Journal of Organometallic Chemistry, 376 (1989) 259–268
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20262

Gas phase reactions of 1,1-dimethylsilabutadiene

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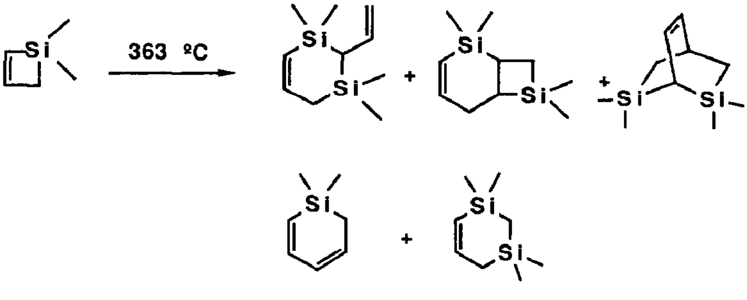
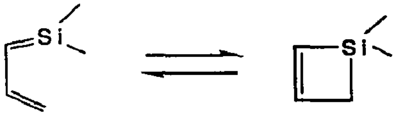
(Received April 17th, 1989)

Abstract

Pyrolysis of 1,1-dimethyl-1-siletene at 363°C in a static reaction vessel produces three major products which are formal dimers of the starting material or the reactive isomer, the siladiene. Reactions with ethylene, propene, vinyltrimethylsilane and butadiene have been examined. Mechanisms leading to the $Si_2C_{10}H_{20}$ products are discussed. The influence of temperature and concentration of coreactant on competing reaction pathways is interpreted.



Conjugation of vicinal π bonds is often indicated by bimolecular reactions across the termini of the π-electron system. In the case of 1,3-silabutadienes (**1**) such bimolecular reactivity has been rarely observed due to the relatively fast rate of intramolecular silene addition to the adjacent vinyl group [1]. Exceptions have been noted in solution when a siladiene regenerated continuously from prolonged photolysis of the siletene in solution was trapped by polar molecules such as methanol and acetone [2,3]. More recently, we have reported cycloadditions between siladienes and organic π-electron systems at higher temperatures in the gas phase, by static pyrolysis of the more stable siletene isomer, **2** [4].



1 2

Table 1

Temperature dependence of product distribution from pyrolysis of **2** [a,b]

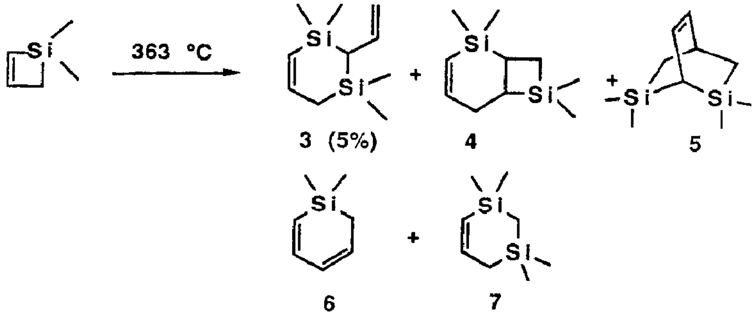
Temperature (°C)	Time (min)	(%) Dec.	**3**	**4**	**5**	**6**	**7**
331	240	58	6	35	55	2	2
363	180	84	9	30	58	1	2
391	75	82	11	24	59	3	3

[a] Initial pressure of **1** was ca. 20 torr. [b] Products were stable under the reaction conditions and % product distributions were based reacted **2**.

Unless the trapping agent was present in much higher concentration than **1** or **2**, cyclic products from combinations **1** or **2** were formed in nearly quantitative yield. In this paper, we report the structures of the $Si_{12}C_{10}H_{20}$ isomers and bimolecular trapping with other organic π-electron reactants. Mechanisms for these reactions have been considered from the kinetic dependence of the product distributions on temperature and trapping agent concentration.

Pyrolysis of vapors (20 torr) of 1,1-dimethyl-1-silacyclobut-2-ene (**2**) at 363°C afforded three major products: 1,1,3,3-tetramethyl-2-vinyl-1,3-disilacyclohex-4-ene (**3**) (9%), 2,2,7,7-tetramethyl-2,7-cyclo[4.2.0]oct-3-ene (**4**) (30%) and 2,2,6,6-tetramethyl-2,6-disilabicyclo[2.2.2]oct-7-ene (**5**) (58%) plus trace amounts 1,1-dimethyl-1-silacyclohexa-2,4-diene (**6**) (1%), 1,1,3,3-tetramethyl-1,3-disilacyclohex-4-ene (**7**) (2%) and unreacted **2** (16%).

