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The regiochemistry of alkenylsilyl, alkenyldisilanyl and alkenylsilyloxy radical cyclizations

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THE REGIOCHEMISTRY OF ALKENYLSILYL, ALKENYLDISILANYL AND ALKENYLSILYLOXY RADICAL CYCLIZATIONS

Iowa State University PH.D. 1984

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The regiochemistry of alkenylsilyl, alkenyldisilanyl and alkenylsilyloxy radical cyclizations

by

Anthony Revis

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
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Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1984

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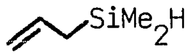
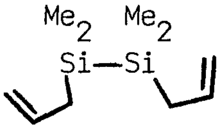
DEDICATION

To my wife, Linda.

NOMENCLATURE

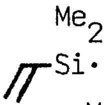
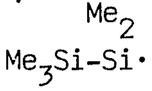
The nomenclature used in this dissertation will, with the exceptions described below, follow the conventions set down by IUPAC. Simple organosilicon compounds will be named as derivatives of silane (SiH_4), while more complicated linear and cyclic systems will be named as sila-analogs of the corresponding carbon system.

Examples:

Me_2SiClH	Dimethylchlorosilane
	Allyldimethylsilane
	1,2-Diallyl-1,1,2,2-tetramethyldisilane
	1,1,3-Trimethyl-1,3-disilacyclopent-4-ene

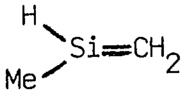
Silicon centered radicals will be named as derivatives of the parent silyl radical ($H_3Si\cdot$). Silicon centered radicals of disilanes will be named as derivatives of the disilanyl radical ($H_3SiH_2Si\cdot$).

Examples:

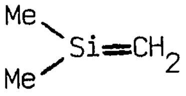
$Me_3Si\cdot$	Trimethylsilyl radical
	Vinyldimethylsilyl radical
 $Me_3Si\text{-}\overset{Me_2}{Si}\cdot$	Pentamethyldisilanyl radical

All compounds containing (p-p) π-bonded silicon will be named as derivatives of silene ($H_2Si{=}CH_2$). Divalent silicon species will be named as derivatives of silylene ($:SiH_2$).

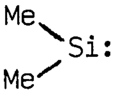
Examples:



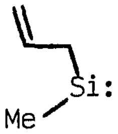
1-Methylsilene



1,1-Dimethylsilene



Dimethylsilylene



Allylmethylsilylene

INTRODUCTION

In the field of free radical chemistry, most of our present knowledge and understanding comes from the work done with carbon-centered radicals. Much of the emphasis has been devoted to intramolecular addition of alkenyl carbon radicals. These reactions often have synthetic utility since a very high degree of selectivity is usually encountered. The Beckwith rules (1) were developed in an attempt to explain the high selectivity observed in intramolecular carbon radical cyclizations. The rules state that lower alkenyl carbon radicals ($\leq C_7$) cyclize in a kinetically preferred exo-fashion. The Beckwith rules have also been extended to include other atoms (2).

The intramolecular addition of silicon-centered radicals has not been as well-studied as its carbon analog. This is surprising when one considers the progress that has been made toward understanding the physical properties, structure and reactivity, and stereochemistry of silicon and other Group IVB radicals. Many generalizations based on silicon radicals, however, are possible as these radicals are found to share many common features with carbon radicals. There are, however, some features that are quite different. Although there were no definitive studies available, it was suggested by the Beckwith rules that cyclization of alkenyl substituted silicon radicals would also favor exo-closure (1).

This dissertation will describe the generation and cyclization of some alkenylsilyl and alkenyldisilanyl radicals. When generated in dilute aromatic solutions, these radicals gave products consistent with an endo-mode of cyclization. This is opposite to that which would be predicted by the Beckwith rules. The generation of silicon radicals in the gas phase from allysilanes is also presented. Depending on the nature of the radical, endo-cyclization or disproportionation to silenes occurs. The silenes then undergo a series of rearrangements to silacyclic products. A new mechanism for the rearrangement of 1,2-diallyltetramethyldisilane to 1,1,3,3-tetramethyl-1,3-disilacyclopentene (3) is put forth. The new mechanism involves a silene to silylene rearrangement (3,4).

Some interesting results on the pyrolytic behavior of some 3-butenylsilanes will be discussed. The initial step in the decomposition of these compounds is found to be carbon-allyl homolysis which generates α-silyl radicals.

Also, described in this dissertation are some attempts to generate silyloxy radicals using allyloxysilanes as precursors. However, no definitive evidence of silyloxy radical cyclization was obtained since the precursors decomposed via alternate but equally interesting pathways.

HISTORICAL

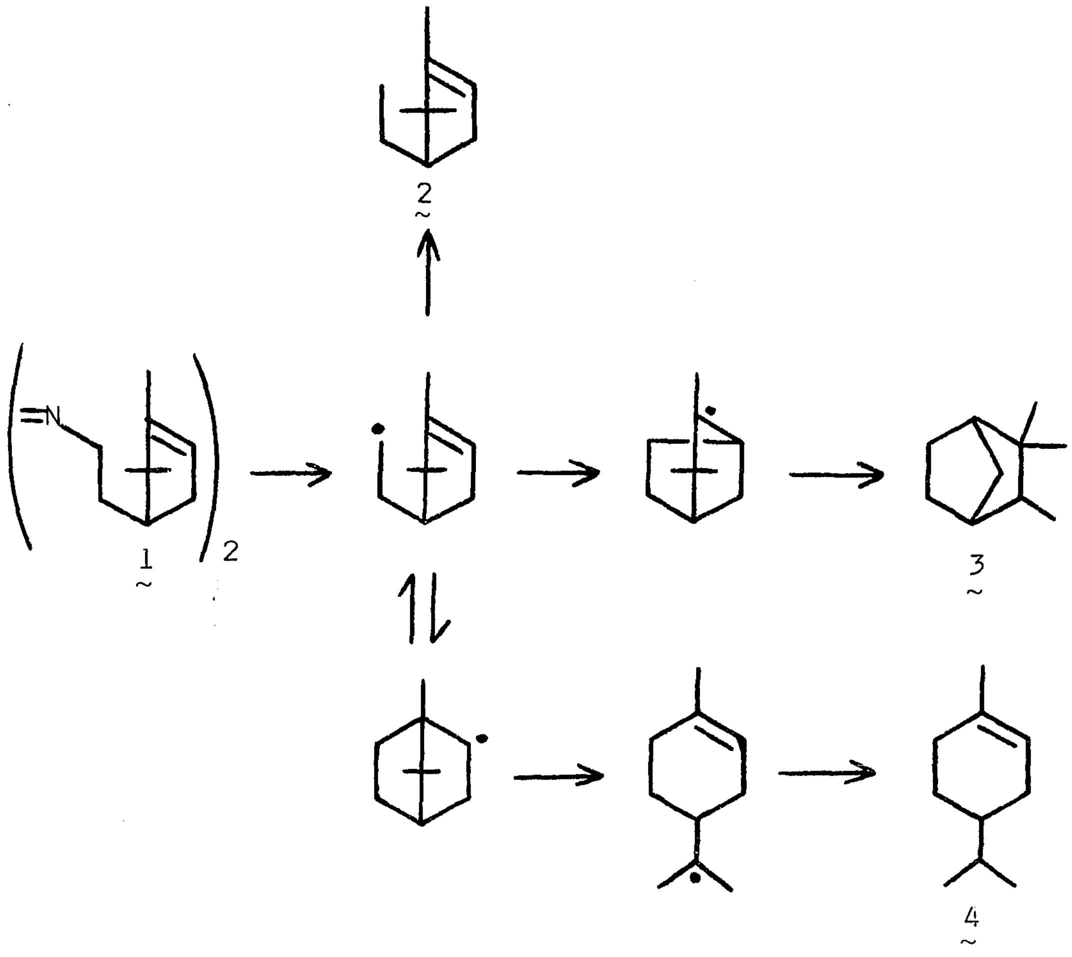
Carbon Radical Cyclization and the Beckwith Rules

A brief summary of the literature pretaining to carbon radical cyclization will be given. Emphasis will be focused on the cyclization and rearrangement of carbon radicals and, therefore, a detailed description of the methods used to prepare them will not be given. The Beckwith rules (1) of radical cyclization will also be discussed. Due to the extensive amount of literature published on the subject of intramolecular addition of radicals, only the material that may be necessary for understanding the work presented in this dissertation will be covered. An excellent review covering radical cyclizations through 1982 and the Beckwith rules has recently been published by Surzur (2).

The 5-hexenyl radical

Perhaps one of the most widely studied intramolecular addition reactions is that of the 5-hexenyl radical. Much of the interest stems from the ease with which it cyclizes and the high yields that are often obtainable. Although the direction of cyclization may vary with changes in the radical structure, the parent 5-hexenyl radical cyclizes with a very high degree of selectivity. The reason for the selectivity will be discussed later in this section. Because the behavior of the 5-hexenyl radical has been well-substantiated, with much kinetic data available on the subject, it is often used as a major carbon radical probe in mechanistic studies.

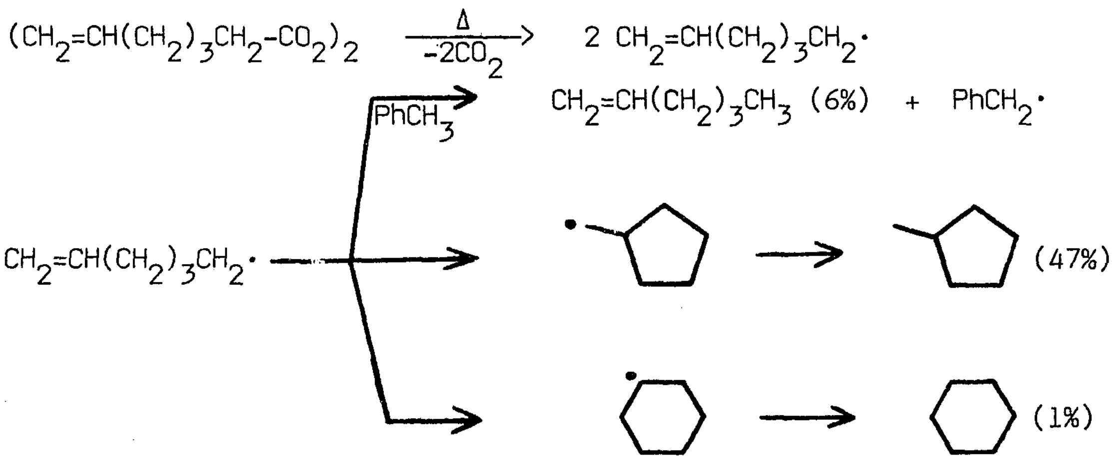
Intramolecular addition of 5-hexenyl radicals was first proposed by Marvel and Vest (5) and Butler and Angelo (6) in 1957. Working independently, they polymerized 1,6-dienes and found that the products lacked unsaturation. They proposed that the initially formed radical must have cyclized. The cyclic radical intermediate was then proposed to initiate a series of propagation steps. Berson and coworkers (7) a short time later reported a simpler case of intramolecular free radical addition. They found that three major products, **2**, **3**, and **4**, were obtainable from the thermal decomposition of 2,2′-bis(azocamphane) **1**. These products were consistent with the occurrence of two distinct



intramolecular additions followed by either hydrogen abstraction giving **3** or beta-scission leading to **4**.

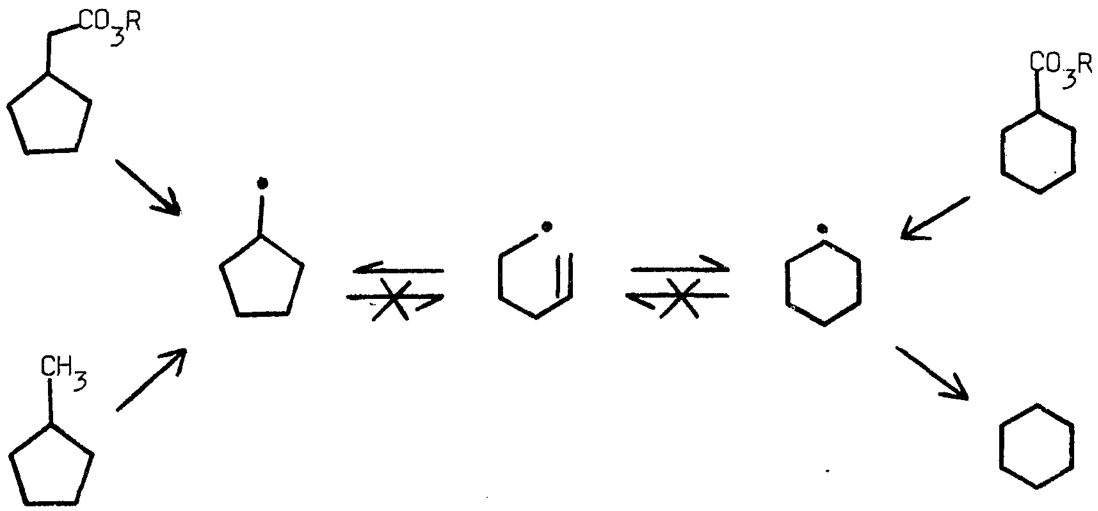
The work of Lamb and coworkers (8) was very instrumental in understanding the behavior of the 5-hexenyl radical. These authors observed that methylcyclopentane was the major product formed from the thermal decomposition (77°C in toluene) of 6-heptenoyl peroxide (Scheme 1).

Scheme 1



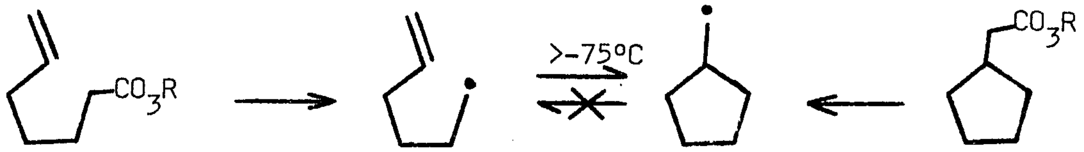
This result was unexpected since methylcyclopentane was derived from a primary radical rather than the thermodynamically more stable secondary radical. Furthermore, the possibility of direct interconversion of the cyclopentylmethyl and cyclohexyl radical was ruled out since, when generated at 77°C from the acyl peroxides in toluene, these radicals gave only methylcyclopentane and cyclohexane, respectively (Scheme 2). Lamb therefore concluded that intramolecular addition of the 5-hexenyl radical was irreversible and that the favored <u>exo</u>-cyclization to methylcyclopentane was under kinetic control.

Scheme 2



More support for the irreversible behavior of the 5-hexenyl radical, as well as its preference for the energetically unfavored exo-cyclized radical, was later given by Walling and Pearson (9). They examined the cyclization of the 5-hexenyl radical at 60° and 120°C when generated from the corresponding mercaptan in excess triethylphosphite containing azobisisobutyronitrile (AIBN) initiator. At the lower temperature, methylcyclopentane was obtained in 43% yield as the only cyclic product. The yield of methylcyclopentane was increased to 50% when the reaction was carried out at 120°C. At 120°C, however, a 3% yield of cyclohexane was also observed.

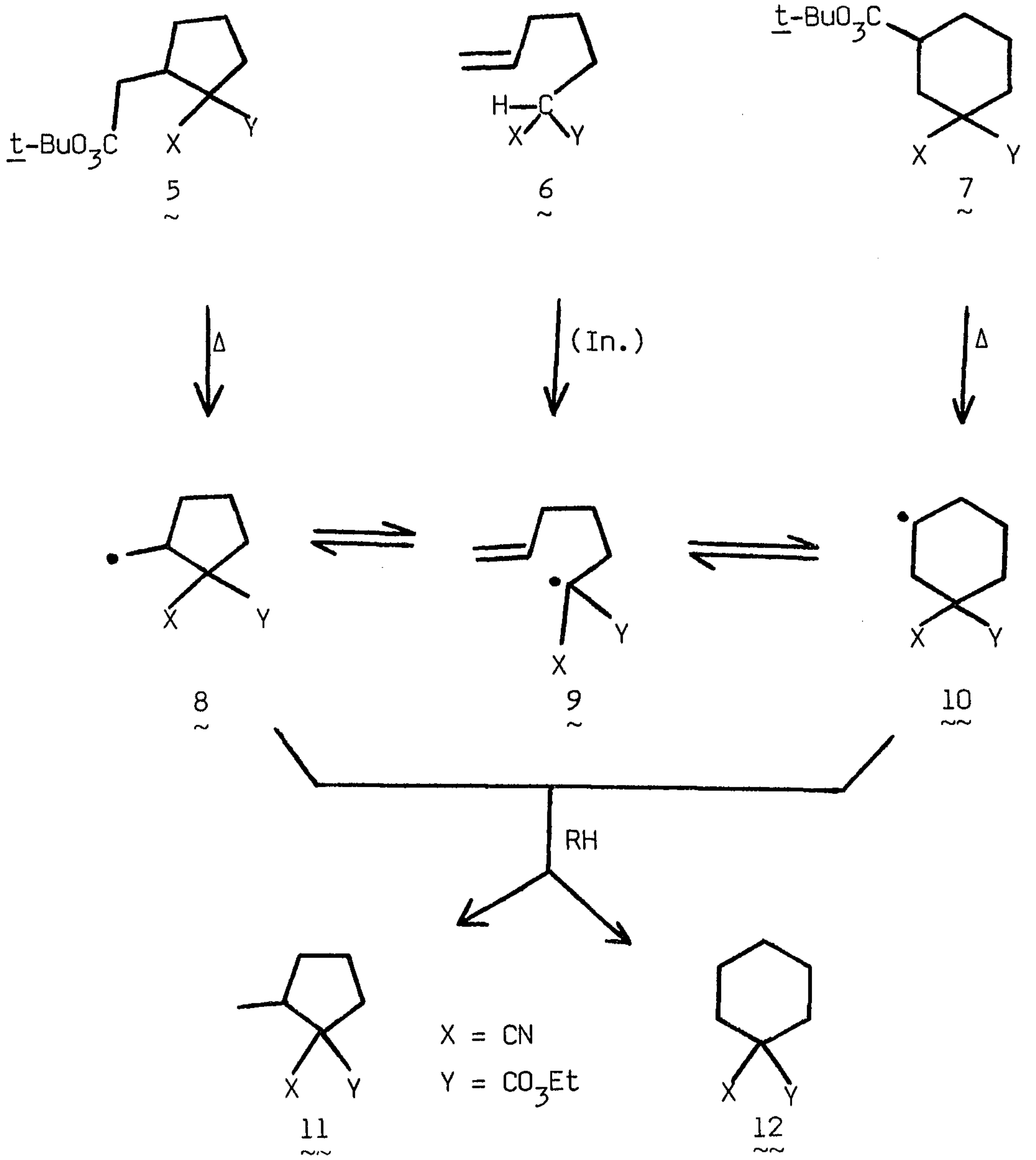
Kochi and Krusic (10) have examined the 5-hexenyl radical using electron spin resonance (ESR). When the 5-hexenyl radical was generated by photolysis (2500 - 3500 Å) of 6-heptenoyl peroxide, its ESR signal was directly observable at -75°C. Upon warming to -35°C, the ESR spectrum of only cyclopentylmethyl radical was seen. At -55°C, both the 5-hexenyl radical and the cyclopentylmethyl radical were detected. The irreversibility of the rearrangement was confirmed by the observation of only the cyclopentylmethyl radical spectrum, even up to 0°C, when this radical was generated by photolysis of cyclopentylacetyl peroxide. These experiments suggest that intramolecular addition of the 5-hexenyl radical occurs predominantly in an irreversible exo-fashion.



Griller et al. (11) and Schmid and Ingold (12) used a similar technique in order to obtain rate constants for the intramolecular addition of the 5-hexenyl radical. The temperature dependent rate constants for the formation of the cyclopentylmethyl radical are: K = 0.34 x 10^2 sec^{-1} at -85°C, k = 17.0 x 10^2 sec^{-1} at -45°C, k = 1.78 x 10^5 sec^{-1} at 40°C. At 25°C, the rate constant was 1.0 x 10^5 sec^{-1}, the activation energy was 7.8 kcal/mol, and the Log A-factor of 10.7.

Substitution at the radical center with a stabilizing group can cause a change in the preferred mode of cyclization. In otherwords, the cyclization process may become reversible. The reversible nature of the 5-hexenyl radical when substituted with stabilizing groups was clearly established by Julia and coworkers (13,14) (Scheme 3). Radicals **8** and **10** were formed from t-butyl peresters **5** and **7**, respectively. The ratio of products **12**/**11** obtained from these radicals was compared to that

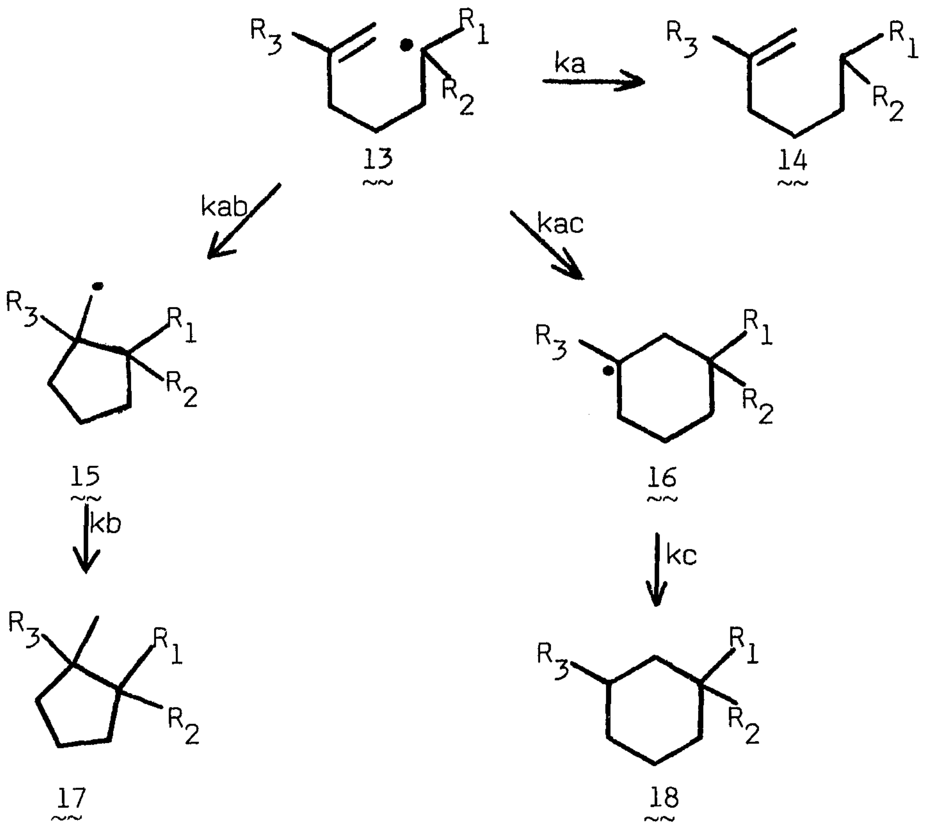
Scheme 3



obtained when radical **9** was formed from the corresponding acyclic derivative **6**. When compound **6** (3.75×10^{-2} mole/liter initial concentration) was heated at 81°C in cyclohexane containing benzoyl peroxide as an initiator (7.5 x 10^{-2} mole/liter initial concentration) the ratio **12**/**11** was 86:14. Thermolysis of perester **5** under the same conditions gave a ratio of 80:20 while thermolysis of the perester **7** afforded a ratio of 85:15. The closeness of these results supports the idea of a reversible process involving the radicals shown in Scheme 3. However, worth noting is that while these cyclizations are reversible, they do not represent a system in equilibrium. In other words, each of the radicals is capable of conversion to products in an irreversible manner. Also, the ratio of 6-membered/5-membered ring products may not always be the same. It has been demonstrated that the ratio is largely dependent on experimental conditions. For example, Julia and Maumy found that when acyclic radical **9** is generated at -70°C under photolytic conditions, the ratio is reversed to 20:80 (**12**/**11**). At this temperature, cyclization must be predominantly a kinetically controlled process. Thus, at low temperatures the behavior of appropriately substituted 5-hexenyl radicals (**9**, X = CN, Y = CO_2Et) parallel that of the parent radical (**9**, X = Y = H). At higher temperatures where the radicals may equilibrate, the thermodynamically more stable cyclohexyl radical **10** is obtained.

The influence of alkyl substituents on the direction of cyclization of the 5-hexenyl radical has also been examined. However, unlike when substituted with stablizing groups, alkyl substituted carbon radicals undergo irreversible cyclization. An extensive study on 1-methyl and 5-methyl substituted 5-hexenyl radicals, as well as the parent 5-hexenyl radical, was done by Walling and Cioffai (15). The radicals were generated between 40° and 70°C from the corresponding bromohexenes and tributylstannane (0.02 mole/liter) in benzene. AIBN was used as the radical initiator. Scheme 4 outlines the competing steps which would

Scheme 4



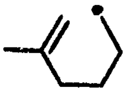
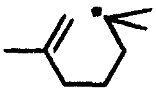
determine the product ratios. Upon examination of the data in Table 1, one finds that cyclization of 5-hexenyl radicals proceeds in good yields. Also, the yield of product 18 is found to increase with increasing stability of the radical center (compare entries 1 and 3, entries 3 and 5). Stabilization of the cyclic radical intermediate also appears

Table 1. Reduction of bromo alkenes by tributylstannane at 70°C

Entry	13	14	% Yield 17	18	Ratio kac/kab
1	R_1=R_2=R_3=H	8.8	90.1	1	< 0.008
2	R_1=R_2=H, R_3=CH_3	17.6	80.0	3.4	0.040
3	R_1=CH_3, R_2=R_3=H	8.7	88.4	2.9	< 0.03
4	R_1=R_3=CH_3, R_2=H	7.9	76.8	15.3	0.15
5	R_1=R_2=CH_3, R_3=H	7.0	79.8	13.2	0.36
6	R_1=R_2=R_3=CH_3	5.4	46.9	47.7	1.28

to play a role in increasing the yield of the thermodynamic product (compare entries 1 and 2, entries 5 and 6). These authors also obtained cyclization rate constants for the six methyl 5-hexenyl radicals. These rate constants are shown in Table 2. Although the reason for the

Table 2. Estimated rate constants for cyclization of 5-hexenyl radicals

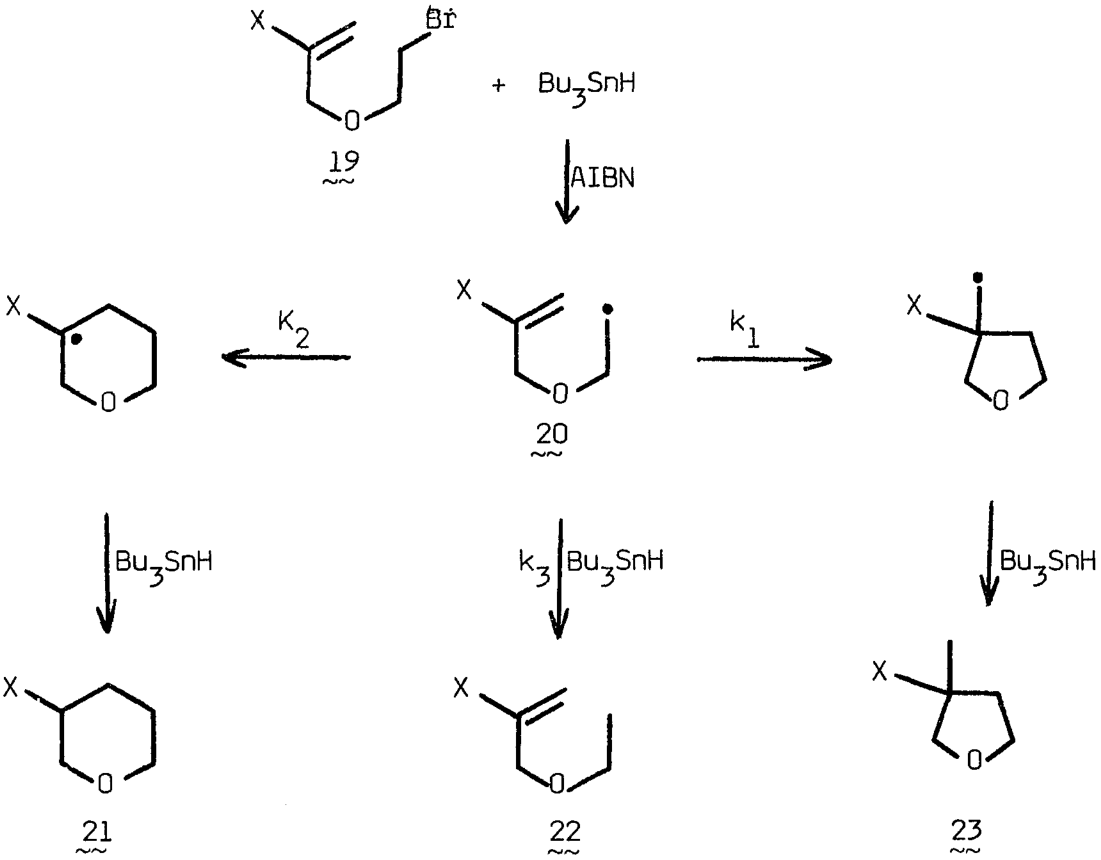
Radical	kab, sec^{-1} x 10^5	kac, sec^{-1} x 10^5
	1.1	< 0.005
	0.9	< 0.024
	0.92	0.19
	0.62	0.54

decrease in kab, or increase in kac, upon substitution is not completely understood, it is clear that alkyl substituents do effect the direction of cyclization. However, there is still a strong preference for the *exo*-mode of addition.

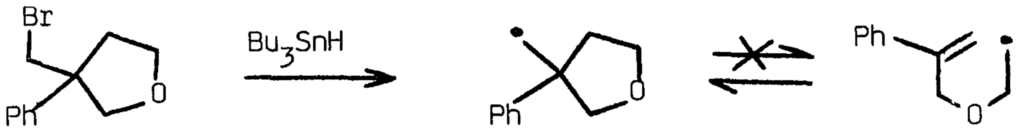
Similar rate data were also obtained by Beckwith and coworkers (16) working with methyl substituted 5-hexenyl radicals. The radicals were prepared by the same methods used by Walling and Cioffai. Beckwith *et al*. suggested that changes in the product ratios were not due to increased stability of the initial radical. In other words, the relatively small change in the ratios was not in accordance with the large differences in formation between primary, secondary, and tertiary radicals. This also suggested that the stability of the incipient radical was not a key factor. Furthermore, they believed that the increased yield of the six-membered ring product was mainly due to a lowering of kab rather than an enhanced kac. The rationale for this belief was not at all made clear. However, the quantitative results support previous findings that alkyl substitution does effect radical cyclization but not so as to change the perferred *exo*-mode.

Butler and Smith (17) have looked at the effect of methyl and phenyl groups at the internal position of the π-bond in the 5-hexenyl radical. The technique used in generating the radical was the same as that reported by Walling and Cioffai (15) and Beckwith *et al*. (16). Scheme 5 outlines the reactions of the two radicals studied. To check the irreversibility of the process, the (3-phenyl-3-tetrahydrofuranyl)-

Scheme 5



methyl radical was generated under the same conditions as radical 20 (90°C, 1.5 mole % AIBN initiator). 3-Phenyl-3-methyltetrahydrofuran was the only product obtained thereby demonstrating the stability of the radical. This result suggests that, once formed, the cyclic radical intermediates in Scheme 5 do not go back to acyclic radical 20. The



relative rates of cyclization as well as the actual product yields at various temperatures are given in Table 3. The product yield of 3-methyltetrahydropyran **23** reaches a maximum of only 3% from 2-methallyloxyethyl **20a**. The 2-(2-phenylallyloxy)ethyl radical **20b**, however, gives 3-phenyltetrahydropyran **23** as the predominant cyclic product. These authors concluded that the controlling factor in the product distribution was the increased stability of the benzylic radical intermediate. Butler and Smith used their kinetic data to estimate the activation energies for the cyclization reactions relative to the activation energy of hydrogen abstraction from tri-n-butylstannane by a primary radical. Wilt et al. (18) calculated the activation energy of the hydrogen abstraction to be between 6.8 and 8.2 kcal/mol based on some published rate constants (19). Since the rate constants for hydrogen abstract of 2-methallyloxyethyl **20a** and 2-(2-phenylallyloxy)ethyl **20b** should be the same,

Table 3. Relative rates of cyclization of **20a** and **20b** with AIBN

Radical	Temp. °C	k_1/k_2	% Yield **21**	**23**
2-Methallyloxyethyl **20a**	40	43	75.2	1.75
	90	30	80.2	2.67
	125	24	79.4	3.22
2-(2-Phenylallyloxy)ethyl **20b**	40	0.55	24.9	45.6
	90	0.52	25.3	48.7
	125	0.50	26.0	51.6

a comparison of the relative activation energies of cyclization was possible. These data are given in Table 4. Based on these values, the

Table 4. Relative activation energies of cyclization of 20a and 20b

Entry	Product	E_A-E_A (H abst.) kcal/mol	kc, s^{-1} at 40°C
1	3-Phenyl-3-methyltetrahydrofuran	1.3 ± 0.25	5.3×10^4
2	3-Phenyltetrahydropyran	1.6 ± 0.25	9.6×10^4
3	3,3-Dimethyltetrahydrofuran	2.2 ± 0.15	6.1×10^4
4	3-Methyltetrahydropyran	3.9 ± 0.3	1.4×10^3

phenyl group seems to cause a 2.4 kcal/mol lowering of the activation energy of cyclization to the pyran ring (compare entries 2 and 4). Stabilization of the incipient radical might also help explain why pyran formation competes more favorably in the phenyl substituted radical than in the methyl system. Also given in Table 4 are the rates of cyclizations (kc) for each product. The total rate constants for cyclization in the methyl and phenyl systems are approximately 6.2×10^4 and 1.5×10^5 s^{-1}, respectively. The fact that the phenyl system is almost twice as fast as the methyl is most likely due to the greater stability of the benzylic radical intermediate leading to the six-membered ring. Therefore, it appears that the proportions of six-membered and five-membered cyclic products is dependent on the activation energies of the competing cyclization pathways. Noteworthy is that cyclization of the 2-(2-phenylallyloxy)ethyl radical 20b still does not overwhelmingly favor *endo*-cyclization.

The 4-pentenyl radical

Attempts by several workers to obtain cyclic products from the 4-pentenyl radical have failed. Gordon and Smith (20) were among some of the earlier workers to recognize the reluctance of the 4-pentenyl radical to cyclize. When the radical was generated by electrolysis of hex-5-enoic acid, Garwood and coworkers (21) observed only radical dimerization. Walling and Pearson (9) prepared the 4-pentenyl radical

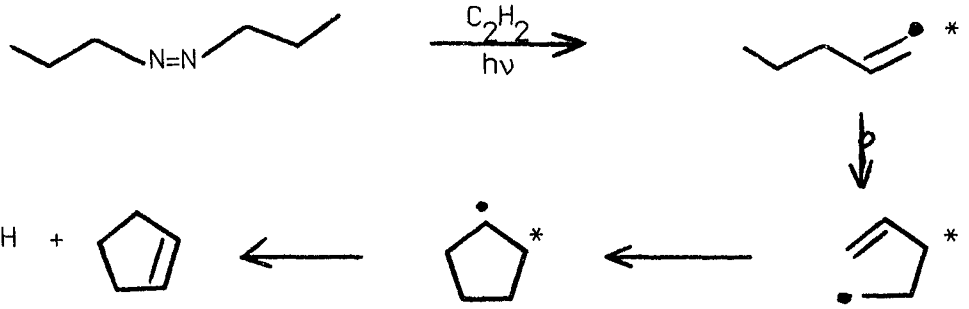
$$\mathrm{CH_2{=}CHCH_2CH_2CH_2CO_2H} \xrightarrow{e-} \mathrm{CH_2{=}CHCH_2CH_2CH_2}\cdot \longrightarrow$$

$$\longrightarrow \mathrm{CH_2{=}CH(CH_2)_6CH{=}CH_2}$$

under the same conditions used to generate the 5-hexenyl radical but were still unable to observe any cyclic product. The 4-pentenyl radical was later generated from 5-hexenoyl peroxide in toluene, but Lamb *et al*. (22) did not obtain any cyclic products.

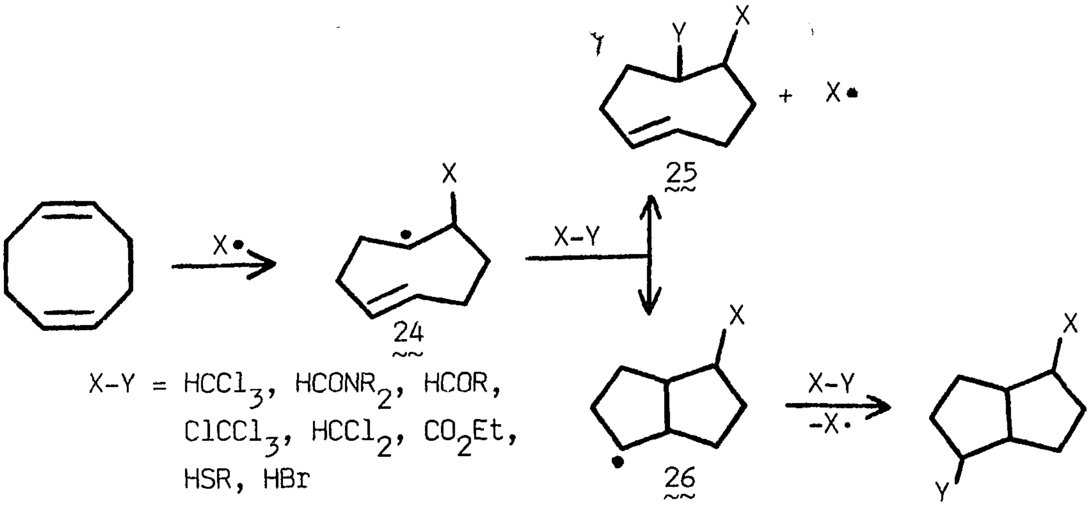
In special cases, cyclization of the 4-pentenyl radical has been observed. In these instances, however, the five-membered (*endo*) cyclic product and not the four-membered (*exo*) cyclic product is the only one observed. For example, the vibrationally excited 4-pentenyl radical has been reported (23) to cyclize to cyclopentene. The 4-pentenyl radical was formed by intramolecular hydrogen abstraction of the 1-pentenyl radical, generated by photolysis of azo-n-propane in the presence of acetylene at 46°C (Scheme 6).

Scheme 6



Another special case of cyclization involving a 4-pentenyl radical has been reported independently by several workers (24,25,26,27). The radical was generated by intermolecular free radical addition to cis,cis-1,5-cyclooctadiene (Scheme 7). The yield of cyclization products was

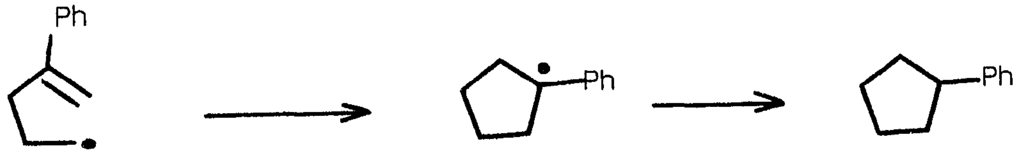
Scheme 7



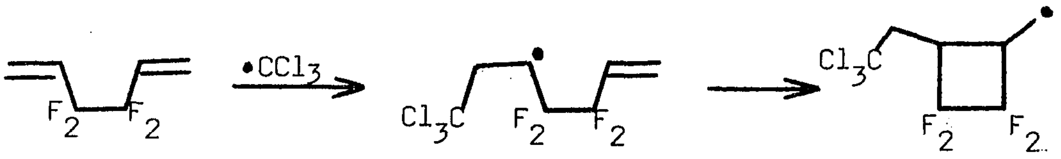
X-Y = $HCCl_3$, $HCONR_2$, HCOR, $ClCCl_3$, $HCCl_2$, CO_2Et, HSR, HBr

as high as 74%. While the cyclization of radical 24 may be viewed as an endo 4-pentenyl closure, it is just as likely that process involves an exo 5-hexenyl radical closure. In all the cases studied, none of the cyclobutyl product was reported.

