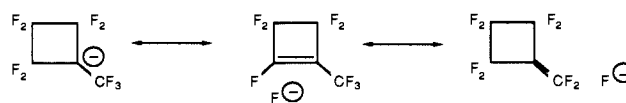


the hyperconjugating structures involving **8A** will be more energetically accessible than those involving **8B**. Thus  $r(C_1-C_2)$  should be shorter than  $r(C_1-C_4)$  as is observed. Furthermore, the hyperconjugating structures involving **8A** should have more s character in the  $C_1-C_2$  bond, making the  $C_2-F$  bonds have more p character. This is consistent with the longer C-F bonds and

the small value found for  $\theta(F_1C_2F_2)$ .



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**Supplementary Material Available:** Table of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

## Kinetics and Mechanisms of $\alpha$ - and $\beta$ -Eliminations of Alkoxysilanes from Saturated and Unsaturated Carbon Frameworks

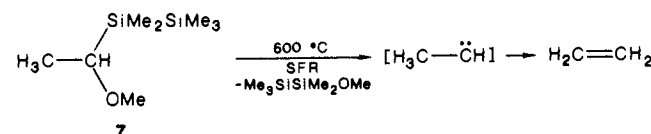
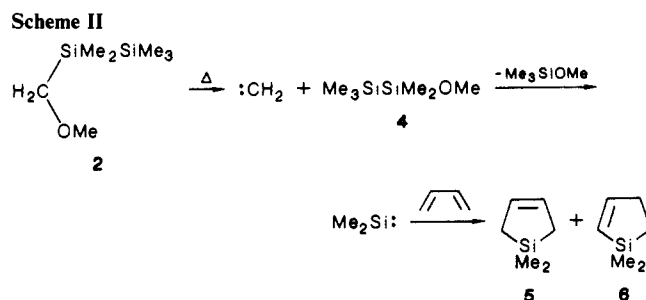
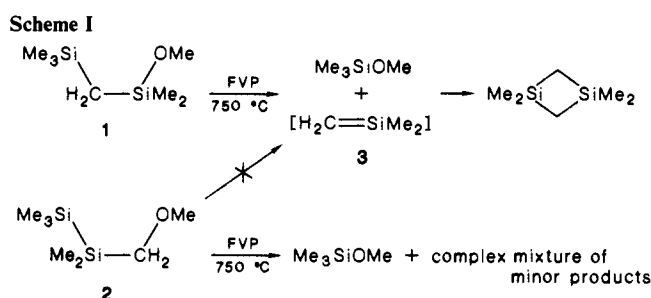
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**Abstract:** Although  $Me_3SiCH_2SiMe_2OMe$  undergoes thermally induced  $\beta$ -elimination of  $Me_3SiOMe$  to afford dimethylsilene, the thermodynamically favorable elimination of  $Me_3SiOMe$  from  $Me_3SiSiMe_2CH_2OMe$  does not occur. From kinetic studies and trapping experiments, this is found to be due to a more favorable  $A$ -factor for three-centered elimination of  $:CH_2$ . Three-centered elimination of  $Me_3SiOMe$  from an  $sp^2$ -hybridized carbon to afford a vinylidene is found to be more facile than the analogous elimination from an  $sp^3$ -hybridized carbon due both to more favorable energy of activation and  $A$ -factor. Thus, silaallene formation from  $H_2C=C(OMe)SiMe_2SiMe_3$  does not occur due to the greater facility of  $\alpha$ -elimination to  $H_2C=C$ .

Thermally induced  $\beta$ -elimination of  $Me_3SiOMe$  from silyl ethers of type **1**, first reported by Gusev'nikov,<sup>1</sup> has proved to be a convenient route to a variety of interesting silenes.<sup>2</sup> One would assume that the analogous elimination from disilanes of type **2** would be much more facile since it would involve breaking the considerably weaker Si-Si and C-O bonds rather than the robust Si-C and Si-O bonds. Indeed, consideration of available bond strengths<sup>3</sup> leads to the conclusion that  $\beta$ -elimination from **2** should be at least 45 kcal/mol more favorable than from **1**. Thus, it was somewhat perplexing to find that flash vacuum pyrolysis (FVP) of **2**, although producing the expected  $Me_3SiOMe$  as the major product, afforded a complex mixture of products, none of which seems (from GCMS analysis) to originate from silene **3**.

