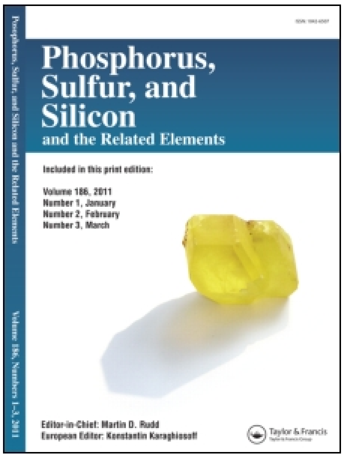

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REARRANGEMENTS OF ALPHA-SILYLSILYLENES TO BETA-SILYLSILYLENES: A MECHANISTIC CONUNDRUM

Myong Euy Lee[a,b]; Marcy A. North[a]; Peter P. Gaspar[a]
[a] Department of Chemistry, Washington University, St. Louis, MO [b] Department of Chemistry, Yonsei University, Kangwondo, South Korea

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REARRANGEMENTS OF ALPHA-SILYLSILYLENES TO BETA-SILYLSILYLENES: A MECHANISTIC CONUNDRUM

MYONG EUY LEE,* MARCY A. NORTH, and PETER P. GASPAR**
Department of Chemistry, Washington University, St. Louis, MO 63130

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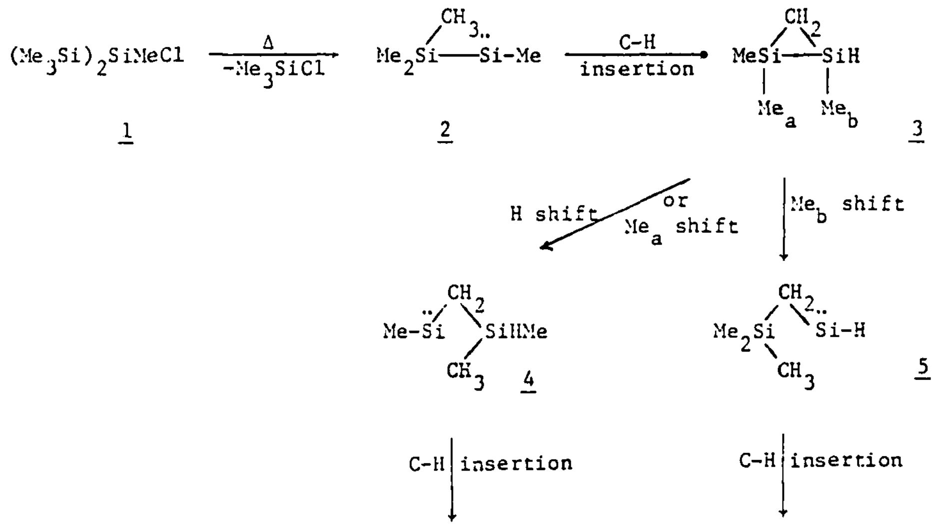
$Me_3SiSiCD_3$: was generated in order to answer the question: does $Me_3SiSiMe$: rearrange to Me_3SiCH_2SiH: via a silene intermediate as suggested by Davidson, or instead via a disilirane, as suggested by Wulff, Goure and Barton. The disilirane mechanism was found to predominate. Transposition of $Me_3SiSiCD_3$: to $CD_3Me_2SiSiMe$: provides evidence for the reversibility of the rearrangement of tetramethyldisilene to methyl(trimethylsilyl)silylene.

Key words: Silylsilylenes; mechanism; disilirane; silene.

A milestone in the evolution of modern organosilicon chemistry was reached a decade ago, when Wulff, Goure, and Barton reported the formation of isomeric 1,3-disilacyclobutanes from the gas-phase pyrolysis of 2-chloroheptamethyltrisilane.[1] This was the first indication of the occurrence of *alpha*-silylsilylene to *beta*-silylsilylene rearrangements, key steps in the mechanism that was suggested by Barton *et al.* to account for the products formed:



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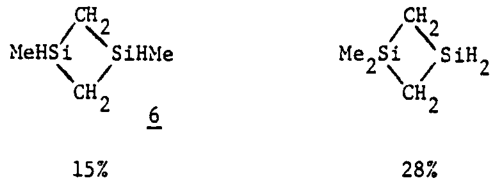
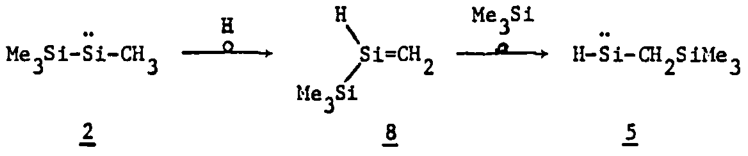
* Permanent address: Department of Chemistry, Yonsei University, Kangwondo 220-13, South Korea.
** Author to whom correspondence should be addressed.



SCHEME I

The formation in higher yield of a product that *requires* the migration of a methyl group during the ring-opening of a disilirane was surprising. While *alpha*-eliminations of acyclic disilanes leading to the formation of silylenes upon the migration of hydrogen, halogen and alkoxy groups are well-known,[2] Davidson and coworkers have found that migration of a methyl group in such a process requires a higher activation energy.[3] Barton and coworkers suggested that the explanation may be the *reversibility* of hydrogen migration, permitting an equilibrium between **3** and **4**. In the intervening years, however, the conversion of $Me_3SiSiMe$: (**2**) to Me_3SiCH_2SiH: (**5**) by a reaction sequence quite different from that shown in Scheme I has become a reasonable alternative.