Wilt and coworkers reported that γ-pheny-4-pentenyl radical cyclized in good yield to phenylcyclopentane (28). Due to an ambiguity in the method used to generate the radical, however, an alternative carbonium ion rearrangement to phenylcyclopentane could not be ruled out.



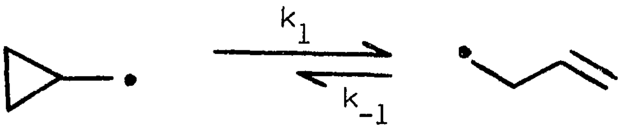
The only example in which a 4-pentenyl radical cyclized to a cyclobutyl compound (exo-mode) was reported by Piccardi et al. (29). The radical was generated similar to a procedure already discussed involving addition of trichloromethyl radical to the π-unit of 3,3,4,4-tetrafluoro-1,5-hexadiene. The authors also report formation of the cyclopentyl derivative (endo-mode).



The 3-butenyl/cyclopropylcarbinyl radical rearrangement

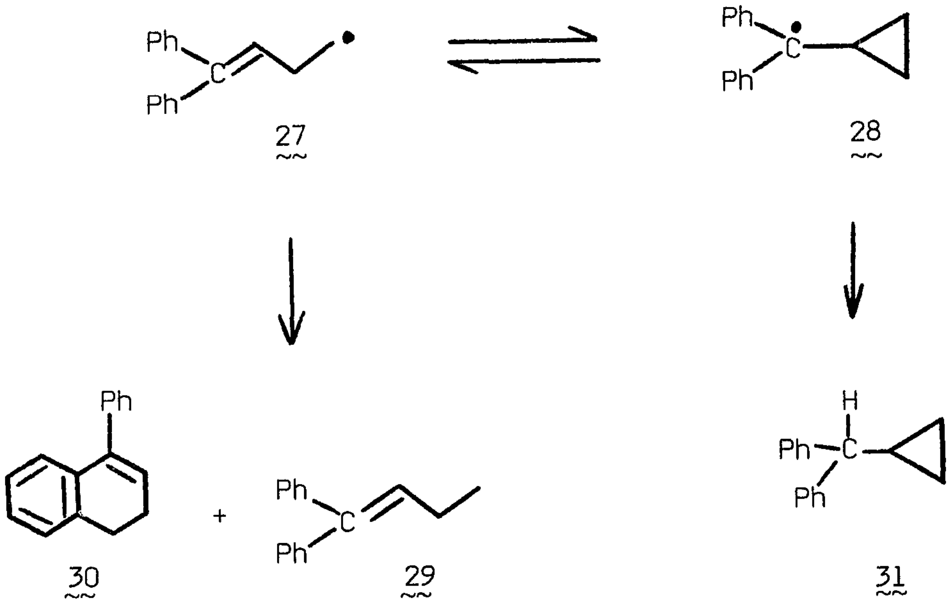
Like the 5-hexenyl radical, the 3-butenyl radical cyclizes in an exo-manner. However, isolation of the cyclized product has not been possible since the reverse reaction is much more facile. Indeed, the cyclopropylcarbinyl to the homoallylic (3-butenyl) radical isomerization is known to be an extremely rapid process in free-radical chemistry (2,30) (Scheme 8). This rearrangement has been used as a major carbon probe in mechanisms involving free-radicals.

Scheme 8



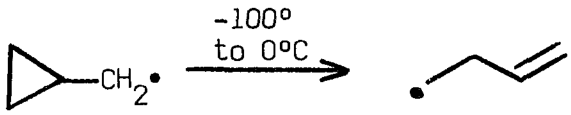
Using ESR techniques and deuterium labeling, Maillard et al. (31) and Effio and coworkers (32) have obtained the rate constants for the isomerization shown in Scheme 8. The rate constant (k_1) for beta-cleavage of the cyclopropylcarbinyl radical, was measured as 1.3 x 10^8 sec^{-1} at 25°C. The energy of activation at 25°C is 5.94 kcal/mole with a Log A-factor of 12.48 sec^{-1}. For the reverse reaction: k_{-1}=9.4 X 10^{-3} sec^{-1} at 40°C, 2.6 x 10^{-4} sec^{-1} at 60°C, 6.2 x 10^4 sec^{-1} at 80°C. The activation energy for the reverse process is 9.09 kcal/mole with a Log A-factor of 10.36 sec^{-1}. Also calculated, was an equilibrium constant of 1.3 x 10^4 at 25°C. These data clearly indicate that the forward reaction, represented by k_1 in Scheme 8, is much more favored than the reverse k_{-1} process. Therefore, isolation of products of the exo-cyclized 3-butenyl radical is not possible.

The facile nature of the reversible rearrangement shown in Scheme 8 was recognized as early as 1967 by Halgren and coworkers (33). They examined the rearrangement of the γ,γ-diphenylallylcarbinyl radical **27** and the diphenylcyclopropylcarbinyl radical **28**. The radicals were generated from the respective t-butyl peracetates at 125°C and afforded compounds **29**, **30** and **31**. Compound **30** was proposed to have arisen from the homoallylic radical **27**. Based on thermodynamic considerations,



the diphenylcyclopropyl radical **28** should be more stable. Therefore, one would expect a higher yield of product **31**. However, the product distribution shown in Table 5 indicates a predominance of products arising from diphenylhomoallylic radical **27**. The beta-scission of the cyclopropylcarbinyl radical far out weighs its thermodynamic stability.

Spectroscopic evidence for the isomerization of the cyclopropylcarbinyl radical to the homoallylic radical was first obtained in 1969. Kochi, Krusic, and Eaton (34) recorded the ESR spectrum of the two species between -140°C and 0°C. The cyclopropylcarbinyl radical was formed by

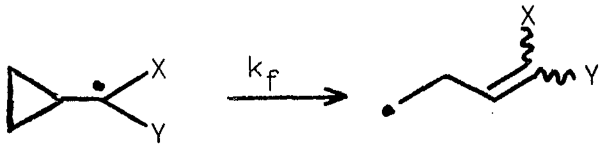


hydrogen abstraction from the methyl group of cyclopropyl methane with photochemically generated t-butoxy radical. Isomerization to the homoallylic radical occurred between -100°C and 0°C.

Table 5. Thermolysis of the peracetates of 27 and 28 at 125°C

Solvent	Perester of		% Yield	
		29	30	31
1,4-cyclohexadiene	27	30.0	11.9	0.3
cyclohexane	27	1.0	26.5	0.1
1,4-cyclohexadiene	28	45.0	11.0	14.6
cyclohexane	28	1.1	23.5	7.5

Substitution at the radical center of the cyclopropylcarbinyl radical has recently been shown to decrease the rate constant for the β-cleavage, k_f, by a factor of about ten (35). The activation energies in the same study were raised on the average by approximately 2 kcal/mol. Such changes in the radical structure, however, still do not make feasible the isolation of the cyclopropyl carbinyl product.

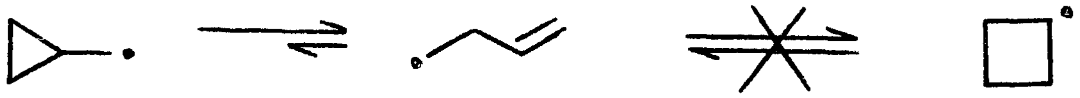


$k_f \approx 2 \times 10^7\ \text{sec}^{-1}$

Ea ≈ 7.2 kcal/mol

a: X = H, Y = $OSiMe_3$; b: X = H, Y = $OSiMe_2Bu^t$; c: X = Me, Y = $OSiMe_3$

In all of the studies done on the isomerization of the cyclopropyl carbinyl to the 3-butenyl radical, and vice versa, products derived from the cyclobutyl radical have never been reported. Several theoretical studies (36,37,38) have looked at the energy differences between the

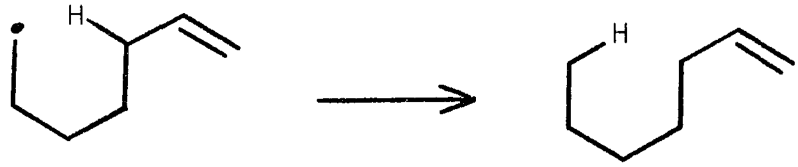


32 33 34

three isomeric radicals. Dewar and Olivella (36) performed some calculations using a spin-unrestricted version of the MINDO/3 procedure together with the associated DFP geometry program. The heats of formation at 25°C for 32, 33, and 34 were 37.9 kcal/mol, 37.4 kcal/mol, and 26.7 kcal/mol, respectively. Although the accuracy of the actual numbers may be questionable, the relative stability of the radicals is quite clear. The cyclobutyl radical must be some 5 to 10 kcal/mol more stable than either of the other two isomers. The reason for the reluctance of 3-butenyl radical 33 to cyclize to cyclobutyl radical 34 may be due to the differences in the transition state geometries of 34 and 32. Dewar and Olivella calculated: ΔH_f = 67.4 kcal/mol for the 33 to 34 transition state, ΔH_f = 50.3 Kcal/mol for the 33 to 32 transition state. Based on these calculations, cyclization to the exo cyclopropylcarbinyl radical should vastly be favored over the endo-closure to 34. More discussion on the transition state geometry will be given in the next section.

Higher homologs of the 5-hexenyl radical

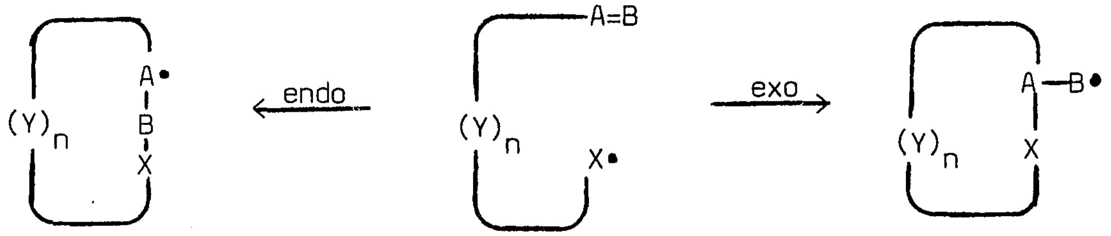
Intramolecular addition of alkenyl radicals having longer chain lengths than the 5-hexenyl radical have not been extensively studied. Cyclization of the higher homologs usually occurs much slower and in reduced yields. Intramolecular 1,5-hydrogen atom transfer is another complication present in the higher homologs of the 5-hexenyl radical. This problem was pointed out by Beckwith and Moad (39) while studing the 6-heptenyl radical. However, when the 6-heptenyl radical (40), as well as the 7-octenyl radical, underwent intramolecular addition, they did so in a predominantly exo-fashion. The ratio of the relative rate constants for the six-membered/seven-membered ring closure was approximately 5:1, while that for the seven-membered/eight-membered ring closure was over 100:1 (39).



The Beckwith rules

Many hypotheses have appeared in the literature in attempts to explain the high selectivity of radical cyclizations, particularly in the case of the 5-hexenyl radical. All of the explanations are based on steric, stereoelectronic, and entropic arguments or some combination of the three. The most frequently employed arguments have been reviewed (2,30). Perhaps the most concise and widely accepted explanation was given by Beckwith *et al*. (1), and Struble *et al*. (41). Their explanation for the observed selectivity was based on a stereoelectronic argument.

The so-called Beckwith rules (1) state that intramolecular addition under irreversible kinetic control in lower alkenyl and alkynyl radicals and related species occurs preferentially in an *exo*-mode. The rules suggest that *exo*-ring closure, **36** to **37**, is kinetically favored over the *endo*-closure of **36** to **35**. Except for the 5-pentenyl radical, for which

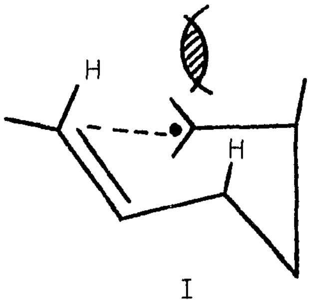


35 **36** **37**

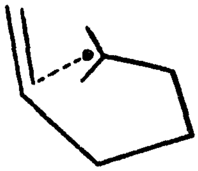
no cyclic products are observed, all of the other alkenyl radical discussed follow this preferred mode of cyclization. Some hetero-centered radicals also follow the Beckwith *exo*-mode of cyclization. Hetero-centered radicals will be discussed in a later section.

Beckwith and coworkers proposed that cyclization of radicals is largely under stereoelectronic control and that the transition state is sterically different from that of cationic cyclizations which usually give the larger ring products. Furthermore, the initial stage of the addition process involves interaction of the planar carbon radical with the lowest unoccupied orbital (LUMO) of the π-system. Theoretical studies of the intermolecular addition of alkyl radicals to double bonds have revealed an early transition state with attack occurring along a line through one end of the double bond and orthogonal to the nodal plane of the π-molecular orbital (42). In other words, as shown in Scheme 9, this occurs best when approach of the radical is along a line extending almost vertically from the p-orbital of one of the π-bonded carbon atoms (IV versus III). Thus, the optimum mode of approach in the 5-hexenyl radical is that which gives the exo-cyclized primary radical. Since the transition state occurs early, and is therefore more reactant-like, there is little effect on product control by stabilization of the incipient radical. Also, note that the 1,3-diaxial steric interactions of a six-membered ring transition state are removed upon forming a five-membered ring (II versus I). Based on these arguments, the kinetically controlled exo-cyclization is preferred for radicals undergoing an irreversible process.

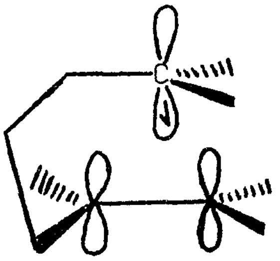
Scheme 9



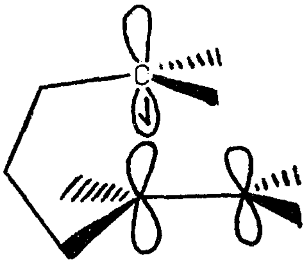
I



II

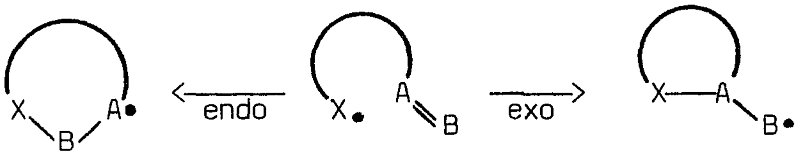


III



IV

The selectivity observed in carbon radical cyclizations is also in keeping with the Baldwin rules for ring closure (43). Following Baldwin's nomenclature, intramolecular addition of alkenyl radicals would involve either an *exo*-trigonal or *endo*-trigonal process. The rules for a



trigonal system are:

1. 3 to 7-*exo*-trigonal are favored;
2. 3 to 5-*endo*-trigonal are disfavored.

The numerical prefixes represent the ring size. Thus, the 5-hexenyl radical, the lower homologs, and the next two higher homologs should favor an *exo*-trigonal (rule 1) process. From the examples given earlier, one sees that this is indeed the case for carbon radicals.

Silicon Radical Cyclizations and Disproportionations

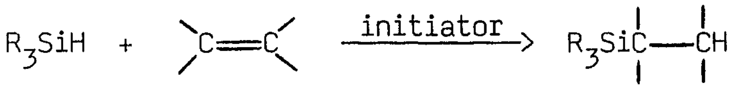
Silicon radicals undergo many of the same type reactions as its carbon analog. But unlike carbon radicals, silicon radicals have been observed to undergo relatively few intramolecular cyclizations.

The most common reactions reported for these radicals are:

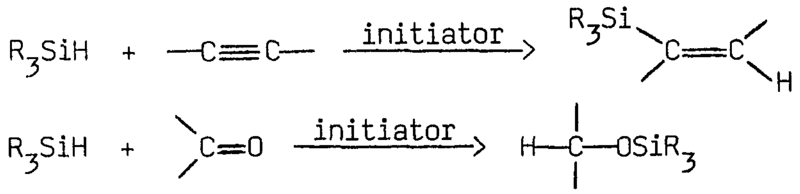
1. Abstraction of halogens (30,44,45)

$$R_3Si\cdot \ + \ RX \longrightarrow R_3SiX \ + \ R\cdot \quad X = Br > Cl > F$$

2. Addition to multiple bonds (46,47,48)



$$R_3SiH \ + \ \rangle C{=}C\langle \ \xrightarrow{\text{initiator}} \ R_3Si\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}H$$



$Cl_3SiH > RCl_2SiH > R_2ClSiH >> R_3SiH$

3. Aromatic substitution (49,50)

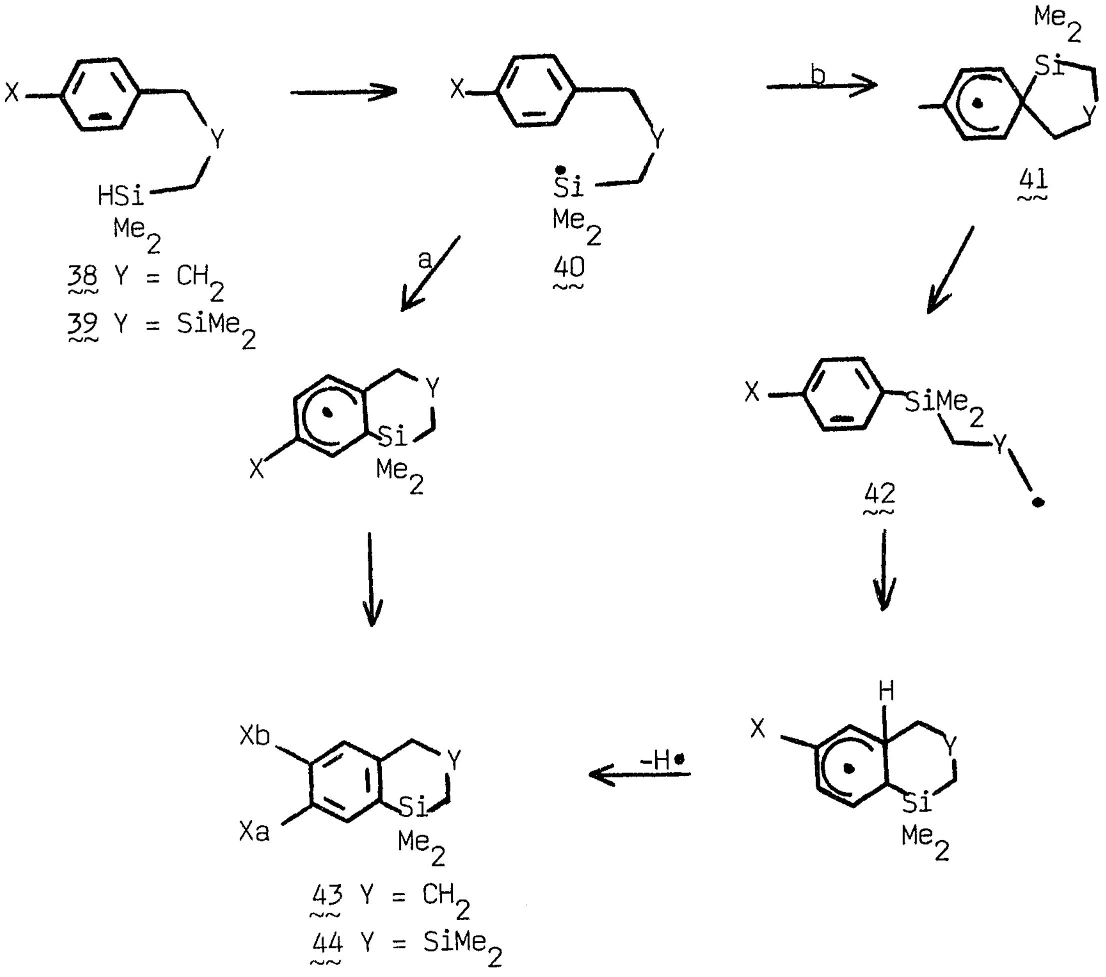
$R_3Si + ArH \longrightarrow ArSiR_3 + H\cdot$

Several methods now exist for generating silicon radicals. Some of the most common methods include mercury photosensitized cleavage of silylhrides (51), decomposition of bis(silyl)mercurials (52,53), and photochemical decomposition of azo compounds (54). There are, however, few good thermal methods of producing silicon radicals. For example, hexaphenyldisilane, in contrast to its carbon analog, does not give triphenylsilyl radical upon thermolysis (55). Hexamethyldisilane, on the other hand, does decompose at 600°C giving the corresponding silicon radical (56). The utility of this method of generating silicon radicals has been limited by other reactions of appropriately substituted disilanes. It is well-known that disilanes undergo α-elimination under thermal conditions when substituted with hydrogen, a halogen or an alkoxy group. Newmann and Schultz have recently generated the trimesitylsilyl radical by irradiation of the corresponding chlorosilane in the presence of an electron rich olefin at -60°C (57). Perhaps the most widely used method of generating silicon radicals is by abstraction of a silylhride by another radical. Several radical initiators (Int·) have been used such as azobisisobutyronitrile (AIBN) and organic peroxides (48,58).

$$R_3SiH + Int\cdot \longrightarrow R_3Si\cdot + IntH$$

One of the first examples of intramolecular cyclization involving a silicon radical was reported by Sakurai and coworkers (59). (3-Phenylpropyl)-dimethysilane **38** was found to give dimethyl-1-silatetralin **43** exclusively upon heating at 135°C (15 hours in a sealed tube) in the presence of di-tert-butyl peroxide (Scheme 10). One mechanism that was

Scheme 10

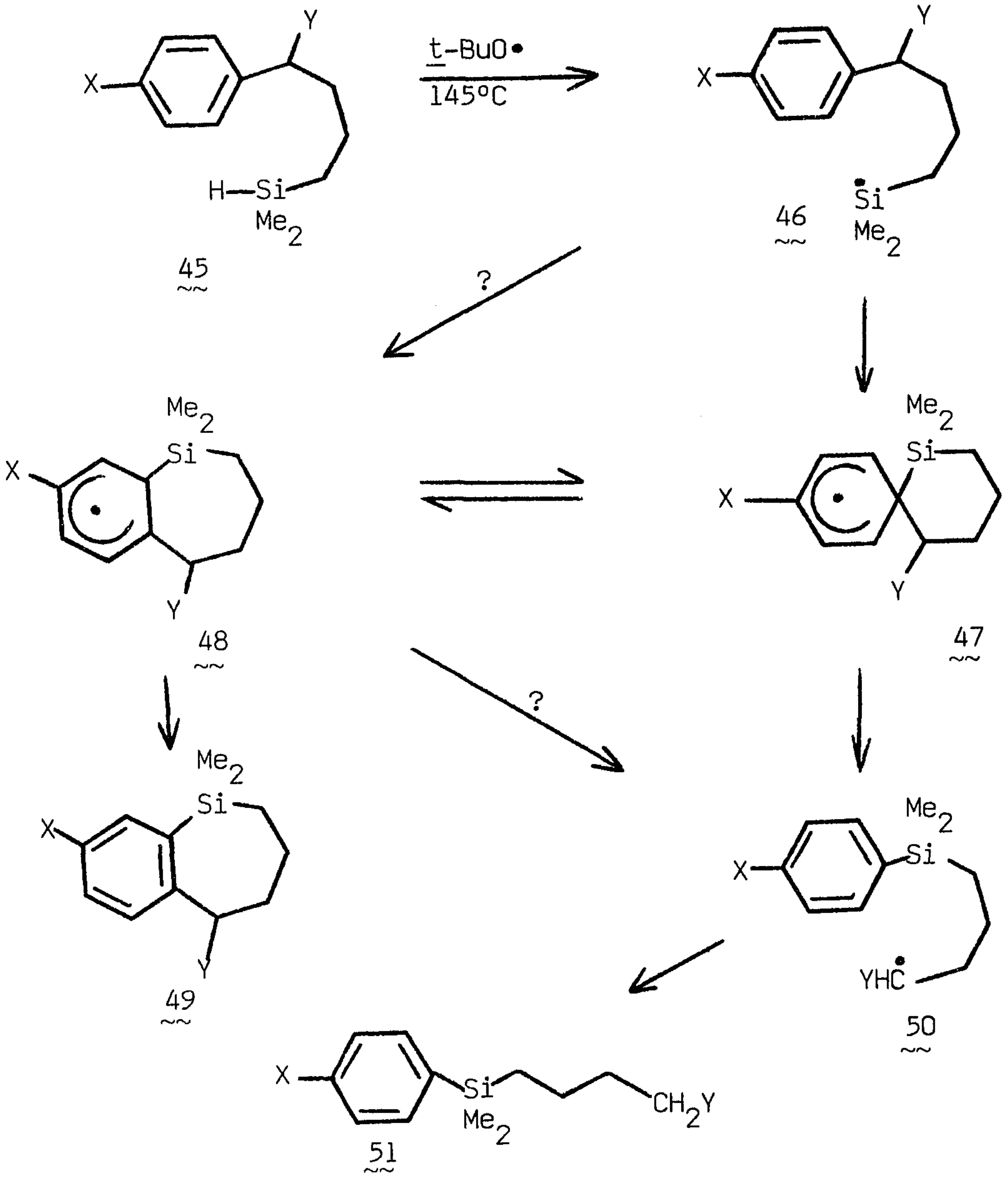


considered to account for product 43 was direct homolytic aromatic substitution in an *endo*-fashion (path a) followed by hydrogen loss. An alternative mechanism, however, may have involved the carbon radical 42 (path b). The para-methyl derivation of 38 (X = CH_3) was subjected to the same reaction conditions in order to distinguish these mechanistic possibilities. Formation of the isomer in which the methyl group was meta to silicon as the sole product led to the conclusion that cyclization occured via path a. The yield of dimethyl-1-silatetralin 43 was 14%. Compound 39 (Y = $SiMe_2$) afforded similar results as those obtained for 38. There was no evidence of having formed a carbon radical intermediate of the type 42.

Migration of a phenyl group from carbon to a silicon radical (40 to 42) was demonstrated later by Sakurai and Hosomi (60). They found that upon heating (4-phenylbutyl)dimethylsilane 45 to 135°C in the presence of di-*tert*-butyl peroxide, both cyclized product 49 and rearranged product 51 were formed (Scheme 11). Their results were explained by a mechanism involving competition between cyclization and rearrangement. From the intermediate spiro radical 47, products may be formed by either ring expansion to 48 or homolysis to carbon radical 50. The possibility of direct cyclization of 46 to 48 was not addressed by these authors.

The scope of this rearrangement was studied by examining a number of compounds of the general formula $ArCHY(CH_2)_nSiMe_2H$. The results are summerized in Table 6. Cyclization products were only observed for n = 2 and n = 3.

Scheme 11



Sakurai et al. (61) have looked at the rearrangement process at temperatures of 370°C and 440°C. The products of this rearrangement are

Table 6. Reaction of X-Ph-CHY(CH_2)nSiMe_2H and di-t-butyl peroxide at 135°C

n	X	Y	Rearrangement	Cyclization
0	H	H	No	No
0	H	H	No	No
0	H	Ph	No	No
1	H	H	No	No
2	H	H	No	Yes
2	H	Me	No	Yes
2	H	Ph	No	Yes
2	p-CH_3	H	No	Yes
3	H	H	Yes	Yes
3	H	Me	Yes	Yes
3	p-CH_3	H	Yes	Yes
4	H	H	No	No
5	H	H	No	No

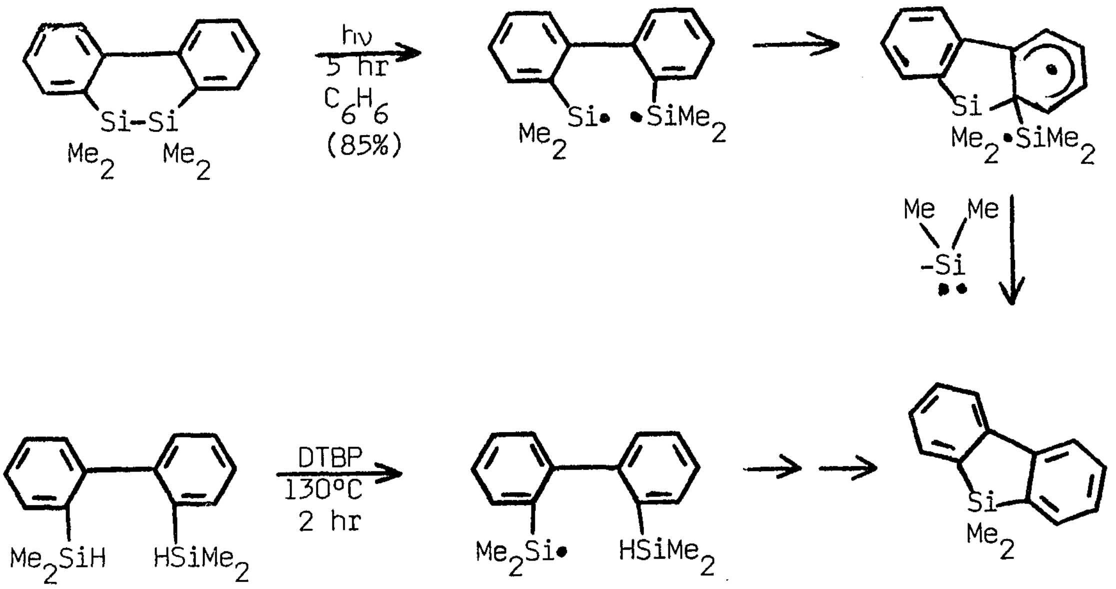
Table 7. Thermal rearrangement of X-Ph-G-$SiMe_2H$

X	G	Temperature °C	Yield
H	CH_2	440	17.3-87.7
p-CH_3	CH_2	440	---
m-CH_3	CH_2	440	---
H	$(CH_2)_2$	370	0
H	$(CH_2)_3$	370	67.5
H	$CH_2SiMe_2CH_2$	370	100
p-CH_3	$CH_2SiMe_2CH_2$	370	100
m-CH_3	$CH_2SiMe_2CH_2$	370	100
H	$(CH_2)_4$	370	38.5
H	$(CH_2)_5$	370	8.7
H	$(CH_2)_6$	370	0

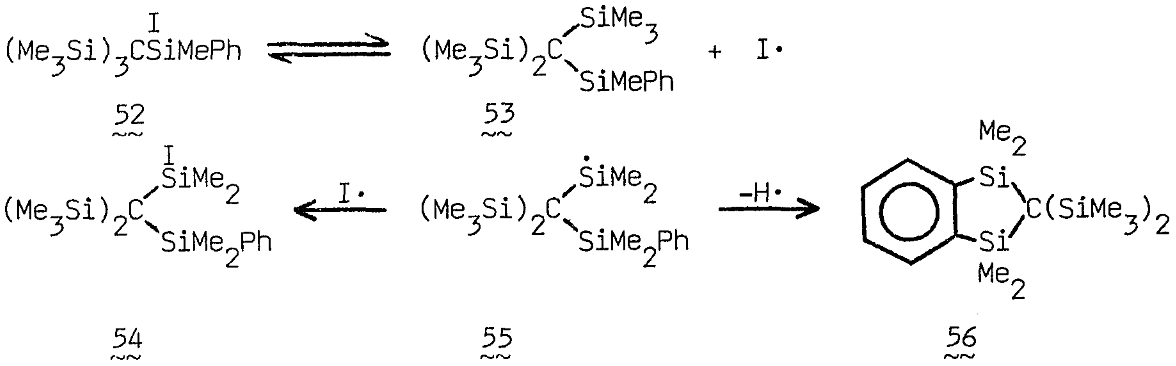
formed via spiro intermediates similar to those already discussed. At these temperatures, however, cleavage occurs much more readily than ring expansion. The data for these rearrangements are given in Table 7.

In a recent communication, Kira *et al*. (62) reported that intramolecular aromatic *ipso*-substitution of a silicon radical was involved in the elimination of dimethylsilylene from photolysis of dibenzo[c,e]-1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene. 9,9-Dimethyl-9-silafluorene was formed in a very high 85% yield. Evidence for the evolvement of a radical intermediate instead of a concerted elimination of dimethylsilylene was obtained when 2,2′-bis(dimethylsilyl)-

biphenyl gave the same product in 76% yield upon heating at 130°C in the presence of di-_tert_-butyl peroxide for 2 hours.

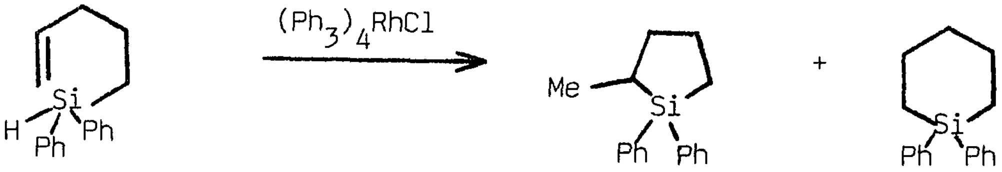


Intramolecular homolytic aromatic substitution of a silicon radical was also demonstrated in the pyrolysis of a [tris(trimethyl)methyl]-diphenylsilyliodide 52 (63). Thermolysis of 52 at 350°C gave a complex



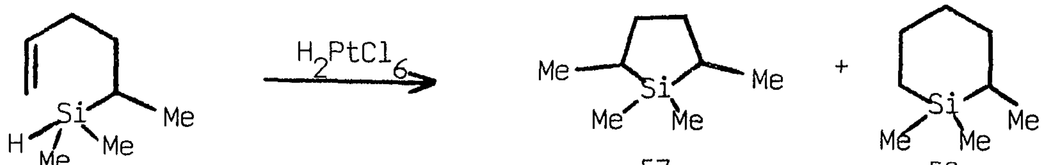
mixture from which 1,3-disilaindene 56 was identified as the major product. Compound 56 was reasoned as having come from homolytic substitution of silicon radical 55.

Most of the intramolecular cyclizations of simple alkenyl silanes have been done with metal catalysts. Several examples of these metal catalyzed cyclohydrosilylations using various metals have been published (64,65,66). Yields of the cyclization product may be as high as 92%.



92.3% 5.8%

Early on, Fessenden and Kray (67) showed that treatment of 5-(dimethylsilyl)-1-hexene with chloroplatinic acid in pentane produced a mixture containing 73% yield of 1,1,2,5-tetramethylsilacyclopentane 57

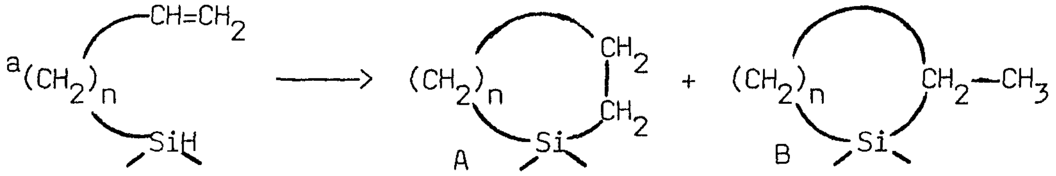


57 (73%) 58 (trace)

and only a trace of 1,1,2-trimethylsilacyclohexane 58. Swisher and Chen (68) reported the only study of systematically varying the chain length of the alkenyl substituent. The results are given in Table 8. Notice that

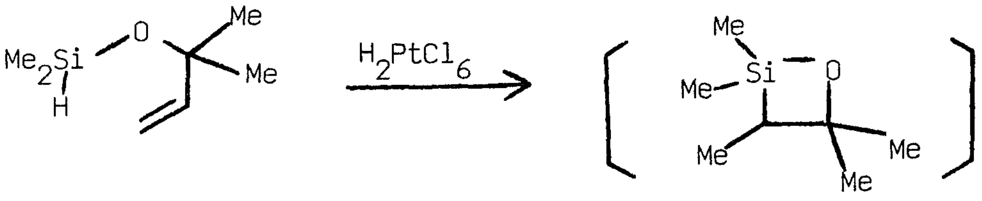
Table 8. Intramolecular hydrosilylation with H_2PtCl_6

n	Total % Yield	% A[a]	% B[a]
0,1	only polymer	--	--
2	46.3	100	0
3	58.1	10	90
4	69.8	47.5	52.5
5	16.4	45.8	54.2
6	2.4	0	100



the endo-cyclization product predominates only in the case of n = 2. In the case of 4-pentenyldimethylsilane (n = 3), Sakurai et al. found similar results (69). In most of the cases reported, it appears the cyclization to the smaller of the rings is the predominant reaction.

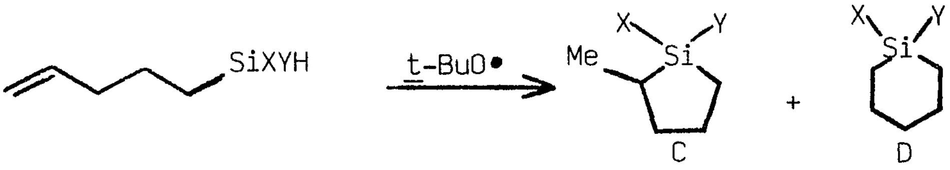
Intramolecular hydrosilylation of vinyldimethylcarbinoxydimethylsilane has also been reported (70). The products formed in this reaction were rationalized as having come from a silaoxetane. However, no silaoxetane was ever isolated or observed spectroscopically.



Sakurai (71) reported a study on the cyclization of some 4-pentenylsilyl radicals generated by abstraction of a silylhride by *tert*-butoxy radical (58,59). Two major cyclic products (type C and type D) were formed when the silanes were heated at 135°C and 30°C in sealed tubes. The results are summerized in Table 9. The reason for the observed selectivity and the distribution of yields was not clear. However, the more bulky groups seem to favor type D while substitution by a more electronegative group appeared to favor type C formation. This work was never published in a complete form.

