1080 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86, 0.93 (2t, 6 H, J = 6 Hz, CH_3CH_2), 0.97 (d, 3 H, J = 6 Hz, CH_3CHCC), 1.24 (d, 3 H, J = 6 Hz, CH_3CHOC), 2.58 (d, 1 H, J = 5 Hz, $CCHHO$), 2.71 (d, 1 H, J = 5 Hz, $CCHHO$), 4.47 (s, 2 H, $C_6H_5CH_2$), 7.31 (b s, 5 H, C_6H_5). Anal. Calcd for $C_{25}H_{38}O_4$: C, 74.59; H, 9.51. Found: C, 74.39; H, 9.36.

Benzyl 2(*S*)-[5(*S*)-Ethyl-3(*S*)-methyl-5-(5(*R*)-ethyl-5-hydroxy-6-(*S*)-methyl-2(*R*)-tetrahydropyranyl)-2(*S*)-tetrahydrofuryl]butyl Ether (5). By the procedure described for the preparation of the alcohols **34**, 120 mg (0.30 mmol) of the epoxide **60** in 3 mL of dry *n*-pentane with 320 mg (1.56 mmol) of copper(I) bromide–dimethyl sulfide complex and 1.4 mL (3.08 mmol) of 2.2 M methyllithium in ether afforded, after chromatography on 10 g of silica gel column with 15% ethyl acetate in petroleum ether, 120 mg (90%) of the alcohol **5**. The spectral characteristics of this material were identical with those of the alcohol derived from degradation of lasalocid A.

2(*S*)-[5(*S*)-Ethyl-3(*S*)-methyl-5-(5(*R*)-ethyl-5-hydroxy-6(*S*)-methyl-2(*R*)-tetrahydropyranyl)-2(*S*)-tetrahydrofuryl]butan-1-ol. To a stirred solution of 0.5 cm (3 mmol) of lithium wire in 10 mL of anhydrous liquid ammonia at −78 °C under argon was added a solution of 54 mg (0.13 mmol) of the monobenzyl ether **5** in 1 mL of dry THF. Cooling was then discontinued (ammonia reflux) and after 1 h, 250 mg (4.7 mmol) of anhydrous ammonium chloride was cautiously added to the reaction mixture. The resulting mixture was then diluted with 20 mL of ether and the ammonia was allowed to evaporate. The resulting suspension was filtered and the solid was washed by trituration with four 10-mL portions of ether. Removal of the solvent at reduced pressure from the combined filtrates and then chromatography of the residue on 10 g of silica gel with 40% ethyl acetate in petroleum ether afforded 42 mg (98%) of the corresponding diol. The spectral characteristics of this material were identical with those of the diol derived from degradation of lasalocid A.

2(*R*)-[5(*S*)-Ethyl-3(*S*)-methyl-5-(5(*R*)-ethyl-5-hydroxy-6(*S*)-methyl-2(*R*)-tetrahydropyranyl)-2(*S*)-tetrahydrofuryl]butanal (61). By the procedure described for the oxidation of the alcohol **33**, 80 mg (0.24 mmol) of the above diol in 3 mL of dry dichloromethane with 10 mg (0.12 mmol) of anhydrous sodium acetate and 133 mg (0.62 mmol) of pyridinium chlorochromate afforded, after chromatography on 10 g of silica gel with 40% ether in petroleum ether, 62 mg (78%) of the aldehyde **61**: evaporative distillation 130–140 °C (0.005 mmHg); $[\alpha]^{22}_D$ −2.5° (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) 3600, 3450, 2750, 1720, 1460, 1390, 1230, 1130, 1100, 1060, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (d, 3 H, J = 6 Hz, CH_3CHCC), 1.18 (d, 3 H, J = 6 Hz, CH_3CHOC), 9.64 (d, 1 H, J = 3 Hz, CHO). Anal. Calcd for $C_{19}H_{34}O_4$: C, 69.90; H, 10.50. Found: C, 69.77; H, 10.44.