It had been proposed in 1976 that an alkylsilylene could rearrange to a silene via a hydrogen shift,[4] and such a transformation,[5,6] followed by the shift of a trimethylsilyl group, can lead to the isomerization of **2** to **5**, as shown in Scheme II below:



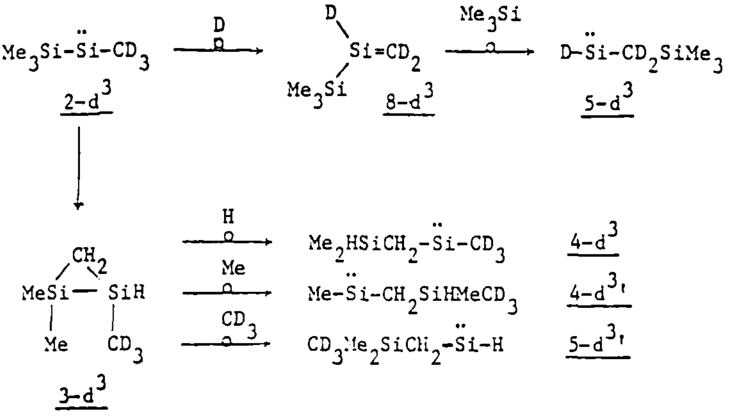
SCHEME II

Davidson and Scampton have suggested that the silene route to Me_3SiCH_2SiH: is *ca.* 10^3 times as rapid as the disilirane route at 850 K, and have obtained good agreement between the ratio of disilacyclobutanes **6** and **7** predicted on the basis of their estimated activation parameters and the experimental values.[5]

The question thus remained unanswered: How does the *alpha*-silylsilylene to *beta*-silylsilylene rearrangement **2** → **5** take place? It was decided to investigate the mechanism of rearrangement of **2** to **5** by employing a label that would distinguish the operation of the *alpha*-silylsilylene, disilirane, *beta*-silylsilylene route of Scheme I from the *alpha*-silylsilylene, silene, *beta*-silylsilylene route of Scheme II. A trideuteromethyl group at the divalent silicon atom serves this function as shown in Scheme III.

Clearly, intermolecular trapping of the *beta*-silylsilylenes is desirable, since Scheme I predicts that intramolecular insertions by the divalent silicon atoms of **4-d**^{3}, **4-d**$^{3'}$, **5-d**^{3} and **5-d**$^{3'}$ into carbon-hydrogen bonds of methyl groups would lead to ambiguous product mixtures. A mixture of the same "isotopomeric" 1,1-dimethyl-

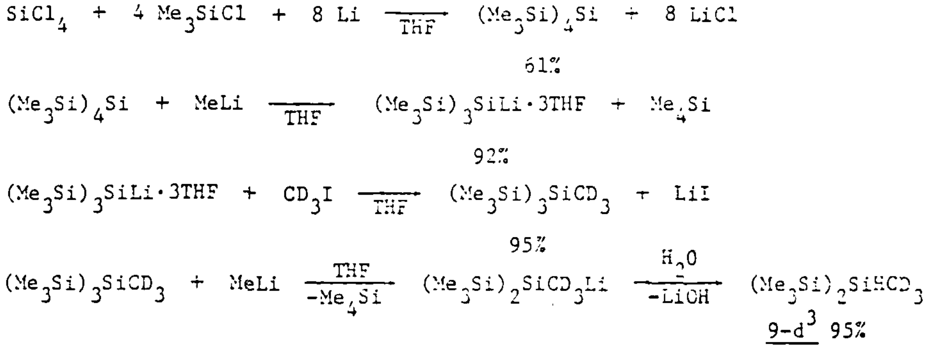
1,3-disilacyclobutanes (**7-d**^{3} and **7-d**$^{3\prime}$)) would be formed by intramolecular insertion from **5-d**^{3} and **5-d**$^{3\prime}$ although in different ratios, and the same "isotopomeric" 1,3-dimethyl-1,3-disilacyclobutanes (**6-d**^{3} and **6-d**$^{3\prime}$), again in different ratios, would be