The changes in percentages of products over the temperature range, 331–391°C are shown in Table 1.



The 60°C variation in temperature did not have a major influence in the distribution of $Si_2C_{10}H_{20}$ isomers. Formation of **5** was little influenced and the changes for **3** and **4** were relatively small increases and decreases, respectively. Since products **3**–**5** very likely originated from combinations of the siladiene **1** with **2** or dimerization, the modest temperature effect was surprising and its interpretation posed mechanistic problems. Several factors might influence the product distribution, not the least of which is the temperature dependence of the mode of siladiene reactivity. Does the silabutadiene react as a delocalized 4π- or as a 2π-electron system with itself or with its thermal precursor **1**, and to what extent is the regioselectivity of addition determined by the electron distribution of the π bond of the coreactant?

Our initial effort to distinguish between these possible modes of cycloaddition was to record the temperature effect on the relative yields of the known 2 + 2 adduct, 1,1-dimethyl-silacyclohex-3-ene (**8**), and the 2 + 4 product, the cyclic 2-ene **9**

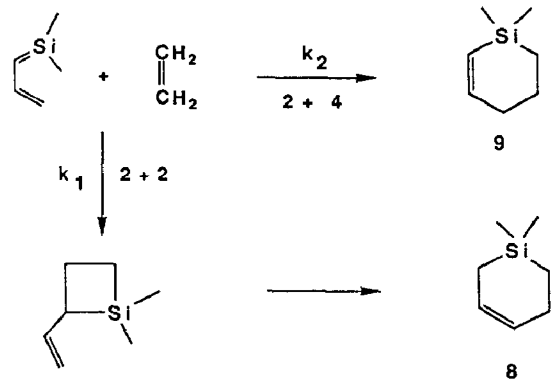


Table 2

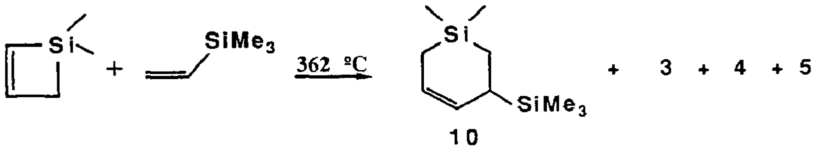
Temperature dependence of **8**/**9**

Temperature (°C)	327.8	335.7	347.1	357.6	370.7	380.1	389.7	±0.1
8/**9**	1.12	1.12	1.113	1.14	1.18	1.20	1.20	±0.02

from reaction of **2** with ethylene (twentyfive-fold excess) [3]. Table 2 shows that higher temperature slightly favors the formation of **8**, the 2 + 2 product, relative to **9**, the product of the 2 + 4 mechanism.

Since ethylene was present in a large excess of **2**, yields of disilane isomers were negligibly small, < 5% of the total. When the ethylene concentration was reduced to a ten-fold excess, isomers accounted for ≈ 30% of the products: **3** (5%), **4** (10%), **5** (15%).

The importance of polarization in the alkene trap is noted in the copyrolysis of **2** and vinyltrimethylsilane (five-fold excess) at 362 °C for 60 minutes. Only one new product, 1,1-dimethyl-5-trimethylsilyl-1-silacyclohex-3-ene (**10**), was formed in 62% yield, probably via ring expansion of the 2 + 2 intermediate, 2-vinyl-3-trimethylsilyl-1,1-dimethyl-1-silacyclobutane, according to the mechanism above. Surprisingly, the ratios of $Si_2C_{10}H_{20}$ isomers: **3** (22%), **4** (10%), and **5** (6%) favored **3**, the product which might easily have been attributed to a 2 + 4 siladiene dimerization. The variation in the relative amounts of the three Si_2 isomers with concentration of vinyltrimethylsilane, *T*, is shown in Table 3.



In contrast to the regioselective cycloaddition of vinyltrimethylsilane and dimethylsilabutadiene, reaction with propene (five-fold excess at 365 °C) afforded the

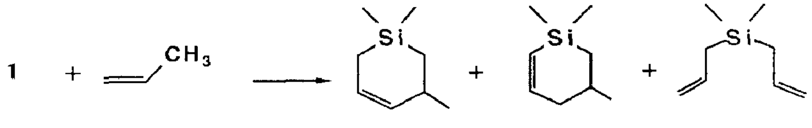
Table 3

Variation in product yields with trapping agent at 362° C [a]

% dec. **2**	Conc. *T*	**3** (%)	**4** (%)	**5** (%)	**10** (%)	**10**/(**3**+**4**+**5**)	**10**/(**4**+**5**)
46	1/1	15	19	23	39	0.7	0.9
70	5/1	22	10	6	62	1.7	3.9
82	10/1	23	8	3	65	1.9	5.9

[a] Pyrolysis time at each concentration was 60 min.

