*, 115.

(9) Withnall, R.; Andrews, L. *J. Am. Chem. Soc.* **1985**, *107*, 2567.

(10) Schaefer, H. F. *Acc. Chem. Res.* **1982**, *15*, 283.

(11) Conlin, R. T.; Kwak, Y.-K. *Organometallics* **1984**, *3*, 918 and references therein.

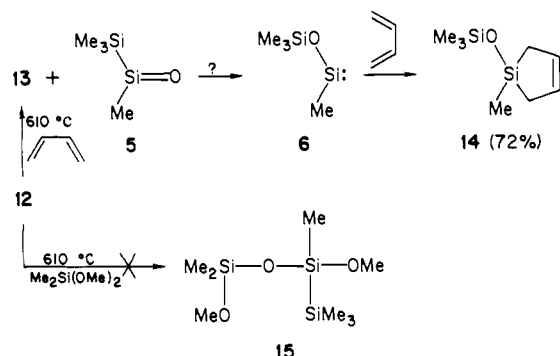
(12) Hussmann, G.; Wulff, W. D.; Barton, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1263.

(13) Davidson, I. M. T.; Thompson, J. F. *J. Chem. Soc., Chem. Commun.* **1971**, 251.

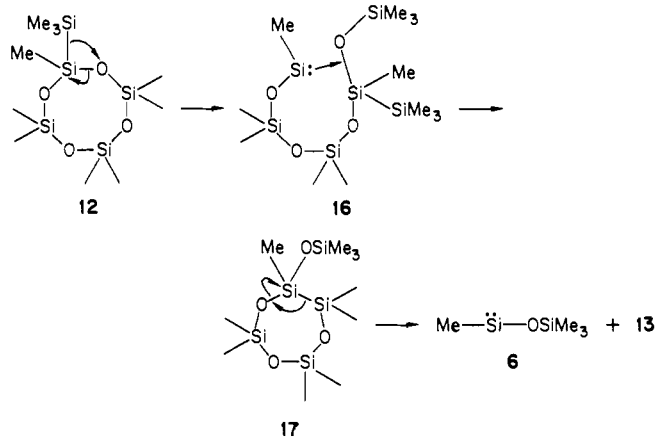
(14) Davidson, I. M. T.; Thompson, J. F. *J. Chem. Soc., Faraday Trans. 1* **1975**, 2260.

(15) This extrusion now suffers badly from the attentions of theory for it has been calculated³ that the insertion reaction $(\text{H}_2\text{SiO})_3 + \text{H}_2\text{Si}=\text{O} \rightarrow (\text{H}_2\text{SiO})_4$ is exothermic by 120.8 kcal/mol.

(16) Gaspar, P. P. In "Reactive Intermediates"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1981, Vol. 2, pp 335-387.