SCHEME III

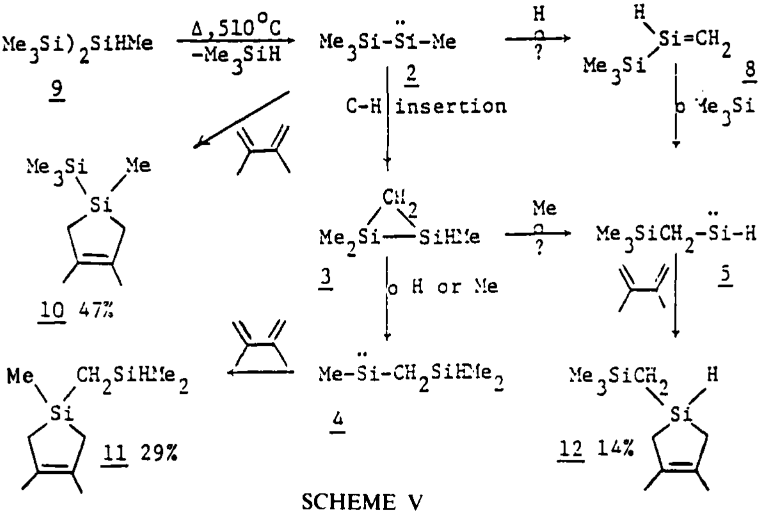
formed by intramolecular insertion from **4-d**^{3} and **4-d**$^{3\prime}$.[7] In contrast, intermolecular addition or insertion reactions of **4-d**^{3}, **4-d**$^{3\prime}$, **5-d**^{3}, and **5-d**$^{3\prime}$ could be predicted to lead to distinct products that reveal the pathways that formed them.

The following synthetic scheme, based on the work of Gilman,[8] and Brook,[9] was adopted to obtain the required silylene precursor:



SCHEME IV

It was decided to employ 2,3-dimethylbutadiene as the trapping agent, despite the complexities of the silylene-diene addition mechanism.[10] Studies with other silylenes had given high yields of 1-silacyclopent-3-enes from this substrate.[11] The system was tested with unlabelled silylene precursor, synthesized by a route analogous to Scheme IV. Flash vacuum pyrolysis of 1,1,1,2,3,3,3-heptamethyltrisilane at 510°C in the presence of a 20-fold excess of trapping agent led to a high combined yield of the 1-silacyclopent-3-enes derived from addition of silylenes **2**, **4**, and **5** to the diene. The results are given in Scheme V:



SCHEME V

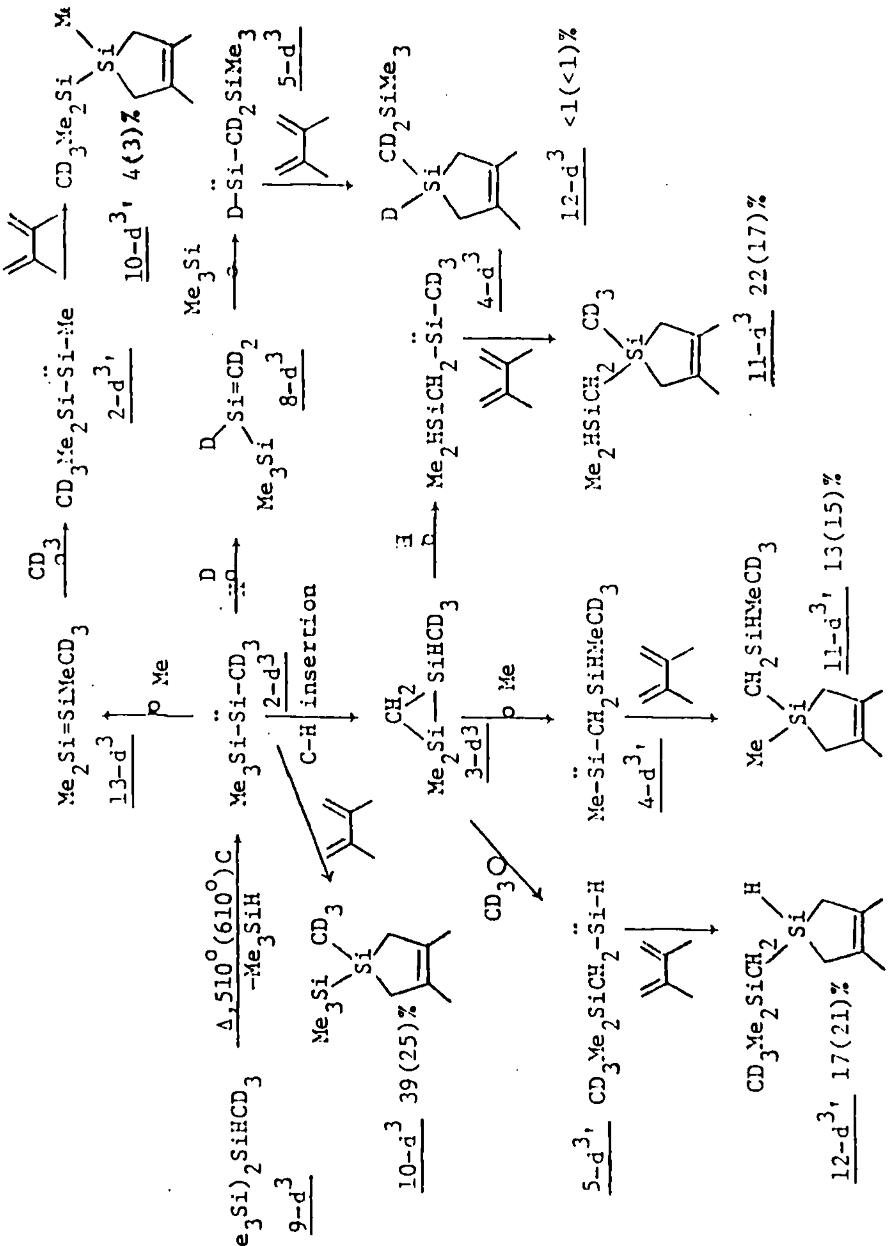
It is interesting to note that the yield of product **12** from the trapping of *beta*-silylsilylene **5** is only half that of **11**, formed by trapping of **4**. This is the reciprocal of the product ratio obtained from intramolecular stabilization of **4** and **5** by Wulff, Goure and Barton, as shown in Scheme I. The difference in the apparent ratios of intermediates **4** and **5** may be due to the change in reaction conditions. Rapid intermolecular trapping of *beta*-silylsilylenes **4** and **5** may interfere with the equilibration of **3** and **4** suggested by Barton.