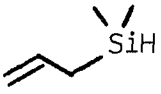
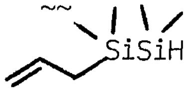
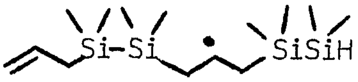
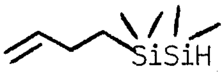
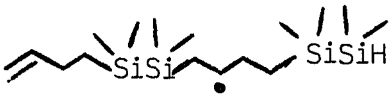
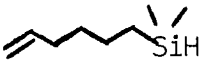
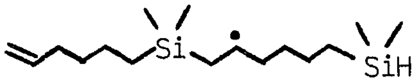
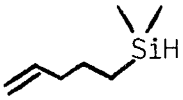
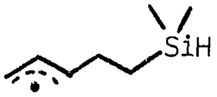
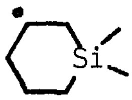
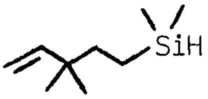
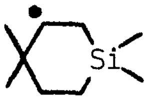
Table 9. Cyclization of 4-pentenylsilane initiated by di-*tert*-butylperoxide

X	Y	% Yield at 135°C		% Yield at 30°C	
		C[a]	D[a]	C[a]	D[a]
Me	Ph	0.65	5.46	1.47	9.48
Ph	Ph	0.74	6.1	3.1	12.6
i-Pr	Cl	3.94	5.47	---	---
Me	Cl	71.6	12.6	4.8	2.9

a 

Very recently, Ingold and coworkers reported an ESR study on the intramolecular addition of some silyl and disilanyl radicals (72). The radicals were formed from the corresponding silyl hydride by abstraction with *tert*-butoxy radicals in cyclopropane at various temperatures. The results are summarized in Table 10. At the silane concentrations (13% w/w) used in their experiments, the intermolecular addition was considerably faster than the cyclization process. Only in

Table 10. ESR hyperfine splitting and assigned structures[a]

Alkenylsilane	Radical Structure	a^H/G	T/K
 60		17.3(4H) 19.5(1H)	295-225
 61		17.6(4H) 19.6(1H)	150-370
 62		17.5(2H) 20.5(1H) 25.2(2H)	295-225
 63		17.0(2H) 21.0(1H) 26.5(2H)	150-255
 64		4.0(1H) 13.8(4H) 14.5(1H)	295
		20.7(1H) 38.5(2H)	240
 65		6.0(1H) 19.5(1H) 36.0(1H)	200-250

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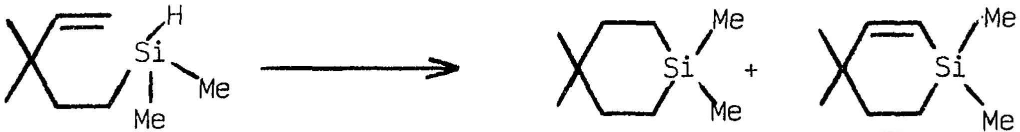
[a] Peroxide decomposition of 3-butenyldimethylsilane, 59, was not reported.

the case of 4-pentenyldimethylsilane 64 and the dimethylpent-4-ene silane 65 was intramolecular cyclization observed. From silane 65, 1,1,4,4-tetramethyl-1-silacyclohexane 66 and 1,1,4,4-tetramethyl-1-silacyclohexene 67 were isolated in 35% and 11% yield, respectively, based on a 92% consumption of hydrido silane 65. No other products were isolated in this work.



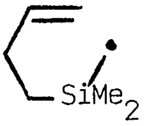
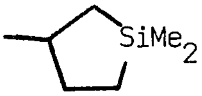
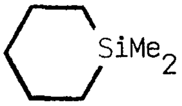
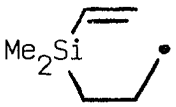
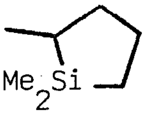
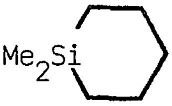
65 66 67

Ingold *et al*. results indicate that *endo*-cyclization predominates over *exo*-cyclization for silicon radicals derived from 64 and 65. This is opposite that which would have been predicted according to the Beckwith rules. Attempts to measure the rate constant for cyclization failed, however, an upper limit of 10^9 sec^{-1} at 173 K and a lower limit of 10^7 sec^{-1} at room temperature were estimated. The estimates were based on similar experiments with triethylsilane and ethylbromide. The absence of an ESR signal for the silyl radicals also suggested a rapid process.

Ingold *et al*. (72) offered an explanation based on bond lengths and configurations at the radical centers for the observed *endo*-regiochemistry. In other words, for the 5-hexenyl radical *endo*-cyclization is disfavored because the carbon radical cannot achieve the proper alignment of p-orbitals for *endo*-closure (Scheme 9). However, with the silicon analog, the increased carbon-silicon bond length allows for optimum alignment of the pyramidal silicon orbital with the terminal p-orbital of the π-system. The reason for the departure of silicon radicals from the Beckwith rules will be discussed in more detail in the Results and Discussion section. Also, some results that are complementary and supportive of Ingold *et al*. will be given; results that were completed prior to their report.

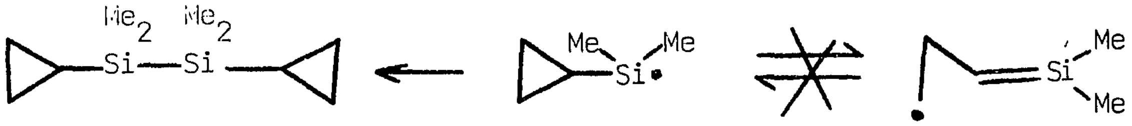
The effect of increased bond length on the direction of cyclization due to silicon was demonstrated earlier by Wilt (73). Wilt examined the intramolecular addition of α-silyl radical 68 and the vinylsilylpropinyl radical 69 and obtained the results shown in Table 11. The radicals were formed by abstraction of the corresponding chlorides or bromides with tri-*n*-butyltin hidride (TBTN) with AIBN initiator. Notice that the increased carbon-silicon bond length in radical 68 leads to predominantly six-membered ring. The γ-silyl group in radical 69 decreases the possibility of overlap with the terminal end of the π-system and,

Table 11. Radical cyclization using tri-*n*-butyltin hydride and azoisobutyronitrile at 366 nm

Radical	% Yield (rel. rate) of Product	
 68	 5(0.5)	 11(1)
 69	 42(15)	 3(1)

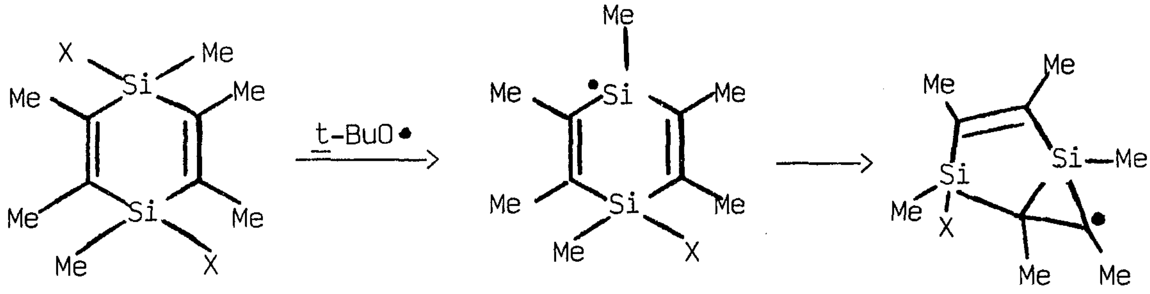
therefore, results in predominantly five-membered ring formation. Although the author did not offer this explanation, based on Ingold *et al.* (72) results and the work to be presented in this dissertation, this seems to be the most reasonable way to explain the observed regioselectivity.

The cyclopropyldimethylsilyl radical 71 is another silicon radical that does not behave like its carbon analog. When cyclopropyldimethylsilyl radical was generated by *tert*-butoxy radical abstraction from the corresponding hydrosilane, only the radical dimer 70 was formed (58). No products were observed that might have come from the rearranged carbon radical 72. The analogous cyclopropylcarbinyl radical undergoes facile ring opening to the 3-butenyl radical as previously discussed. The dicyclopropylsilyl and tricyclopropylsilyl radicals also fail to rearrange (71).



70 71 72

Intramolecular cyclization to form a silacyclopropane has been reported to occur and the ESR spectrum of the cyclized radical recorded (74). When the 1,4-disilacyclohexadiene silyl radical 74 was generated by free radical abstraction of a hydrogen or deutrium from the corresponding hydrosilane 73, the ESR spectrum produced was consistent with having formed the silacyclopropyl carbon radical 75. Although this occurs formally by cyclization onto a vinyl group, it may also be viewed as an *exo*-closure of a 4-pentenyl silyl radical.

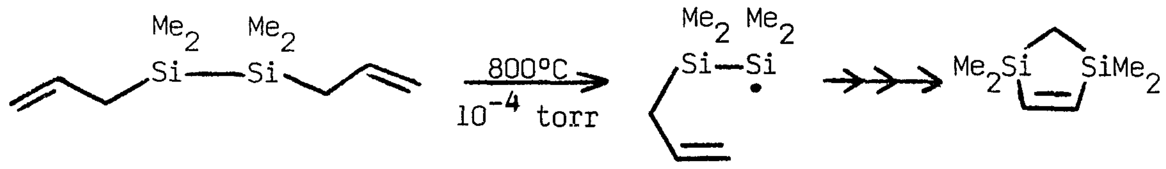


73 X = H, D 74 75

As previously mentioned, there exist very few good thermal silicon radical generators. Davison and Wood (75), however, did report that the pyrolysis of trimethylallylsilane formed trimethylsilyl radical and propenyl radical as the main primary process. Between 580° and 730°C the reaction was first order, with an Arrhenius A-factor of $10^{15.9}$ sec^{-1}

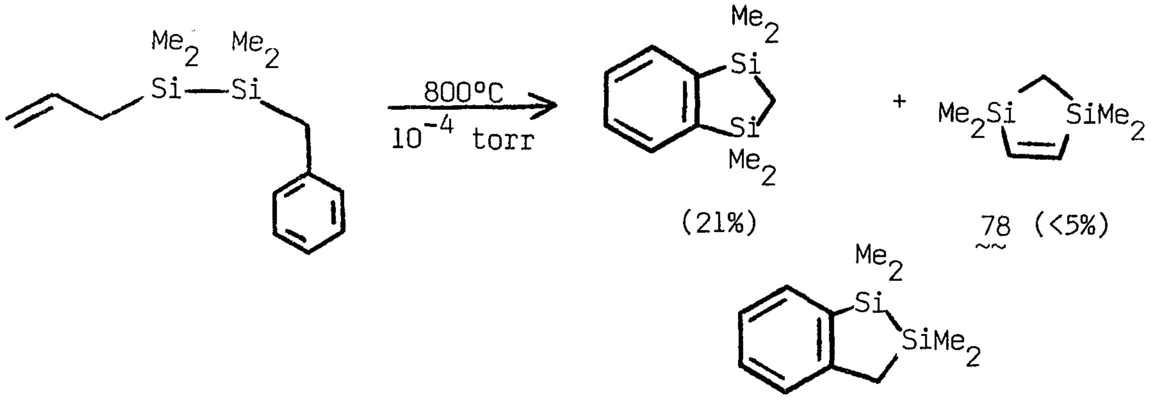
and an activation energy of about 73 kcal/mol. At low pressure, the radicals gave trimethylsilane and propene; but at high pressure bimolecular reactions between the trimethylsilyl radical and trimethylallylsilane lead to tetramethylsilane (TMS) and trimethylvinylsilane. Cleavage of the allyl-silicon bond replaced mechanisms involving methyl loss (76) and methylene extrusion (77) that were previously envolked to account for the trimethylvinylsilane formed in this pyrolysis.

Barton and Jacobi have used allyl and benzyl cleavage to prepare disilanyl radicals in the gas phase (3). Thus, upon the pyrolysis of 1,2-diallyl-tetramethyldisilane 76 at 800°C in a vacuum (1 X 10^{-4} mm Hg), 1,1,3,3-tetramethyl-1,3-disilacyclopentene **78** was produced in 51% yield. They rationalized that the first step in the process was homolysis of



76 **77** **78**

the allyl-silicon bond giving the disilanyl radical **77**. Radical **77** could then undergo a sequence of rearrangements on to the observed product **78**. A more detailed mechanism on the rearrangement of **77** to **78** will be given in the Results and Discussion section. A new mechanism for the formation of **78** from diallyldisilane **76** will also be discussed. Similar products are formed when 1-allyl-2-benzyltetramethyldisilane is pyrolyzed under the same conditions. However, the 1,2-disilaindane, formed in 29% yield, must have come from direct intramolecular aromatic substitution of 2-benzyl-1,1,2,2-tetramethyldisilanyl radical.



(21%) **78** (<5%)

(29%)

Other allylsilanes have been suggested to decompose via a concerted retroene elimination of propene to form silenes. This topic will be dealt with in the Results and Discussion section.

Until recently, the disproportionation of silicon radicals was thought to be a minor process. Indeed some early studies with methylsilyl, dimethylsilyl, and trimethylsilyl radicals generated photochemically (Hg6($^3P_1$)) supported this belief (78). Since then, several investigations have been done to advance the understanding of this reaction.

Kinetic data is now available on the rate of combination (kc) of silicon radicals. Watts and Ingold (79) using electron paramagnetic spectroscopy techniques obtained a bimolecular rate of combination of trimethylsilyl radical equal to 5.5 X 10^9 M^{-1} sec^{-1} in solution.

$$2\ Me_3Si\cdot \xrightarrow{kc} Me_3SiSiMe_3$$

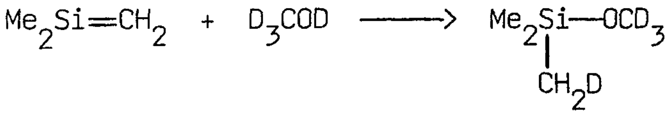
This value was much higher than that of 3.16 X 10^2 M^{-1} sec^{-1} previously calculated by Thynne (80). Watts and Ingold did not observe any significant amount of disproportionation occurring. The rate of combination, kc, has also been measured in the gas phase. In a short communication, Cadman et al. (81,82) reported kc to be 1.78 X 10^{11} M^{-1} sec^{-1} using a rotating sector technique between 44° and 126°C. The combination reaction was found to be competitive with abstraction of chlorine from methyl chloride. These authors also did not report any products derived from disproportionation (82).

A relative ratio for kd/kc of 0.046 was reported a short time after by Strausz and coworkers (83) but they gave no experimental basis for

$$2\ Me_3Si\cdot \xrightarrow{kd} Me_2Si{=}CH_2 + Me_3SiH$$

the ratio. It was not until 1980 when Strausz et al. reported that upon photolysis of bistrimethylsilyl mecury at room temperature, an almost identical kd/kc ratio of 0.05 ± 0.01 was obtained (84).

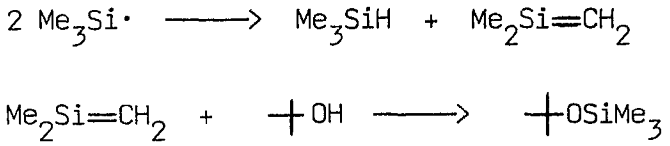
Tokach and Koob (85,86) were among the first to obtain evidence for the disproportionation of a silyl radical to a silene at room temperature. Mercury photosensitized reaction of trimethylsilane with added perdeuterated methanol gave deuterated trimethylmethoxysilane in good yield.



$$Me_2Si{=}CH_2 + D_3COD \longrightarrow Me_2\underset{\displaystyle CH_2D}{\underset{|}{Si}}{-}OCD_3$$

This was the expected product of methanol trapping of dimethylsilene. The kd/kc value obtained at 25°C was 0.31 ± 0.08.

Gaspar and coworkers have also demonstrated that disproportionations of silicon radicals is important in solution chemistry. In some kinetic ESR experiments at short reaction times, hexamethyldisilane and tert-butyl alcohol were the only compounds formed from the photolysis of trimethylsilane and di-tert-butyl peroxide (87). They concluded that radical recombination was the exclusive mode of self-reaction for trimethylsilyl radicals. At longer irradiation times, however, a third product was formed (88). The product was identified as tert-butoxy-trimethylsilane which was believed to have come from trapping of dimethyl-



$$2\ \mathrm{Me_3Si\cdot} \longrightarrow \mathrm{Me_3SiH} + \mathrm{Me_2Si{=}CH_2}$$

$$\mathrm{Me_2Si{=}CH_2} + -\!\!\!\!+\mathrm{OH} \longrightarrow -\!\!\!\!+\mathrm{OSiMe_3}$$

silene with tert-butyl alcohol. At short reaction times, the low concentration of tert-butyl alcohol did not allow for efficient trapping of the disproportionation product. With excess tert-butyl alcohol added, the trapping occurred immediately. A value of 0.2 for kd/kc was measured at 25°C. The disproportionation process must be very fast since the combination reaction is near the diffusion controlled limit ($k_c = 5.5 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$).

Other examples of disproportionation of free silicon radicals in solution are found in the literature (89,90,91). Further elaboration on them is not necessary.

Evidence for the disproportions of silicon radicals in the gas phase comes from some early work of Davidson and Lambert with trimethylsilane (92,93). Pyrolysis of trimethylsilane in a quartz stirred-flow reactor between 670°C and 758°C gave 1,3-dimethyl-1,3-disilacyclobutane and tetramethyl-1,3-disilacyclobutane along with hydrogen and methane. The intermediate silenes that characteristically give 1,3-disilacyclobutanes (94) were accounted for by a mechanism involving bimolecular disproportionation.

$$\cdot CH_2SiMe_2H \quad + \quad HMe_2Si\cdot \quad \longrightarrow \quad Me_3SiH \quad + \quad MeHSi{=}CH_2$$

$$\cdot CH_2SiMe_2H \quad + \quad Me_3Si\cdot \quad \longrightarrow \quad Me_3SiH \quad + \quad Me_2Si{=}CH_2$$

$$\cdot CH_2SiMe_2H \quad + \quad \cdot CH_2SiMe_2H \quad \longrightarrow \quad Me_3SiH \quad + \quad Me_2Si{=}CH_2$$

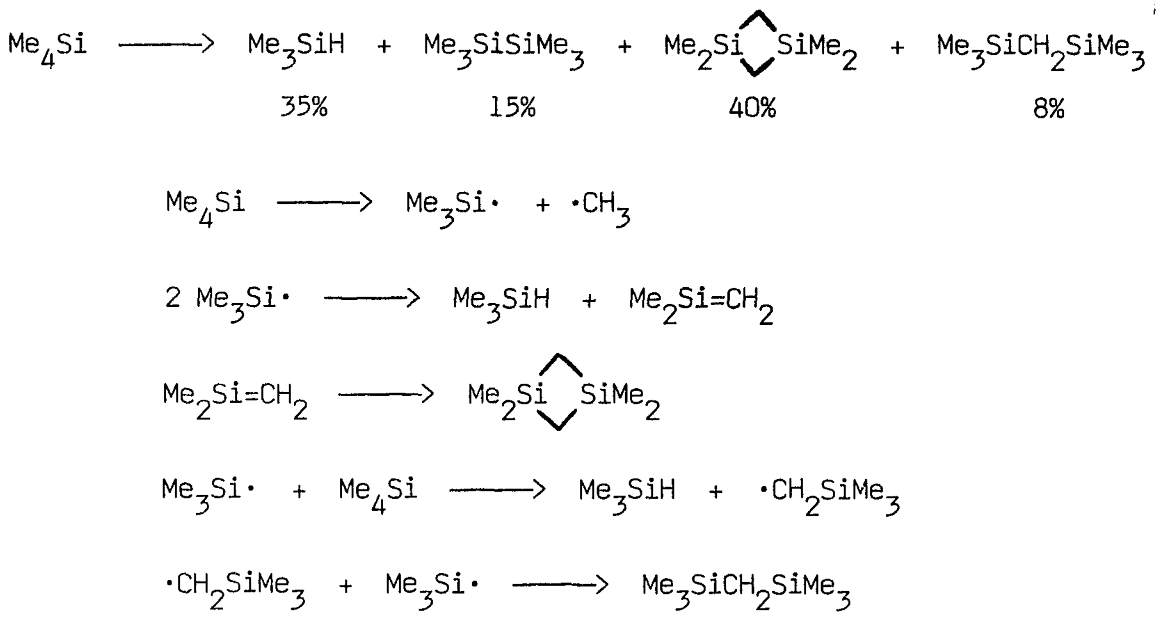
Other workers investigating the decomposition of trimethylsilane have suggested unimolecular formation of the silenes via homolytic bond cleavages (95,96). This would require loss of another methyl or hydrogen radical from the first-formed radical intermediate. Very recently, Ring *et al*. (97) have reported such a unimolecular disproportionation. The radicals were generated from dimethysilane using a single pulse shock tube reactor between 677°C and 1027°C. Reaction times were approximately 300 μsec.

$$\cdot CH_3 \quad + \quad Me_2SiH_2 \quad \longrightarrow \quad \cdot CH_2SiMeH_2$$

$$\cdot CH_2SiMeH_2 \quad \longrightarrow \quad CH_2{=}SiH_2 \quad + \quad \cdot CH_3$$

Clifford and coworkers (98) investigated the flow pyrolysis of tetramethylsilane between 537° and 707°C (0.1-30 mm Hg). Moderate yields of trimethysilane (35%), tetramethyl-1,3-disilacyclobutane (40%), hexamethyldisilane (15%), and tetramethyl-2,4-disilapentane (8%) were formed as the major products along with methane and ethane gas. Scheme 12 outlines the proposed mechanism that accounts for these products. The activation energy for the homolysis of the $Si{-}CH_3$ bond was measured as 67.6 kcal/mol. This value is much lower than the bond dissociation

Scheme 12



energy of 89.4 kcal/mol calculated by Walsh (99). Based on the product data, a kd/kc value of 1.2 was estimated. Notice that formation of the silene occurs via bimolecular disproportionation.

Baldwin _et_ _al_. used computer-aided numerical calculations to reinvestigate the kinetics of the thermal decomposition of trimethylsilane and tetramethylsilane (100). The experiments were carried out using the "pulsed stirred-flow" technique between 567°C and 782°C. They arrived at two rather long chain mechanisms in which formation of the silene intermediate occurs via unimolecular homolysis of either an methyl-silicon or a hydrogen-silicon bond (89 kcal/mol and 90 kcal/mol, respectively (99)).

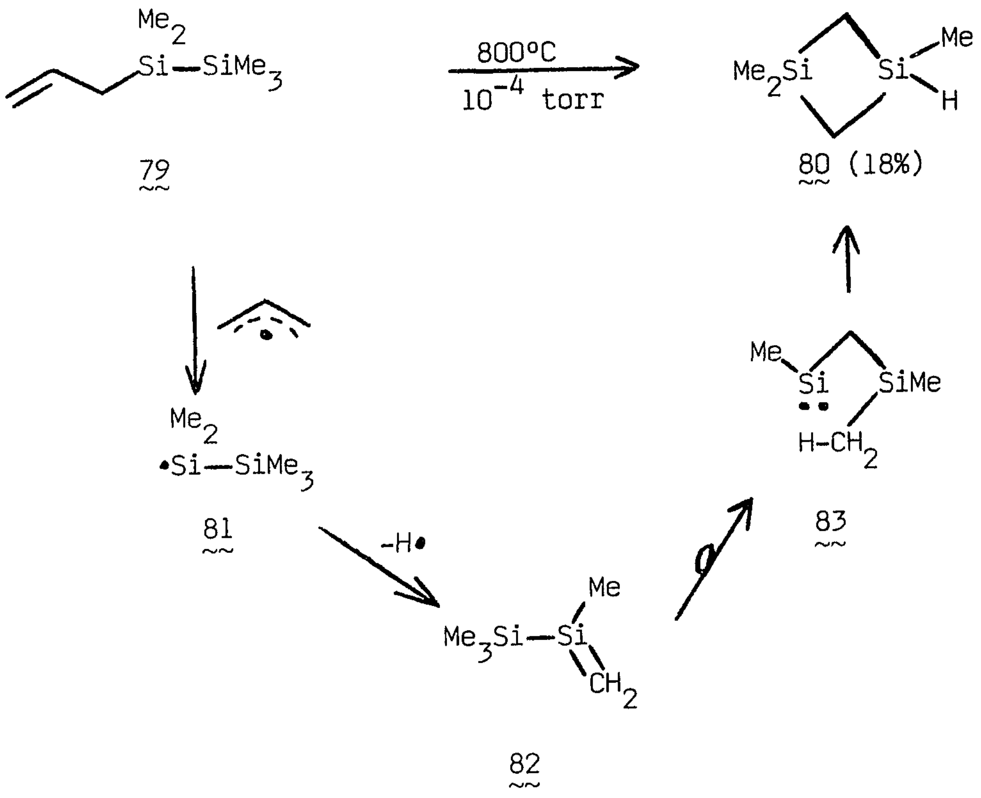
$$Me_3SiCH_2\cdot \longrightarrow Me_2Si{=}CH_2 + CH_3\cdot$$

$$Me_2HSiCH_2\cdot \longrightarrow Me_2Si{=}CH_2 + H\cdot$$

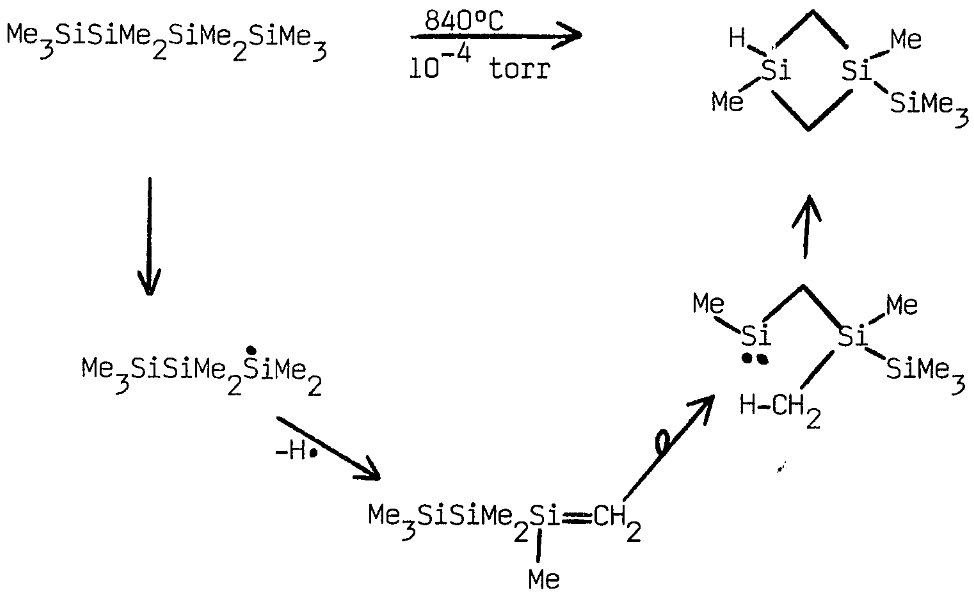
$$Me_2HSiCH_2\cdot \longrightarrow MeHSi{=}CH_2 + CH_3\cdot$$

Disproportionation of a silyl radical generated at 800°C by homolysis of a silicon-allyl bond has been reported (3). Pyrolysis of 1-allylpentamethyldisilane 79 gave trimethyl-1,3-disilacyclobutane 80 in 18% yield. 80 Was reported to have come from rearrangement of the silene which was formed upon disproportionation of pentamethyldisilanyl radical (Scheme 13). Similarly, Barton *et al*. showed that pyrolysis of deca-

Scheme 13



methyltetrasilane gave heptamethyltrisilanyl radical which underwent disproportionation to the silene (4). Subsequent silene to silylene rearrangement gave the observed product. Further discussion on the silene to silylene rearrangement (82 to 83 Scheme 13) will be given in the Results and Discussion section.



Cyclization of Other Heterocentered Radicals

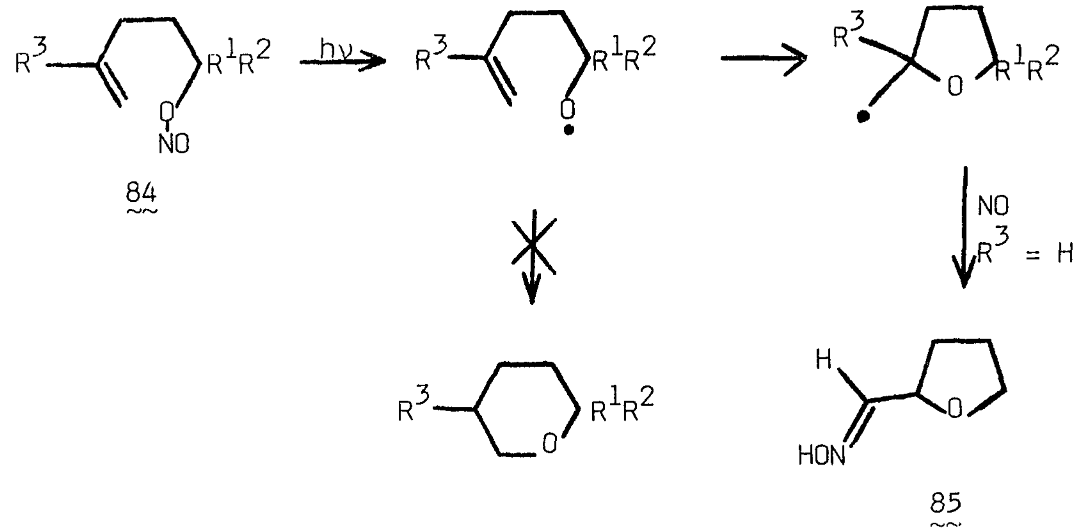
Just as with silicon, intramolecular additions of other heteroatomic radicals have been studied much less than those cyclizations involving carbon radicals. Much of the work with heteroatomic free radicals has been done since the middle nineteen sixties. In general, these species are governed by the same features controlling carbon radical cyclization. In this section, a brief review of the literature on alkoxyl and germanium radicals will be considered. Surzur has published an excellent review on the intramolecular addition of other heteroatomic radicals including sulfur, nitrogen, phosphorus, and peroxy radicals (2).

Alkoxyl radicals

Many of the early attempts to cyclize alkoxyl radicals failed. One of the main problems was the tendency of alkoxyl radicals to abstract allylic hydrogen (101). Also, many of the radical precursors themselves undergo cyclization via ionic pathways (102).

Most of the work on intramolecular addition of alkoxyl radicals has been done by Surzur and coworkers (103). Several substituted nitrite esters were found to cyclize under photolytic conditions. Yields of oxime 85 were usually between 50% and 60% when run at low concentrations in benzene (104,105) (Scheme 14). Products derived from the six-membered

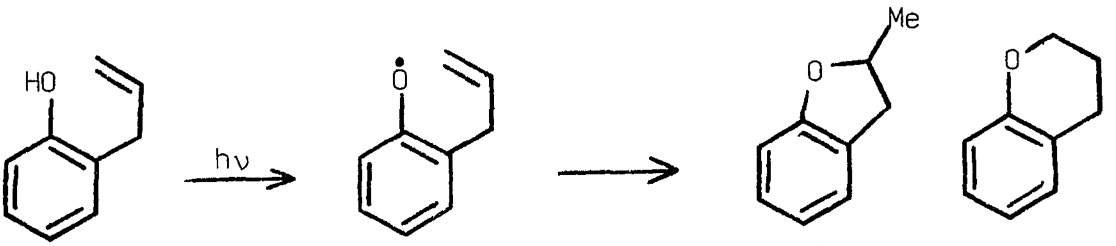
Scheme 14



ring radical were not detected, even for R_3 = Me which gave some six-membered ring product in the 5-hexenyl case (Scheme 4 and Table 1). Rieke and Moore (106,107) obtained similar results in ESR experiments on alkoxyl radicals generated by the identical method. All attempts to observe the six-membered ring cyclized product by varing the concentration of starting nitrile easter **84** were unsuccessful. The highest yield of oxime **85** ($R_1 = R_2 = R_3$ = H) was 68%. Neither Rieke and Moore or Clerici *et al*. (108) were able to isolate any cyclic products using lower homologs of **84**.

The results on alkoxyl radical cyclization seem to parallel those of the all carbon 5-hexenyl radical. Thus, extending the Beckwith rules of radical cyclization to include simple alkoxyl radical is valid.

There is evidence that aryloxyl radicals also cyclize in a Beckwith *exo*-fashion. For example, photolysis of substituted 2-allyphenol gave benzofuran **86** and chroman **87** in a 90:10 ratio (109,110). The ratio was found to vary only slightly with the substituent on the ring (111).



86 **87**

(90) : (10)

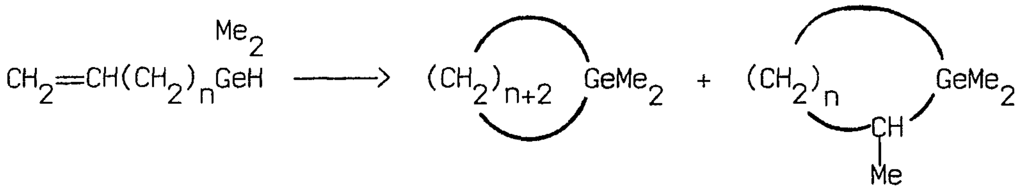
Germanium radicals

Some recent work on the intramolecular addition of alkenyldimethylgermanium radicals has raised questions about extension of the Beckwith rules beyond row one radicals. Mochida and Asami (112), and Mochida and Miyagawa (113) have investigated the cyclization of germanium radicals of various chain lengths generated by free radical abstraction of the corresponding hydrogermane. The reactions were carried out in sealed tubes with benzene solvent and azobisisobutyronitrile (AIBN) or dibenzoyl peroxide (BPO) as iniators at 42°C or 80°C, respectively. The results are summarized in Table 12. The predominant direction of cyclization is clearly endo, which is exactly opposite that of analogous carbon radicals. However, this is in keeping with the studies of Ingold et al. (72) on silyl radicals. Mocida and Asami concluded that endo-closure is preferred for intramolecular addition of germanium radicals because of the stability of the incipient secondary radical and, to a greater extent, the increased carbon-germanium bond length. The longer carbon-germanium bond distance enables the cyclization to bypass the geometric restraints that force the analogous carbon system to cyclize in an exo-fashion.

Table 12. Ring closure reactions of ω-alkenyldimethylgermanes

N	**ii**[a]	mmol (Initiator)	**iii**[a]	% Yield Based on consumed **i**[a]
2	0.007	(AIBN)	0	2.3
	0.112	(BPO)	0	17.4
3	0.042	(AIBN)	trace	70.6
	0.042	(BPO)	trace	80.8
4	0.108	(AIBN)	0.016	27.9
	0.201	(BPO)	0.051	90.3
5	0.008	(AIBN)	0	17.8
	0.041	(BPO)	0	12.5

[a]



i **ii** **iii**

RESULTS AND DISCUSSION

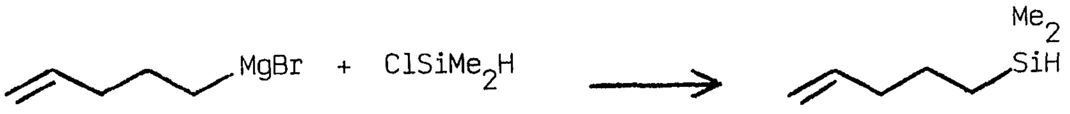
There were two main questions that this study on alkenylsilyl radical intramolecular additions had hoped to address. One question was whether the so-called Beckwith rules could be extended to include silicon-centered radicals. In other words, do alkenylsilyl radicals cyclize to the kinetic _exo_-product, as is well known for carbon radicals, or do they cyclize in an _endo_-fashion? After the work reported in this dissertation was completed, Ingold and coworkers (72) published an ESR study that suggest a preference for _endo_-closure of silyl radicals. The other question was; if silyl radicals do cyclize regioselectively, will the techniques used to generate the radical and acquire cyclic products be synthetically useful? The work reported herein will answer both of these questions.

Generation and Cyclization of Alkenylsilyl and Alkenyldisilanyl Radicals in Solution

At the inception of this project, there existed only a single mention (in a review article) of a systematic study of "simple" alkenylsilyl radical cyclization (71). However, those systems possessing aromatic rings as the alkenyl unit were known (59,60,61). Sakurai (71) reported that di-_tert_-butyl peroxide initiated intramolecular hydrosilylation of substituted 4-pentenylsilane produced a confusing picture of substituent control of both regiochemistry and yield (see Historical section Table 9). This work has never been published in a complete form. Very recently, and after the work reported here was completed, Ingold, Davies _et al_. (72) published a report which describes an ESR study of the radicals formed during photolysis of di-*tert*-butyl peroxide (DTBP) and several alkenyldimethylsilanes. No evidence for the cyclization of 3-butenylsilyl radicals was found, and in all cases intermolecular radical addition was found to predominate. However, it was demonstrated that 4-pentenylsilyl radicals strongly favored *endo*-cyclization over *exo*-cyclization (see Historical section Table 10). Since in only one case were products actually isolated and identified, the findings reported in this section will be complementary and supportive of the conclusions of Ingold and coworkers with regard to pentenylsilyl radical cyclizations and will present a new picture of butenylsilyl radical intramolecular reactions. Also, to be reported in this section is a new picture of cyclopropyldimethylsilyl radical (58) and allyldimethylsilyl radical.

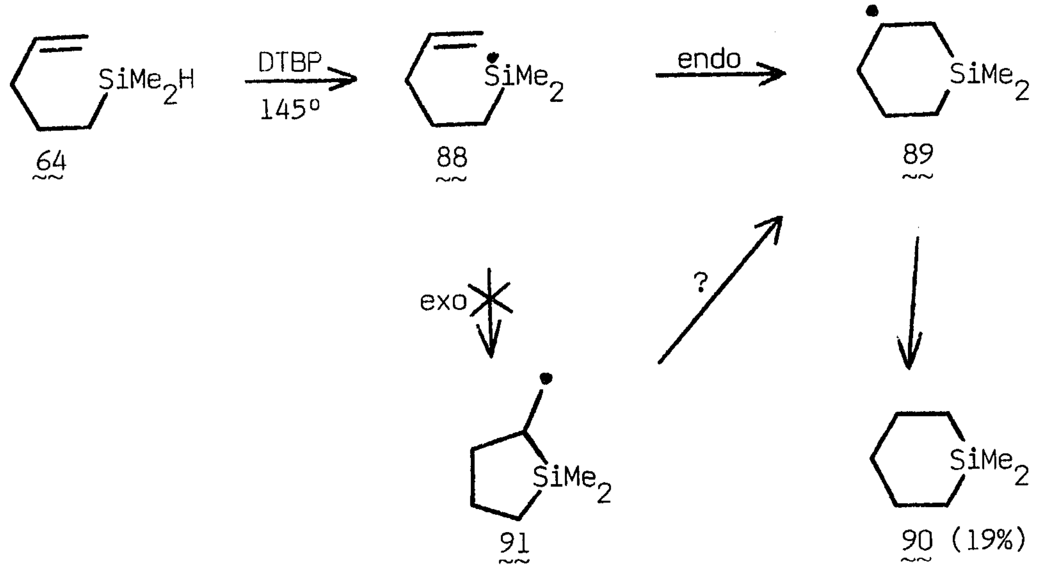
The abstraction of a silyl hydride by a *tert*-butoxy radical, generated thermally from DTBP, was used to prepare the alkenylsilyl radicals in solution. The reactions were carried out in degassed sealed pyrex ampoules with either benzene or *tert*-butylbenzene as the solvent. No effect of solvent change was noted.

In order to provide a close comparison with the classic 5-hexenyl radical, hydrogen abstraction from the analogous silyl hydride **64** was effected. 4-Pentenyldimethylsilane **64** (114) was prepared by Grignard coupling of 4-pentenylmagnesium bromide and dimethylchlorosilane in 70%



64

yield. Heating a 1% solution of 64 and DTBP (2:1) in benzene at 145°C for 4 hours afforded a product mixture which contained, in addition to 48% unreacted 64, a 19% yield (GC) of a sole, major volatile product, 1,1-dimethyl-1-silacyclohexane 90 (114,115). Compound 90 was isolated pure by preparative GC, and its spectral properties matched with those of an authentic sample of 90. Therefore, it appears that under these conditions radical 88 undergoes cyclization in an *endo*-fashion. Careful examination of the product mixture by GC-mass spectra (GCMS) revealed no significant products isomeric with the major product.

