THERMAL REACTIONS OF FOUR-MEMBERED RINGS CONTAINING SILICON OR GERMANIUM

DISSERTATION

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By

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The synthesis of E- and Z-1,1,2,3-tetramethylsilacyclobutanes is described. Pyrolysis of either isomer at 398.2 °C provides the same products but in different amounts: propene, E- and Z-2-butene, allylethyldimethylsilane, dimethylpropylsilane, the respective geometric isomers, 1,1,2,3,3-pentamethyl-1,3-disilacyclobutane, 1,1,1-ethyldimethyl-2,2,2-vinyldimethyl-disilane and E- and Z-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutane. Mechanisms involving di- and trimethylsilenes are described for disilane formation and rate constants of the elementary steps for the fragmentation reactions are reported.

Photochemically generated dimethylsilylene in the hydrocarbon solution inserts into the cyclic Ge-C or Si-C bonds of 1,1-dimethylgerma- or silacyclobutane to produce 1-germa-2-sila- or 1,2-disilacyclopentane. The relative reactivities of 1,1-dimethylgerma- and silacyclobutanes toward the dimethylsilylene have been determined. The carbenoid resulting from the cuprous chloride catalyzed decomposition of diazomethane at 25 °C in cyclohexane reacts with 1,1-dimethylgermacyclobutane to give, surprisingly

1,1,5,5-tetramethyl-1,5-digermacyclooctane as the major product. The reactions of the carbenoid with 1,1-dimethylsilacyclobutane are described.

The kinetics of gas phase thermal decomposition of 1,1-dimethylgermacyclobutane has been studied over the temperature range, 684 - 751 K at pressures near 14 Torr. The Arrhenius parameters for the formation of ethylene are k_1 $(s^{-1}) = 10^{(14.6 \pm 0.3)}$ exp $(62.7 \pm 2.9$ kcal $mol^{-1}/RT)$ and those for the formation of propene and cyclopropane are k_2 $(s^{-1}) = 10^{(14.0 \pm 0.1)}$ exp $(60.4 \pm 2.8$ kcal $mol^{-1}/RT)$.

Static gas phase pyrolyses of 1,1-dimethyl-1-silacyclobutene, DMSCB, in the presence of a variety of alkenes and alkynes at 260 - 365 °C have been studied. Our experimental results suggest that under these conditions the DMSCB ring opens to 1,1-dimethyl-1-silabutadiene, which either recyclizes to DMSCB or reacts with alkenes or alkynes in competing 4 + 2 and 2 + 2 cycloadditions.

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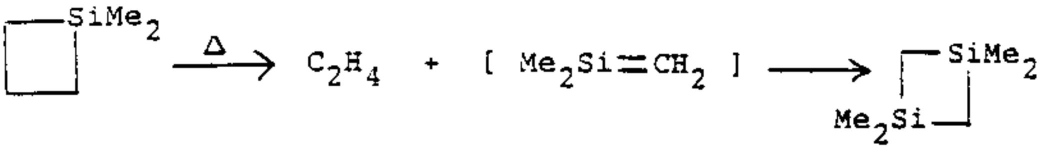
CHAPTER 1

KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION OF E- AND Z- 1,1,2,3-TETRAMETHYLSILACYCLOBUTANE

Introduction

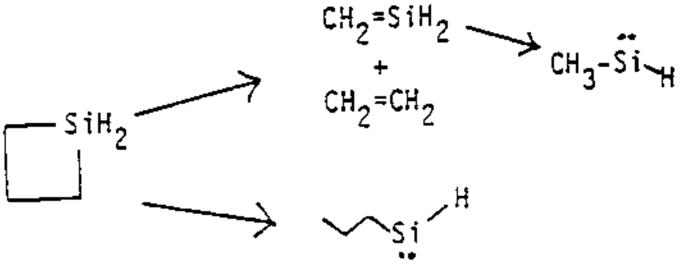
The interest in compounds containing a silicon-carbon double bond (silenes) started with the report of Nametkin and coworkers[1] who found that gas-phase thermal decomposition of 1,1-dimethylsilacyclobutane yields 1,1,3,3-tetramethyl-1,3-disilacyclobutane and ethylene.

(eq 1-1)

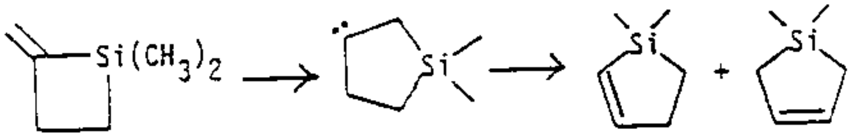


Chemical trapping[2] and kinetic studies[3] of Gusel'nikov and coworkers suggested that silenes are the primary reactive intermediates in the gas-phase thermal decomposition of 1,1-dimethylsilacyclobutane. Different substituents on the silicon atom in the four-membered ring have allowed us to understand the reactivity of a large number of silenes formed in the 2 + 2 cycloreversion of the substituted silacyclobutanes.[4] So far, for these substituted silacyclobutanes, in only two cases have mechanistic deviations from thermal reactions of analogous hydrocarbons been observed.

In the first, Barton and Davidson[5] discovered a minor pathway for the decomposition of hydridosilacyclobutane, an α hydrogen migration to the adjacent ring methylene which competes with the major pathway,[6] fragmentation to hydridosilenes. It is known that hydridosilenes thermally isomerize to methylsilylenes[7] (eqn 1-2). In the other, Conlin, Huffaker, and Kwak reported that thermal ring expansion of 2-methylene-1,1-dimethylsilacyclobutane yielded a cyclic carbene to the near exclusion of fragmentation to allene and 1,1-dimethylsilene[8] (eqn 1-3).



(eqn 1-2)

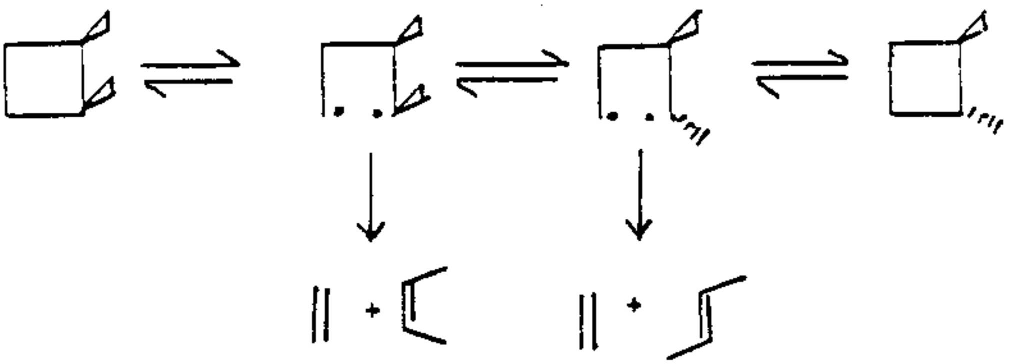


(eqn 1-3)

A first step in these two ring-opening processes is cleavage of a Si-C bond in conjection with additional molecular reorganization. In these two atypical examples the original C-C bonds seem to remain intact until secondary processes lead to stable products. However, Barton,[9] Sommer[10] and Weber[11] bonds seem to remain intact until secondary processes lead to stable products. However, Barton,[9] Sommer[10] and Weber[11] have reported that C-C bond-breaking precedes cleavage of the Si-C bond for the usual thermal decomposition of silacyclobutanes.

Theoretical and experimental studies have suggested that 1,4-biradicals are transients in the 2 + 2 fragmentation of most four-membered rings. This hypothesis is based on the observation that the stereochemical marker is not maintained in the products. The loss of the original stereochemistry in the alkene products from the 2 + 2 cycloreversion has been explained by processes in which some bond rotation competes with β-scission and recyclization

(eqn 1-4)



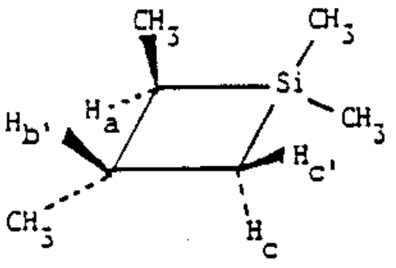
steps. The stereochemistry of a 1,4-diyl, perturbed by a heavier atom such as silicon, has not been studied. We consider such a stereochemistry by using two methyls groups, substituted on C_2 and C_3 of E- and Z-1,1,2,3-tetramethylsilacyclobutane **1** as mechanistic probes. The synthesis of E- and Z-**1** is described. Mechanism of the thermal decomposition of **1** and rate constants of the elementary steps for the fragmentation reactions are reported. A recent report of the magnitude of stabilization of radical centers either α[13] or β[14,15] to a silicon atom may contribute to the interpretation of the work described here. The extent to which the rules of orbital symmetry, based on a Huckel description of symmetrical π-bonds, influence the formation of metalloethylenes from a metallocyclobutane deserves close scrutiny.

Results and Discussion

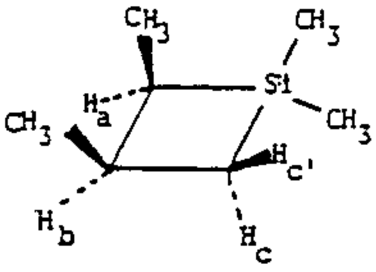
Synthesis of Z- and E-1,1,2,3-tetramethylsilacyclobutane 1

The first attempts of this synthesis, hydrosilylation of 3-bromo-2-methyl-1-butene[16] with dimethylchlorosilane in the presence of a catalytic amount of chloroplatinic acid were unsuccessful due to the rapid loss of HBr from the allylic position. However, hydrosilylation of 3-chloro-2-

methyl-1-butene[17] with dimethylchlorosilane afforded (3-chloro-2-methylbutyl) dimethylchlorosilane in high yield (>85%). Ring closure to a mixture of E- and Z-1,1,2,3-tetramethylsilacyclobutane **1**, was accomplished with either Na/K in xylene (45% yield) or Mg in THF (70%). The ratios of E to Z isomers were similar for both metal/solvent systems: 3:2 with NaK/xylene and 4:3 with Mg/THF, however, the latter method was preferred.[18] The structure of **1** was confirmed by spectroscopic data including nmr, mass spectra, ir and elemental analysis as described in the experimental section.



E-1



Z-1

The configurations of the E- and Z-**1** isomers were determined by the proton and carbon nmr spectra. In the proton nmr spectra of the diastereomers, H_b' of the E-isomer is significantly more shielded than is H_b of the Z-isomer (1.74 and 2.51 ppm, respectively). Such interactions between a hydrogen and a vicinal cis methyl group, as in E-**1**, has been described previously in the assignment of the configurations of E- and Z-2,3-dimethyloxetanes.[19] In addition, carbon nmr spectra distinguish between cis and trans substituted four-membered rings. For example, the carbon-bonded methyl chemical shifts of Z-**1** are found further upfield, 9.23 and 19.18 ppm, than those observed for E-**1**, 13.46 and 24.06 ppm. Similar shielding of the methyl groups in the Z isomer relative to the E isomer is known for 2,3-dimethyloxetane[19] (13.0 and 16.9 : 17.5 and 22.8, respectively) and for Z- and for E-1,2-dimethylsilacyclobutane[20] (-7.0 and 15.6 : -2.3 and 17.3, respectively).

Pyrolysis product distribution

Both E- and Z-tetramethylsilacyclobutane isomers, when pyrolyzed separately at 398 °C provide the same products. Although the quantitative product distributions are slightly different from one isomer to the other, they fall in the following ranges: propene **3** (+1,1,2-trimethylsilene), 65-75%; Z- and E-2-butenes **2** and **4**, respectively, (+1,1-dimethylsilene) 4-10%; allyl(ethyl)dimethylsilane **5**, 7-12%; dimethyl(propyl)vinylsilane **6**, 2-4%. Geometric isomerization also is variable according to the starting isomer and reaction time; however, it does not exceed 19% in any case. Dimerization of the resulting silenes from either isomer afforded the following disilanes: 1,1,2,3,3-pentamethyl-1,3-disilacyclobutane **7**, 2-3%; 1,1,1-

ethyldimethyl-2,2,2-vinyldimethyldisilane **8**, 1%; and E- and Z-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutane **9** and **10**, 9-11% and 16-18% respectively. In addition to these major products, some minor products were detected by GC (less than 1%). When pyrolysis was carried out in the presence of added air, the percentages of these minor products increased significantly, suggesting that they result from reaction with traces of oxygen in the system. Tables 1-8 and 1-9 in the experimental section show the product distributions associated with the major pathways in pyrolysis of E-**1** and Z-**1**. The following table shows the observed percentage distributions:

			Product		
Reactant	(3)	(2) + (4)	(5)	(6)	Isomer
Z-1	66.0 ± 2.2	5.4 ± 9.0	8.1 ± 0.5	3.0 ± 0.6	16.9 ± 2.2
E-1	72.4 ± 3.6	9.3 ± 1.0	10.4 ± 1.5	2.6 ± 0.9	5.6 ± 5.1

In the case of Z-**1** the product distribution is nearly time independent but for E-**1** it is not. At low conversion the amount of geometric isomer (i.e. Z-**1**) is high (ca 12%) but falls to a low value (< 1%) at high conversions due to its greater thermal instability.

Measurements of Z- and E-2-butenes, **2** and **4** respectively, suggest predominant retention of stereochemistry in these decompositions. In the case of Z-**1** the starting isomer decomposition gives 79 ± 3% Z-2-butene (**2**) up to 50% conversion but for the E-1 case the amount of E-2-butene (**4**) is 85 ± 3% up to 70% conversion. For both cases the retention of stereochemistry decreases with increasing conversion.

Kinetic Analysis

The large number of products and simultaneous interconversion and decomposition of both starting isomers complicate a kinetic analysis of this system. To simplify these problems we used a kinetic modeling rather than an oversimplified modeling to logarithmic (i.e., first order) decay plots. In this method the coupled first order rate processes of scheme 1-1 were integrated using a numerical integration routine which calculates the product distribution from either isomer as a function of time using a trial set of rate constants.[21] At any time of interest, comparison can be made with the experimental product distribution. Rate constants were then adjusted and the calculations repeated until the differences between calculated and observed product distribution were minimized. Table 1-1 shows the final values for the rate constants.

Scheme 1-1

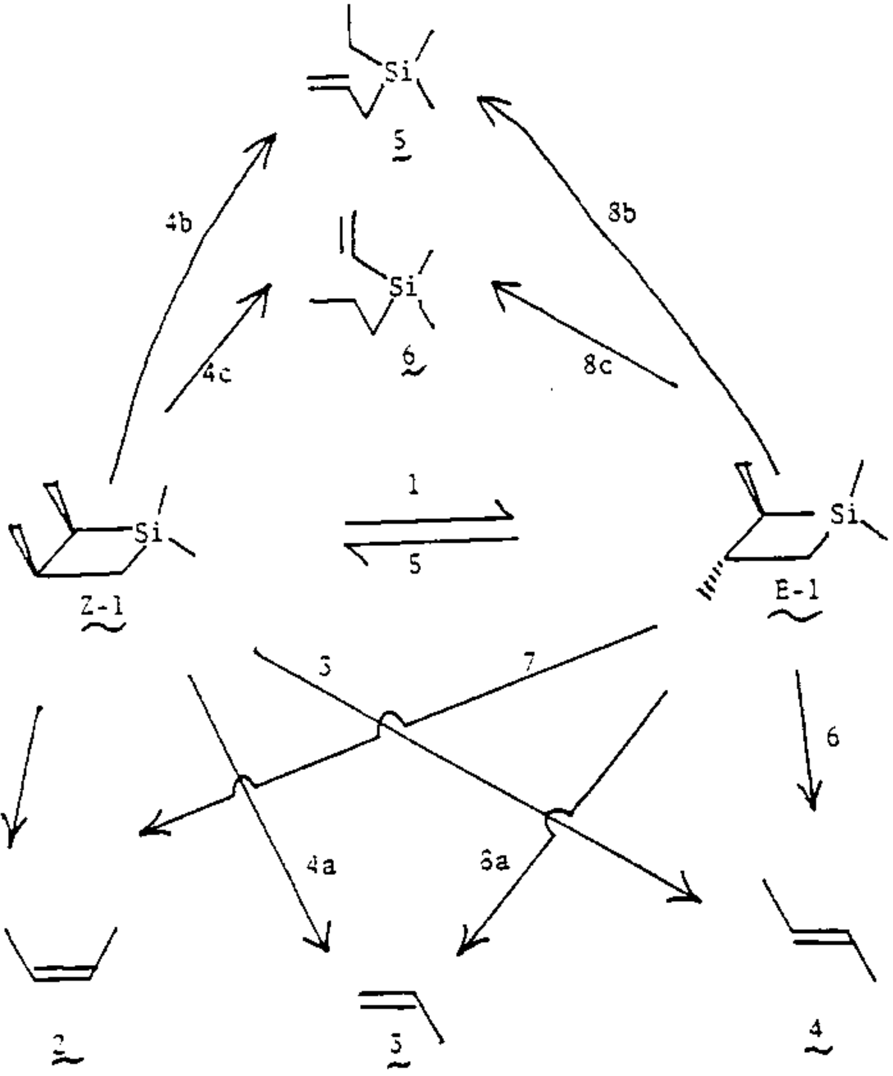


Table 1-1. Optimized rate constants for the thermal decomposition and isomerization of E- and Z-1 at 398 °C.

Z-1 Step[a]	k/s^{-1}	Uncertainty	E-1 Step[a]	k/s^{-1}	Uncertainty
1	1.30×10^{-4}	± 5%	5	2.40×10^{-5}	± 15%
2	3.00×10^{-5}	± 6%	6	1.45×10^{-5}	± 6%
3	6.92×10^{-6}	± 12%	7	2.50×10^{-6}	± 12%
4	5.38×10^{-4}	± 3%	8	1.60×10^{-4}	± 3%
4a	4.63×10^{-4}	± 3%	8a	1.34×10^{-4}	± 5%
4b	5.58×10^{-5}	± 7%	8b	2.14×10^{-5}	± 10%
4c	1.86×10^{-4}	± 16%	8c	4.99×10^{-6}	± 30%
Overall	7.05×10^{-4}	± 2%	Overall	2.01×10^{-4}	± 2%

[a] $k_4 = k_{4a} + k_{4b} + k_{4c}$ and $k_8 = k_{8a} + k_{8b} + k_{8c}$

Figures 1-1 and 1-2 show the product distribution of Z-**1** and E-**1** respectively, via the major pathways. Figure 1-3 shows the extent of loss of stereo-label in the product 2 butenes. The solid line in each of the three figures is the calculated value. Figures 1-2 and 1-3 allow the following comments: (i) a maximum in Z-**1** during decomposition of E-**1** (Fig. 1-2) and (ii) changes in the ratios of 2-butene isomers with time due to the secondary decomposition of the stereo-isomer of the starting material in each case (Fig. 1-3). This later effect is more noticeable in the case of the decomposition of E-**1**.

Discussion

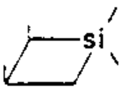
General

Table 1-2 shows the breakdown pathways in the thermal decomposition of E- and Z-**1** at 398.2 ^{o}C which shows that propene formation is the major fragmentation path in both

Table 1-2. Analysis of pathways in the thermal decomposition of E- and Z-**1** at 398.2 ^{o}C.

Pathway		Z-**1** %	E-**1** %
Fragmentations:	total	70.9	75.0
	propene	65.7	66.5
	2-butenes	5.2	8.5
Isomerizations:	total	29.0	25.0
	geometric	18.4	11.9
	structural	10.6	13.1

Fig. 1-1

Product Distribution in Pyrolysis of  at T=398.2 °C

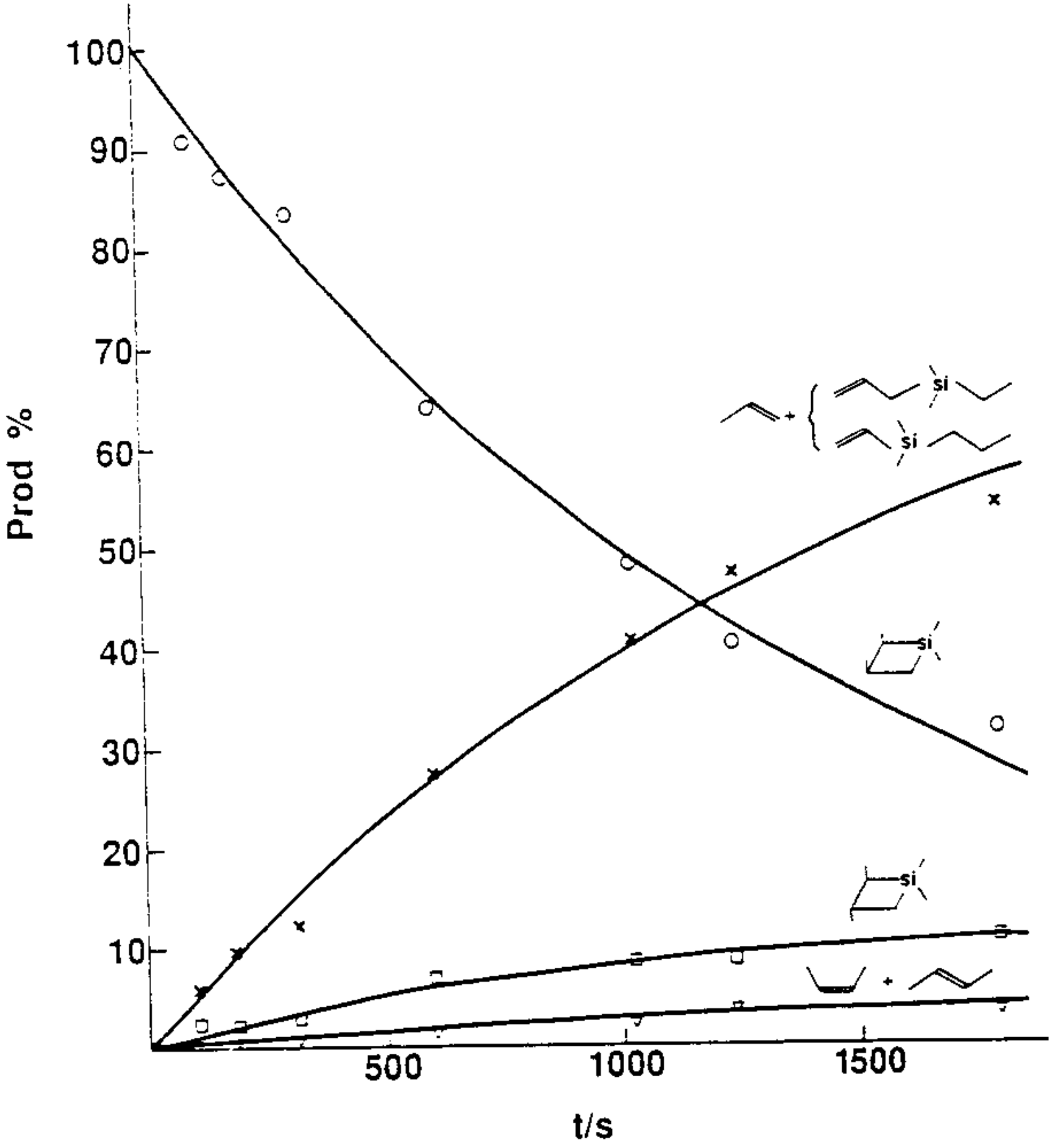


Fig. 1-2

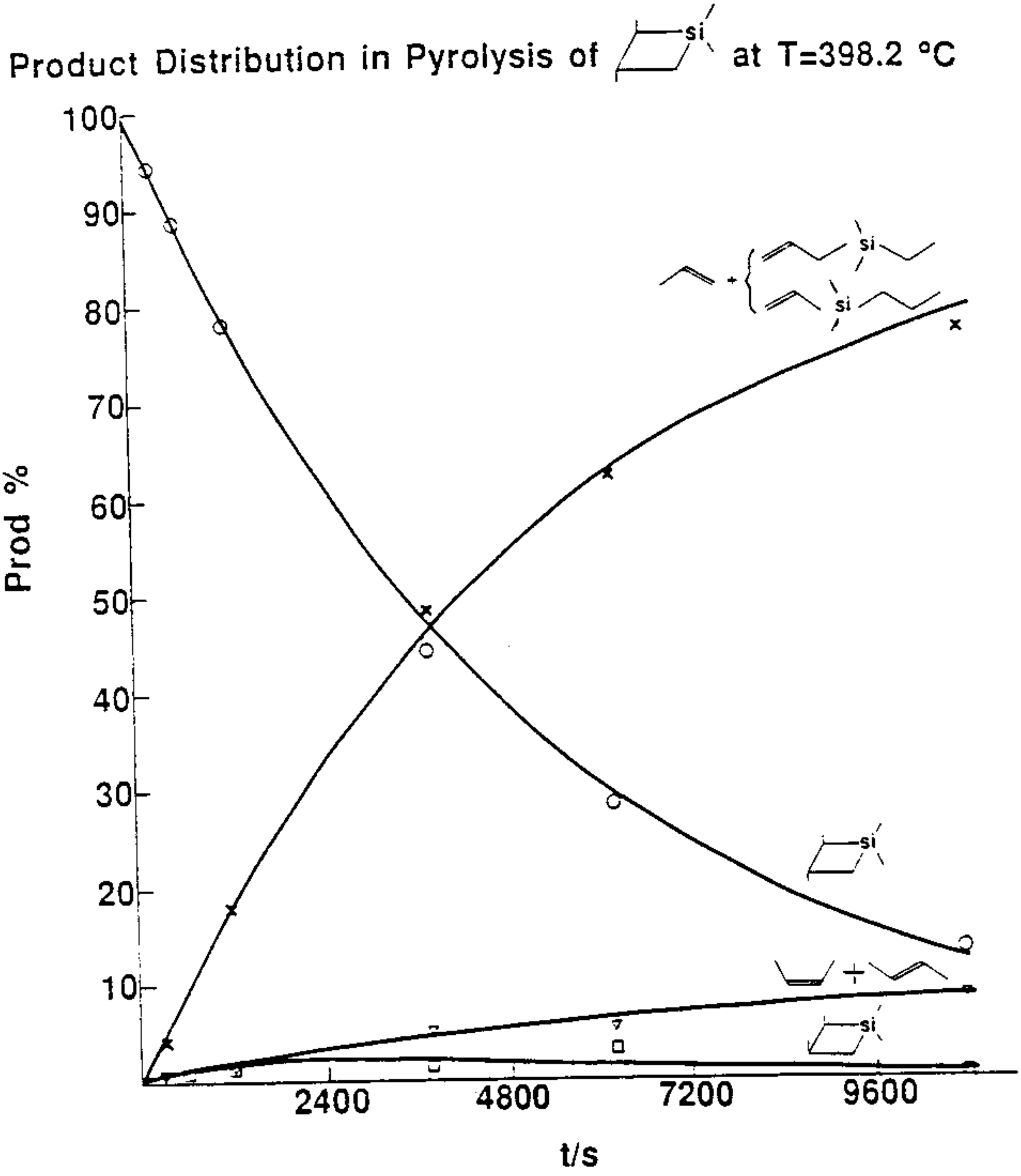
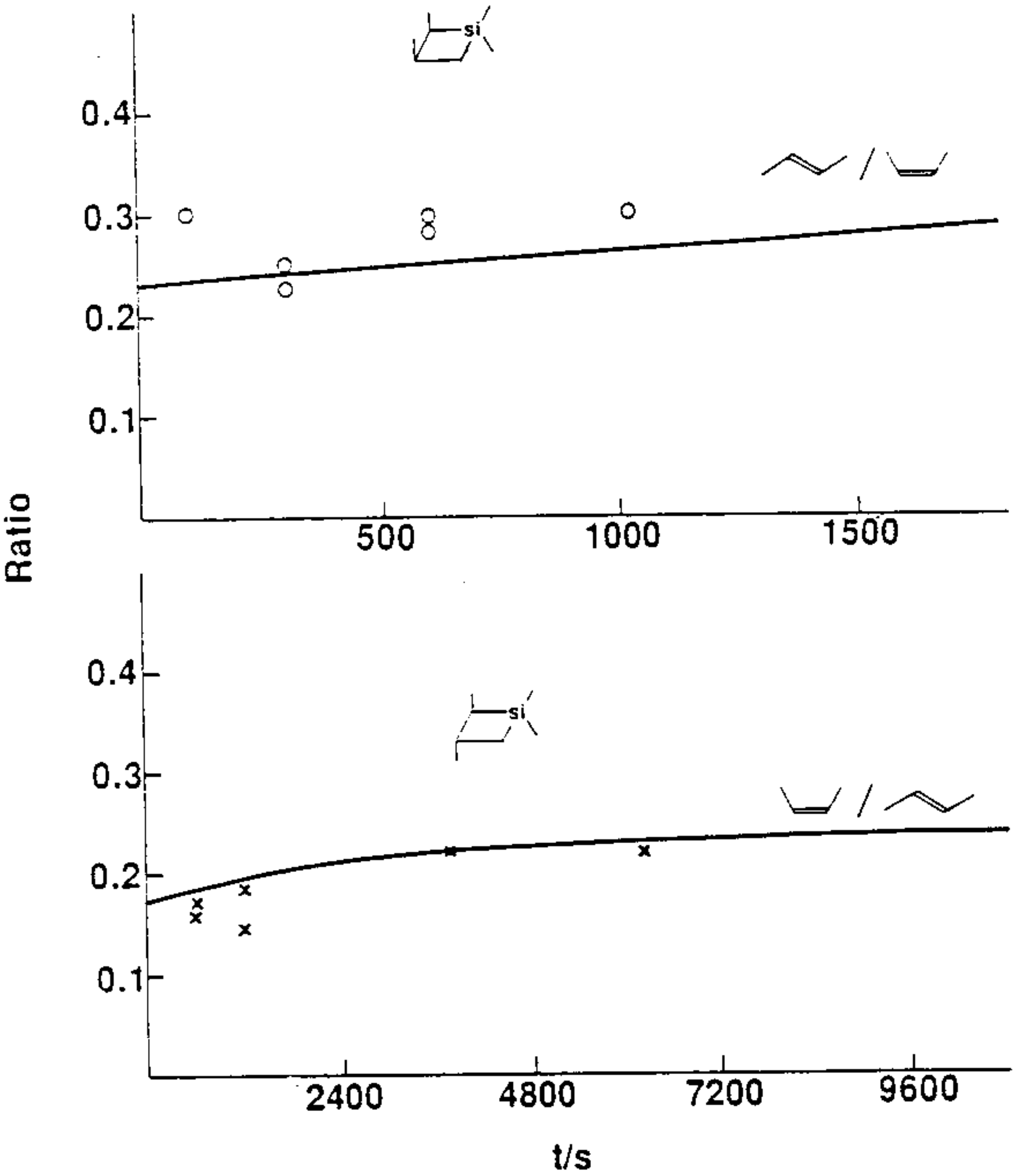

Product Distribution in Pyrolysis of
si
at T=398.2 °C
Prod %
100
90
80
70
60
50
40
30
20
10
2400
4800
7200
9600
t/s
si
si
si
si

Fig. 1-3 Butene Ratios in 1,1,2,3-Tetramethy-1-silacyclobutane Pyrolysis T=398°C.



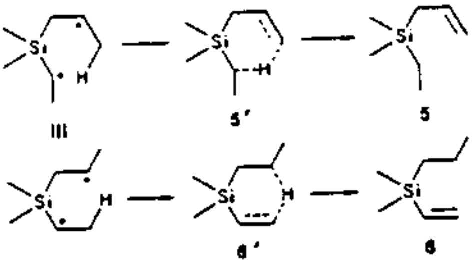
cases. Although Z-**1** decomposes 3.5 times faster (Table 1-1) than E-**1**, the pattern of decomposition is fairly similar for both isomers. The greater geometric isomerization of Z-**1** relative to E-**1** can be explained in terms of relief of repulsion due to cis-vicinal methyl groups interaction in the four-membered ring. However, this is not great enough to prevent formation of any Z-**1** from E-**1**. It appears that structural isomerizations are fairly similar for both isomers.

Fragmentation

Propene formation is the major fragmentation path in the thermal decomposition of E- and Z-**1**. This is consistent with homolysis of the more substituted carbon-carbon bond. Butene formation is the minor path which involves cleavage of the least substituted carbon-carbon bond and should be relatively immune to the methyl group interactions which are relieved in the major fragmentation path. A major difficulty in the analysis of the minor 2-butene formation pathway is the relatively small yield of butene relative to propene products. The extent of retention of stereochemistry in the 2-butene fragment is obtained either by extrapolation of the ratio to zero conversion or by using the ratios of corresponding rate constants. For Z-**1**, $k_2/k_3 = 4.3$ (±0.5) and for E-**1**, $k_6/k_7 = 5.8$ (±0.7). Stereospecificity of 2-butene formation is high in both cases, suggesting that second-bond breaking (Si-C bond) competes effectively with bond-rotation, if a diradical intermediate is assumed (see later).

Structural isomerization

It is known from pyrolysis of 1,1,2-trimethylsilacyclobutane **11**[9] and 1,1,3-trimethylsilacyclobutane **12**[22] that migration of a hydrogen from an exocyclic methyl group to β- or α-ring carbon produces significant isomerization products: ethyldimethylvinylsilane, 10%,[9] and allyltrimethylsilane, 20%[22] respectively. Similarly, we observe formation of allylethyldimethylsilane **5** and dimethylpropylvinylsilane **6** from the analogous isomerization pathways in both E- and Z-**1** pyrolyses. From the relative product ratios in the pyrolyses of trimethylsilacyclobutanes mentioned above, one might expect that **5** is the major acyclic isomer. Within experimental error, the ratio 5:6, 3.6 is the same for both E- and Z-**1**. It should be noted that formation of these acyclic isomers, **5** and **6**, from both E- and Z-**1**, can be accommodated by previously proposed[23] six-membered ring transition states requiring cleavage of the more substituted carbon-carbon bond (Scheme 1-2). Preference of **5** over **6** might be related



Scheme. 1-2

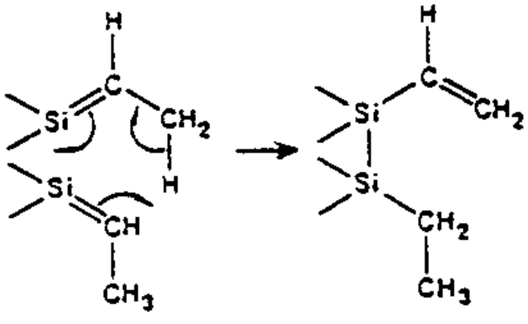
to the extra stability (and therefore lower reactivity) of the radical center β to the silicon atom compared to that α to silicon (see later), thus favoring reaction via transition state 5′ rather than 6′.

Dimerization

The formation of intermediates 1,1,2-trimethylsilene **13** and 1,1-dimethylsilene **14** from **1** are confirmed by the presence of silene dimers **7-10**. The absence of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (a dimer from **14**) is probably due to the low concentration of **14** and the smaller probability that two such reactive species will collide. The disilanes **9** and **10** are formed by the head to tail dimerization of **13**. It has been reported that this dimerization occurs without an activation enthalpy.[23]

The product 1,1,1-ethyldimethyl-2,2,2-vinyldimethyldisilane **8** is an interesting dimer. Recently, Brook[24] has reported that a variety of stable 1,1-bis(trimethylsilyl)-2-trimethylsiloxysilenes dimerize to 1,2-disilacyclobutanes, in head to head fashion. Similarly, trimethylsilene **13** might dimerize to 1,1,2,2,3,4-hexamethyl-1,2-disilacyclobutane in head to head fashion. This disilacyclobutane might undergo rearrangement to yield acyclic disilane **8** by analogy to octamethyl-1,2-disilacyclobutane.[25,26] Another possible mechanism which does not involve 1,2-disilacyclobutane is the ene addition of one molecule of silene **13** to another, to yield **8** in a single step (Scheme 1-3).[27]

Scheme 1-3



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Comparison with other four-membered ring pyrolyses.

E- and Z-**1** are compared to the hydrocarbon analogues, E- and Z-1,2-dimethylcyclobutane **15**. Table 1-3 shows the kinetic information and relative product distributions from the decomposition of E- and Z-1,2-dimethylcyclobutane[28] at 398 °C. Similar distributions have been obtained more recently by Wang and Chickos.[29] This pattern is similar to that for the E- and Z- silacyclobutane, methylated at C(2) and C(3).