Flow pyrolysis of **9-d**^{3}, the precursor to the labelled silylene **2-d**^{3} at two different temperatures led to the results shown in Scheme VI. These point rather definitely to a minor role, at most, for silene intermediates in the rearrangement of *alpha*-silylsilylenes to *beta*-silylsilylenes under these reaction conditions.

The distribution of the labelled isomers was determined by integration of the ^{1}H and ^{2}H NMR spectra of the structural isomers isolated by preparative gas-chromatography: **10** (mixture of **10-d**^{3} and **10-d**$^{3'}$), **11** (mixture of **11-d**^{3} and **11-d**$^{3'}$), and **12** (>95% **12-d**$^{3'}$, <1% yield of **12-d**^{3} found[12]). The low yield of **12-d**^{3} and the formation of **12-d**$^{3'}$, indicate that the rearrangement of methyl(trimethylsilyl)silylene **2** to trimethylsilylmethylsilylene **5** occurs predominantly, under these reaction conditions, via formation of a disilirane intermediate **3** followed by ring opening with methyl-migration, as suggested by Wulff, Goure and Barton.[1] The rearrangement of methyl(trimethylsilyl)silylene **2** to trimethylsilylmethylsilylene **5** via 1-trimethylsilylsilene **8** was at most a minor pathway, contributing less than 5% relative to rearrangement via disilirane **3**.

Despite the impressive results obtained from modelling of silylene reactions with the use of estimated activation parameters,[3,5] the present results underscore the need for direct measurement of the rate constants and their temperature dependences for elementary steps in complex reaction sequences.

In addition to establishing a disilirane intermediate in the rearrangement of **2** to **5**, the presence of the trideuteromethyl group permits the first experimental estimates of the relative rates of processes that consume disilirane **3-d**^{3}. It may safely be assumed that the intramolecular Si—H insertions by divalent silicon centers that


(Me3Si)2SiHCD3
9-d3
Δ, 510°(610°)C
-Me3SiH
Me3Si-Si-CD3
2-d3
Me2Si=SiMeCD3
13-d3
~Me
~CD3
CD3Me2Si-Si-Me
2-d3'
CD3Me2Si
10-d3', 4(3)%
~D
Me3Si
D
Si=CD2
8-d3
~Me3Si
D-Si-CD2SiMe3
5-d3
D
CD2SiMe3
12-d3 <1(<1)%
C-H insertion
Me3Si
CD3
10-d3 39(25)%
Me2Si—SiHCD3
CH2
3-d3
~H/D
Me2HSiCH2-Si-CD3
4-d3
Me2HSiCH2
CD3
11-d3 22(17)%
~Me
Me-Si-CH2SiHMeCD3
4-d3'
Me
CH2SiHMeCD3
11-d3', 13(15)%
~CD3
CD3Me2SiCH2-Si-H
5-d3'
CD3Me2SiCH2
H
12-d3', 17(21)%

lead **4-d**^{3} and **4-d**$^{3\prime}$ to revert back to **3-d**^{3} occur at the same rate, since these processes differ by only a secondary isotope effect. Therefore the ratio of **4-d**^{3} and **4-d**$^{3\prime}$ depends on the relative rates of H-migration and Me-migration in the ring-opening of **3-d**^{3}. The ratio of the products, **11-d**^{3} from **4-d**^{3} and **11-d**$^{3\prime}$ from **4-d**$^{3\prime}$ suggests that the ratio of the rates of H-migration and Me-migration (per Me-group) is *ca.* 3.4:1.

The observation that the yield of **12-d**$^{3\prime}$ is higher than that of **11-d**$^{3\prime}$ can be understood when it is noted that **4-d**$^{3\prime}$, whose addition forms **11-d**$^{3\prime}$, can revert to disilirane **3-d**^{3} via Si—H insertion, not available for reversion of **5-d**$^{3\prime}$, whose adduct is **12-d**$^{3\prime}$. If all methyl group migrations in the ring opening of **3-d**^{3} occurred at the same rate, a yield of **12-d**$^{3\prime}$ higher than that of **11-d**^{3} would require that the rate of reversion of **4-d**$^{3\prime}$, (and also of **4-d**^{3}) to **3-d**^{3} be more than twice the rate of silylene addition to 2,3-dimethylbutadiene. Since Me-migration and CD_3-migration in the ring opening of **3-d**^{3} are not degenerate processes, an alternative explanation for the ratio of the products **12-d**$^{3\prime}$ and **11-d**$^{3\prime}$ is simply that CD_3-migration is more rapid than Me-migration, per methyl group.