4(*S*)-[5(*S*)-Ethyl-3(*S*)-methyl-5-(5(*R*)-ethyl-5-hydroxy-6(*S*)-methyl-2(*R*)-tetrahydropyranyl)-2(*S*)-tetrahydrofuryl]hexan-3-ol. To a stirred solution of 62 mg (0.19 mmol) of the aldehyde **61** in 4 mL of dry THF at −78 °C under argon was added 0.72 mL (0.58 mmol) of an 0.8 M solution of ethylmagnesium bromide in THF. The resulting solution was stirred at 0 °C for 30 min, treated with 5 mL of saturated aqueous NH_4Cl, and then diluted with 25 mL of ether. The organic phase was separated, washed with 10 mL of saturated aqueous NH_4Cl and 10 mL of saturated aqueous NaCl, and then dried ($MgSO_4$). After removal of the solvents at reduced pressure and chromatography of the residue on 10 g of silica gel with 50% ether in petroleum ether, there was obtained 60 mg (89%) of a diastereoisomeric mixture of the corresponding alcohols: evaporative distillation 120–130 °C (0.005 mmHg); IR ($CHCl_3$) 3600, 3500, 1460, 1380, 1130, 1100, 1060, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (d, 3 H, J = 6 Hz, CH_3CHOC).

4(*R*)-[5(*S*)-Ethyl-3(*S*)-methyl-5-(5(*R*)-ethyl-5-hydroxy-6(*S*)-methyl-2(*R*)-tetrahydropyranyl)-2(*S*)-tetrahydrofuryl]hexan-3-one (3). By the procedure described for the preparation of the aldehyde **61**, 35 mg (0.10 mmol) of the above alcohols in 1 mL of dry dichloromethane with 50 mg (0.23 mmol) of pyridinium chlorochromate afforded, after chromatography on 10 g of silica gel with 35% ether in petroleum ether, 31.4 mg (90%) of the ketone **3**. The spectral and physical data obtained on this ketone were identical with those of the same ketone obtained from the reverse aldol of lasalocid A (X537A).

Silacyclobutene Synthesis via Intramolecular Cyclization of Unsaturated Silylenes

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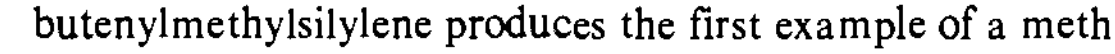
Abstract: Flash vacuum pyrolysis of methoxydisilanes is used to generate 1-, 2-, and 3-propenylsilylenes. Each of these silylenes affords siletene (silacyclobutene) products although the mechanistic origins are probably different in each case. Isobutenylmethylsilylene produces the first example of a methylenesilacyclobutane, and this ring is shown to undergo a remarkable rearrangement to 1,3-dimethylsiletene.

In view of the rich harvest of novel cyclic hydrocarbons which have been generated from intramolecular additions of alkenylcarbenes,[1] it is surprising that the chemistry of only vinylsilylene has been investigated to date.[2] As part of a systematic study of intramolecular reactions of silylenes, we have studied the chemistry of 1-, 2-, and 3-propenylsilylenes and report here that all afford the silacyclobutene ring.

It has been known since 1963 that allylcarbenes undergo intramolecular π addition to produce bicyclo[1.1.0]butanes.[1,3]



thus, in hopes of producing the first example of a 1-silabicyclo[1.1.0]butane, we generated allylsilylene **2** by the thermally induced α elimination of Me_3SiOMe from disilane **1** (680 °c, horizontal quartz chip packed tube (10^{-4} torr). An 87% mass recovery was realized in the flash vacuum pyrolysis (FVP) and Me_3SiOMe was formed in 68% yield. The only other major product was 1-methylsiletene (**3**) (25%, 37% based on Me_3SiOMe). By analogy with carbene chemistry, **3** could have arisen via π addition to form silabicyclo[1.1.0]butane **4**, followed by homolysis of the internal ring bond[4] and hydrogen migration, or by cyclization of 1-sila-1,3-butadiene **5**, as 1-sila-1,3-butadienes are known to close to siletenes.[6] Formation of **5** could arise from 1,2-hydrogen migration to silicon in **2**. However, the thermal rearrangement of a silylene to a silene by hydrogen migration has never been observed.[7] Alternatively, **3** might arise directly from

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(1) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971; pp 332–342.

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

(3) Lemal, D. M.; Menger, F.; Clark, G. W. *J. Am. Chem. Soc.* **1963**, *85*, 2529.

(4) This is not the path of bicyclo[1.1.0]butane which thermally isomerizes to 1,3-butadiene through cleavage of two external ring bonds.[5]

(5) Doering, W. von E.; Coburn, J. F., Jr. *Tetrahedron Lett.* **1965**, 991.

(6) Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *216*, C5.