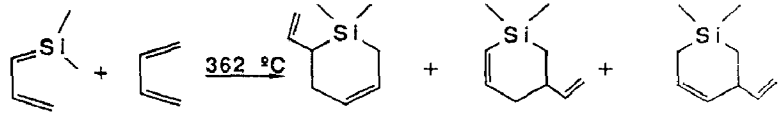
rearranged 2 + 2 product, 1,1,5-trimethyl-1-silacyclohex-3-ene (**11**) (45%), the 4 + 2 adduct, 1,1,5-trimethyl-1-silacyclohex-2-ene (**12**) (26%) and, the 'ene' product, diallyldimethylsilane [5] (**13**) (6%) along with the **3** (16%), **4** (2%), and **5** (4%).



11 **12** **13**

+ **3** + **4** + **5**

Generation of the siladiene transient with the highly reactive butadiene trap (twentyfold excess at 365 °C) produced three cycloadducts: 1,1-dimethyl-6-vinyl-1-sila-cyclohex-3-ene (**14**) (37%), 1,1-dimethyl-5-vinyl-1-silacyclohex-2-ene (**15**) (20%), 1,1-dimethyl-5-vinyl-1-silacyclohex-3-ene (**16**) (42%) and suppressed formation of the $Si_2H_{10}H_{20}$ products.



14 (37) **15** (20) **16** (42)

Discussion

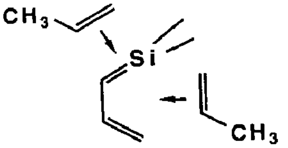
Bimolecular reaction. The data in Table 2 for reaction of **1** with ethylene were obtained under conditions where **8** and **9** did not interconvert and the formation of other products, Si_2 isomers, was negligible. Therefore the ratio of silacyclohexenes **8** and **9** is a measure of k_1/k_2 and can serve as a simple organic π-electron group to investigate the relative energetics of the 2 + 2 and 2 + 4 cycloadditions [6].

The ratio, k_1/k_2, can be expressed by the Arrhenius equation: $\ln(\mathbf{8}/\mathbf{9}) = \ln(A_1/\ln A_2) + (E_2 - E_1)/RT$. The value, $\log(A_1) - \log(A_2)$, 0.35 ± 0.04, is consistent with a larger $\Delta S^{\ddagger}$ and a "looser" transition state for the nonstereospecific 2 + 2 cycloaddition of k_1 compared to the more ordered stereospecific 2 + 4 path of k_2. It is the entropic effect, however, that is primarily responsible for the somewhat faster 2 + 2 cycloaddition. Surprisingly, the "symmetry allowed" 4 + 2 cycloaddition proceeds with a slightly higher enthalpy, $E_2 - E_1 = 1.0 \pm 0.2$ kcal/mol. Theory has predicted a larger electron density on C2 than on C4 of the 1-silabuta-1,3-diene

[7] and a greater coulombic attraction between C2 of the siladiene and the π-electrons of ethylene may account for the lower activation enthalpy of k_1 relative to k_2.

The reaction between vinyltrimethylsilane and the silabutadiene produced only one adduct and was selected for study of the dependence of formation of the $Si_2C_{10}H_{20}$ isomers on trapping agent concentration. The effect of increasing the concentration of vinylsilane is expected to raise the amount of this adduct and to reduce the formation of $Si_2C_{10}H_{20}$ isomers. Although the yield of **10** did increase: 39%, 62%, to 65% (see Table 3), as the ratio of trapping agent/silacyclobutene was varied from 1/1, 5/1, to 10/1, the increase was somewhat less than linear in trapping agent concentration.