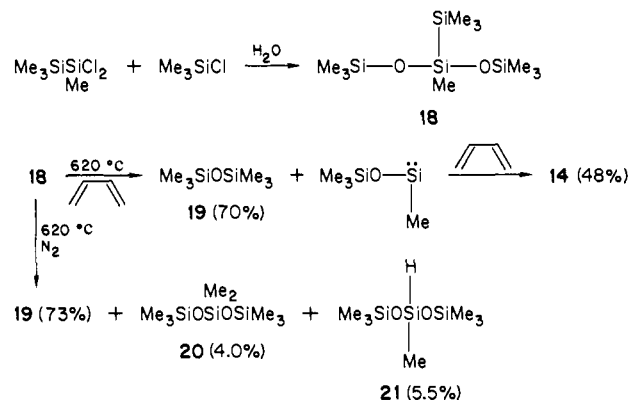


methylsiloxy)silylene (**6**). However, it does not demand that **6** arises from isomerization of silanone **5**. Indeed, pyrolysis of **12** (610 °C, N_2 flow) in the presence of excess dimethyldimethoxysilane did not produce any of the desired product of silanone insertion, disiloxane **15**. Thus, while this result could be accommodated by isomerization of **5** to **6** at a rate greater than that of the bimolecular reaction of **6** and $\text{Me}_2\text{Si}(\text{OMe})_2$, or by complete decomposition of the unobserved **15** via a reductive elimination of Me_3SiOMe , one is forced to consider alternative routes from **12** to silylene **5**. As alkoxydisilanes have long been known¹⁶ to undergo reductive elimination of alkoxy silanes to produce silylenes, the possibility that **12** isomerizes to silylene **16** is very real. Intramolecular Si–O insertion (another precedented silylene reaction¹⁷) by **16** would yield siloxane **17** which could produce silylene **6** and **13** by a second reductive elimination. The only argument against this pathway is the fact that no butadiene trapping of silylene **16** is observed.



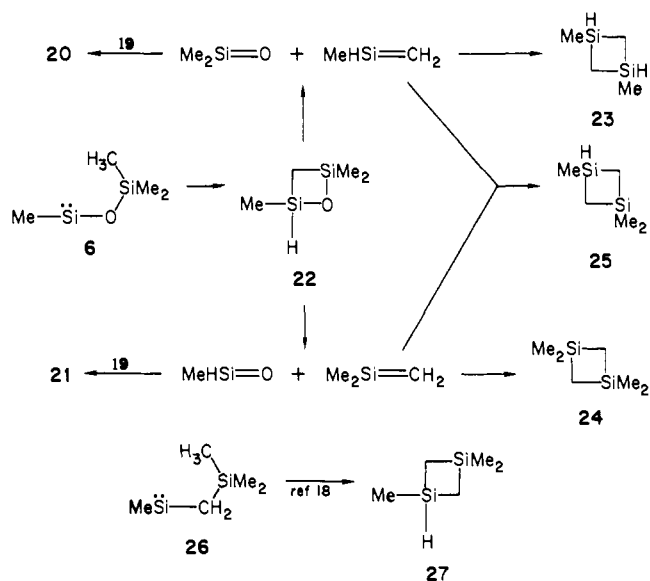
The isomerization of silylene **6** to silanone **5** by 1,2-silyl migration from oxygen to silicon was also investigated. Slow addition of water to a stirring solution of 1,1-dichlorotetramethyldisiloxane and excess chlorotrimethylsilane afforded a 31% yield of disiloxane **18**, the desired thermal precursor to **6**. Pyrolysis of **18** was carried out at 620 °C with butadiene as the carrier gas to produce hexamethyldisiloxane (**19**) (70%) and the expected product of butadiene trapping of **6**, silacyclopentene **14** (48%). In the absence of butadiene, the pyrolysis of **18** formed one major product, **19** (73%), and only small amounts of other volatile silicon-containing products. The two most abundant of the minor products could be isolated and were identified as octamethyltrisiloxane (**20**, 4.0%) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (**21**, 5.4%). The yields of **20** and **21** more than doubled to 10% and 14%, respectively, in the flash vacuum pyrolysis (850 °C, ca. 10^{-4} torr) of **18** with excess **19**. In neither pyrolysis was there any evidence for the presence of silanone **5**.

The origins of trisiloxane products **20** and **21** are of considerable interest as the most obvious route would involve insertion of silanones, $\text{Me}_2\text{Si}=\text{O}$ and $\text{MeHSi}=\text{O}$, into an Si–O bond of disiloxane **19**. These silanones can be formed from the decompo-



sition of a common precursor, disilaoxetane **22**, produced from intramolecular C–H insertion by silylene **6**. The analogous reaction of silylene **26** to form 1,3-disilacyclobutane (**27**) is known to proceed efficiently.¹⁸

Supportive evidence for the intermediacy and decomposition of disilaoxetane **22** is the GCMS identification of disilacyclobutanes **23**, **24**, and **25** among the minor products from the neat pyrolysis of **18**. These are the known dimers of the two silenes expected from the decomposition of **22**.