Table 1-3. Kinetics of pathways for decomposition of E- and Z-1,2-dimethylcyclobutane.[28]

Reactant	Product	log A (s^{-1})	Ea(kcal mol^{-1})	$10^5 k/s^{-1}$ (398.2 °C)	%
Z-**15**	$2C_3H_6$	15.48	60.4	6.60	69
	$C_4H_8 + C_2H_4$	15.57	63.0	1.16	12
	E-**15**	14.81	60.1	1.77	19
	butene stereochemistry: E/Z ~ 0.56 (14% conversion)				
E-**15**	$2C_3H_6$	15.45	61.6	2.50	70
	$C_4H_8 + C_2H_4$	15.46	63.4	0.665	19
	Z-**15**	14.57	61.3	0.413	12
	butene stereochemistry: Z/E - 0.13 (14% conversion)				

The following are the differences between the two four-membered ring systems: (i) Z-**1** decomposes about 9.1 times faster than Z-**15**, but E-**1** reacts about 6.4 times faster than E-**15**. (ii) Although structural isomerization products from hydrogen shifts occur only from the C-methylated silacyclobutane, the percentages of geometric isomerization (i.e. E/Z) are almost identical for **1** and **15**. (iii) Formation of propene relative to butene, via a split at the more substituted carbon-carbon bond, occurs more readily in the silacyclobutane than the cyclobutane (Table 1-4). Probably, this is due to the slightly different geometries of cyclobutane and silacyclobutane. Because the C-C-C bond angle of the silacyclobutane ring is greater than that of the cyclobutane, the methyl groups on C(2) and C(3) in **1** are expected to be closer to each other than the methyl groups in **15**. This might cause additional strain in silacyclobutane, which gives the higher propene/butene ratio. (iv) Although, differences in the stereochemistry of 2-butene formation are observed, our data do not allow definitive statements for mechanistic interpretation.[30] As shown below (Table 1-5) Z-**1** gives relatively more stereoretention than the carbon analogue (Z-**15**), while E-**1** provides similar stereoretention to E-**15**. However, in both four-membered ring systems, the E-isomers fragment with greater stereospecificity than the Z-isomers.

Table 1-4. Ratios of fragmentation pathways in E- and Z-**1** compared with E- and Z-**15**.

Ratio[a]	Z-**1**	E-**1**	Z-**15**	E-**15**
$\frac{\text{Propene}}{\text{2-butenes}}$	12.5	7.9	5.8	3.7

a In the cases of E- and Z-**15**, propene yields are halved to take account of reaction symmetry

Table 1-5. Comparison of 2-butene stereochemistry resulting from the decomposition of Z-**1**, Z-**15**, E-**1** and E-**15**.

Product Ratio	Z-1	5-15	Product Ratio	E-1	E-15
$\frac{\text{E-2-butene}}{\text{Z-2-butene}}$	0.23 ± .05	0.56	$\frac{\text{Z-2-butene}}{\text{E-2-butene}}$	0.16 ± .03	0.13

Tables 1-6 and 1-7 provide kinetic parameters for methyl substituted silacyclobutanes and cyclobutanes respectively. Following are the comments about the tables: (i) In the silacyclobutane cases, the presence of one methyl group at the 2 or 3 position accelerates decomposition by a factor of approximately 3 relative to 1,1-dimethylsilacyclobutane **16**. In contrast, this rate enhancement is about twice that observed for methylcyclobutane. (ii) Surprisingly, a second C-methyl group increases the rate of decomposition by a factor of 35 for Z-**1** and 10 for E-**1**. However, the effect of two vicinal methyl groups on cyclobutane is significantly smaller. (iii) It should be noted that Z-**1** decomposes 3.5 times faster than E-**1** and Z-**15** reacts 2.5 times faster than E-**15**. The rate enhancements of methyl substituted silacyclobutane suggest that transition states for the silacyclobutane systems are more stable than the transition states for the cyclobutanes. Unfortunately, the absence of the Arrhenius parameters for E- and Z-**1**, makes it impossible to distinguish between an entropy or enthalpy effect.

Thermochemistry

Bond dissociation enthalpies as well as substitutent effects may be estimated by using thermochemical kinetics.[32] As an example, the well-known fragmentation of cyclobutane (assumed as a hypothetical biradical process), is compared to that dimethylsilacyclobutane.

Table 1-6. Kinetic parameters and relative rate constants for decomposition of selected silacyclobutanes.

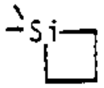
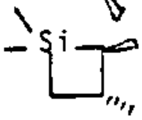
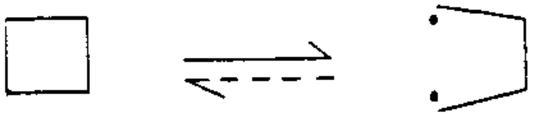
molecule	log A (s^{-1})	Ea (kcal mol^{-1})	10^4 k/s^{-1} (398.2 C)	rel. rate	ref.
	15.64	62.5	0.20	1	2,36
	15.45	60.6	0.53	2.7	31
	16.39	63.3	0.62	3.1	22
	-----	----	7.00	35	This Work
	-----	----	1.97	10	This work

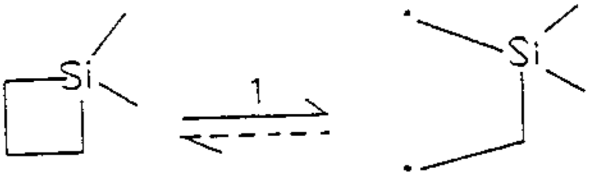
Table 1-7. Kinetic parameters and relative rate constants for the decomposition of slected cyclobutanes.

molecule	log A (s^{-1})	Ea (kcal mol^{-1})	10^4 k/s^{-1} (398.2°C)	rel. rate	ref.
	15.6	62.5	0.18	1	35
	15.64	62.0	0.29	1.6	37
	15.68	61.0	0.67	3.7	38
	15.68	60.8	0.78	4.3	28
	15.67	62.0	0.31	1.7	28



The enthalpy ΔH^o for ring opening of cyclobutane might be estimated by using the bond dissociation enthalpy of the central bond of n-butane and the ring strain enthalpy of cyclobutane, i.e., $\Delta H^o = D(C-C)$ - ring strain.[33] Substituting corresponding values in the above,[34] gives ΔH^o (kcal mol^{-1}) = 86.5 - 26.2 = 60.3. The reported experimental activation energy is 62.5 kcal mol^{-1}.[35] The discrepency between the two numbers, 2.2 kcal mol^{-1}, may be attributed to the activation barrier for recombination of the 1,4-methylene radicaloid centers.

In the case of dimethylsilacyclobutane decomposition, there are two possible sites of initial ring opening: the silicon-carbon or carbon-carbon bond. Barton, et al.[9] used a methyl group, substituted on C(2) as a mechanistic probe. They found that carbon-carbon cleavage is the major fragmentation path producing the isolated silene products. Our thermochemical analysis, therefore, considers (i) whether biradical formation from cleavage of a C-C bond has a significant energetic advantage over that for an Si-C bond and (ii) whether the energy involved parallels the experimental activation energy. For this purpose the decomposition of dimethylsilacyclobutane is considered here.[3,36] First we examine C-C bond breaking:



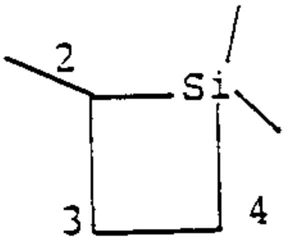
In this case the most significant influences on the activation enthalpy are: (i) carbon-carbon bond strength, (ii) ring strain, and (iii) stabilization effects of the silicon atom on developing α- and β-radical sites, i.e., $\Delta H^o_1 = D(C\text{-}C)$ - ring strain - stabilization effects. Experimental studies have suggested that α and β stabilization effects of silicon are 0.5[13] and 3.0[14,15] kcal/mol respectively. Recent application of group additivity to organosilicon compounds[39] gives an estimate of the ring strain for 1,1-dimethylsilacyclobutane of $E_s = 22 \pm 3$ kcal mol^{-1}. Substituting corresponding values in the equation above gives ΔH^o (kcal mol^{-1}) $= 86.5 - 22 - 3 - 0.5 = 61$. In comparison to the known experimental activation energy $E_a \doteq 62.5$ kcal mol^{-1} there is but a small difference. This difference between the numbers, 1.5 kcal mol^{-1}, again suggests a very small barrier for ring closure.

Secondly, we consider Si-C bond breaking:

In this analysis, ΔH_1°, 61 kcal mol^{-1}, from above, is compared to the calculated ΔH_2° for silicon-carbon bond cleavage. The appropriately modeled silicon-carbon bond dissociation energy for comparison is that which produces a tertiary silyl radical and a primary carbon radical as in D(Et-$SiMe_3$). From the application of the group additive methods estimate[39] for ΔH_f° (Me_3SiEt) and known ΔH_f° values for $SiMe_3$[13] and C_2H_5,[34] we estimate D(Me_3Si-Et) to be 87.2 kcal mol^{-1}. With the same E_s, 22 kcal mol^{-1}, and assuming that there are not any special interaction effects of silicon with the developing radical center, the barrier for silicon-carbon bond cleavage ΔH_2°, become 65.2 kcal mol^{-1} (87.2 - 22 = 65.2). This value is higher than the experimental activation energy and effectively rules out initial cleavage at the Si-C bond.

If the activation entropies for C-C and Si-C cleavage are quite similar, the ratio of the respective rate constants k_1 to k_2 at 400 °C, a typical temperature for static pyrolyses, is $\exp(\Delta H_2 - \Delta H_1)/RT \approx 23$. The assumption that fragmentation is initiated at a carbon-carbon bond in dimethylsilacyclobutane is consistent with the available thermochemistry. At higher temperatures, 700°C, more typical of those utilized in flash vacuum pyrolysis experiments, the ratio of k_1/k_2 is ≈ 9.

The effects of methyl groups on the enthalpies of cleavage of the two types of bonds in silacyclobutanes, Si-C and C-C, are not known. However, the similarity of the Arrhenius parameters for 1,1,2- and 1,1,3-trimethylsilacyclobutanes suggests an insignificant difference between the two. Interestingly, these arguments, while supporting the conclusion of Barton et al.[9] that initial C-C cleavage represents the major reaction path for 1,1,2-trimethylsilacyclobutane, tend to point up the probability that the minor reaction path also occurs with initial C-C cleavage (the less substituted C-C bond). Thus in 1,1,2-trimethylsilacyclobutane, the C_3 - C_4 fragmentation is still favored over Si-C_2 breaking. With conclusion that initial C-C bond breaking is dominant, the explanation for more marked methyl group substituent effects in silacyclobutanes as opposed to cyclobutanes becomes more elusive. Since the energetic advantage of C-C over Si-C bond breaking apparently derives in large part from the



stabilization of the β-radical center by silicon, an explanation first offered by Barton et al.[9], then the methyl groups may offer some small but subtle modifications (enhancements) to this interaction and also possibly to the α-interaction.[40] In addition, pyrolysis of silacyclobutane containing unsaturated carbon substitutents such as phenyl and vinyl groups placed on the 2- and 3- ring carbon atoms respectively, support the situation described above. For example, pyrolysis of 2-phenyl-1,1-dimethylsilacyclobutane gives the E- and Z-2,4-diphenyl-1,1,3,3-tetramethyldisilacyclobutane and < 5%, if any, styrene.[11] Also, in the thermal fragmentation of the highly substituted 3-vinyl-2-(trimethylsilyl)methyl-1,1-dimethylsilacyclobutane, formation of each of the six isolated products could be attributed to an initial C-C bond cleavage.[41] In all other silacyclobutane pyrolyses, with exceptions of hydridosilacyclobutanes and 2-methylene-1,1-dimethylsilacyclobutane, described earlier and possibly 1,1-dichlorosilacyclobutane,[42] product analyses do not require any initial Si-C bond cleavage.

Experimental

Proton nmr spectra were obtained on a Hitachi Perkin-Elmer R24B 60-MHz spectrometer with CH_2Cl_2 as an internal standard and carbon nmr spectra were recorded on a JEOL FX902 spectrometer using D_2O or $CDCl_3$ as a lock solvent. All chemical shifts are reported in ppm downfield from external TMS. High resolution (360-MHz) nmr spectra of E-**1** and Z-**1** were obtained on a Nicolet spectrometer at the regional NSF facility at the Colorado State University or on a Varian 300-MHz VXR spectrometer at UNT. Infrared spectra were carried out in gas phase cells (10 torr of sample) on a Perkin-Elmer 1330 spectrometer calibrated to polystyrene. Preparative gas chromatography was performed on a Varian 90A GLC (thermal conductivity detector). When the reaction products were not isolated, yields were determined chromatographically with cyclohexane as an internal standard and predetermined response factors for the organosilanes. Analytical gas chromatography was carried out on a HP 5840A GLC (flame ionization detector) equipped with a Valco gas sampling port. Mass spectra were obtained on a HP 5970A mass selective analyzer coupled to a HP 4790A gas chromatograph. Elemental analyses were performed by the Midwest Center for Microanalysis and exact mass measurements were determined by the Midwest Center for Mass Spectrometry.

Synthesis of (3-chloro-2-methylbutyl)dimethylchlorosilane)

To a 25 mL three-neck flask containing 5.0g (49 mmol) of 3-chloro-2-methyl-1-butene[14] and hexachloroplatinic acid, 200 mg, dimethylchlorosilane (5.2 g, 55 mmol) was added dropwise over a period of 1 hour. The mildly exothermic reaction was stirred for 2 hours at room temperature and for 10 hours at 55 °C. The reaction mixture was cooled, flash distilled in order to separate the products from the catalyst and then slowly heated until unreacted dimethylchlorosilane was removed. Analytical gas chromatography (10% SP2100 on Supelcoport, 10 ft) indicated two diastereomers present in >85% yield. Samples of the diastereomers were purified but not separated by preparative gc (20% OV-17 on Chromobsorb W, 10 ft, 60 °C) for subsequent characterization. ^1H nmr (neat mixture) δ: 0.70 (6H, s, $(CH_3)_2Si$), 1.22 (2H, d, J = 6.7 Hz, CH_2-Si), 1.35 (3H, d, J = 7.1 Hz, CH_3CSi), 1.65 (3H, d, J = 6 Hz, CH_3CCl), 2.21 (1H, m CH), 4.12 (1H, m CH); ^{13}C nmr (neat mixture) δ: 2.73 (q), 17.36 (t), 18.86 (t) 21.47 (q) 21.98 (q) 22.37 (q), 23.80 (q), 36.48 (d), 36.74 (d), 64.96 (d), 65.09 (d); m/e (% rel. int.): 137 (67), 135 (100), 115 (41), 113 (60), 95 (99), 93 (98), 54 (78).

Synthesis of E- and Z-1,1,2,3-tetramethyl-1-silacyclobutane-1

A mixture of 8.6 g (4.3 mmol) of the diastereomers was added to 3.1 g of magnesium in 100 mL of THF and mechanically stirred at 25 °C for 2 hours at room temperature and 55 °C for 16 hours. The reaction mixture was cooled in an ice bath and a saturated solution of ammonium chloride was added. The copious precipitate was filtered and washed with ether. The combined filtrates were placed in a separatory funnel and washed successively with water, 5% $NaHCO_3$, brine, water, and dried with Na_2SO_4. The products **E-1** and **Z-1**, obtained in 70% yield, were concentrated by distillation and chromatographically purified (20% OV-17 on Chromobsorb W, 0.25 in x 25 ft). With the oven temperature at 55 °C and a flow rate of 50 mL/min, product retention times were 10.5 min for the E- and 16.5 min for the Z-isomer.

E-1: ^1H nmr (neat) δ: 0.17 (3H, s, CH_3Si), 0.21 (3H, s, CH_3Si), 0.42 (1H, dd, J = 12.60 Hz, J = 10.82 Hz, CH_cSi), 0.78 (1H, app q, CH_aSi), 0.95 (3H, d, J = 7.2 Hz, CH_3CSi), 1.08 (3H, d, J = 6.4 Hz, CH_3CCSi), 1.10 (1H, m, $CH_{c'}Si$), 1.74 (1H, m, $CCH_{b'}C$); ^{13}C nmr (neat) δ: -5.66 (q), 0.52 (q), 13.46 (q), 20.74 (t), 24.06 (q), 31.28 (d), 36.22 (d); ^{29}Si nmr (neat)'δ: 7.68; IR (gas): 2955(s), 2912(s), 2877(s), 1467(m), 1253(w), 1145(w), 1067(w), 1042(w), 981(m), 972(m), 845(s), 822(s), 732(m); GC/MS (%rel. int.): 128 (10), 113

(4), 87 (12), 86 (94), 73 (16), 72 (55), 59 (44), 58 (100), 55 (11), 45 (15), 44 (22), 43 (48); elemental analysis: calcd C = 65.52, H = 12.57, found C = 65.26, H = 12.58.

Z-**1**: ^{1}H nmr (neat) δ: 0.19 (3H, s, CH_3Si), 0.23 (3H, s, CH_3Si), 0.66 (1H, dd, J = 12.86 Hz, J = 7.71 Hz, $CH_{c'}Si$), 0.95 (3H, d, J = 8.0 Hz, CH_3CSi), 1.00 (3H, d, J = 7.02 Hz, CH_3CCSi), 1.10 (1H, ddd, J = 12.86 Hz, 7.71 Hz, 4.10 Hz, CH_cSi), 1.38 (1H, app q, $CH_{a'}Si$), 2.51 (1H, app q, $CCH_{b'}CSi$); ^{13}C nmr (neat) δ: -2.60 (q), -1.37 (q), 9.23 (q), 9.18 (q), 20.35 (t), 24.45 (d), 30.37 (d); ^{29}Si nmr (neat) δ 10.97; IR (gas): 2955(s), 2925(s), 2882(s), 1464(m), 1255(s), 1157(w), 1067(w), 975(m), 967(m), 847(s), 805(s), 707(m); GC/MS (rel. int.): 128 (9), 113 (5), 87 (11), 86 (100), 73 (15), 72 (56), 59 (36), 58 (91), 45 (12), 44 (20), 43 (41); elemental analysis: calcd C = 65.52, H = 12.57, found C = 65.09, H = 12.37.

Pyrolysis Kinetics. These were carried out in static reactors in the vapor phase at both Reading[43] and Denton using equipment previously described.[14,44] The products of E-**1** and Z-**1**, alkenes **2-4** and silanes **5-10** are known compounds. For identification purposes, gas chromatographic retention times were characterized with samples obtained commercially or synthesized independently. A number of different columns were used for analysis. In Denton, alkene separations were achieved on a 3% picric acid/graphite column (3ft x 0.125 in, 50 °C) and silanes on a SP2100 column, described earlier or an SP2250 (15% w/w #100 Supelcoport, 10 ft x 0.125 in, 100 °C). At Reading, a Silicon Fluid column (15% on 60/80 Chromosorb P, 12 ft x 0.125 in) separated the alkenes at 0 °C and the silanes at 80 °C. In both laboratories, detection was by FID and relative product yields on each column were based on calibrated gas mixtures for alkene products. It was however, assumed that silane isomers had identical response factors. With the complex product mixtures produced in these pyrolyses, it was found more convenient and reliable to compare hydrocarbon and silane yields relative to cyclohexane as an inert internal standard (as mixtures with E-1 and Z-1 prior to a series of runs).

Tables 1-8 and 1-9 show the time evolution of the distribution of major products (and reactants) in pyrolysis mixtures at 398.2 ± 0.3 °C. A number of other runs, carried out at different pressures of reactant (1-6 Torr) or at higher pressures with added inert gas N_2 up to 25 Torr indicated no pressure dependence on the rate constants.

Ratios of Z- and E-2-butenes, **2** and **4** respectively, were also determined during the present experiments and were found to be very sensitive to the presence of adventitious air, which tended (i) to increase yields of **2** and **4** and (ii) to equilibrate ratio of **2/4**. After careful degassing of the

Table 1-8. Mixture compositions from pyrolysis of Z-1

			% Composition			
Time sec	Reactant (Z-1)	Propene (3)	2-Butene (2)+(4)	(E-1)	(6)	(5)
100	91.16	4.63	0.36	2.51	0.32	1.02
180	87.50	8.20	0.60	2.36	0.38	0.96
310	83.53	10.62	0.95	3.06	0.54	1.30
600	64.01	23.25	1.63	6.86	1.27	2.99
1020	48.32	35.07	2.46	8.63	1.36	4.15
1230	40.25	41.17	3.74	8.77	1.45	4.61
1800	31.72	46.59	3.56	10.63	1.61	5.88

Table 1-9. Mixture compositions from pyrolysis of E-1

			% Composition			
Time sec	Reactant (E-1)	Propene (3)	Butene (2)+(4)	(Z-1)	(6)	(5)
300	94.45	4.27	0.61	0.67	tr	tr
600	88.80	9.03	1.17	1.00	tr	tr
1200	78.16	16.01	2.08	1.66	tr	2.09
3780	44.51	41.95	5.16	1.68	0.95	5.75
6240	28.60	52.32	5.77	(3.21)	1.96	8.14
10800	13.53	63.04	8.73	0.45	2.96	11.29

tr = trace

reactants, reproducible ratios were found which were independent of reactant starting pressure. These are shown in the results section.

Synthesis of allylethyldimethylsilane 5[45] To a solution of allyl Grignard (from allylbromide, 4.0 g, 33 mmol and Mg, 3.0 g, 125 mmol in 30 mL of diethyl ether) in a 100 mL, 3-neck round bottom flask, equipped with a reflux condenser, dropping funnel and magnetic stirring bar was added 1.73 g, 14 mmol of chloro(ethyl)dimethylsilane. The reaction mixture was stirred for 2 h at room temperature and for 1 h at 45 °C until the chlorosilane had disappeared. The reaction mixture was then poured onto a 50 mL solution of cold saturated ammonium chloride. The organic layer was separated, washed with H_2O and dried over anhydrous sodium sulfate (gc yield = 60% on OV-17 as described above). The authentic sample was used to identify 5 from the kinetic pyrolyses. ^{13}C nmr (neat) δ: -5.07 (q), 6.05 (t), 6.50 (q), 22.24 (t), 112.11 (t), 133.96 (d).

Synthesis of dimethylpropylvinylsilane 6[46] To a solution of propyl Grignard (from bromopropane, 4.1 g, 33 mmol and Mg, 3.0 g, 125 mmol in 30 mL of diethyl ether) in a 100 mL 3-neck round bottom flask equipped with a reflux condenser, dropping funnel and magnetic stirring bar was added 1.70 g, 14 mmol of chloro(dimethyl)vinylsilane. The reaction mixture was stirred at room temperature for 2 h and at 45 °C for 1 h until the chlorosilane had disappeared. The typical

Grignard workup afforded 6, 70% g.c. yield (20% SF-96 on Chromabsorb W, 1/4 in x 20 ft.) ^{13}C nmr (neat) δ: -4.10 (q), 16.84 (t), 17.60 (q), 17.63 (t), 130.51 (t), 138.32 (d).

Synthesis of 1,1,1-ethyldimethyl-2,2,2-vinyldimethyl-1,2-disilane 8[47] To a 100 mL flask containing 0.5 g (71 mmol) of Li wire (1/4 in x 1/8 in pieces) and 50 mL of tetrahydrofuran (THF), under Ar, was added a solution of 2.0 g (16 mmol) of chloroethyldimethylsilane, 2.0 g (16.3 mmol) of chloro(dimethyl)vinylsilane. The flask was immersed in a water filled ultrasound laboratory cleaner[48] and after 3h, the liquid in the flask was flash distilled under vacuum. Product **8** was isolated by fractional distillation, 40% yield (1.12g, bp 77 °C/30 Torr). ^{13}C nmr (neat) δ: -5.07 (q), -4.55 (q), 6.50 (t), 7.61 (q), 130.19 (t), 138.50 (d).

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CHAPTER 2

THE INSERTION OF DIMETHYLSILYLENE INTO SILICON AND GERMANIUM-CARBON BONDS

Introduction

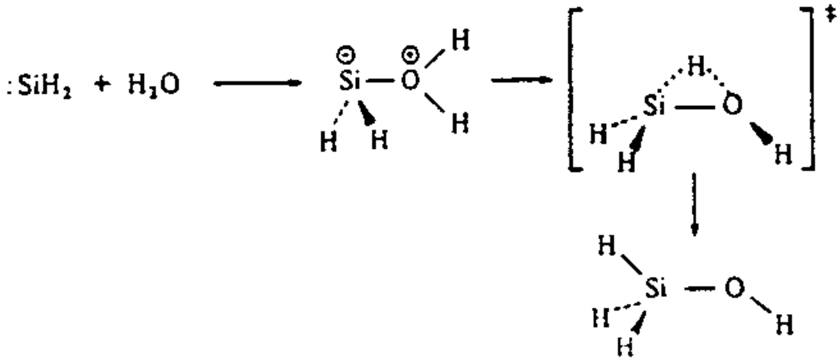
Silylene chemistry has been actively studied since the mid-1960s.[1] One of the first methods of the preparation of dimethylsilylene was suggested by Gilman and co-workers in its reverse Diels-Alder extrusion from several bicyclic precursors.[2] However, extrusion of silylenes from disilanes remains one of the most important preparation methods for their thermal generation. Subsequently, polysilanes have been used as precursors for the photochemical generation of silylenes.[1] Kumada and co-workers studied the photolysis of dodecamethylcyclohexasilane, and found that photolysis yields dimethylsilylene and the corresponding cyclopentasilane.[3]

$$\text{cyclo-}(Me_2Si)_6 \xrightarrow{h\nu} Me_2Si: \quad + \quad \text{cyclo-}(Me_2Si)_5$$

Gorden[4] reported theoretical calculations for the insertion of $:SiH_2$ into the H_2 molecule to form SiH_4. These calculations predict a 8.6 kcal/mol barrier for this insertion; the corresponding experimental valve is 5.5 kcal/mol.[5] A similar calculation for insertion of $:CH_2$ into

H_2 showed no barrier. Also, the calculations for the insertion of SiH_2 into the O-H bond have been shown that insertions involve initial coordination of an oxygen lone pair of electrons with the empty 3p orbital of the silylene to form a stable zwitterionic complex which then rearranges to silanol (E_a = 23.4 kcal/mol)[6].

(ref. 2-1)



Weber and Steele[7] reported the isotope effect in the hydrogen migration step for the reactions of Me_2Si: with ethanol, kH/kD=2.3 (ether) and for insertion into the Si-H bond of n-butyldimethylsilane, kH/kD=1.4 (ether). Gu and Weber[8] have found that Si-H and Si-OR bonds of polysilanes are more reactive toward silylene than the corresponding substituted monosilanes. They have shown that $Me_3SiSiHMe_2$ is 1.5 times as reactive toward Me_2Si: than n-$BuMe_2SiH$ and $Me_3SiSiMe_2OEt$ is about seven times as reactive as Me_3SiOMe. these results were used to explain the formation of higher silanes from the reactions of monosilanes with Me_2Si:.

$$\text{cyclo-(Me}_2\text{Si)}_6 + \text{HSiMe}_3 \xrightarrow[\substack{[\text{Me}_2\text{Si}]:[\text{H-Si}] \\ 1:3}]{h\nu}$$

$$\underset{28.5\%}{\text{HSiMe}_2\text{SiMe}_3} + \underset{22\%}{\text{H(SiMe}_2)_2\text{SiMe}} + \quad \text{(ref. 2-1)}$$

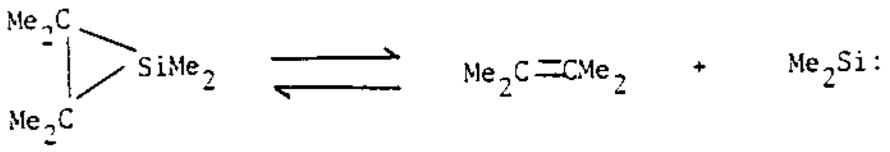
$$\text{H(SiMe}_2)_3\text{SiMe}_3 \;\; 11\%$$

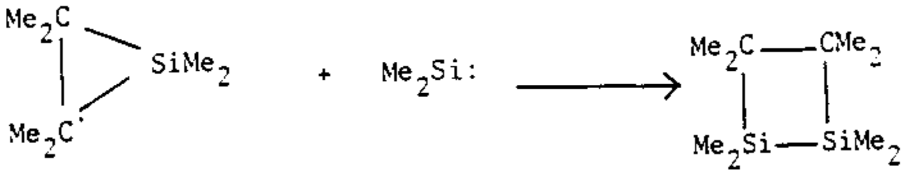
$$\text{cyclo-(Me}_2\text{Si)}_6 + \text{EtOSiMe}_3 \xrightarrow[\substack{[\text{Me}_2\text{Si}]:[\text{O-Si}] \\ 1:2}]{h\nu}$$

$$\underset{10\%}{\text{EtOSiMe}_2\text{SiMe}_3} + \underset{25\%}{\text{EtO(SiMe}_2)_2\text{SiMe}_3} +$$

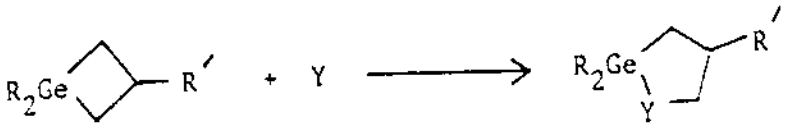
$$\text{EtO(SiMe}_2)_3\text{SiMe}_3 \;\; 32\%$$

So far there is only one example of the insertion of silylene into the Si-C bond, reported by Seyferth's[9] group. They found that hexamethylsilacyclopropane decomposes thermally at 70 °C, and yields dimethylsilylene which it subsequently inserts into the Si-C bond of silacyclopropane and produces octamethyl-1,2-disilacyclobutane.





A number of reactions involving insertion into a Ge-C ring bond of germacyclobutanes have been reported.[10,11]

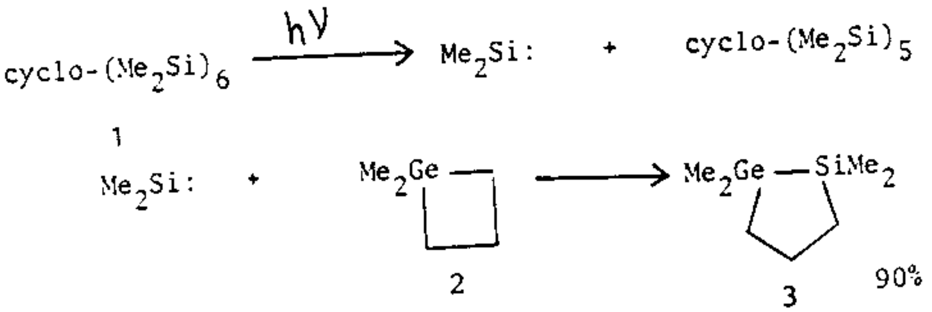


$Y = S, SO_2, :CCl_2, Me_2Ge:$; $R' = H$, alkyl

The insertion of dimethylsilylene into the cyclic Ge-C or Si-C bonds of 1,1-dimethylgerma- or silacyclobutane, however, have not been studied. We consider such reactions and report the relative reactivities of 1,1-dimethylgerma- and silacyclobutanes toward the dimethylsilylene. Also, the reactions of the carbenoid resulting from the cuprous chloride-catalyzed decomposition of diazomethane with dimethylgerma- or silacyclobutane are described.

Results and Discussion

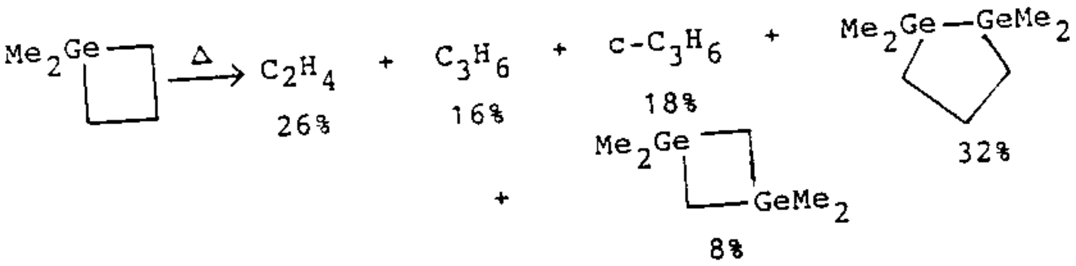
The photolysis of dodecamethylcyclohexasilane (**1**) in the presence of an eight fold excess of 1,1-dimethyl-1-germacyclobutane (**2**) in cyclohexane at 254 nm at room temperature gave 1,1,2,2-tetramethyl-2-germasilacyclopentane 3 in 90% yield. On the basis of the polarizability of the



(eqn 2-1)

Ge-C bonds, together with the ring strain of the germacyclobutanes which induce high chemical reactivity[10,11] product **3** might have been expected. The insertion of dimethylgermylene into the cyclic Ge-C bond of dimethylgermacyclobutane has been reported.[12]

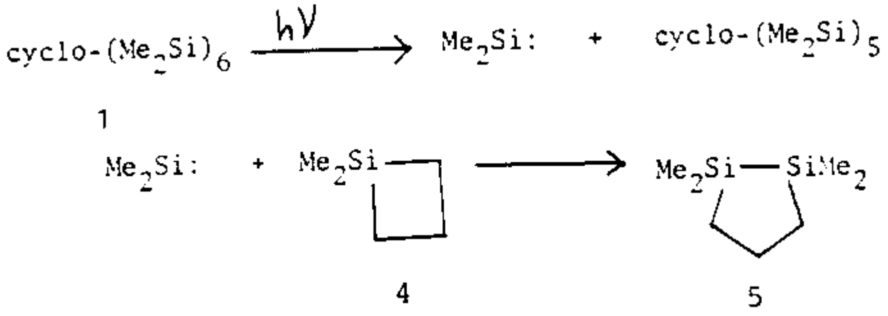
(eqn 2-2)



Equation 2-1 shows the first example of the insertion of dimethylsilylene into the cyclic Ge-C bond of **2**.

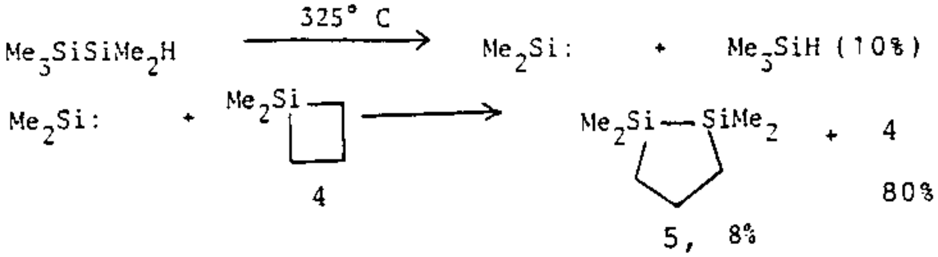
When photolysis of a mixture of **1**, **2** and triethylsilane, with the ratios of 1:5:5 respectively was carried out for four hours, the ratio of the Si-H insertion product, triethyldimethyldisilane to **3** was 38 to 1. This is not surprising since it has been known that alkylsilanes containing Si-H bond are good traps for silylene.

Similarly, photolysis of **1** in the presence of an eight fold excess of 1,1-dimethyl-1-silacyclobutane (**4**) in n-heptane at room temperature gave 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**5**) in a lower yield (8%). This demonstrates that the Ge-C bond of **2** is more reactive toward the silylene insertion than the Si-C bond of the homolog **4**.


(eqn 2-3)

In a competition experiment, photolysis of a mixture of **1**, **2** and **4**, with the ratios of 1:5:5 respectively, was monitored for 7.5 hours. The ratio of **3** to **5** was 3.5 to 1.0 and remained constant as a function of photolysis time. Again, this experiment indicates that silylene inserts more slowly into the cyclic Si-C bond of **4** than into the cyclic Ge-C bond of **2**.

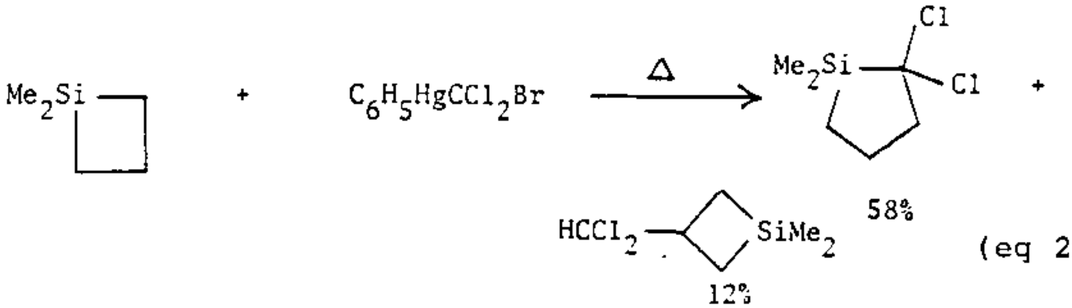
Pentamethyldisilane has been used as a precursor for the thermal generation of silylene.[13] Pyrolysis of pentamethyldisilane and a ten-fold excess of 1,1-dimethylsilacyclobutane, **4** in a 500 mL closed pyrolysis vessel at 325 °C gave **5** in 8% yield.