One possible explanation for the surprising dichotomy between the thermolyses of **1** and **2** would be that **2** eschews  $\beta$ -elimination in favor of  $\alpha$ -elimination<sup>4</sup> to produce  $:CH_2$ , a process that is not available to **1**. Carbene formation by reductive elimination of  $Me_3SiOR$  is a well-established process<sup>7</sup> although to our knowledge the internal competition between  $\alpha$ - and  $\beta$ -elimination presented in **2** has never been probed. Thus, the complexity of the pyrolysate



from **2** could be explained by initial  $\alpha$ -elimination of  $:CH_2$  followed by a second  $\alpha$ -elimination of  $:SiMe_2$  from the resulting disilane **4**. The generation of two highly reactive intermediates from each molecule of **2** would virtually guarantee a complex product

(1) Nametkin, N. S.; Gusev'nikov, L. E.; Volnina, E. A.; Vdovin, V. M. *Dokl. Akad. Nauk SSSR* **1975**, *220*, 386.

(2) (a) Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. C. *Tetrahedron Lett.* **1981**, *22*, 7. (b) Barton, T. J.; Burns, G. T. *J. Organomet. Chem.* **1981**, *216*, C5. (c) Barton, T. J.; Vuper, M. *J. Am. Chem. Soc.* **1981**, *103*, 6788. (d) Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 2006.

(3) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(4) This is also known to be the case for the decomposition of  $CHF_2C-F_2SiCl_3$ <sup>5</sup> and  $CHF_2CF_2SiMe_3$ .<sup>6</sup>

(5) Haszeldine, R. N.; Robinson, P. J.; Williams, W. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1013.

(6) Haszeldine, R. N.; Parkinson, C.; Robinson, P. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1018.

(7) Atwell, W. H.; Weyenberg, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 3438. Brook, A. G.; Dillon, P. J. *Can. J. Chem.* **1969**, *47*, 4377.

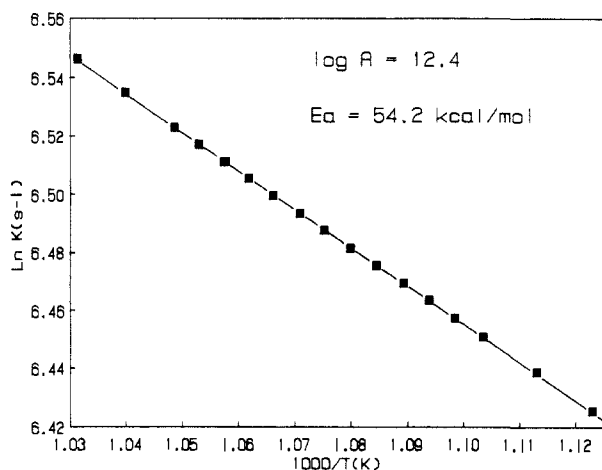


Figure 1. Arrhenius plot for the formation of  $\text{Me}_3\text{SiOMe}$  from **1** in SFR.

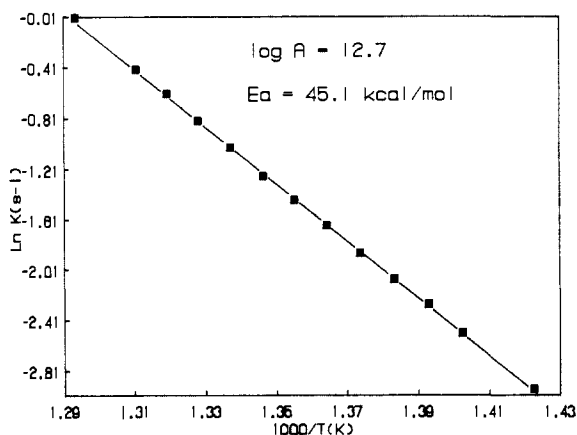


Figure 2. Arrhenius plot for the formation of  $\text{Me}_3\text{SiOMe}$  from **9** in SFR.

mixture. Evidence for the formation of  $:\text{SiMe}_2$  was obtained by flow-coppyrolysis of **2** and butadiene at  $620^\circ\text{C}$  to obtain the expected addition products, silacyclopentenes **5** and **6**. Evidence for carbene formation was obtained by pyrolysis of disilanyl ether **7** to obtain ethylene as the exclusive low molecular weight product.

