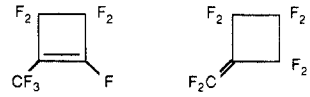
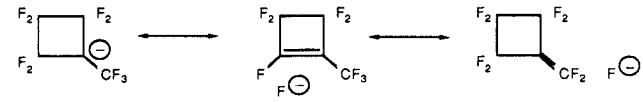


8A 8B

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 $\theta(F_1C_2F_2)$.



Acknowledgment. W. Mahler, T. Fukunaga, and B. E. Smart are thanked for helpful discussions. L. Lardear is acknowledged for invaluable help in the X-ray structure determination.

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

Kinetics and Mechanisms of α- and β-Eliminations of Alkoxysilanes from Saturated and Unsaturated Carbon Frameworks

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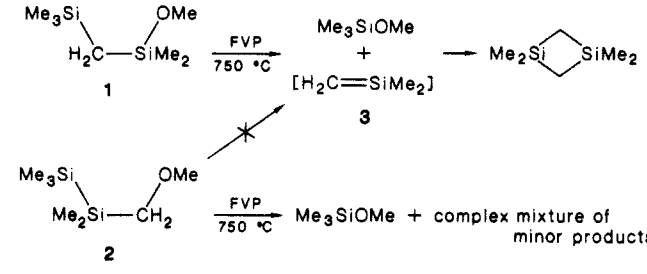
Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011, and the Ames Laboratory—Department of Energy, Ames, Iowa 50011. *Received September 21, 1987*

Abstract: Although $Me_3SiCH_2SiMe_2OMe$ undergoes thermally induced β-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 α-elimination to $H_2C{=}C:$.

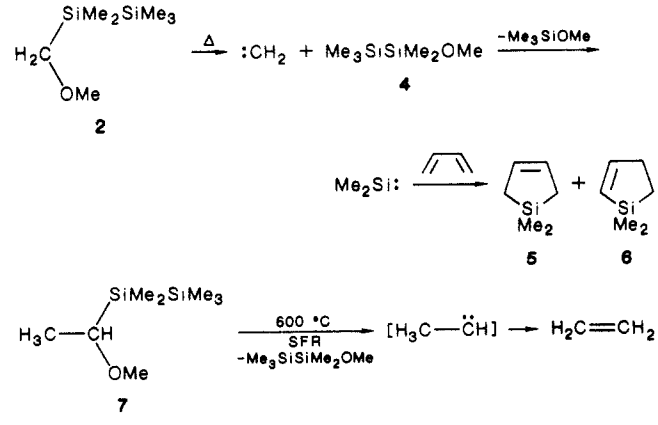
Thermally induced β-elimination of Me_3SiOMe from silyl ethers of type **1**, first reported by Gusel'nikov,[1] has proved to be a convenient route to a variety of interesting silenes.[2] One would assume that the analogous elimination from disilanes of type **2** would be much more facile since it would 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[3] leads to the conclusion that β-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 β-elimination in favor of α-elimination[4] 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[7] although to our knowledge the internal competition between α- and β-elimination presented in **2** has never been probed. Thus, the complexity of the pyrolysate from **2** could be explained by initial α-elimination of $:CH_2$ followed by a second α-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

Scheme I



Scheme II



(1) Nametkin, N. S.; Gusel'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 $CHF_2CF_2SiCl_3$[5] and $CHF_2CF_2SiMe_3$.[6]
(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.

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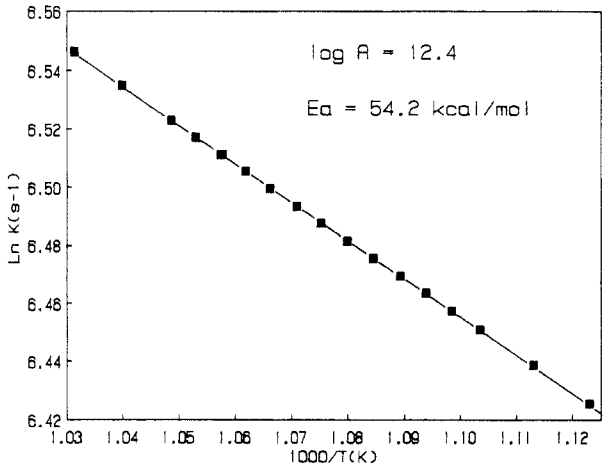


Figure 1. Arrhenius plot for the formation of Me_3SiOMe from **1** in SFR.