A further conclusion may be drawn from the formation of **10-d**$^{3\prime}$, a product indicative of the 'transposition'[6] of **2-d**^{3} to **2-d**$^{3\prime}$, a silylene-to-silylene rearrangement that is degenerate in the absence of label. In light of the evidence presented for a disilene intermediate in a related non-degenerate transposition,[6] it is safe to suggest that **2-d**^{3} rearranges to **2-d**$^{3\prime}$, via disilene **13-d**^{3}. Evidence is thus finally at hand that the rearrangement of tetramethyldisilene **13** to methyl(trimethylsilyl)silylene **2**, a seminal discovery by Wulff, Goure and Barton, is *reversible*. In recognition of the stimulus provided by this discovery for the development of organosilicon chemistry in the past decade, we propose that this reaction be called the Barton rearrangement.

EXPERIMENTAL

General Data. All preparative reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen or argon. Solvents were dried using standard techniques. All air-sensitive liquids and the dried solvents were transferred by standard syringe or double-needle techniques.

^{1}H- ^{2}H- and ^{13}C-NMR spectra were recorded on Varian XL-300 and VXR-500 FT spectrometers. Combined gas chromatography-mass spectroscopy was performed on a Finnegan 3200 mass spectrometer operating at an ionizing energy of 70 eV. Analytical gas chromatography was carried out on a Gow-Mac model 39-750 instrument with a flame ionization detector employing a 10 ft ⅛ inch o.d. stainless steel column with 15% DC-200 on Chromosorb-W. Preparative gas chromatography was done on an instrument constructed in this laboratory, with a thermal conductivity detector employing Gow-Mac code 13-002 dual rhenium tungsten filaments and a 15 ft ¼ inch o.d. aluminum column with 10% DC-200 silicone oil on ABS Anakrom 60/80 mesh packing or a 10 foot ¼ inch o.d. aluminum column with 10% SE-30 silicone oil on ABS Anakrom 60/80 mesh packing.

Reported yields are based on the unrecovered silylene precursor and were determined by gas chromatography with the aid of an internal standard, hexadecane. Gas chromatographic response factors were determined for most of the isolated products. Response factors for isomeric products of similar structure were in some cases assumed to be equal. For a few products that could not be isolated in pure form, response factors were estimated from those for similar structures.

In the case of pairs of deuterated products differing only in the positions of the labels, **10-d**^{3} and **10-d**$^{3\prime}$, **11-d**^{3} and **11-d**$^{3\prime}$, **12-d**^{3} and **12-d**$^{3\prime}$, the individual yields were determined by first obtaining the total yields of each product pair by gas chromatography, and then measuring the ratio of each pair of isolated products from the integration of the ^{2}H NMR spectrum.

Materials. Tetrakis(trimethylsilyl)silane: synthesized by the method of Gilman and Smith.[13]

Lithiotris(trimethylsilyl)silane $(Me_3Si)_3SiLi$ 3THF: synthesized by the method of Gutekunst and Brook.[14]

Methyltris(trimethylsilyl)silane. To a stirred solution of 5.2 g (11 mmol) lithiotris(trimethylsilyl)silane in 100 ml dry THF under a nitrogen atmosphere in an ice-water bath was slowly added 2.0 ml (12 mmol) CH_3I from an air-tight syringe. After 2 h stirring the reaction mixture was worked up and fractionally distilled to yield 2.5 g (87%) methyltris(trimethylsilyl)silane bp 106–7°C (30 torr) (lit. 94–5°C (8 torr)[15]: ^1H NMR (C_6D_6) δ 0.575 (s, 27H, $SiMe_3$), 0.488 (s, 3H, SiMe).

1,1,1,2,3,3,3-Heptamethyltrisilane 9. To a stirred solution of 10 g (38 mmol) methyltris(trimethylsilyl)silane in 150 ml dry THF under a nitrogen atmosphere at room temperature was slowly added 33 ml (45 mmol) of a 1.4 M solution of methyllithium-lithium bromide complex in Et_2O (Aldrich). After 3 d stirring the reaction mixture was hydrolyzed with deionized water. The organic layer was separated and combined with hexane extracts of the aqueous layer and dried over anhydrous sodium sulfate. GC analysis indicated a 95% yield of 1,1,1,2,3,3,3-heptamethyltrisilane, isolated by evaporation of solvent and preparative gas chromatography: ^1H-NMR (C_6D_6) δ 0.141 (d, 3H, J = 4.5 Hz, SiMe), 0.163 (s, 18H, $SiMe_3$), 3.370 (q, 1H, J = 4.5 Hz, Si—H); MS (70 eV) *m/e* (relative intensity) 190 (M^+, 12), 175 (12), 131 (7), 116 (32), 102 (34), 101 (24), 73 (100), 59 (13).

Trideuteromethyltris(trimethylsilyl)silane. To a stirred solution cooled in a water-ice bath of 18 g (38 mmol) $(Me_3Si)_3SiLi$ 3THF (white crystals) dissolved in 150 mL dry THF under a nitrogen atmosphere was added 3.2 mL (49 mmol) CD_3I (99.5 + atom % D, Aldrich, d = 2.276) from a disposable syringe. Upon addition of the CD_3I, the yellow-green reaction mixture turned colorless. After 1 h stirring, GLC analysis indicated that the reaction was complete, giving a 95% yield of trideuteromethyltris(trimethylsilyl)silane, which was isolated as described above for 1,1,1,2,3,3,3-heptamethyltrisilane. ^1H-NMR (C_6D_6) δ 0.580 (s, 27H, $SiMe_3$).