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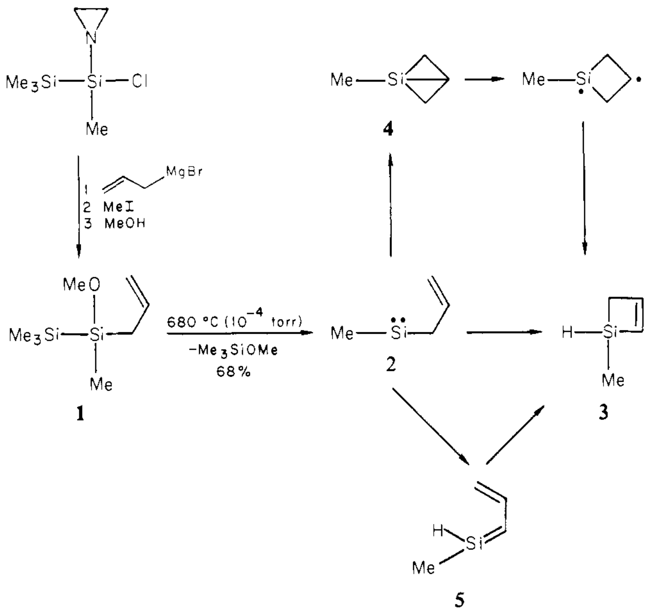
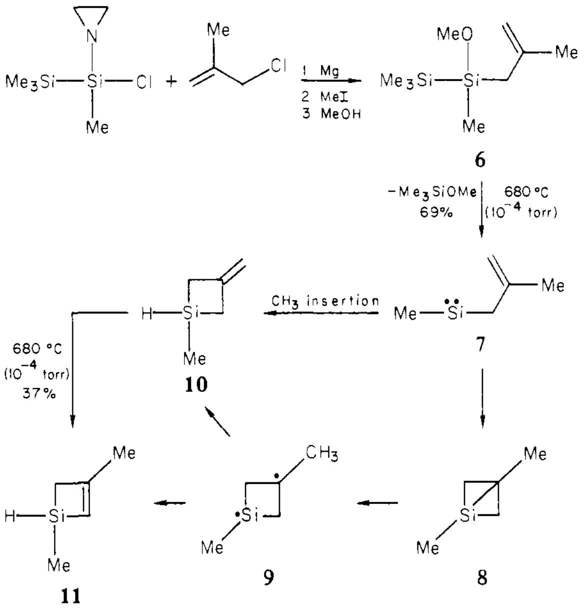


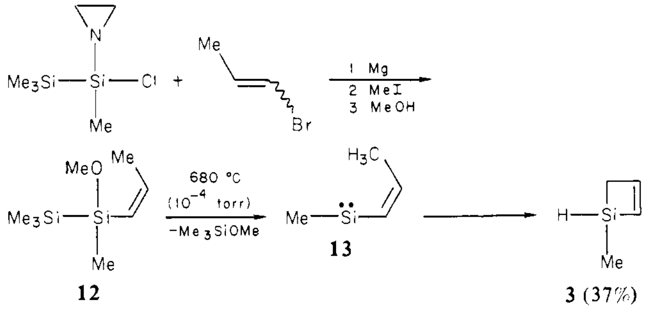
silylene insertion into a terminal vinyl C–H bond. As this process has never been observed for the more reactive carbenes, it seems unlikely, and we favor the route involving the intermediacy of silabicyclo[1.1.0]butane **4**.

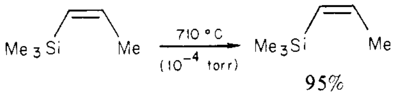
In an attempt to demonstrate generality for this synthesis of siletenes, silylene **7** was generated by FVP of disilane **6** (680 °C (10^{-4} torr)). Indeed, the expected 1,3-dimethylsiletene **11** was formed in 20%. However, the major product from **7** was 1-methyl-2-methylene-1-silacyclobutane (**10**, 41%). Again it is possible to rationalize the formation of both **10** and **11** from π addition of **7** to form silabicyclo[1.1.0]butane **8**. Homolysis of the central ring bond of **8** leads to 1,3-diradical **9** which can serve as the precursor of either **10** or **11** via hydrogen migration. Alternatively **10** could be formed directly from **7** by silylene insertion into a methyl C–H bond.[9] Indeed, it is quite likely that