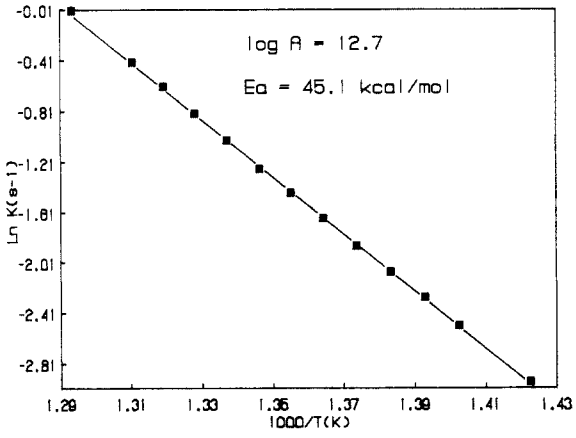


Figure 2. Arrhenius plot for the formation of Me_3SiOMe from **9** in SFR.

mixture. Evidence for the formation of $:SiMe_2$ was obtained by flow-copyrolysis of **2** and butadiene at 620 °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 α-elimination is favored over β-elimination, we are aware of no kinetic studies that could provide an answer. Thus, a kinetic investigation of the thermolyses of **1** and of α-silyl ether **8** was undertaken with use of a pulsed, stirred-flow reactor (SFR) modeled after the system described by Davidson.[8] Decomposition of **1** was carried out over a temperature range of 618–697 °C following the rate of Me_3SiOMe 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 Me_3SiOMe 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.[9] For comparison the decomposition of 1-methoxy-2-(trimethylsilyl)ethane (**9**) was examined in the SFR. The thermolysis, which cleanly produced Me_3SiOMe and ethylene, was followed by the formation of the alkoxysilane over the temperature range of 430–500 °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

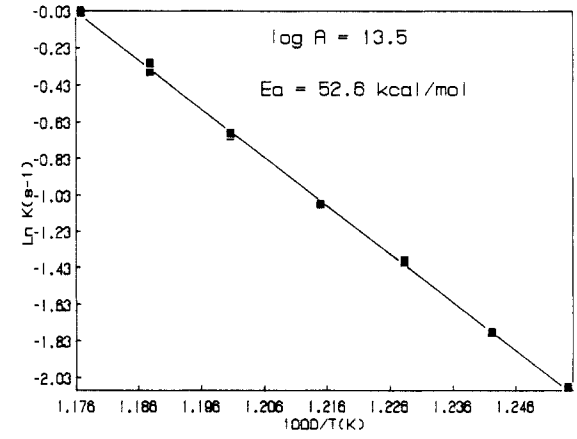


Figure 3. Arrhenius plot for the formation of Me_3SiOMe from **8** in SFR.

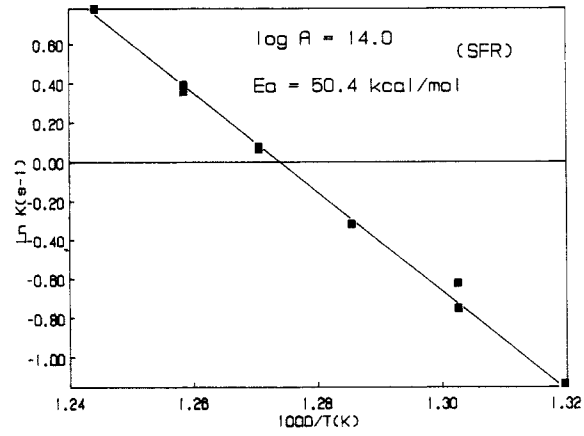
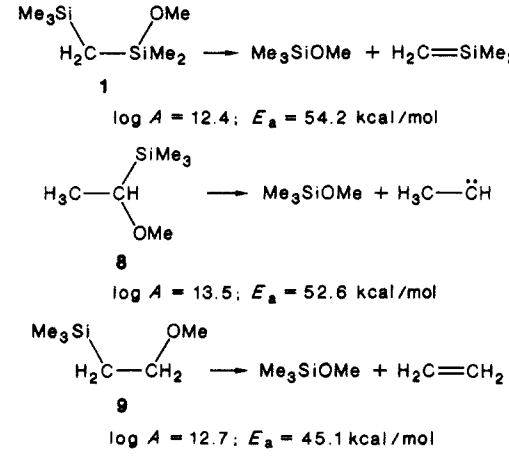


Figure 4. Arrhenius plot for the formation of Me_3SiOMe from **10** in SFR.