(eqn 2-4)

It appears that the thermally generated silylene in the gas phase at 325 °C inserts into the cyclic Si-C bond of silacyclobutanes in the same fashion as the photochemically one in the solution at the room temperature.

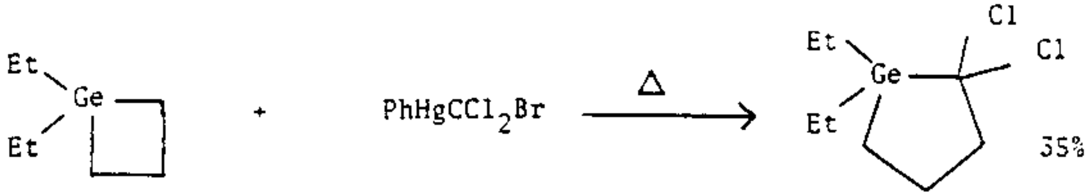
Seyferth and co-workers have extensively investigated the reactions of dichlorocarbene generated from pyrolysis of phenylbromodichloromethylmercury and dimethylsilacyclobutanes. They found that insertion occurs in the cyclic Si-C bonds as well as C-H bonds β to the silicon atom.[10,11,14]



(eq 2-5)

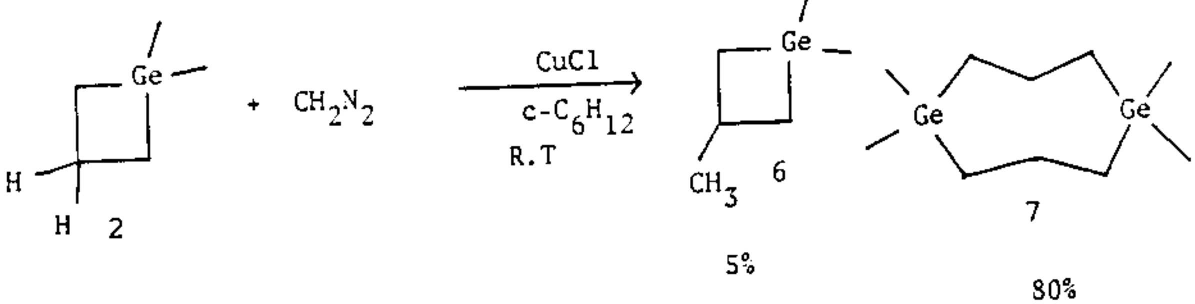
However, the reaction of 1,1-diethylgermacyclobutane with dichlorocarbene gives only 2,2-dichloro-1,1-diethyl-1-germacyclopentane in a lower yield (35%).[10,11]

(eq 2-6)



These reactions led us to investigate the analogous methylene insertion reaction. It has been found that the carbenoid species which previously had been shown to be inert to alkanes did, however, insert into the C-H bonds of hexamethyldisilane. Furthermore, the activation of C-H bonds toward carbenoid insertion also occurred for organotin and to a lesser extent for organogermanium compound.[15] We found that the carbenoid resulting from the cuprous chloride catalyzed decomposition of diazomethane at the room temperature in cyclohexane reacts with dimethylgermacyclobutane **2** to give 1,1,3-trimethyl-1-germacyclobutane **6** (5%) and surprisingly 1,1,5,5-tetramethyl-1,5-digermacyclooctane **7** as the major product (80%).

(eq2-7)

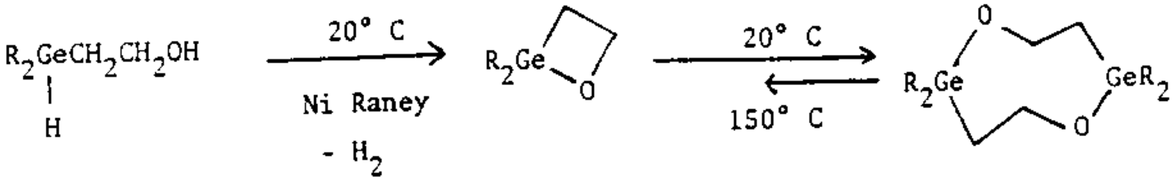


Product **6** is formed by the insertion of the carberoid, resulting from the copper catalyzed decomposition of diazomethane, into the C-H bonds β to the germanium atom of **2**. In order to insure that product **6** is produced from the carbenoid and not free methylene, it was necessary to preclude stray light as the source of a suprious result. When the reaction of diazomethane with **2** was repeated in the absence of cuprous chloride but otherwise under conditions identical with those which produced products **6** and **7**, the GC analysis indicated that no product was formed. Formation of product **7**, a dimer of **2** is surprising. It appears that the carbenoid resulting from the copper catalyzed decomposition of diazomethane has an important role in the formation of **7**. When the reaction was repeated in the absence of diazomethane at room temperature no product was formed, but at 110 °C all of the 1,1-dimethylgermacyclobutane disappeared and an uncharacterized polymeric material was formed.

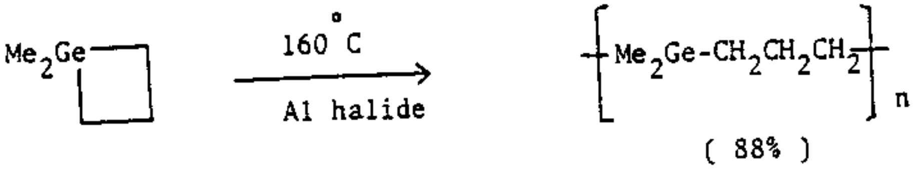
$$2 + \mathrm{CuCl} \xrightarrow[\mathrm{c\text{-}C_6H_{12}}]{\mathrm{R.T}} \text{no reaction} \qquad \text{(eq 2-8)}$$

$$2 + \mathrm{CuCl} \xrightarrow[\mathrm{c\text{-}C_6H_{12}}]{110^\circ\ \mathrm{C}} \text{wax (polymer ?)} \qquad \text{(eq 2-9)}$$

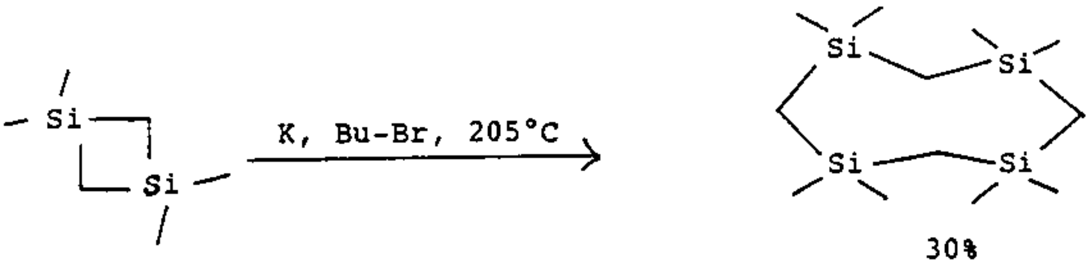
Equation 2-7 shows the first example of the dimerization of **2** in the presence of the transition metal salt. The following reaction shows the dimerization of dialkyl-2-germaoxatane at 20 °C.[16]



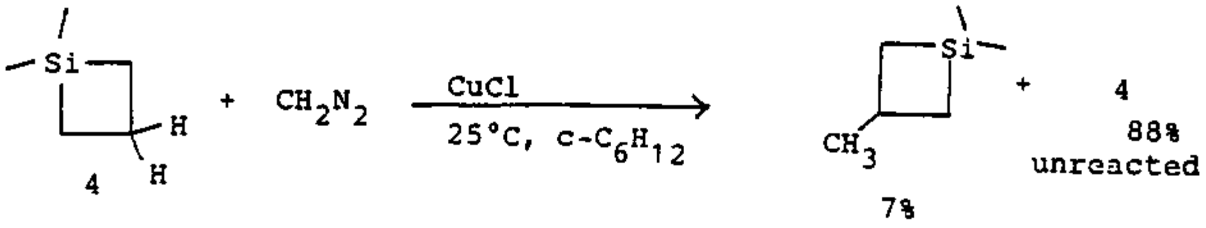
It has been reported that 1,1-dimethylgermacyclobutane **2** undergoes polymerization at 160 °C in the presence of aluminum halides to give a high-molecular weight polymer.[13]



Also, dimer of 1,1,3,3-tetramethyl-1,3-disilacyclobutane has been prepared.[17a]



Finally, we found that the carbenoid resulting from the cuprous choride catalyzed decomposition of diazomethane at room temperature in cyclohexane reacts with 1,1-dimethylsilacyclobutane **4** to produce 1,1,3-trimethyl-1-silacyclobutane **8** (7%) and unreacted **4** (88%). Surprisingly, no product corresponding to the dimerization of **4** was formed.

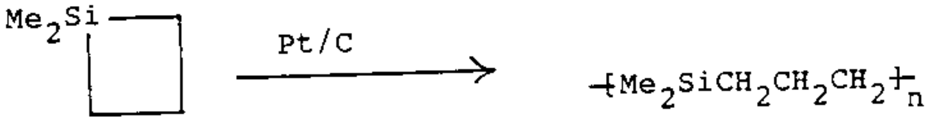


When the reaction was repeated in the absence of diazomethane at room temperature no product was produced, but at 95 °C an uncharacterized polymeric material was formed.

$$4 \quad + \quad CuCl \xrightarrow[c\text{-}C_6H_{12}]{25°C} \text{no reaction}$$

$$4 \quad + \quad CuCl \xrightarrow[c\text{-}C_6H_{12}]{95°C} \text{wax (polymer?)}$$

Polymerization of 1,1-dimethylsilacyclobutane in the presence of platinum has been reported.[17b]



Experimental

General data. Proton and carbon nmr spectra, mass spectra, analytical gas chromatography and preparative gas chromatography were performed as described in Chapter 1. Yields were calculated from response factors using cyclohexane or n-heptane as internal standards. Photolysis were carried out in a Rayonet photochemical reactor (RPR-100) equipped with 254 nm lamps. Pyrolysis were performed as described in Chapter 1. Compounds **4** and triethylsilane were purchased from Petrarch, **2** was synthesized as described in Chapter 3. Pentamethyldisilane was synthesized by the reduction of chloropentamethyldisilane using LAH in ether. Cyclo-$(Me_2Si)_6$ was synthesized by the referenced procedures.[18]

1-Photolysis of dodecamethylcyclohexasilane in 1,1-dimethyl-1-germacyclobutane.--A solution of 0.49 g (3.4 mmol) of 1,1-dimethyl-1-germacyclobutane and 0.15g (0.4 mmol) of dodecamethylcyclohexasilane were placed in a 5 mm quartz nmr tube and irradiated at 254 nm for 215 minutes. The reaction mixture was flash distilled under vacuum. Preparative GC of the liquid afforded 1,1,2,2-tetramethyl-2-germasilacyclopentane (**3**) 90% gc yield (20% OV-17 on chromosorb W, 1/4 in. x 20 ft.) **3**:^1H nmr (neat) ppm o.12 (6H,S,CH_3Si), 0.17 (6H,S,CH_3Ge),[19] 0.61 (2H, t, J = 6.5 HZ, CH_2Si), 0.77 (2H, t, J = 7.2 HZ, CH_2Ge), 1.61 (2H, app quintet, CCH_2C); ^{13}C nmr (neat) ppm -4.75(q), -3.45(q), 19.51(t), 19.96(t), 23.54(t); GC/MS:m/e(relative intensity), 205 (48), 204 (27), 203 (37), 202 (15), 201 (27), 189 (25), 187 (22), 185 (15), 165 (16), 163 (58), 162 (30), 161 (60), 160 (16), 159 (46), 147 (25), 145 (21), 117 (18), 113 (29), 111 (19), 99 (18), 89 (39), 87 (38), 85 (26), 73 (100), 59 (43), 45 (26), 43 (29).

2-Photolysis of dodecamethylcyclohexasilane in 1,1-dimethyl-1-silacyclobutane.--A solution of 0.34 g (3.4 mmol) of 1,1-dimethyl-1-silacyclobutane, 0.15g (0.4 mmol) of dodecamethylcyclohexasilane and 0.1 g (1 mmol) of n-heptane irradiated for 10 hours. The procedure in experiment 1 was applied to purify the product. Preparative GC on the OV-17 column gave 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**5**) 8% g.c. yield. ^{13}C nmr (neat) ppm:-4.10(q), 18.79(t), 22.43(t):^{1}H nmr and mass spectral data agree with previously reported values.[20]

3-Photolysis of dodecamethylcyclohexasilane in 1,1-dimethyl-1-germacyclobutane and triethylsilane.--A mixture of 112 mg (0.77 mmol) of 1,1-dimethyl-1-germacyclobutane, 90 mg (0.77 mmol) of triethylsilane and 54 mg (0.16 mmol) of dodecamethylcyclohexasilane irradiated for 4 hours. The ratio of the Si-H insertion product, triethyldimethyldisilane to **3** was 38 to 1.0.

4-Photolysis of dodecamethylcyclohexasilane in 1,1-dimethyl-1-germacyclobutane and 1,1-dimethyl-1-silacyclobutane.--A solution of 109 mg (1.1 mmol) of 1,1-

dimethyl-1-silacyclobutane, 157 mg (1.1 mmol) of 1,1-dimethyl-1-germacyclobutane and 75 mg (0.2 mmol) of dodecamethylcyclohexasilane was irradiated for 7.5 hours. The ratio of 1,1,2,2-tetramethyl-2-germasilacyclopentane **3** to 1,1,2,2-tetramethyl-1,2-disilacyclopentane **5** was 3.50 to 1.0 and remained constant as a function of photolysis time.

5-Cuprous chloride.[15]--A solution of 7.6 g (0.06 mol) anhydrous sodium sulfite in 50 ml of water was added slowly at room temperature to a stirred solution of 10 g (.06 mol) of $CuCl_2,2H_20$ in 10 ml of water. The mixture became dark brown and then white cuprous chloride precipitated slowly. After stirring the mixture for 30 minutes, the precipitate and supernatant liquid were then poured into a liter of water containing 1 g of sodium sulfite and 2 ml of concentrated HCl. The mixture was again stirred for 30 minutes. The pale white precipitate was then allowed to settle, and the supernatant liquid was carefully decanted. The cuprous chloride was quickly transferred to a suction filter and washed in succession with 25 ml of dilute sulfurous acid, 100 ml of acetic acid, 90 ml of absolute ethanol and finally with 90 ml of anhydrous ether. The cuprous chloride was then quickly removed to an oven and dried at 100 ^{o}C for 20 minutes.

6-Acetylmethylurea.[15,22]--Acetamide (54 g, 1 mol) and bromine (88 g, 0.55 mol) was placed in a 4-liter beaker. Then a solution of 40 g (1 mol) of sodium hydroxide in 180 ml of water was added dropwise. The mixture was stirred and gently heated by a steam bath until effervescence occurred. Finally, the mixture was cooled in an ice bath for an hour, and then white crystaline acetylmethylurea was collected by suction filtration in greater than 80% yield. It was used without any further purification.

7-N-nitrosomethylurea.[15]--A mixture of acetylmethylurea (40 g, 0.34 mol) and concentrated HCl (40 ml) was heated on a steam bath for 15 minutes. The solution was diluted with an equal volume of water and cooled at 5 °C in an ice bath. A cold saturated solution of sodium nitrite (30 g, 0.43 mol) in 110 ml of water was added slowly with stirring. The mixture was kept in the ice bath for an additional 10 mintes and then filtered and washed with 10 ml of ice-cold water. Air drying gave approximately 26 g of N-nitrosomethyl-urea (NMU) as pale yellow crystals melting at 122-124 °C.

8-Diazomethane in Decalin.[15]--A 500 ml round bottom flask with smooth glass necks was fitted with a thermometer and mechanical stirring in cork stoppers. To the flask was added 30 g of a 40% aqueous KOH solution and 100 ml of decaline. The two phase mixture was then cooled to 0 °C and a safety shield was placed in front of the flask. Nitrosomethylurea (10 g, 97 mmol) was added to the flask in 0.5 g portions at such a rate that the reaction temperature never exceeded 5 °C. The mixture was stirred for an additional 20 minutes, and the bright yellow organic layer was quickly decanted into a glass cylinder (3 cm x 25 cm) cooled in a dry ice-isopropanol bath. The diazomethane solution was stored in this manner until further use.

9-Catalytic decomposition of diazomethane by cuprous chloride in 1,1-dimethyl-1-germacyclobutane.--A diagram of the apparatus is shown in Fig. 2-1. At room temperature diazomethand from the decaline solution was swept in a stream of argon (flow rate, 5 ml/min) into a 10 cm test tube, A, containing a stirring bar, 1 g (6.9 mmol) of 1,1-dimethyl-1-germacyclobutane (**2**), 150 mg of cuprous chloride and 1 ml of cyclohexane. In order to minimize the evaporative loss, a spiral condenser B was connected to a recirculating cold bath maintained at 0 °C. A cold finger C containing a dry ice-isopropanol bath was attached above the spiral condenser. In order to prevent the formation of a free carbene, it was necessary to shield the entire system from light. After five hours, nearly all of the diazomethane was transferred to the test tube. The reaction mixture was flash distilled under vacuum. Preparative GC of the liquid afforded 1,1,3-trimethyl-1-germacyclobutane (**6**) 5% and 1,1,5,5-tetramethyl-1,5-digermacyclooctane (**7**) 80% gc yield (20% OV-17 on chromosorb W, 1/4 in. x 20 ft.). When the reaction was repeated in the absence of diazomethane at room temperature no product was formed, but at 110 °C a polymeric material which was not characterized

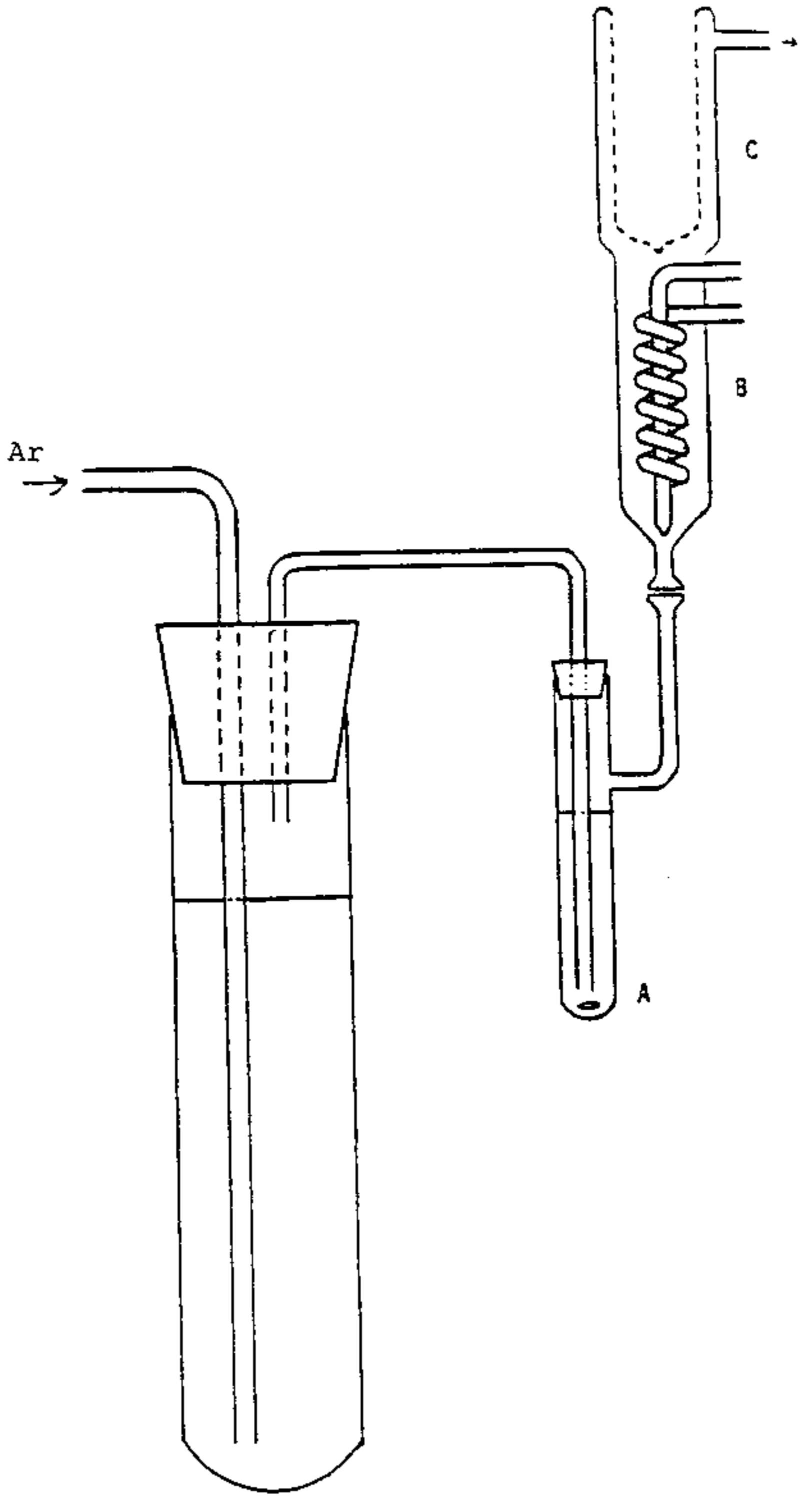


Fig. 2-1 A diagram of apparatus for the reaction of diazomethane and 1,1-dimethylgerma- or silacycobutane.

was formed. Also, the reaction of **2** with diazomethane but in the absence of cuprous chloride was repeated, the GC analysis indicated that no product was formed.

6: ^{1}H NMR (neat) ppm 0.28 (3H, s, $GeCH_3$), 0.30 (3H, s, $GeCH_3$), 0.80 -1.45 (4H, 2 sets of m, $GeCH_2$) .90 (3H, d, J=7.10 Hz), 2.42 (1H, m, SiCCH); ^{13}C nmr (neat) ppm -1.17 (q), 1.56 (q), 27.18 (q), 28.22 (t), 30.69 (d); GC/MS, m/e (relative intensity) 159 (32), 119 (100), 118 (32), 117 (69), 115 (56), 105 (36), 103 (31), 89 (38), 87 (28).

7: ^{1}H nmr (neat) ppm 0.04 (12H, s, $GeCH_3$) 0.75 (8H, m, CH_2Ge), 1.32 (4H, app quintet, $GeCCH_2$); ^{13}C nmr (neat) ppm 1.62 (q), 17.49 (t), 22.95 (t); GC/MS m/e (relative intensity) 295 (1), 293 (1), 291 (1), 269 (4), 267 (11), 265 (15), 263 (14), 227 (19), 225 (67), 224 (27), 223 (91), 222 (24), 221 (98), 220 (19), 219 (50), 217 (20), 211 (25), 209 (33), 207 (37), 205 (24), 203 (11), 121 (31), 119 (100), 118 (27), 117 (78), 115 (50), 107 (17), 105 (71), 104 (24), 103 (53), 101 (38), 91 (17), 89 (35), 87 (27), 85 (15), 43 (74), 47 (15), 41 (88).

10-Copper catalyzed decomposition of diazomethane in 1,1-dimethylsilacyclobutane.--At room temperature vapors of diazomethane were swept by argon (flow rate, 5 ml/min) from the decalin solution into a mixture of 0.76 g (7.6 mmol) of 1,1-dimethylsilacyclobutane (**4**), 1.5 ml cyclohexane and 150 mg of cuprous chloride (the apparatus in the previous experiment was used). After six hours, transfer of the gaseous diazomethane was nearly complete. The reaction mixture was flash distilled under vacuum. The GC analysis of the liquid on a SP2100 column showed 1,1,3-trimethyl-1-silacyclobutane **8** (7%) as the only product and unreacted **4** (88%). When the reaction was repeated in the absence of diazomethane at room temperature no product was formed, however at 95 °C an uncharacterized polymeric material was formed.

11-Static pyrolysis of pentamethyldisilane and 1,1-dimethyl-1-silacyclobutane.--Pyrolysis of 10 torr of pentamethyl-disilane and 100 torr of 1,1-dimethyl-1-silacyclobutane, **4** in a 500 ml reaction bulb immersed in a molten salt bath at 325 °C for 16 hours gave 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**5**) in 8% yield.

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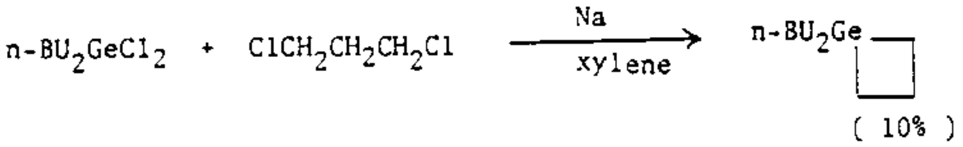
CHAPTER 3

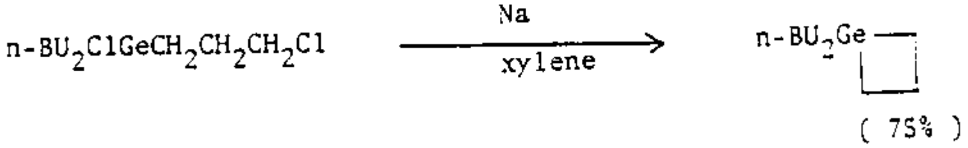
KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION OF 1,1-DIMETHYL-1-GERMACYCLOBUTANE

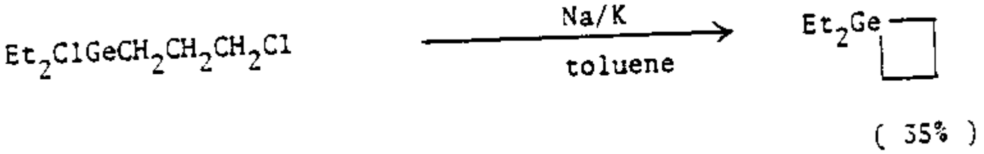
Introduction

The first synthesis of germacyclobutanes was reported by Mazerolles, Lesbre and Dubac[1,2] by the condensation of dialkyldichlorogermanes and 1,3-dichloropropane in the presence of sodium:

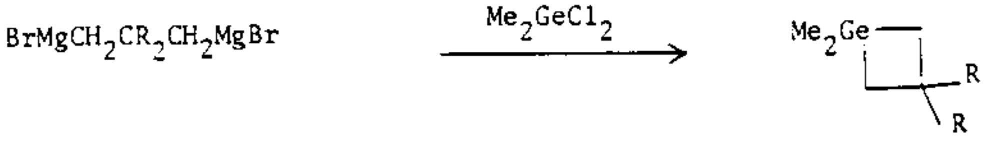


However, cyclization of γ-chloropropylchlorogermanes with Na or Na/K gave a higher yield:[1,2]

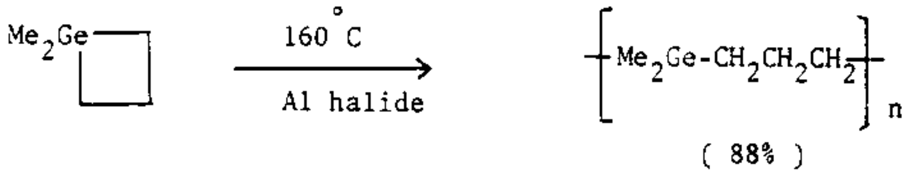




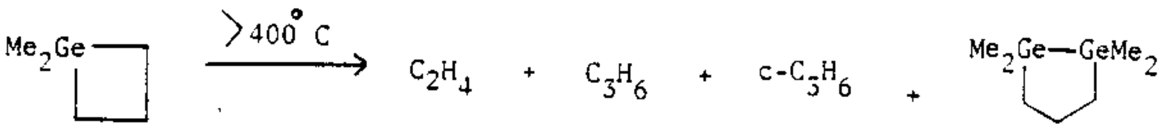
Recently, Bickelhaupt[3] reported a convenient synthesis of germacyclobutanes in more than 95% yield which involves the reaction of the di-Grignard reagents, $BrMgCH_2CR_2CH_2MgBr$ (R=H, Me) with dichlorodimethylgermane:



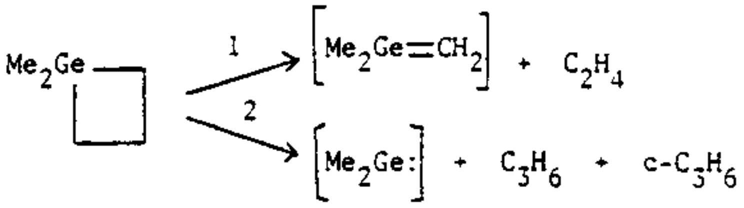
In 1969 Nametkin's group[4] reported that 1,1-dimethylgermacyclobutane undergoes polymerization at 160 °C in the presence of aluminum halides to yield a high-molecular weight polymer:

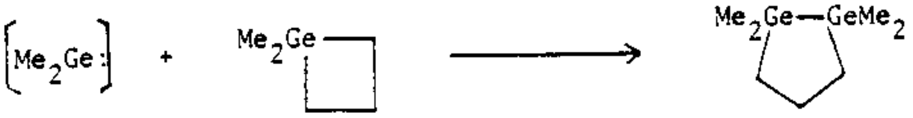


Later the same group[5] looked at the pyrolysis of 1,1-dimethylgermacyclobutane, specifically; static and pulsed flow systems at temperatures of 400 to 450 °C and 550 to 600 °C:



The following mechanism for the decomposition of 1,1-dimethylgermacyclobutane was proposed:





They suggested that pathway (1) involves the formation of 1,1-dimethyl-1-germaethylene. However, 1,1,3,3-tetramethyl-1,3-digermacyclobutane, (a dimer of the germaethylene) was not detected. Pathway (2) involves the formation of dimethylgermylene which subsequently inserts into the cyclic Ge-C bond of the starting material and yields 1,1,2,2-tetramethyl-1,2-digermacyclopentane. Similar pathways were reported for the fragmentation of dimethylgermacyclobutane upon electron impact.[5,6,7]

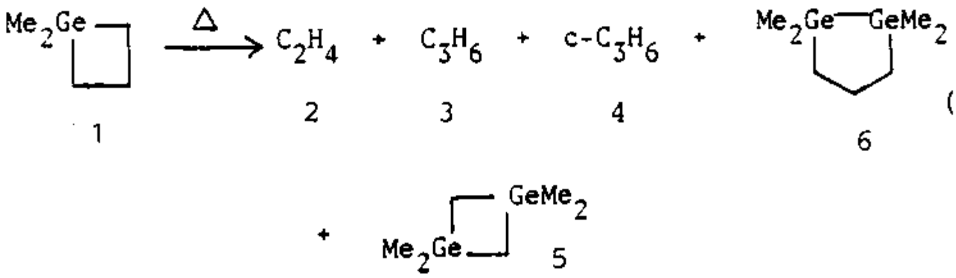
Since both pathways are involved in the formation of the reactive intermediates (the germaethylene and the germylene) the proposed mechanism is lacking of evidence. Kinetics and trapping experiments are needed to support the mechanism.

Results and Discussion

1,1-dimethylgermacyclobutane (**1**) was synthesized by the Bickelhaupt's method;[3] however, some modifications were applied (see the experimental section).

Pyrolysis product distribution

Static pyrolysis of 1,1-dimethylgermacyclobutane (**1**) in a 250 ml quartz vessel submerged in a molten-salt bath from 411 to 476 °C yielded ethylene (**2**), propene (**3**), cyclopropane (**4**), 1,1,3,3-tetramethyl-1,3-digermacyclobutane (**5**) and 1,1,2,2-tetramethyl-1,2-digermacyclopentane (**6**) (eqn 3-1)



(eqn 3-1)

Tables 3-1 and 3-2 show the product distributions for two typical temperatures. The distributions appear to be nearly time-invariant. Our experimental results agree with the proposed mechanism of Gusel'nikov[7] (Scheme 3-1). 1,1,3,3-tetramethyl-1,3-digermacyclobutane (**5**) in equation 3-1 clearly is formed by dimerization of 1,1-dimethylgermaethylene (**7**). However, Gusel'nikov's group[5] did not detect this dimer from the gas phase pyrolysis of **1**. Product **6** is formed by the insertion of dimethylgermylene

Table 3-1. Product distributions in pyrolysis of **1** at 428 °C

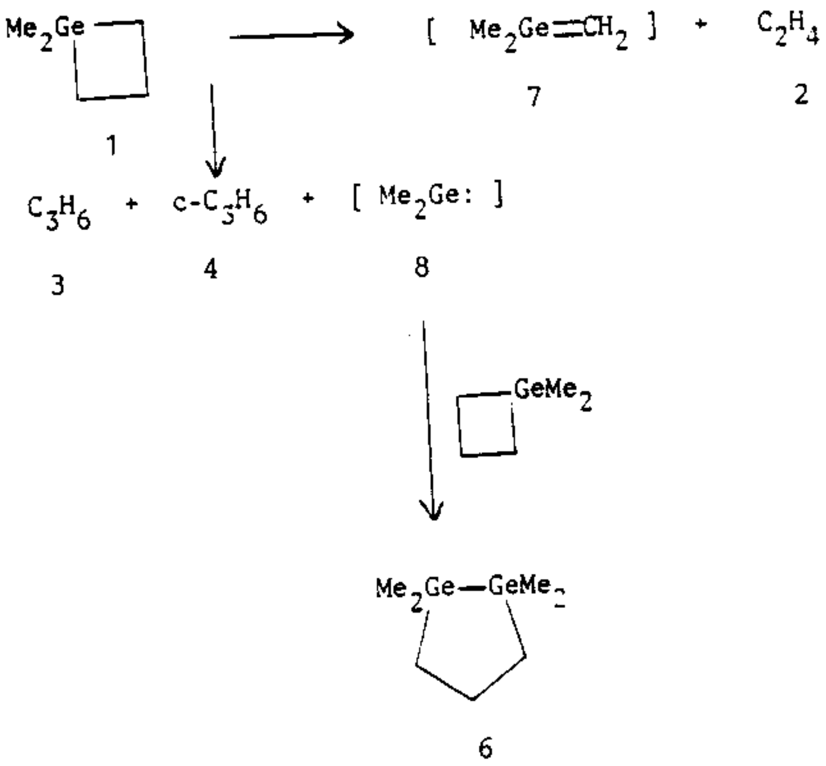
% Conversion of 1	**Reaction time (min)**	**2%**	**3%**	**4%**	**5%**	**6%**	**(3 + 4)/2**
5.3	30	26.1	27.4	19.4	7.20	19.9	1.79
10.5	60	28.5	22.0	20.6	8.10	20.8	1.49

Table 3-2. Product distributions in pyrolysis of **1** at 470.6 °C

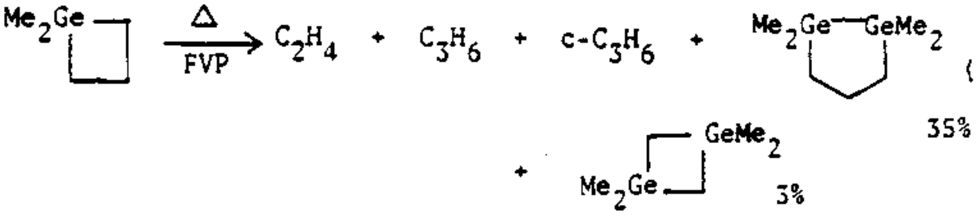
% Conversion of 1	**Reaction time (min)**	**2%**	**3%**	**4%**	**5%**	**6%**	**(3 + 4)/2**
26.3	13	26.0	16.7	17.8	9.30	30.2	1.33
49.6	28	26.0	15.8	17.7	8.20	32.3	1.29

(**8**) into the cyclic Ge-C bond of **1** (Scheme 3-1). The ratio of **(3 + 4)/2** in tables 1 and 2 suggests that fragmentation is predominated by dimethylgermylene formation. However, this predomination slightly decreases by increasing the temperature.