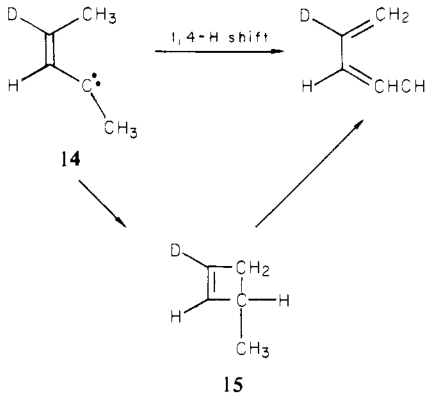
10 is the sole initial product of **7** since we find that **10** isomerizes exclusively to **11** under the reaction conditions. The isomerization of **10** to **11** is surprising in view of the fact that the analogous isomerization of methylenecyclobutane has never been observed in the extensive studies on the thermolysis of this system.[11]

If allylic C–H insertion were really the origin of **10**, then siletene **3** should also be produced by 1-propenylsilylene **13**. Indeed, pyrolysis of *cis*-1-propenyldisilane **12** (680 °C (10^{-4} torr)) afforded only two volatile products, Me_3SiOMe (79%) and **3** (37%, 47% based on Me_3SiOMe). Certainly the formation of **3** from **13** is most reasonably rationalized by direct methyl C–H insertion. The possibility that **13** first rearranges to silylene **2** is rendered unlikely by the observation that *cis*-1-trimethylsilylpropene undergoes FVP (710 °C (10^{-4} torr) 95% recovery) without structural or stereochemical isomerization.





With regard to the mechanism of the conversion of silylene **13** to siletene **3**, it is of interest to consider the recent report by Perez of the thermal generation of the exactly analogous carbene **14**.[12]



The object of that work was to determine whether the sole product, 1,3-pentadiene, was formed by a 1,2- or 1,4-hydrogen shift, and by a deuterium labeling experiment the Argentinean group concluded that the product resulted from a 1,4-shift of hydrogen. In view of our results and in consideration of their reaction conditions (800 °C (0.1 torr)), we would suggest that 1,3-pentadiene is not formed by a direct 1,4-shift of hydrogen but rather through initial C–H insertion to form cyclobutene **15** which undergoes electrocyclic ring opening to the observed product with the same labeling results.

It is far less obvious what should be expected of the isomeric 2-propenylsilylenes. Quite surprisingly, we find that generation of 2-propenylsilylene **17** through FVP of 2-propenyldisilane **16** also affords siletene **3** (16%) as the only product isomeric with **17**. That silylene **17** is actually produced in this thermolysis was convincingly demonstrated by copyrolysis of **16** and 2,3-di-

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(7) The reverse rearrangement of a silene to a silylene via 1,2-hydrogen migration is a highly controversial subject.[8] However, the possibility of conjugation in **5** certainly should make the **2** → **5** transformation more attractive than when only alkyl ssubstituents are present.

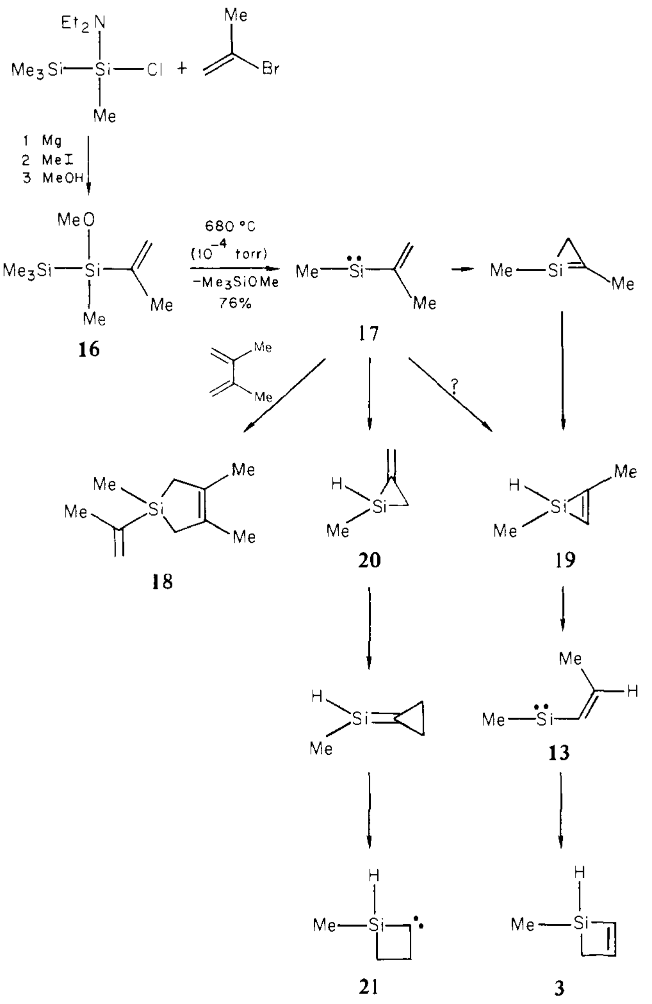
(8) Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1982**, *1*, 210.