Scheme III



derived from a combination of the strength of the Si–O bond in **1** and the weakness of the incipient Si–C π-bond.

Decomposition of **8** was studied in the SFR system from 524 to 579 °C by following the rate of Me_3SiOMe 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[12] for 1,2-eliminations of silyl halides from α-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[13] following the rate of disappearance of **8** contin-

(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 HBr from *i*-, *n*-, *sec*-, and *t*-BuBr has A-factors ranging from 13.0 to 13.5,[10] while HCN elimination from *i*-PrCN has a log A of 12.1.[11]

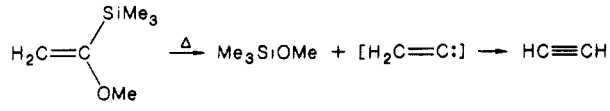
(10) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; J. Wiley and Sons: New York, 1976; p 111.

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

(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



10

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

uously by mass spectroscopy. The resulting Arrhenius parameters of log A = 13.3 ± 0.1 and E_a 52.0 ± 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, α-elimination is much faster (more than 2 500 times at 600 °C) than β-elimination largely due to a more favorable A-factor. Thus, β-elimination in **2** has no chance to compete with α-elimination. Such information is crucial in the future design of thermal precursors of reactive species.

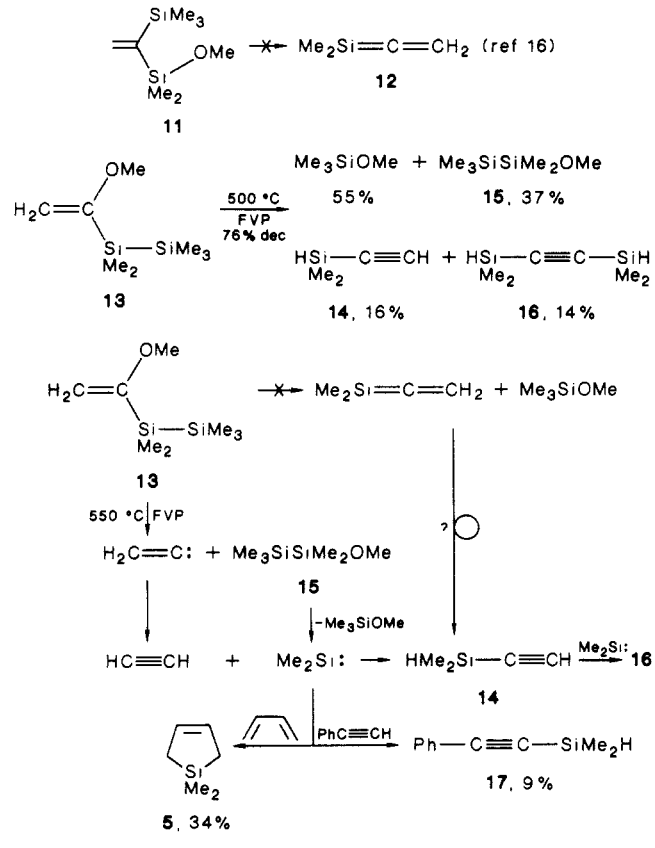
With the activation parameters for α-elimination to a saturated carbene in hand, it was of interest to compare these values with those for the analogous elimination to produce an unsaturated carbene.[14] Thus, the thermolysis of 1-methoxy-1-(trimethylsilyl)ethene (**10**) was studied in both the SFR (485–530 °C) (Figure 4) and LPP (403–462 °C). In the SFR, the clean decomposition of **10** to acetylene and Me_3SiOMe was followed through the formation of the alkoxysilane, 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 β-elimination route to silenes as exploited with systems of type **1** cannot be extended to the production of 1-silaallenes. We have already reported[15] on the thermochemistry of 1-(dimethylmethoxysilyl)-1-(trimethylsilyl)ethene **11** which does not decompose by extrusion of Me_3SiOMe. We have now investigated the thermolysis of its isomer (1-methoxyethenyl)pentamethyldisilane (**13**) and find that like **2** it prefers α-elimination to β-elimination. Flash vacuum pyrolysis of **13** at 550 °C does indeed afford Me_3SiOMe and (dimethylsilyl)-acetylene (**14**) from which it could be argued that β-elimination had occurred to produce silaallene **12** which rearranged[16] to **14**. However, the concomitant formation of methoxydisilane **15** and bis(dimethylsilyl)acetylene (**16**) strongly suggests that this is actually an α-elimination of **13** to produce vinylidene, which isomerizes to acetylene, and **15**, which undergoes an α-elimination to afford Me_3SiOMe and Me_2Si:. Thus, the formation of alkynes **14** and **16** would be ascribed to reaction of acetylene and one or two molecules of Me_2Si:.[17] Conclusive evidence for the formation of Me_2Si: 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 Me_2Si:/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 Me_2Si: as evidenced by the yield of Me_3SiOMe, 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. ^1H and ^{13}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.