Relative amounts of the $Si_2C_{10}H_{20}$ isomers showed a marked and unusual variation with different ratios of trapping agent. As the vinyltrimethylsilane concentration increased, the yield of **3** did also. This result is not expected if **3** were produced by a second order reaction of **1** and suggests that dimerization of the reactive silabutadienes is not the exclusive source of **3**. Formation of **4** and **5** decreased inversely with increasing amounts of vinyltrimethylsilane as expected for a first order dependence on the concentration of starting **2**. The peculiar enhancement in the yield of **3** was also noted when propene was the coreactant and will be discussed later. It is interesting that the steric effect of the methyl group of propene



also favors a transition state in which the unsubstituted methylene carbon of the alkene added exclusively to the silicon atom of the siladiene. Propene, unlike vinyltrimethylsilane, allows products from both the 2 + 4 and 2 + 2 pathways, silacyclohex-2- and -3-enes, respectively, in a ≈ 1/2 ratio.

The three different vinylsilacyclohexenes **14**, **15**, and **16** are cycloadducts involving 2 and 4 π-electron components of both the siladiene and butadiene. One of the vinyl groups of either of the diene reactants, butadiene or the siladiene, is unreactive in the cycloaddition path and provides a label in the following mechanistic analysis. The cyclic-3-ene **14** appears to originate from a 2 + 4′ reaction of the siladiene and a vinyl group of butadiene. The cyclic-3-ene **15** might arise from a 4 + 2′ cycloaddition between butadiene and the Si–C π bond of the siladiene.

Isolation of **16**, the major product, suggests that a 2,3-divinylsilacyclobutane intermediate undergoes a 1,3-silicon shift.

Formation of $Si_2C_{10}H_{20}$ products. The gas phase dimerization of the hydrocarbon, butadiene, may offer a basis for comparison [8*,9]. The major adduct, 4-vinylcyclohexene (93%), formed by a 4 + 2 cycloaddition is accompanied by smaller amounts of *trans*-1,2-divinylcyclobutane (5%) and *cis,cis*-1,5-cyclooctadiene (2%), presumably from ring expansion of the *cis*-1,2-divinylcyclobutane.

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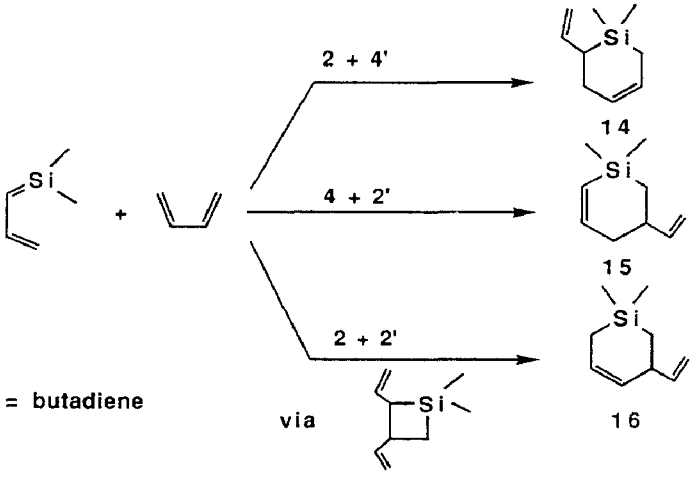
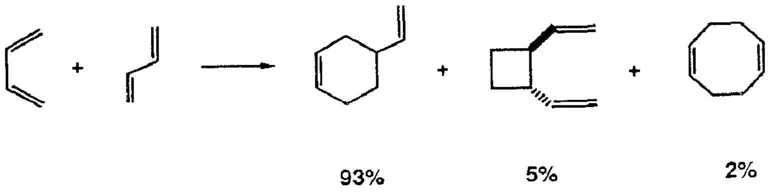
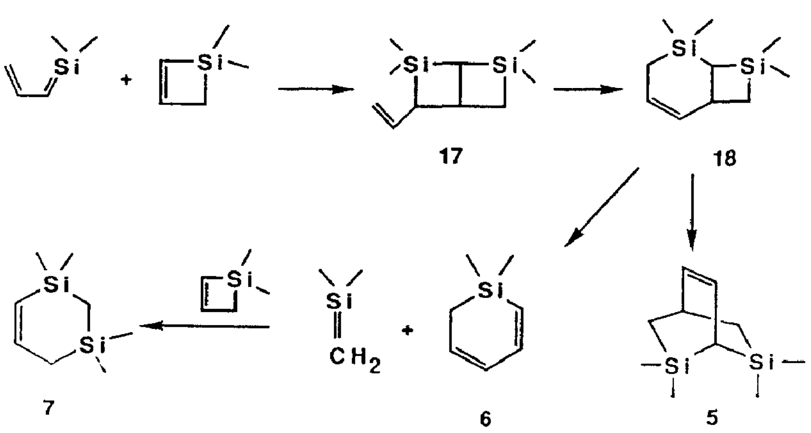
* Reference number with asterisk indicates a note in the list of references.