Scheme 3-1



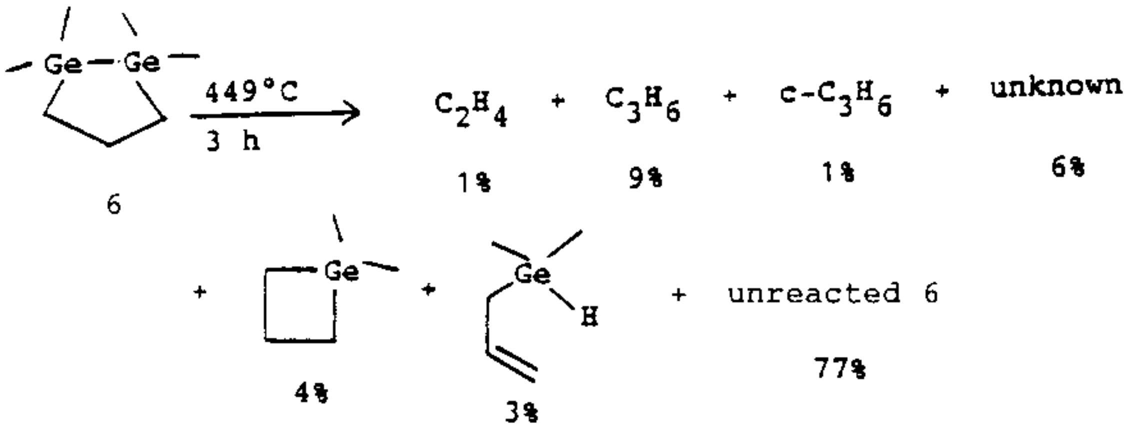
Similarly, flow vacuum pyrolysis of 1,1-dimethylgermacyclobutane in a quartz tube at 553 °C (54% decomposition) yielded ethylene, propene, cyclopropane, 1,1,3,3-tetramethyl-1,3-digermacyclobutane, and 1,1,2,2-tetramethyl-1,2-digermacyclopentane (eqn 3-2):



(eqn 3-2)

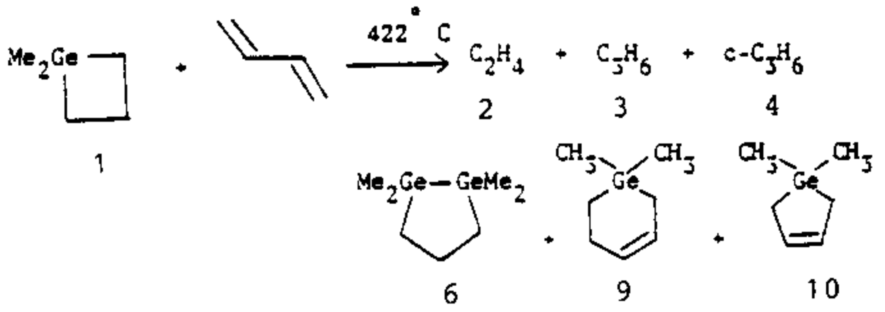
Since no special precautions were taken to prevent loss of the vapors during analysis of the flow pyrolysis experiments exact yield of the volatile products are not available.

In order to find out whether cyclopropane comes from secondary decomposition of 1,1,2,2-tetramethyl-1,2-digermacyclopentane (**6**) or from fragmentation of 1,1-dimethylgermacyclobutane (1), neat pyrolysis of **6** was carried out at 449 °C for 3 h. Under these conditions only 1% cyclopropane (**4**) was formed. Thus, decomposition of **6** is not the major source of cyclopropane.



Trapping reaction

Static pyrolysis of 1,1-dimethylgermacyclobutane (**1**) in the presence of butadiene at 422 °C (16% conversion) was performed. In addition to the volatile and the insertion products which were observed in the neat pyrolysis of **1**, products **9** (1,1-dimethylgermacyclohex-3-ene) and **10** (1,1-dimethylgermacyclopent-3-ene) were formed (eqn 3-3):



(eqn 3-3)

Table 3-3 shows the product distributions with a ratio of **1** to butadiene; 1:1 respectively and Table 3-4 is the product distributions with a ratio of **1** to butadiene; 1:4.5 respectively. Product **9** is the first example of the 1,1-dimethylgermaethylene trapping product in the gas phase which is formed probably via a [4 + 2] cycloaddition pathway. Product **10** is formed by a 1,4 addition of dimethylgermylene to butadiene (Scheme 3-2). It has been reported that this 1,4 addition proceeds via a concerted [4 + 2] cheletropic mechanism.[8-10]

Scheme 3-2

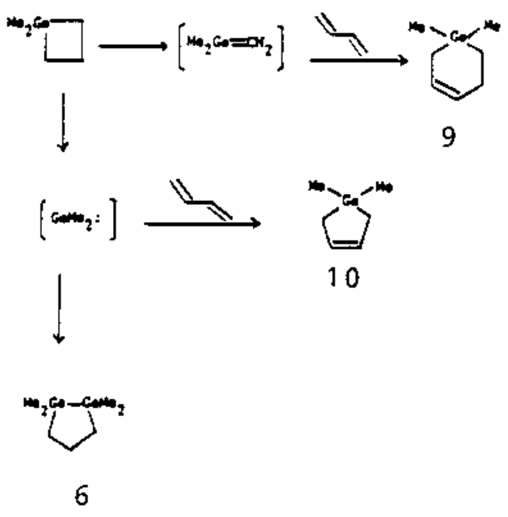


Table 3-3. Product distributions in pyrolysis of **1** in the presence of butadiene; ratio of butadiene to **1** is equal to 1:1

Reaction time (min)	**2%**	**3%**	**4%**	**6%**	**9%**	**10%**	**$^{9}/_{10}$**
35	20.4	17.8	12.5	22.3	24.4	2.6	8.58
70	23.5	16.1	14.4	19.6	24.6	1.8	10.89

Table 3-4. Product distributions in pyrolysis of **1** in the presence of butadiene; ratio of butadiene to **1** is equal to 4.5:1

Reaction time (min)	**2%**	**3%**	**4%**	**6%**	**9%**	**10%**	**$^{6}/_{10}$**
35	22.7	20.6	10.8	11.4	24.2	10.3	1.11
70	26.3	18.4	11.4	12.5	23.8	7.6	1.64

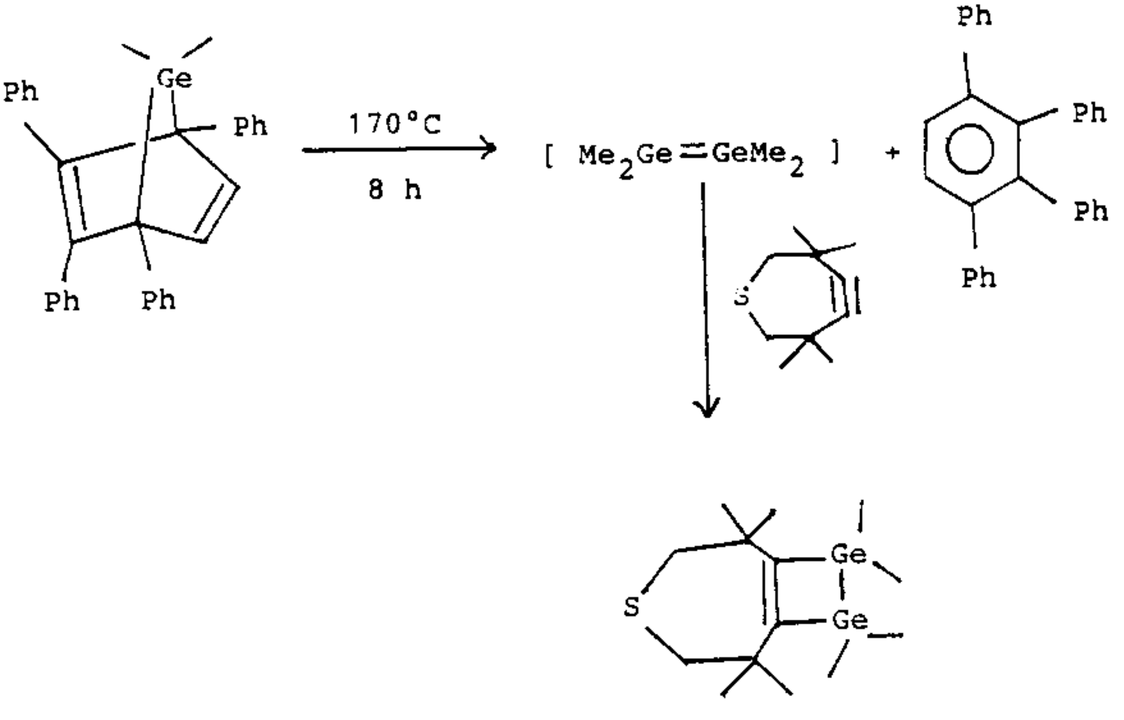
The ratio of **6/10** in Table 3-3 suggests that dimethylgermylene (**8**) reacts faster (about 10 times) with the cyclic Ge-C bond of **1** than with the butadiene. Surprisingly, even in the presence of a 4.5 fold excess of butadiene (Table 3-4) still dimethylgermylene reacts faster (about 1.4 times) with the cyclic Ge-C bond of **1** than with butadiene. Also it is interesting to note that this insertion effectively competes with the [4 + 2] cycloaddition of 1,1-dimethygermaethylene and butadiene. The insertion of the photochemically generated dimethylsilylene into the cyclic Ge-C bond of **1** has been reported in Chapter 2.

Likewise, flow vacuum pyrolysis of 1,1-dimethygermacyclobutane in the presence of a ten fold excess of butadiene at 496 °C (10% decomposition) yielded the same products as observed in the static pyrolysis case at 422 °C in the presence of butadiene. The distribution of the germanium containing products are shown in Table 3-5.

Table 3-5. Products distribution of the flow vacuum pyrolysis of 1 in the presence of a 10 fold excess of butadiene at 496 °C

6%	**9%**	**10%**
26.4	33.7	25.7

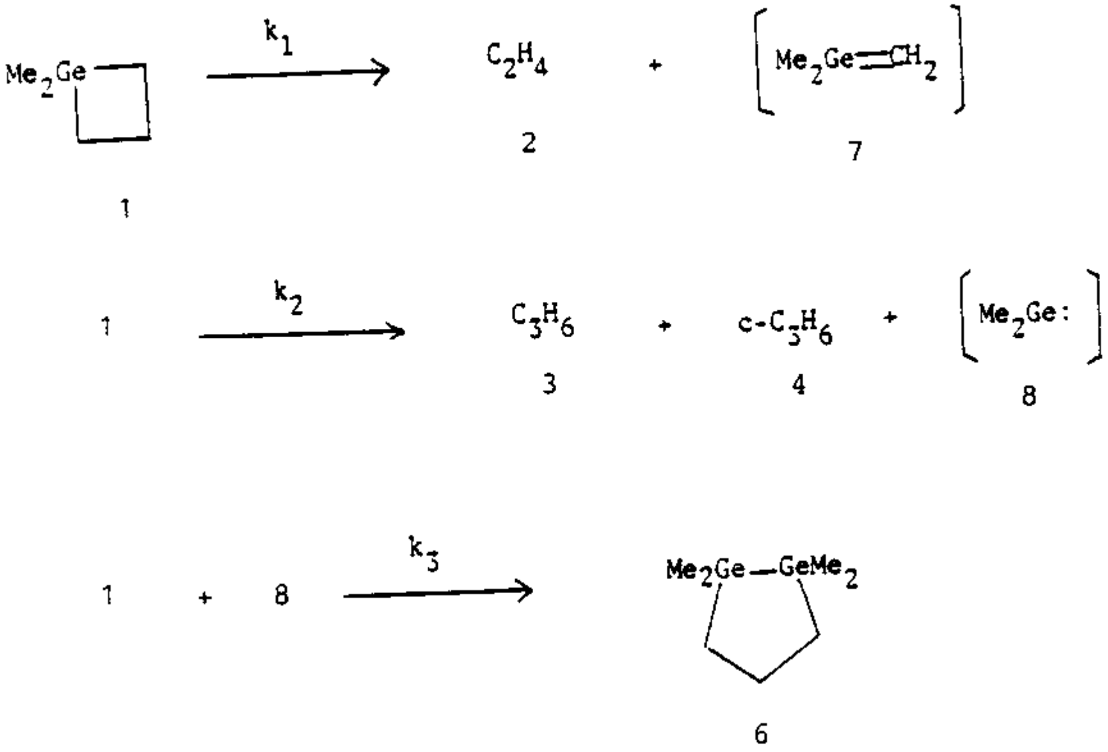
Attempts to trap dimethylgermaethylene (**7**) and dimethylgermylene (**8**) with a 20 fold excess of acetylene in vacuum flow pyrolysis of **1** at 500 to 600 °C were unsuccessful. We observed only products which were reported in the neat flow pyrolysis of **1**. Also, trapping of **7** and **8** with acetylene in static pyrolysis of **1** at 450 °C failed. However, trapping of the thermally generated digermene in the presence of a heterocyclic acetylene has been reported.[11]



Kinetics

Rate constants for the thermal fragmentation of 1 and for the formation of 2 and (3 + 4) at ten different temperatures from 684 to 751.3 K have been determined. Scheme 3-3 shows the kinetics pathways.

Scheme 3-3



The rate of disappearance of 1 is

$$\frac{-d[1]}{dt} = k_1[1] + k_2[1] + k_3[1][8] \qquad \text{(eqn 3-4)}$$

The steady-state approximation for [8] gives

$$\frac{d[8]}{dt} = k_2[1] - k_3[1][8] = 0 \qquad \text{(eqn 3-5)}$$

Solution for [8] gives

$$[8] = k_2/k_3 \qquad \text{(eqn 3-6)}$$

Substitution of equation 3-6 to equation 3-4 gives

$$\frac{-d[1]}{dt} = k_1[1] + k_2[1] + \frac{k_2k_3[1]}{k_3} \qquad \text{(eqn 3-7)}$$

$$\frac{-d[1]}{dt} = [k_1 + 2k_2][1] \qquad \text{(eqn 3-8)}$$

$$\frac{-d[1]}{dt} = k_{obs}[1] \qquad \text{(eqn 3-9)}$$

$$k_{obs} = k_1 + 2k_2 \qquad \text{(eqn 3-10)}$$

$$[1] = [1]_o \exp(-k_{obs}t) \qquad \text{(eqn 3-11)}$$

$$\ln[1] = \ln[1]_o - k_{obs}t \qquad \text{(eqn 3-12)}$$

The slope of the plot of ln[1] versus time gives k_{obs}, [1] is the concentration of I at time t, can be calculated:

$$[1] = 100 - ([2] + [3] + [4] + [6]) \qquad \text{(eqn 3-13)}$$

[2], [3], [4], [6] are the % yield of each of those individual products at time t.

The rate constants for formation of 2 and (3 + 4) can be calculated by the following equations.[12]

$$[2] = [2]_o + \frac{k_1[1]_o}{k_{obs}} (1-\exp{-k_{obs}t}) \qquad \text{(eqn 3-14)}$$

$$[3 + 4] = [3 + 4]_o + \frac{k_2[1]_o}{k_{obs}} (1-\exp{-k_{obs}t}) \qquad \text{(eqn 3-15)}$$

A plot of [2] versus (1-exp-k_{obs}t) gives a straight line with a slope of:

$$(\text{slope})_1 = \frac{k_1[1]_o}{k_{obs}} \qquad \text{(eqn 3-16)}$$

Similarly, a plot of [3 + 4] versus (1-exp-k_{obs}t) gives a straight line with a slope of:

$$(\text{slope})_2 = \frac{k_2[1]_o}{k_{obs}} \qquad \text{(eqn 3-17)}$$

From equations 3-16 and 3-17, the ratio of k_2/k_1 can be calculated.

$$\frac{(\text{slope})_2}{(\text{slope})_1} = k_2/k_1 \qquad \text{(eqn 3-18)}$$

Therefore, k_1 and k_2 can be calculated by solving equations 3-10 and 3-18. By knowing k_1 and k_2 the rate constant for the thermal fragmentation of 1 can be calculated (eqn 3-19).

$$k_f = k_1 + k_2 \qquad \text{(eqn 3-19)}$$

Table 3-6 gives the time dependence of starting material (s.m.), 1, at 716.7 K.

Table 3-6. Change in concentration of 1 with time at 716.7K (correlation coefficient; 0.999)

Time (sec)	Remaining s.m. (1, %)	ln[1]
800	91.4 (9)	4.5152
1200	88.0 (9)	4.4773
1600	84.2 (8)	4.4332
2000	80.3 (8)	4.3858
2400	76.0 (7)	4.3307
2800	72.4 (6)	4.2822

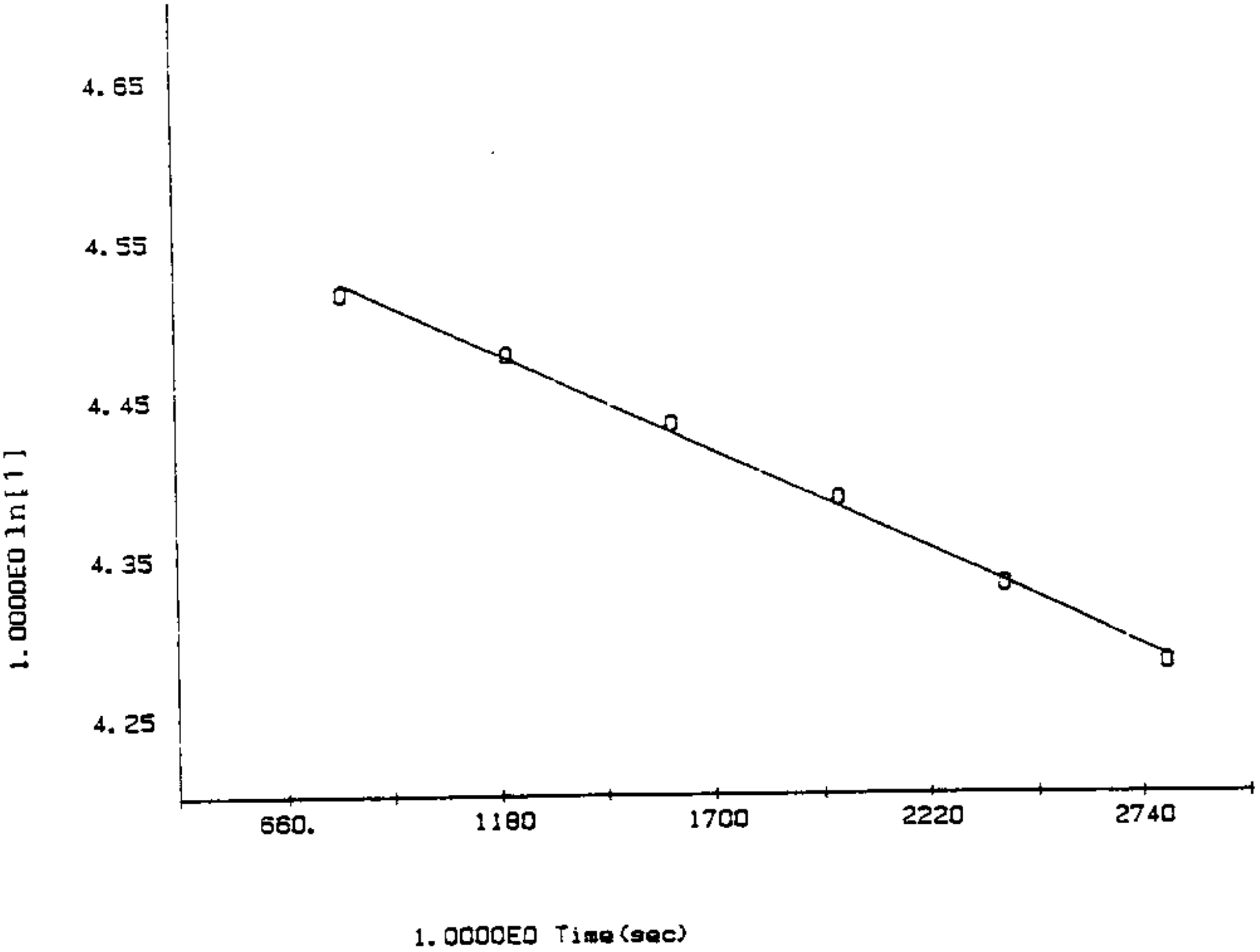


Fig. 3-1 A plot of ln[1] vs time (sec) at 716.7 K .

A plot of ln[1] versus time (sec) provided a good straight line (Figure 3-1). The slope of the straight line was calculated by using a least squares program.[13] From the slope, $k_{obs} = 1.18 \times 10^{-4}$ sec^{-1}, was calculated. Table 3-7 shows the time dependence of products **2** and (**3** + **4**) at 716.7 K. Figures 3-2 and 3-3 show the plot of [**2**] and [**3** + **4**] versus ($1-\exp-k_{obs}t$) respectively. Equations 3-10 and 3-18 were used to calculate k_1 and k_2; $k_1 = 3.40 \times 10^{-5}$ sec^{-1}, $k_2 = 4.21 \times 10^{-5}$ sec^{-1}. k_{obs} of **1**, rate constants for the thermal fragmentation of **1** (k_f, eqn 3-19) and for the formation of **2** and (**3** + **4**) are listed in Tables 3-8 and 3-9 at different temperatures from 684.0 to 751.2 K.

The plots for the fragmentation of 1 and for the formation of 2 and (3 + 4) in Figures 3-4, 3-5 and 3-6 respectively gave Arrhnius parameters with good straight lines (correlation coefficient, 0.999). The Arrhenius parameters are listed in Table 3-10.

The Eyring plots, (Figures 3-7 through 3-9) of ln (k_f/T) vs 1/T, of ln (k_1/T) vs 1/T and ln (k_2/T) vs 1/T provided values of activation parameters as calculated by the method of least squares (correlation coefficient 0.999). Activation parameters are summarized in Table 3-11.

Table 3-7. Time dependence of concentrations of products 2 and (3 + 4) at 716.7 K

Time (sec)	2%	3%	4%	(3 + 4)%	$(1-\exp-k_{obs}\ t)\times10^2$ [a]
800	2.30 (1)	2.46 (1)	1.73 (1)	4.19 (1)	9.01
1200	3.58 (2)	3.22 (3)	2.65 (1)	5.87 (3)	13.2
1600	4.92 (5)	3.94 (3)	3.61 (4)	7.55 (4)	17.2
2000	5.82 (4)	4.41 (3)	4.26 (3)	8.67 (3)	21.1
2400	7.11 (4)	5.03 (2)	5.08 (2)	10.1 (2)	24.7
2800	7.79 (5)	5.43 (3)	5.62 (4)	11.1 (3)	28.2
R[b]	0.998			0.998	

[a] $k_{obs} = 1.18 \times 10^{-4}$ sec^{-1} at 716.7 K

[b] R: correlation coefficient

Table 3-8. Temperature dependence of k_{obs} of 1,1-dimethylgermacyclobutane (1)

Temp. K	$k_{obs} \times 10^5$/sec^{-1}
683.9 (1)	1.37 (2)
689.9 (1)	1.89 (5)
698.4 (1)	3.51 (1)
706.6 (1)	5.91 (2)
716.7 (1)	11.5 (3)
721.5 (1)	15.3 (7)
728.9 (1)	23.3 (3)
737.4 (1)	33.7 (5)
743.6 (1)	51.1 (7)
751.2 (1)	75.4 (6)

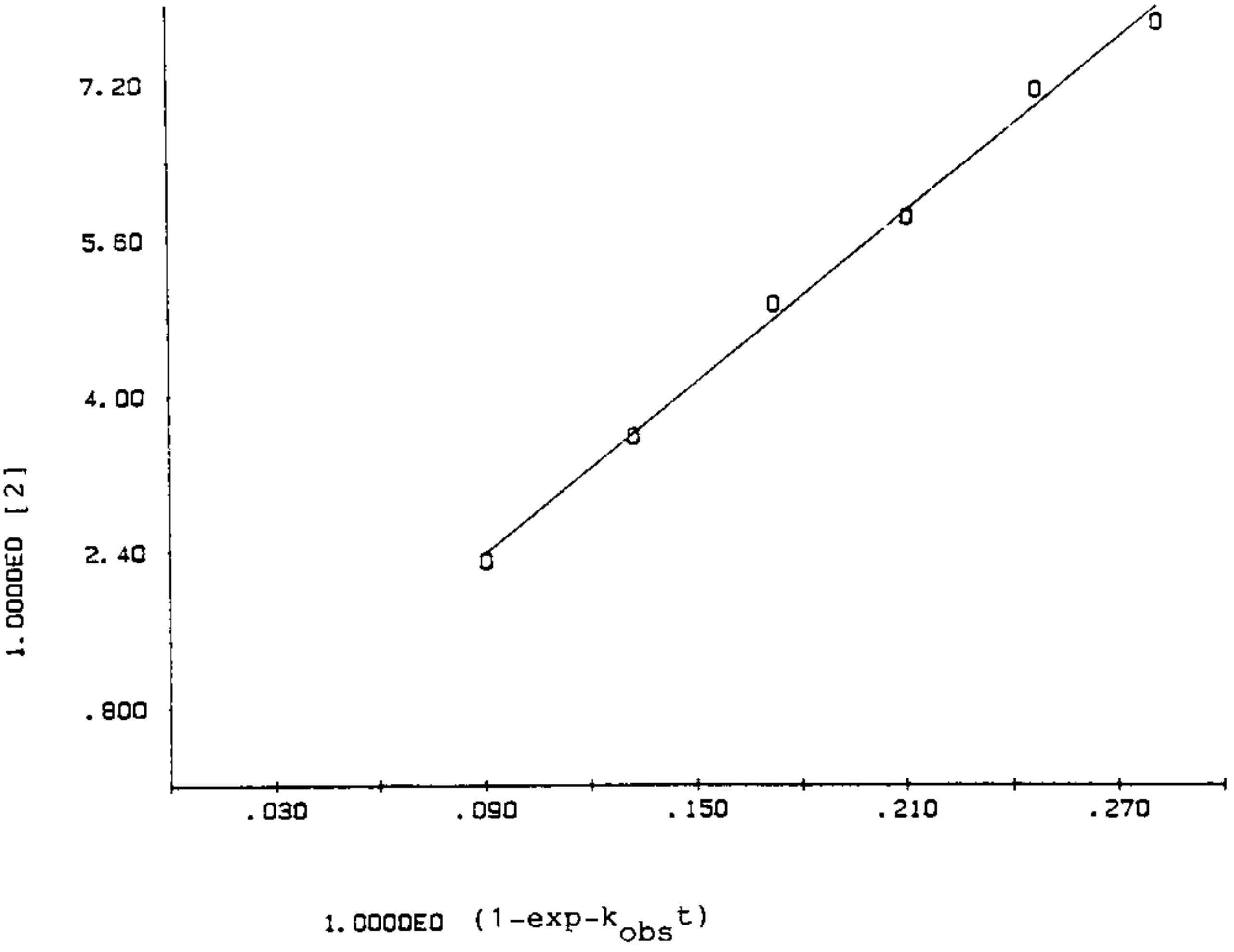


Fig. 3-2 A plot of [2] vs [1-exp(k_{obs}t)].

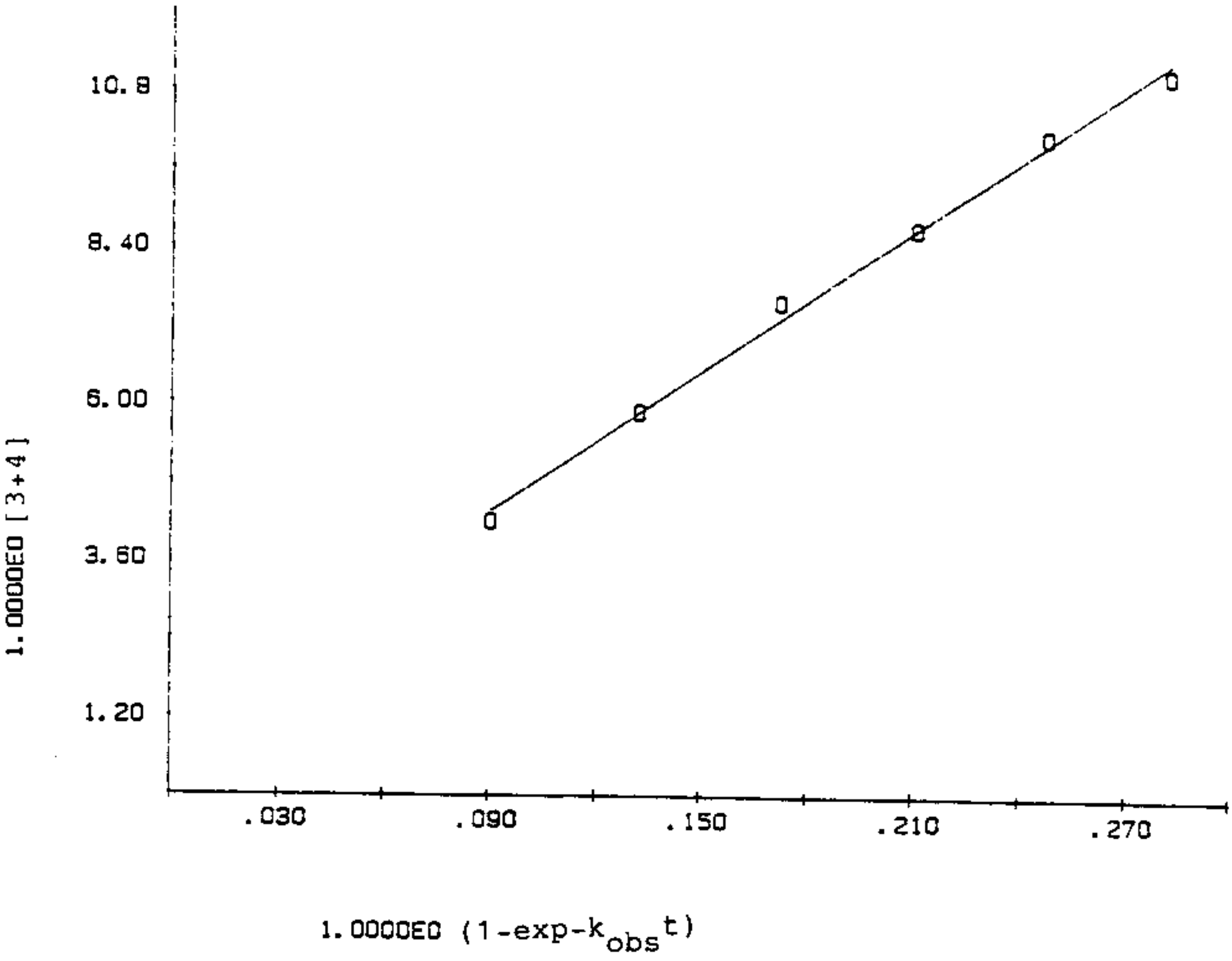


Fig. 3-3 A plot of [3 + 4] vs [1-exp(k_{obs}t)] .

Table 3-9. Rate constants for formation of 2 and (3 + 4) and thermal fragmentation of 1

Temp. K	$k_1 \times 10^5/\mathrm{sec}^{-1}$ [a]	$k_2 \times 10^5/\mathrm{sec}^{-1}$ [a]	$k_f \times 10^5/\mathrm{sec}^{-1}$ [b]
683.9 (1)	0.37 (3)	0.49 (5)	0.86 (5)
689.9 (1)	0.54 (4)	0.70 (7)	1.24 (7)
698.4 (1)	0.85 (1)	1.33 (2)	2.18 (2)
706.6 (1)	1.52 (6)	2.20 (2)	3.72 (6)
716.7 (1)	3.13 (6)	4.18 (2)	7.31 (6)
721.7 (1)	4.42 (18)	5.46 (9)	9.88 (18)
728.9 (1)	6.75 (6)	8.27 (12)	15.0 (12)
737.4 (1)	10.2 (1)	11.7 (7)	21.9 (7)
743.6 (1)	14.8 (9)	18.2 (10)	33.0 (10)
751.2	21.8 (3)	26.8 (2)	48.6 (3)
R	0.9990	0.9990	0.9990

[a] rate constants are calculated by equations 3-10 and 3-18
[b] $k_f = k_1 + k_2$
k1 rate constants for formation of 2
k2 rate constants for formation of (3 + 4)

Table 3-10. Arrhenius parameters for fragmentation of 1 and formation of 2 and (3 + 4)

Reaction	Ea; kcal/mol	$\mathrm{Log}_{10}A$ (sec^{-1})
$1 \xrightarrow{k_f} 2 + 3 + 4$	61.7 ± 0.6	14.6 ± 0.2
$1 \xrightarrow{k_1} 2$	63.1 ± 0.8	14.7 ± 0.3
$1 \xrightarrow{k_2} 3 + 4$	60.7 ± 0.8	14.0 ± 0.3

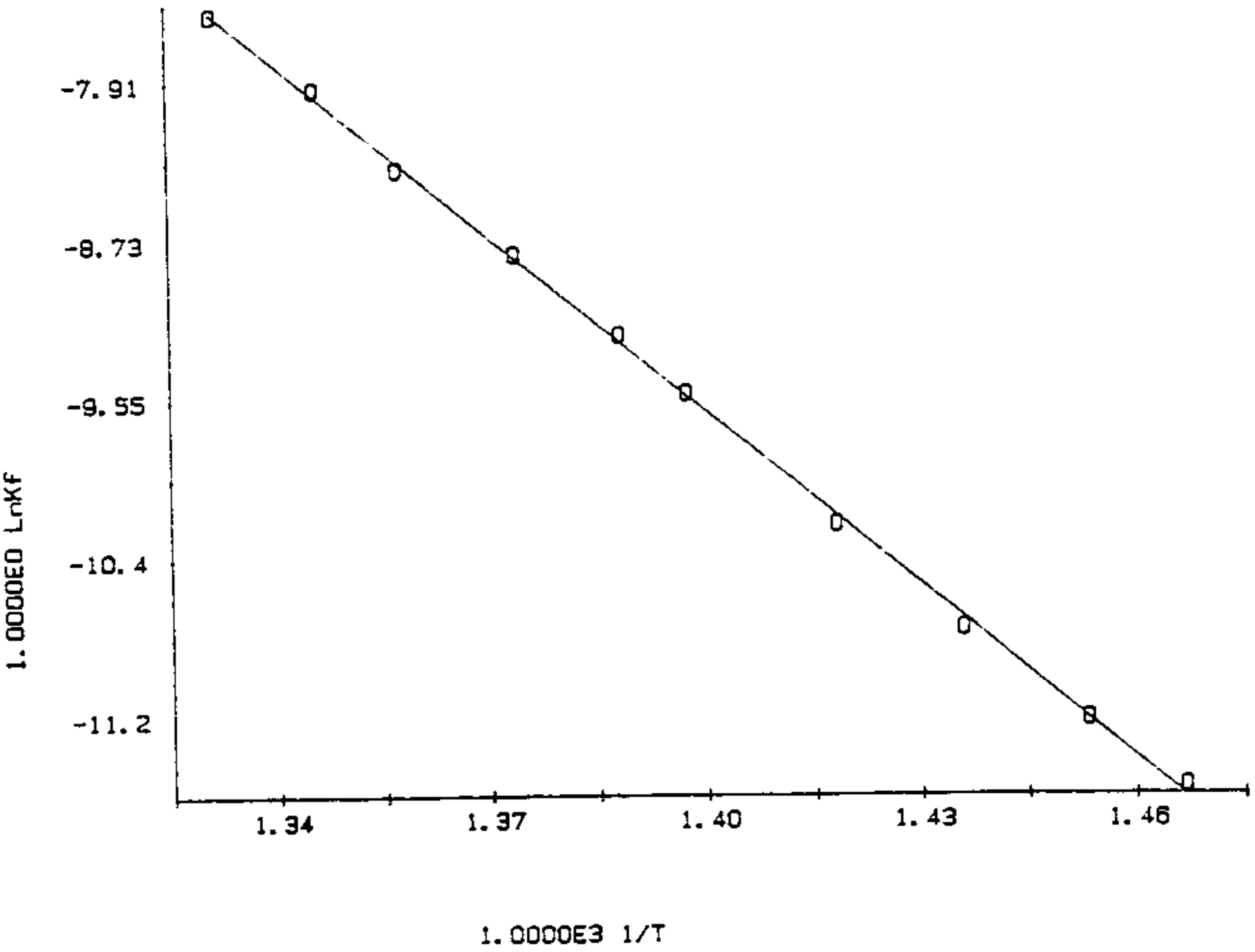


Fig. 3-4 Arrhenius plot of ln $k_{fragmentaion}$ vs 1000/T .