1,1,1,3,3,3-Hexamethyl-2-trideuteromethyltrisilane **9-d^3**. To a stirred solution cooled in a water-ice bath of 9 g (34 mmol) of $(Me_3Si)_3SiCD_3$ in 100 mL dry THF under an argon atmosphere was added dropwise 38 mL (57 mmol) of a 1.4 M solution of methyllithium-lithium bromide complex in Et_2O (Aldrich). After 48 h stirring at room temperature, GLC analysis indicated that the reaction was 98% complete. The reaction mixture was hydrolyzed with deionized water, and the organic layer was separated and combined with pentane extracts of the aqueous layer, and then dried with anhydrous sodium sulfate overnight. After removal of the solvent under reduced pressure a 95% yield of $(Me_3Si)_2SiHCD_3$ was obtained and purified by preparative gas chromatography. ^1H-NMR (C_6D_6) δ 0.168 (s, 18H, $SiMe_3$), 3.360 (s, 1H, SiH); MS (70 eV) *m/e* (relative intensity) 193 (M^+, 10), 178 (13), 120 (10), 119 (38), 105 (44), 104 (16), 76 (52), 73 (100) 59 (8).

Gas-Phase Pyrolyses. The flow vacuum pyrolyses were carried out in a vertical, unpacked quartz tube, 10 ml i.d. × 18 cm, incorporated in a vacuum flow system that has been described previously.[6] The hot zone was passivated by treatment with hexamethyldisilazane (1.5 mL evaporated through the system at reaction temperature) before each pyrolysis experiment. A gaseous mixture of silylene precursor and trapping agent was delivered from a 1 L reservoir through a ball-type flow meter and the pressure in the system was measured just upstream from the hot-zone by a calibrated thermocouple vacuum gauge. Residence times were less than one-tenth s. The reaction mixture was trapped ca. 12 cm downstream from the hot-zone in a U-trap immersed in liquid N_2. After a pyrolysis experiment, typical duration 2 to 4 min, the reaction mixture was subjected to a preliminary fractionation by trap-to-trap distillation in the vacuum line to which the pyrolysis flow system is attached. Further separation and isolation of products was carried out by gas chromatography, with transfer of products via septum-capped ampoules and gas-tight syringes.

Pyrolysis of 1,1,1,2,3,3,3-Heptamethyltrisilane **9** *in the Presence of 2,3-Dimethyl-1,3-butadiene.* A mixture of 51 mg (0.27 mmol) **9** and 440 mg (5.37 mmol) 2,3-dimethyl-1,3-butadiene was degassed in the reservoir and then evaporated with an infrared heat-gun before being passed during a 2 min period through the hot-zone at 510°C, 2 torr total pressure, residence time 2 ms. The pyrolysis was repeated three times under the same conditions and the product mixtures were combined. Conversion of **9** was ca. 80%. The products were separated by gas chromatography on a DC-200 column and consisted of: a mixture of 1,1- and 1,3-dimethyl-1,3-disilacyclobutanes **6** and **7** (3%), 1,3,4-trimethyl-1-trimethylsilyl-1-silacyclopent-3-ene **10** (47%), 1,3,4-trimethyl-1-(dimethylsilyl)methyl-1-silacyclopent-3-ene **11** (29%), and 3,4-dimethyl-1-(trimethylsilyl)methyl-1-silacyclopent-3-ene **12** (14%). Spectroscopic data for compounds **10**, **11**, and **12** are given in Table I. Exact mass determinations: calculated for $C_{10}H_{22}Si_2$ (**10**–**12**) 198.1260; measured 198.126 (**10**), 198.126 (**11**), 198.125 (**12**).

TABLE I

NMR and MS data for reaction products from the flow pyrolysis of 1,1,1,2,3,3,3-heptamethyltrisilane **9** and 1,1,1,3,3,3-hexamethyl-2-trideuteromethyltrisilane **9-d^3** in the presence of 2,3-dimethylbutadiene

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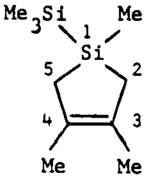
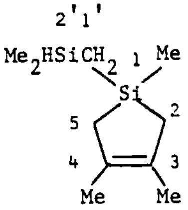


10

^{1}H NMR (C_6D_6) δ 0.112 (s, 9H, $SiMe_3$), 0.168 (s, H, SiMe), 1.499 (m, Δδ = 0.198), J_{gem} = 17.0 Hz, C_2—H, C_5—H), 1.734 (s, 6H, C_3—Me, C_4—Me)

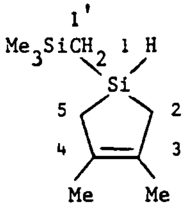
mass spectrum, *m/e* (relative intensity) 198 (parent, 42), 183 (52), 125 (98), 124 (26), 123 (47), 116 (29), 109 (36), 97 (23), 85 (16), 83 (24), 73 (base, 100), 59 (45)