Formation of **5**, the major product in our neat pyrolyses, requires sequential isomerization of silacyclobutane rings. The absence of a temperature dependence may be due the compensating effects of several competing reaction pathways in a multi-step reaction. Of a variety of possible pathways, we favor one in which both 2- and 3-vinylsilacyclobutane intermediates **17** and **18** undergo ring expansions shown.

The symmetry allowed sila-sigmatropic rearrangement of 2-vinylsilacyclobutanes to silacyclohex-3-enes, similar to **17** → **18**, has been described previously as a thermally facile processes at 350 °C [4]. Ring expansion of **18**, a 3-vinylsilacyclobutene, also a well-precedented pathway [10], provides correct postioning of the silicon



atoms in **5**. Additional evidence for an intermediate such as **18** comes from the isolation of minor amounts of secondary products: the conjugated silacyclohexadiene **6** and the disilacyclohexene **7**. Formation of these two products might be reasonably accommodated by fragmentation of the labile **18** to 1,1-dimethylsilene and **6**. The silene, in a large excess of **1** or **2**, could be trapped efficiently to yield **7**. In the presence of trapping agents, products from these secondary pathways were not detected.

The regiospecific formation of disilabicyclo[4.2.0.]oct-3-ene (**4**) appears to proceed from the least hindered approach of the silabutadiene to the double bond of the starting silacyclobutene. Kinetic trapping studies support this view. The combined product yields for **4** and **5** decrease nearly in same proportion that **10** increases as expected for a pathway in which both starting material **2** and vinyltrimethylsilane compete for the siladiene intermediate.


4

At higher reaction temperature the concentration of **1** increases as does the probability of dimerization of the silabutadiene. Accordingly the yield of **3** increases (Table 1). The structural similarity between the major hydrocarbon dimer, 4-vinylcyclohexene, from butadiene dimerization and **3** suggests that the silabuta-1,3-diene also reacts with itself in a 4 + 2 or 2 + 2 manner. However the increase in **3** with greater concentrations of the trapping agent suggests that it is not formed exclusively by a simple bimolecular reaction of two transient silabutadienes **1**. The origin of the enhanced yields of **3** relative to **4** and **5**, especially in the presence of propene and vinyltrimethylsilane, is not obvious to us [11*].

Additional factors which cold affect relative amount of **3** are (1) the barriers for *s-cis* and *s-trans* isomerization of **1** as well as the reactivity of each rotational isomer [12*], (2) possible reversibility of the initial 2 + 2 cycloaddition, and (3) the formation of silabicyclo[1.1.0]butane as a reservoir for a transient which selectively reacts to produce **3**.

Experimental

General data. Proton NMR spectra were recorded on a Hitachi Perkin–Elmer R24B 60-MHz spectrometer using methylene chloride as an external standard and carbon NMR spectra were obtained on a JEOL FX 90Q spectrometer with D_2O or $CDCl_3$ as a lock solvent. High resolution NMR spectra were obtained on a Varian 300-MHz VXR spectrometer and chemical shifts are reported in ppm downfield from external tetramethylsilane. Preparative gas chromatography was performed on a Varian 90A GLC (thermal conductivity detector). Analytical gas chromatography was performed on a HP 5840A GLC (flame ionization detector) equipped with a Valco gas sampling port. Low resolution mass spectra were determined on a HP 5970A mass selective analyzer coupled to a HP 5790A gas chromatograph. High resolution mass spectra were obtained at the Mass Spectrometry Facilities at Massachusetts Institute of Technology.

Static pyrolysis of 1,1-dimethyl-1-siletene 2 [5]. Vapors of **2** (20 torr) were pyrolyzed at temperatures from 330 to 390 °C in a 500 ml closed vessel attached to a high vacuum line. The results are shown in Table 1 of the text. In a typical experiment three major products of molecular formula $Si_2C_{10}H_{20}$ were formed: 1,1,3,3-tetramethyl-2-vinyl-1,3-disilacyclohex-4-ene (**3**) (9%), 2,2,7,7-tetramethyl-2,7-disilabicyclo[4.2.0]oct-3-ene (**4**) (30%), and 2,2,6,6-tetramethyl-2,6-disilabicyclo-[2.2.2]oct-7-ene (**5**) (58%) plus small amounts 1,1-dimethyl-1-silacyclohexa-2,4-diene (**6**) and 1,1,3,3-tetramethyl-1,3-disilacyclohex-4-ene (**7**). Products were isolated by preparative GC on the OV-17 column (20% OV-17 on Chromosorb W, 1/4 in. × 20 ft.).