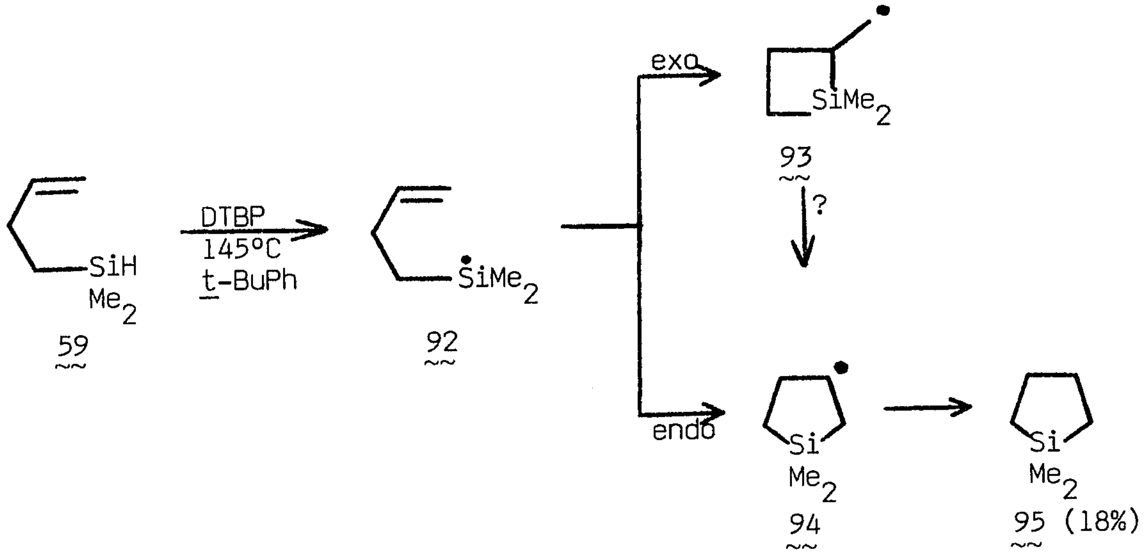


Although the *endo*-cyclization of 88 is an apparent violation of the Beckwith rules, caution must be exercised in interpretation of this result as it is possible that initially formed *exo*-radical 91 rearranges to *endo*-radical 89. Such a rearrangement seems unlikely since radical 89 (and not 91) has been identified as arising from 64 in the ESR studies of

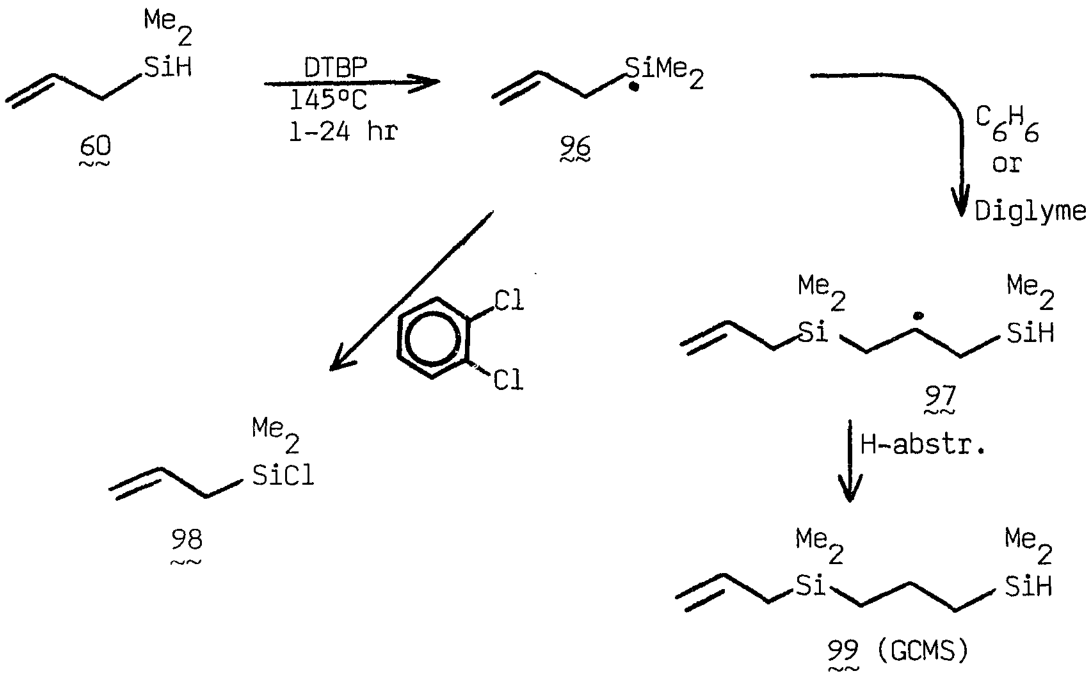
Ingold and coworkers (72). Therefore, it is reasonable to assume that *endo*-cyclization of **88** has occurred in a dramatic reversal from the behavior of the analogous carbon-centered radical.

A similar procedure was used to examine the next lower homology. Thus, when 3-butenyldimethylsilane **59** (114) was heated at 145°C in the presence of DTBP for 12 hours, only one major volatile product was isolated by preparative GC along with 9% of unreacted **59**. The compound was identified as 1,1-dimethylsilacyclopentane **95** (114,115) which was present in 18% yield by GC. The spectra of **95** exactly matched that of an authentic sample prepared by magnesium-induced coupling of 1,4-dibromobutane and dimethyldichlorosilane. The GCMS data revealed no other isomeric products. Therefore, in contrast to Ingold and coworkers (72), who saw no evidence of intramolecular reaction of radical **92**, it appears that under the reaction condition reported here, **59** not only cyclizes, but does so in an *endo*-fashion. One must again exercise caution in interpreting this result due to the possibility of rearrangement of *exo*-radical **93** to *endo*-radical **94**. Unfortunately, there seems to be no definitive results on the cyclization of 4-pentenyl radicals in the literature for comparison of **59** with the carbon analog (see Historical section on 4-pentenyl radicals).

Several attempts to observe cyclic products of allyldimethylsilyl radical **96** failed. Based on GCMS data, the only product formed when a solution of allyldimethylsilane **60** and DTBP (2:1) in *tert*-butylbenzene or diglyme was heated up to 24 hours had a molecular weight equal to

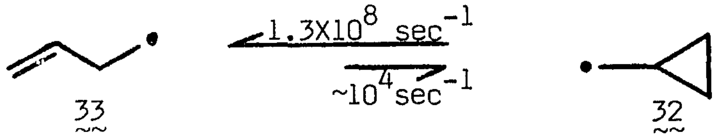


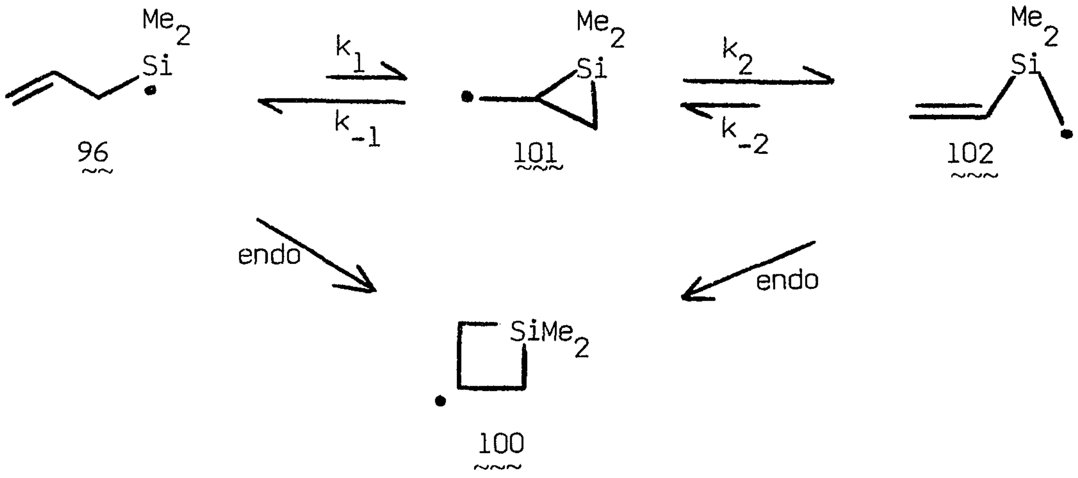
twice that of 60. Such a compound can be accounted for by intermolecular attack of the radical 96 on 60 followed by hydrogen abstraction. Ingold and coworkers (72) observed this type of intermolecular addition in their ESR studies (see Historical section Table 10). The dimer product of 60 was never present in high enough yield to make isolation possible. When the reaction was carried out in o-dichlorobenzene as the solvent, allyldimethylchlorosilane 98 was one of the major products along with chlorobenzene as evidenced by GCMS. Since it is well-known that silicon-centered radicals abstract halogens from haloaromatic compounds (30), this is taken as evidence for having formed radical 96.



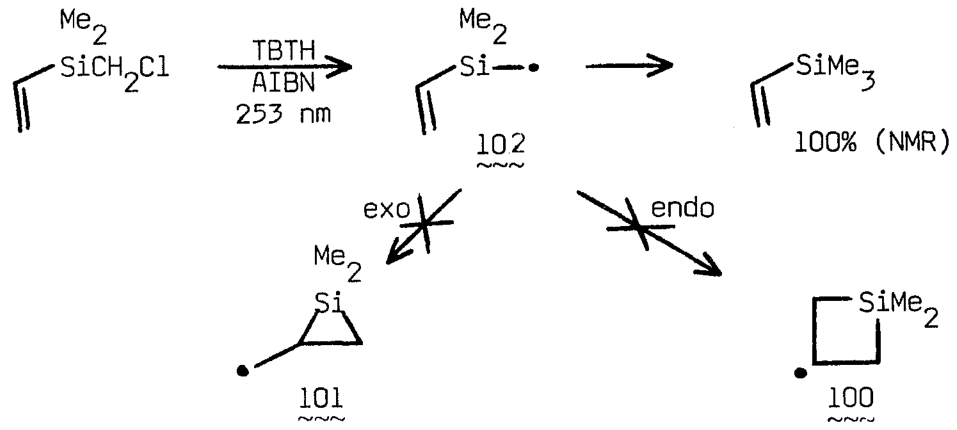
The apparent reluctance of radical 96 to cyclize is similar to that which is known for the 3-butenyl carbon radical. In other words, observation of cyclized products from the 3-butenyl radical 33 is not possible due to the facile β-cleavage of the cyclopropyl carbinyl radical 32. Therefore, analogous cyclization of silyl radical 96, k_1, may be much slower than the reverse β-cleavage, k_{-1}.

Alternatively, allyldimethylsilyl radical 96 could cyclize to silacyclobutyl radical 100. In fact, *endo*-closure of 96 should be the preferred mode of cyclization. On the other hand, if *exo*-cyclization



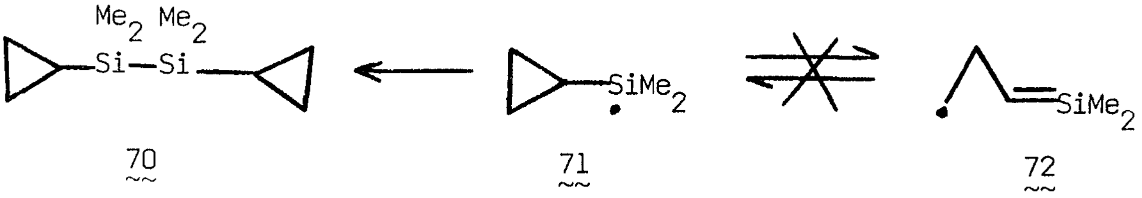


were to occur and k_2 is faster than k_{-1}, then α-silyl radical 102 would be formed by cleavage of the weaker carbon-carbon bond (99,116). The absence of trimethylvinylsilane (GCMS analysis) suggests that 102 was not formed. However, the absence of trimethylvinylsilane is not conclusive evidence since Wilt's (73) work would support cyclization of 102 to silacyclobutyl radical 100. Careful examination of the GCMS data revealed no silacyclobutyl products or dimer of allyldimethylsilyl radical 96. To better address the issue, radical 102 was independently generated. Thus, when a benzene or pentane solution of chloromethyldimethylvinylsilane (1.2% w/w) was photolyzed (rayonet, 253 nm) in the presence of tri-*n*-butylstannane (TBTH) and AIBN initiator, NMR showed quantitative



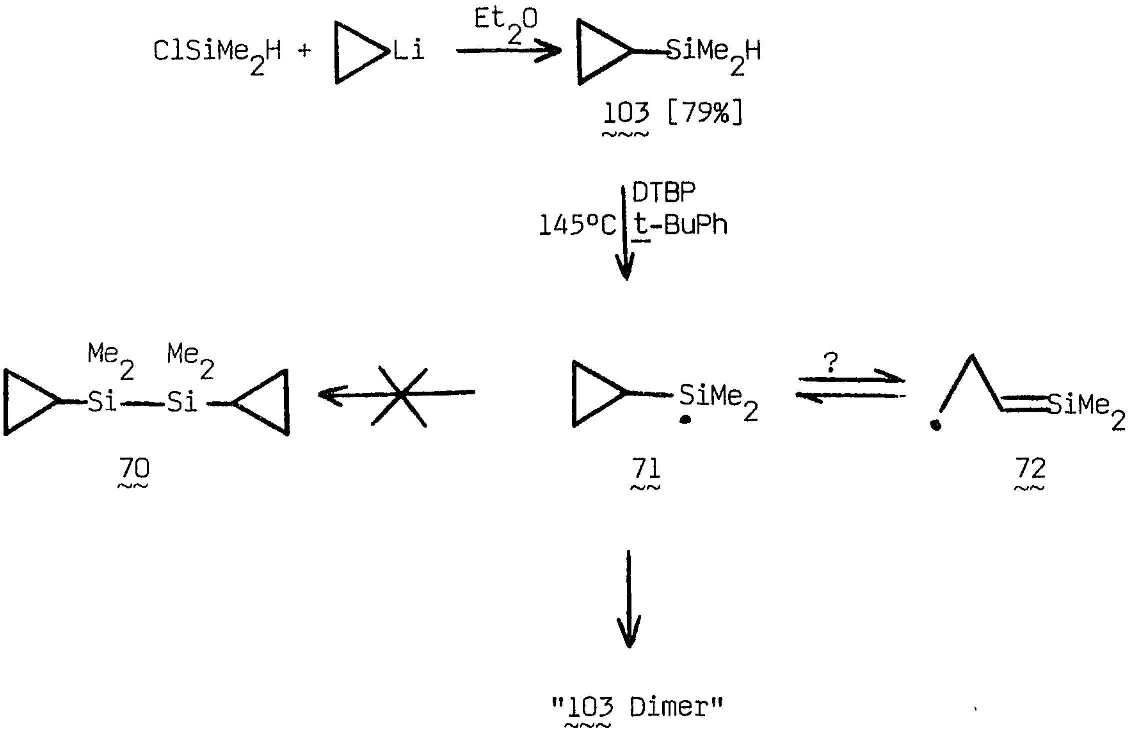
conversion to trimethylvinylsilane. Therefore, at least under the conditions reported here, hydrogen abstraction is much more competitive than *endo*- or *exo*-closure. This tends to suggest that radical 102 was not formed in the peroxide decomposition of silane 60.

The absence of a radical dimer was puzzling since similar dimers have been reported in the literature. For example, Sakurai and coworkers (58) found that cyclopropylsilyl radical 71, generated by hydrogen abstraction with *tert*-butyl peroxide at 140°C, dimerizes in good yield. No evidence for β-cleavage to 72 was reported for what is apparently a very stable radical. Having found that allyldimethylsilyl radical did



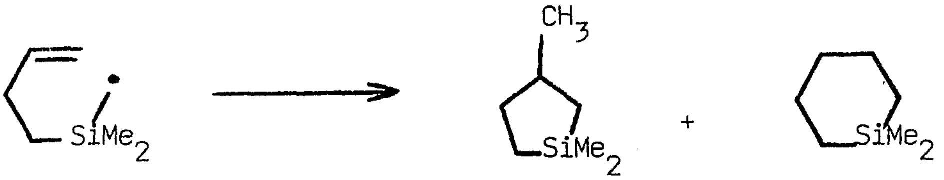
not dimerize under almost identical conditions lead to a reinvestigation of the cyclopropyldimethylsilyl radical 71.

Cyclopropyldimethylsilane 103 was prepared in 79% yield by addition of dimethylchlorosilane to a solution of cyclopropyllithium in ether (117). The reaction of 103 was then carried out as described for allyldimethylsilane 60 using DTBP initiator in *tert*-butylbenzene solvent. The only product that could be identified by GCMS other than unreacted 103 had a molecular weight equal to twice that of 103. There was no product present that had a molecular weight equal to radical dimer 70. Although the conditions used are almost identical, the results presented here do not support those previously published by Sakurai *et al*. (58).



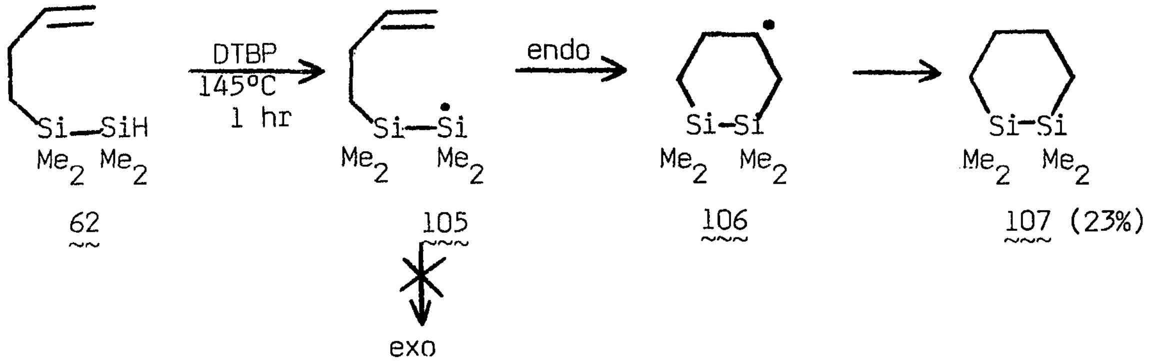
However, like Sakurai *et al.*, there was no evidence of having formed silene radical 72.

Wilt has demonstrated that substitution by a silyl group α to the radical center significantly alters the preferred mode of cyclization (73) (see Historical section on silicon radical cyclization). Thus, α-silyl radical 68 was found to give predominantly *endo*-cyclized product 90 which is opposite to that of the well studied 5-hexenyl radical (*exo*-mode). Wilt's results, coupled with those already presented in this section, created an interest in the chemistry of α-silasilyl radicals. Therefore, a systematic study on the intramolecular cyclization of disilanyl radicals was undertaken.



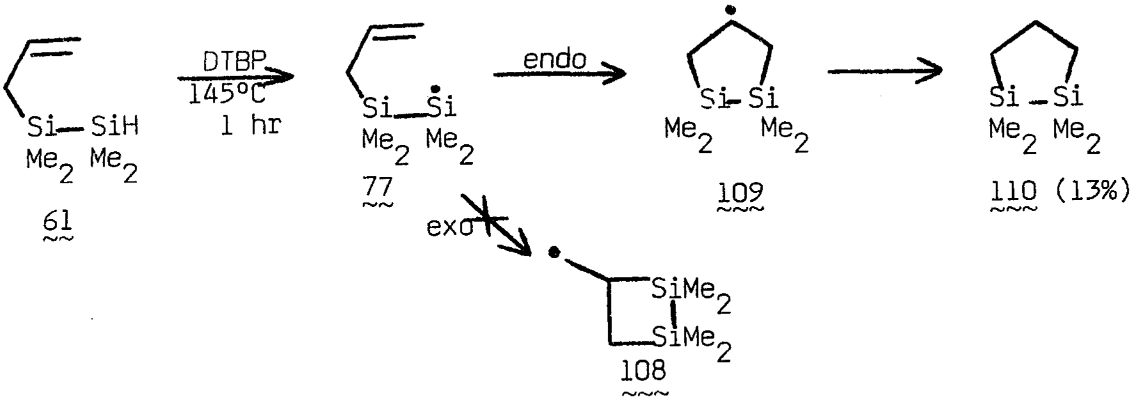
68 104 (5%) 90 (11%)

Analog extension of the 5-hexenyl system to a disilanyl radical was accomplished by synthesis of 62 via magnesium-induced coupling of 1,2-dichloro-1,1,2,2-tetramethyldisilane and 4-bromo-1-butene followed by lithium aluminum hydride ($LiAlH_4$) reduction. After heating a 1% benzene solution of 62 with DTBP for 1 hour at 145°C, only 11% of 62 remained. The sole major volatile product (23%) was isolated by preparative CG and spectrally identified as 1,1,2,2-tetramethyl-1,2-disilacyclohexane 107 (118). Thus, substitution of a second silicon in the radical chain does not deter the cyclization of 105 from an *endo*-pathway.



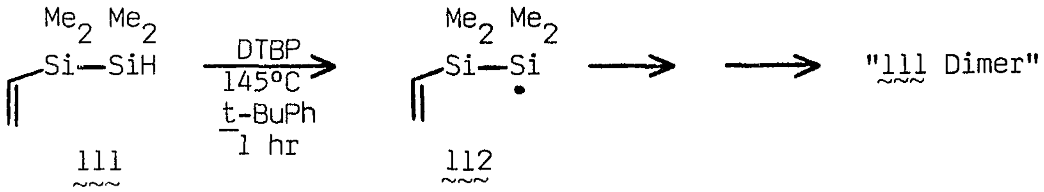
Ingold and coworkers (72) recently reported that disilanyl radical 105 gave no ESR evidence for intramolecular reaction (see Historical section Table 10). However, the results presented here clearly demonstrate that cyclization occurs and does so in an *endo*-fashion. To check the spectral assignment of 107, an authentic sample was prepared by magnesium-induced coupling of 1,2-dichloro-1,1,2,2-tetramethyldisilane and 1,4-dibromobutane. All of the spectral properties and GC retention times exactly matched.

The radical produced from hydrogen abstraction from allyldisilanyl hydride 61 was also reported (72) to provide no ESR evidence for intramolecular cyclization. However, heating a 1% solution of 61 in benzene at 145°C for 1 hour afforded a product mixture which contained, in addition to 14% unreacted 61, a 13% yield (GC) of a sole, major volatile product, 1,1,2,2-tetramethyl-1,2-disilacyclopentane 110 (118). Thus, the lower homologous disilanyl radical also undergoes apparent predominant or exclusive intramolecular π-addition in an *endo*-sense. The formation of *endo*-radical 109 may be simply another manifestation of the well-known



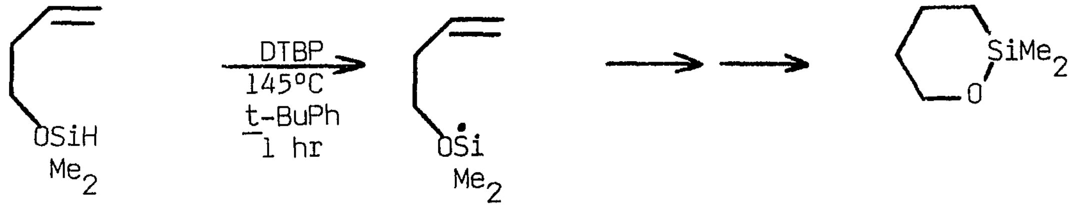
stability of β-silyl radicals as 109 possesses two β-silyl substituents. Even so, the net result is thermodynamic rather than kinetic control over cyclization.

Vinyldisilanyl hydride 111 failed to undergo intramolecular hydrosilylation when treated with DTBP in *tert*-butylbenzene and heated at 145°C for 1 hour. The only volatile product that could be identified by GCMS had a molecular weight equal to twice that of 111. Therefore, it seems reasonable to assume that radical 112, like 96 and 71, underwent intermolecular addition to starting hydride 111 followed by hydrogen abstraction. The "111 dimer" was not present in high enough yield to be isolated.



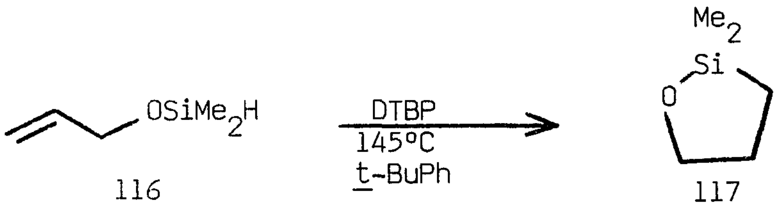
To further explore the effect of heterosubstitution at the α-position, butenyloxydimethylsilane 113 (119) was prepared in 80% yield by the reaction of 4-butenyl alcohol and dimethylchlorosilane with an added equivalent of pyridine. All of 113 was reacted after 1 hour at 145°C in the presence of DTBP, and the only major volatile product was found to be 2,2-dimethyl-2-silaoxacyclohexane 115 (120,121) formed in 24% yield. This clearly demonstrates that substitution with oxygen at the α-position does not deter the preferred endo-mode of cyclization of silicon radicals.

113 (80%)



113 114 115 (24%)

Unfortunately, attempts to establish the generality of alkenyloxysilyl radical intramolecular addition by examining the next lower homolog failed. When allyloxydimethylsilane 116 (122) was treated with DTBP and heated at 145°C for various time periods, no significant amount of cyclic products were ever observed. By GCMS a trace (<1%) of a compound having a molecular weight equal to that of 117 (70,121,122) was present. However, optimization of the yield of this product was not possible and therefore, one hesitates to draw any conclusion.



116

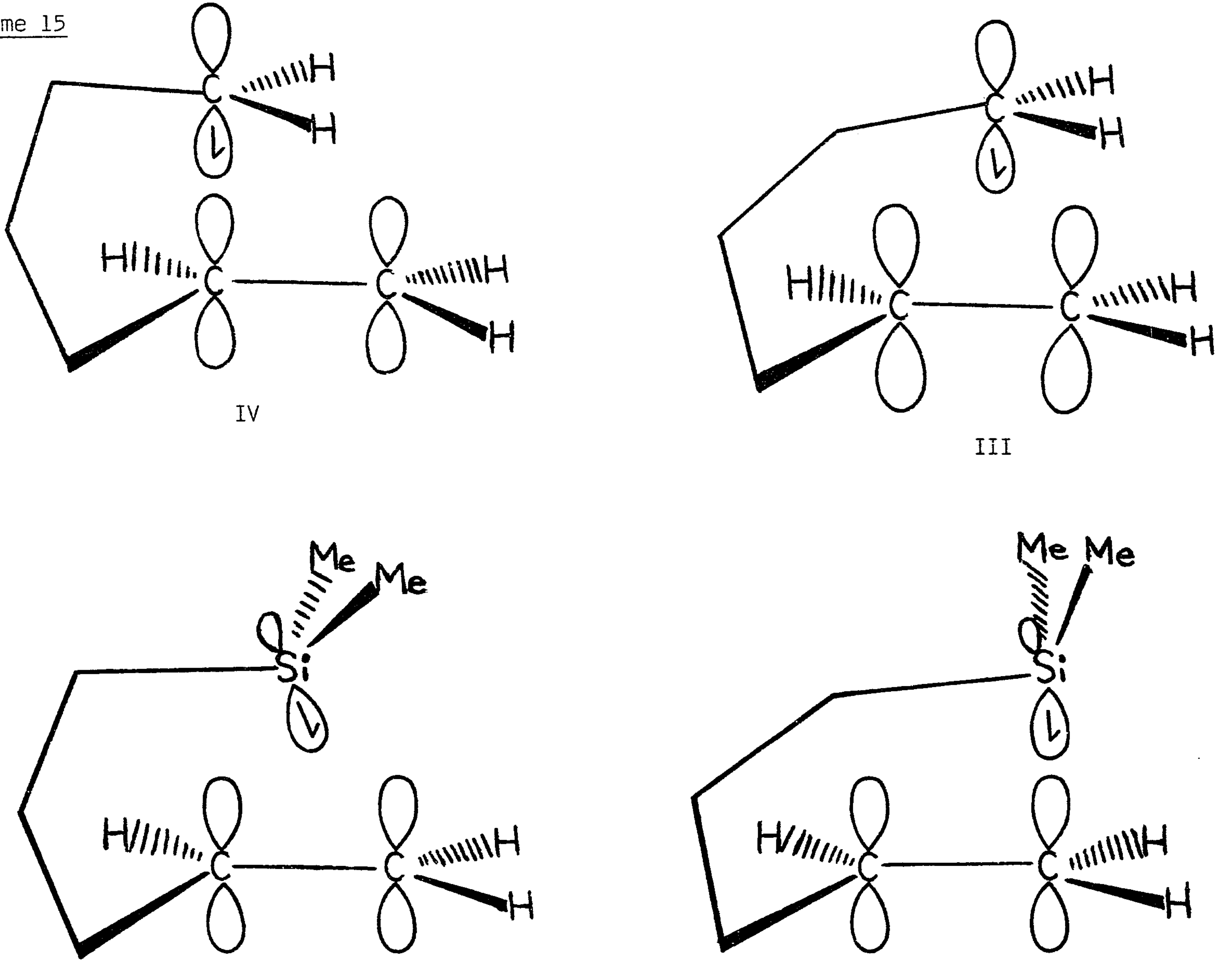
117
(not observed)

The results presented in this section coupled with those of Ingold and coworkers (72), as well as those of Mochida and Miyagawa (113) for the analogous cyclizations of alkenyldimethylgermyl radicals, make it abundantly clear that the extension of the Beckwith rules for homolytic ring closure cannot be extended beneath carbon in Group IV. Since the reasons for the contrathermodynamic behavior of the carbon-centered radicals are not totally clear (2), it is not possible to pinpoint the origins of the changeover in behavior with certainty. Certainly, the most obvious and most likely responsible differences are the increased chain length due to the longer bonds to silicon (both in the chain and for the incipient silicon-carbon bond in the activated complex), and the pyramidal configuration of silicon radicals (71) as opposed to the planar configuration of carbon radicals.

Examination of the orbital picture of the transition state geometry leading to product provides a rationale for the changeover in the regiochemistry of silyl radical cyclizations. Beckwith and coworkers (1,16) proposed that cyclization of 5-hexenyl radical gave the kinetic *exo*-product because the carbon radical could not properly align with the terminal p-orbital of the π-system (see Historical section on the Beckwith rules). In other words, the initial bonding interaction in carbon radical cyclizations must involve structure **IV** (Scheme 15). However, with silicon radicals, structure **V** is much easier to achieve because of the longer silicon-carbon bond. Therefore, the thermodynamic *endo*-mode is preferred. A transition state geometry analogous to **V** should be favored even more in the case of disilanyl radicals which are now shown to cyclize in a thermodynamic *endo*-fashion. Also, the pyramidal nature of the silicon radicals aids in relief of some of the intervening steric factors that may effect the regiochemistry. The possible role of these stereoelectronic factors has also been discussed by Ingold and coworkers (72) and have been used to explain the results of Wilt's (73) study on α-silyl radical intramolecular additions.

Having found abstraction of a silyl hydride by another radical to be a good method of generating silicon radicals, the use of radical initiators other than DTBP was examined. Both di-benzoyl peroxide (BP) and azobisiosobutyronitrile (AIBN) were tried. Only in the case of butenyloxydimethylsilane **113** with BP was any evidence of cyclization

Scheme 15



IV

III

VI

V

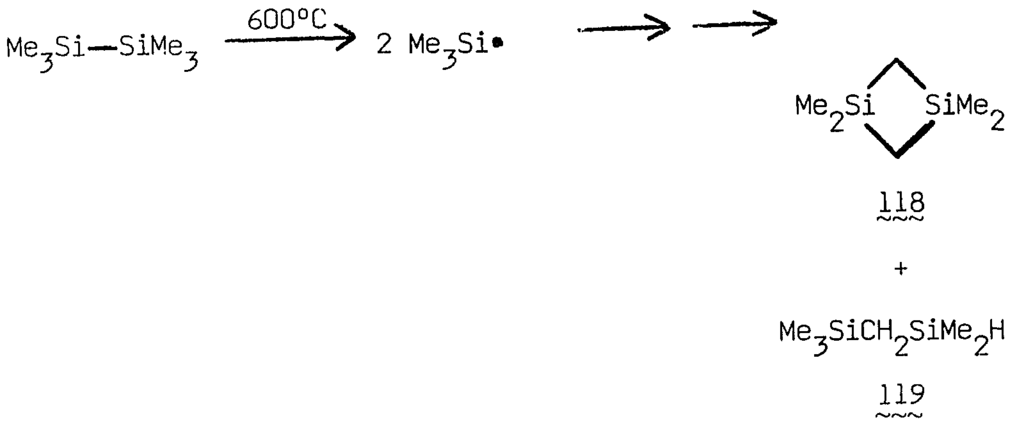
obtained. Thus, when a solution of **113** and BP (4.3:1) in *o*-dichlorobenzene was heated at 110°C for 3½ hours, NMR showed two multiplets (δ 0.55 and δ 1.20-1.90) and a new singlet in the silicon-methyl region (δ ca. 05) which were similar to those found for 2,2-dimethyl-2-silaoxacyclohexane **115**. The ratio of **113** to **115** was approximately 5:1. All other attempts to use BP at 110°C and AIBN at 45°C failed.

In summary, intramolecular addition of alkenylsilyl and alkenyldisilanyl radicals proceeds in a regiospecific *endo*-fashion when generated by hydrogen abstraction from the corresponding silane with *tert*-butoxy radical. The preference for *endo*-closure is also observed for alkenyloxysilyl radicals. These results are opposite those which are known for the well studied analogous carbon-centered radicals. Therefore, the Beckwith rules (1) can not be extended to include silyl radicals when generated under these conditions. Silyl radicals having total chain lengths of four atom units were found not to cyclize nor dimerize. Instead, these radicals appear to undergo intermolecular addition followed by hydrogen abstraction.

The average yield of cyclic product was approximately 20% based on reacted starting material. The relatively low yields are most likely due to competition between intramolecular and intermolecular reactions. Therefore, this technique as a route to silacyclic compounds does not rival the existing methods. Carrying out the experiments at infinite dilution should theoretically increase the yield of intramolecular cyclization. However, this would also greatly decrease the synthetic utility.

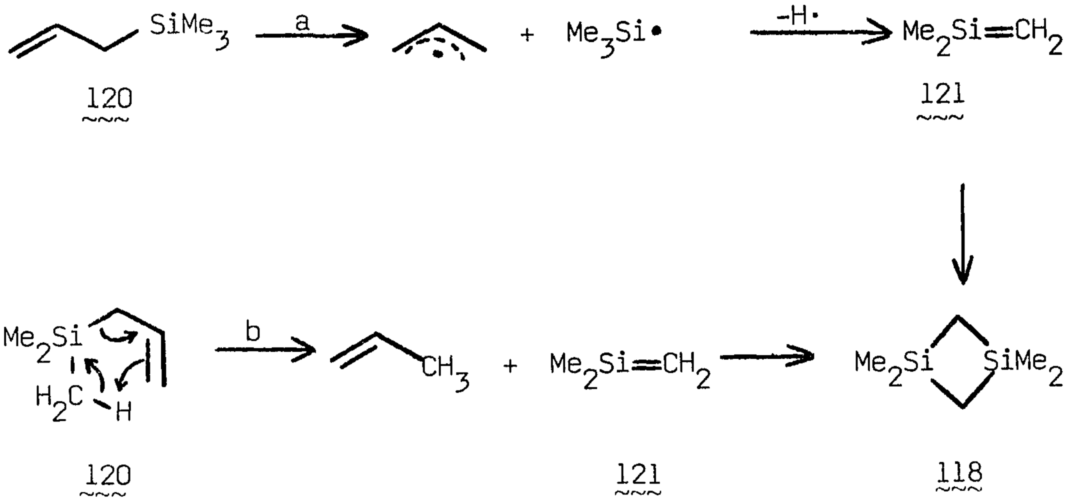
Gas Phase Generation and Reactions of Silicon Radicals

There are few good thermal silicon radical generators. However, hexamethyldisilane has been shown to decompose to trimethylsilyl radical at 600°C via homolysis of the silicon-silicon bond (56). The reaction affords 1,1,3,3-tetramethyl-1,3-disilacyclobutane **118** and **119** (123) as the major products. A complex bimolecular mechanism, which was found to be pressure dependent, was written to account for the observed products (124,125,126,127). The complex behavior of this reaction has limited its worth as a silyl radical generator.



Allylsilanes have also been reported to give silyl radicals under pyrolytic conditions. For example, trimethylallylsilane **120** gave trimethylsilyl radical when pyrolyzed in a stirred-flow system between 580° and 730°C (75). The trimethylsilyl radical was reported to then undergo bimolecular disproportionation to dimethylsilene **121** which dimerized in a head-to-tail fashion affording **118** (Scheme 16, path a). Since the

Scheme 16

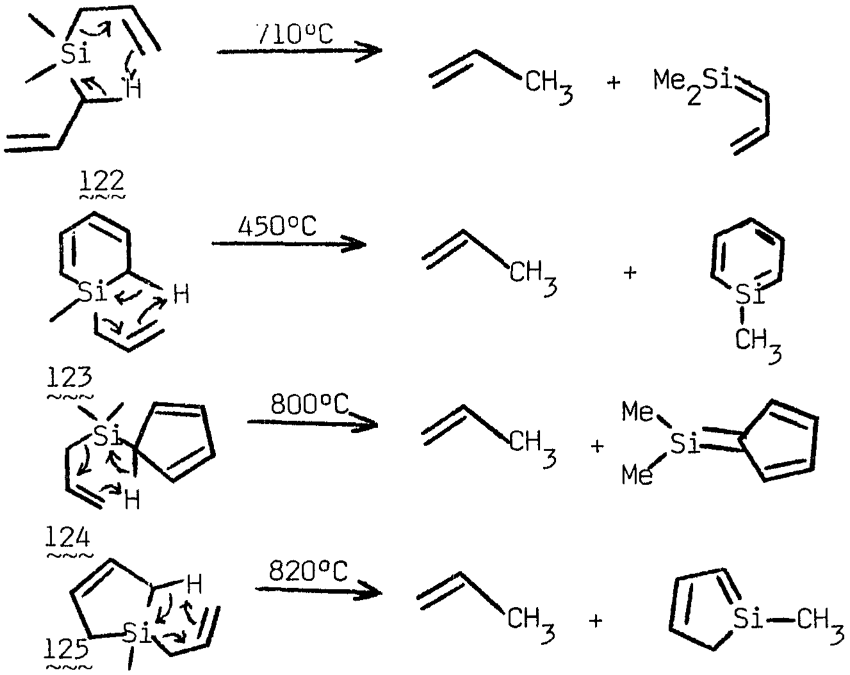


activation energy (73 kcal/mole) was found to be very close to the calculated silicon-allyl bond dissociation energy, these authors concluded that the concerted retroene elimination (path b) was a minor process (75).

Recently, however, Barton and coworkers (128) have reinvestigated the gas-phase thermal decomposition of allyltrimethylsilane using deuterium labeling and kinetic studies of variable pressure. Although homolysis of the silicon-allyl bond (path a) does occur at high pressure, the main primary mode of unimolecular decomposition for allyltrimethylsilane when pyrolysed at low pressure is via a concerted retroene elimination of propene (path b). An activation energy of 55 kcal/mol was obtained for the concerted process which is approximately 18 kcal/mol less than the silicon-allyl bond dissociation energy.