As to the question of why  $\alpha$ -elimination is favored over  $\beta$ -elimination, we are aware of no kinetic studies that could provide an answer. Thus, a kinetic investigation of the thermolyses of **1** and of  $\alpha$ -silyl ether **8** was undertaken with use of a pulsed, stirred-flow reactor (SFR) modeled after the system described by Davidson.<sup>8</sup> Decomposition of **1** was carried out over a temperature range of  $618$ – $697^\circ\text{C}$  following the rate of  $\text{Me}_3\text{SiOMe}$  formation. On the basis of 21 rate determinations in this temperature range, the Arrhenius plot (Figure 1) gave the first-order rate constant for formation of  $\text{Me}_3\text{SiOMe}$  as  $\log k_1 = (12.4 \pm 0.1) - [(54200 \pm 300)/2.3RT]$ . The activation energy of  $54$  kcal/mol eliminates the possibility of a homolytic process, and the  $A$ -factor of  $12.4$  is consistent with that of a four-center transition state.<sup>9</sup> For comparison the decomposition of 1-methoxy-2-(trimethylsilyl)ethane (**9**) was examined in the SFR. The thermolysis, which cleanly produced  $\text{Me}_3\text{SiOMe}$  and ethylene, was followed by the formation of the alkoxy silane over the temperature range of  $430$ – $500^\circ\text{C}$ . The resulting Arrhenius plot (Figure 2) yielded the first-order rate constant as  $\log k_1 = (12.7 \pm 0.1) - [(45000 \pm 200)/2.3RT]$ . The gratifyingly similar  $A$ -factors are strong evidence that both **1** and **9** decompose via four-centered transition states, while the difference in  $E_a$ 's is

(8) Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 972.

(9) For example, the elimination of  $\text{HBr}$  from *i*-, *n*-, *sec*-, and *t*- $\text{BuBr}$  has  $A$ -factors ranging from  $13.0$  to  $13.5$ ,<sup>10</sup> while  $\text{HCN}$  elimination from *i*- $\text{PrCN}$  has a  $\log A$  of  $12.1$ .<sup>11</sup>

(10) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; J. Wiley and Sons: New York, 1976; p 111.

(11) Dastor, P. N.; Emovan, E. U. *Can. J. Chem.* **1973**, *51*, 366.

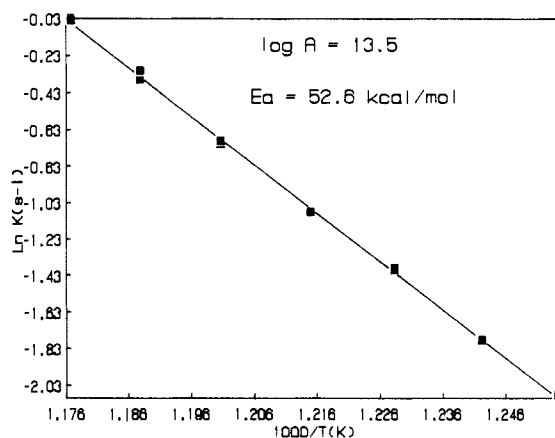


Figure 3. Arrhenius plot for the formation of  $\text{Me}_3\text{SiOMe}$  from **8** in SFR.