3: ^{3}H NMR ($CDCl_3$) δ 0.03 (3H, s, $SiCH_3$), 0.08 (9H, s, $Si(CH_3)_2$ and $SiCH_3$), 1.30 (1H, d, *J* 9.40 Hz, SiCHSi), 1.45 (2H, m, $SiCH_2C{=}C$), 4.78 (2H, m, $CH_2{=}CCSi_2$), 5.55 (1H, app d, *J* 12.50 Hz, SiCH=C), 5.60 (1H, m, $Si_2CCH{=}C$), 6.70 (1H, d of t, *J* 12.50 Hz 6.04 Hz and *J* 6.04 Hz, CH=CSi); ^{13}C NMR ($CDCl_3$) δ −4.10 (q), −2.70 (q), −2.30 (q), −1.20 (q), 18.30 (t), 23.52 (d), 111.21 (t), 129.02 (d), 135.76 (d), 145.19 (d); GC/MS, *m/e* (relative intensity) 196 (33), 181 (67), 168 (37), 153 (39), 131 (24), 98 (59), 97 (30), 96 (64), 83 (87), 73 (100), 69 (39), 59 (66), 45 (37), 43 (91). exact mass calc. for $Si_2C_{10}H_{20}$ 196.1104, obs. 196.1100.

4: ^{1}H NMR ($CDCl_3$) δ −0.02 (6H, s, $Si(CH_3)_2$), 0.05 (6H, s, $Si(CH_3)_2$), 0.85 (2H, m, CH_2–Si), 2.08 (2H, m, CH_2–C=C), 2.25 (1H, d of t, *J* 14.30 Hz, *J* 6.42 Hz, SiCHCSi), 2.82 (1H, m, SiCHCSi), 5.98 (1H, app d, *J* 13.5 Hz, Si–CH=C), 6.78 (1H, d of t, *J* 13.5, *J* 7.54 Hz, Si–C=CH; ^{13}C NMR, (neat) δ 0.32 (q), 0.64 (q), 16.05 (d), 21.76 (t), 31.75 (d), 36.06 (t), 130.60 (d), 146.78 (d); gc/ms, *m/e* (relative intensity) 196 (16), 181 (57), 179 (22), 168 (71), 153 (34), 122 (44), 109 (56), 108 (31), 96 (50), 95 (28), 83 (35), 73 (100), 72 (54), 59 (73), 45 (30), 43 (83); exact mass calcd for $Si_2C_{10}H_{20}$ 196.1104, found 196.1100.

5: ^{1}H NMR ($CDCl_3$) δ −0.05 (6H, s, $SiMe_{exo}$), 0.15 (6H, s, $SiMe_{endo}$), 0.50 (2H, d of d, *J* 14.06 Hz, *J* 2.20 Hz, $SiCH_{endo}$), 0.75 (2H, d of d, *J* 14.06 Hz, *J* 4.58 Hz, $SiCH_{exo}$), 1.25 (1H, d, *J* 7.23 Hz, $SiCH_cSi$), 3.08 (1H, m, CCH_bC), 5.90 (1H, app t, *J* 7.23 Hz, SiCCH=C), 6.04 (1H, app, t, *J* 7.23 Hz, SiCC=CH); ^{13}C NMR ($CDCl_3$) δ −0.22 (q), 0.38 (q), 17.87 (d), 20.89 (t), 30.70 (d), 130.15 (d), 131.88 (d); GC/MS, *m/e* (relative intensity) 196 (65), 181 (86), 153 (31), 129 (35), 122 (67), 109 (53), 108 (87), 73 (100), 59 (78), 43 (72); exact mass calc. for $Si_2C_{10}H_{20}$ 196.1104, found 196.1100.

The temperature dependence of the pyrolysis of 2 and ethylene. Static vacuum pyrolysis of 1,1-dimethylsiletene (**1**) (6 torr) and ethylene (≈ 150 torr) was carried out over the temperature range 327.8–389.7 °C in a 250 ml quartz reaction vessel. The apparatus has been described previously [4]. Aliquots of the pyrolysate (ca. 10 torr) were analyzed at 15–30 minute intervals over 1–2 h. Ratios of **8**/**9** were determined by GC on a SP-2100 column (10% on Chromosorb W, 1/8 in. × 12 ft.). The ratios **8**/**9** were determined to be time invariant and recorded at seven temperatures given in Table 2. Under these reaction conditions, no secondary decomposition of either **8** or **9** was observed.