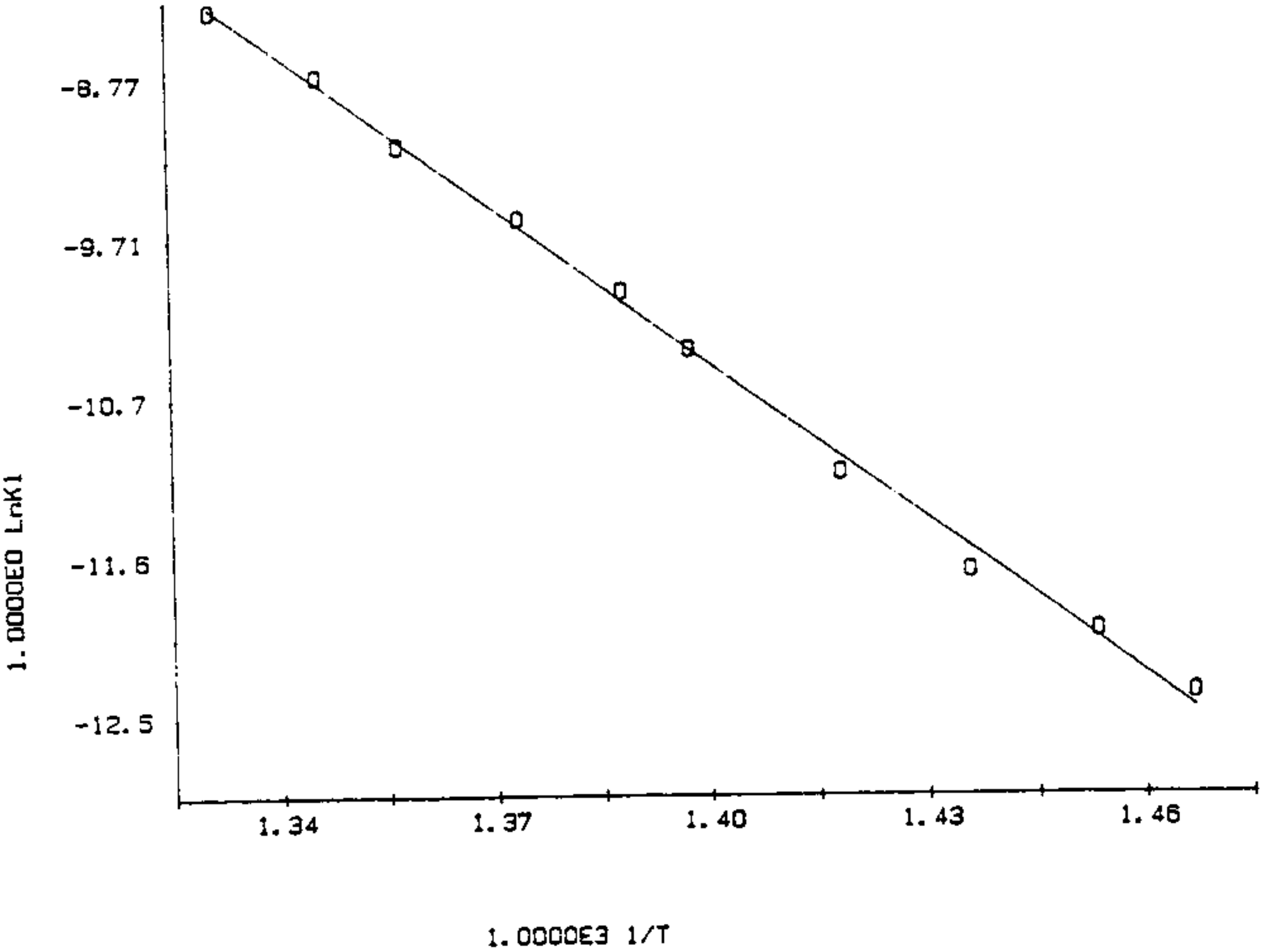


Fig. 3-5 Arrhenius plot of ln k_1 vs 1000/T .

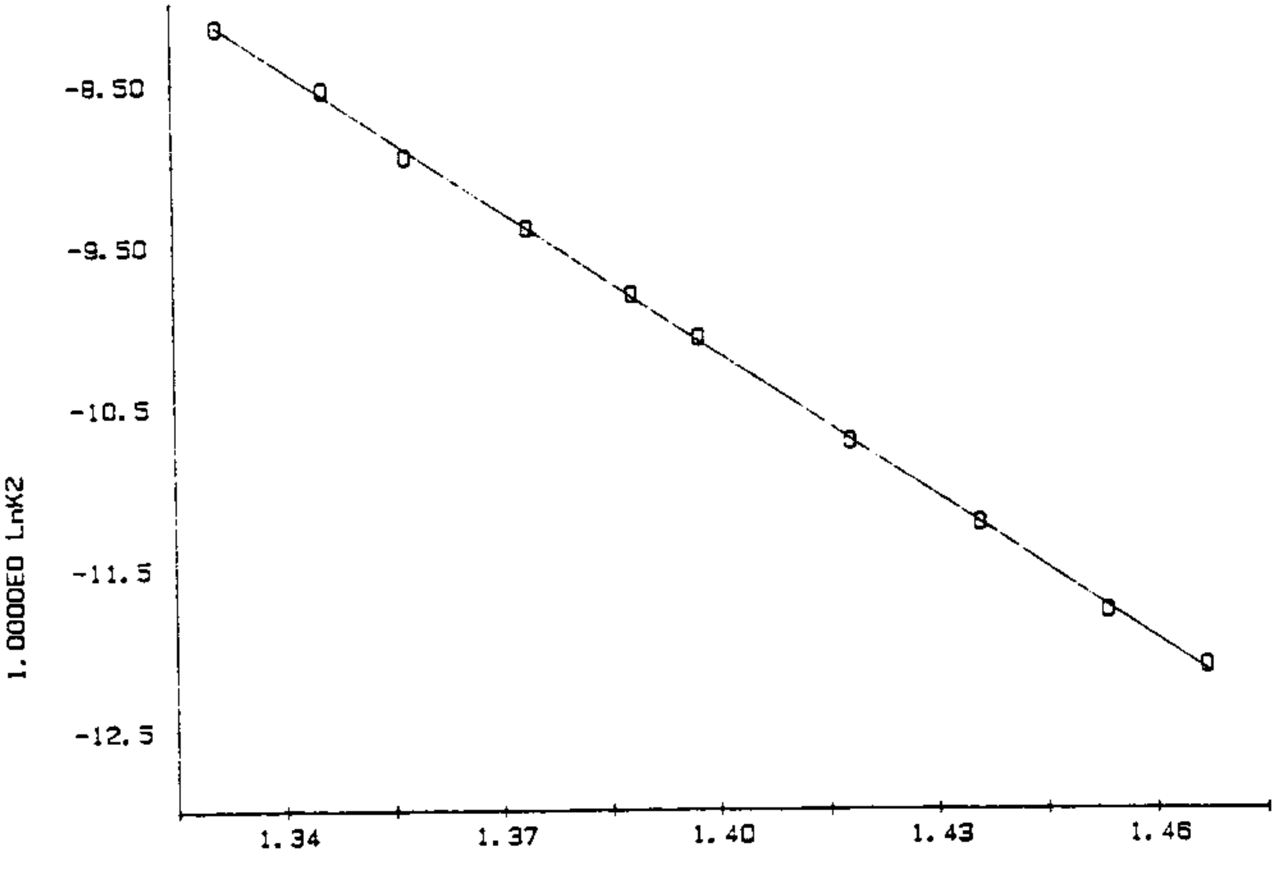


Fig. 3-6 Arrhenius plot of $\ln k_2$ vs 1000/T .

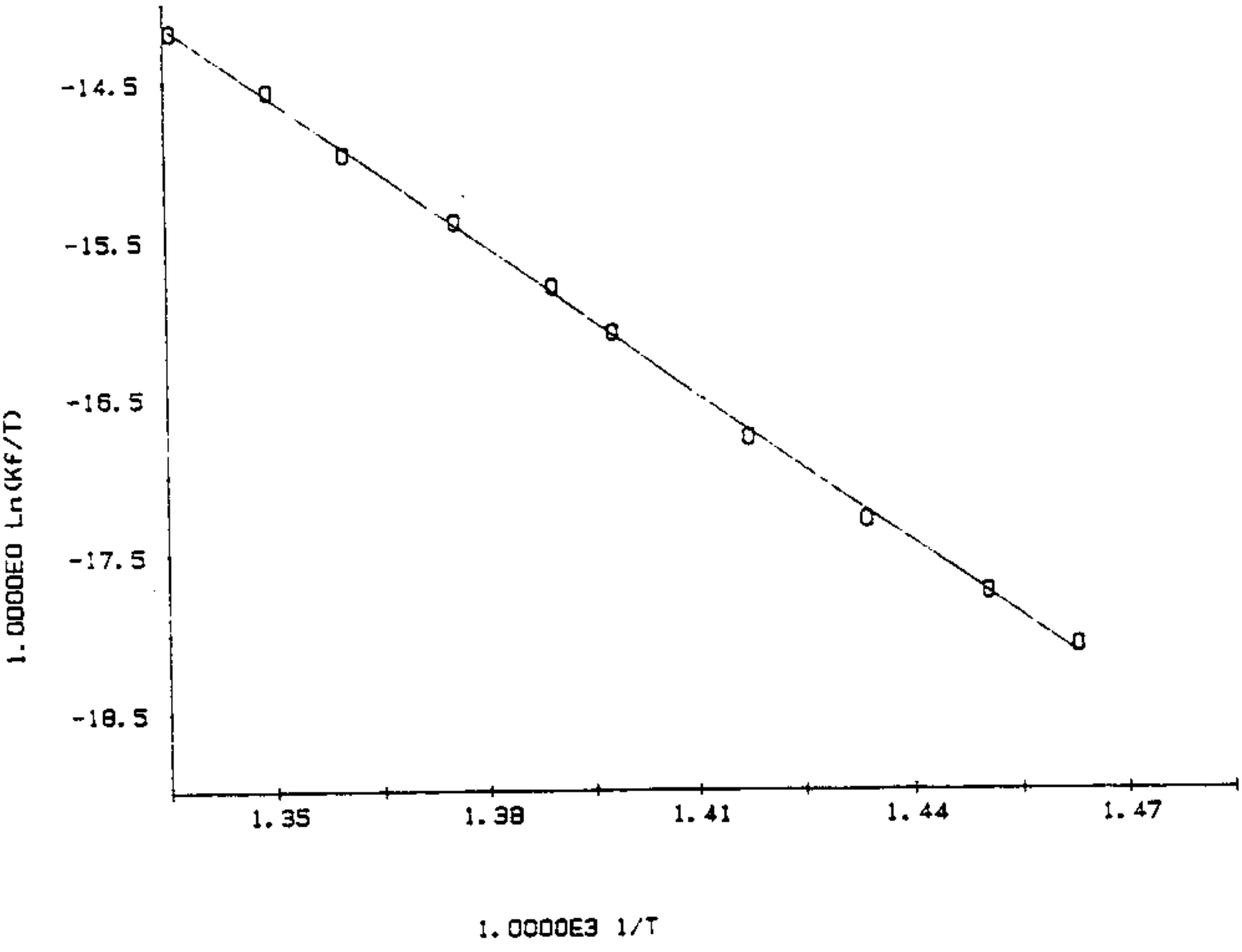
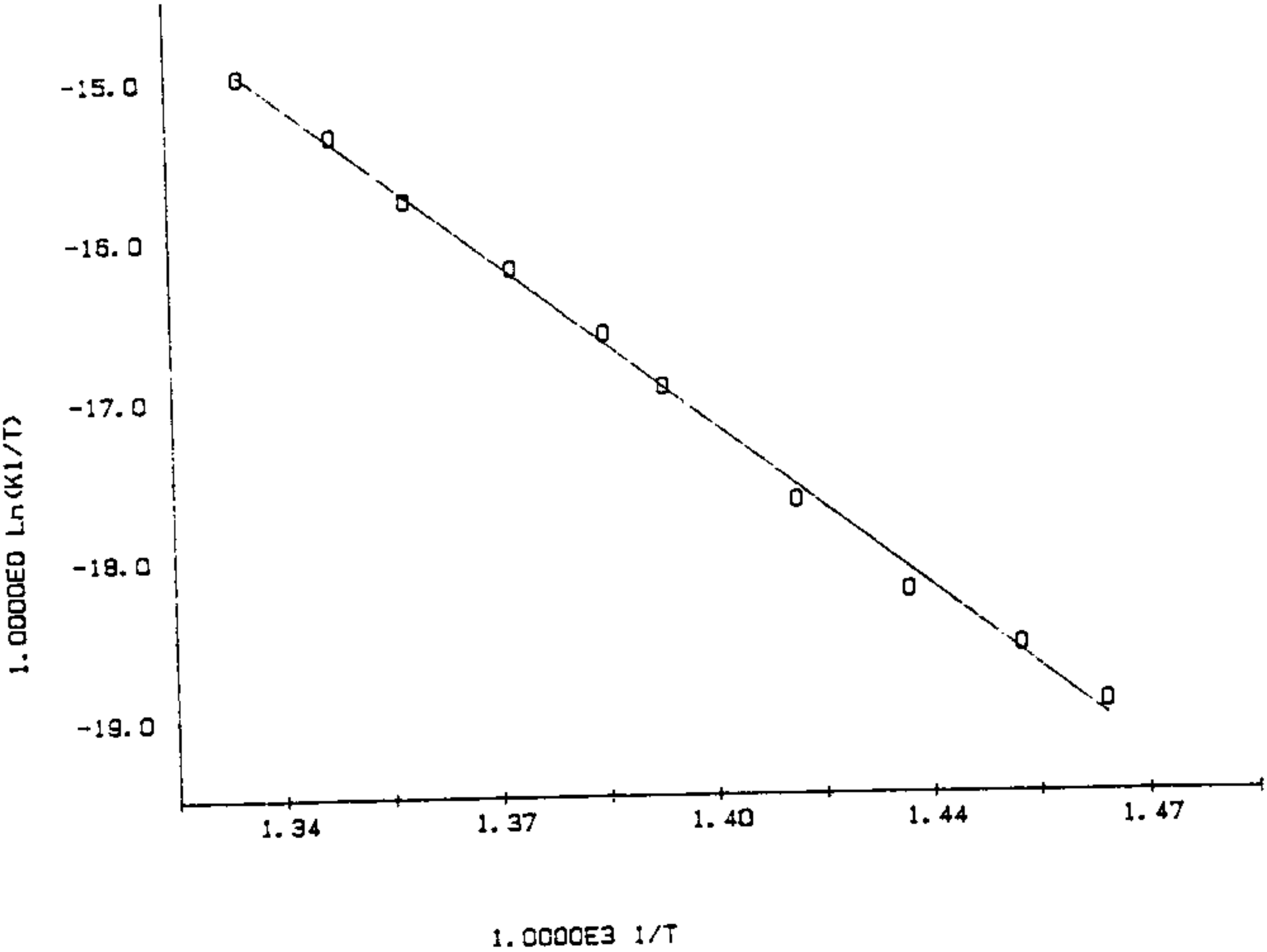


Fig. 3-7 Eyring plot of ln $(k_{frag.}/T)$ vs 1000/T .



Eig. 3-8 Eyring plot of ln(k_1/T) vs 1000/T.

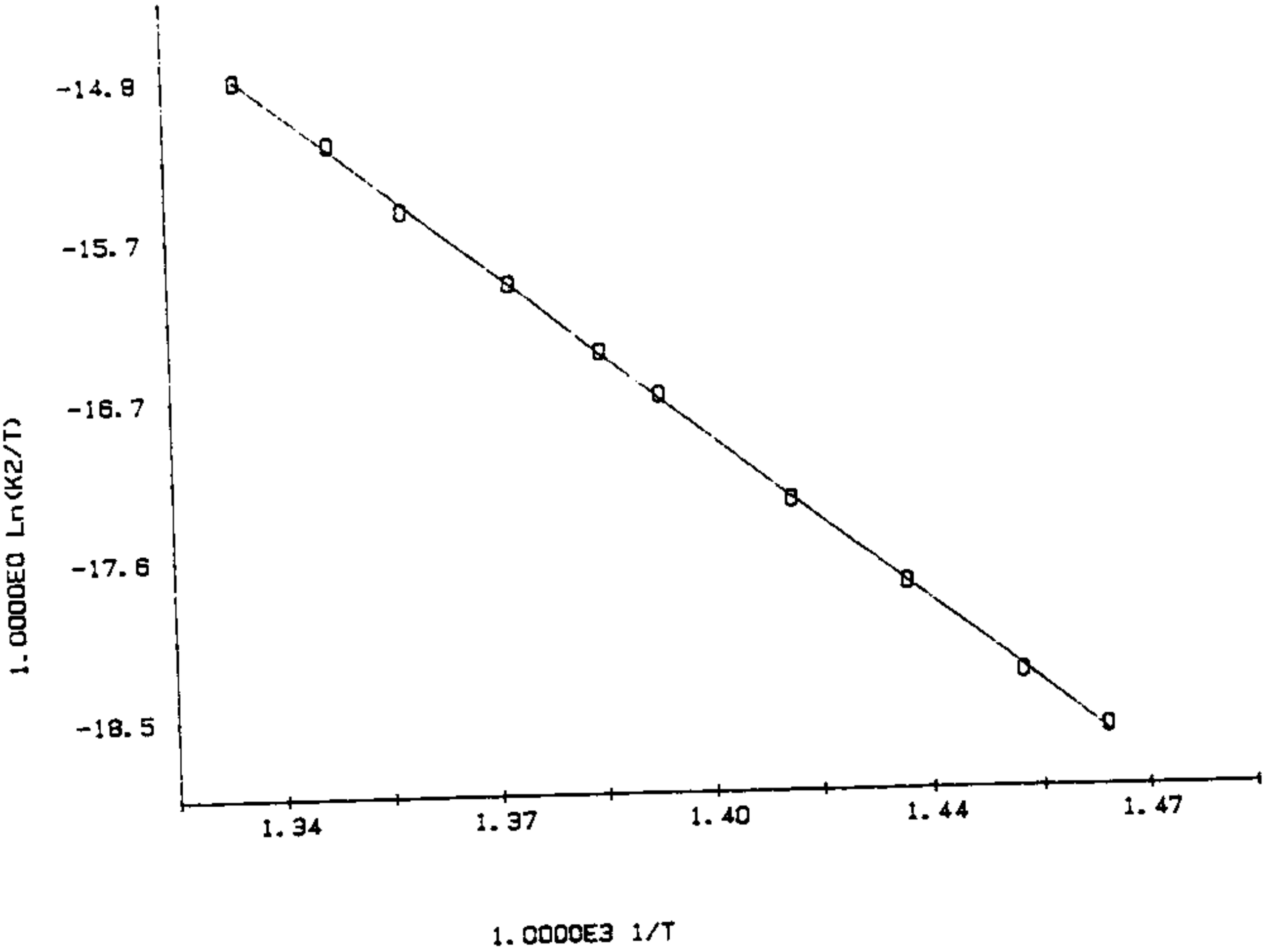


Fig. 3-9 Ering plot of ln (k_2/T) vs 1000/T .

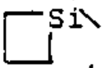
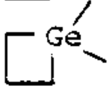
Table 3-11. Activation parameters for fragmentation of **1** and formation of 2 and (3 + 4)

Reactions	$\Delta S^{\neq}$= cal/mol deg[a]	$\Delta H^{\neq}$= kcal/mol[a]
$1 \xrightarrow{k_f} 2 + 3 + 4$	6.0 ± 0.9	60.3 ± 0.6
$1 \xrightarrow{k_1} 2$	6.5 ± 1.2	61.7 ± 0.8
$1 \xrightarrow{k_2} 3 + 4$	3.3 ± 1.1	59.1 ± 0.8

[a] $\ln (K/T) = \ln (k/h) - \frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R}$

Kinetic parameters for 2 + 2 cycloreversion of group 4 cyclobutanes are given in table 3-12. It shows that the activation energies are nearly the same. However, the bond dissociation energies (enthalpies) of group 4 acyclic compounds are not the same (table 3-13). A question which arises here is that, despite the difference in the bond dissociation energies of group 4 acyclic compounds, why are

Table 3-12. Kinetic parameters for 2 + 2 cycloreversion of Group 4 cyclobutanes.

molecule	Log A(s^{-1})	Ea(kcal mol^{-1})	ref.
	15.6	62.5	14
	15.6	62.5	15
	14.6	63.1	This work

the activation energies for the 2 + 2 cycloreversion of cyclobutanes the same?

Table 3-13. Bond dissociation energies (enthalpies) of Group 4 acyclic compounds.

molecule	BD (kcal mol^{-1})	ref.
CH_3-C(Me)$_3$	84	16
CH_3-Si(Me)$_3$	90	17
CH_3-Ge(Me)$_3$	76	18

In order to find out whether decomposition of 1,1-dimethylgermacyclobutane (**1**) proceeds through consecutive or parallel reactions, the following general consecutive reactions have been considered.

$$A \xrightarrow{k_1} B \xrightarrow{k_1'} C$$

In this case compound A converts to compound B with rate constant k_1 and B converts to compound C with rate constant k_1'. The concentration of A, B and C are shown in fig. 3-10[19].

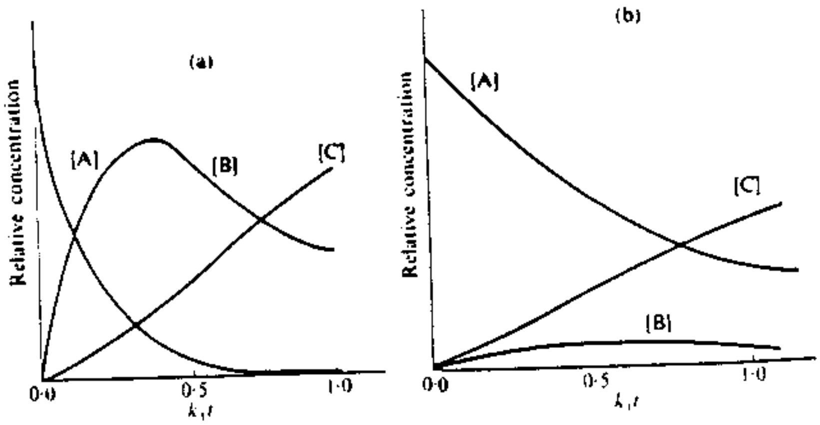
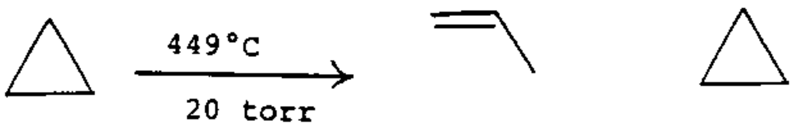


Fig.3-10 The concentration of reactants, intermediates, and products for two consecutive first-order reactions. (a) $k_1 = 10k_1'$. (b) $k_1 = 0{\cdot}1k_1'$.

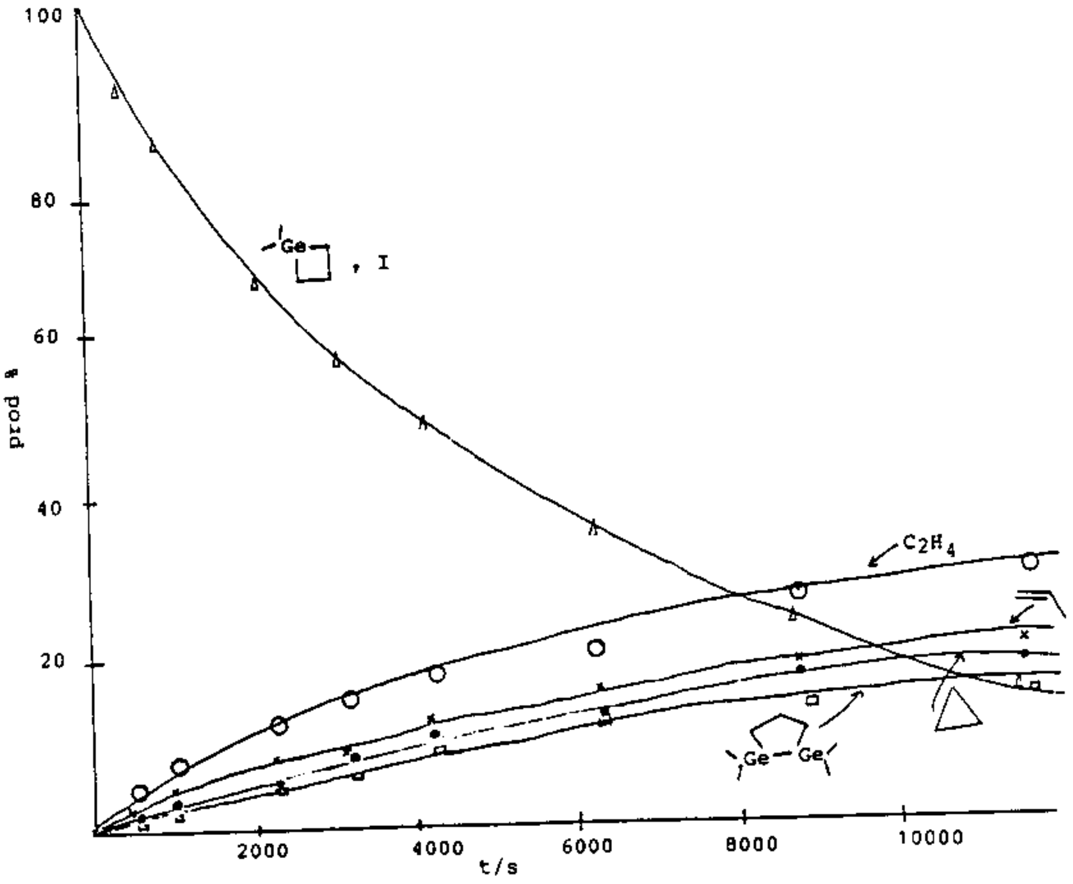
It shows that if the course of the reaction were followed by analyzing for A, curve A would be obtained; if it were followed by measuring the concentration of the end product C, curve C would result; and finally if only the intermediate product B were determined, it would be found that its concentration would rise to a maximum and then fall off, as shown by curve B. We applied a similar idea to the decomposition of 1,1-dimethylgermacyclobutane (**1**). Product distribution of **1** at 450 ^{o}C is shown at fig. 3-11. It appears that as 1,1-dimethylgermacyclobutane (**1**) starts to decay, products; ethylene, propene, cyclopropane and 1,1,2,2-tetramethyl-1,2-digermacyclopentane start to form. As shown in the figure (3-11), we do not see any product decays during the course of the decomposition of **1**. This suggests that pyrolysis of **1** is not involved in the consecutive reactions, probably proceeding through parallel reactions.

The possibility of the formation of propene from the secondary decomposition of cyclopropane was examined by performing the pyrolysis of cyclopropane at 449 ^{o}C. Following is the product distribution:



1 h	2.3%	97.7%
3 h	3.3%	96.7%

Fig. 3-11 Product distribution of 1,1-dimethylgermacyclobutane at 450 °C.



As shown in the above, after 3 hr. only 3% propene was formed along with 97% of unreacted cyclopropane. This indicates that the decomposition of cyclopropane is not the major source of propene.

In addition, to find out whether propene comes from excited (hot) cyclopropane or from the decomposition of 1,1-dimethylgermacyclobutane (**1**), pyrolysis of **1** in the presence of a 40 fold excess of argon (inert gas) was carried out. No changes in the rate constant of the decomposition of **1** or the ratio of cyclopropane to propene compared to the neat pyrolysis of **1** were observed. This suggests that propene does not come from the excited (hot) cyclopropane, but probably forms from the decomposition of **1**.

Experimental

Preparative gas chromatography, proton NMR, carbon NMR, mass spectra were performed as described in Chapter 1. Analytical gas chromatography was performed on a HP 5840A GLC (flame ionization detector) equipped with a Valco gas sampling port. For GC analysis, SP-2100 (10% on 80/100 Supelcoport, 1/8 in. x 13 ft.) was used.

Pyrolysis kinetics was carried out in a 250 ml quartz vessel submerged in a molten-salt bath (eutectic mixture, 50% $NaNO_2$, 7% $NaNO_3$, and 53% KNO_3, m.p 142 ^{o}C) which was insulated by Aqua-Cell (diatomite, Johns-Manville Co.). A Thermotrol proportional controller (230 volts) model 1053A (GCA Precision Scientific) with a model 1183 platinum resistance temperature detector was used to control the temperature. In addition, a stainless steel mineral insulated heating element (220 volts) from Chromalox Comfort Conditioning Division was used as a heating element. Temperature was measured by a Chromel-Alumel thermocouple (Type K) which was connected to a Leeds & Northrup Type K-3 potentiometer with a null detector (Leeds & Northrup, 9828 D.C. Null Detector). Temperature was constant to ±0.1 ^{o}C. The thermocouple was held in the center of the molten-salt bath. A Brooklyn thermometer (range: 298 to 355 ^{o}C) was used to calibrate the thermocouple derived temperatures. Vapors of 1,1-dimethylgermacyclobutane (**1**) were introduced into the quartz reaction vessel through a vacuum line. Initial pressure of **1** for kinetics were measured by a model PDR-C-2 pressure gauge (MKS Instrument Co.) and model 227 AHS-A-100 Baratron (MKS Instrument Co.).

Typically, each kinetic/pyrolysis run was sampled six times by removing a small portion of pyrolysate (about 1.5 torr) from the reaction vessel (into a small section of the vacuum line. We used an average of 2 GC runs for each point in a rate constant and at least six points were used for each rate constant plot. Rate constants and activation parameters were calculated by using a least square program.[13] (In most cases correlation coefficients of 0.999 were obtained; however, in a few cases correlation coefficients were 0.998.)

The role of surface effects on the course of the decomposition of **1** is minimal as suggested by a comparison of rate constants obtained in packed and unpacked reaction vessel at 716.2 K. With a 12 fold increase in the surface to volume ratios, the change in the rate constant for decomposition was <5%.

Flow vacuum pyrolyses were accomplished in a quartz tube (10 mm i.d. x 30 cm) wrapped with nichrome ribbon, covered with asbestos tape and connected to a vacuum line. The quartz tube was seasoned with hexamethyldisilazane before each use. Residence times in the hot zone ca. 1/10 seconds and pressures were 1-5 torr. A 0.8 mm aperture attached at the end of the hot zone was used to control the residence time and pressure.

The product yields from flow vacuum pyrolyses were based on the amount of decomposition of starting material (**1**) and determined chromatographically with predetermined response factors for the organogermane products. In both static and flow pyrolyses the response factor of 1,1-dimethylgermacyclobutane (**1**) was assumed to be one and the product response factors were determined based on the response factor of **1** (Table 3-14).

Table 3-14. Response factors on HP 5840A GLC

Compound	Response factors[a]
1	1.00 (1)
2	0.51 (2)
3	0.70 (1)
4	0.70 (2)
5	0.57 (3)
6	0.76 (1)
9	0.70 (1)
10	0.55 (2)

[a] The following equation was used to calculate the response factors:

$$R.F = \frac{mmol_1}{mmol_{product}} \times \frac{area_{product}}{area_1}$$

1,1-Dimethylgermacyclobutane (**1**) was synthesized by the Bickelhaupt's method;[3] however, some modifications were applied. Tetramethylgermane was synthesized by modified synthesis of tetramethyltin[20] and dimethyldichlorogermane was synthesized by the Kumada's method.[21]

1-Synthesis of tetramethylgermane.[20]--Magnesium 87.47 g (3.64 mol) and 1050 ml n-butyl ether (dried over LAH) was placed in a 2L three-neck flask fitted with a cold condenser, an addition funnel, and a mechanical stirrer. Then a solution of 173.2 ml of iodomethane (2.78 mol) in 173 ml of n-butyl ether was added dropwise through the additional funnel. Gentle reflux was maintained during this addition. The reaction mixture was stirred for six hours at room temperature and then 100 g (0.46 mol) of tetrachlorogermane was added dropwise, stirred for four hours at room temperature and one hour at reflux. Simple distillation was applied to remove product and some n-butyl ether.

Finally, fractional distillation (using glass helicoils column) of the distillate afforded 41 g tetramethylgermane (65% yield) purity 96%, bp 42 to 43 ^{o}C/760 mmHg.

2-Synthesis of dichlorodimethylgermane.[21]--To a 250 ml three-neck flask containing 41.3 g (0.31 mol) of tetramethylgermane and 83.2 g (0.62 mol) of $AlCl_3$, was added dropwise 48.8 g (0.62 mol) of acetyl chloride. The reaction mixture was stirred for three days at room temperature. Then 100 ml of dry CH_2Cl_2 was added, flash distilled in order to separate the product and solvent from the catalyst. Finally, dichlorodimethylgermane was isolated by fractional distillation, 61% yield (33 g, bp 123 to 124 °C/760 mmHg).

3-Synthesis of 1,1-dimethylgermacyclobutane.[3,22]--In a one liter three-neck flask fitted with a cold condenser, an addition funnel, and a mechanical stirrer was added to 12 g (0.5 mol) of Mg and 750 ml of dry ether. Then a solution of 17.2 g (85 mmol) of 1,3-dibromopropane in 100 ml dry ether was added slowly to the flask through the addition funnel in a period of 2 hr. After stirring the reaction mixture at room temperature for 24 hours, 7.8 g (45 mmol) of dichlorodimethylgermane was added and stirred for four hours at room temperature. The reaction mixture was treated with 150 ml of saturated NH_4Cl and successfully washed with water, 5% $NaHCO_3$, water and dried over Na_2SO_4. After distillation, using glass helicoils column we obtained 2.7 g (19 mmol) of 1,1-dimethylgermacyclobutane (**1**), 42% yield, purity ~95%, bp 118 to 119 °C/760 mmHg. ^{13}C NMR (neat) δ: -0.26(q), 20.16(t), 21.39(t).

4-Static pyrolysis of 1,1-dimethylgermacyclobutane (1).--Pyrolysis of **1** (13.7 torr, 1.8×10^{-4} mol) from 411 to 476 °C was performed in a 250 ml quartz vessel in a fused salt bath. the results for two typical temperatures are shown in Tables 3-1 and 3-2.

5-Flow vacuum pyrolysis of 1.--Vapors from 0.6 g (4.1 mmol) of 1,1-dimethylgermacyclobutane (**1**) at a rate of 100 mg/15 min were pyrolyzed in a quartz tube at 553 °C (trap to trap distillation of the reaction mixture by using slush baths: dry-ice isopropanol (-78 °C) and toluene/liquid N_2 bath (-95 °C) was applied to separate the gaseous products from the less volatile products). Ethylene (**2**), propene (**3**) and cyclopropane (**4**) were gaseous products. 1,1,3,3-tetramethyl-1,3-digermacyclobutane (**5**) and (**6**) were the only germanium containing products. At 553 °C under this pyrolysis condition decomposition of **1** was 54% and **5** and **6**, were formed in 3% and 35% yields respectively. Preparative GC of V and VI were performed on a SF-96 column (20% on Chromosorb W, 1/4 in. x 20 ft.). Spectral characteristics of **5** and **6** were identical with those previously reported.[7,23,24]

5: ^{13}C nmr (neat) δ: 2.47 (q), 10.53 (t).
6: ^{13}C nmr (neat) δ: -3.97 (q), 20.55 (t), 24.45 (t).

6-Static pyrolysis of 1,1-dimethylgermacyclobutane (1) with butadiene.--Static pyrolysis of **1** (7.2 torr) and 1,3-butadiene (7.2 torr) was carried out at 421.8 °C in a fused salt bath. GC analysis of a small aliquot of pyrolysate (about 5 torr) at each reaction time was performed on a SP-2100 column (1/8 in. x 12 ft.). In addition to the volatile and insertion products which were observed in the neat pyrolysis of **1**, products **9** (1,1-dimethylgermacyclohex-3-ene, 24.4%) and **10** (1,1-dimethylgermacyclopent-3-ene, 2.6%) were formed. A similar experiment, but with a different ratio of **1** (6.2 torr) to 1,3-butadiene (27.9 torr) was done at the same temperature (see Tables 3-3 and 3-4 in the Results and Discussion section).

7-Vacuum flow pyrolysis of 1,1-dimethylgermacyclobutane (1) with butadiene.--Vapors from 0.4 g (2.8 mmol) of **1** were pyrolyzed at a rate of 75 mg for 15 minutes in the presence of a 10 fold excess of 1,3-butadiene at 496 °C. Decomposition of **1** was 10% and bulb-to-bulb distillation of pyrolysate using the same slush bath described earlier followed by preparative on an OV-17 column (20% on Chromosorb W 45/60, 1/4 in. x 20 ft.) provided three germanium containing products: 1,1,2,2-tetramethyl-1,2-digermacyclopentane (**6**, 26.4%), 1,1-dimethylgermacyclohex-3-ene (**9**, 33.7%) and 1,1-dimethylgermacyclopent-3-ene (**10**, 25.7%).