In summary, the first evidence for a silanone-to-silylene rearrangement has been found, but an alternative mechanism cannot be ruled out at this time. No evidence for the reverse reaction, isomerization of a siloxysilylene to a silylsilanone, could be found. However, evidence for silanone production from decomposition of a siloxysilylene was found and interpreted as proceeding via cyclization to a 1,3-disilaoxetane and extrusion of silanone from this intermediate. Further work is in progress in an attempt to gain definitive evidence for (or against) the silanone-to-silylene rearrangement.

Experimental Section

General. Routine ^1H NMR spectra were recorded on a Varian Model EM-360 spectrometer. High-resolution ^1H and ^{13}C NMR was obtained on a Bruker WM-300 spectrometer. Infrared (IR) spectra were recorded on a Beckman IR-4250 spectrometer. Gas chromatograph–mass spectra (GCMS) were recorded on a Finnegan Model 4023 mass spectrometer. Exact mass measurements were obtained on an AEI MS-902 spectrometer. All mass spectra were recorded at 70 eV. Ultraviolet (UV) spectra were obtained on a Perkin-Elmer 320 spectrophotometer. Gas chromatographic (GC) data were obtained on a Varian-Aerograph Model 3700, 1700, or 920 or Fischer/Victoreen Series 4400 gas chromatograph. GC yields were determined with internal standards and predetermined re-

(17) Weber, W. P.; Soysa, H. S.; Okinoshima, H. *J. Organometal. Chem.* **1966**, *133*, C17.

(18) Barton, T. J.; Wulff, W. D.; Goure, W. F. *J. Am. Chem. Soc.* **1978**, *100*, 6236.

sponse factors. All melting points (mp) were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

Preparation of 1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(trimethylsilyl)cyclotetrasiloxane (12) and 1,3,5-Trimethyl-1,3,5-tris(trimethylsilyl)cyclotrisiloxane (13). To 3.01 g (0.017 mol) of 1,1-dichlorotetramethylidisilane¹⁹ contained in 70 mL of THF was slowly added 3 mL of H₂O. After stirring for 10 h, the solution was extracted with saturated aqueous NaCl. The organic layer was separated and dried over MgSO₄ and the solvent removed to afford a white semisolid. The D₄ analogue **12** was isolated and purified by crystallization from the residue with MeOH: 0.93 g (44%): NMR (CDCl₃) δ 0.05 (s, 9 H), 0.12 (s, 3 H); IR (KBr) 2955, 2895, 1240, 1040 cm⁻¹; mass spectrum, (21 eV) *m/e* (% rel intensity) 528 (0.01), 513 (2.7), 455 (66), 309 (39), 249 (43), 233 (86), 131 (100), 73 (26), calcd for C₁₅H₄₅O₄Si₈ (M⁺ - CH₃) 513.14723, measd 513.14706; mp 94-95 °C. The D₃ analogue **13** was isolated from the residue by preparative GC (8 ft 15% SE-30): NMR (CDCl₃) δ 0.21 (s, 3 H), 0.12 (s, 9 H); mass spectrum, *m/e* (% rel intensity) 396 (0.7), 381 (1.4), 323 (13), 265 (2.3), 249 (3.7), 205 (4.6), 189 (5.2), 174 (15), 147 (11), 131 (48), 116 (12), 73 (100), calcd for C₁₂H₃₆O₃Si₆ 396.12801, measd 396.12946.