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 N_2. Pressures were measured by an ion gauge placed behind a liquid 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.[8] 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[13] and is continuously monitored by the VG SX-300.

Synthesis of (Trimethylsilyl)(dimethylmethoxysilyl)methane (1).[1] Preparation of **1** was accomplished in two steps in overall isolated yield of 34%. Quenching of Me_3SiCH_2MgCl with Me_2SiCl_2 afforded $Me_3SiCH_2SiMe_2Cl$ (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 $Me_3SiCH_2SiMe_2Cl$ 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); ^1H NMR ($CDCl_3$) δ −0.14 (2 H, s), 0.02 (9 H, s), 0.10 (6 H, s), 3.38 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 0.03, 1.13, 4.14, 49.94.

Synthesis of (Methoxymethyl)pentamethyldisilane (2). Disilane **2** was prepared by the method of Tamao and Kumada.[18] Characterization was by ^1H 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 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

(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.
(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}H NMR ($DCCl_3$) δ 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}C NMR ($DCCl_3$) δ −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) cm^{-1}. Anal. Calcd for $C_8H_{20}OSi_2$: C, 51.00; H, 10.70. Found: C, 50.85; H, 10.97.

Synthesis of (1-Methoxyethyl)pentamethyldisilane (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 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 Et_2O added, the aqueous layer discarded, and the organic layer washed twice with 10 mL of H_2O before drying over Na_2SO_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}H NMR ($DCCl_3$) δ 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}C NMR ($DCCl_3$) δ −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) cm^{-1}. Anal. Calcd for $C_8H_{22}OSi_2$: 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.[19]

Synthesis of 1-Methoxy-1-(trimethylsilyl)ethene (10). Ether **10** was synthesized by the route reported by Soderquist.[20]

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 H_2, and the mixture was stirred for 6 days. The bomb was washed out with 15 mL of Et_2O 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}H NMR ($DCCl_3$) δ 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}C NMR ($DCCl_3$) δ −3.85, 14.34, 58.20, 71.34; IR (neat) 1248 (s), 864 (s), 839 (s) cm^{-1}. Anal. Calcd for $C_6H_{16}OSi$: C, 54.48; H, 12.19. Found: C, 54.83; H, 12.54.

(19) Pola, J.; Schraml, J.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3158.

(20) Soderquist, J. A.; Hsu, G. J. *Organometallics* **1982**, *1*, 830.

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 Me_3SiOMe (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 (5×10^{-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 Me_3SiOMe (55%), **15** (37%), **14** (16%), and **16** (14%) were isolated by preparative GC and characterized by GCMS, GCIR, and ^{1}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 Me_3SiOMe (42%) and silacyclopentene **5** (34%) were isolated by preparative GC and characterized by GCMS, ^{1}H NMR, and ^{13}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 (5×10^{-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 Me_3SiOMe (22%), **15** (21%), and **17** (9%) were isolated by preparative GC and identified by GCMS, GCIR, and ^{1}H NMR.

Acknowledgment. We are indebted to the National Science Foundation for support of this work. The Department of Energy, Materials Sciences Division, is gratefully acknowledged for the support of Dr. Ijadi-Maghsoodi and for funding which made possible the construction of the SFR and LPP systems.

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; Me_3SiCH_2MgCl, 13170-43-9; Me_2SiCl_2, 75-78-5; $Me_3SiCH_2SiMe_2Cl$, 13683-11-9; methyl vinyl ether, 107-25-5; chloropentamethyldisilane, 1560-28-7; 1,3-butadiene, 106-99-0; phenylacetylene, 536-74-3.