(**9**) ^{13}C nmr (neat) δ: -3.25 (q), 11.31 (t), 13.20 (t), 22.56 (t), 127.13 (d), 129.93 (d); ^{1}H nmr (neat) δ: 0.14 (6H, S, CH_3Ge), 0.73 (2H, t, J = 6.4 HZ, CCH_2Ge), 1.32 (2H, app d, J = 4.2 HZ, $C{=}CCH_2Ge$), 2.18 (2H, m, $GeCCH_2$), 5.71 (2H, m, CH = CH); mass spectral data agree with previously reported values.[25]

(**10**) ^{13}C nmr (neat) δ: -2.73 (q), 18.66 (t), 130.77 (d): Proton NMR, IR, and mass spectral data agree with previously reported values.[12,26,27]

8-Vacuum flow pyrolysis of 1,1-dimethylgermacyclobutane with acetylene.--Pyrolysis of vapors from 0.5 g (3.5 mmol) of **1** with a 20 fold excess of acetylene were carried out at 500 to 600 °C. Same products as the neat pyrolysis case were obtained; however, no products corresponding to acetylene aducts were observed.

9-Pyrolysis kinetics.--These were carried out in the vapor phase over the temperature range, 690 to 751.3 K at pressure near 13.5 torr in a fused salt bath. GC analysis of a small portion (about 1.5 torr) of the pyrolysis mixture at each reaction time was done on a Sp-2100 column (1/8 in. x 12 ft.). The rate constants for the fragmentation of 1,1-dimethylgermacyclobutane (**1**) and for the formation of **2** and (**3** + **4**) were summarized in Table 3-9.

10-Static pyrolysis of 1,1,2,2-tetramethyl-1,2-digermacyclopentane 6.--Pyrolysis of **6** (5 torr) at 449 °C for 3 hr. in a 250 mL pyrolysis vessel gave ethylene (less than 1%), propene (9%), cyclopropane (1%), unknown monogermane (6%), 1,1-dimethylgermacyclobutane **1** (4%), allyldimethylgermane **11** (3%) and unreacted **6** (77%).

(**11**) ^{1}H nmr (neat) δ: 0.028 (6H, d, J= 3.3 Hz, $Ge(CH_3)_2$) 1.54 (2H, app d, J=8.1 Hz, CH_2Ge), 3.65 (1H, app quintet, J=3.3 Hz, GeH), 4.60 (2H, m, CH_2=C), 5.50 (1H, m, CCH=C); ^{13}C nmr (neat) δ: -5.73 (q), 21.26 (t), 112.30 (t), 135.72 (d); GC/MS, m/e (relative intensity) 146 (5), 107 (21), 105 (100), 104 (45), 103 (70), 102 (19), 101

(55), 100 (13), 91 (19), 89 (88), 88 (29), 87 (68), 85 (47), 75 (13), 74 (16), 73 (15), 72 (12).

11-Static pyrolysis of cyclopropane.--Cyclopropane (20 torr) were pyrolized for 3 hr. at 449 °C in a 250 ml pyrolysis vessel. We found that under these conditions only 3% propene is formed.

12-Static pyrolysis of 1,1-dimethylgermacyclobutane 1 in the presence of excess Ar.--Pyrolysis of germacyclobutane **1** (14 torr) in the presence of argon (556 torr) at 430 °C was monitored from 1200 to 6500 sec. No changes in the rate constant of decomposition of **1** or the ratio of cyclopropane to propene compared to the neat pyrolysis of **1** were observed.

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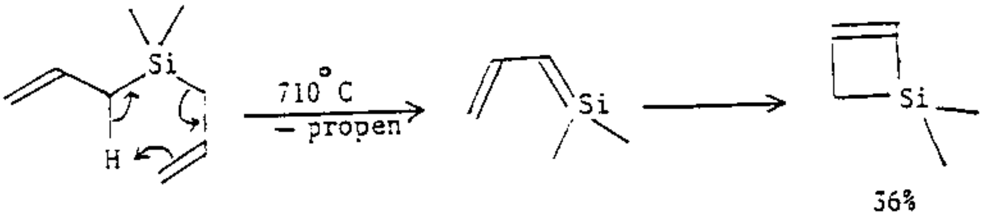
CHAPTER 4

THE REACTIONS OF 1,1-DIMETHYL-1-SILA-1,3-BUTADIEN

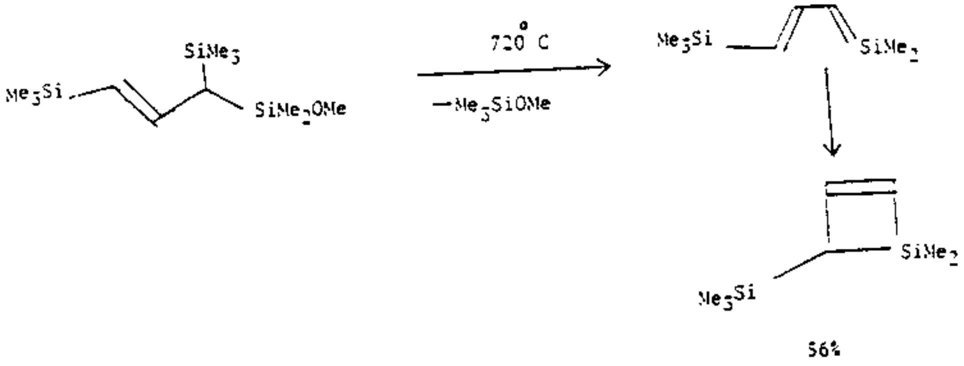
Introduction

In the past twenty years, much work on the reactivities and properties of compounds containing a silicon-carbon double bond (silenes), which are reactive intermediates in many reactions, have been reported.[1,2] However, little work on silabutadienes has been described.[3,4,5]

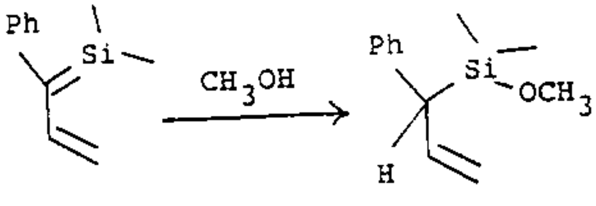
In 1978 Block and Revelle[3] discovered that vacuum flash-pyrolysis of diallyldialkysilanes yielded silacyclobutenes. The formation of these products was explained in terms of cyclization of the silabutadiene intermediates formed through a retroene elimination of propene:



Later, Barton and Burns[4] found that vacuum flash-pyrolysis of 1,3-bis(trimethylsilyl)-3-dimethylmethoxysilylpropene afforded 1,1-dimethyl-4-trimethylsilyl-1-silacyclobutene in a satisfactory yield. This reaction was viewed as proceeding through a β-elimination of Me_3SiOMe to produce an intermediate 1-sila-1,3-butadiene which closed to give the unsaturated ring:



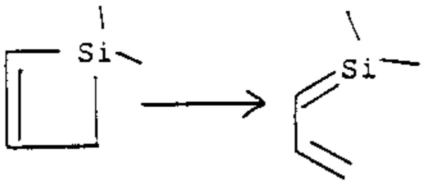
In liquid-phase studies, bimolecular reactions of acetone and methanol with the photochemically generated 1,1-dimethyl-1-sila-2-phenyl-1,3-butadiene, which was produced from the corresponding silacyclobutene, have been reported.[5] Addition of the O-H bond of methanol to the silicon-carbon double bond of siladiene was reported to be the primary product:



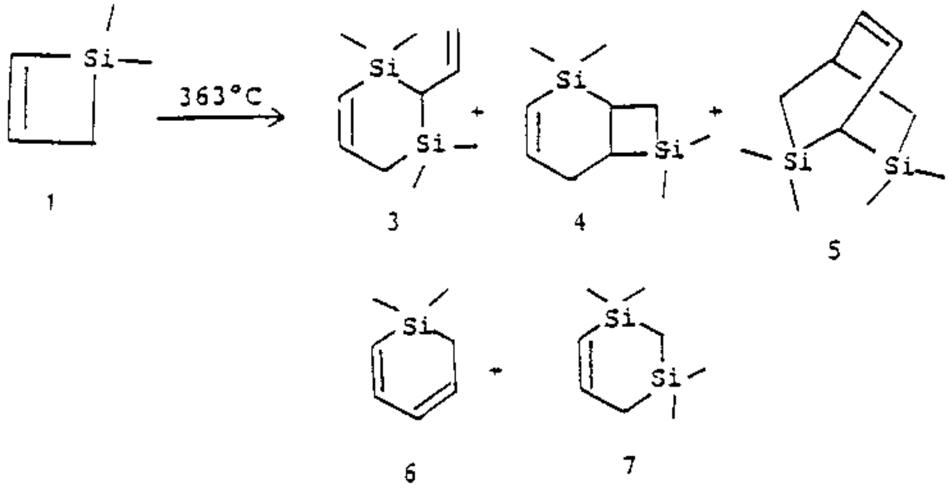
Photolysis, in the presence of acetone produced evidence for a 4 + 2 cycloaddition.[6] However, the interpretation of that result has been questioned.[7] A thermal reaction of 2-phenyl-1-siladiene with acetone has been reported, and evidence for 4 + 2 and 2 + 2 cycloadditions between the siladiene and acetone were also described.[5] Bimolecular reactions of the formally conjugated siladiene with alkenes and alkynes, however, have not been studied. We consider such reactions and address the mechanisms of both 2 + 2 and 2 + 4 cycloadditions.

Results and Discussion

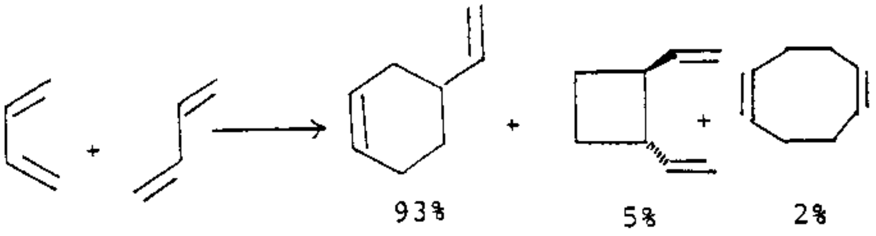
Dimerization of 1,1-dimethyl-1-silabuta-1,3-diene.-- It has been reported that silenes, if not stabilized by bulky substituents, dimerize very fast but the analogous reactions of 1-silabuta-1,3-dienes are not known.[2] Silene in the presence of an intramolecular trap such as a nearby carbon-carbon double bond reduces the chance for the formation of dimers from silabutadiene.[8]



We have found that dimerization of silabutadiene can be achieved at high temperature in a closed pyrolysis vessel where the 1-silabuta-1,3-diene is continuously reproduced from its more stable isomer, a 1-silacyclobut-2-ene. Static pyrolysis of 1,1-dimethyl-1-silacyclobut-2-ene **1** at 363 °C provides three major products, $Si_2C_{10}H_{20}$ dimers of **1**: 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 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 the unreacted **1** (16%).



Whether the $Si_2C_{10}H_{20}$ isomers form from dimerization of siladiene **2** or from reaction of **2** with unreacted **1** raises mechanistic questions. In contrast, the gas phase dimerization of the hydrocarbon, butadiene[9] gives the 4 + 2 cycloaddition adduct, 4-vinylcyclohexene (93%) along with 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.



It is interesting to note that the analogy between dimerization of 1-silabutadiene and of butadiene is diminished by the significantly smaller concentration of the π-bonded silene. However, the effect of temperature on the product distribution in Table 4-1 can provide mechanistic parallels to the dimerization of butadiene.

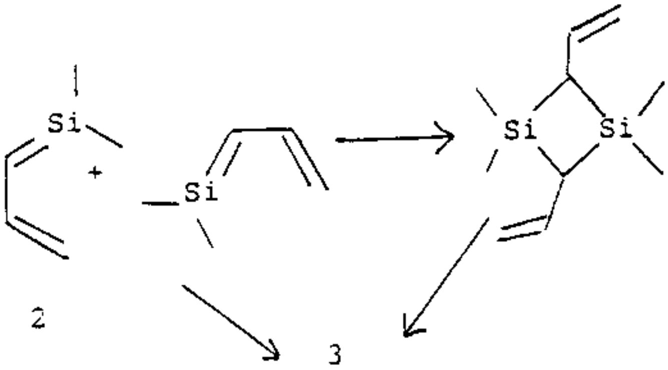
Table 4-1. Temperature dependence of product distribution from pyrolysis of **1**.[a,b]

Temp. 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

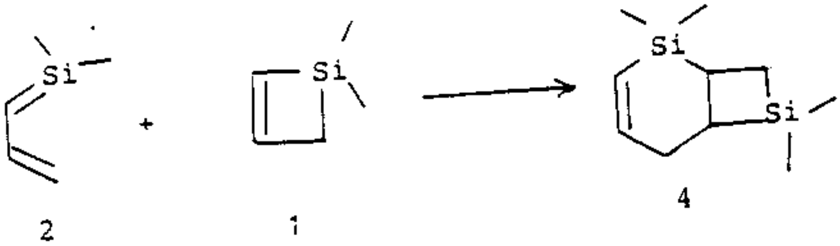
[a] in all pyrolyses, the initial pressure of **1** was 20 torr.
[b] all products are stable under the reaction conditions.

At higher reaction temperature the concentration of **2** increases, suggesting that the probability of dimerization of the silabutadiene is enhanced, so the yield of **3** increases. The structural similarity between 4-

vinylcyclohexene and **3** indicates that silabutadiene **2** also reacts with itself in a 4π + 2π fashion. We cannot, however, disregard the possibility that siladiene **2** initially dimerizes in the usual head to tail oreintation to form 1,1,3,3-tetramethyl-2,4-divinyl-1,3-disilacyclobutane which isomerizes to **3**

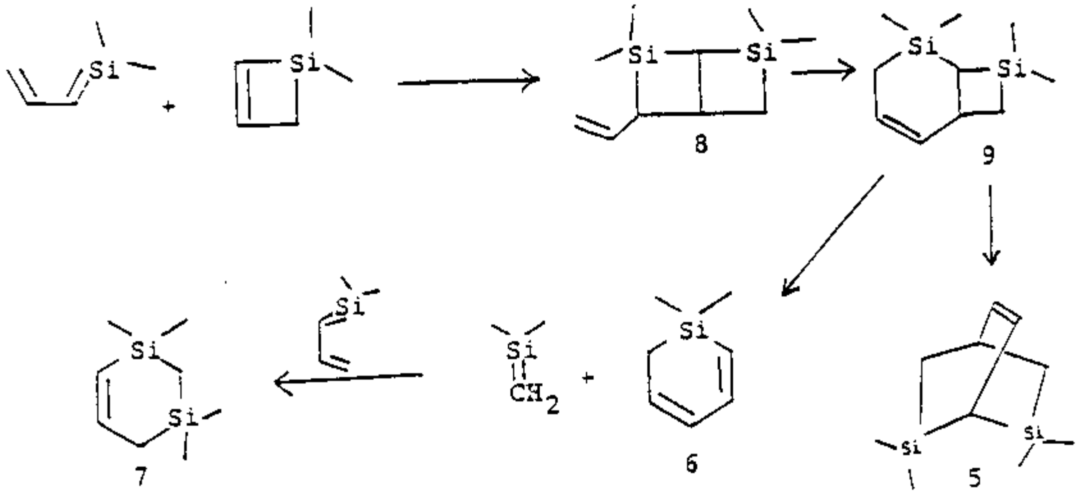


Supporting the mechanistic interpretation for greater amount of **3** from dimerization of **2** by either mechanism is the relative decrease in **4** (Table 4-1), the product anticipated from the cycloaddition between **2** and the carbon-carbon π-bond of **1**.



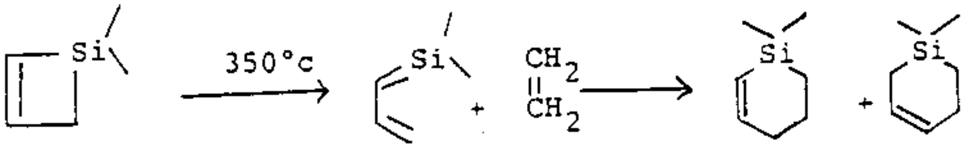
Product **5**, the major product might be formed through a sequential isomerization of silacyclobutane rings. The lack of a temperature dependence on the formation of **5** is surprising and possibly due to compensating effects of several different reaction rates in a multi-step mechanism. A possible pathway leading to **5** may be involved in both 2- and 3-vinylsilacyclobutane intermediates **8** and **9** which then undergo ring expansions as shown below:

Scheme 4-1



Rearrangement of **8** to **9** may be considered an example of the 1,3-sila-sigmatropic shift previously reported for the ring expansion of 2-vinylsilacyclobutanes to a silacyclohex-3-ene.[10] Also, the ring expansion of 3-vinylsilacyclobutanes to a silacyclohex-3-ene has been observed to be a thermally facile process in a flow system at 450 °C.[11] Formation of minor amounts of secondary products **6** and **7** may serve as evidences for an intermediate such as **9**. Fragmentation of **9** might produce 1,1-dimethylsilene and **6**. Trapping of the silene in the pressence of a large excess of **1** or **2** could yield **7**.

Reactions of 1,1-dimethylsilabutadiene 2 with alkenes.--Static pyrolysis of 1,1-dimethylsilacyclobutene **1** in the presence of a twenty-fold excess of ethylene at 350 °C produces 1,1-dimethyl-1-silacyclohex-2-ene **10** (45%) and the cyclic 3-ene **11** (51%) in nearly quantitative yield.

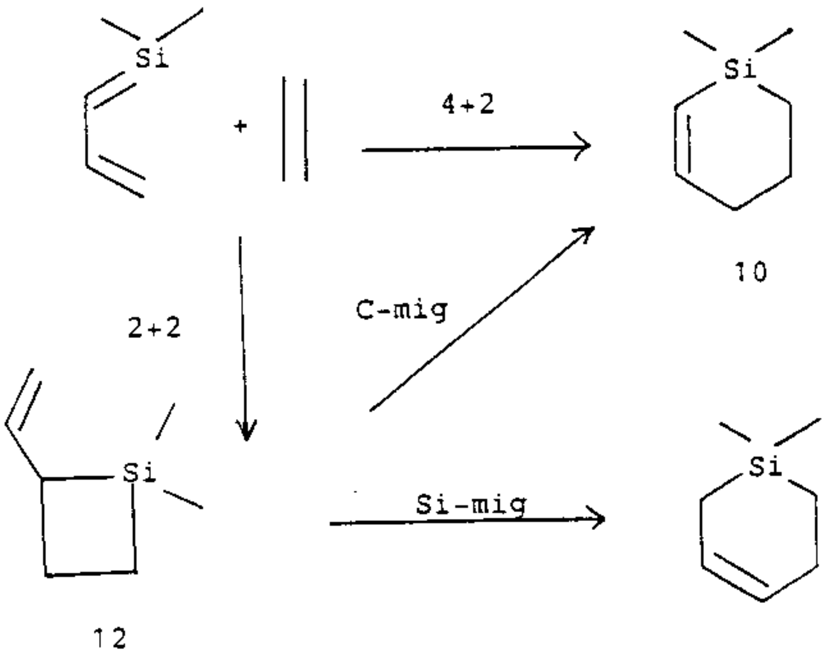


10 11

45% 51%

Formation of the 2-ene might be expected from a Diels-Alder type cycloaddition between ethylene and the siladiene. However, observation of the 3-ene raises mechanistic concerns about the primary thermal pathways. A possible explanation for the formation of **11** is the 2 + 2 cycloaddition between siladiene **2** and ethylene to form the unknown 2-vinyl-silacyclobutane **12** (Scheme 4-2). A ring expansion via a 1,3-silyl shift to the terminal methylene of the allyl group could yield **11**. Since the Si-C bond

Scheme 4-2



10

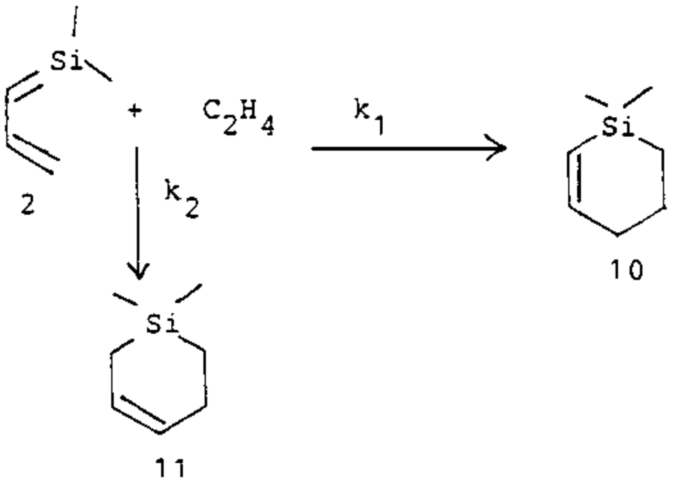
12

11

dissociation energy (89 kcal/mol) is slightly greater than the corresponding C-C bond (87 kcal/mol),[12] it is possible that some, if not all, of **10** is formed by cleavage of the weaker C-C bond of **12**.

It appears that the ratio of [**11**] to [**10**] is nearly independent of the reaction time (1-3 hr.) and as shown in Table 4-2 the ratio is slightly temperature dependent at temperatures ranging from 601 to 663 K. From Table 4-2 we can determine the activation energy difference between the formations of **11** and **10**.

Consider the following scheme:



From the above scheme, the rates of formations of **10** and **11** are

$$d[\mathbf{10}]/dt = k_1[\mathbf{2}][C_2H_4] \tag{4-1}$$

$$d[\mathbf{11}]/dt = k_2[\mathbf{2}][C_2H_4] \tag{4-2}$$

Integration of equations 4-1 and 4-2 from t = 0 to t = t gives equations 4-3 and 4-4 respectively:

$$[\mathbf{10}] = k_1[\mathbf{2}][C_2H_4]t \tag{4-3}$$

$$[\mathbf{11}] = k_2[\mathbf{2}][C_2H_4]t \tag{4-4}$$

The ratio of products **11** to **10** at a given time is obtained by dividing equation 4-4 by equation 4-3.

$$[\mathbf{11}]/[\mathbf{10}] = k_2/k_1 \tag{4-5}$$

We can express the temperature dependence of equation 4-5 according to the Arrhenius relationship, $k = Ae^{-Ea/RT}$, as follows:

$$\ln([\mathbf{11}]/[\mathbf{10}]) = \ln(A_2e^{-E_2/RT}/A_1e^{-E_1/RT}) \qquad (4-6)$$

$$\ln([\mathbf{11}]/[\mathbf{10}]) = \ln(A_2/A_1) + (E_1-E_2)/RT \qquad (4-7)$$

The plot of ln([**11**]/[**10**]) vs. 1/T using data in Table 4-2 shown in Figure 4-1 is linear. From the slope of the plot we could obtain the activation energy difference between the formations of **11** and **10** (E_1-E_2).

$$E_1-E_2 = 1.04 \pm 0.13 \text{ kcal/mol}$$

$$\log(A_2/A_1) = 0.35 \pm 0.04$$

correlation coefficient = 0.96

Table 4-2. Ratios of [**11**] to [**10**] at 601 to 663 K.[a]

Temperature K	[**11**]/[**10**]
601	1.12 ± 0.01
609	1.12 ± 0.01
620	1.13 ± 0.01
631	1.14 ± 0.02
644	1.18 ± 0.02
653	1.20 ± 0.01
663	1.20 ± 0.01

[a] Products **11** and **10** are stable under the reaction conditions.

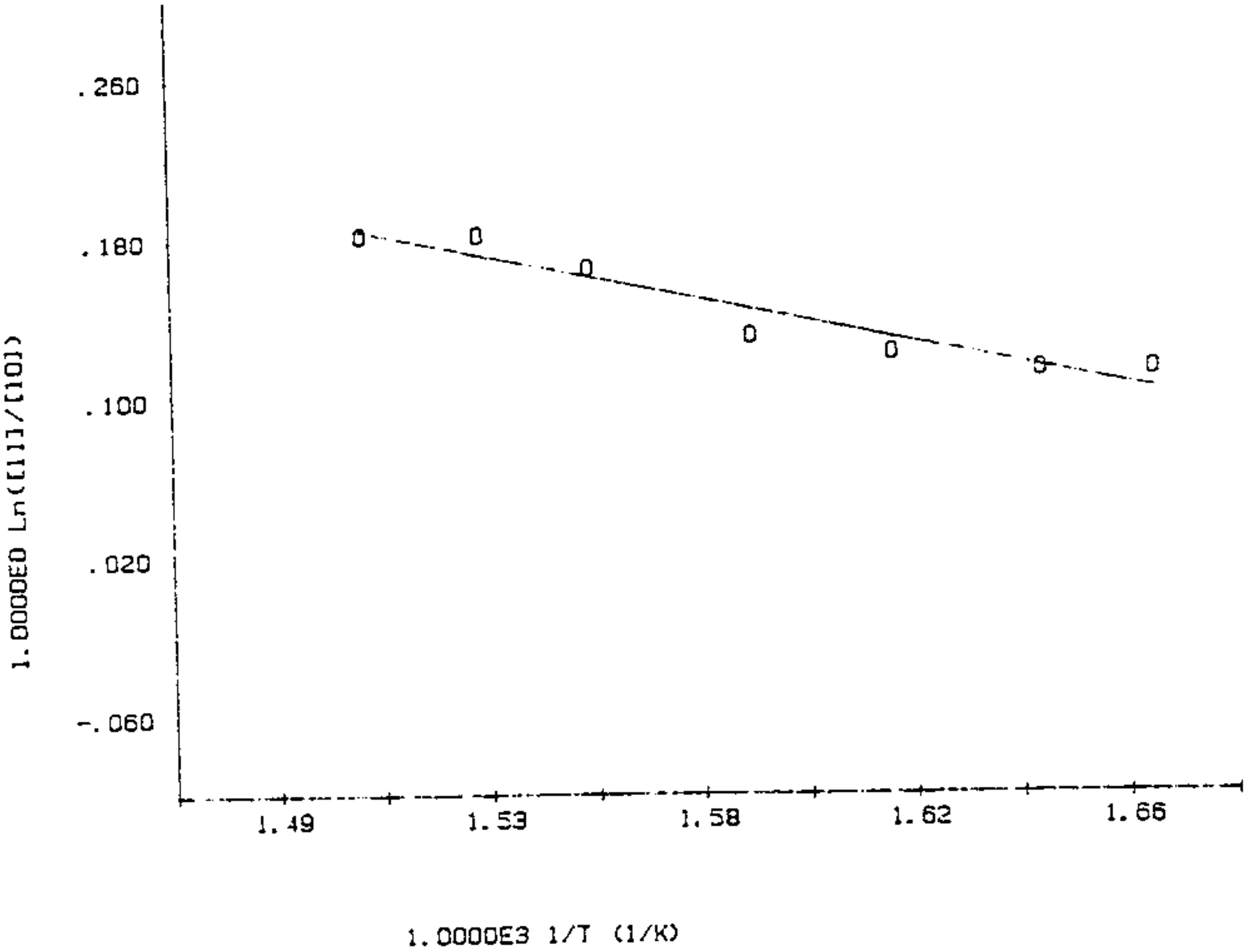
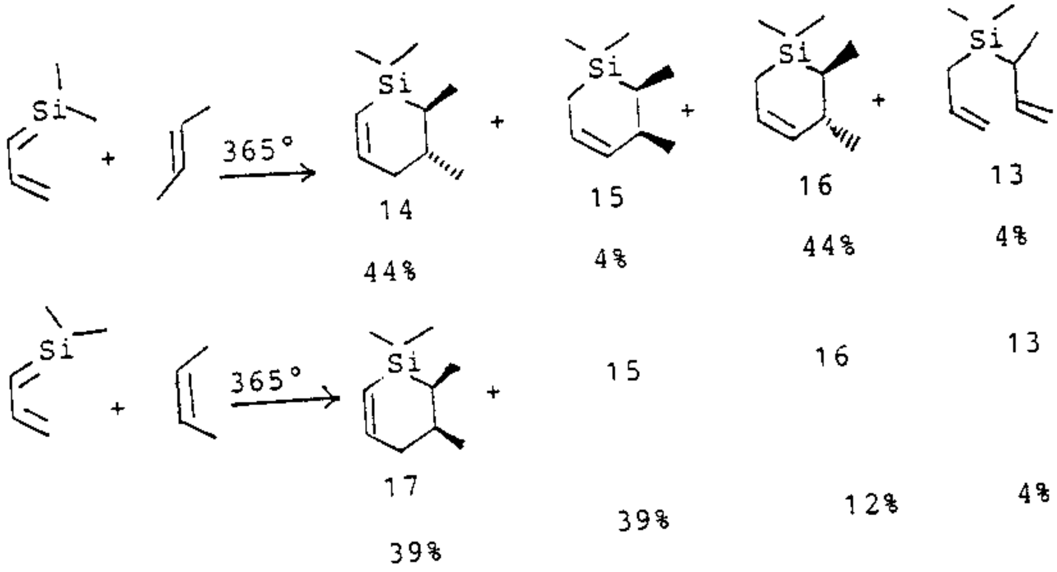


Fig. 4-1 A plot of ln ([11]/[10]) vs. 1000/T.

Pyrolysis of **1** with a twenty-fold excess of trans-2-butene at 365 °C provides four adducts of **2** and the butene: the acyclic 3,4,4-trimethyl-4-silahepta-1,6-diene **13** (4%); trans-1,1,5,6-tetramethyl-1-silacyclohex-2-ene **14** (44%) and cis and trans-1,1-5,6-tetramethyl-1-silacyclohex-3-ene **15** and **16**, (4% and 44%), respectively. Reaction of **2** with cis-2-butene also produces four adducts: **13** (4%) cis-1,1,5,6-tetramethyl-1-silacyclohex-2-ene **17** (39%) along with **15** and **16**, (39% and 12%), respectively.[13]



The cyclic-2-enes, **14** and **17** are formed stereospecifically (>99%), suggesting that despite the highly polarized and unsymmetrical distribution of four π electrons[14] of siladiene **2**, the 4 + 2 cycloaddition between **2** and an alkene is an orbital symmetry allowed process.[15]

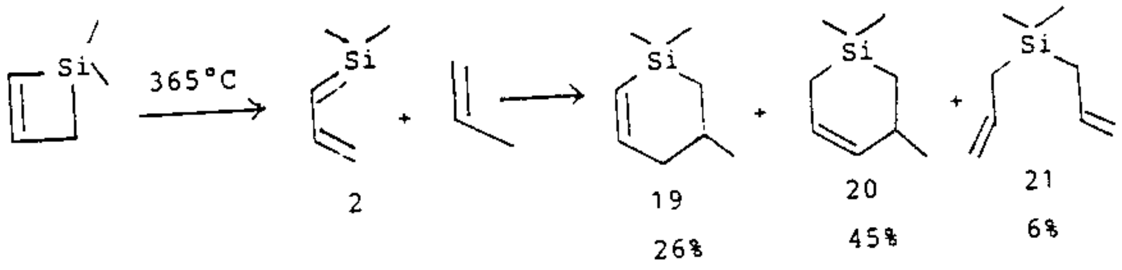
The cyclic-3-enes, **15** and **16** indicate slight scrambling in product stereochemistry. The mechanism of the formation of **15** and **16** involves in a process in which alkene stereochemistry is partially lost. In the case of E-2-butene, retention of the trans relation between adjacent methyls in the cyclic 3-ene is 92% but only 76% from Z-2-butene.

A possible explanation is that the Si-C double bond of siladiene **2** reacts with slight non-stereospecifically with 2-butene to yield the substituted 2-vinyl-1-silacyclobutane **18**. So far, the stereochemistry of the 2 + 2 cycloaddition of silenes to alkenes is not known. It has been shown that E- and Z-1,1,2,3-tetramethyl-1-silacyclobutane each decompose with ≥ 20% loss of starting stereochemistry in the 2-butene product.[16] Microscopic reversibility then dictates that the 2 + 2 cycloaddition of silene to alkenes also proceed with some loss of stereochemistry in formation of the four-membered ring.

A ring expansion of the diastereomeric intermediates **18** via a 1,3-silyl shift to the terminal methylene of the allyl group could yield the **E** and **Z** isomers **15** and **16**. This rearrangement may serve as an example of the 1,3-sila-sigmatropic shift previously observed to occur with inversion of configuration at the migrating silicon center.[17] It should be noted that facile ring expansion via silicon migration prevents the 1,5 sigmatropic hydrogen shift previously reported for pyrolysis of substituted 3-vinylsilacyclobutanes.[11] Since cyclic 2-enes **14** and **17** are formed stereospecifically, it indicates that they do not come from any C-C ring expansion of diasteromeric **18**. Further, **18** does not appear to decompose to silenes and substituted 1,3-dienes.

As we have shown earlier the major cycloaddition product of **2** and ethylene is the 2 + 2 adduct (53%) and similarly, in reactions with **E**- and **Z**-2-butenes, the forbidden products predominate. Surprisingly, the rate of the forbidden and partially stereospecific 2 + 2 cycloaddition is slightly faster than that of the allowed and stereospecific 4 + 2.[18] Regardless of the fact that the rules of orbital symmetry correctly describe the stereochemistry of 4 + 2 and 2 + 2 cycloaddition of **2** and 2-butenes, they do not account for the faster rate of the forbidden reaction. Possibly the polarization of 2, known to have greater negative charge density on C(2) than C (4),[14] might emphasize the importance of coulombic forces in such cycloadditions.[19]

Reaction of 2 with propene. Static pyrolysis of **1** and a five-fold excess of propene at 365 °C gives 1,1,5-trimethyl-1-silacyclohex-2-ene **19** (26%), 1,1,5-trimethyl-1-silacyclohex-3-ene **20** (45%), diallyldimethylsilane **21** (6%) and 3 dimers of **1** (22%).

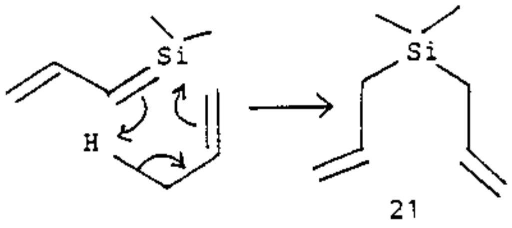


+ dimer 3 + dimer 4 + dimer 5

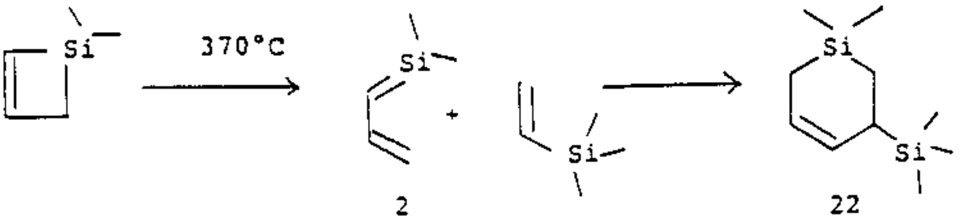
16% 2% 4%

This reaction shows the regioselectivity of 4 + 2 and 2 + 2 cycloadditions of **2** and propene, indicating that the less substituted side of the π-bond of propene bonds with the silicon of siladiene **2**. The product diallyldimethylsilane **21** may derive from the "ene" reaction of propene and the silene end of **2** (Scheme 4-3). It should be noted that at lower temperature, the amounts of the trapping products decrease, but the yield of dimers increases. For example, pyrolysis of **1** and a ten-fold excess of propene at 345 °C gives **19** (22%), **20** (39%), **21** (5%), **3** (13%), **4** (8%) and **5** (12%).