(9) Intramolecular alkyl C–H insertion by silylenes can be an extremely efficient process.[8,10]

(10) Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236. Gusel'nikov, L. E.; Lopatnikova, E.; Polyakov, Yu. P.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1980**, *253*, 1387.

(11) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 90–94.

(12) Perez, J. D.; Yranzo, G. I. *J. Org. Chem.* **1982**, *47*, 2221.



methyl-1,3-butadiene, an efficient silylene trap. The copyrolysis afforded silacyclopentene **18** (51% yield) as expected from addition of **17** to the diene. With considerable trepidation, we suggest that here the origin of **3** involves isomerization of silirene **19** to silylene **13**. Indeed, we have very recently obtained independent evidence for this very isomerization in the reactions of hydrido- and silylsilylenes with acetylenes.[13] An alternative route not involving **13** can be envisioned as proceeding through isomerization of silamethylenecyclopropane **20** to carbene **21**. Further studies must be carried out to provide any mechanistic distinction.

Experimental Section

General Data. Proton NMR spectra were recorded on a Varian Model EM-360 spectrometer. GC mass spectral data were collected at 70 eV on a Finnegan Model 4023 mass spectrometer. Exact mass measurements were obtained on an AEI MS-902 mass spectrometer. Gas chromatographic separations were performed on a Varian-Aerograph Series 1700 gas chromatograph. Unless otherwise specified, all yields are NMR yields calculated from internal standards and are absolute.

1-Aziranyl-1-chlorotetramethyldisilane. To a stirred solution of 7.50 g (0.174 mol) of azirane in 100 mL of freshly distilled ether (from CaH_2) at −78 °C under a nitrogen atmosphere was added 75.0 mL of 2.40 M *n*-butyllithium in hexane (0.18 mol). After the mixture was stirred for 30 min at −78 °C, this solution was transferred via cannula to a stirred solution of 32.79 g (0.175 mol) of 1,1-dichlorotetramethyldisilane in 250 mL of dry Et_2O at −78 °C over a 30-min period. The mixture was allowed to warm to room temperature and then stirred for 4 h. After removal of salts by Celite filtration, the filtrate was concentrated by rotary evaporation. Distillation of the residue at 62–65 °C (0.5 torr) afforded 23.04 g of 1-aziranyl-1-chlorotetramethyldisilane: ^1H NMR (CCl_4) δ 0.23 (s, 9 H), 0.52 (s, 3 H), 1.74 (s, 4 H).

1-Allyl-1-methoxytetramethyldisilane (1). To a stirred solution of 0.0232 mol of allylmagnesium bromide in 40 mL of Et_2O was added 3.64 g (0.0188 mol) of 1-aziranyl-1-chlorotetramethyldisilane (vide supra). After the mixture was stirred for 30 min, 2.0 mL of CH_3I was added, followed by 2.50 mL of CH_3OH. The reaction was stirred overnight, then diluted with hexane, and filtered through Celite. The filtrate was concentrated by rotary evaporation. Distillation afforded 2.04 g (58%) of **1**: bp 45–46 °C (1 torr); ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), (s, 3 H), 1.82 (d, $J = 8$ Hz, 2 H), 3.50 (s, OMe, 3 H), 4.62–5.12 (m, 2 H, $=CH_2$), 5.45–6.22 (m, 1 H); mass spectrum, *m/e* (rel intensity) 188 (7), 173 (21), 147 (100), 131 (18), 117 (43), 73 (82); calcd for $C_8H_{20}OSi_2$ (M^+), *m/e* 188.10528; measd, *m/e* 188.10484.