Several examples of retroene eliminations of allylsilanes possessing α-methylene groups have been published. Some examples are summarized below. The facile concerted retroene elimination of propene from allylsilanes has perhaps limited the use of these compounds as generators of silicon radicals in the gas phase.

Examples | reference



122 — 129

123 — 130

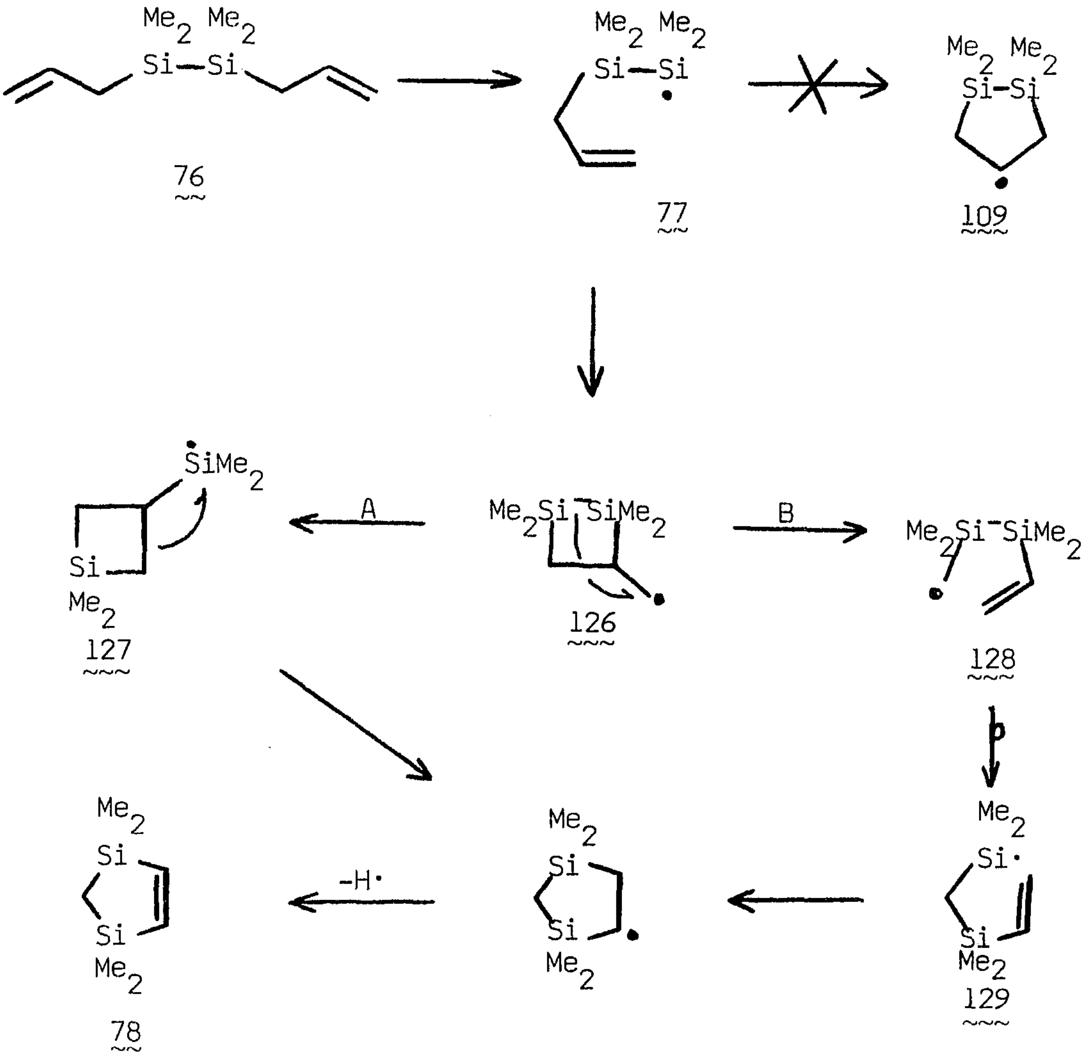
124 — 131

125 — 132

Much of the work reported in this section was stimulated by a report by Barton and Jacobi (3) on the gas phase generation of allyltetramethyldisilanyl radical 77. They found that vacuum-flow pyrolysis of 1,2-diallyl-1,1,2,2-tetramethyldisilane 76 cleanly afforded 1,1,3,3-tetramethyl-1,3-disilacyclopentene 78 in 51% yield. In order to rationalize the formation of product 78, these authors offered the mechanism outlined in Scheme 17. The first step involved formation of disilanyl radical 77 by homolytic cleavage of the silicon-allyl bond.

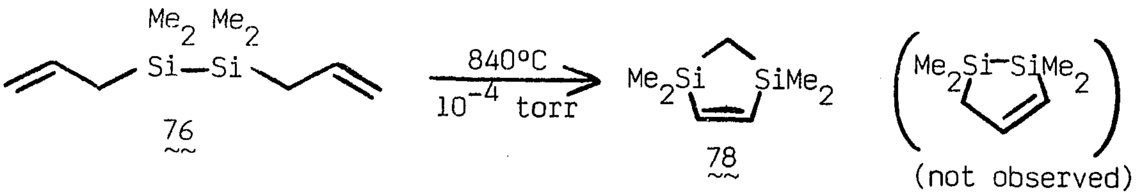
It was proposed that 77 underwent *exo*-closure to afford 126, in keeping with the Beckwith rules, and not *endo*-closure to 109 since no products of this ring system were found. *Exo*-cyclized radical 126 could conceivably go on to 78 via cleavage of the carbon-carbon bond (path B) or by silicon-silicon bond homolysis (path A) followed by combination with the carbon-centered radical and subsequent rearrangement.

Scheme 17

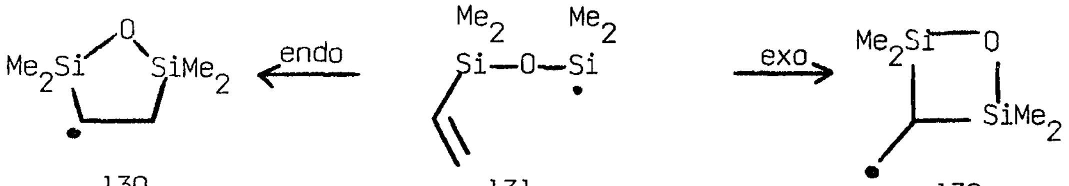


Although the reaction conditions are quite different, the results presented in the previous section of this dissertation on the generation and cyclization of radical **77** (sealed tube, 145°C, DTBP in benzene), coupled with the ESR studies of Ingold, Davies and coworkers (72), suggest that *endo*-closure to **109** should be favored over the *exo*-mode. Therefore, a reinvestigation of the thermal decomposition of 1,2-diallyl-1,1,2,2-tetramethyldisilane **76** was undertaken. The pyrolytic behavior of some other allylsilanes was also examined.

In order to establish the correctness of the product composition, the pyrolysis of **76** was repeated under similar reaction conditions as those reported by Barton and Jacobi (3). Thus, when **76** was slowly distilled through a quartz tube heated to 840°C under vacuum (1 X 10^{-4} mm Hg), only one major product was formed. The compound was isolated by fractional distillation and identified as **78**. The yield of **78** was 60%. The clean formation of rearranged 1,3-disilacyclic **78** is consistant with the previous report (2).



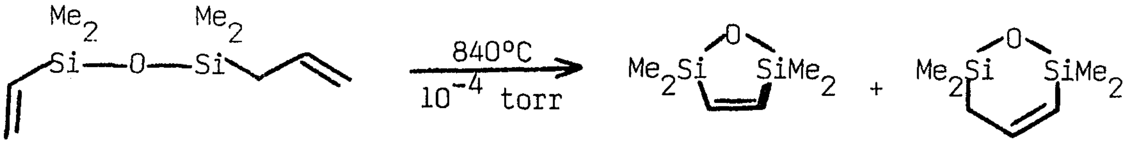
Two of the key steps in the previously reported mechanism, outlined in Scheme 17, involved either rearrangement of **128** to **129** or rearrangement of **126** to **127**. Both pathways would require cleavage of a silicon-silicon bond (bond dissociation energy approximately 80 kcal/mole (99)). If either of these rearrangements were somehow circumvented, observation of the first formed cyclic intermediate might be possible. A likely candidate for this might be the analogous disiloxanyl radical 131. The



130 131 132

rational behind this choice is that in order for a rearrangement analogous to that described by Barton and Jacobi (3) (Scheme 17) to occur, cleavage of a very strong silicon-oxygen bond (bond dissociation energy approximately 128 kcal/mole (99)) must take place. Such a cleavage is very unlikely. Therefore, one might expect to obtain products directly derivable from the ring system of *exo*-radical 132 or the *endo*-closure radical 130.

Cleavage of an silicon-allyl bond was chosen as a possible method of generating radical 131 in the gas phase. Thus, 1-allyl-3-vinyl-1,1,-3,3-tetramethyldisiloxane 133 (133) was prepared in 28% yield (yield not optimized) by sequential addition of vinyllithium and allylmagnesium bromide to a solution of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane. Upon pyrolysis of 133, two major products were formed. They were identified based on their spectral characteristics as 3,3,5,5-tetramethyl-3,5-disila-4-oxycyclopentene 134 and 4,4,6,6-tetramethyl-4,6-disila-5-oxycyclohexene 135 in 18% and 15% yield, respectively. The yields are based on 66% reacted 133. Clearly no rearrangement has

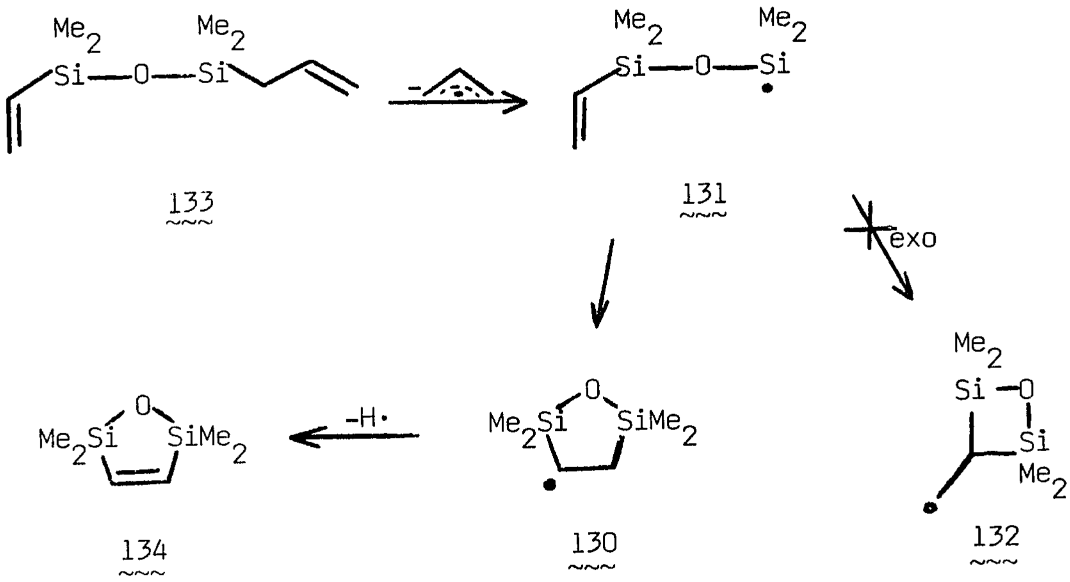


133 134 (18%) 135 (15%)

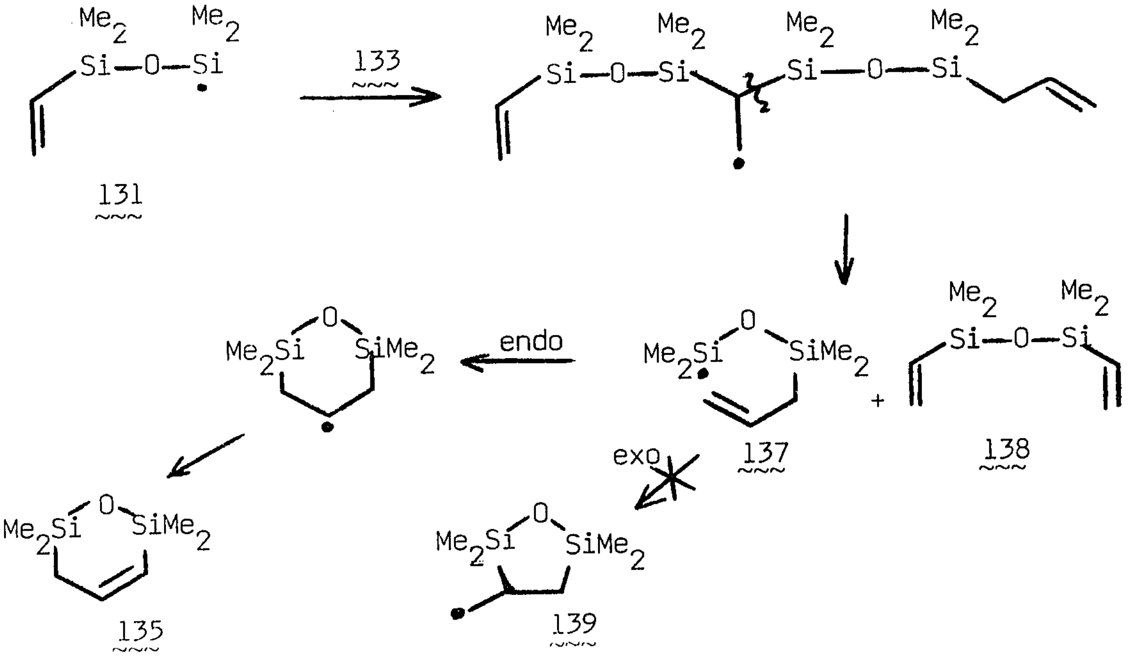
occurred in this reaction. The mechanism which is believed to best account for the observed products is given in Scheme 18. Initial homolysis of the silicon-allyl bond would afford vinyldisiloxy radical 131. *Endo*-cyclization, "anti-Beckwith" mode, of 131 followed by loss of hydrogen would give 134. Likewise, 135 is most reasonably explained by *endo*-cyclization of radical 137. The formal lose of a vinyl group must have occured by a bimolecular process involving attack of 131 on 133 to form a radical adduct which could undergo cleavage to 137 and 1,3-divinyl-1,1,3,3-tetramethyldisilane 138. The absence of products having either the 132 or the 139 ring system suggest that *exo*-closure did not take place. However, cyclization to an *exo*-radical cannot be ruled out since either the radical or its products may not be stable under the reaction conditions. While this may be true for 1,3-disiloxatane 132 (134), *exo*-radical 139 should yield a stable product. No significant amount of products were observed for either of these ring systems.

Scheme 18

Part A



Part B

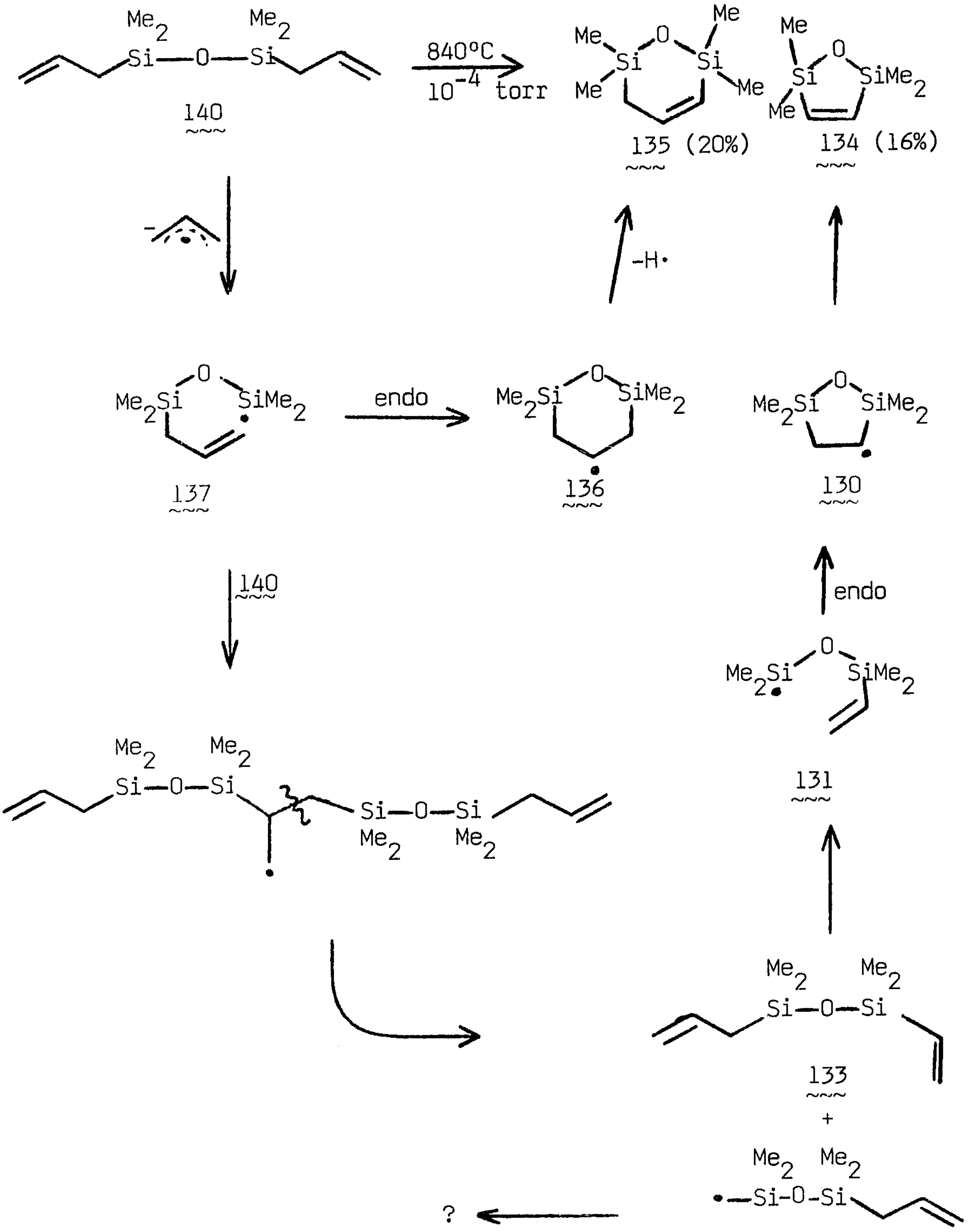


Even though it is possible that the *exo*-radicals may have rearranged to *endo*-radicals, the net result is formation of the thermodynamic rather than the kinetic cyclic products.

1,3-Divinyl-1,1,3,3-tetramethyldisilane 138, though proposed to be formed in the pyrolysis of 133 via the mechanism shown in Scheme 18 (part B), was absent from the reaction mixture. This is not too surprising since either of the radicals formed under these conditions could initiate bimolecular cleavage of one of the vinyl groups, analogous to that which gives 137, to afford radical 131. However, a pure sample of 138 (Petrarch) is stable up to 840°C in a vacuum (1 X 10^{-4} mm Hg).

In order to establish that compound 135 was formed from cyclization of radical 137 (formally a vinyl loss), the pyrolysis of 1,3-diallyl-1,1-3,3-tetramethyldisiloxane 140 (135) was carried out under the same conditions (840°C, 1 X 10^{-4} mm Hg). As predicted, 135 was formed as the major product in 20% yield based on 74% reacted 140. Also present in the product mixture was a 16% yield of 134. The mechanism given in Scheme 19 for the formation of 135 and 134 supports the contention that silyl radicals generated in the gas phase cyclize in an *endo*-fashion affording the thermodynamic product. Most likely, 134 was formed by intermolecular attack of radical 137 on the π-bond of 140 to give a radical adduct which upon cleavage would give 133 and α-silyl radical 141. Similar α-silyl radicals have been shown by Wilt (73) to undergo intramolecular

Scheme 19

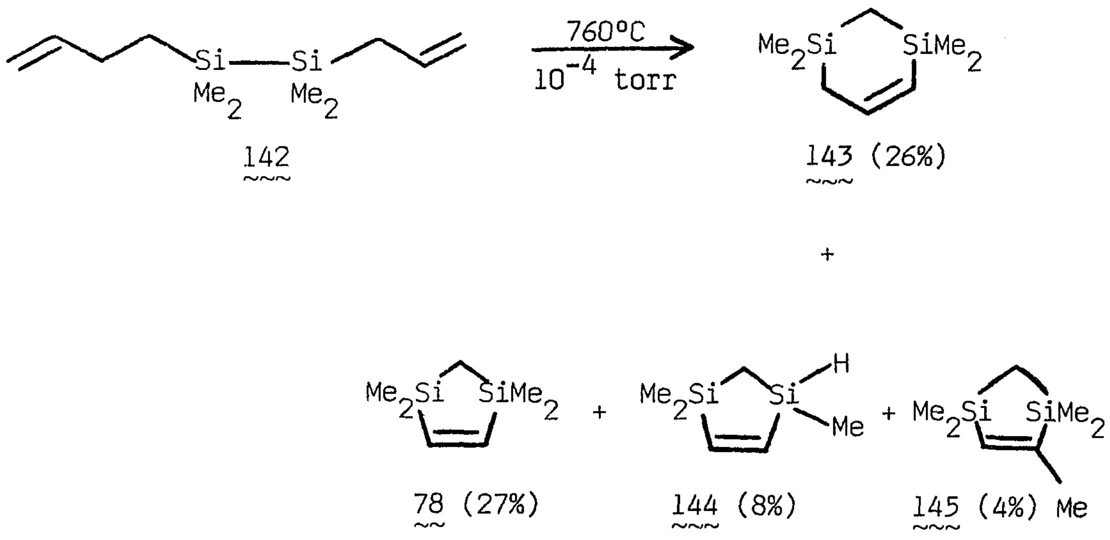

840°C
10-4 torr
140
135 (20%)
134 (16%)
-H·
endo
137
136
130
endo
140
131
133
+
?

cyclization in solution (see Historical section on Silicon Radical Cyclizations). No products having a ring system or a $C_7H_nSi_2O$ molecular formula that might be derivable from 141 could be found in the GCMS. Thermally generated α-silyl radicals will be discussed in the next section.

Based on the above examples, homolytic cleavage of the silicon-allyl bond of disiloxanes is a good method of generating a silyl radical in the gas phase. The cyclic products derived from these radicals are most reasonably explained by endo-closure followed by disproportionation. One must, therefore, conclude that silyl radicals in the gas phase also do not follow the Beckwith rules. If this is correct, the reported exo-cyclization of allyltetramethyldisilanyl radical 77 under pyrolytic conditions (3) is even more puzzling, especially when one might expect that the high temperatures used would favor thermodynamic rather than kinetic control (136).

To further explore the thermal behavior of allyldisilanes, 2-(3-butenyl)-1-allyl-1,1,2,2-tetramethyldisilane 142 was prepared by sequential magnesium-induced coupling of 4-bromo-1-butene and allyl bromide with 1,2-dichloro-1,1,2,2-tetramethyldisilane. Upon pyrolysis of 142 at 760°C in a vacuum (1 X 10^{-4} mm Hg), four major products were isolable by preparative GC. Based on their spectral properties, the compounds were identified as 1,1,3,3-tetramethyl-1,3-disilacyclohexene 143 (137), 78 (3), 1,1,3-trimethyl-1,3-disilacyclopentene 144, and

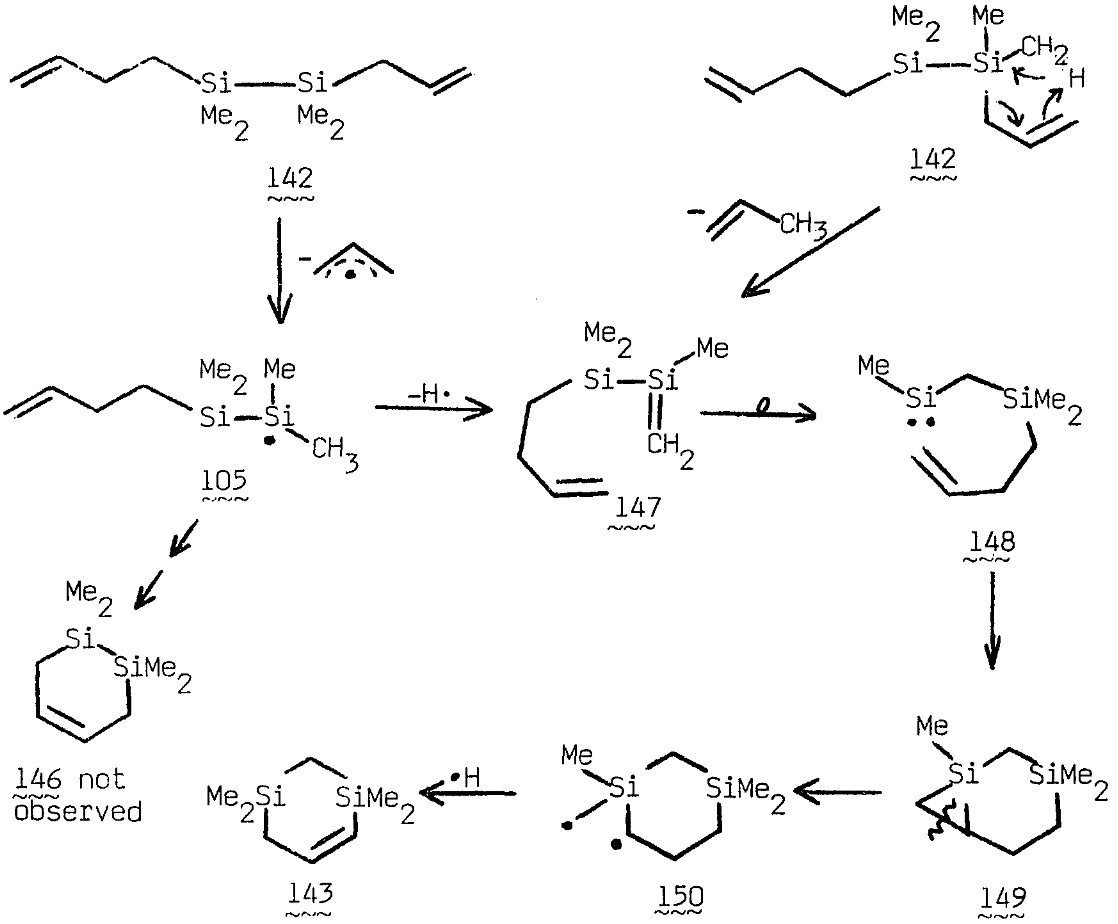
1,1,3,3,5-pentamethyl-1,3-disilacyclopentene 145. The yields of these products are given below based on 78% decomposition of 142. Although



these products may be rationalized as having formed via silyl radical cyclization followed by rearrangement (similar to that published for the conversion of 76 to 78 in Scheme 17) such a mechanism now seems unlikely. It is particularly unlikely that the contrathermodynamic exo-closure would be an important step in the transformation. An alternative route to these 1,3-disilacyclics is given in Schemes 20, 22, and 23.

It is proposed that butenyldisilanyl radical 105 is formed by homolysis of the silicon-allyl bond (Scheme 20). However, instead of undergoing intramolecular addition to the π-bond, 105 disproportionates

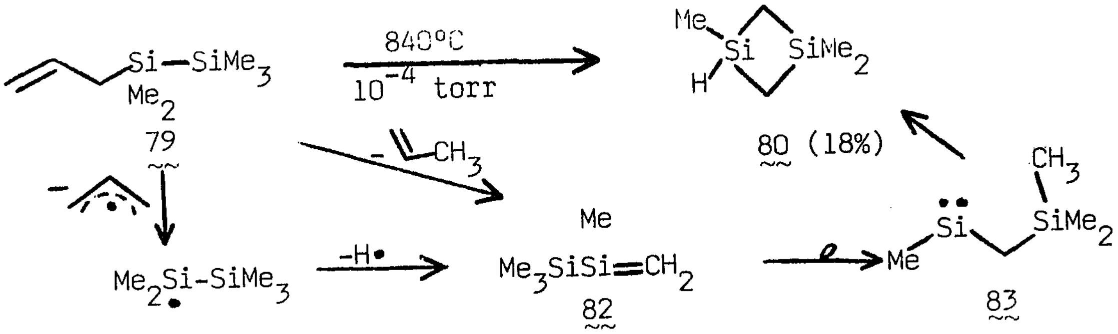
Scheme 20

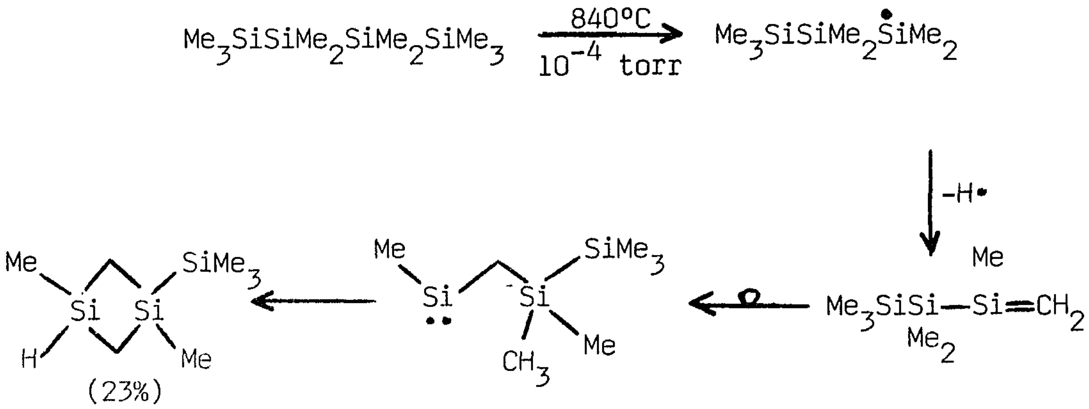


to the silene 147. Silene 147 could then undergo a 1,2-silyl shift (3,4) affording silylene 148 which upon intramolecular π-insertion would give the bicyclic disilane 149. Cleavage of the weaker carbon-carbon bond of the silacyclopropane ring followed by hydrogen migration in biradical 150 affords 143. Since each of the steps in Scheme 20 has literature precedence (*vida infra*), this mechanism seems most reasonable.

With the available data, it is not possible to differentiate between a stepwise or concerted retroene process. Based on the recent work of Barton and coworkers (128), the concerted elimination of propene from allylsilanes is an important mode of decomposition.

Disproportionation of disilanyl radicals to form silenes that undergo silene to silylene rearrangement is not an uncommon phenomenon when the radicals are generated under pyrolytic conditions. For example, Barton and Jacobi demonstrated that 80 was formed in 18% yield from 79 (3) via a similar mechanism. A direct retroene elimination to silene 82 from 79 was not ruled out in this study. Barton and coworkers have published other examples of silene to silylene rearrangement (4,138,139).

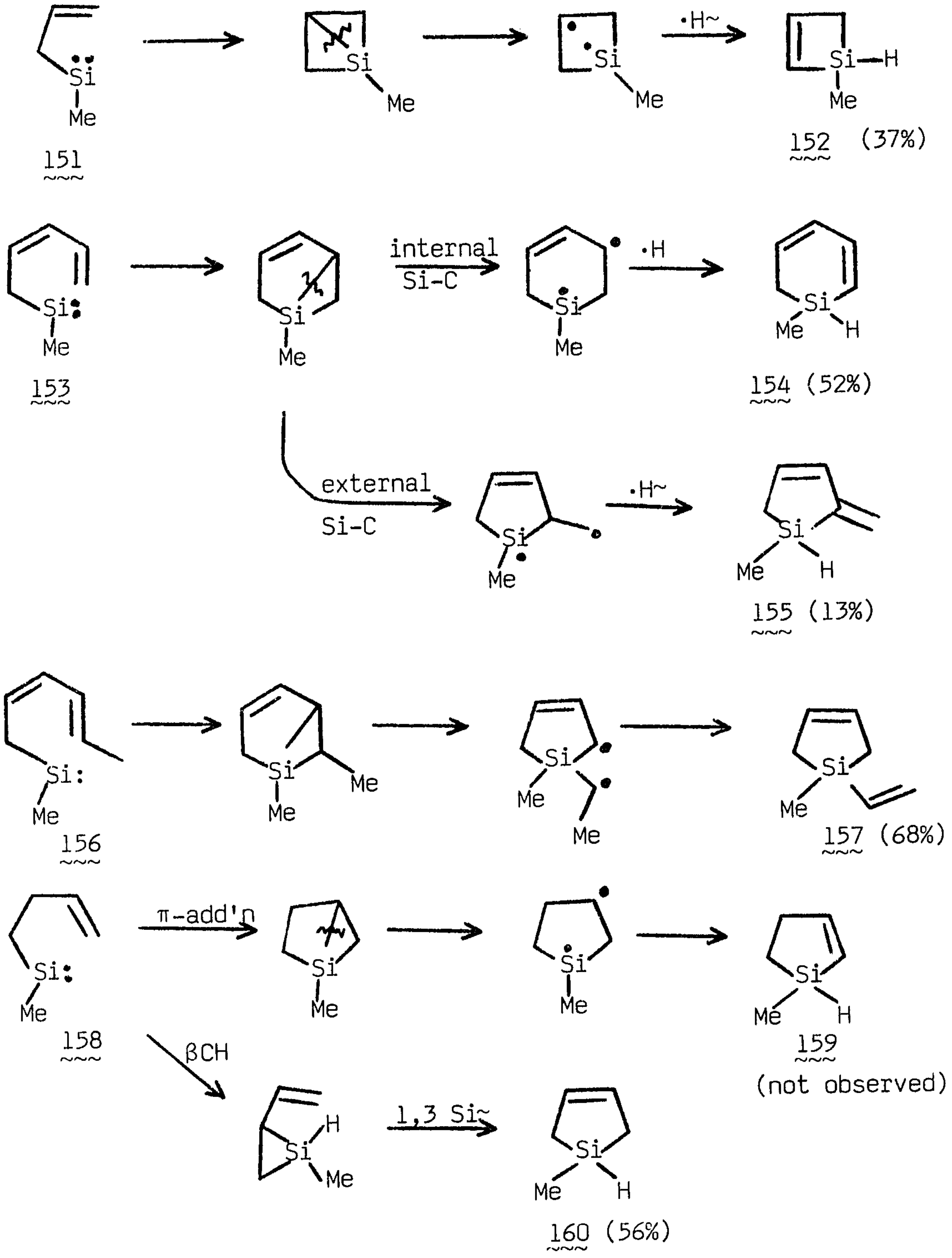




Intramolecular insertion of silylenes into π-bonds is not without literature precedent. Recently, Barton and Burns (140) reported that flash-vacuum pyrolysis generated allylmethylsilylene 151 and methyl-1-(2,4-hexadienyl)silylene 153 isomerized to the corresponding hydrido silacyclics in good yields (Scheme 21). They suggested that this occurred via initial intramolecular π-addition to form silacyclopropyl intermediates followed by homolysis of the internal silicon-carbon bond and hydrogen migration. In the case of 153, some product was also observed that would come from homolysis of the external silicon-carbon bond, e.g. 155. Substitution by a methyl group on the hexadiene moiety as in 156 altered the expected mode of cleavage and gave a product, 157, which was reported to have been formed by cleavage of the weaker carbon-carbon bond (99). Interestingly, none of the intramolecular π-addition product 159 was observed for the simpler 3-butenylmethylsilylene 158. The mechanism that was invoked to account for 56% yield of 160 was initial silylene insertion into an allylic hydrogen to form an intermediate vinylsilacyclopropane which could undergo a 1,3-silyl migration. All of the silylenes were generated at 680°C in a vacuum (1 X 10^{-4} mm Hg) by α-elimination of trimethylmethoxysilane from the corresponding methoxydisilanes.