Vacuum Pyrolysis of 12. The D₄ analogue **12** (0.191 g) was sublimed (90 °C, 1 × 10⁻⁴ torr) through a horizontal quartz tube packed with quartz chips and heated to 780 °C. The pyrolysate (0.13 g) was collected in a liquid nitrogen cooled trap and analyzed by GCMS. Three major components were observed: unreacted **12** (ca. 25%), **13** (ca. 20%) (both identified by spectral comparison to authentic samples), and an unidentified product whose mass spectrum was consistent with loss of methyl(trimethylsilyl)silylene from **12** (ca. 30%) [mass spectrum *m/e* (% rel intensity) 412 (1.4), 397 (3.9), 339 (28), 282 (2.1), 265 (3.8), 252 (2.5), 190 (3.5), 147 (7.9), 116 (100), 73 (12)]. The yield of these products was approximated from relative peak areas. The complexity of the pyrolysate prohibited their isolation. Numerous isomers of **12**, **13**, and the unidentified product and other unidentified volatile products were also formed.

Pyrolysis of 12 with Butadiene or with Nitrogen. The D₄ analogue **12** (0.219 g) dissolved in 0.8 mL of benzene was slowly dropped through a vertical quartz tube packed with quartz chips and heated to 610 °C. Butadiene was used as the carrier gas (40 mL/min). The pyrolysate was collected in a dry ice/isopropyl alcohol cooled trap and initially analyzed by GCMS. The three major components were identified: recovered starting material **12** (67% completion), **13** (11%), and **14** (72%). Starting material and the D₃ analogue were identified by comparison with their mass spectra to those of an authentic sample. Compound **14** was isolated by preparative GC (8 ft 10% OV101) and identified based on the following spectra data: NMR (CDCl₃) δ 0.33 (s, 9 H), 0.48 (s, 3 H), 1.40 (br s, 4 H), 5.91 (br s, 2 H); mass spectrum, *m/e* (% rel intensity) 186 (20), 171 (47), 143 (17), 117 (100), 73 (65), 59 (31), calcd for C₈H₁₈O_{Si₂} 186.08996, measd 186.08894. Pyrolysis of **12** in identical fashion, except nitrogen (30 mL/min) was substituted for butadiene as the carrier gas, afforded a complex mixture of at least 20 volatile products. The D₃ analogue **13** (21%) was identified as the major product based on retention time and comparison of its mass spectrum to that of an authentic sample.

Pyrolysis of 12 with Butadiene. The D₃ analogue **13** (0.153 g) dissolved in 400 μL of benzene was copolylyzed with butadiene as the carrier gas (40 mL/min) according to the previously described procedure. Analysis of the pyrolysate by GCMS revealed that **13** had decomposed to several products, all formed in low yield (91% completion). The silylene trapping product **14** (11%) was identified by comparison of its mass spectrum to that of an authentic sample.

Pyrolysis of 12 with Dimethyldimethoxysilane. The D₄ analogue **12** (0.192 g) dissolved in 0.8 mL of dimethyldimethoxysilane was dropped through a vertical quartz tube packed with quartz chips and heated to 610 °C. Nitrogen was used as the carrier gas (30 mL/min). After collection in a dry ice/isopropyl alcohol cooled trap, the pyrolysate was analyzed by GCMS. No evidence for formation of the expected methyl(trimethylsilyl)silanone insertion product (**15**) was found. As in pre-

vious described pyrolysis of **12** in the absence of butadiene, numerous (>20) unidentified products were formed. The major product was identified as 1,3-dimethoxytetramethyldisiloxane based on spectral comparison to an authentic sample. Pyrolysis of dimethyldimethoxysilane also afforded this product.

Preparation of Bis(trimethylsilyloxy)(trimethylsilyl)methylsilane (18). 1,1-Dichlorotetramethylidisiloxane (2.81 g, 0.015 mol) and trimethylchlorosilane (4.10 g, 0.038 mol) were added to 100 mL of THF. To this stirring solution was added 6.0 g (0.076 mol) of pyridine followed by the slow addition of 2.5 mL of H₂O. After stirring for 12 h, 100 mL of pentane was added and the resulting solution was extracted with saturated aqueous HCl. Following separation of the organic layer and drying over MgSO₄, the solvent was removed. Compound **18** was isolated from the residue by preparative GC (10 ft 10% OV101): 31%; NMR (CDCl₃) δ 0.15 (s, 18 H), 0.11 (s, 3 H), 0.10 (s, 9 H); ¹³C NMR (CDCl₃) δ -2.3, 2.1, 3.4; IR (neat) 2965, 2900, 1260, 1075, 1040, 845 cm⁻¹; mass spectrum *m/e* (% rel intensity) 294 (0.3), 279 (1.9), 221 (42), 191 (12), 147 (8.8), 117 (7.9), 73 (100), 59 (5.4), calcd for C₁₀H₃₀O₂Si₄ 294.13230, measd 294.13238.