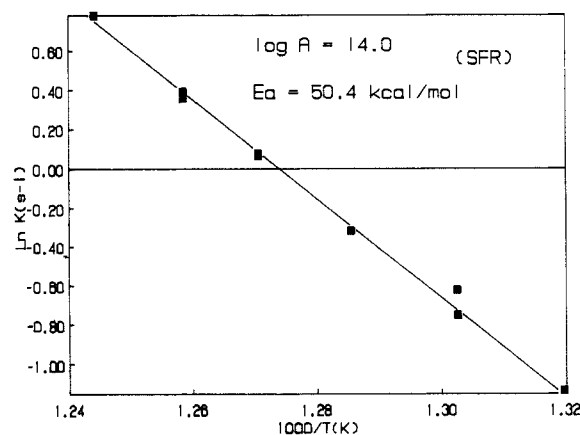
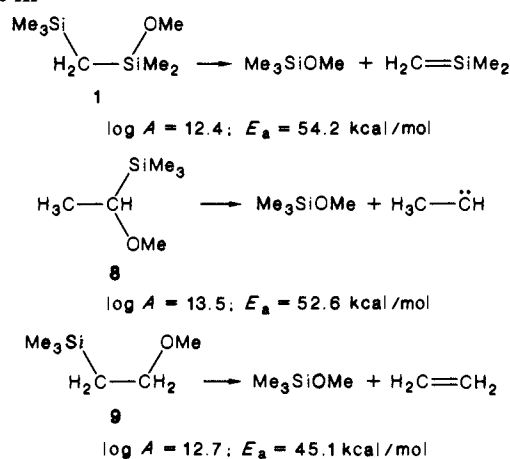


Figure 4. Arrhenius plot for the formation of  $\text{Me}_3\text{SiOMe}$  from **10** in SFR.

#### Scheme III



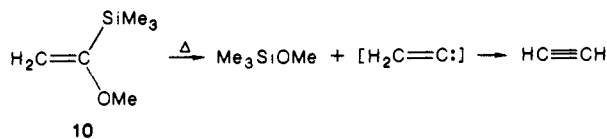
derived from a combination of the strength of the  $\text{Si}-\text{O}$  bond in **1** and the weakness of the incipient  $\text{Si}-\text{C}$   $\pi$ -bond.

Decomposition of **8** was studied in the SFR system from  $524$  to  $579^\circ\text{C}$  by following the rate of  $\text{Me}_3\text{SiOMe}$  formation. The Arrhenius plot (Figure 3) from 14 rate determinations gave the first-order rate constant as  $\log k_1 = (13.5 \pm 0.1) - [52600 \pm 400]/2.3RT]$ . The  $A$ -factor of  $13.5$  is a reasonable value for a three-center transition state, although reported values<sup>12</sup> for 1,2-eliminations of silyl halides from  $\alpha$ -halosilanes range from  $10.8$  to  $15.2$ . As a check on the validity of our activation parameters, the thermolysis of **8** was also followed in a low-pressure-pyrolysis (LPP) system<sup>13</sup> following the rate of disappearance of **8** contin-

(12) Robinson, P. J. *React. Kinet.* **1975**, *1*, 93–160.

(13) Davidson, I. M. T.; Ostah, N. A.; Seyferth, D.; Duncan, D. P. *J. Organomet. Chem.* **1980**, *187*, 297.

## Scheme IV



SFR:  $\log A = 14.0 \pm 0.3$ ,  $E_a = 50.4 \pm 1.0$   
 LPP:  $\log A = 13.6 \pm 0.2$ ,  $E_a = 49.3 \pm 0.7$

ously by mass spectroscopy. The resulting Arrhenius parameters of  $\log A = 13.3 \pm 0.1$  and  $E_a = 52.0 \pm 0.6$  kcal/mol were within experimental error the same as those obtained in the SFR.

It is of considerable interest to note that although the activation energies for the decompositions of **1** and **8** are within 2 kcal/mol,  $\alpha$ -elimination is much faster (more than 2500 times at 600 °C) than  $\beta$ -elimination largely due to a more favorable  $A$ -factor. Thus,  $\beta$ -elimination in **2** has no chance to compete with  $\alpha$ -elimination. Such information is crucial in the future design of thermal precursors of reactive species.

With the activation parameters for  $\alpha$ -elimination to a saturated carbene in hand, it was of interest to compare these values with those for the analogous elimination to produce an unsaturated carbene.<sup>14</sup> Thus, the thermolysis of 1-methoxy-1-(trimethylsilyl)ethene (**10**) was studied in both the SFR (485–530 °C) (Figure 4) and LPP (403–462 °C). In the SFR, the clean decomposition of **10** to acetylene and  $\text{Me}_3\text{SiOMe}$  was followed through the formation of the alkoxyasilane, while the rate of decay of **10** was followed in the LPP system. Although the scatter produced larger error limits than observed for **1** or **8**, it is clear that the more facile production of vinylidene is due to both a more favorable  $A$ -factor and activation energy.