Silene to silylene rearrangement followed by π-insertion, not *exo*-cyclization of the disilanyl radical, is offered as an alternative mechanism for the formation of 78 from 76. Thus, retroene elimination

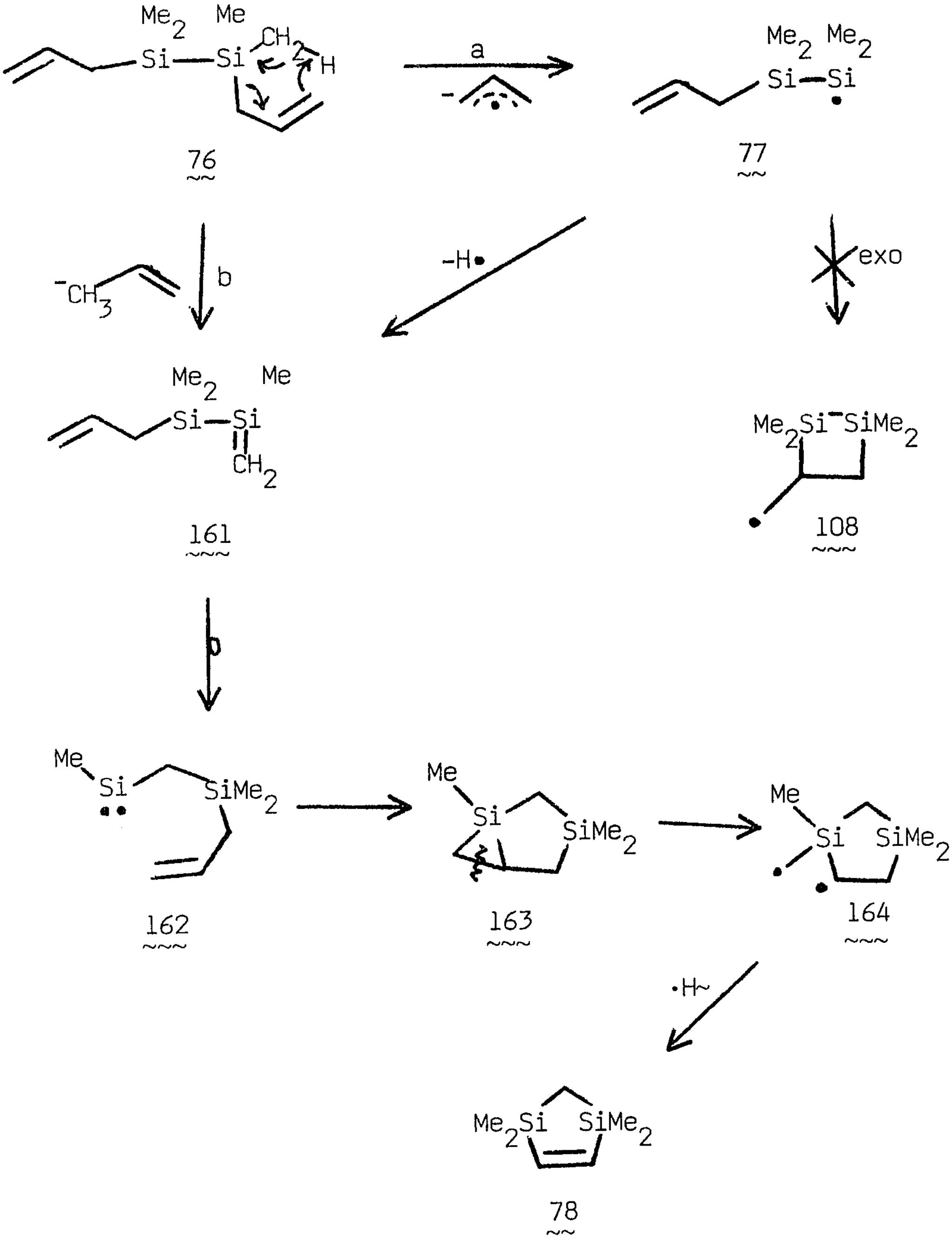
Scheme 21


Si
Me
151
Si
Me
Si
Me
·H~
Si—H
Me
152 (37%)
Si
Me
153
Si
Me
internal
Si-C
Si
Me
·H
Si
Me
H
154 (52%)
external
Si-C
Si
Me
·H~
Si
Me
H
155 (13%)
Si:
Me
156
Si
Me
Me
Si
Me
Me
Si
Me
157 (68%)
Si:
Me
158
π-add'n
Si
Me
Si
Me
Si
Me
H
159
(not observed)
βCH
H
Si
Me
1,3 Si~
Si
Me
H
160 (56%)

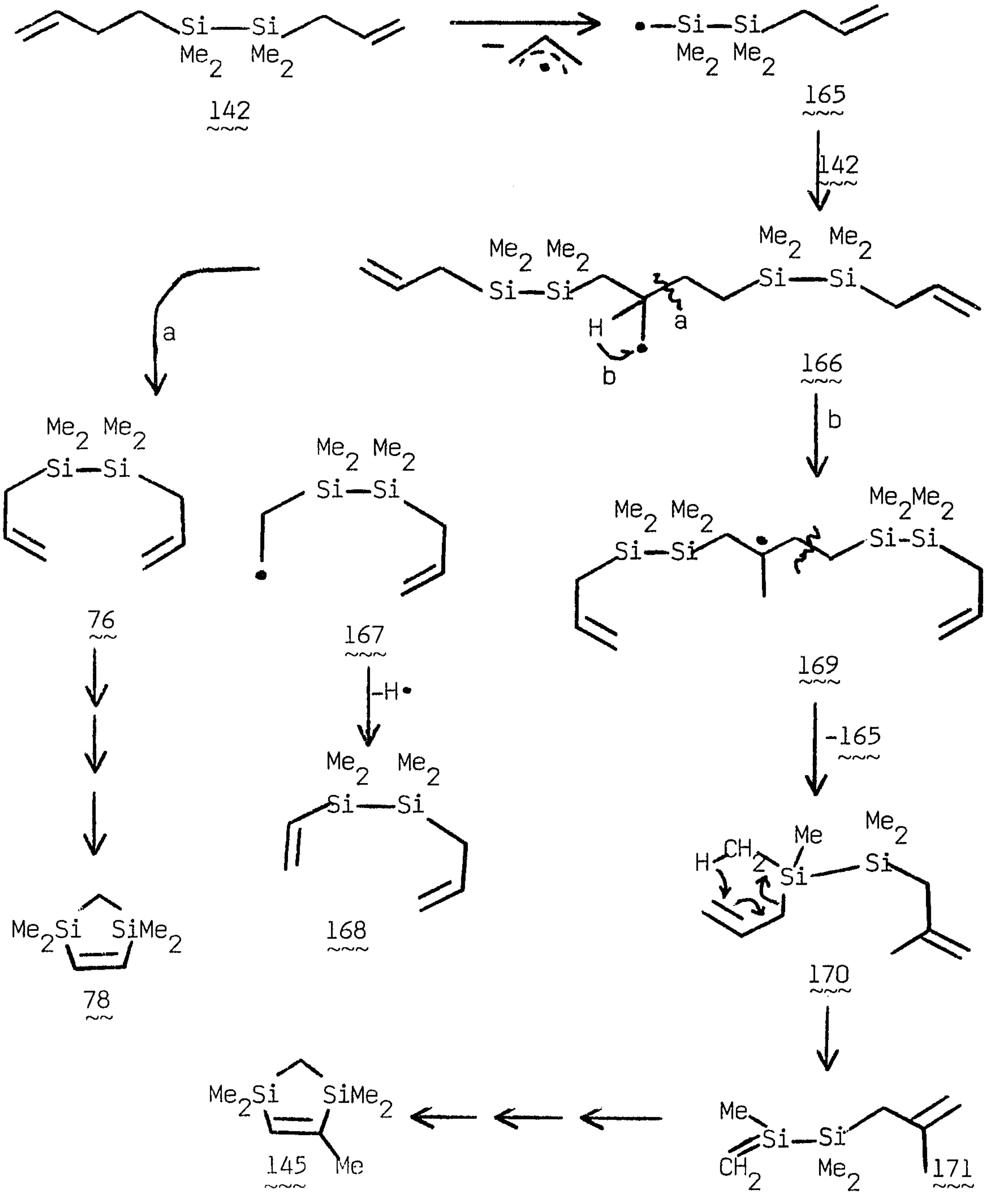
of propene from **76** would give silene **161** which after a 1,2-silyl shift followed by π-insertion of silylene **162** affords silacyclopropyl compound **163** (Scheme 22). Cleavage of the weaker carbon-carbon bond of **163** followed by hydrogen migration gives product **78**. Although the radical cyclization mechanism proposed by Barton and Jacobi (3) (Scheme 17) is reasonable, the results presented here, not to mention the cleanliness of the reaction, suggest otherwise. However, based on product analysis, it is not possible to differentiate between a stepwise (path a) and a concerted (path b) retroene process.

It is interesting to find that **78** is also formed in the pyrolysis of the butenyldisilane **142**. To account for this observation, a bimolecular route to the 1,2-diallyldisilane **76** which cleanly gives **78** is invoked (Scheme 23). The mechanism starts with the homolysis of the carbon-allyl bond of the butenyl group of **142** to form the α-silyl radical **165**. Evidence for this type cleavage is forthcoming. Intermolecular addition of **165** to the π-bond of **142** would give radical adduct **166** which could decompose to the observed products by two pathways. β-Cleavage of **166** (path a) would give **76** which decomposes to **78** via the mechanism outlined in Scheme 22. It is conceivable that unimolecular homolysis of the butenyl group followed by disproportionation of the resulting silyl radical could also give silene intermediate **161** which rearranges to product. However, based on some work done on the thermal behavior of 3-butenylsilanes, this type cleavage is believed to be less important. The work on 3-butenylsilanes will be presented in the next section.

Scheme 22

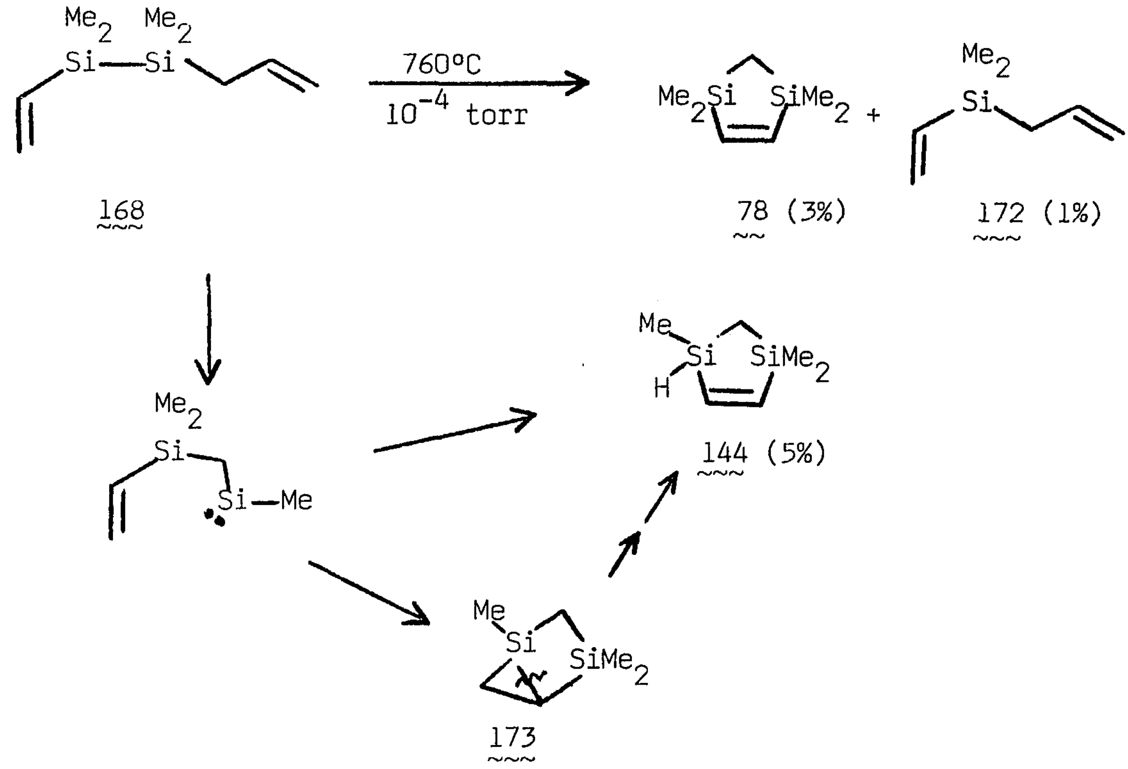


Scheme 23



Path b is offered as a possible route to 145. Thus, 1,2-hydrogen migration in radical adduct 169 followed by β-cleavage affords 170. Retroene elimination to propene and silene 171 followed by a 1,2-silyl shift, π-insertion, carbon-carbon bond homolysis of the intermediate silacyclopropane, and hydrogen migration would give the minor product 145.

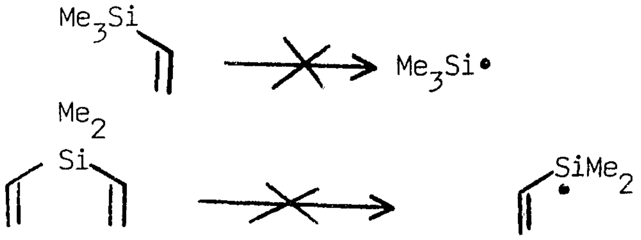
β-Disilanyl radical 167, the other fragmentation product of path a in Scheme 23, is believed to lead to 1,1,3-trimethyl-1,3-disilacyclopentene 144 via 168. In order to check this possibility, 1-allyl-2-vinyl-1,1,2,2-tetramethyldisilane 168 (141) was independently synthesized and pyrolyzed under the same conditions; namely 760°C at 1 X 10^{-4} mm Hg. Analysis of the pyrolysate showed a complex mixture of products with a mass recovery of 77%. The major volatile products and the corresponding yields are shown below. Although one hesitates to make strong mechanistic conclusions based on such a low yield process, the presence of 144 in the product mixture is at least in keeping with retroene elimination from 168 followed by silene to silylene rearrangement on to product 144. Note, however, that cleavage of the internal silicon-carbon bond of the silacyclopropyl ring in 173 occurs. Although silicon-carbon bond rupture is the usual expectation for a monocyclic silacyclopropane (124), there is literature precedent for carbon-carbon bond cleavage as well. Carbon-carbon bond homolysis has been invoked to explain the products obtained from ring-expansion reactions between silylenes and cyclic dienes such as cyclopentadiene (142), 1,3-cyclooctadiene (143), and furans (144).

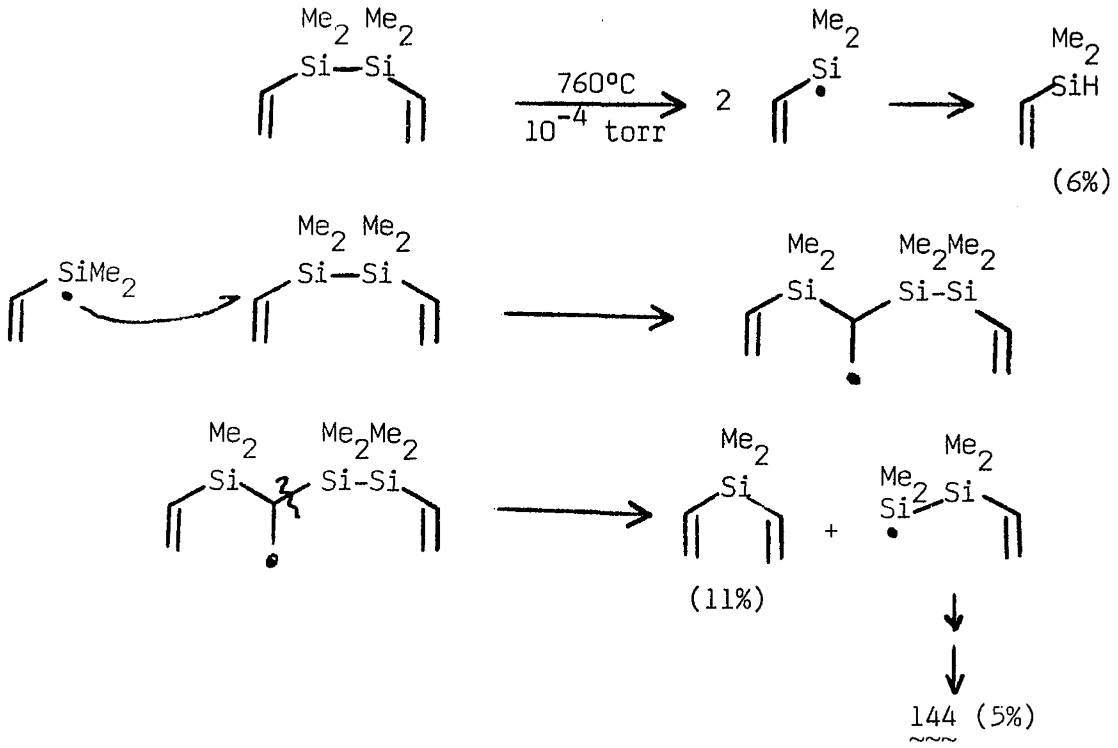


Formation of vinylallyldimethylsilane 172 (1%) most likely occur by reductive-elimination of dimethylsilylene. However, a radical process is also possible. Examination of the GC trace at column temperatures between 200°-230°C (15 ft., 20% OV-101/Chromosorb W) revealed a very complex mixture of high molecular weight products. None were isolable.

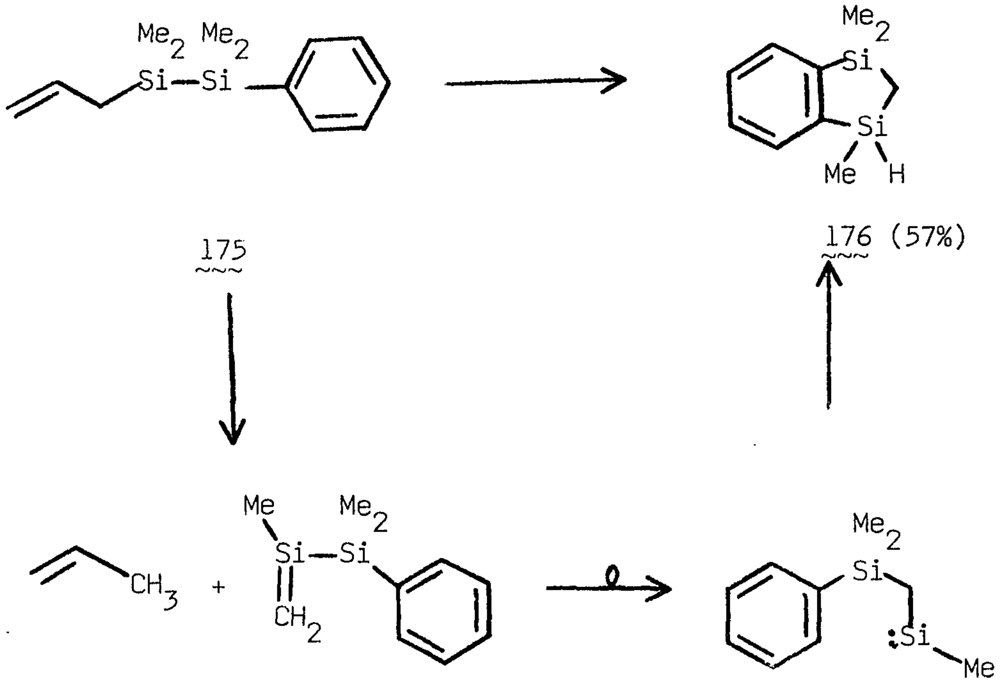
1,3-Disilacyclopentene 78, the only other volatile product, was rationalized as having been formed via allyldisilanyl radical 77 which disproportionates to silene 161 (see Scheme 22). What amounts to formally a loss of ethylene must occur through radical initiated cleavage of the vinyl group from 168. Therefore, stepwise silene formation is believed to be just as important as the concerted retroene process.

Evidence that suggests that simple homolytic cleavage of the vinyl group does not take place was obtained when both trimethylvinylsilane and divinyldimethylsilane were pyrolyzed under the identical conditions (760°C, 1 X 10^{-4} mm Hg). In both cases, quantitative recovery of starting material was obtained. Also, to demonstrate that radical-initiated cleavage of the vinyl group is possible, 1,2-divinyl-1,1,2,2-tetramethyldisilane 174 was pyrolyzed. At 760°C, homolysis of the silicon-silicon bond should occur (56) and furnish a radical source for the propagation step. As predicted, the pyrolysis of 174 afforded a 84% mass recovery of pyrolysate that contained a 5% yield of 144. Also present in the complex mixture was vinyldimethylsilane (6%), dimethyldivinylsilane (11%), and an unexplainable 5% yield of trimethylvinylsilane. The yields are based on 35% recovered 174. The major components of the pyrolysis were non-volatile compounds as evidenced by GC analysis on a 15 ft., 20% OV-101/Chromosorb W column between 200°-230°C. None of them were isolable.





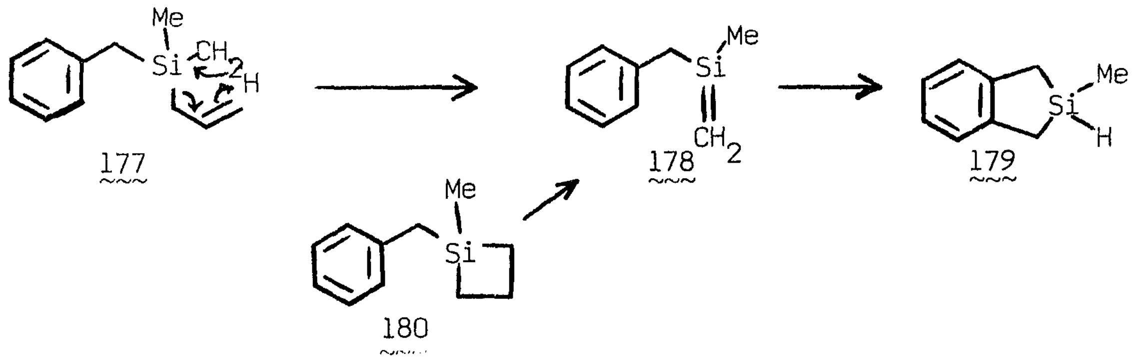
To remove the complications caused by having a butenyl or vinyl group in the molecule, the pyrolysis of 1-allyl-2-phenyl-1,1,2,2-trimethyldisilane 175 was carried out. At 770°C (1 X 10^{-4} mm Hg), 80% of the mass was recovered and GC analysis showed only one product along with unreacted 175 (35%). The compound was identified as 1,1,3-tetramethyl-1,3-disilaindane 176 which was present in a very clean 57% yield as based on consumed 175. Although other mechanisms may certainly be envisioned, the one that seems to best fit the conversion of 175 to 176 involves retroene elimination of propene followed by silene to silylene rearrangement. The silylene could then conceivably give 176 by inserting into the phenyl hydrogen or π-addition followed by cleavage and hydrogen migration.



The results reported here suggest that the pyrolytic decomposition of allyldisilanes occurs preferentially via retroene elimination to form silenes. This is different from what is observed for allyldisiloxanes that give cyclic products derived from the corresponding silyl radical. It is not clear, however, whether a stepwise process or a concerted retroene elimination of propene is involved. Surely, a stepwise silyl radical disproportionation mechanism must be involved in what are formally ethylene losses (78 from 168 and 144 from 174). Although the results are consistent with silene formation followed by rearrangement, none of the characteristic silene dimers (94) were ever observed.

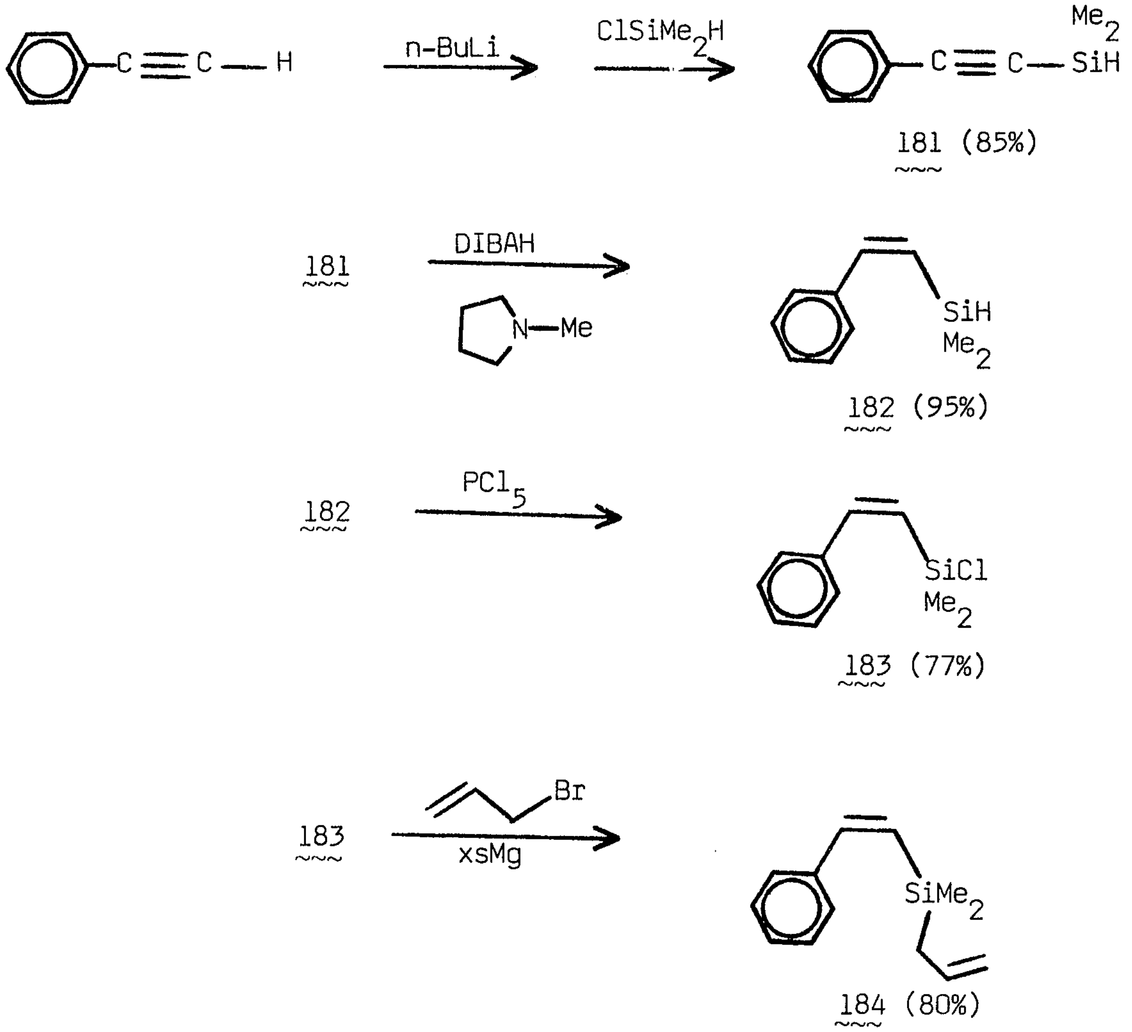
The obvious way to acquire evidence for the intermediacy of a silene or silylene species is by chemically intercepting them with known traps. Butadiene was chosen as a trap since it is well-known to undergo efficient reactions with silenes (145,146) and silylenes (147). However, flow pyrolysis of 168 and 175 with butadiene as the carrier gas between 500°C and 620°C did not give any of the characteristic cycloaddition products of the corresponding silene or silylene. In both cases, a very complex mixture of many products was obtained. These experiments do not rule out the intermediacy of these reactive species, however, since any radicals formed may also be trapped by butadiene. Such may be the case in a stepwise retroene process.

Similar results were reported by Goure (148) who proposed that 2-methyl-2-silaindane 179 resulted from intramolecular cyclization of silene 178 which was produced from retroene elimination of propene from 177. He too was unable to trap the silene. However, independent generation of 178 from silacyclobutane 180 also gave 179 thereby supporting his mechanism. Approximately ten other products were also formed.

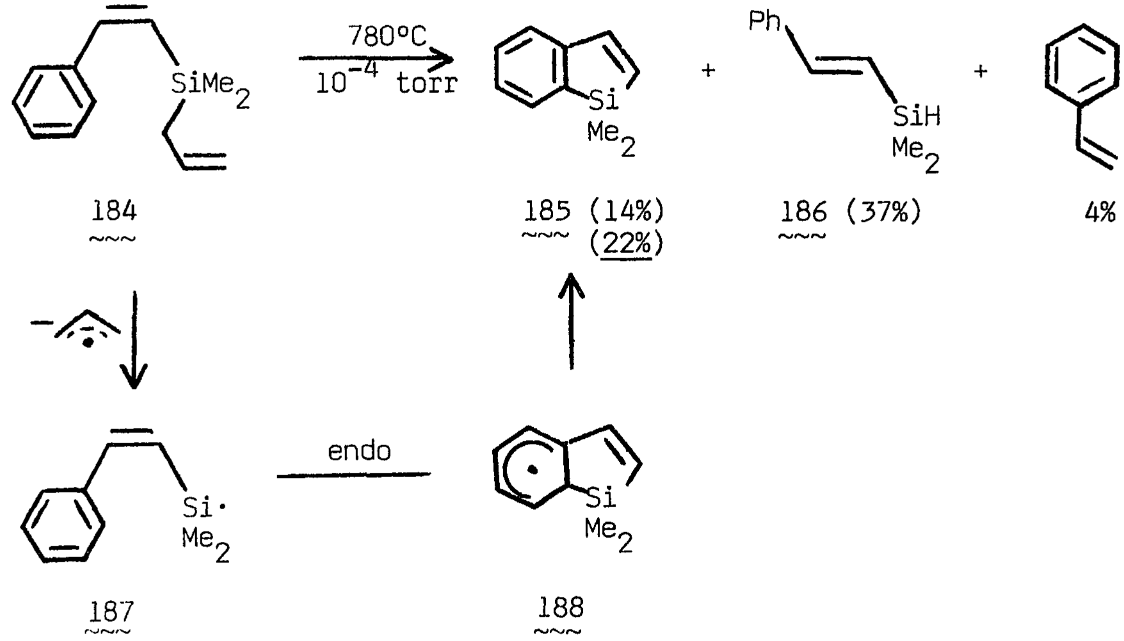


In order to try and understand the factors influencing simple homolytic cleavage of the silicon-allyl bond to give silyl radicals and retroene elimination affording silenes, the thermal behavior of another type allylsilane was looked at. *Cis*-2-phenyl-1-(allyldimethylsilyl)ethylene **184** was synthesized by the route outlined below. Thus, an etheral solution of phenylacetylene was metalated at -78°C with *n*-butyllithium (149) followed by refluxing and addition of dimethylchlorosilane to afford **181** in 85% yield. Diisobutylaluminum hydride (DIBAH) reduction to **182** in the presence of one equivalent of N-methylpyrrolidine was accomplished in 95% yield by a literature procedure (150). The corresponding chlorosilane was obtained in 77% yield by treatment of a pentane slurry of **182** with phosphorus pentachloride. Magnesium-induced coupling of **183** and allylbromide then gave 80% yield of **184**. The *cis*-stereochemistry was confirmed by the 15.1 Hz coupling constants of the vinyl hydrogens as evidenced by NMR spectroscopy.

When **184** was pyrolyzed at 780°C (1 X 10^{-4} mm Hg) two major products were formed along with 5% unreacted **184** and a 4% yield of styrene. The compounds were isolated by preparative GC and identified as *trans*-2-phenyl-1-(allydimethylsilyl)ethylene **186** (37%) (coupling constant = 20.0 Hz for the vinyl hydrogens) and 1,1-dimethyl-1-silaindene **185** (14%) (151). The yield of **185** goes up to 22% when corrected for the *cis*/*trans* isomerization product **186**. Offered as a likely mechanism for the formation of **185** is generation of silyl radical **187**, by homolytic

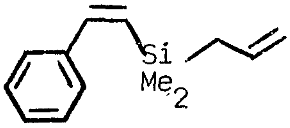
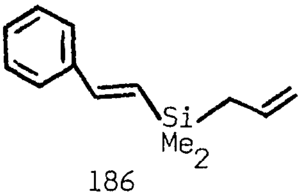


cleavage of the allyl bond, which cyclizes in an *endo*-fashion on to the "butadiene portion" of the ring to given radical intermediate 188. Rearomatization of 188 by loss of hydrogen afforded ample driving force for the formation of 1-silaindene 185. This is but another example of the cyclization of alkenylsilyl radicals in a regiospecific "anti-Beckwith" fashion. There was no evidence of a retroene elimination occurring in this pyrolysis. Therefore, one should not be lead to believe that all allylsilanes decompose by a retroene pathway. A possible explanation for the dichotomous behavior of these allylsilanes will be given in the summary.



Whether or not *trans*-2-phenyl-1-(allyldimethylsilyl)ethylene **186** would give 1-silaindene **185** was also a question of interest. Therefore, **186** and **184** were pyrolyzed under exactly the same conditions. The results are summarized in Table 13. The relative mole ratios are based on GC areas and it is assumed that the GC response factors for **184**, **185** and **186** are about the same. 1-Silaindene **185** is indeed formed from the *trans* compound **186**. However, from the relative mole ratios one finds that

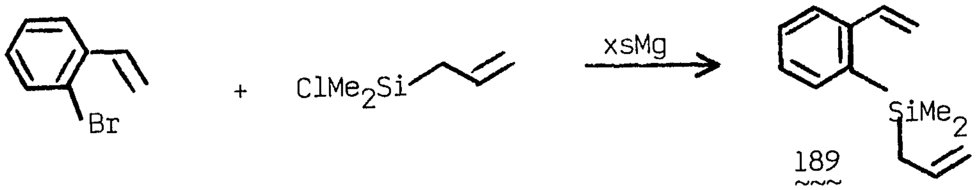
Table 13. Pyrolysis of 184 and 186 at 780°C (1 X 10^{-5} mm Hg)

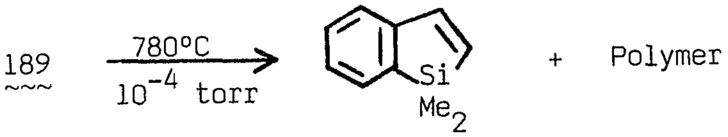
Starting Material	Relative mole Ratio			Relative % Yield		
	184	185	186	184	185	186
 184	1.0	4.4	5.3	9.3	41.1	49.5
 186	1.0	2.5	5.4	11.2	28.1	60.7

the yield of 185 is almost half that obtained from the *cis*-isomer. Quite interesting is the almost identical ratio of 184 to 186 obtained in both experiments. Although this is probably a fortuitous occurrence and the ratios may not represent an equilibrium concentration, it does suggest that equilibrium conditions should favor 186. This would not be unexpected based on simple thermodynamic grounds. If one assumes that all of the 1-silaindene 185 is formed from the *cis*-isomer, the *cis*/*trans* ratio (184:186) obtained on pyrolyzing 186 is reduced to 1:1.5. However, from 184 the ratio remains the same. Therefore, one is reluctant to believe that either set of ratios represents an equilibrium concentration.

To remove the possibility of *cis*/*trans* isomerization, (*o*-vinylphenyl)allyldimethylsilane 189 was synthesized by magnesium-induced coupling of allyldimethylchlorosilane and *o*-bromostyrene (Aldrich).

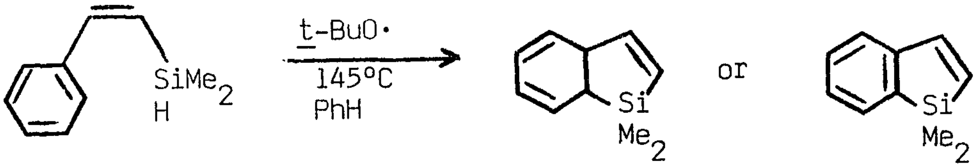
However, pyrolysis of **189** at 780°C (1 X 10^{-4} mm Hg) afforded a yellow viscous oil in 68% mass recovery. Although GC analysis did reveal some **185** in the pyrolysate (based on GC retention time), the major component was by far polymeric. In retrospect, since thermal polymerization of styrene is well-known, this result should not have been unexpected.





185 (GC)

Since abstraction of a silyl hydride by *tert*-butoxy radical was found to be a good method of generating silyl radicals, an attempt was made to prepare radical **187** in solution. However, when a 1% solution of **182** in benzene was heated at 145°C in the presence of di-*tert*-butyl peroxide, no cyclic products were observed. Starting silyl hydride **182** was the major product present even after heating for 24 hours. This result was quite surprising in view of the earlier work presented in this dissertation along with that of Kira *et al*. (62).



182

(not observed)

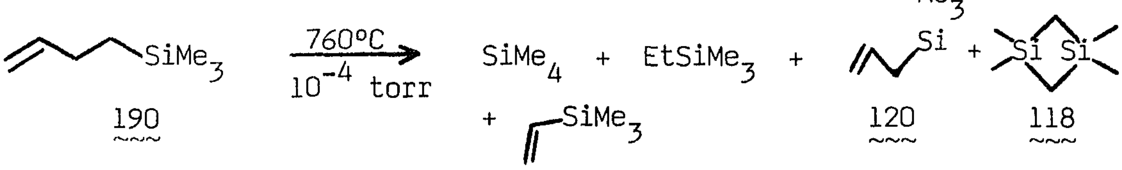
In summary, the pyrolysis of allylsilanes affords both silyl radicals and silenes. The intermediate formed is dependent on the structure of the allylsilane. For example, when allyldisilanes are decomposed under pyrolytic conditions, the products formed are most reasonably accounted for via silene intermediates. The silenes are formed either by step wise or concerted propene elimination. A silene mechanism and not the previous proposed radical cyclization mechanism is therefore believed to be involved in the very clean formation of 1,1,3,3-tetramethyl-1,3-disilacyclopentene **78** from 1,2-diallyl-1,1,2,2-tetramethyldisilane **76**. On the other hand, pyrolysis of allyldisiloxanes and allylvinylsilanes (**184**) affords silyl radicals by homolysis of the silicon-allyl bond. These silyl radicals undergo intramolecular cyclization in an *endo*-fashion.

Although there is evidence in the literature that suggest that silyl radicals are not stabilized to any significant extent by adjacent groups (99,152), the results presented here may suggest otherwise. In other words, perhaps disiloxanyl radicals and vinylsilyl radicals (**184**) are sufficiently stabilized to undergo cyclization. However, disilanyl radicals may suffer facil β-cleavage due to the instability of these species. Even if this explanation is not correct, the general trend may certainly be a helpful "rule-of-thumb" toward predicting which process will take place.

Pyrolytic Decomposition of 3-Butenylsilanes

One of the key steps proposed in the decomposition of 2-(3-butenyl)-1-allyl-1,1,2,2-tetramethyldisilane **142** to 1,1,3,3-tetramethyl-1,3-disilacyclopentene **78** is homolysis of the carbon-allyl bond of the butenyl unit (Scheme 23). Simple calculations based on published bond dissociation energies (99) (D Si-C = 89 kcal/mol, D C-allyl = D C-C 88 kcal/mol - 14 kcal/mol allylic stabilization = 74 kcal/mol) show that the carbon-allyl bond should be almost 15 kcal/mol weaker than the carbon-silicon bond in **142**. There are no published experimental data in support of this hypothesis. Therefore, the pyrolysis of some 3-butenylsilanes was undertaken.

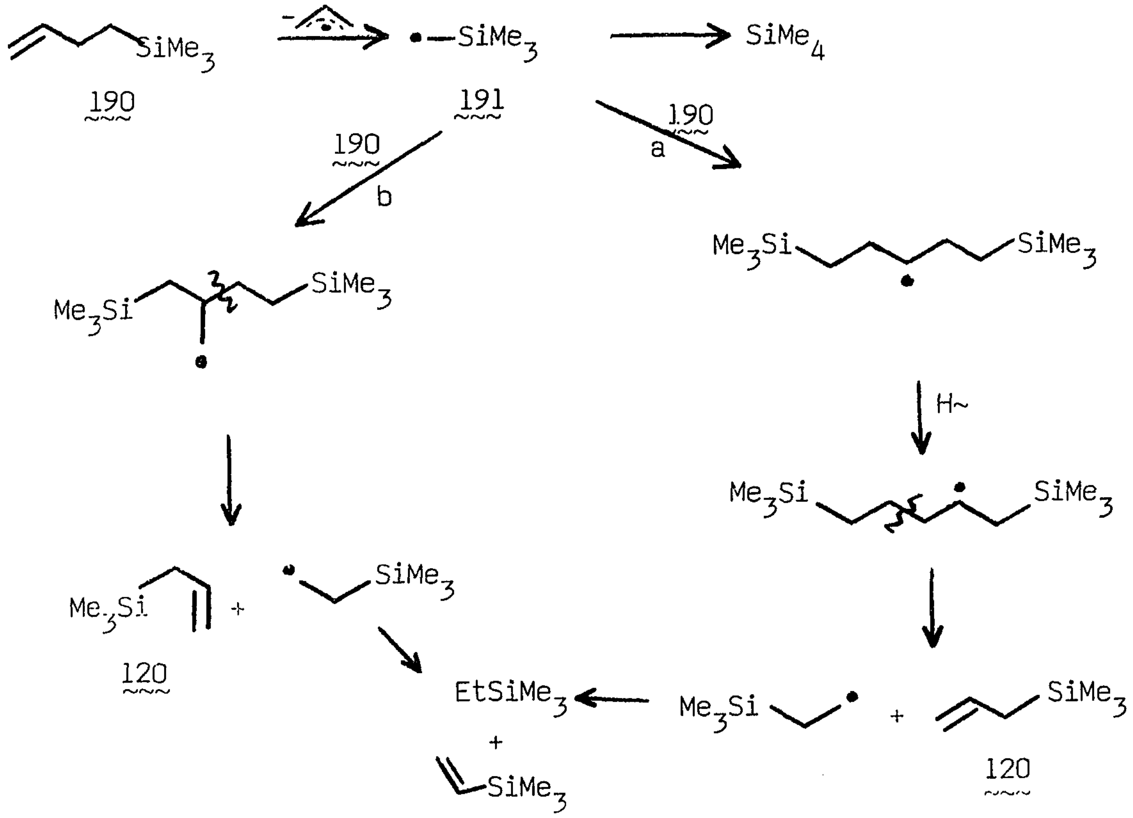
In order to look at the primary products of decomposition, 3-butenyltrimethylsilane **190** (153) was pyrolysed at 760°C in a vacuum (1 X 10^{-4} mm Hg). Under these conditions, only 10% decomposition of **190** occured. Five major products were identifiable by comparing the GCMS data of the pyrolysate with that of the known compounds. The products were tetramethylsilane (TMS), vinyltrimethylsilane, ethyltrimethylsilane, allyltrimethylsilane **120**, and 1,1,3,3-tetramethyl-1,3-disilacyclobutane **118**. The molar ratios of these compounds were approximately 2:1:2:2:1, respectively. All of the observed products may be rationalized as having



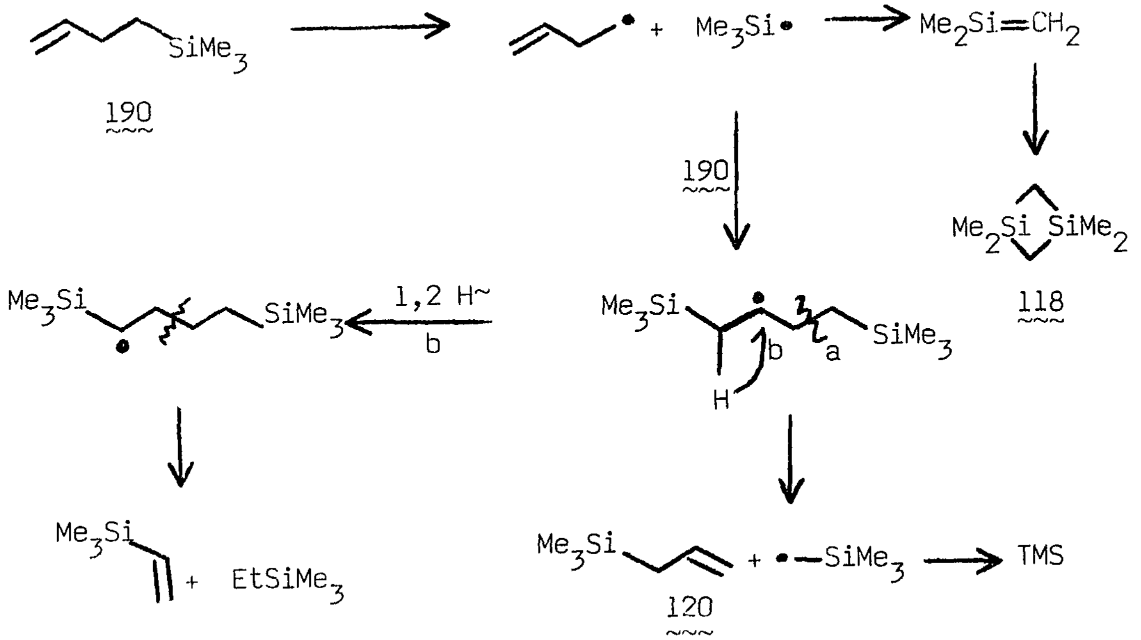
190 **120** **118**

been formed via the mechanism outlined in Scheme 24. The presence of TMS in the pyrolysate seems to demand cleavage of the carbon-allyl bond followed by hydrogen abstraction. Although other mechanisms are possible, they seem very unlikely. Intermolecular addition of the "TMS radical" to the π-bond of 187 followed by cleavage or hydrogen migration and homolysis (path a or path b) could give three of the other products. It is likely that 1,3-disilacyclobutane 118, a known head to tail dimer of dimethylsilene (94), is formed from trimethylallylsilane 120 via retroene elimination to the corresponding silene (128).