11

^{1}H NMR (C_6D_6) δ −0.243 (d, 2H, $J_{2'1'}$ = 3.9 Hz, $C_{1'}$—H), 0.070 (d, 6H, *J* = 3.6 Hz, $Si_{2'}$—Me), 0.151 (s, 3H, Si_1—Me), 1.378 (m, 4H, Δδ = 0.084, J_{gem} = 18.5 Hz, C_2—H, C_5—H), 1.730 (s, 6H, C_3—Me, C_4—Me), 4.195 (nonet, 1H, *J* = 3.9 Hz, $Si_{2'}$—H)

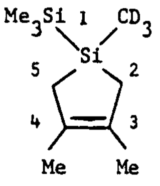
mass spectrum, *m/e* (relative intensity) 198 (parent, 16), 183 (13), 157 (11), 156 (54), 155 (30), 142 (17), 141 (base, 100), 129 (14), 116 (13), 101 (13), 73 (30), 59 (18)



12

^{1}H NMR (C_6D_6) δ −0.257 (d, 2H, $J_{11'}$ = 4.8 Hz, $C_{1'}$—H), 0.057 (s, 9H, $SiMe_3$), 1.469 (m, 4H, Δδ = 0.300, J_{gem} = 17.9 Hz, C_2—H, C_5—H), 1.704 (s, 6H, C_3—Me, C_4—Me), 4.402 (septet, 1H, $J_{1'1}$, J_{21}, J_{51} = 3.6 Hz, Si_1—H)

mass spectrum, *m/e* (relative intensity) 198 (parent, 12), 157 (13), 156 (58), 155 (22), 141 (base, 100), 142 (16), 129 (15), 116 (16), 101 (25), 83 (12), 73 (29), 59 (26).

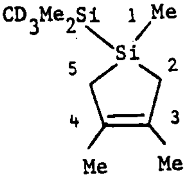


10-d^3

^{1}H NMR (C_6D_6) δ 0.111 (s, 9H, $SiMe_3$), 1.498 (m, 4H, δ = 0.193, J_{gem} = 16.8 Hz, C_2—H, C_5—H), 1.732 (s, 6H, C_3—Me, C_4—Me)

^{2}H NMR (C_6D_6) δ 0.100 (s, 3D, Si_1—Me)

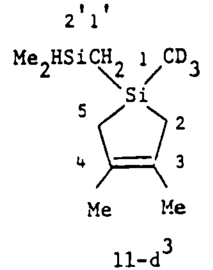
mass spectrum (mixture of **10-d^3** and **10-d$^{3'}$**), *m/e* (relative intensity) 201 (parent, 14), 186 (18), 128 (base, 100), 127 (30), 126 (36), 125 (28), 119 (43), 109 (40), 86 (23), 76 (81), 73 (92), 62 (62), 59 (40).



10-d$^{3'}$

^{1}H NMR^a (C_6D_6) δ 0.167 (s, 6H^a, $SiMe_2$), 0.167 (s, 3H, Si_1—Me), 1.498 (m, 4H^a, δ = 0.193, J_{gem} = 16.8 Hz, C_2—H, C_5—H), 1.732 (s, 6H, C_3—Me, C_4—Me)

^{2}H NMR (C_6D_6) δ 0.048 (s, 3D, $SiMe_3$)

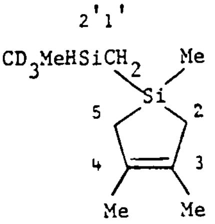


11-d³

^{1}H NMR^b (C_6D_6) δ −0.248 (d, 2H, $J_{2'1'}$ = 3.9 Hz, $C_{1'}$—H), 0.073 (d, 6H^b, $J_{2'H,Me}$ = 3.9 Hz, $Si_{2'}$—Me), 1.389 (m, 4H^b, Δδ 0.084, J_{gem} = 18.5 Hz, C_2—H, C_5—H), 1.743 (s, 6H^b, C_3—Me, C_4—Me), 4.220 (nonet, 1H^b, J = 3.9 Hz, $Si_{2'}$—H)

^{2}H NMR (C_6D_6) δ 0.087 (s, 3D^b, Si_1—Me)

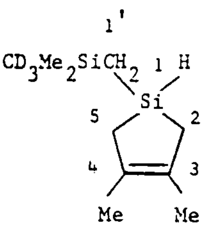
mass spectrum (mixture of **11-d³** and **11-d³′**), *m/e* (relative intensity) 201 (parent, 11), 184 (10), 159 (99), 158 (59), 145 (33), 144 (base, 100), 143 (35), 141 (79), 132 (39), 119 (49), 104 (51), 76 (71), 73 (33), 62 (54), 59 (51)



11-d³′

^{1}H NMR^b (C_6D_6) δ −0.248 (d, 2H, $J_{2'1'}$ = 3.9 Hz, $C_{1'}$—H), 0.073 (d, 3H^b, $J_{2'H,Me}$ = 3.9 Hz, $Si_{2'}$—Me), 0.158 (s, 3H, Si_1—Me), 1.389 (m, 4H^b, Δδ = 0.084, J_{gem} = 18.5 Hz, C_2—H, C_5—H), 1.743 (s, 6H^b, C_3—Me, C_4—Me), 4.227 (sextet, 1H^b, J = 3.9 Hz, $Si_{2'}$—H)