Lastly, we note that the  $\beta$ -elimination route to silenes as exploited with systems of type **1** cannot be extended to the production of 1-silaallenes. We have already reported<sup>15</sup> on the thermochemistry of 1-(dimethylmethoxysilyl)-1-(trimethylsilyl)ethene **11** which does not decompose by extrusion of  $\text{Me}_3\text{SiOMe}$ . We have now investigated the thermolysis of its isomer (1-methoxyethenyl)pentamethyldisilane (**13**) and find that like **2** it prefers  $\alpha$ -elimination to  $\beta$ -elimination. Flash vacuum pyrolysis of **13** at 550 °C does indeed afford  $\text{Me}_3\text{SiOMe}$  and (dimethylsilyl)acetylene (**14**) from which it could be argued that  $\beta$ -elimination had occurred to produce silaallene **12** which rearranged<sup>16</sup> to **14**. However, the concomitant formation of methoxydisilane **15** and bis(dimethylsilyl)acetylene (**16**) strongly suggests that this is actually an  $\alpha$ -elimination of **13** to produce vinylidene, which isomerizes to acetylene, and **15**, which undergoes an  $\alpha$ -elimination to afford  $\text{Me}_3\text{SiOMe}$  and  $\text{Me}_2\text{Si:}$ . Thus, the formation of alkynes **14** and **16** would be ascribed to reaction of acetylene and one or two molecules of  $\text{Me}_2\text{Si:}$ .<sup>17</sup> Conclusive evidence for the formation of  $\text{Me}_2\text{Si:}$  in the pyrolysis of **13** was obtained through copyrolysis of **13** and butadiene at 450 °C in a flow system to obtain the usual silylene addition product, silacyclopentene **5** in 34% yield. Evidence for the validity of the assumption of  $\text{Me}_2\text{Si:}/\text{acetylene}$  origin for products came from copyrolysis of **13** and phenylacetylene to obtain adduct **17**, no **16**, and only a trace of **14**. Although the yield of **17** appears disconcertingly low, relative to the formation of  $\text{Me}_2\text{Si:}$  as evidenced by the yield of  $\text{Me}_3\text{SiOMe}$ , it actually represents a respectable 41% trapping efficiency. Thus, we conclude that there is no reason to suggest the intermediacy of silaallene **12** in the pyrolysis of **13**.

## Experimental Section

**General.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Nicolet Model NT-300 spectrometer. GCMS data were obtained at 70 eV on a HP 5970 mass selective detector coupled with a HP 5890 capillary GC.

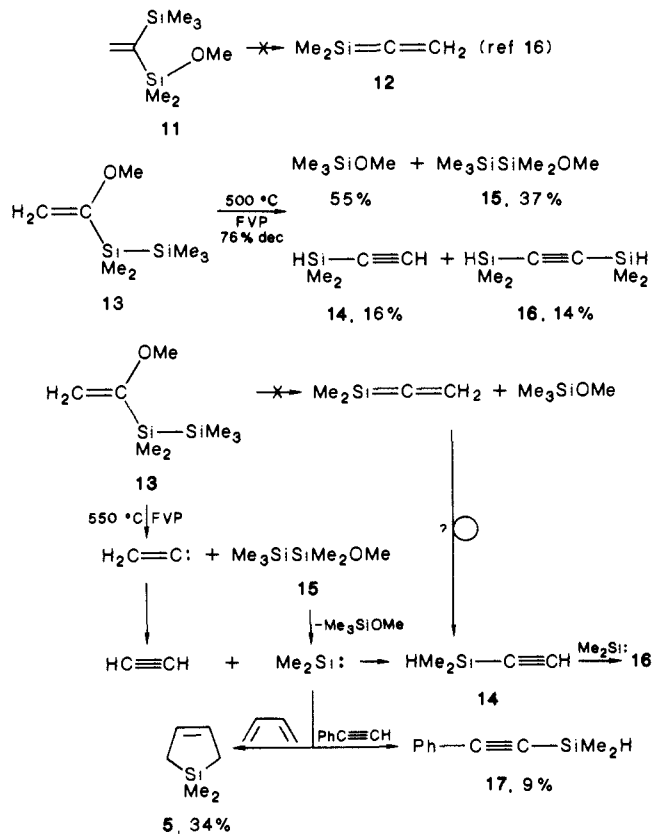
(14) Barton, T. J.; Groh, B. L. *J. Org. Chem.* **1985**, *50*, 158; *J. Am. Chem. Soc.* **1985**, *107*, 7221.