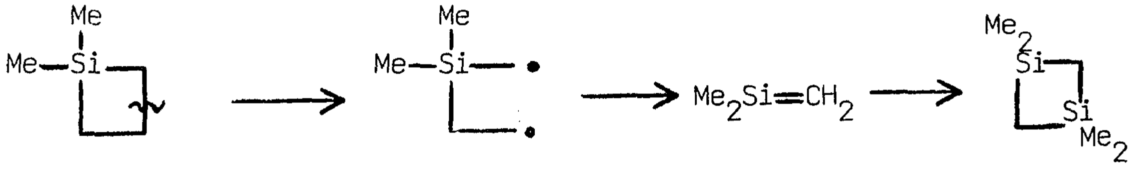
Scheme 24



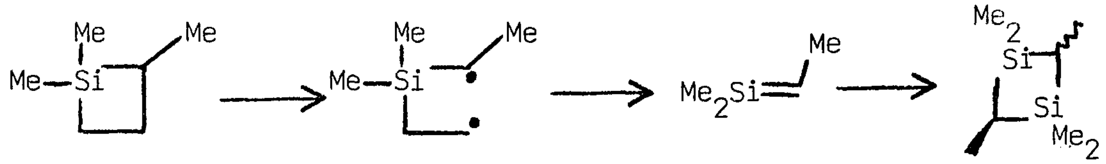
The best alternative to the mechanism outlined in Scheme 24 would involve cleavage of the butenyl-silicon bond (89 kcal/mol) generating trimethylsilyl radical. Attack of trimethylsilyl radical on 190 would give a radical adduct that could also give the observed products. Trimethylsilyl radical is known to give 118 (92,93) via 1,1-dimethylsilene (94). However, based on bond energies and some other results to be presented, this author favors Scheme 24.



Gas phase precursors of α-silyl radicals are scarce. One of the few examples in which an α-silyl radical is formed in the gas phase is in the thermal decomposition of 1,1-dimethylsilacyclobutane 192. Under pyrolytic conditions, 192 was shown to undergo unimolecular decomposition to dimethylsilene via initial homolytic fission of the carbon-carbon bond (154). The characteristic silene dimer 118 was isolated. The Arrhenius parameters were identical to those known for cyclobutane; namely log $_{10}A$ = 15.64 and E_a = 62.6 kcal/mol. Barton and coworkers (155) demonstrated that other silacyclobutanes decompose via α-silyl radicals when they pyrolyzed 1,1,2-trimethyl-1-silacyclobutane 193 in a nitrogen-flow system between 520° and 680°C. Again, silene dimers were formed. Working with 2-methyl and 2-phenyl substituted 1,1-dimethyl-1-silacyclobutane, Golino et al. (156) concluded that carbon-carbon bond cleavage occurred at least twenty times faster than silicon-carbon homolysis. Other workers have also examined the thermal decomposition of 1,1-dimethyl-1-silacyclobutane, and various substituted derivatives (157,158), and have reached similar conclusions.



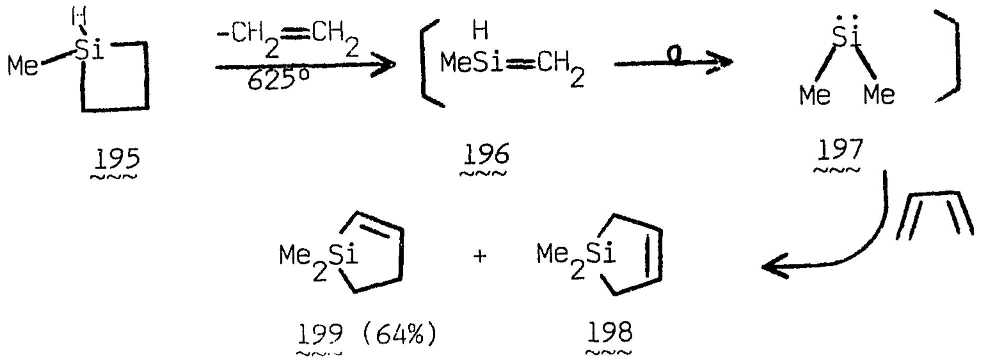
192 118



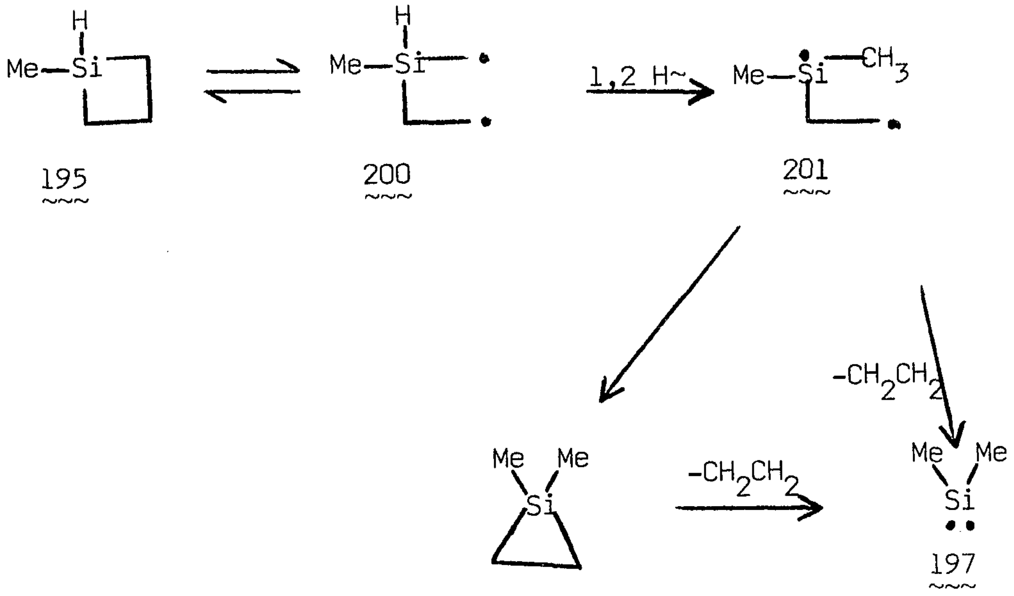
193 194

Conlin and Wood (159) recently reported that the pyrolysis of 1-methyl-1-silacyclobutane 195 affords dimethylsilylene 197 which could be trapped in excellent yield. They proposed that initially formed methylsilene 196 underwent 1,2-hydrogen migration to dimethylsilylene 197.

Support for this migration was offered by Drahnek et al. (160) and Arrington et al. (161), who reported that photochemically generated 196 isomerizes to 197 at 100 K. Shortly there after, Barton et al. (4) presented evidence that under their thermal conditions, 196 does not isomerize to 197. Only the silene trapped product of 2,3-dimethylbutadiene along with the silene dimer were observed when 196 was generated at 450°C from the Diels-Alder adduct of 1-methyl-1-silacyclohexadiene and perfluoro-2-butyne. Total product yields were approximately 66%. Since no products derived from dimethylsilylene 197 were present, these authors offered an alternative mechanism to the isomerization of 196 to 197. Their mechanism (Scheme 25) involved 1,2-hydrogen migration from α-silyl radical 200 followed by either direct cleavage to 197 or recombination followed by silylene extrusion from 1,1-dimethylsilacyclopropane. Based on some theoretical studies on the isomerization of 196 to 197 by Goddard et al. (162) who calculated the energy barrier of the reaction to be 41 kcal/mol, and most recently by Nagase and Kudo (163) who predict a 40 kcal/mol activation energy, an alternate mechanism to that proposed by Colin and Wood (159) deserves some consideration.



Scheme 25



However, 1,2-hydrogen migration from silicon to a carbon-centered radical, such as suggested by Barton et al. (4), has never been reported. In fact, very few 1,2-migrations from silicon to carbon-centered radials are known. One example of 1,2-migration, however, has been reported to occur in the gas phase. Shiina and Kumada (164) showed the hexamethyldisilane readily rearranges to (trimethylsilylmethyl)-dimethylsilane 119 and trimethylsilane 202 at 600°C. One of the key

$$Me_3SiSiMe_3 \xrightarrow{600°C} \underset{119}{Me_3SiCH_2SiMe_2H} + \underset{202}{Me_3SiH}$$

steps in the proposed chain mechanism was 1,2-trimethylsilyl migration to silyl radical **204**. The rearrangement must have an appreciable barrier of activation since when generated in solution, between 80°C and 124°C, no rearrangement occurs (165,166).

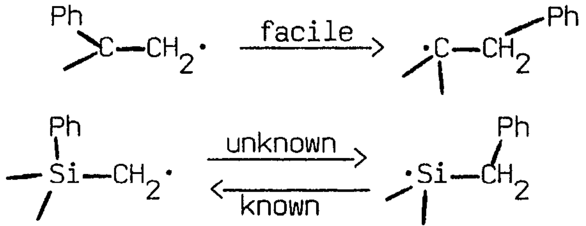
$$Me_3SiSiMe_3 \longrightarrow 2\ Me_3Si\cdot$$

$$Me_3Si\cdot + Me_3SiSiMe_3 \longrightarrow \underset{\mathbf{202}}{Me_3SiH} + \underset{\mathbf{203}}{\cdot CH_2SiMe_2SiMe_3}$$

$$\underset{\mathbf{203}}{\cdot CH_2SiMe_2SiMe_3} \xrightarrow{\Omega} \underset{\mathbf{204}}{Me_3SiCH_2SiMe_2\cdot}$$

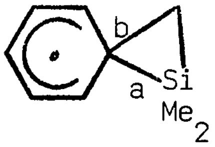
$$\underset{\mathbf{204}}{Me_3SiCH_2SiMe_2\cdot} + Me_3SiSiMe_3 \longrightarrow \mathbf{119} + \mathbf{203}$$

The reason for the apparently high barrier to 1,2-migrations from silicon to carbon-centered radicals in solution is not clear. Furthermore, it is somewhat puzzling when one considers the many documented cases of 1,2-migrations involving all carbon systems. For example, 1,2-phenyl shift from carbon to a carbon-center radical is well known. Although this migration proceeds with a rate constant of only 59 sec^{-1} (167,168), other aromatics migrate with rate constants of about 10^3 sec^{-1} (169, 170). The analogous phenyl shift from silicon to carbon is unobserved (171). However, the reverse process of migration from carbon to a silicon-centered radical does occur. Since these rearrangements most likely proceed via *ipso*-attack on the aromatic ring, as opposed to migration across the frontier orbitals, the transition state leading to **206** from **205**, and vis versa, should be the same. Wilt *et al*. (172), therefore,



205 206

proposed that the stability of α-silyl radical 205, and not the stain of the intermediate, prevented the rearrangement. The intermediate proposed by Wilt and coworkers was the spiro-silacyclopropyl radical 207.

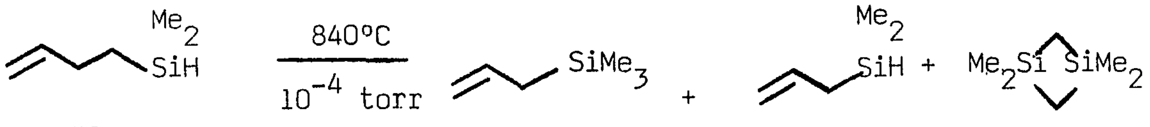


207

Examination of 207 leads one to suggest an alternative explanation for the absence of 1,2-phenyl migrations from silicon to carbon. Namely, based on bond strengths, bond a should be weaker than bond b (99). Therefore, once intermediate 207 is formed, whether from α-silyl radical 205 or silyl radical 206, the product obtained should result from homolysis of the weaker bond a. This explanation also seems to fit the reported observations. However, since migration of hydrogen, as well as simple alkyl groups, would probably involve frontier orbitals, this explanation can not be extended to these substituents.

The pyrolysis of 3-butenylsilanes, which appear to give α-silyl radicals, may prove useful in looking at 1,2-hydrogen shifts from silicon to carbon-centered radicals. To examine this, the pyrolysis of 3-butenyldimethylsilane 59 was carried out. At 840°C, flash-vacuum pyrolysis

(1 X 10^{-4} mm Hg) of 59 afforded cleanly two major products but with only a 56% mass recovery. The compounds were isolated by preparative GC and identified as allyltrimethylsilane 60 (4%), and trimethylsilane 188 (17%). The yields are based on 75% consumption of 62. A trace amount (<1%) of 1,1,3,3-tetramethyl-1,3-disilacyclobutane 189 was detected by GCMS.

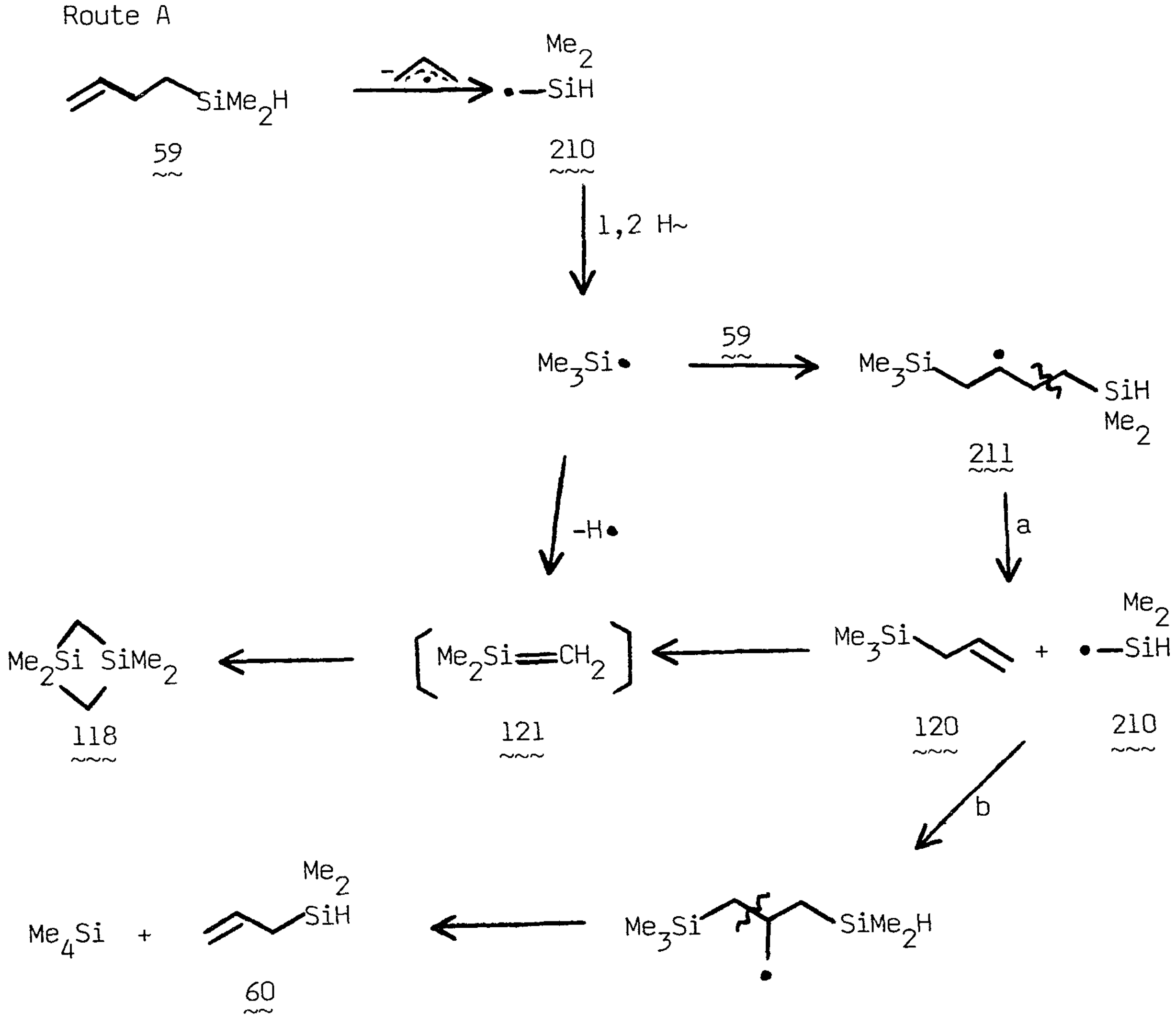


59 120 (17%) 60 (4%) 118 (<1%)

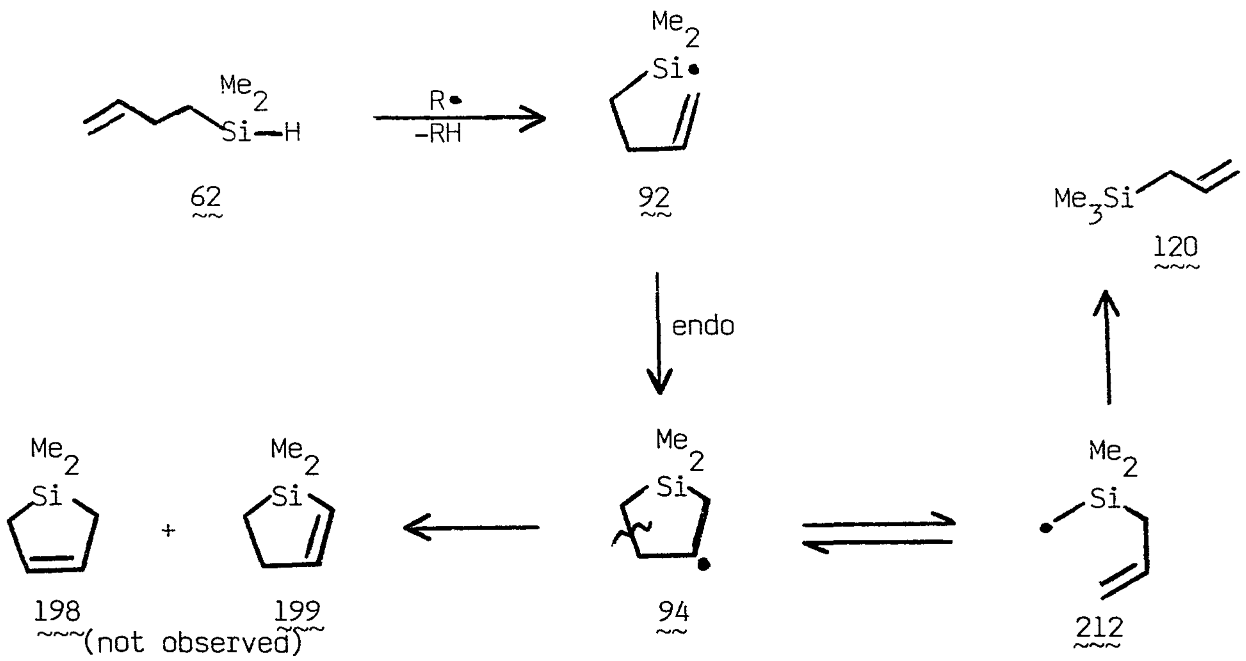
Three reasonable mechanisms (Scheme 26) may be envisioned to account for the observed products. However, the mechanism that this author believes best accounts for the observed products is route A. Homolysis of the carbon-allyl bond as the initial step, which affords α-silyl radical 210, seems reasonable based on bond strengths (99) coupled with what was demonstrated for 3-butenyltrimethylsilane 190. 1,2-Hydrogen migration in 210 followed by intermolecular addition of trimethylsilyl radical to 59 would give radical adduct 211 which could decompose to products via path a and path c.

Although the route A mechanism is certainly consistent with the products formed, it is not demanded. One alternative, route B, could involve *endo*-closure of silyl radical 92 followed by β-cleavage and hydrogen abstraction. Since it is unlikely that 92 would be formed by simple homolytic cleavage of the silicon-hydrogen bond (D Si-H = 90 kcal/mol (99)), it would have to occur via hydrogen abstraction by some

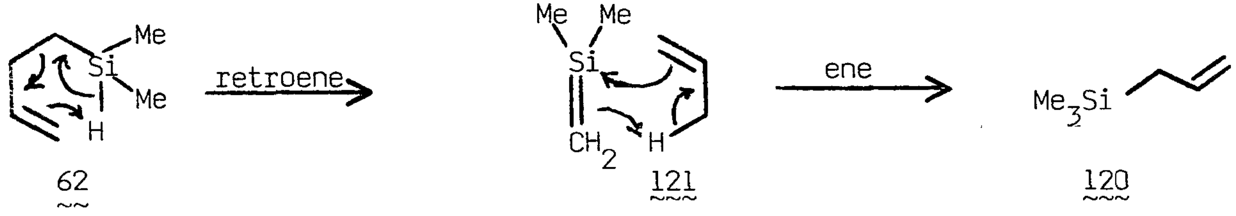
Scheme 26


Route A
SiMe2H
59
Me2
SiH
210
1,2 H~
Me3Si•
59
Me3Si
SiH
Me2
211
-H•
a
Me2Si SiMe2
118
Me2Si=CH2
121
Me3Si
+
Me2
SiH
120
210
b
Me4Si
+
Me2
SiH
60
Me3Si
SiMe2H

Route B



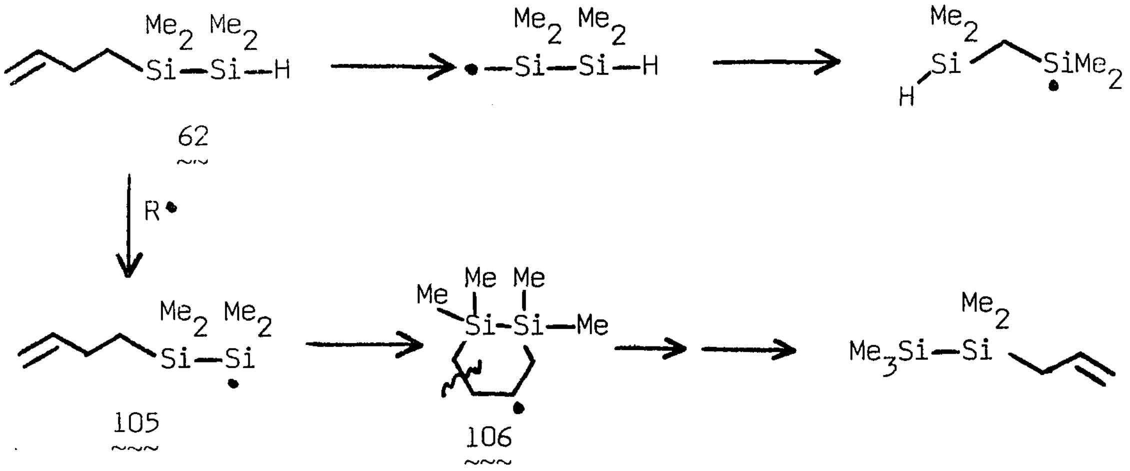
Route C



other radical (R·). Furthermore, the absence of both **198** and **199** in the pyrolysates tends to argue against route B. However, it appears that consideration of the differences in the relative rates of addition of a silyl radical to a π-bond versus abstraction of a silyl hydride by another radical should allow for distinction between route A and route B. It seems reasonable to assume that R· is a carbon-centered radical. Unfortunately, there are very little kinetic data available to make a good comparison. Although Choo and Gaspar (173) obtained a rate constant of $1.7 \pm 1.0 \times 10^{5}\ M^{-1}\ sec^{-1}$ for the addition of trimethylsilyl radical to ethylene at 20°C, no data is available on the abstraction of a silyl hydride by an alkyl radical at this temperature. The only data found on the abstraction reaction was published by Berkley *et al.* (174). They reported a rate constant of $7.1 \times 10^{7}\ M^{-1}\ sec^{-1}$ for the abstraction of the hydrogen from trimethylsilane by methyl radical at 200°C.

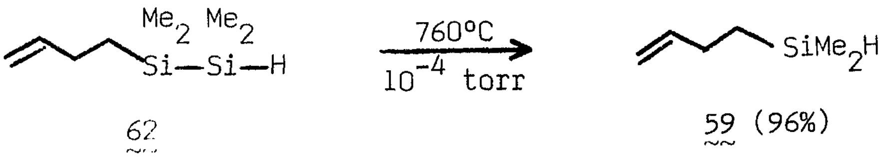
Even if kinetic data were available to make such a comparison, it would still not eliminate route C (Scheme 26). Although retroene elimination off of a silylhydride is without literature precedence, the ene reaction of 1,1-dimethylsilene and propene is known (175,176,177). The activation energy for the ene reaction was recently estimated to be between 12 and 17 kcal/mol (128). However, route C mechanism does not explain the presence of dimethylallylsilane **60**.

In order to explore further the possibility of hydrogen abstraction to form silyl radical **92** (route B, Scheme 26), the thermal decomposition of hydride disilane **62** was examined. It was believed that the primary mode of thermal decomposition of **62** should also be via cleavage of the carbon-allyl bond of the butenyl unit. If this were true, then two very interesting pathways to further reactions would be available to this α-disilanyl radical. One of the radicals formed could conceivably abstract the silicon hydrogen from **62** to form disilanyl radical **105**. Endo-cyclization of **105** would give **106**, which in accordance with route B



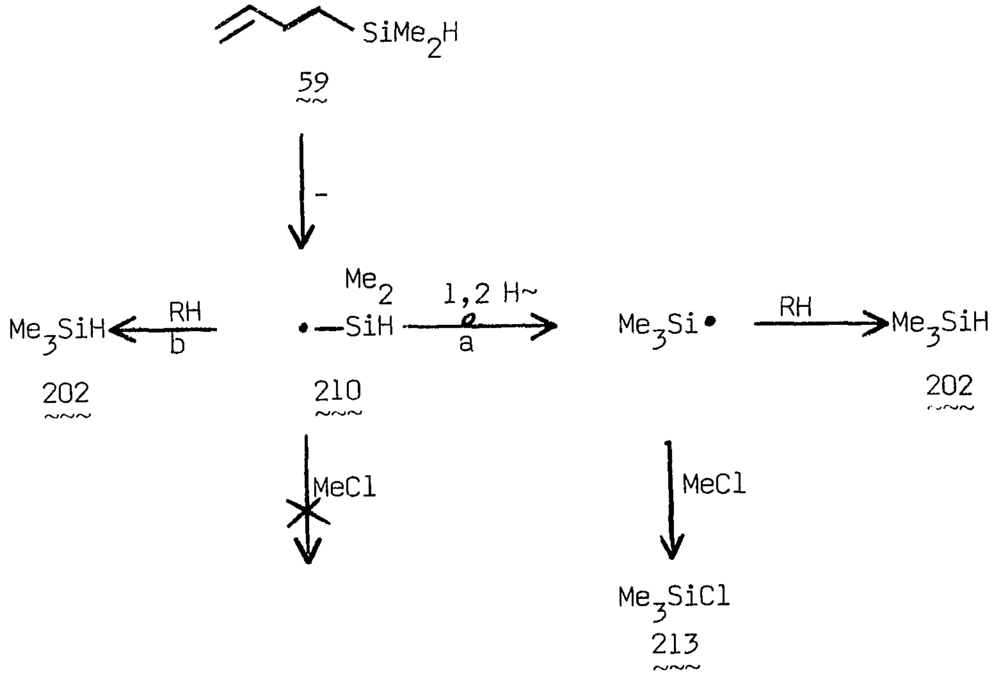
of Scheme 26, would yield 1-allylpentamethyldisilane **79**. The other alternative would be for the α-disilanyl radical (**R**·) to undergo a 1,2-silyl shift (164).

However, when **62** was pyrolyzed at 760°C (1 X 10^{-4} mm Hg) only one product, 3-butenyldimethylsilane **59**, was formed in a very clean 96% yield based on 94% consumption of **62**. This product is most reasonably explained as coming from the well-known reductive-elimination of dimethylsilylene.



Just as the work presented herein was being completed, Davidson (178) communicated to us some kinetics that was done on 3-butenyldimethylsilane 59. He found trimethylsilane 202 to be the major thermal decomposition product of 59. There are two reasonable pathways by which 202 could be formed (Scheme 27). Path a would involve 1,2-hydrogen migration in α-silyl radical 210 followed by hydrogen abstraction by trimethylsilyl radical, while path b would involve direct hydrogen abstraction of radical 210. Since it is well-known the silicon-centered radicals abstract halogens from alkyl and aryl halides, excess methylchloride was added and the reaction repeated. Under these conditions, trimethylsilane 202 was suppressed and trimethylchlorosilane 213 formed. This result is consistent with the formation of trimethylsilyl radical via 1,2-hydrogen migration. Davidson did not report any 3-butenyl-

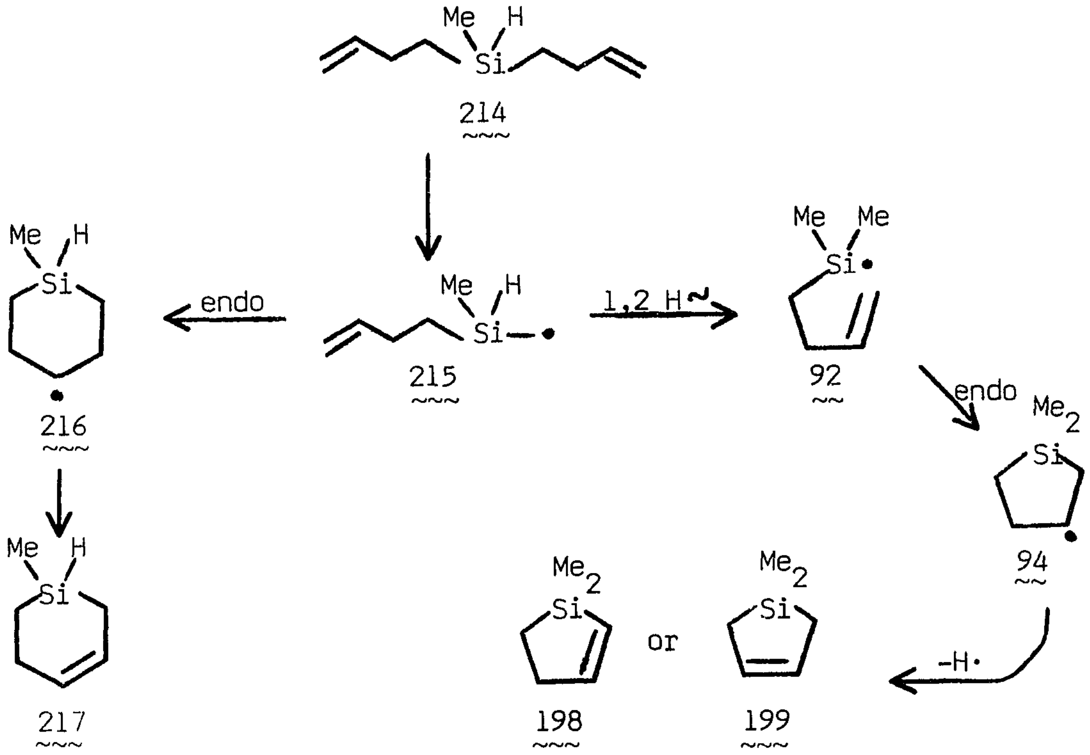
Scheme 27



dimethylchlorosilane which would be formed by methyl chloride trapping of silyl radical **92** (Scheme 24). Davidson also estimated a 44 kcal/mol barrier for the rearrangement.

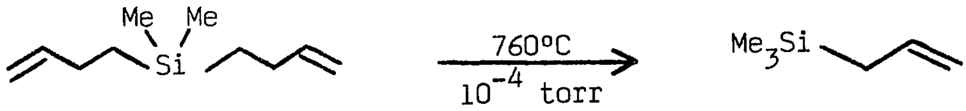
These results not only demonstrate that 3-butenylsilanes thermally decompose via silicon-allyl cleavage, but also suggest that the corresponding hydrido silane undergoes what must be a very rapid 1,2-hydrogen migration.

To try and obtain at least a quantitative measure of just how fast the 1,2-hydrogen migration was, a competition experiment between cyclization and hydrogen migration was designed. The compound chosen for the study was di(3-butenyl)methylsilane **214** which was prepared in 63% yield by magnesium-induced coupling of two equivalents of 4-bromo-1-butene and methyldichlorosilane. It was expected that upon pyrolysis of **214**, either of two processes, or a combination thereof, would take place. 1,2-Hydrogen migration in α-silyl radical **215** followed by intramolecular addition of the silyl radical, **92**, would give products of the silacyclopentyl ring system. But based on Wilt's (73) work on similar radicals in solution, **215** should cyclize in an *endo*-fashion to silacyclohexyl radical **216**. The product ratios should reflect the relative rates of the two pathways. Flash-vacuum pyrolysis (1 X 10^{-4} mm Hg) of **214** at 730°C afforded only a 37% mass recovery of pyrolysate. GC analysis revealed a very complex mixture of volatile compounds of which the major product was isolated (preparative GC, 9 ft, 20% OV-101/Chromosorb W, 130°C) and identified by NMR and mass spectrum as allyldimethyl-



silane **60**. By comparison with known mass spectra (137,179), GCMS showed that both **198** and **199** were present in the pyrolysate. Also by GCMS, two other isomers of **198** and **199** ($C_6H_{12}Si$) were also present. Although at a much lower temperature, 630°C, the mass recovery of pyrolysate went up to 79%, the complexity of the product mixture did not change. Only about 5% to 10% of **214** was consumed at 630°C.

In retrospect, it had not been established that α-silyl radicals cyclize in the gas phase. Therefore, the pyrolysis of di(3-butenyl)-dimethylsilane **218** was carried out (Scheme 28). Compound **218** should give α-silyl radical **68** which has been shown to undergo predominantly *endo*-closure in solution (73) (see Historical section, Table 11). Vacuum pyrolysis of 218 at 760°C (1 X 10^{-4} mm Hg) afforded trimethylallylsilane 120 as the major product formed in 32% yield based on 86% consumption of 218. Also formed were small amounts (<3% each) of about seven other volatile products. The formation of trimethylallylsilane 120 was quite surprising as it was totally unexpected.



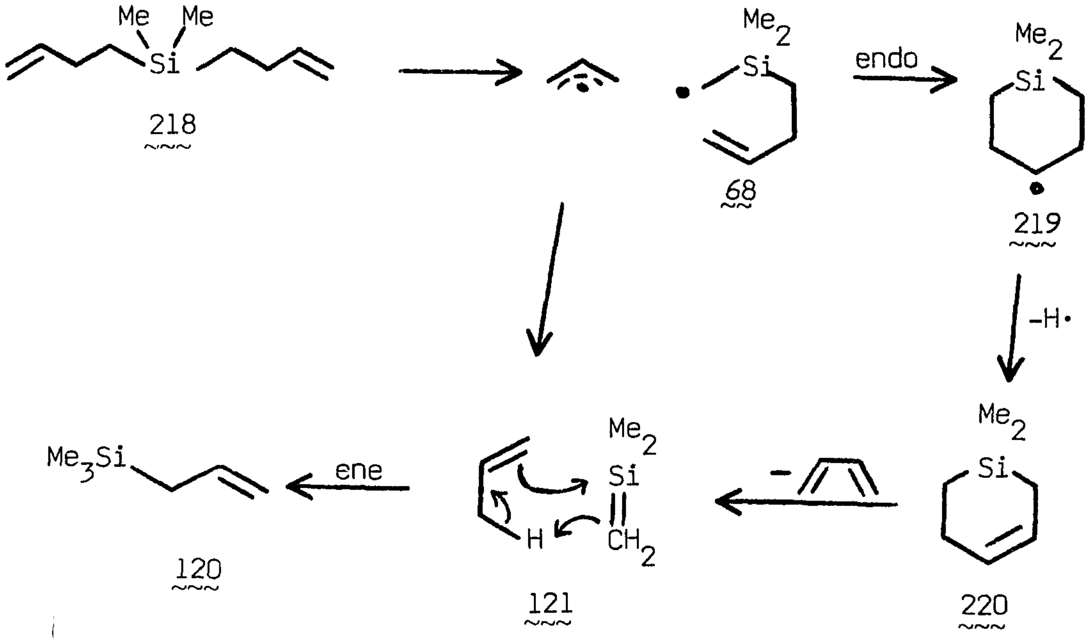
218

120 (32%)

Two very interesting mechanistic possibilities are envisioned to account for the formation of trimethylallylsilane 120 from 218. Scheme 26 outlines a route in which α-silyl radical 68 undergoes the expected *endo*-closure (73) followed by disproportionation of 219 giving 1,1-dimethyl-1-silacyclohex-3-ene 220. Under the reaction conditions, however, 220 could decompose via retro-Diels-Alder reaction to dimethylsilene 121 and butadiene. Ene reaction of 121 with propene (175) could then give trimethylallylsilane 120. Barton (180), in some unpublished results, has evidence that silacyclohex-3-enes decompose via retro-Diels-Alder reactions. However, this might not be a concerted process. Whether concerted or stepwise, the result is the production of a silene unit.