Scheme 4-3



Reaction of 2 with trimethylvinylsilane. Pyrolysis of **1** with a five-fold excess of trimethylvinylsilane at 370 °C in a closed pyrolysis vessel produces 1,1-dimethyl-5-trimethylsilyl-1-silacyclohex-3-ene **22** (43%) along with 3 dimers of **1** (57%):



2 22

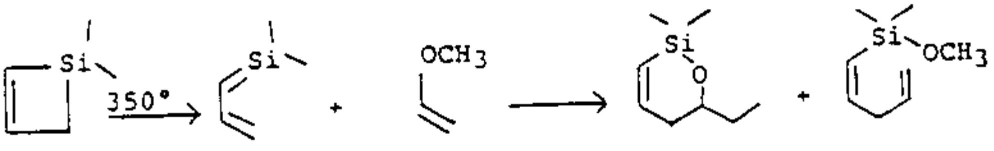
43%

+ dimer 3 + dimer 4 + dimer 5

50% 3% 4%

Surprisingly, in this reaction no product corresponds to the 4 + 2 cycloaddition of **2** and trimethylvinylsilane is produced.

Reaction of 2 with methyl vinyl ether. Static pyrolysis of 1 and a fifteen-fold excess of methyl vinyl ether at 350 °C provides 2,2-dimethyl-6-ethyl-1-oxa-2-silacyclohex-3-ene **23** (33%), 2,2-methylmethoxy-2-silahepta-3,6-diene **24** (36%), unknown A (8%), unknown B (9%) and 3 dimers of **1** (14%).

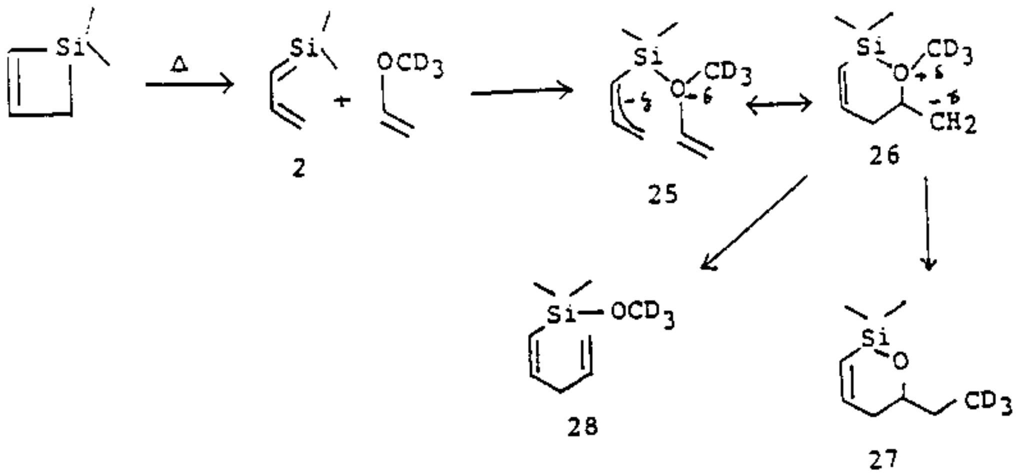


2 23 (33%) 24 (36%)

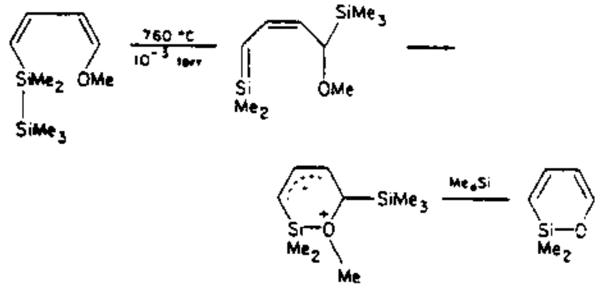
+ unknown A (8%) + unknown B (9%) + 3 (10%) + 4 (1%) + 5 (3%)

Formation of **23** and **24** raise mechanistic concerns about the primary pathways. Theoretical studies have shown that in siladiene **2** silicon has positive charge density but, C_2 and C_4 have negative charge density. However, C_2 has greater negative charge density than C_4.[14] Also, it has been known that silenes are reactive toward ethers and produce a donor-acceptor type complex.[20] The use of a labeled methyl vinyl ether such as methyl-d_3 vinyl ether represents a subtle but very effective method of determining specific information about the bonds that are involved in the above reaction. A likely rationale is that lone pair electrons on oxygen of methyl-d_3 vinyl ether add to the silene end of siladiene 2 to form a partially polarized species (**25**) which has a resonance form (**26**). Migration of the CD_3 group to the partially negatively charged methylene group produces **27**. Cleavage of the cyclic C-O bond of **26** gives **28** (Scheme 4-4).

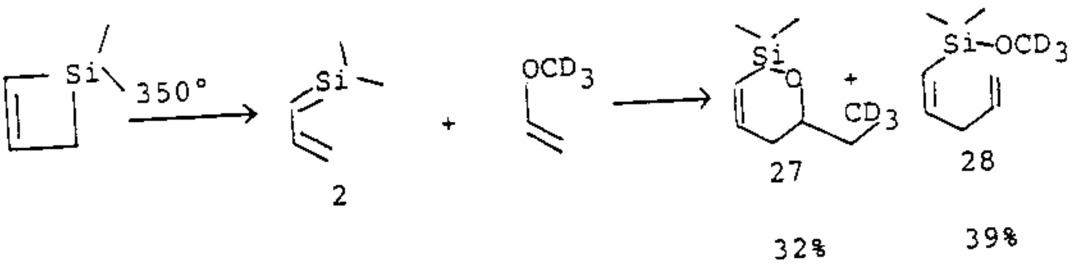
Scheme 4-4



An example of a partially polarized species similar to **25** has been reported in the following reaction.[21]

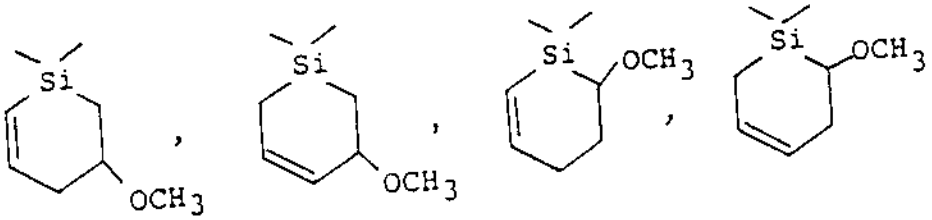


Our experimental results from reaction of **1** and methyl-d_3 vinyl ether are consistent with the proposed mechanism and

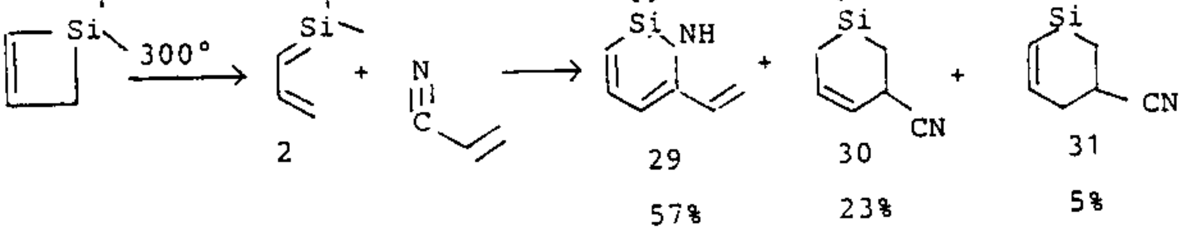


clearly show that the CD_3 group in the cyclic and acyclic products originated from methyl-d_3 vinyl ether.

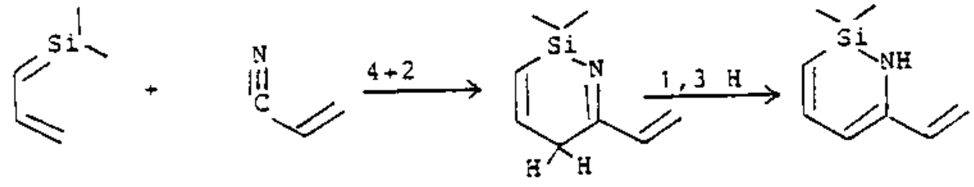
Attempts to isolate and identify unknowns A and B were unsuccessful. However, GC/MS suggests that both A and B have the same molecular weight as **23** and **24** (MW = 156). following are the structural possibilities for A and B.



Reaction of 2 with acrylonitrile. Pyrolysis of **1** and a five-fold excess of acrylonitrile at 300 °C gives 2,2-dimethyl-6-vinyl-1-hydrido-2-silapyridine **29** (57%), 5-cyano-1,1-dimethyl-1-silacyclo-hex-3-ene **30** (23%) and 5-cyano-1,1-dimethyl-1-silacyclo-hex-2-ene **31** (5%).

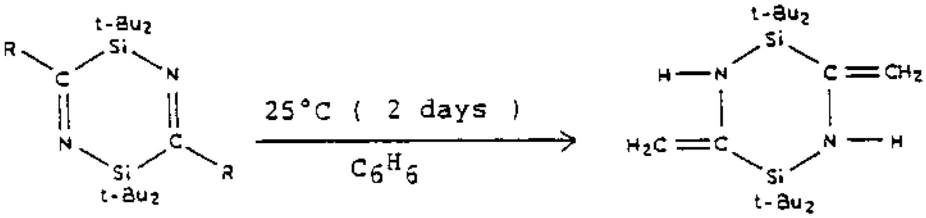


A possible path leading to the major product (**29**) may be involved in the following mechanism.

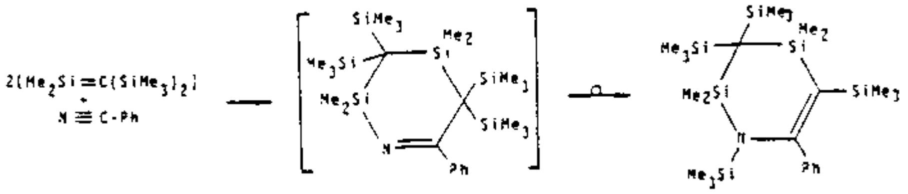


2 32 29

Rearrangement of **32** to **29** may be compared to the following reactions.[22]

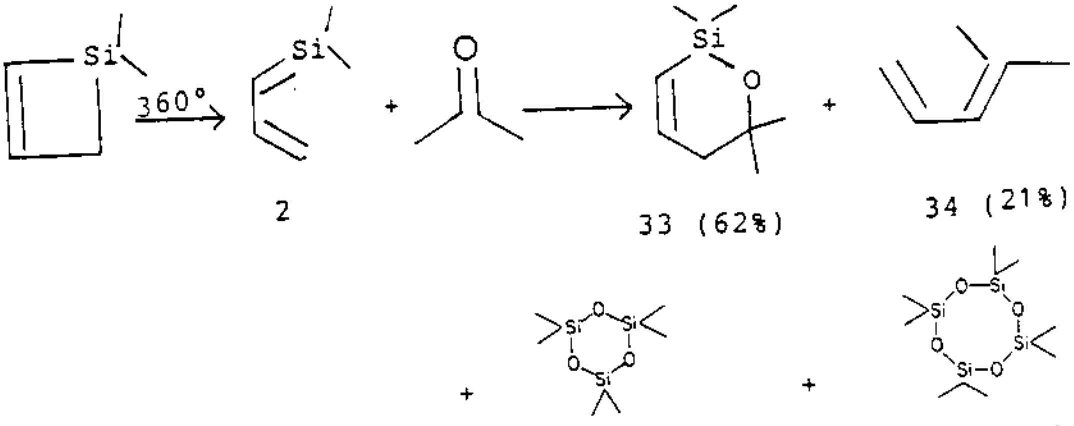


R= CH_3



It is interesting to note that in the reaction of butadiene with acrylonitrile only carbon-carbon double bonds react with butadiene to give the 4 + 2 adduct in high yield. However, in the case of siladiene the carbon-nitrogen triple bond acts as a better dienophile than the carbon-carbon double bond, resulting in a high yield of product **29**.

Reaction of 2 with acetone. Static copyrolysis of 1 and a five-fold excess of acetone at 360 °C yields 2,2,6,6-tetramethyl-1-oxa-2-silacyclohex-3-ene **33** (62%), 4-methyl-1,3-pentadiene **34** (21%), hexamethylcyclotrisiloxane **35** (12%) and octamethylcyclotetrasiloxane **36** (3%).



2

33 (62%)

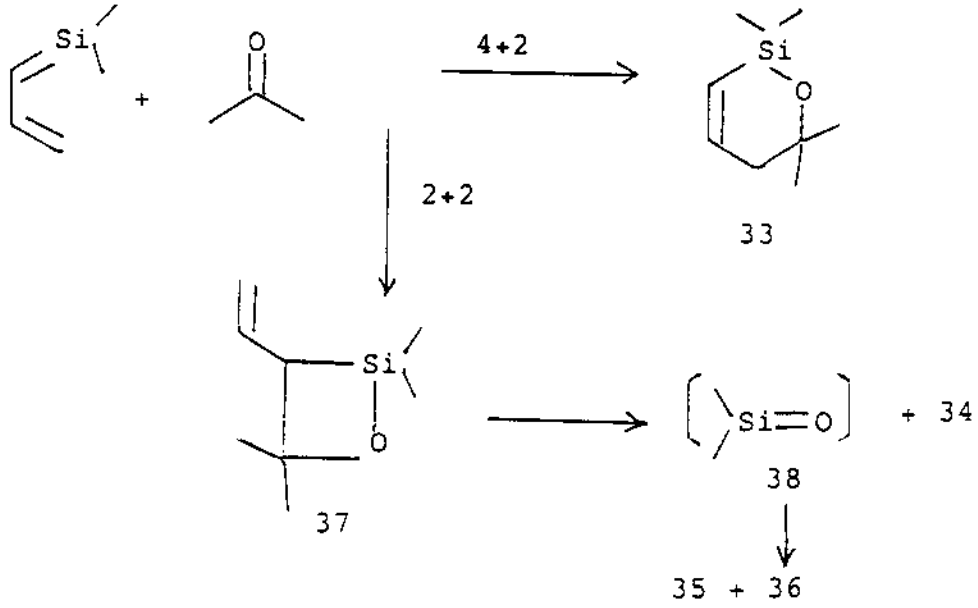
34 (21%)

35 (12%)

36 (3%)

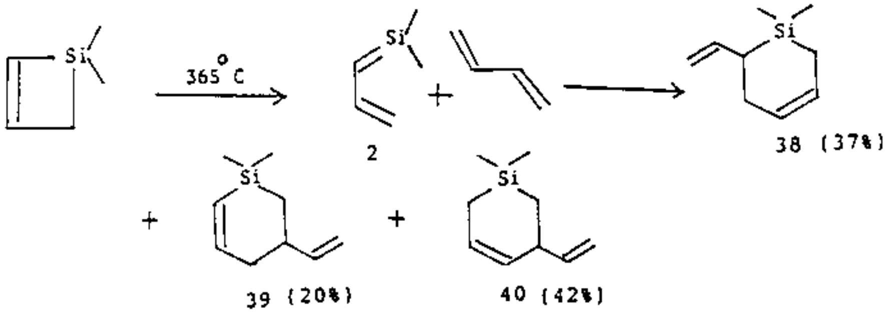
Formation of product **33** might be expected from a 4 + 2 cycloaddition between siladiene **2** and acetone. A 2 + 2 cycloaddition between **2** and acetone would result in the unstable 2,2,4,4-tetramethyl-2-sila-1-oxatane **37** which decomposes to dimethylsilanone **38** and 4-methyl-1,3-pentadiene **34**. Cyclization of **38** gives **35** and **36** (Scheme 4-5).

Scheme 4-5

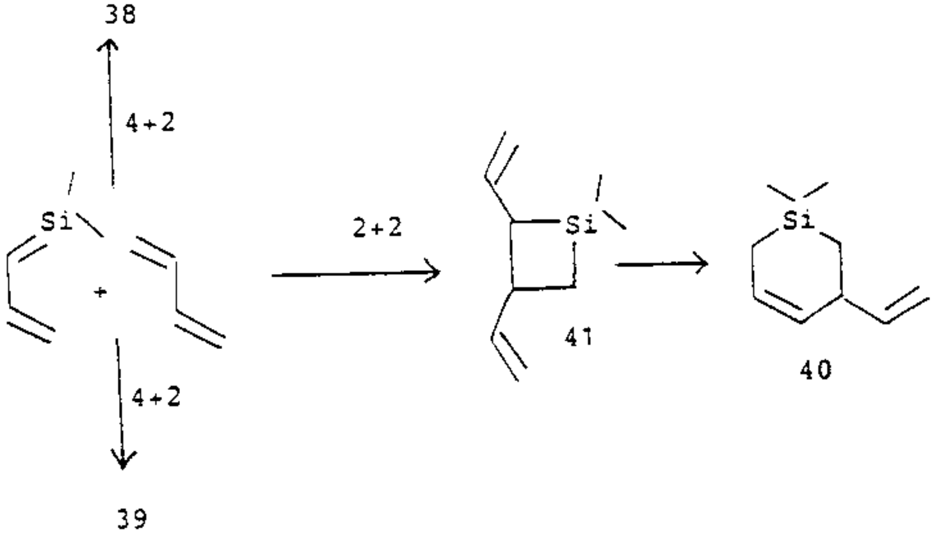


A similar mechanism for the thermal reaction of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene and acetone has been reported.[5]

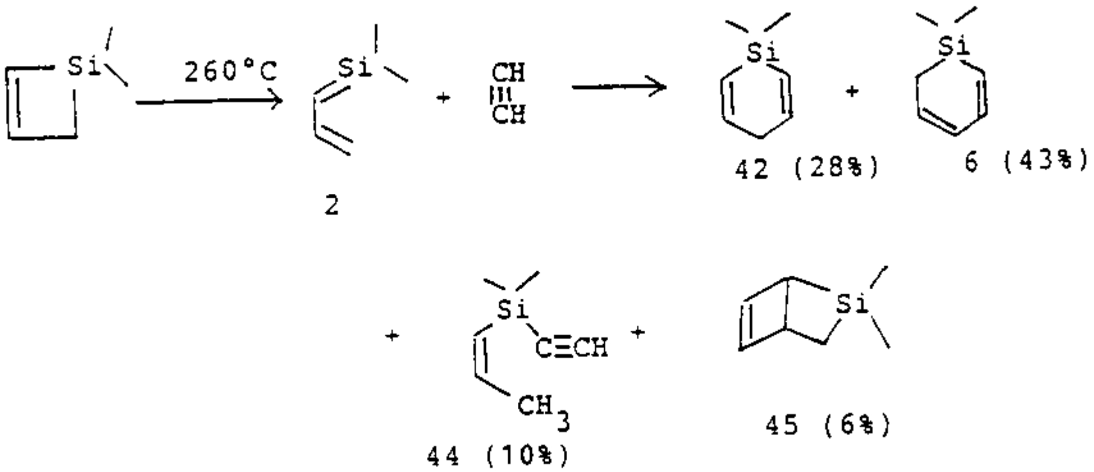
Reaction of 2 with butadiene. Pyrolysis of **1** in the presence of a twenty-fold excess of butadiene in a closed pyrolysis vessel at 365 °C affords 1,1-dimethyl-6-vinyl-silacyclohex-3-ene **38** (37%), 1,1-dimethyl-5-vinyl-silacyclohex-2-ene **39** (20%) and 1,1-dimethyl-5-vinyl-silacyclohex-3-ene **40** (42%).



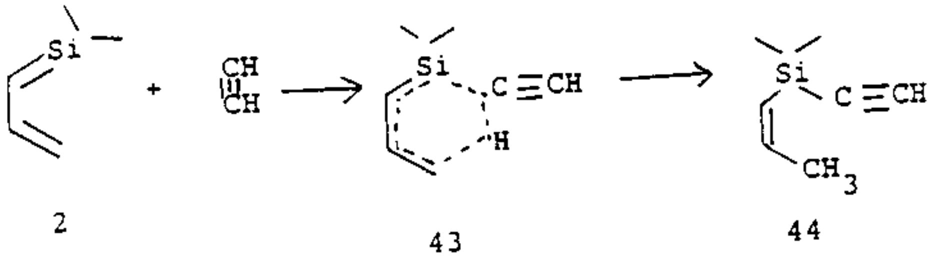
Product **38** is formed via a 4 + 2 cycloaddition between butadiene and the silene end of **2**. However, product **39** is produced from a 4 + 2 cycloaddition between siladiene **2** and the vinyl end of butadiene. A possible rational for the formation of **40** is the 2 + 2 cycloaddition between the silene end of **2** and the vinyl portion of butadiene to give the unstable 2,3-divinylsilacyclobutane **41**. The ring expansion of **41** via a 1,3-silyl shift to the terminal methylene of the allyl group could yield **40**. It should be mentioned that no ethylene was formed in this reaction.



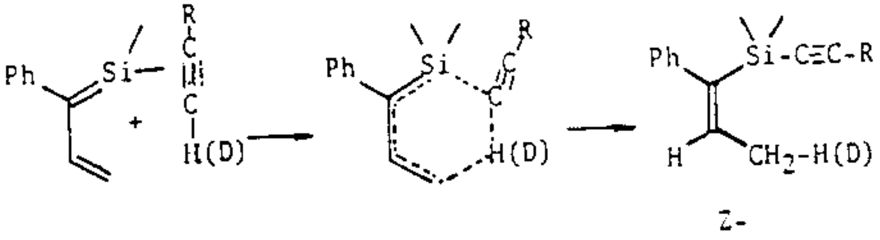
Reaction of 2 with acetylene. Static pyrolysis of **1** with a twenty-fold excess of acetylene at 260 °C gives 1,1-dimethyl-1-silacyclohexa-2,5-diene **42** (28%), 1,1-diemthyl-1-silacyclohexa-2,4-diene **6** (43%), Z-3,3-dimethyl-3-silahex-4-ene-1-yne **44** (10%) and 2,2-diemthyl-2-silabicyclo[2.2.0]hex-5-ene **45** (6%).



Compounds **42** and **6** are the expected 4 + 2 and 2 + 2 cycloaddition products between acetylene and siladiene **2**. Observation of products **44** and **45** is interesting. Formation of the acyclic z isomer **44** requires that siladiene **2** to be in a S-cis form. Partially negatively charged carbon (C_4) of siladiene **2** abstracts hydrogen from acetylene through a six member ring transition state to produce **44**. Possibly the polarities of the C-H bond of acetylene and siladiene **2** may emphasize the importance of the ionic transition state.



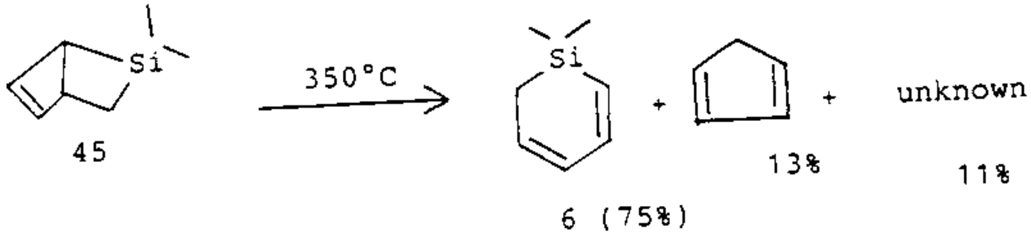
Similar behavior has been observed in the reaction of 1,1-dimethyl-1-sila-2-phenyl-1,3-butadiene with trimethylsilylacetylene.[23]



$$\frac{k_H}{k_D} = 1.20 +0.02$$

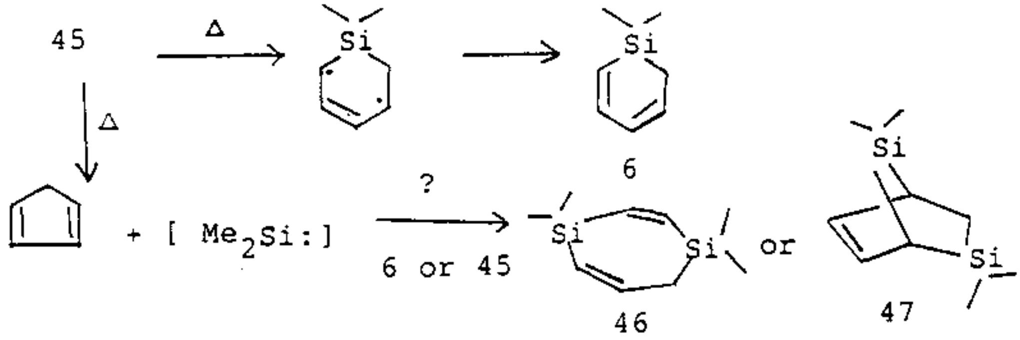
Since the deuterium labeling experiment showed a very small isotope effect on the reaction, the possibility of the six-membered ring transition state was suggested.

A possible explanation for the formation of silabicyclic **45** is the 2 + 2 cycloaddition between acetylene and the carbon-carbon π-bond of silacyclobutene **1**. The possibility that some of the conjugated cyclic diene (**6**) comes from the ring opening of silabicyclic **45** raises a mechanistic question. We found that static pyrolysis of silabicyclic **45** at 350 °C produces conjugated cyclic diene **6** (75%), cyclopentadiene (13%) and an unknown (11%) which has a molecular weight of 182 (GC/MS). This molecular weight corresponds to the molecular weight of the product from the reaction between dimethylsilylene and the cyclic diene or the starting bicyclic **45** and the silylene. The possibilities include compounds **46** or **47** in Scheme 4-6.

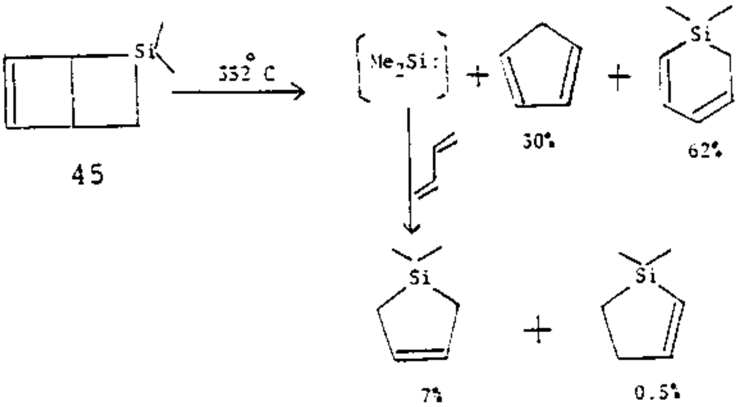


Following is the possible mechanism for the ring opening of the silabicyclic compound.

Scheme 4-6

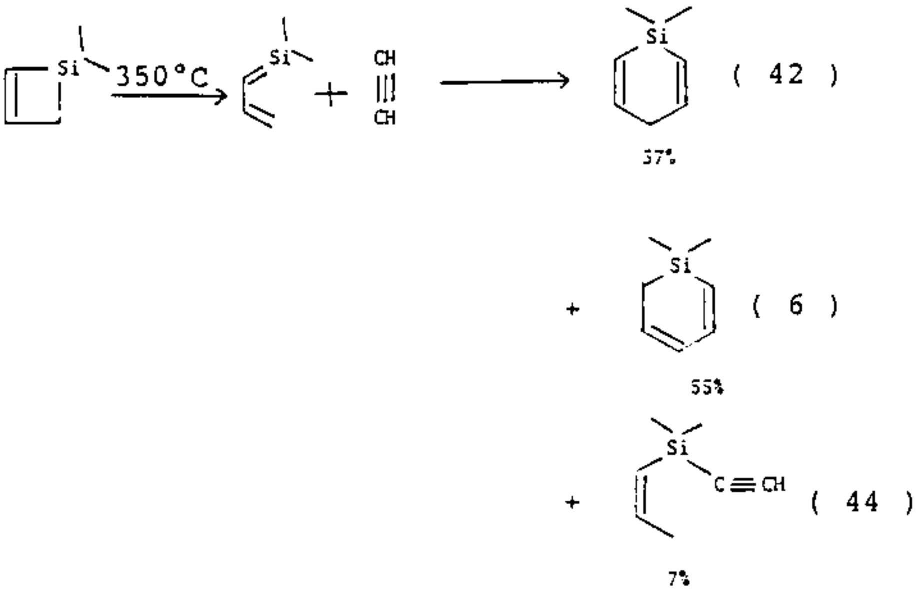


It appears that this ring opening is not a symmetry allowed process, because in the resulting six-membered ring product, a conjugated diene can not exist in an s-trans form. The alternative mechanism is a 1,4 diradical which then rearranges to the conjugated cyclic diene. We have been able to trap the reactive intermediate dimethylsilylene by using butadiene as a trapping agent in the copyrolysis of silabicyclic 45 and butadiene.



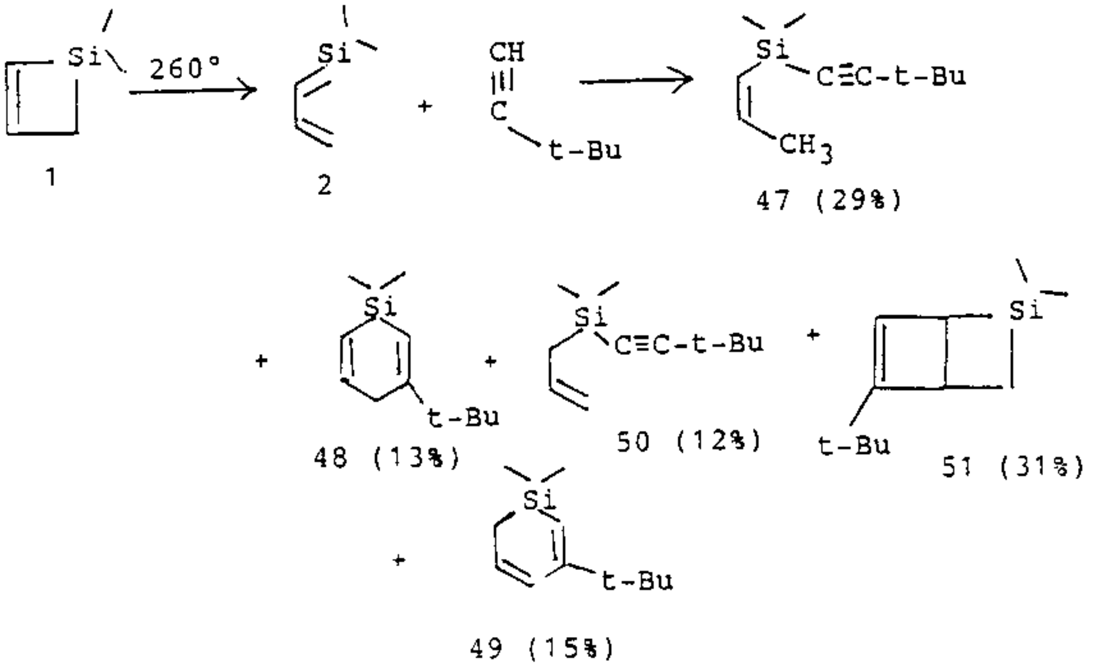
The two silacyclopentene compounds are the products from the raction between intermediate dimethylsilylene and butadiene.

Finally, we found that at the higher temperature (350 °C), the reaction of silacyclobutene **1** and acetylene provides only three products: unconjugated cyclic diene **42** (37%), conjugated cyclicdiene **6** (55%) and the acyclic **Z-44** (7%). However, neither bicyclic **45** or cyclopentadiene are formed at the higher reaction temperature, suggesting that all three products are produced from the reaction between acetylene and siladiene **2**.

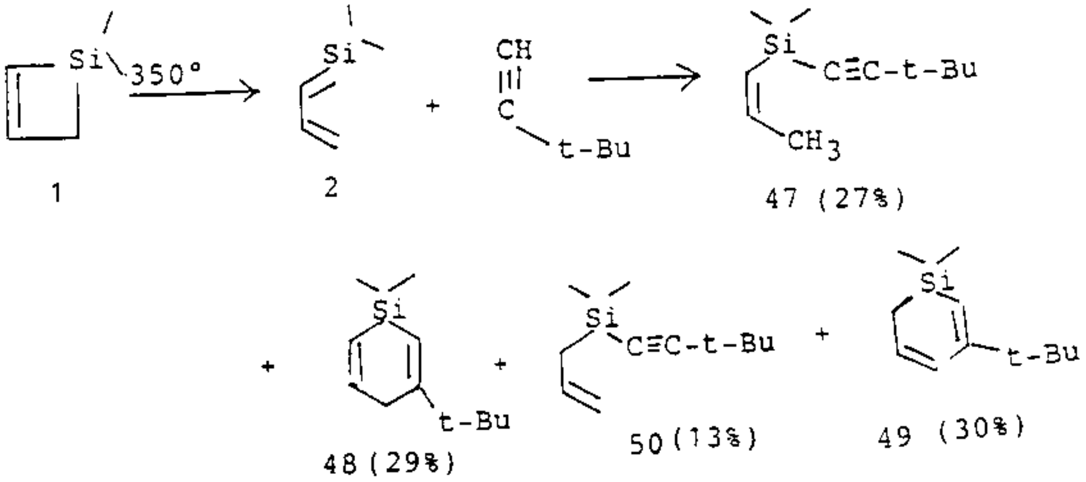


It should be noted that the ratio of conjugated cyclic diene **6** to unconjugated cyclic diene **42** is about 3 to 2 and remains constant from 260 to 356 °C. This indicates that even at the lower reaction temperature, silabicyclic **45** does not have a noticable influence on the amount of conjugated cyclic diene **6**.

Reaction of 2 with t-butylacetylene. Pyrolysis of **1** in the presence of an eight-fold excess of t-butylacetylene at 260 °C in a closed pyrolysis vessel affords Z-4,4,7,7-tetramethyl-4-silaocta-2-ene-5-yne **47** (29%), 1,1-dimethyl-3-t-butyl-1-silacyclohexa-2,5-diene **48** (13%), 1,1-dimethyl-3-t-butyl-1-silacyclohexa-2,4-diene **49** (15%), 4,4,7,7-tetramethyl-4-silaocta-1-ene-5-yne **50** (12%) and 2,2-dimethyl-5-t-butyl-2-silabicyclo[2.2.0]hex-5-ene **51** (31%).



Interestingly, the yield of **51**, the product anticipated from the 2 + 2 cycloaddition between t-butylacetylene and the carbon-carbon π-bond of **1** is relatively higher than that of silabicyclic **45**, the product from the acetylene reaction under the same condition. However, the yields of unconjugated cyclic diene **48** and conjugated cyclic diene **49** are relatively lower than those of **42** and **6** in the acetylene case. Probably the steric hindrance of the t-butyl group reduces the rate of the 4 + 2 and 2 + 2 cycloaddition between siladiene **2** and t-butylacetylene. This interpretation is consistent with higher yields of the acyclic products (**Z-47** and **50**) than that of **Z-44**, the product from the acetylene reaction under the same condition. A possible explanation for the formation of acyclic **50** is abstraction of hydrogen from t-butylacetylene by partially negatively charged carbon (C_2) of siladiene **2**. Again, at a higher temperature (350 °C) the yields of unconjugated cyclic diene **48** and conjugated cyclic diene **49** are relatively lower than those of **42** and **6**, in the acetylene reaction under the same condition. Also, at higher temperaure the yields of the acyclic products (**Z-47** and 50) is higher than that of **Z-44** in the acetylene case under the same condition.



1 2 47 (27%) 48 (29%) 50 (13%) 49 (30%)

It appears that the ratio of conjugated cyclic diene **49** to unconjugated **48** is about 1 to 1 and remains constant from 260 to 355 °C.

Experimental

General Data. Proton and carbon NMR spectra, IR and mass spectra were obtained as described in the previous chapters. Analytical gas chromatography and preparative gas chromatography were performed on the same instruments mentioned in Chapter I. Pyrolyses were carried out in a 250 or 500 mL reaction bulb immersed in a molten salt bath as described in Chapter III. Product yields from pyrolyses were based on the amount of decomposition of starting material and determined chromatographically with cyclohexane as an internal standard and predetermined response factors for the organosilanes. Compound 1,1-dimethyl-1-silacyclobutene 1 was synthesized by the referenced procedures.[3]

Static pyrolysis of 1,1-dimethyl-1-silacyclobutene 1.--Pyrolysis of vapors (20 torr) of 1 in a 500 mL closed pyrolysis vessel from 331 to 391 °C was performed. The results are shown in Table 4-1 in the results and discussion section. Three major products, $Si_2C_{10}H_{20}$ dimers of **1**: 1,1,3,3-tetramethyl-2-vinyl-1,3-disilacyclohex-4-ene **3**, 2,2,7,7-tetramethyl-2,7-disilabicyclo[4.2.0]oct-3-ene **4** and 2,2,6,6-tetramethyl-2,6-disilabicyclo[2.2.2]oct-7-ene **5** plus trace amounts 1,1-dimethyl-1-silacyclo-hexa-2,4-diene **6** and 1,1,3,3-tetramethyl-1,3-disilacyclohex-4-ene **7** were isolated by the preparative GC on the OV-17 column (20% OV-17 on chromosorb **W**, 1/4 in. x 20 ft.).