(15) Bain, S.; Ijadi-Maghsoodi, S.; Barton, T. J. *Organometallics* **1987**, *6*, 1136.

(16) Barton, T. J.; Burns, G. T.; Goure, W. F.; Wulff, W. D. *J. Am. Chem. Soc.* **1982**, *104*, 1149.

(17) Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1983**, *2*, 199. Haas, C. H.; Ring, M. A. *Inorg. Chem.* **1975**, *14*, 2253.

## Scheme V



Quantitative GC analysis was accomplished with use of predetermined response factors and *n*-decane as an internal standard. Preparative GC separations were performed on a Varian Model 920 instrument. Flash vacuum pyrolyses (FVP) were carried out by slowly distilling compounds through a heated, seasoned, horizontal quartz pyrolysis tube (16 mm i.d., 200 mm long) packed with quartz chips, with product collection in a trap cooled with liquid  $\text{N}_2$ . Pressures were measured by an ion gauge placed behind a liquid  $\text{N}_2$  trap and are typically an order of magnitude lower than in the reaction zone. The stirred flow reactor (SFR) system is modeled after that described by Davidson.<sup>8</sup> Our SFR system uses a 60 mL/min He flow to sweep the material through the reactor into a Varian 6000 GC (FID) and has the option of diverting the separated products into a VG SX-300 quadrupole mass spectrometer for mass analysis. The low-pressure pyrolysis (LPP) is designed after that described by Davidson<sup>13</sup> and is continuously monitored by the VG SX-300.

**Synthesis of (Trimethylsilyl)(dimethylmethoxysilyl)methane (1).**<sup>1</sup> Preparation of **1** was accomplished in two steps in overall isolated yield of 34%. Quenching of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  with  $\text{Me}_2\text{SiCl}_2$  afforded  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{Cl}$  (bp 56–58 °C (20 Torr)) in 47% yield. To a stirring mixture of LiOMe in THF at –78 °C, obtained by addition of 8.2 mL (2.5 M, 21 mmol) of *n*-BuLi in hexane to 1.0 g (31 mmol) of methanol in 15 mL of THF, was added 3.4 g (19 mmol) of  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{Cl}$  over 10 min. After being stirred at –78 °C for 0.5 h, the mixture was warmed to room temperature. Trap-to-trap distillation was followed by fractional distillation with a 7-cm column packed with glass helices to afford 2.4 g (14 mmol, 73%) of **1**: bp 54–55 °C (26 Torr); GCMS (70 eV)  $m/e$  (% relative intensity) 163 (7.5), 162 (16), 161 (M – 15, 100), 131 (68), 115 (6.4), 89 (12), 73 (31), 59 (56), 45 (26), 43 (24);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  –0.14 (2 H, s), 0.02 (9 H, s), 0.10 (6 H, s), 3.38 (3 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.03, 1.13, 4.14, 49.94.

**Synthesis of (Methoxymethyl)pentamethyldisilane (2).** Disilane **2** was prepared by the method of Tamao and Kumada.<sup>18</sup> Characterization was by  $^1\text{H}$  NMR and GCMS.