Pyrolysis of 2 with vinyltrimethylsilane. Combinations of **2** and vinyltrimethylsilane in molar ratios 1/1, 1/5, and 1/10 were mixed in the liquid phase, repeatedly degassed and transferred to a heated vacuum line prior to pyrolysis in a 500 ml reaction vessel. After 60 minutes at 361 °C, the reaction mixture was condensed to an adjacent liquid N_2 cooled trap containing several µl of hexane carrier. The low volatility of the products required special care in the analysis. The following products: 1,1-dimethyl-5-trimethylsilyl-1-silacyclohex-3-ene (**10**) (43%), **3** (50%), **4** (3%) and **5** (4%) were identified from the spectroscopic data below or from coinjections of authentic materials. 10: 1H NMR (neat) δ −0.28 (9H, s, $SiMe_3$), −0.24 (6H, s, $SiMe_2$), 0.30 (2H, app t, *J* 9.02 Hz, $SiCH_2CSi$), 0.86 (2H, m, CH_2–C=C), 1.30 (1H, m, SiCH–C=C), 5.27 (2H, m, CH=CH); ^{13}C NMR (neat) δ −3.83 (q), −2.13 (q), 9.56 (t), 12.48 (t), 23.31 (d), 123.40 (d), 129.80 (d); *m/e* (relative intensity) 198 (7), 196 (18), 181 (27), 179 (10), 168 (14), 155 (11), 153 (15), 131 (12), 129 (10), 125 (14), 124 (20), 122 (15), 110 (27), 109 (31), 98 (31), 97 (17), 96 (31), 95 (18), 85 (25), 83 (41), 81 (11), 73 (100), 72 (13), 69 (16), 59 (59), 55 (17), 45 (25), 43 (49), 31 (10), exact mass calc. for $Si_2C_{10}H_{22}$ 198.1260, obs. 198.1254.

Pyrolysis of 2 with propene. Propene (100 torr) and dimethylsiletene (**2**) (20 torr) were pyrolyzed in a 500 ml closed vessel at 365° C for 2 h. Three new products were isolated by preparative gas chromatography on the previously described OV-17 column: 1,1,5-trimethyl-1-silacyclohex-3-ene (**11**) (45%), 1,1,5-trimethyl-1-silacyclohex-2-ene (**12**) (26%), diallyldimethylsilane (**13**) (6%), **3** (16%), **4** (2%) and **5** (4%).

11: ^1H NMR (neat) δ −0.30 (3H, s, $SiCH_3$), −0.28 (3H, s, $SiCH_3$), 0.03 (1H, d of d, *J* 10.180 Hz, *J* 8.10 Hz, Si–CHC) 0.51 (1H, d of d, *J* 10.80 hz, *J* 4.02 Hz, Si–CHC), 0.75 (3H, d, *J* 6.22 Hz, CH_3C), 0.80 (2H, m, $SiCH_2C$=C), 1.91 (1H, m, SiC–CHC), 5.00 (1H, app d, *J* 11.20 Hz, SiC–CH=C), 5.24 (1H, m, $SiC–C=CH)_3$ ^{13}C NMR (neat) δ −3.12 (q), −1.95 (q), 12.55 (t), 20.81 (t), 25.75 (q), 28.81 (d), 124.46 (d), 136.17 (d); *m/e* (relative intensity) 140 (32), 125 (31), 98 (100), 72 (43), 59 (53), 43 (47); exact mass calc. for SiC_8H_{16} 140.1021, obs. 140.1023.

12: ^1H NMR (neat) δ −0.34 (3H, s, $SiCH_3$), −0.31 (3H, s, $SiCH_3$), 0.01 (1H, d of d, *J* 11.07 Hz, *J* 6.75 Hz, Si–CHC), 0.36 (1H, app d, *J* 11.07 Hz, SiCHC), 0.64 (3H, d, *J* 6.01 Hz, CH_3C), 1.44 (2H, m, CH_2C=C), 1.56 (1H, m, SiC–CH), 5.27 (1H, app d, *J* 14.10 Hz, SiCH=C), 6.27 (1H, d of d of d, *J* 14.10 Hz, *J* 5.08 hz, *J* 2.62 Hz, SiC=CH); ^{13}C NMR (neat) δ −1.95 (q), −1.76 (q) 21.33 (t), 26.34 (d), 28.09 (q), 39.15 (t), 126.16 (d), 147.36 (d); *m/e* (relative intensity) 140 (27), 125 (38), 99 (17), 98 (100), 97 (27), 83 (47), 59 (62), 55 (14), 43 (39), 39 (10); exact mass calc. for SiC_8H_{16} 140.1021, obs. 140.1023.