3:^{1}H NMR ($CDCl_3$) δ 0.03(3H, S, $SiCH_3$), 0.08 (9H, S, $Si(CH_3)_2$, $SiCH_3$), 1.30 (1H, d, J = 9.40 Hz, SiCHSi), 1.45 (2H, m, $SiCH_2C{=}C$); 4.78 (2H, m, $CH_2{=}C$), 5.55 (1H, app d, J = 12.50 Hz, SiCH=C), 5.60 (1H, m, $Si_2C{-}CH{=}C$), 6.70 (1H, t of d, J = 12.50 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, t of d, J = 14.30 Hz, J = 6.42 Hz, SiCHCSi), 2.82 (1H, m, SiCHCSi), 5.98 (1H, app d, J = 13.50 Hz), 6.78 (1H, t of d, J = 13.50, 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, H_{endo}), 0.75 (2H, d of d, J = 14.06 Hz, J = 4.58 Hz, H_{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 cald for $Si_2C_{10}H_{20}$ 196.1104, found 196.1100.

6:^{13}C NMR (neat) δ -1.89 (q), 13.46 (t), 125.70 (d), 125.96 (d), 127.26 (d), 140.98 (d)[24].

7:^{13}C NMR (neat) δ -1.24 (t), -0.65 (q), 0.52 (q), 18.53 (t), 129.28 (d), 144.82 (d)[11].

Static pyrolysis of 1 with ethylene.--Pyrolysis of **1** (15 torr) and ethylene (300 torr) in a 500 mL closed vessel at 350 °C for 2 hr. gave 1,1-dimethyl-1-silacyclohex-2-ene **10** (45%) and 1,1-dimethyl-1-silacyclohex-3-ene **11** (51%).

10:^{13}C NMR (neat) δ -2.12 (q), 11.83 (t), 20.87 (t), 30.87 (t), 126.35 (d), 148.01 (d).[25]

11:^{13}C NMR (neat) δ -2.96 (q), 9.91 (t), 12.90 (t), 22.50 (t), 125.40 (d), 129.70 (d).[1,2]

Pyrolysis of 1 with trans-2-butene.--Static pyrolysis of **1** (12 torr) and trans-2-butene (240 torr) was carried out for 2.5 hr. at 365 °C. GC analysis of the reaction mixture on the SP2100 Column (1/8 in. x 12 ft.) indicated the following products: the acyclic 3,4,4-trimethyl-4-silahepta-1,6-diene **13** (4%); trans-1,1,5,6-tetramethyl-1-silacyclohex-2-ene **14** (44%) and cis and trans-1,1,5,6-

tetramethyl-1-silacyclohex-3-ene **15** and **16** (4% and 44%), respectively. Similar reaction with cis-2-butene also provided four adducts: 13(4%) cis-1,1,5,6-tetramethyl-1-silacyclohex-2-ene **17**(39%) along with **15** and **16**, (39% and 12%) respectively. All of the products were isolated by the preparative GC on the DCQF1 Column (20% DCQF1 on chromosorb W, 1/4 in. x 20 ft.).

Synthesis of 3,4,4-trimethyl-4-silahepta-1,6-diene 13.[17]--In a 150 mL, three-neck round bottom flask, equipped with a reflux condenser, dropping funnel and a mechanical stirrer was added to 1.13 g (47 mmol) of magnesium turnings and 30 mL of THF. Then a solution of 4.30 g (47 mmol) of 3-chloro-1-butene (Aldrich) in 15 mL of THF was added slowly to the flask through the dropping funnel. During the addition of the halide the reaction temperature remained 40 to 50 ^{o}C and the addition was completed for 1.5 hr. The reaction mixture was refluxed for 20 min., cooled to 30 ^{o}C, and then 4.68 g (35 mmol) of allylchlorodimethylsilane (Petrarch) in 15 mL of THF was added. The addition was completed for 1 hr., 20 mL THF was added and the mixture was refluxed for 2 hr. The reaction mixture was cooled and then poured onto a 50 mL solution of cold saturated amonium chloride. The organic layer was separated, washed with H_2O and dried over anhydrous sodium sulfate (GC yield = 50% on 20% SF-96 on chromosorb W, 1/4 in. x 20 ft.). The authentic sample was used to identify **13** from the pyrolyses. **13** ^{1}H NMR (neat) δ -

0.47 (3H, s, MeSi), -0.46 (3H, s, Mesi), 0.63 (3H, d, J=7.11 Hz, CH_3-C-Si), 1.09 (3H, m, Si-CH_2-C=C & CH-Si), 4.30 (2H, m, CH_2=C(C)Si), 4.47 (2H, m, CH_2=C-C-Si), 5.32 (2H, m, C=CH-C-Si & C=CH-C(C)Si); ^{13}C NMR (neat) δ -6.31 (q), 12.55 (q), 21.07 (t), 26.08 (d), 110.09 (t), 112.69 (t), 133.89 (d), 140.33 (d); MS m/e (rel. int.) 113 (M - C_3H_5) (37), 99 (46), 85 (32), 71 (24), 59 (100), 43 (34). exact mass calculted for M - 41, SiC_6H_{13}, 113.0786, found 113.0788.

14 ^1H NMR ($CDCl_3$) δ -0.03 (3H, s, CH_3-Si), 0.02 (3H, s, Me-Si), 0.47 (1H, m, Si-CH-C), 0.95 (3H, d, J=7.02 Hz, CH_3-C-Si), 0.98 (3H, d, J=6.60 Hz, CH_3-C-C-Si), 1.60 (1H, m, HC-C-Si), 1.84 (1H, 3 sets of m, H_aC-C-C-Si), 2.23 (1H, 2 sets of m, H_bC-C-C-Si), 5.67 (1H, br d, J=14.90 Hz, Si-CH=C), 6.63 (1H, d of d of d, J=14.90, J=5.20, J=3.00 Hz, Si-C=CH); ^{13}C NMR (neat) δ -5.07 (q), -3.51 (q), 12.22 (q), 20.42 (q), 23.47 (d), 33.68 (d), 39.93 (t), 126.16 (d), 147.22 (d); MS m/e (rel. int.) 154 (17), 139 (12), 126 (11), 111 (15), 98 (100), 83 (45), 73 (70), 59 (60), 43 (44). exact mass calculated for SiC_9H_{18} 154.1178, found 154.1180.

15 ^1H NMR ($CDCl_3$) δ 0.027 (3H, s, CH_3-Si), 0.032 (3H, s, CH_3-Si), 0.86 (3H, d, J=6.03 Hz, CH_3-C-Si), 1.03 (3H, d, J=7.20 Hz, CH_3-C-C-Si), 1.13 (1H, d of d of d, J=6.10 Hz, J=3.20 Hz, J=1.80 Hz, Si-CH_a-C=C), 1.19 (1H, d of d of d, J=6.10 Hz, J=2.00 Hz, J=1.50 Hz, Si-CH_b-C=C), 1.25 (1H, d of q, J=6.03 Hz, J=3.10 Hz, Si-CH-C-C), 2.48 (1H, m, Si-C-CH-C), 5.37 (1H, d of d of d, J=12.00 Hz, J=3.20 Hz, J=1.50 Hz, C=CH-C-Si), 5.67 (1H, m, CH=C-C-Si); ^{13}C NMR (neat) δ -4.09 (q), -3.32 (q), 9.11 (q), 11.52 (t), 19.06 (q), 20.49 (d), 32.98 (d), 124.34 (d), 134.36 (d); MS m/e (rel. int.) 154 (34), 139 (20), 126 (32), 112 (27), 99 (19), 98 (100), 86 (63), 83 (39), 73 (41), 59 (73), 58 (92), 43 (63). exact mass calculated for SiC_9H_{18} 154.1178, found 154.1171.

16 ^1H NMR (neat) δ -0.19 (3H, s, CH_3Si), -0.14 (3H, s, CH_3Si), 0.29 (1H, m, CH-Si), 0.82 (3H, d, J=8.00 Hz, CH_3-C-Si), 0.86 (2H, m, CH_2-Si), 0.90 (3H, d, J=7.30 Hz, CH_3CCS_i), 1.85 (1H, m, CH-C-Si), 5.32 (1H, br d, J=12.60 Hz, C=CH-C-Si), 5.57 (1H, m, CH=C-C-Si); ^{13}C NMR (neat) δ -6.44 (q), -3.58 (q), 12.81 (q), 12.81 (t), 21.07 (q), 22.76 (d), 36.61 (d), 123.62 (d), 136.17 (d); MS m/e (rel. int.) 154 (31), 139 (12), 126 (27), 113 (13), 112 (27), 111 (18), 99 (18), 98 (100), 86 (56), 83 (40), 73 (45), 59 (73), 58 (79), 43 (63). exact mass calculated for SiC_9H_{18} 154.1178 found 154.1180.

17 ^1H NMR ($CDCl_3$) δ 0.03 (3H, s, CH_3-Si), 0.07 (3H, s, CH_3-Si), 0.83 (1H, m, CH-Si), 0.87 (3H, d, J=6.10 Hz, CH_3-C-Si) 0.98 (3H, d, J=6.50 Hz, CH_3-C-C-Si), 1.95 (1H, m, HC-C-Si), 2.01 (2H, m, CH_2-C-C-Si), 5.63 (1H, br d, J=14.00 Hz, Si-CH=C), 6.60 (1H, d of d of d, J=14.00, 4.30, J=3.10 Hz, HC=C-Si); ^{13}C NMR (neat) δ -4.36 (q), -2.21 (q), 7.93 (q), 19.77 (q), 20.81 (d), 31.34 (d), 34.92 (t), 125.11 (d), 146.77 (d). MS m/e (rel. int.) 154 (16), 139 (14), 126 (12), 111 (16), 98 (100), 85 (13), 83 (55), 73 (88), 59

(79), 45 (18), 43 (50). exact mass calculated for SiC_9H_{18}, 154.1178, found 154.1171. NOE difference spectra confirmed the configurational assignments of **14** and **17**. For **17**, irradiation of the methyne proton on C(6) at 0.83 δ, enhanced the signal of the cis methyne proton on C(5) at 1.95 δ. Similarly, irradiation at 1.95 δ enhanced the signal at 0.83 δ. No NOE effects on the ring methyne hydrogens were observed from analogous experiments in **14**.

Pyrolysis of 1 with propene.--Propene (100 torr) and dimethylsilacyclobutene **1** (20 torr) were pyrolyzed in a 500 mL closed vessel at 365 °C for 2 hr. In addition to 3 dimers of **1** four new products were produced: 1,1,5-trimethyl-1-silacyclohex-2-ene **19** (26%), 1,1,5-trimethyl-1-silacyclohex-3-ene **20** (45%), diallyldimethylsilane **21** (6%), dimer **3** (16%), dimer **4** (2%) and dimer **5** (4%). The new products were isolated by preparative GC on the OV-17 column.

19: ^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_2-C=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); GC/MS, 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.

20: ^1H NMR (neat) δ -0.30 (3H, s, $SiCH_3$), -0.28 (3H, s, $SiCH_3$), 0.03 (1H, d of d, J=10.80 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); ^{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); GC/MS, m/e (relative intensity) 140 (32), 125 (31), 99 (14), 98 (100), 97 (24), 85 (29), 83 (35), 72 (43), 59 (53), 55 (13), 43 (47), 39 (15); exact mass calc. for SiC_8H_{16} 140.1021, obs. 140.1023.

Pyrolysis of 1 with trimethylvinylsilane.--Static pyrolysis of 15 torr of **1** and 75 torr of trimethylvinylsilane (Petrarch) in a 500 mL pyrolysis vessel at 370 °C for 2 hr. provided 1,1-dimethyl-5-trimethylsilyl-1-silacyclohex-3-ene **22** (43%), dimer **3** (50%), dimer **4** (3%) and dimer **5** (4%).

22: ^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); GC/MS, 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.

Synthesis of methyl-d_3 vinyl ether.[26]--Mercuric acetate (0.25 g, 0.8 mmol), n-butyl vinyl ether (5 g, 50 mmol) (Aldrich) and methanol-d_4 (1.78 g, 50 mmol) (Aldrich) were placed in a 25 mL round bottomed flask. The flask was attached to a closed system fractional distillation apparatus that was equipped with a cold receiver (-78 °C) and had a fractional column (20 cm) packed with glass helicoils. The fractional column was kept at 0 °C during the course of the reaction. The mixture in the flask was heated at 60 °C for 2 hr. and during this time the product was collected in the receiving flask and at the end of the reaction it was transferred under vacuum into a gas bulb storage vessel. We obtained 1.70 g (30 mmol, 57% yield) of methyl-d_3 vinyl ether. ^{13}C NMR (neat) δ 53.69 (m, CD_3), 83.69 (t), 152.84 (d).

Pyrolysis of 1 with methyl vinyl ether.--Pyrolysis of **1** (15 torr) and methyl vinyl ether (225 torr) in a 500 mL closed vessel at 350 °C for 2 hr. yielded 2,2-dimethyl-6-ethyl-oxa-2-silacyclohex-3-ene **23** (33%), 2,2-methylmethoxy-2-silahepta-3,6-diene **24** (36%), unknown A (8%), unknown B (9%), dimer **3** (10%), dimer **4** (1%) and dimer **5** (3%). The structural possibilities for A and B are shown in the Result and Discussion section.

A similar reaction with methyl-d_3 vinyl ether produced 2,2-dimethyl-6-ethyl(d_3)-1-oxa-2-silacyclohex-3-ene **27** (31%), 2-methyl-2-methoxy(d_3)-2-silahepta-3,6-diene **28** (35%), unknown C (9%), unknown D (9%), dimer **3** (10%), dimer **4** (1%) and dimer **5** (2%). Major products **23**, **24**, **27** and **28** were isolated by the preparative GC on a DCQF1 column (20% DCQF1 on Chromosorb W, 1/4 in. X 20 ft.)

23: ^{1}H NMR ($CDCl_3$) δ 0.08 (6H, s, $SiMe_2$), 0.86 (3H, t, J=7.12 Hz, CH_3C), 1.57 (2H, quintet, J=7.12 Hz, CH_2 outside of the ring), 2.16 (2H, m, CH_2-C=C), 3.80 (1H, quintet, J=7.12 Hz, CHO), 5.75 (1H, app d, J=13.20 Hz, SiCH=C), 6.74 (1H, t of d, J=13.20 Hz, J=4.80 Hz, Si-C=CH); ^{13}C NMR ($CDCl_3$) δ -0.32 (q), -0.23 (q), 10.16 (q), 30.03 (t), 36.03 (t), 72.92 (d), 127.01 (d), 147.19 (d); GC/MS, m/e (relative intensity) 156 (9), 141 (22), 139 (25), 128 (12), 127 (100), 99 (16), 98 (52), 83 (32), 75 (38), 61 (15), 59 (16), 45 (24), 43 (19).

24: ^{1}H NMR ($CDCl_3$) δ 0.22 (6H, s, $SiMe_2$), 2.88 (2H, app t J=7.50 Hz, CH_2C=C), 3.42 (3H, s, OCH_3), 5.10 (2H, m, CH_2=C), 5.46 (1H, d, J=14.13 Hz, SiCH=C) 5.85 (1H, m, Si-C=CH), 6.40 (1H, quintet, J=7.47 Hz, CCH=C); ^{13}C NMR (neat) δ -1.36 (q), 37.13 (t), 49.22 (q), 114.58 (t), 126.93 (d), 135.84 (d), 147.22 (d); GC/MS, m/e (relative intensity) 141 (M-CH_3) (66), 124 (40), 113 (22), 111 (28), 109 (58), 89

(63), 75 (67), 59 (100), 45 (22), 43 (21), 39 (17); exact mass calc. for $SiC_7H_{13}O$, M-15, 141.0736, obs. 141.0742.

27: ^1H NMR ($CDCl_3$) δ 0.12 (6H, s, $Si(CH_3)_2$), 1.60 (2H, app d, J=7.13 Hz, CH_2CD_3), 2.15 (2H, m, CH_2-C=C), 3.82 (1H, quintet, J=7.12 Hz, CHO) 5.77 (1H, d, J=13.22 Hz, SiCH=C), 6.76 (1H, t of d, J=13.24 Hz, J=4.86 Hz, SiC=CH); ^{13}C NMR ($CDCl_3$) δ -0.51 (q), -0.40 (q), 9.91 (m, CD_3), 30.44 (t), 35.92 (t), 72.84 (d), 127.08 (d), 147.24 (d); GC/MS, m/e (relative intensity) 159 (13), 144 (20), 142 (27), 128 (14), 127 (100), 99 (16), 98 (61), 83 (43), 75 (39), 61 (17), 59 (17), 47 (10), 45 (31), 43 (30).

28: ^1H NMR ($CDCl_3$) δ 0.18 (6H, s, $Si(CH_3)_2$), 2.82 (2H, app t J=7.42 Hz, CH_2C=C), 5.08 (2H, m, CH2=C), 5.44 (1H, d, J=14.11 Hz, SiCH=C), 5.82 (1H, m, Si-C=CH), 6.41 (1H, quintet, J=7.45 Hz, CCH=C); ^{13}C NMR (neat) δ -1.37 (q), 37.07 (t), 49.23 (m, OCD_3), 114.52 (t), 127.00 (d), 135.97 (d); GC/MS, m/e (relative intensity) 144 (M-CH_3) (67), 124 (42), 115 (18), 112 (23), 109 (66), 92 (81), 78 (100), 62 (77), 60 (67), 59 (20), 46 (22), 45 (12), 43 (24), 41 (11).

Unknown A: GC/MS m/e (relative intensity) 156 (6), 109 (5), 90 (8), 89 (100), 59 (59), 58 (6), 45 (8), 43 (9), 41 (9), 39 (11), 31 (6).

Unknown B: GC/MS, m/e (relative intensity) 156 (15), 142 (13), 141 (100), 124 (11), 113 (12), 111 (29), 109

(34), 89 (24), 75 (73), 61 (7), 59 (71), 45 (19), 43 (15), 39 (11), 31 (7).

Unknown C: GC/MS, m/e (relative intensity) 93 (11), 92 (100), 62 (18), 60 (50).

Unknown D: GC/MS, m/e (relative intensity) 159 (19), 145 (15), 144 (97), 112 (22), 109 (39), 92 (29), 78 (100), 62 (62), 60 (36), 46 (21), 43 (17).

Pyrolysis of 1 with acrylonitrile.--Static pyrolysis of **1** (15 torr) with acrylonitile (75 torr) in a 500 mL pyrolysis vessel at 300 °C for 2 hr. provided 2,2-dimethyl-6-vinyl-1-hydrido-2-silapyridine **29** (57%, bright yellow) 5, cyano-1,1-dimethyl-1-silacyclo-hex-3-ene **30** (23%) and 5-cyano-1,1-dimethyl-1-silacyclo-hex-2-ene **31** (5%). These products were isolated by preparative GC (DC-710, 20% on chromosorb W, 1/4 in. x 16 ft.).

29: ^{1}H NMR (neat) δ -0.26 (6H, s, Si$(CH_3)_2$, 3.48 (1H, broad S, NH), 4.62 (3H, m, CH=CH_2), 5.05 (1H, app d, J=16.46 Hz, SiCH=C), 5.68 (1H, d of d, J=16.46 Hz, J=13.13 Hz, SiC=CH), 6.41 (1H, d of d, J=13.13 Hz, J=6.57 Hz, SiC=C-CH); ^{13}C NMR (neat) δ 3.83 (q), 103.98 (d), 110.09 (t), 116.01 (d), 136.17 (d), 142.08 (s), 142.67 (d); IR (neat, KBr) cm^{-1} 3374 (w), 2959 (s), 2926 (w), 2867 (w), 1582 (m), 1527 (m), 1419 (m), 1415 (m), 1397 (w), 1259 (s), 1165 (w), 1095 (m), 1076 (s), 1043 (s), 1038 (s), 942 (w), 839 (m), 801 (s), 780 (s), 705 (w); GC/MS, m/e (relative intensity), 151 (21), 137 (13), 136 (100), 108 (13), 67

(7), 43 (10), exact mass cald for $SiC_8H_{13}N$ 151.0817, found 151.0826.

30: ^1H NMR ($CDCl_3$) δ 0.05 (3H, s, $SiCH_3$), 0.06 (3H, s, $SiCH_3$), 1.03 (1H, d of d J=5.92 Hz, J=3.20 Hz, SiCHC), 1.07 (1H, d of d J=5.92 Hz, J=2.84 Hz, SiCH'C), 1.27 (2H, m, $SiCH_2C$=C), 3.35 (1H, m, CHC N), 5.58 (1H, broad d J=11.12 Hz, SiCCH=C), 5.95 (1H, m, SiCC=CH); ^{13}C NMR ($CDCl_3$) δ -2.74 (q), -1.95 (q), 12.71 (t), 15.42 (t), 25.40 (d), 122.80 (s), 124.49 (d), 130.58 (d); GC/MSS, m/e (relative intensity) 151 (25), 150 (34), 136 (28), 111 (63), 109 (51), 86 (29), 85 (26), 84 (100), 72 (56), 67 (22), 66 (35), 58 (20), 55 (22), 54 (22), 53 (20), 44 (29), 43 (73), 39 (24); exact mass cald for $SiC_8H_{13}N$ 151.0817, found 151.0826.

31: ^1H NMR ($CDCl_3$) δ, 0.10 (6H, s, $Si(CH_3)_2$), 0.94 (1H, d of d J=8.42 Hz, J=3.40 Hz, SiCHC), 1.02 (1H, d of d J=8.42 Hz, J=2.92 Hz, SiCH'C), 2.40 (2H, m, CH_2C=C), 2.82 (1H, m, CHC N), 5.76 (1H, d, J=14.74 Hz, SiCH=C), 6.55 (1H, t of d J=14.74 Hz, J=2.75 Hz, SiC=CH); ^{13}C NMR ($CDCl_3$) δ -2.10 (q), 1.41 (q), 16.41 (t), 26.92 (d), 33.21 (t), 122.80 (s), 127.69 (d), 144.50 (d), GC/MS, m/e (relative intensity) 151 (17), 136 (24), 111 (16), 110 (21), 109 (100), 98 (23), 83 (28), 70 (13), 67 (15), 66 (15), 55 (17), 44 (12), 43 (41), 39 (13), 32 (18), exact mass cald for $SiC_8H_{13}N$, 151.0817, found 151.0826.

Static pyrolysis of 1 with acetone.--Acetone (75 torr) and silacyclobutene **1** (15 torr) were pyrolyzed in a 500 mL closed vessel at 360 °C for 2 hr. Gas chromatography analysis of the pyrolysate showed 2,2,6,6-tetramethyl-1-oxa-2-silacyclohex-3-ene **33** (62%), 4-methyl-1,3-pentadiene **34**[28] (21%), hexamethylcyclotrisiloxane **35**[5] (12%) and octamethylcyclotetrasiloxane **36**[5] (3%). We isolated these products by preparative GC (20% OV-17 on Chromosorb W, 1/4 in. x 16 ft.)

33: ^{1}H NMR ($CDCl_3$) δ 0.16 (6H, s, $Si(CH_3)_2$), 1.32 (6H, s, $C(CH_3)_2$), 2.23 (2H, app d J=5.20 Hz, CH_2), 5.85 (1H, app d, J=12.32 Hz, SiCH=C), 6.70 (1H, t of d, J=12.32 Hz, J=5.20 Hz, SiC=CH); ^{13}C NMR ($CDCl_3$) δ 0.85 (q), 30.17 (q), 41.50 (t), 72.60 (s), 127.35 (d), 145.57 (d); GC/MS, m/e (relative intensity) 156 (24), 141 (83), 127 (15), 123 (20), 115 (47), 99 (16), 98 (97), 83 (64), 75 (100), 72 (15), 61 (27), 59 (17), 55 (12), 47 (16), 45 (42), 43 (39), 41 (14), 39 (23); exact mass cald. for $C_8H_{16}SiO$ 156.0970, found 156.0972.

Pyrolysis of 1 with butadiene.--Static pyrolysis of **1** (15 torr) and 1,3-butadiene (300 torr) in a 500 mL closed vessel at 350 °C for 2.5 hr. gave 1,1-dimethyl-6-vinyl-silacyclohex-3-ene **38** (37%), 1,1-dimethyl-5-vinyl-silacyclohex-2-ene **39** (20%) and 1,1-dimethyl-5-vinyl-silacyclohex-3-ene **40** (42%). These products were isolated by preparative GC on an OV-17 column.

38: ^{1}H 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, m, 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 from vinyl group), 6.67 (1H, d of d of d, J=13.5 Hz, 6.0 Hz, 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); GC/MS, m/e (relative intensity), 152 (7), 137 (19), 124 (11), 109 (62), 99 (8), 98 (100), 95 (12), 92 (11), 83 (62), 81 (11), 73 (22), 72 (17), 69 (10), 67 (11), 59 (42), 55 (17), 53 (14), 45 (14), 44 (10), 43 (52), 39 (16), 31 (10); exact mass cald. for SiC_9H_{16} 152.1021, found 152.1020.

39: ^{1}H 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_2-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 from vinyl group), 6.69 (1H, d of d of d J=14.1 Hz, J=5.4 Hz, 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); GC/MS, m/e (relative intensity) 152 (19), 137 (24), 124 (47), 109 (72), 99 (10), 98 (94), 95 (16), 93 (13), 92 (30), 85 (27), 84 (11), 83 (100), 81 (15), 78 (14), 73 (41), 72 (36), 71 (15), 69 (15), 67 (17), 59 (71), 58 (17), 55 (28), 54 (11), 53 (23), 45 (20), 44 (16), 43 (80), 42 (10), 41 (13), 39 (28), 31 (15); exact mass cald. for SiC_9H_{16} 152.1021, found 152.1020.

40: ^1H NMR ($CDCl_3$) δ -0.04 (3H, s, $SiCH_3$), 0.06 (3H, s, $SiCH_3$), 1.21 (2H, d of d J = 6.5, 1.8 Hz, $SiCH_2C{=}C$), 1.75 (1H, app q, J=7.3 Hz), 2.25 (2H, m, $SiCH_2CC{=}C$), 4.84 (2H, m, $CH_2{=}C$), 5.58 (1H, m, CH=C from vinyl group), 5.65 (1H, t of d J = 15.1, 6.5 Hz, SiCCH=C), 5.36 (1H, m, SiCC=CH); ^{13}C NMR (neat) δ -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), 99 (11), 98 (100), 95 (11), 92 (12), 83 (83), 73 (16), 72 (24), 67 (13), 59 (74), 58 (15), 55 (20), 53 (17), 45 (15), 44 (11), 43 (61), 39 (25), 31 (14); exact mass cald. for SiC_9H_{16} 152.1021, found 152.1020.

Pyrolysis of 1 with acetylene.--Static pyrolysis of 10 torr of **1** and 200 torr of acetylene in a 500 mL pyrolysis vessel at 260 °C for 8 hr. provided 1,1-dimethyl-1-silacyclohexa-2,5-diene **42** (28%), 1,1-dimethyl-1-silacyclohexa-2,4-diene **6**[24] (43%), Z-3,3-dimethyl-3-silahexa-4-ene-1-yne **44** (10%) and 2,2-dimethyl-2-silabicyclo[2.2.0]hex-5-ene **45** (6%). All of the products were isolated by preparative GC on the SF-96 column (20% SF-96 on Chromosorb W, 1/4 in. X 20 ft.)

42: ^{13}C NMR (neat) δ -0.95 (q), 33.42 (t), 125.60 (d), 144.17 (d).

44: ^{1}H NMR ($CDCl_3$) δ 0.10 (6H, s, $Si(CH_3)_2$), 1.62 (3H, d, J=7.30 Hz, CH_3C=C), 2.15 (1H, s, CH C), 5.18 (1H, d, J=13.12 Hz, SiCH=C), 6.15 (1H, quintet J=7.30 Hz, SiC=CH); ^{13}C NMR ($CDCl_3$) δ -0.39 (q) 18.79 (q), 88.79 (s), 93.70 (d), 125.70 (d), 145.47 (d); GC/MS, m/e (relative intensity) 124 (3) 110 (12), 109 (100), 83 (54), 69 (41), 59 (8), 53 (29), 43 (32) 39 (9).

45: ^{1}H NMR ($CDCl_3$) δ 0.12 (3H, s, $SiCH_3$), 0.16 (3H, s, $SiCH_3$), 0.90 (2H, m, $SiCH_2$), 1.35 (2H, m, CHC=C), 6.30 (1H, broad d, J=11.50 Hz, SiCCH=C), 7.65 (1H, broad d, J=11.50 Hz, SiCC=CH); ^{13}C NMR ($CDCl_3$) δ -3.50 (q), -0.90 (q), 0.20 (t), 18.73 (d), 23.94 (d), 126.81 (d), 153.48 (d); GC/MS, m/e (relative intensity) 124 (16), 110 (12), 109 (100), 83 (16), 81 (26), 67 (9), 59 (23), 55 (11), 53 (12), 43 (35), 39 (9).

A similar reaction but at higher temperature (350 °C) gave only three products: unconjugated cyclicdiene **42** (37%), conjugated cyclicdiene **6** (55%) and the acyclic **Z**-44 (7%).

Static pyrolysis of silabicyclic 45.--Pyrolysis of **45** (10 torr) at 350 °C for 1.5 hr. in a 250 mL pyrolysis vessel gave 1,1-dimethyl-1-silacyclohexa-2,4-diene **6** (75%), cyclopentadiene (13%) and unknown **46** (11%) which has a molecular weight of 182 (MS). This might correspond to

1,1,4,4-tetramethyl-1,4-disilacyclohepta-2,5-diene **46**. However, the complete identity of this compound is not confirmed. We have only GC/MS information (also, see Result and Discussion section). Unknown **46**: GC/MS, m/e (relative intensity) 182 (19), 187 (22), 109 (39), 108 (100), 93 (13), 73 (89), 59 (31), 45 (17), 42 (44).

Pyrolysis of 45 and butadiene.--Static pyrolysis of silabicyclic **45** (5 torr) and 1,3-butadiene (100 torr) at 350 ^{o}C for 1 hr. in a 250 mL reaction vessel provided conjugated cyclic diene **6** (61%), cyclopentadiene (30%), 1,1-dimethyl-1-silacyclopent-3-ene (7%) and 1,1-dimethyl-1-silacyclopent-2-ene (1%).[27]

The temperature dependence of the pyrolysis of 1 and ethylene.--The static vacuum pyrolysis of 1,1-dimethylsilacyclobutene **1** (3 torr) and ethylene (60 torr) was done over the temperature range 601-663 K, in a 250 mL quartz reaction vessel. Sampling of a small portion of pyrolysate (~15 torr) from the reaction vessel at intervals 15 min. from 1 min. to 65 min. was performed. Typically there were four aliquots for each experiment. The ratio of **11/10** was determined by analysis of the pyrolysate on SP-2100 GC column (10% on chromosorb W, 1/8 in. x 12 ft.). We found that the ratio of [**11**] to [**10**] is nearly independent of the reaction time (1-3 hr.). These ratios at seven different temperatures from 601 to 663 K are listed in Table 4-2 in the Result and Discussion section.

Pyrolysis of 1 with t-butylacetylene-- Dimethylsilacyclobutene **1** (15 torr) and t-butylacetylene (120 torr) were pyrolyzed in a 500 ml pyrolysis vessel at 260 °C for 8 hr. Five products were produced: Z-4,4,7,7-tetramethyl-4-silaocta-2-ene-5-yne **47** (29%), 1,1-dimethyl-3-t-butyl-1-silacycolohexa-2,5-diene **48** (13%), 1,1-dimethyl-3-t-butyl-1-silacyclohexa-2,4-diene **49** (15%), 4,4,7,7-tetramethyl-4-silaocta-1-ene-5-yne **50** (11%) and 2,2-dimethyl-5-t-butyl-silabicyclo [2•2•0] hex-5-ene **51** (31%).

The same reaction but at higher temperature (350 °C) provided only four products: acyclic **Z-47** (27%), unconjugated cyclic diene **48** (29%), conjugated cyclic diene **49** (30%) and acyclic **50** (13%). All of the products were isolated by preparative GC (20% OV-17 on chromosorb W. 1/4 in. x 16 ft.).

47: ^{1}H NMR (neat) δ -0.23 (6H, s, $Si(CH_3)_2$), 0.77 (9H, s, $(CH_3)_3C$), 1.45 (3H, d, J=7.0 Hz, $CH_3C{=}C$), 4.84 (1H, d, J=13.2 Hz, SiCH=C), 5.75 (1H, app quintet, J=7.0 Hz, SiC=CH; ^{13}C NMR (neat) δ -0.07 (q), 18.34 (q), 27.70 (s), 30.63 (q), 80.83 (s), 115.29 (s), 127.13 (d), 143.79 (d); GC/MS, m/e (relative intensity) 180 (13), 166 (16), 165 (100), 139 (11), 125 (34), 123 (67), 109 (15), 97 (25), 83 (20), 73 (11), 67 (13), 59 (19), 43 (20); exact mass calc. for $SiC_{11}H_{20}$ 180.1334, obs. 180.1336.

48: ^{1}H NMR ($CDCl_3$) δ 0.06 (6H, s, $Si(CH_3)_2$), 1.02 (9H, s, $(CH_3)_3C$), 1.35 (2H, d, J=2.1 Hz, CH_2C=C), 5.55 (1H, s, CH=C-t-BU), 6.00 (2H, broad s, SiCH=CH); ^{13}C NMR (neat) δ -1.95 (q), 12.87 (t), 28.81 (q), 36.61 (s), 114.32 (d), 126.61 (d), 127.39 (d), 160.56 (s); GC/MS, m/e (relative intensity) 180 (27), 165 (38), 124 (19), 123 (100), 109 (47), 95 (22), 83 (13), 73 (18), 59 (38), 57 (29), 43 (20), 41 (11); exact mass calc for $SiC_{11}H_{20}$ 180.1334, obs. 180.1336.

49: ^{1}H NMR ($CDCl_3$) δ 0.04 (6H, s, $Si(CH_3)_2$), 1.04 (9H, s, $(CH_3)_3C$), 1.40 (2H, broad s, $SiCH_2$), 5.65 (2H, m, SiCH=C, SiCCH=C), 6.70 (1H, d of d, J=13.1 Hz, J=7.0 Hz, SiCC=CH); ^{13}C NMR (neat) δ -2.67 (q), 14.24 (t), 28.48 (q), 36.74 (s), 117.57 (d), 123.03 (d), 142.67 (d), 148.07 (s); GC/MS, m/e (relative intensity) 180 (49), 166 (15), 137 (20), 123 (100), 121 (22), 109 (51), 107 (17), 106 (22), 105 (20), 97 (13), 95 (23), 93 (15), 91 (16), 83 (18), 81 (15), 73 (69), 69 (20), 67 (17), 59 (92), 58 (15), 57 (29), 55 (18), 53 (16), 45 (14), 43 (39), 41 (20), 39 (21); exact mass calc. for $SiC_{11}H_{20}$ 180.1334, obs. 180.1336.

50: ^{1}H NMR (neat) δ -0.20 (6H, s, $Si(CH_3)_2$), 0.65 (9H, s, $(CH_3)_3C$), 2.40 (2H, broad s, $SiCH_2$), 5.32 (2H, m, CH_2=C), 6.12 (1H, m, SiCCH=C), GC/MS m/e (relative intensity) 180 (4), 165 (52), 124 (16), 123 (100), 110 (11), 109 (69), 95 (19), 83 (11), 73 (12), 69 (11), 59

(30), 57 (42), 43 (20), 41 (12); exact mass calc. for $SiC_{11}H_{20}$ 180.1334, obs. 180.1336.

51: ^1H NMR (neat) δ 0.10 (6H, s, $Si(CH_3)_2$), 0.13 (2H, m, CH_2Si), 0.80 (1H, m, CHSi), 1.15 (9H, s, $(CH_3)_3C$) 1.90 (1H, m, SiCCH), 5.00 (1H, broad s, CH=C); ^{13}C NMR (neat) δ -2.99 (q), -0.46 (q), 0.45 (t), 18.53 (d), 23.02 (d), 29.39 (q), 36.35 (s), 114.58 (d), 175.90 (s); GC/MS m/e (relative intensity) 180 (12), 165 (36), 124 (17), 123 (100), 109 (49), 95 (22), 83 (13), 73 (19), 69 (12), 59 (46), 57 (33), 43 (25), 41 (12); exact mass calc. for $SiC_{11}H_{20}$ 180.1334, obs. 180.1336.

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