**Synthesis of (1-Methoxyethenyl)pentamethyldisilane (13).** To a solution of methyl vinyl ether (3.70 g, 63.7 mmol) in 30 mL of THF at –78 °C under  $\text{N}_2$  was slowly added 52.7 mmol of *t*-BuLi (31.0 mL of 1.7 M solution in pentane). The mixture was allowed to warm to 0 °C and stirred for an additional 0.5 h during which time the color changed from yellow to colorless. After being cooled to –78 °C, a solution of chloropentamethyldisilane (7.70 g, 46.1 mmol) in 10 mL of THF was added

(18) Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1966**, *5*, 226.

via syringe after which the mixture was warmed to room temperature and stirred for 20 h. After trap-to-trap distillation, fractional distillation yielded GC-pure **13** (5.9 g, 68%); bp 64–66 °C (20 Torr); GCMS (70 eV)  $m/z$  (% relative intensity) 187 ( $M - 1$ , 0.8), 173 ( $M - 15$ , 23), 89 (100), 84 (43), 73 (92), 59 (79), 58 (40), 45 (47), 43 (33);  $^1\text{H NMR}$  ( $\text{DCCl}_3$ )  $\delta$  0.05 (9 H, s), 0.14 (6 H, s), 3.49 (3 H, s), 4.22 (1 H, d,  $J = 2.0$  Hz), 4.60 (1 H, d,  $J = 2.0$  Hz);  $^{13}\text{C NMR}$  ( $\text{DCCl}_3$ )  $\delta$  -4.91, -2.27, 54.09, 93.34, 170.64; IR (neat) 3096 (w), 2951 (s), 2897 (m), 1580 (m), 1246 (s), 1209 (s), 1040 (s), 891 (m), 835 (s), 800 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_8\text{H}_{20}\text{OSi}_2$ : C, 51.00; H, 10.70. Found: C, 50.85; H, 10.97.

**Synthesis of 1-Methoxyethylpentamethyldisilane (7).** A solution of **13** (0.9 g, 4.8 mmol) and hydrazine (1.85 g, 58 mmol) in 30 mL of MeOH was refluxed (100 °C bath) for 30 h with continuous bubbling of  $\text{O}_2$  through the solution. After reflux the total volume was only ca. 10 mL. After the solution was cooled to 0 °C, HCl (5 mL, 0.1 N) was added, the mixture stirred for 1 h, 50 mL of  $\text{Et}_2\text{O}$  added, the aqueous layer discarded, and the organic layer washed twice with 10 mL of  $\text{H}_2\text{O}$  before drying over  $\text{Na}_2\text{SO}_4$ . After filtration the ether was removed by distillation to leave 0.3 g of crude **7** which was further purified by preparative gas chromatography. **7**: GCMS  $m/e$  (% relative intensity) 175 ( $M - 15$ , 5), 148 (6), 131 (19), 89 (60), 86 (35), 73 (100), 59 (80), 58 (34), 45 (49), 43 (39);  $^1\text{H NMR}$  ( $\text{DCCl}_3$ )  $\delta$  0.04 (3 H, s), 0.06 (9 H, s), 0.1 (3 H, s), 1.20 (3 H, d,  $J = 7.9$  Hz), 3.05 (1 H, q,  $J = 7.3$  Hz), 3.30 (3 H, s);  $^{13}\text{C NMR}$  ( $\text{DCCl}_3$ )  $\delta$  -6.56, -6.13, -1.77, 15.18, 58.11, 71.25; IR (neat) 2951z(s), 2895 (m), 1244 (s), 1103 (s), 1076 (s), 833 (s), 797 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_8\text{H}_{22}\text{OSi}_2$ : C, 50.46; H, 11.65. Found: C, 50.10; H, 11.95.

**Synthesis of 1-Methoxy-2-(trimethylsilyl)ethane (9).** Ether **9** was synthesized by the route reported by Chvalovsky.<sup>19</sup>

**Synthesis of 1-Methoxy-1-(trimethylsilyl)ethene (10).** Ether **10** was synthesized by the route reported by Soderquist.<sup>20</sup>