Pyrolysis of 2 with butadiene. Static pryolysis of **2** (15 torr) and 1,3-butadiene (300 torr) in a 500 ml closed vessel at 350° C for 2.5 h. afforded 1,1-dimethyl-6-vinyl-silacyclohex-3-ene (**140** (37%), 1,1-dimethyl-5-vinyl-silacyclohex-2-ene (**15**) (20%) and 1,1-dimethyl-5-vinyl-silacyclohex-3-ene (**16**) (42%). Products were separated and isolated by preparative GC on OV-17.

14: ^1H NMR ($CDCl_3$) δ 0.05 (3H, s, $SiCH_3$), 0.07 (3H, s, $SiCH_3$), 0.49 (1H, app t, *J* 13.5 Hz, SiCH), 0.85 (1H, broad d, *J* 13.5 Hz, SiCH), 1.86 (1H, t of d of d, *J* 17.7, 11.1, 2.4 Hz, SiCHC=C), 1.70 2H, CH_2–C=C), 4.90 (2H, m, CH_2=C) 5.70 (1H, t of d, *J* 13.5 Hz, *J* 1.2 Hz, SiCCH=C), 5.85 (1H, m, CH=C), 6.67 (1H, d of d of d, *J* 13.5, 6.0, 2.5 Hz, SiCC=CH); ^{13}C NMR (neat) δ −1.95 (q), −1.69 (q), 18.08 (t), 36.48 (t), 36.81 (d), 110.74 (t), 126.41 (d), 145.60 (d), 146.96 (d); *m/e* (relative intensity), 152 (7), 137 (19), 109 (62), 98 (100), 83 (62), 73 (22), 59 (42), 43 (52); exact mass cald. for SiC_9H_{16} 152.1021, found 152.1020.

15: ^1H NMR ($CDCl_3$) δ −0.02 (3H, s, $SiCH_3$), 0.07 (3H, s, $SiCH_3$), 1.65 (2H, m, $SiCH_2$), 1.86 (1H, m, SiCCH), 2.08–2.30 (2H, 2 sets of m, CH–C=C), 4.85 (2H, m, CH_2=C), 5.70 (1H, app d *J* 14.1 Hz, SiCH=C), 5.88 (1H, d of d of d *J* 17.1 Hz, *J* 10.5 Hz, *J* 6.6 Hz, CH=C), 6.69 (1H, d of d of d, *J* 14.1 Hz, *J* 5.4 Hz, and *J* 2.4

Hz, SiC=CH); ^{13}C NMR (neat) −4.89 (q), −3.64 (q), 26.08 (t), 30.24 (t), 31.08 (d), 109.96 (t), 125.70 (d), 139.42 (d), 147.81 (d); *m/e* (relative intensity) 152 (19), 137 (24), 124 (47), 109 (72), 98 (94), 92 (30), 85 (27), 83 (100), 73 (41), 72 (36), 59 (71), 43 (80); exact mass calc. for SiC_9H_{16} 152.1021, found 152.1020.

16: ^1H NMR ($CDCl_3$0 δ −0.4 (3H, s, $SiCH_3$), −0.33 (3H, s, $SiCH_3$), 0.84 (2H, m, CH_2Si), 1.37 (1H, app quintet, *J* 7.3 Hz), 1.92 (2H, m, $CH_2C=C$), 4.44 (2H, m, $CH_2=C$), 5.23 (1H, m, CH=C), 5.29 (1H, m, SiCCH=C), 5.36 (1h, d of d, *J* 11.0 Hz, *J* 6.5 Hz, SiCC=CH); ^{13}C NMR (neat), −6.25 (q), −3.90 (q), 12.55 (t), 28.55 (t), 29.46 (d), 110.29 (t), 124.98 (d), 128.37 (d), 139.29 (d); GC/MS, *m/e* (relative intensity) 152 (23), 137 (14), 124 (25), 109 (46), 98 (100), 83 (83), 59 (74), 43 (61); exact mass calc. for SiC_9H_{16} 152.1021, found 152.1020.

Acknowledgement

Support of this research from the R.A. Welch Foundation and the Dow Corning Corporation is gratefully acknowledged. We also thank Dr. C.E. Costello of the Mass Spectrometry Facility at the Massachusetts Institute of Technology for high resolution mass spectra.

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