^{2}H NMR (C_6D_6)δ 0.001 (3D^b, $Si_{2'}$—Me)



12-d³′

^{1}H NMR (C_6D_6) δ −0.261 (d, 2H, $J_{11'}$ = 4.2 Hz, $C_{1'}$—H), 0.055 (s, 6H, $Si_{2'}$—Me), 1.472 (m, 4H, Δδ = 0.298, J_{gem} = 17.4 Hz, C_2—H, C_5—H), 1.707 (s, 6H, C_3—Me, C_4—Me), 4.408 (septet, 1H, $J_{1'1}$, J_{21}, J_{51} = 3.6 Hz, Si_1—H)

^{2}H NMR (C_6D_6) δ 0.028 (s, 3D, $Si_{2'}$—Me)

mass spectrum, *m/e* (relative intensity) 201 (parent, 8), 186(7), 184(7), 159 (62), 158 (37), 144 (base, 100), 143 (25), 141 (52), 132 (26), 119 (27), 104 (29), 76 (62), 73 (29), 62 (32), 59(32).

Pyrolysis of 1,1,1,3,3,3-Hexamethyl-2-trideuteromethyltrisilane **9-d³** *in the presence of 2,3-dimethyl-1,3-butadiene.* A mixture of 60 mg (0.31 mmol) **9-d³** and 505 mg (6.16 mmol) 2,3-dimethyl-1,3-butadiene was placed in the reservoir, degassed, and then gasified using an infrared 'heat gun'. This reaction mixture was allowed to flow during a 2 min period through the hot-zone at 510°C, 2 torr, residence time 1 ms. The pyrolysis was repeated twice under the same conditions and the pyrolysates were combined. After removal of the low-boiling fraction (trimethylsilane and dimethylbutadiene) by trap-to-trap distillation in the vacuum line from a water-ice bath to liquid nitrogen, the higher-boiling fraction was analyzed and separated by gas chromatography. Conversion of **9-d³** was found to be *ca.* 80%. The products obtained (and their yields) were: 3,4-dimethyl-1-trideuteromethyl-1-trimethylsilyl-1-silacyclopent-3-ene **10-d³** (39%), 1,3,4-trimethyl-1-dimethyl(trideuteromethyl)-1-silacyclopent-3-ene **10-d³′** (4%), 1-dimethylsilylmethyl-3,4-dimethyl-1-trideuteromethyl-1-silacyclopent-3-ene **11-d³** (22%), 1,3,4-trimethyl-1-methyl(trideuteromethyl)silylmethyl-1-silacyclopent-3-ene **11-d³′** (13%), and 1-dimethyl(trideuteromethyl)silylmethyl-3,4-dimethyl-1-silacyclopent-3-ene **12-d³′** (17%).

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[a] Since the spectra of **10-d³** and **10-d³′** were obtained from mixtures of the two, the the areas of those peaks in the NMR spectra of the minor isomer **10-d³**, that overlapped with those of the major isomer **10-d³** are assumed values. This does *not* affect the assay of the mixtures.

[b] Since the spectra of **11-d³** and **11-d³′** were obtained from mixtures of the two, the areas of those peaks in the NMR spectra that were identical or that overlapped are assumed values. This does not affect the assay of the mixtures.

A mixture of 85 mg (0.44 mmol) **9-d**^{3} and 580 mg (7.10 mmol) 2,3-dimethyl-1,3-butadiene was prepared as above and allowed to flow during a 3 min period through the hot zone at 610°C, 2 torr, residence time 2 ms. Conversion of **9-d**^{3} was complete. After fractionation and analysis as described above the products (and their yields) were found to be: **10-d**^{3} (25%), **10-d**$^{3'}$ (3%), **11-d**^{3} (17%), **11-d**$^{3'}$ (15%), and **12-d**$^{3'}$ (17%). Spectroscopic data are given in Table I for compounds **10-d**^{3}, **10-d**$^{3'}$, **11-d**^{3}, **11-d**$^{3'}$ and **12-d**^{3}.

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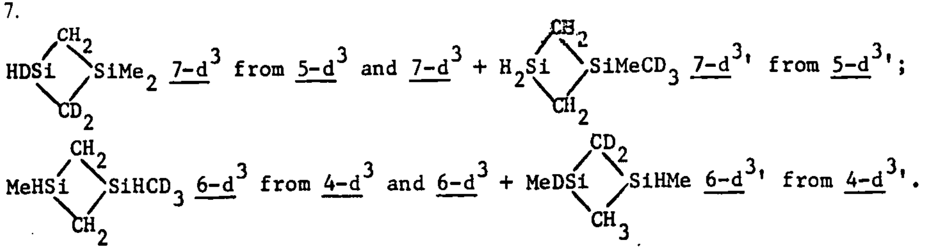

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12. A small peak at δ −0.3 in the ^{2}H NMR spectrum of **12-d**$^{3'}$ could be due to the CD_2 peak of **12-d**^{3} (although no distinct Si—D peak was observed), but its area would represent a less than 1% yield of **12-d**^{3}.
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