Vacuum Pyrolysis of 1. Neat **1** (0.6687 g, 3.56 mmol) was distilled (25 °C (1 × 10^{-4} torr)) through a 1-ft horizontal quartz tube packed with quartz chips and heated at 680 °C. The pyrolysate was collected in a liquid N_2 cooled trap and constituted a 87% mass recovery (0.5795 g). Analysis of the pyrolysate by both GC (20 ft, 20% SE-30 on Chromosorb W) and NMR revealed two products. The major product was identified as Me_3SiOMe (68%) by spectral comparison with an authentic sample. The second product was identified as 1-methylsiletene (25%, 37% based on Me_3SiOMe) **3**: ^1H NMR (C_6D_6) δ 0.17 (d, 3 H, $J = 4$ Hz, collapses to s with $h\nu$ at δ 4.98), 1.54 (2 H, center of doubled AB with $J = 18$, 2 Hz, collapses to AB quartet, $J = 18$ Hz, with $h\nu$ at δ 6.90), 4.98 (apparent pentet, actually overlapped d of q, both *J*'s ca. 4 Hz, 1 H, SiH), 5.92 (d, $J = 7$ Hz, 1 H), 6.89 (m, 1 H, collapses to d of d, $J = 7$, 4 Hz, with $h\nu$ at δ 1.54); mass spectrum, *m/e* (rel intensity) 84 (27), 83 (25), 69 (100), 58 (72); calcd for SiC_4H_8 (M^+), *m/e* 84.0395; measd, *m/e* 84.0393.

2,4,5,5-Tetramethyl-4-methoxy-4,5-disilahex-1-ene (6). To a stirred suspension of excess magnesium turnings in 35 mL of dry THF was added 15 mL of a THF solution containing 2-methyl-3-chloropropene (2.784 g, 0.0307 mmol) and 1-aziranyl-1-chlorotetramethyldisilane (5.01 g, 0.0259 mol) at a rate sufficient to maintain a gentle reflux. After the mixture was stirred for 3 h at room temperature, the solution was decanted from the excess Mg and diluted with hexane. CH_3I (5.0 mL) was then added and followed by MeOH (5 mL). After the mixture was stirred for 1 h, the solution was filtered through Celite and the filtrate concentration by rotary evaporation. Distillation of the residue afforded 2.30 g (44%) of **6**: bp 35–37 °C (0.2 torr); ^1H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 0.25 (s, 3 H), 1.76 (m, 5 H, allylic methyl and methylene, collapses to two s with $h\nu$ at δ 4.59), 3.46 (s, 3 H, OMe), 4.59 (m, 2 H, collapses to AB q with $h\nu$ at δ 1.76); mass spectrum, *m/e* (rel intensity) 202 (M^+, 8), 187 (22), 147 (100), 133 (21), 117 (41), 89 (39), 73 (67), 59 (41); calcd for $C_9H_{22}OSi_2$, *m/e* 202.1209; measd, *m/e* 202.1207.

Vacuum Pyrolysis of 6. Neat **6** (0.2911 g, 1.44 mmol) was distilled (25 °C (1 × 10^{-4} torr)) through a horizontal quartz-packed tube heated at 680 °C with an 82% mass recovery (0.2380 g). GC and NMR analysis of the pyrolysate revealed three major products, and these were isolated by preparative GC (20 ft, 20% SE-30 on Chromosorb W, temperature programmed from 70 °C at 2 deg/min). The first eluted product was Me_3SiOMe (69%); the second was identified as 1,3-dimethylsiletene (**11**, 20%): ^1H NMR (C_6D_6) δ 0.30 (d, 3 H, $J = 4$ Hz, collapses to s with $h\nu$ at δ 5.04), 1.48 (center of AB q, 2 H, $J = 16$ Hz), 1.78 (br s, 3 H, collapses to s with $h\nu$ at δ 0.30), 5.75 (br s, 1 H); mass spectrum, *m/e* (rel intensity) 98 (M^+, 100), 97 (45), 83 (99), 58 (35), 55 (32); calcd for $C_5H_{10}Si$, *m/e* 98.0552; measd, *m/e* 98.0549. The third product was identified as 1-methyl-3-methylene-1-silacyclobutane (**10**, 41%): ^1H NMR[14] (C_6D_6) δ 0.15 (d, 3 H, $J = 4$ Hz, collapses to s with $h\nu$ at δ 4.49), 1.89 (4 H, center of d of d of d of d of d, $J_{CC'} = 16$ Hz, $J_{CD} = 2$ Hz, $J_{C'D} \simeq 3$ Hz, $J_{BC} \sim J_{BC'} \sim J_{AC} \sim J_{AC'} \sim 2$ Hz, collapses to overlapped d of d of d of d (tripled AB q) with $h\nu$ at δ 4.49, collapses to d of d of d (doubled AB q) with $h\nu$ at δ 4.88, $J = 16$, 2, and 3 Hz), 4.49 (m, 1 H, SiH, collapses to d of d, $J = 2$, 3 Hz with $h\nu$ at δ 0.15), 4.88 (pentet, $J = 2$ Hz, collapses to s with $h\nu$ at δ 1.89, 2 H); mass spectrum, *m/e* (rel intensity) 98 (M^+, 72), 97 (46), 83 (100), 71 (11), 70 (28), 59 (11), 58 (51), 55 (32); calcd for $C_5H_{10}Si$, *m/e* 98.0552, measd, *m/e* 98.0548. FVP of **10** (680 °C (10^{-4} torr)) produced a mixture of **10** and **11** (1:0.55). FVP of **11** (0.0480 g, 0.49 mmol) at 680 °C (10^{-4} torr) produced only unreacted **11**.