Pyrolysis of 18 with and without Butadiene. Trisiloxane **18** (0.390 g) was dropped through a vertical quartz tube packed with quartz chips and heated to 620 °C. Butadiene was used as the carrier gas (40 mL/min). The pyrolysate (98% completion) was collected in a dry ice/isopropyl alcohol cooled trap. The two major silicon-containing products were isolated by preparative GC (8 ft 10% OV101) and identified as hexamethylidisiloxane (**19**) (70%) and **14** (48%) based on comparison of their GCMS and ¹H NMR spectra to those of authentic samples. An identical pyrolysis of **18** (0.213 g), except nitrogen was used as the carrier gas (30 mL/min), afforded a yellow pyrolysate (0.181 g, 96% completion) from which hexamethylidisiloxane (73%) was identified by GCMS as the major product. Several minor products were also formed. The two minor products formed in highest yield were identified as octamethyltrisiloxane (4.0%) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (5.4%) based on comparison of their mass spectra to an authentic sample or to that previously reported.²⁰

Vacuum Pyrolysis of 18 with Added Hexamethylidisiloxane. Hexamethylidisiloxane (1.0 mL) and **18** (0.189 g) were flash-distilled (100 °C, 1 × 10⁻² torr) through a horizontal quartz tube packed with quartz chips and heated to 850 °C. The pyrolysate was collected in a liquid nitrogen cooled trap. The three major components were isolated by preparative GC (8 ft 10% OV101) and identified as starting material (61% completion), **21** (14%) [NMR (CCl₄) δ 0.13 (s, 18 H), 0.21 (d, 3 H, *J* = 3 Hz), 4.95 (q, 1 H *J* = 3 Hz); IR (neat) 2965, 2140, 1255, 1055, 840 cm⁻¹; mass spectrum, *m/e* (% rel intensity) 222 (0.5), 221 (2.8), 207 (66.2), 191 (3.5), 175 (1.1), 133 (11), 96 (20.3), 73 (100)], and **20** (10%) [NMR (CCl₄) δ 0.15 (s, 18 H), 0.19 (s, 6 H); mass spectrum, *m/e* (% rel intensity) 221 (52), 205 (4.0), 147 (5.2), 133 (9.5), 103 (15), 73 (100), 59 (12)].

Vacuum Pyrolysis of 18 with No Added Trap. Trisiloxane **18** (0.125 g) was slowly distilled (55 °C, 1 × 10⁻³ torr) through a horizontal quartz tube packed with quartz chips and heated to 850 °C. The pyrolysate (0.091 g) was collected in a liquid nitrogen cooled trap and analyzed by GCMS. The two major components were identified as hexamethylidisiloxane (in significant, but undetermined, yield) and starting material. Minor products (<5% yield) were identified by comparison of their mass spectrum to that previously reported: **20**, **21**, **23**²¹ [mass spectrum, *m/e* (% rel intensity) 166 (84), 115 (19), 101 (100), 99 (22), 85 (12), 69 (17)]; **25**²² [mass spectrum, *m/e* (% rel intensity) 130 (53), 129 (7), 115 (100), 99 (6), 73 (31), 59 (14)]; and **24**²³ [mass spectrum, *m/e* (% rel intensity) 144 (24), 129 (100), 101 (12), 73 (13), 59 (25)].

Acknowledgment. The support of this work by the National Science Foundation is gratefully acknowledged.

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