**Synthesis of 1-Methoxy-1-(trimethylsilyl)ethane (8).** In a stainless steel bomb equipped with stirrer were placed **10** (2.7 g, 21 mmol) and Pd/C (0.1 g, 5%). The bomb was charged with 600 psi  $\text{H}_2$ , and the mixture was stirred for 6 days. The bomb was washed out with 15 mL of  $\text{Et}_2\text{O}$  and fractional distillation yielded GC-pure **8** (1.1 g, 8.5 mmol, 40%); bp 54–55 °C (125 Torr); GCMS  $m/e$  (% relative intensity) 117 ( $M - 15$ , 19), 89 (27), 73 (100), 59 (40), 45 (28), 43 (32);  $^1\text{H NMR}$  ( $\text{DCCl}_3$ )  $\delta$  0.00 (9 H, s), 1.19 (3 H, d,  $J = 7.3$  Hz), 2.90 (1 H, q,  $J = 7.3$  Hz), 3.32 (3 H, s);  $^{13}\text{C NMR}$  ( $\text{DCCl}_3$ )  $\delta$  -3.85, 14.34, 58.20, 71.34; IR (neat) 1248 (s), 864 (s), 839 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_6\text{H}_{16}\text{OSi}$ : C, 54.48; H, 12.19. Found: C, 54.83; H, 12.54.

**Copyrolysis of 2 and 1,3-Butadiene.** The copyrolysis was conducted in a vertical tube furnace with use of a quartz chip packed tube (16 mm i.d., 200 mm long) with butadiene (60 mL/min) as the carrier gas. The addition rate for **2** (130 mg) was ca. 25 mg/min (via syringe). GC and GCMS analysis and comparison with authentic samples revealed the major products to be  $\text{Me}_3\text{SiOMe}$  (19%), **5** (8%), and **6** (4%) with the yields corrected for 11% unreacted **2**.

**FVP of 13.** FVP of **13** (135 mg) was conducted at 550 °C ( $5 \times 10^{-4}$  Torr) by slow distillation of **13** through the pyrolysis tube and collection at -196 °C. After addition of a measured amount of *n*-decane as an internal standard, the yields were measured (after individual calibration) by GC. The yields are corrected for the 24% recovery of **13**. The major products  $\text{Me}_3\text{SiOMe}$  (55%), **15** (37%), **14** (16%), and **16** (14%) were isolated by preparative GC and characterized by GCMS, GCIR, and  $^1\text{H NMR}$ .

**Copyrolysis of 13 and 1,3-Butadiene.** Pyrolysis of **13** (244 mg) was conducted in a vertical quartz chip packed tube to 450 °C by dropwise addition via syringe (through a septum) at a rate of ca. 10 mg/min. The tube was continuously swept with butadiene at a rate of 60 mL/min. The pyrolysate was collected at -78 °C and an internal standard of decane was added. Yields were determined by GC and are corrected for 27% recovery of **13**. The products  $\text{Me}_3\text{SiOMe}$  (42%) and silacyclopentene **5** (34%) were isolated by preparative GC and characterized by GCMS,  $^1\text{H NMR}$ , and  $^{13}\text{C NMR}$  comparison with authentic samples.

**Copyrolysis of 13 and Phenylacetylene.** A mixture of **13** (92.3 mg, 0.491 mmol) and phenylacetylene (89.1 mg, 0.874 mmol) was pyrolyzed by codistillation ( $5 \times 10^{-4}$  Torr) through a horizontal quartz chip packed tube heated to 550 °C. The pyrolysate was analyzed by GC with *n*-decane as the internal standard, and the yields are corrected for 16% unreacted **13**. The major products  $\text{Me}_3\text{SiOMe}$  (22%), **15** (21%), and **17** (9%) were isolated by preparative GC and identified by GCMS, GCIR, and  $^1\text{H NMR}$ .

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**Registry No.** **1**, 5180-93-8; **2**, 5089-54-3; **5**, 16054-12-9; **6**, 18187-50-3; **7**, 113380-60-2; **8**, 113380-61-3; **9**, 18173-63-2; **10**, 79678-01-6; **13**, 113403-33-1; **14**, 1777-04-4; **15**, 18107-29-4; **16**, 34664-55-6; **17**, 87290-97-9;  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ , 13170-43-9;  $\text{Me}_2\text{SiCl}_2$ , 75-78-5;  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{Cl}$ , 13683-11-9; methyl vinyl ether, 107-25-5; chloropentamethyldisilane, 1560-28-7; 1,3-butadiene, 106-99-0; phenylacetylene, 536-74-3.

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