(*Z*)-4,5,5-Trimethyl-4-methoxy-4,5-disilahex-2-ene (12). To a stirred suspension of excess Mg turnings in 30 mL of THF was added 2.0 mL (2.816 g, 0.0233 mol) of 1-bromopropene (technical grade mixture of *E* and *Z* isomers) in a 30-min period. After the reaction was complete, 2.325 g (0.012 mol) of 1-aziranyl-1-chlorotetramethyldisilane was added in one portion. The solution was stirred for 2 h at room temperature and

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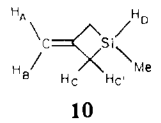
[13] Barton, T. J.; Burns, S. A.; Burns, G. T., submitted for publication.

[14] Structure:



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then decanted from the excess Mg. Addition of 4.0 mL of CH_3I was followed by addition of 5.0 mL of CH_3OH. After the mixture was stirred for 1 h, the solution was diluted with hexane, filtered through Celite, and concentrated by rotary evaporation. The residue was separated by GC (20 ft, 20% SE-30 on Chromosorb W with a temperature program of 130–200 °C at 2 deg/min) to afford 0.4288 g (19%) of **12**: ^1H NMR ($DCCl_3$) δ 0.10 (s, 9 H), 0.27 (s, 3 H), 1.82 (d of d, J = 7 Hz, J = 1 Hz, collapses to d with J = 7 Hz with $h\nu$ at 5.46, 3 H), 3.40 (s, 3 H, OMe), 5.46 (d of q, J = 14 Hz, J = 1 Hz, collapses to d with J = 14 Hz with $h\nu$ at 1.82, 1 H), 6.46 (apparent sextet, actually overlapped d of q, J = 14 Hz, J = 7 Hz, collapses to d with J = 14 Hz with $h\nu$ at 1.82, 1 H); mass spectrum, m/e (rel intensity) 188 (M^+, 15), 173 (100), 132 (60), 115 (55), 88 (40), 73 (50); calcd for $C_8H_{20}OSi_2$, m/e 188.1053; measd 188.1049.

Vacuum Pyrolysis of 12. Neat **12** (0.4288 g, 2.28 mmol) was distilled (25 °C (10^{-4} torr)) through a horizontal quartz-packed tube heated at 680 °C and an 87% mass recovery was obtained. GC and NMR analysis revealed two products: Me_3SiOMe (79%) and **3** (37%, 47% based on Me_3SiOMe). Both were isolated by preparative GC and identified by spectral comparison with authentic samples.

Vacuum Pyrolysis of (*Z*)-1-Trimethylsilylpropene. Neat (*Z*)-1-trimethylsilylpropene was distilled through a horizontial, quartz-packed tube at 710 °C (10^{-4} torr). A 95% mass recovery of unchanged (by GC and NMR) material was obtained.

Synthesis of 1-(Diethylamino)-1-chlorotetramethyldisilane. To a stirred solution of 24.501 g (0.131 mol) of 1,1-dichlorotetramethyldisilane in 200 mL of Et_2O was added 0.136 mol of lithium diethylamide in 100 mL of Et_2O in a 30-min period. After the mixture was stirred for 3 h, the solution was filtered through Celite and then concentrated by rotary evaporation. Distillation of the residue afforded 16.7 g (57%) of the title compound: bp 51–53 °C (0.1 torr); ^1H NMR ($DCCl_3$) δ 0.21 (s, 9 H), 0.49 (s, 3 H), 1.04 (t, J = 7 Hz, 4 H), 2.92 (q, J = 7 Hz, 6 H).

1-Methoxy-1-(2-propenyl)tetramethyldisilane (16). To a stirred suspension of excess Mg turnings in 50 mL of Et_2O was added 2.50 mL (0.0281 mol, 3.405 g) of 2-bromopropene over 1 h. The solution was stirred for an additional hour and then quenched with 4.788 g (0.214 mol) of 1-(diethylamino)-1-chlorotetramethyldisilane (vide supra) in one portion. This solution was stirred for 10 h and then decanted from the excess Mg. The solution was diluted with an equal volume of hexane and cooled to 0 °C, and 5.0 mL of MeI, followed by an excess of MeOH/NaOMe, was added. After the mixture was stirred for 1 h, the solution was filtered through Celite and concentrated by rotary evaporation. The residue was flash distilled (ca. 40 °C (0.1 torr)), and the distillate was then separated by GC (20 ft, 20% SE-30 on Chromosorb W, 140–200 °C at 2 deg/min) to afford 0.898 g (23%) pure **16**: ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 0.20 (s, 3 H), 1.74 (overlapped d of d, $J = J'$ = 1.5 Hz, 3 H), 3.34 (s, 3 H, OMe), 5.17 (overlapped d of q, J = 3 Hz, J = 1.5 Hz, collapses to d with J = 3 Hz with $h\nu$ at 1.74, 1 H), 5.51 (overlapped d of q, J = 3 Hz, J = 1.5 Hz, collapses to d with J = 1.5 Hz with $h\nu$ at 1.74, 1 H); mass spectrum, m/e (rel intensity) 188 (25), 173 (100), 132 (80), 88 (95), 73 (80), 58 (80); calcd for $C_8H_{20}OSi_2$, m/e 188.1053; measd, m/e 188.1051.

Vacuum Pyrolysis of 16. Neat **16** (0.7200 g, 3.83 mmol) was distilled (25 °C (10^{-4} torr)) through a horizontal, quartz-packed tube heated at 680 °C to afford an 82% mass recovery. The two products, Me_3SiOMe (76%) and 1-methylsiletene (16%), were isolated by preparative GC and identified by spectral comparison with authentic samples.

Copyrolysis of 16 and 2,3-Dimethyl-1,3-butadiene. A solution of **16** (0.1976 g, 1.05 mmol) and 2.3-dimethylbutadiene (0.5328 g, 6.50 mmol) was slowly dripped directly into a vertical 1-ft quartz tube packed with quartz chips and heated at 510 °C. The system was continuously swept by a stream of N_2 at ca. 30 mL/min. An 84% mass recovery (0.6104 g) was achieved. Other than Me_3SiOMe, the only product was 1,2,4-trimethyl-4-(2-propenyl)-4-silacyclopentene (**18**): 51%; ^1H NMR ($DCCl_3$) δ 0.32 (s, 3 H), 1.47 (br s, 4 H, allylic CH_2), 1.78 (br s, 6 H, allylic Me), 1.90 (overlapped d of d, 3 H, $J = J'$ = 1.5 Hz, collapses to s with $h\nu$ at $\sim\delta$ 5.5), 5.35 (overlapped d of q, J = 3 and 1.5 Hz, collapses to d of J = 3 Hz with $h\nu$ at δ 1.90, 1 H), 5.61 (overlapped d of q, J = 1.5, 3 Hz, collapses to d with J = 3 Hz with $h\nu$ at δ 1.90, 1 H); mass spectrum, m/e (rel intensity) 166 (M^+, 100), 151 (35), 125 (50), 124 (32), 123 (30), 111 (30), 109 (47), 59 (45); calcd for $C_{10}H_{18}Si$, m/e 166.1178; measd m/e 166.1175.

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Registry No. 1, 84602-62-0; **6**, 84602-63-1; **10**, 84602-64-2; **11**, 84602-65-3; **12**, 84002-66-4; **16**, 84602-67-5; **18**, 84602-68-6; 1-aziranyl-1-chlorotetramethyldisilane, 83134-73-0; azirane, 151-56-4; 1,1-dichlorotetramethyldisilane, 4518-99-4; allyl bromide, 106-95-6; methyl trimethylsilyl ether, 1825-61-2; 1-methylsiletene, 84602-69-7; 2-methyl-3-chloropropene, 563-47-3; (*E*)-1-bromopropene, 590-15-8; (*Z*)-1-bromopropene, 590-13-6; (*Z*)-1-trimethylsilylpropene, 4964-02-7; 1-(diethylamino)-1-chlorotetramethyldisilane, 83134-74-1; 1,1-dichlorotetramethydisilane, 4518-99-4; 2-bromopropene, 557-93-7; 2,3-dimethyl-1,3-butadiene, 513-81-5; lithium diethylamide, 816-43-3.