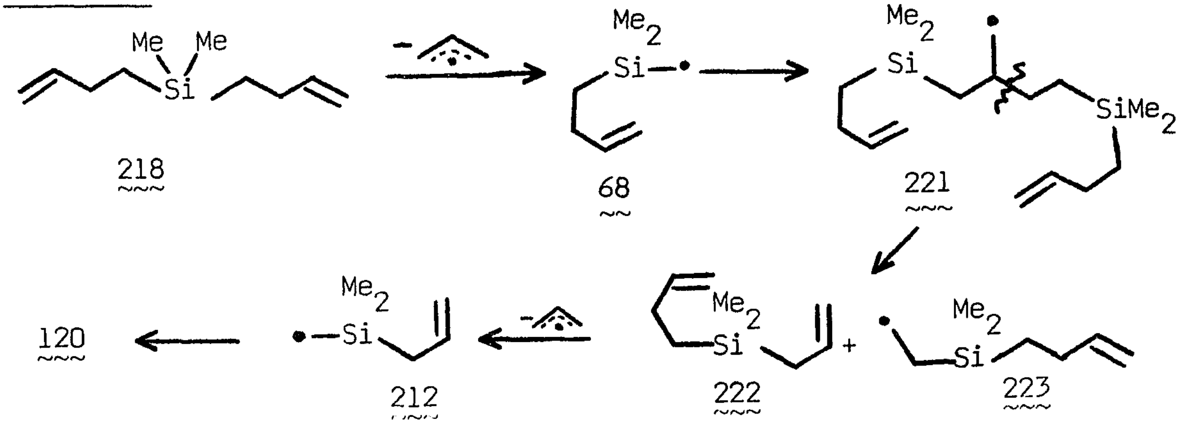
The other reasonable route to 188, Scheme 29, also starts with homolytic cleavage of the carbon-allyl bond of 218 to form α-silyl radical 68. However, instead of *endo*-closure or *exo*-closure, radical 68 might

Scheme 28

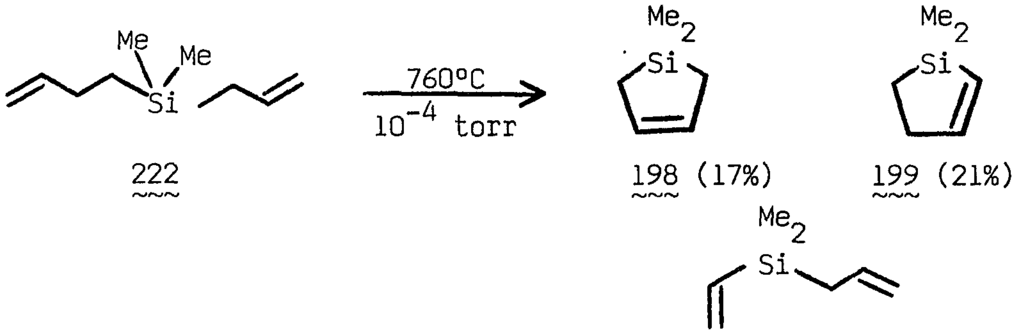


undergo intermolecular addition with 218 to form radical adduct 221. β-Cleavage of adduct 221 would give (3-butenyl)allyldimethylsilane 222 which upon cleavage followed by hydrogen abstraction would afford 120. The other fragmentation product, radical 223, might decompose to some of the minor products in the pyrolysate.

Scheme 29



Experiments designed to check for a silene intermediate, as proposed in Scheme 28, could lead to complicated results since radicals are trapped by the same compounds used to intercept silenes. However, support for the mechanism outlined in Scheme 29 could be obtained by independently pyrolyzing (3-butenyl)allyldimethylsilane **222**. Thus, **222** (181) was prepared in 70% preparative GC yield (9 ft, 20% OV-101/Chromosorb W, column temperature 120°C) by reaction of excess allylmagnesium bromide and (3-butenyl)chlorodimethylsilane. When **222** was pyrolyzed at 760°C (1 X 10^{-4} mm Hg), 77% of the mass was recovered and analyzed by GC. Three major products were formed in about a 1:1:1 ratio along with 25% unreacted **222**. The compounds could not be separated by GC and were, therefore, isolated as a mixture of the three. They were identified, by matching the NMR and GCMS with that of the known compounds (137,179), as 1,1-dimethyl-1-silacyclopent-3-ene **198** (21%), 1,1-dimethyl-1-silacyclopent-2-ene **199** (17%), and allyldimethylvinylsilane **172** (20%). The yields are based upon consumed **222**. Absolutely no trimethylallylsilane **120** could be found in the pyrolysate upon careful examination of the GCMS.



222

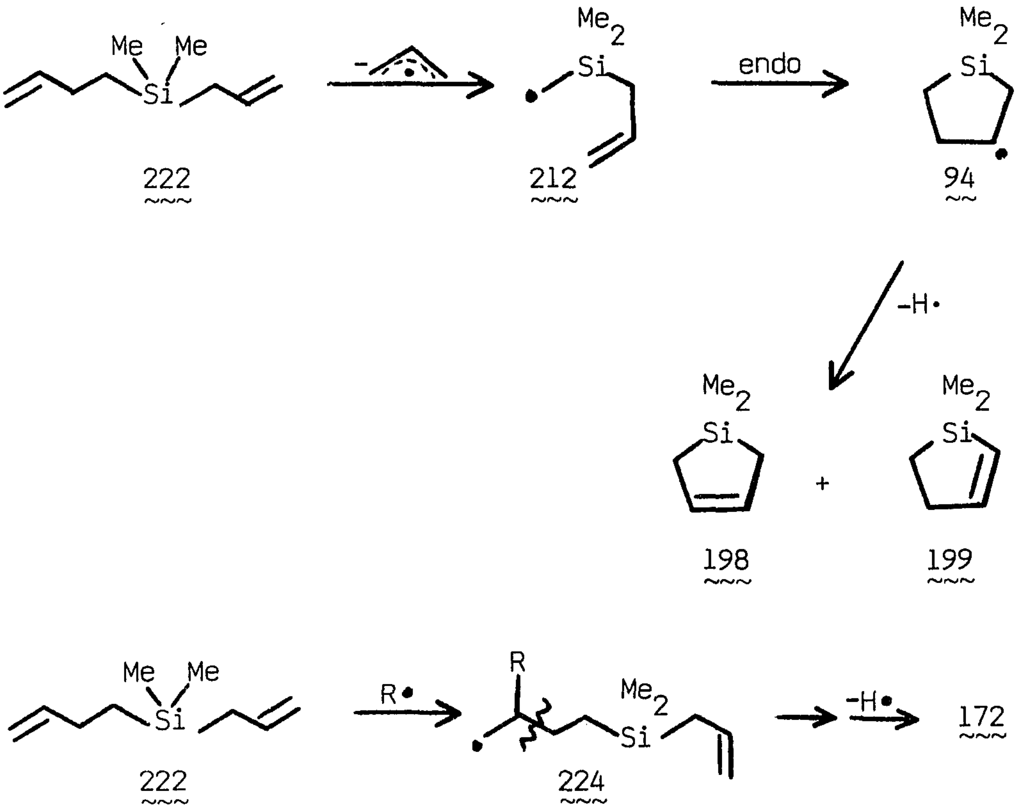
198 (17%)

199 (21%)

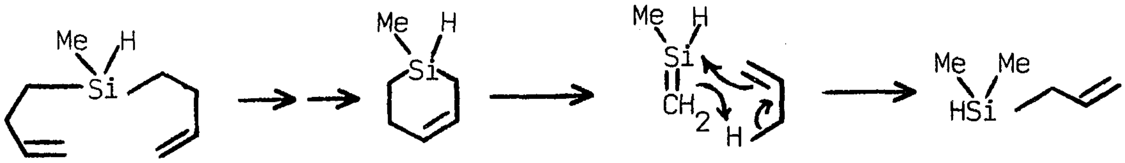
172 (20%)

Mechanistically, the presence of 198 and 199 is quite significant in that they are most likely formed via *endo*-cyclization of α-silyl radical 212 (Scheme 30). Therefore, the mechanism outlined in Scheme 29 for the formation of trimethylallylsilane 120 from dibutenylsilane 218 is believed to be non-operative. Since 212 closes intramolecularly in an *endo*-fashion, it is possible that 68 could have *endo*-cyclized to 219 and proceeded to 120 via the mechanism outlined in Scheme 26. Therefore, of the two possibilities presented here, formation of trimethylsilane 120 via an ene reaction is favored. Furthermore, cyclization

Scheme 30



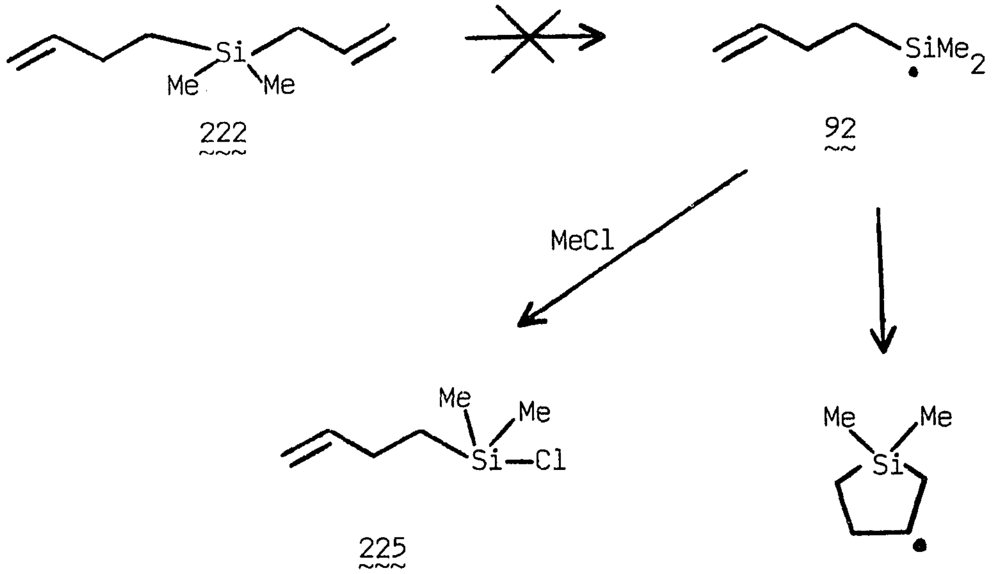
of an α-silyl radical, followed by retro-Diels-Alder reaction and subsequent ene reaction, could account for the observation of dimethylallysilane 60 as the major product of the thermal decomposition of di(3-butenyl)methylsilane 214 (discussed on page 116). In otherwords, retro-Diels-Alder reaction of 217 followed by ene reaction of 1-methylsilene and propene would give 60.



214 217 60

The formation of silacyclopentyl radical 94 from radical 212, which gives 198 and 199, is related to another mechanistic question posed earlier in this section. Route B in Scheme 24 was proposed as an alternative means of forming trimethylsilane 120 from 59. Although this mechanism was dismissed on the basis of some methyl chloride trapping experiments (178), β-cleavage of *endo*-closed silacyclopentyl radical 94 followed by hydrogen abstraction was worth consideration; especially since it is possible that cyclization may be faster than halogen abstraction. However, since silacyclopentyl radical 94 is most likely formed during the thermal decomposition of 222 (Scheme 30), from which absolutely no trimethylsilane 190 is found, then route B in Scheme 24 is even less believable.

Although it is now clear that cleavage of a carbon-allyl bond does occur quite readily in 3-butenylsilanes, there is the possibility that silicon-allyl cleavage could have occured in 222. Furthermore, *endo*-cyclization of the corresponding silyl radical, 92, would give the same silacyclopentyl radical, 94, formed from *endo*-closure of α-silyl radical 212. Therefore, product analysis does not alow for a mechanistic distinction. However, when the pyrolysis of 222 was repeated in a flow system at 540°C with methyl chloride as the carrier gas, GC analysis showed no peaks present that corresponded to (3-butenyl)dimethylchlorosilane 225. Had the silyl radical been responsible for the observed products, it should have been trapped by methyl chloride. Furthermore, the relative ratios of the products formed with methyl chloride and without methyl chloride did not change.



222

92

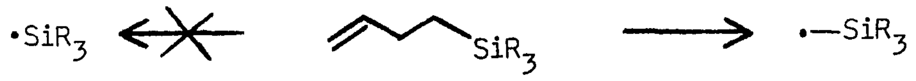
225

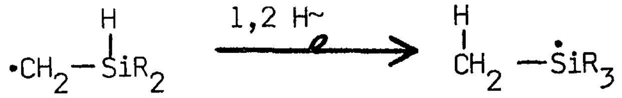
(not observed)

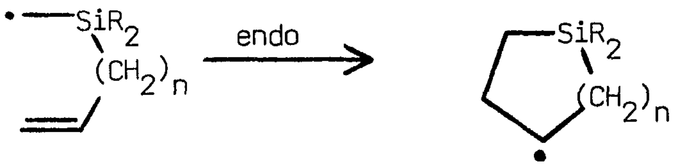
94

In summary, the decomposition of 3-butenylsilanes start with cleavage of the carbon-allyl bond affording α-silyl radicals. The next best alternative, silicon-butenyl cleavage, is found not to occur as readily. This is certainly in keeping with what would be predicted based on published bond energies (99).

The first clear example of 1,2-migration of hydrogen from silicon to a carbon-centered radical was demonstrated in the pyrolysis of 3-butenyldimethylsilane 59. 1,2-Migration of hydrogen was found to be quite competitive with other reactions of the thermally generated α-silyl radical. Also, when substituted with another alkenyl group, these α-silyl radicals are found to undergo intramolecular cyclization in an *endo*-fashion.

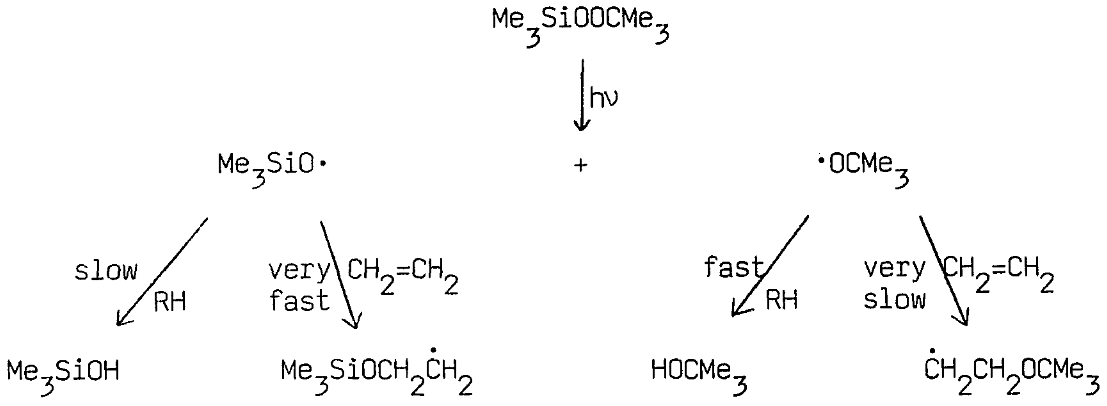






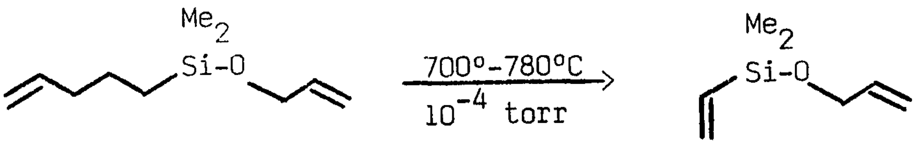
Gas Phase Generation and Reactions of Alkenylsilyloxy Radicals

The addition of silyloxy radicals to olefins is a well-established process. Edge and Kochi have studied the intermolecular addition of trimethylsilyoxy radical to various olefins, such as ethylene, propene and butadiene, by ESR (182). The radical was generated by photolysis of trimethylsilyl tert-butyl peroxide. Although no quantitative data were reported, it was demonstrated the trimethylsilyloxy radical added to olefins much faster than the analogous tert-butoxy radical. Also, hydrogen abstraction by trimethylsilyloxy radical was shown to be a minor process. However, no reports of intramolecular cyclization of silyloxy radicals could be found in the literature. Intramolecular addition of alkoxyl radicals is known (2) (see the Historical section on alkoxyl radical cyclization).



Having clearly demonstrated that silyl radicals, both in solution and in the gas phase, do not cyclize in a Beckwith exo-fashion, a systematic study on the intramolecular closure of silyloxy radicals was undertaken. As was the case with silyl radicals, the degree of *endo*- versus *exo*-closure and the synthetic utility of the cyclization were questions of primary interest. In order to maximize the probability of intramolecular addition, a gas phase generator of alkenylsilyloxy radicals was desired. Pyroltyic cleavage of an allyl group seemed to be a good candidate. Therefore, a series of alkenylallyloxysilanes were synthesized and examined as possible gas-phase precursors to silyloxy radicals.

(4-Pentenyl)allyloxydimethylsilane 226 was prepared in 66% yield by addition of 4-pentenyldimethylchlorosilane 225 to an ether solution containing one equivalent each of allyl alcohol and pyridine. Pyrolysis of 226 gave one major product at 700°C (1 X 10^{-5} mm Hg) along with 77% of 226. The product was present in 25% yield based on reacted 226, and was identified as vinylallyloxydimethylsilane 227. The yield of 227 was reduced to 12% when 78% of 226 was consumed at 780°C (1 X 10^{-4} mm Hg). One possible route to 227 would envolve *endo*-closure of silyloxy radical

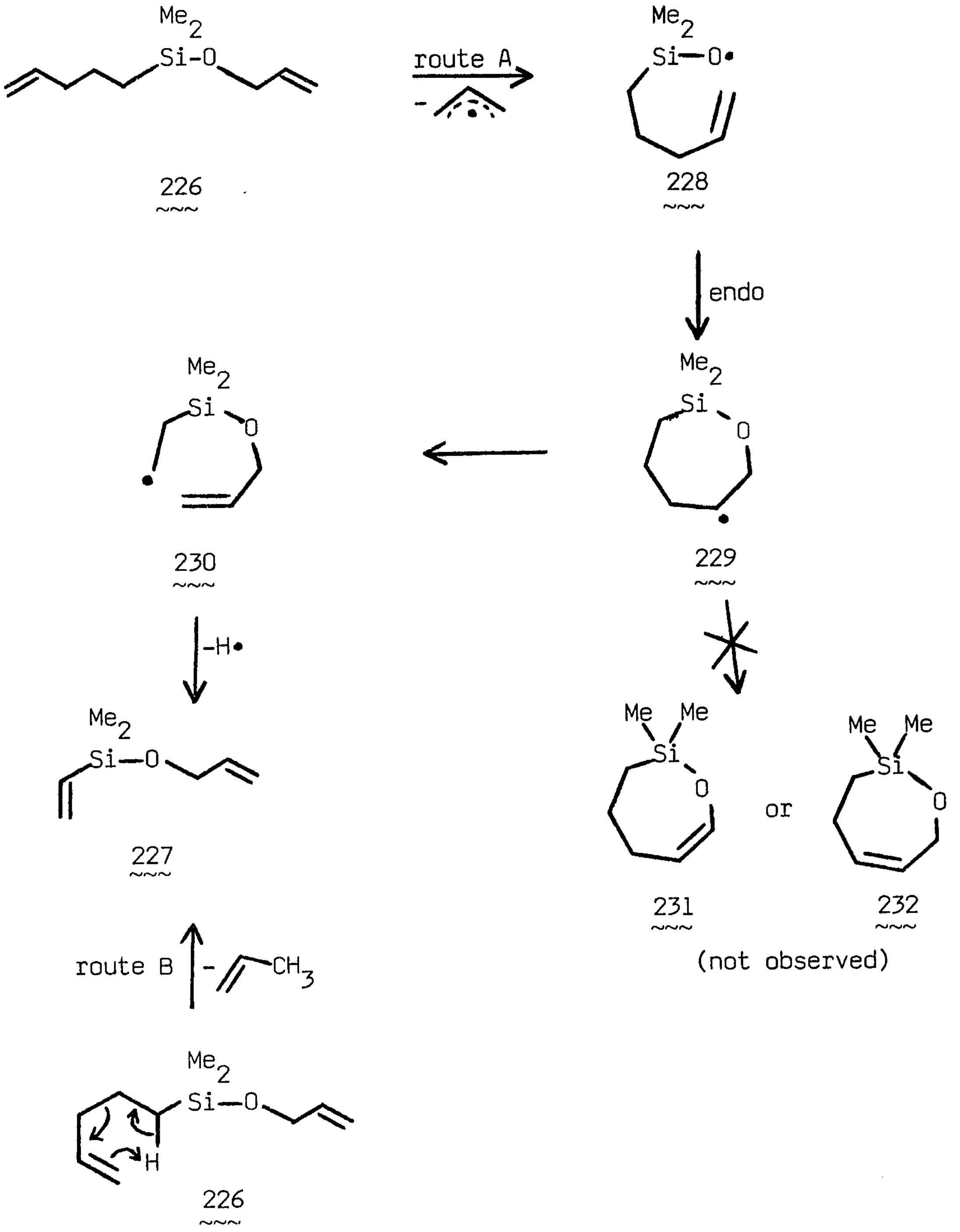


226

227 (12-25%)

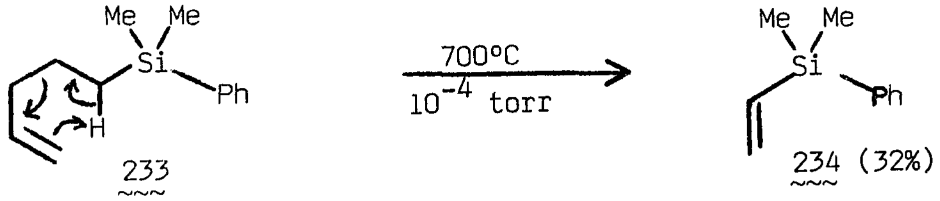
228 followed by β-cleavage of 229 and loss of hydrogen from 230 (Scheme 31, route A). Although this mechanism is certainly consistent with the formation of 227, the complete absence of 231 and 232 from the pyrolysate (83% mass recovery) may suggest otherwise. Based on previous observations,

Scheme 31


Me$_2$
Si-O
226
route A
Me$_2$
Si—O•
228
endo
Me$_2$
Si
O
229
Me$_2$
Si
O
230
-H•
Me$_2$
Si—O
227
Me Me
Si
O
231
or
Me Me
Si
O
232
(not observed)
route B
CH$_3$
Me$_2$
Si—O
H
226

some loss of hydrogen from 229 would be expected. An alternative mechanism (route B, Scheme 31) would involve an all-carbon concerted retroene elimination of propene. If route B of Scheme 31 is operative, then replacement of the allyloxy group by a thermally non-labile group should not alter the course of this reaction.

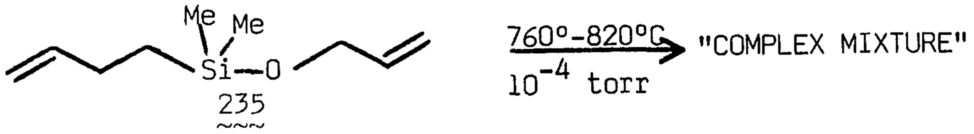
Indeed, pyrolysis of 4-pentenylphenyldimethylsilane 233 at 700°C gave 32% yield of vinyldimethylphenylsilane 234 (183) as predicted. The yield of 234 was reduced to 19% at 780°C accompanied by formation of dimethylphenylsilane (10%) (184) and allyldimethylphenylsilane (6%) (185); formed most likely via radical processes. The yields are based on consumed 233. Since the formation of 234 must undoubtedly occur via a retroene process, it seems reasonable that a retroene mechanism (route B, Scheme 31) and not the silyloxy radical pathway (route A, Scheme 31) accounts for the formation of 227 from 226. The temperature requirement for these retroene reactions are in keeping with those reported by Egger and Vitins (186) for the retroene formation of propene and butadiene from hepta-1,6-diene.



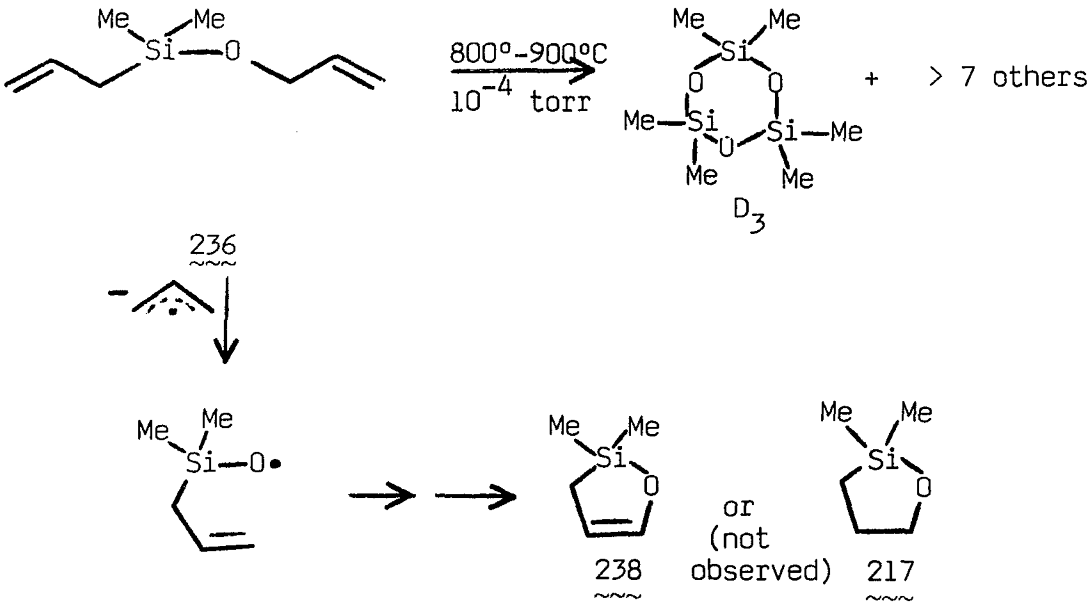
233

234 (32%)

In order to remove the possibility of retroene elimination, the next lower homolog of 226 was examined. However, when 3-butenylallyloxydimethylsilane 235 was pyrolyzed at 760°C (1 X 10^{-5} mm Hg), only 69% of the mass was recovered which consisted of *ca.* 80% 235. A complex mixture of about nine volatile products made up the other 20%. None were present in high enough yields to be isolated. On increasing the pyrolysis temperature to 820°C, a very complex mixture of greater than fifteen products was formed; none were major. The mass recovery dropped to 44%. Obviously, the thermal decomposition of 235 is a complex problem which is probably aided by the presence of a 3-butenyl group (see the section on the Pyrolytic Decomposition of 3-Butenylsilanes).

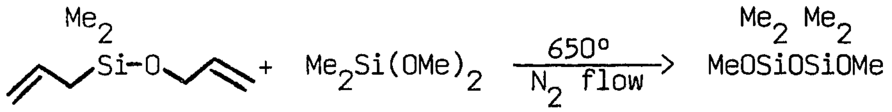


Allyloxyallyldimethylsilane 236 was the next homolog examined in the series which lead to some interesting results. When 236 was pyrolyzed between 800° and 900°C in a vacuum (1×10^{-4} mm Hg), more than eight products were formed as evidenced by GC. GCMS analysis revealed that hexamethylcyclotrisiloxane (D_3) was one of the products present in the mixture. Other compounds had molecular formulas consistent with isomers of 236, 236 plus dimethylsilanone ($Me_2Si{=}O$), and isomeric D_3. The major product throughout this temperature range was unreacted 236. There were no compounds present by GCMS that had molecular formulas consistent with either 238 or 117. However, it is possible that these compounds might not have been stable under the reaction conditions. Whether the primary products formed from 236 are stable or not, the presence of D_3 in the pyrolysate suggested that dimethylsilanone, or an equivalent thereof, was generated in the reaction.



Silanones have received much attention in the literature and much of the chemistry and many of the reactions of these reactive intermediates appears to be understood (158,187,188). One of the main reactions is trimerization to form D_3 analogs which is widely accepted as diagnostic for the presence of a silanone. Another well-known reaction of silanones is silicon-oxygen bond insertion (189). This reaction has been used to chemically trap these intermediates. One of the most frequently used trapping reagents is dimethyldimethoxysilane 239 (190).

A copyrolysis of 236 and a ten fold excess of dimethyldimethoxysilane was carried out to trap any dimethylsilanone that may have been formed. The reaction was done in a nitrogen-flow system (35 mL/min) through a quartz tube heated to 650°C. Analysis of the pyrolysate by GC showed one major product along with dimethyldimethoxysilane **239**. The compound was identified as sym-dimethoxytetramethyldisiloxane **238** (190) which was present in 99% yield. Since **240** is the known dimethylsilanone



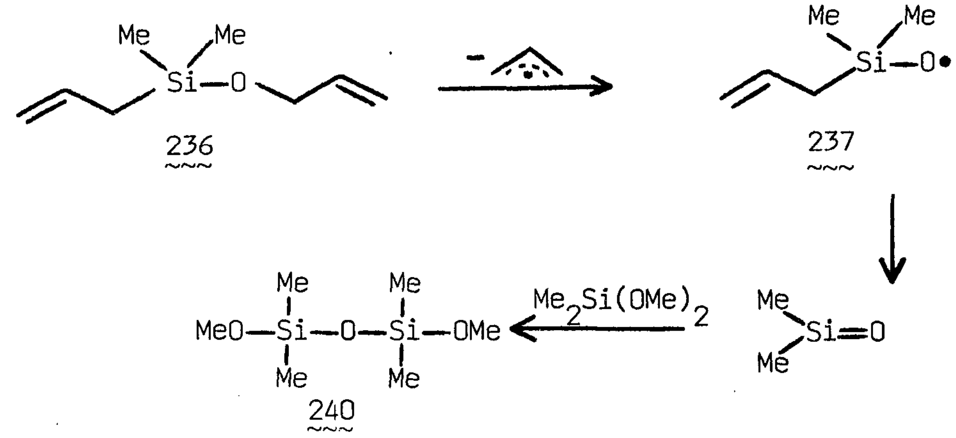
236 **239** **240** (99%)

(93%)

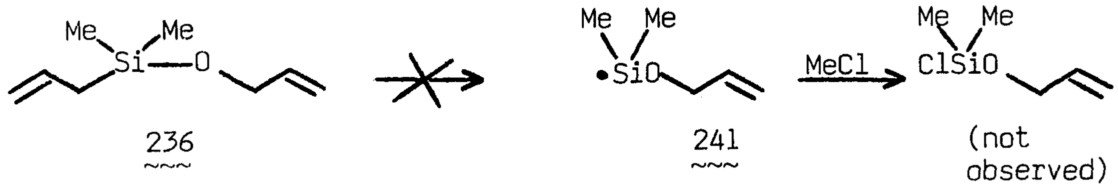
trap (189), the mechanism in Scheme 32 is offered. Namely, homolytic cleavage of the oxygen-allyl bond would give allyldimethylsilyloxy radical **237**. β-Elimination of radical **237** via silicon-allyl cleavage would give dimethylsilanone which in the presence of excess dimethyldimethoxysilane **239** undergoes insertion affording **240**. Since dimethyldimethoxysilane **239** has also shown to give **240** (191), **239** was pyrolysed under identical conditions. The yield of **240** from dimethyldimethoxysilane **239** was approximately 2% which makes the actual yield of **240** from allyloxyallydimethylsilane **236** 93%.

It is just as likely that the initial cleavage in the decomposition of **236** could occur at the silicon-allyl bond. The bond dissociation energies for a silicon-carbon (89.3 kcal/mol (99)) and an oxygen-carbon (85 kcal/mol (192)) bond are too close to argue for predominance of either cleavage. However, the previously used methyl chloride trapping experiment could allow for the distinction as initial cleavage of the silicon-allyl bond would give the corresponding silyl radical which

Scheme 32

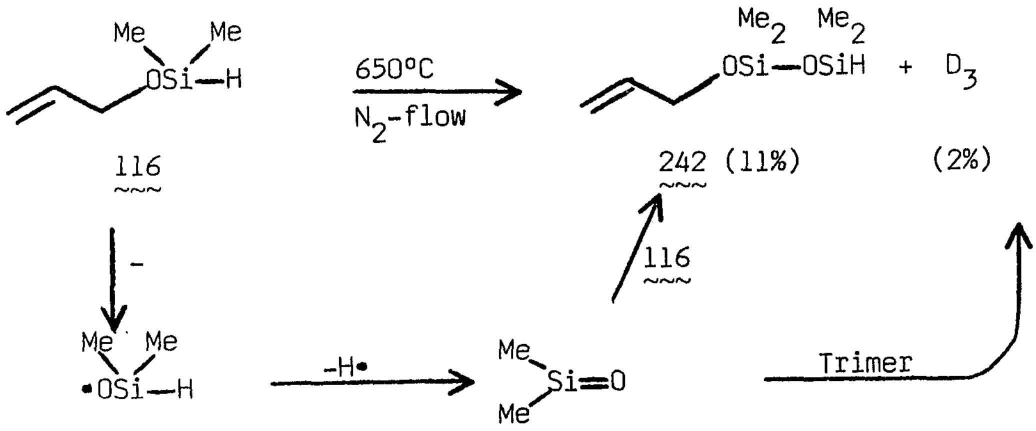


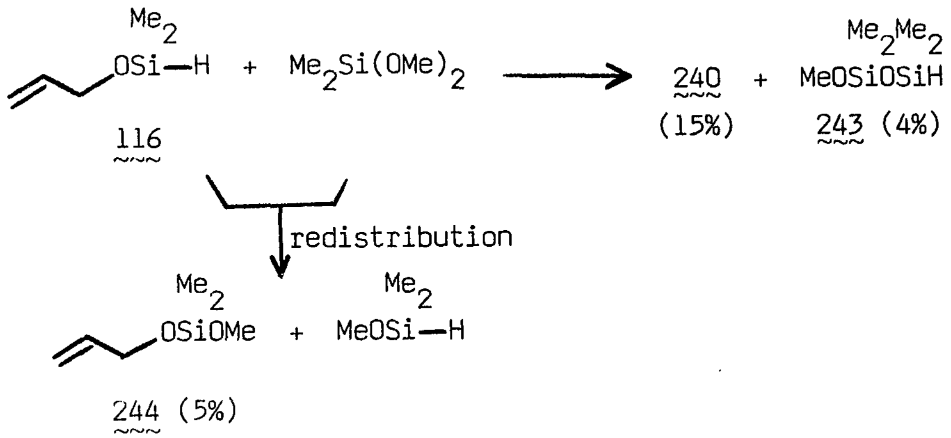
should abstract chlorine from methyl chloride. Thus, when 236 was pyrolyzed in a methyl chloride-flow system (35 mL/min), in a temperature range where only a minimum amount of decomposition of 236 would take place (500°C-560°C), no allyloxychlorodimethylsilane was found in the pyrolysate by GCMS. This suggested that oxygen-allyl cleavage (Scheme 32), and not silicon-allyl cleavage is the initial step in the formation of dimethylsilanone from 236. Evidence that a reaction takes place in the presence of methyl chloride is seen in the formation of D_3 (GCMS) in this temperature range.



Although several methods exist for the formation of a silanone unit (158,187,188), the thermolysis of allyloxyallyldimethylsilane is certainly one of the highest yield generators. Furthermore, it has an major advantage over other methods because of the simplicity of the precursor which is easily prepared from commercially available starting materials.

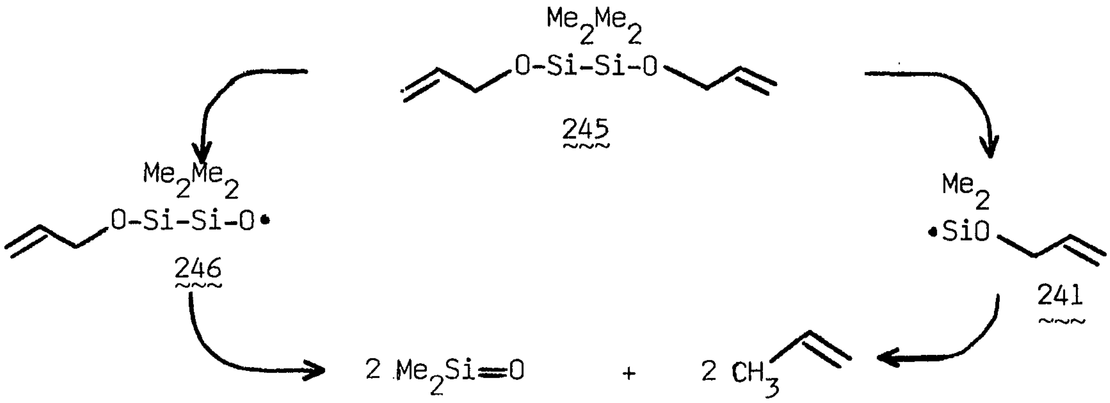
It is important that the second leaving group in the decomposition to dimethylsilanone be capable of stabilizing the radical. This was demonstrated when allyloxydimethylsilane 116 was pyrolyzed at 650°C in a nitrogen-flow system (35 mL/min). Only 38% of the total mass was recovered and, although GC analysis showed only two volatile silicon products, they were present in very poor yields. However, a very complex mixture of none isolable high molecular materials were seen by GC with no recovered 116. The two volatile compounds were identified as allyloxy-1,1,3,3-tetramethyldisiloxane 242 (11%) (193) and D_3 (2%); presumably formed via the intermediacy of dimethylsilanone. The presence of dimethylsilanone was checked by copyrolyzing 116 with dimethyldimethoxysilane 239 under the same conditions. A 15% yield (corrected for self-decomposition of 239) of sym-dimethoxytetramethyldisiloxane 240 was obtained. The other two products, 243 (4%) and 244 (5%), are most likely formed by a combination of a redistribution reaction (194) and silanone trapping.



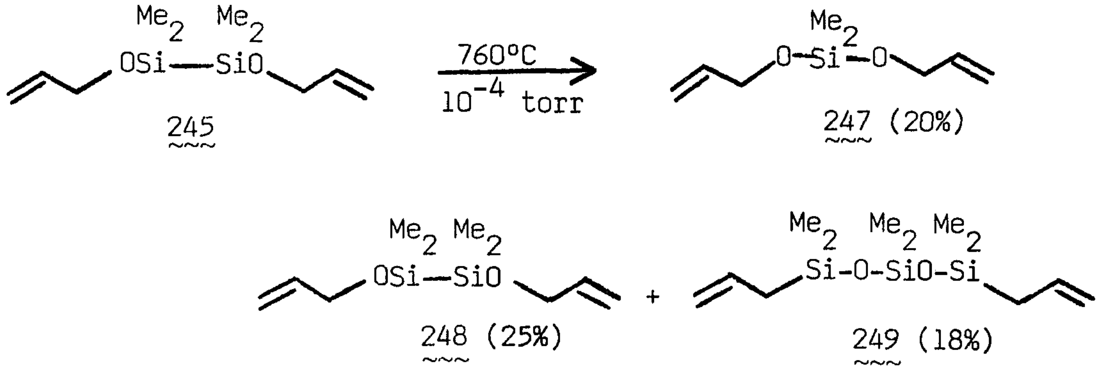


Therefore, the pyrolysis of allyloxydimethylsilane 116 not only demonstrates the importants of a second radical stabilizing group, but also demonstrates that oxygen-allyl cleavage does take place. The alternative would involve silicon-hydrogen cleavage followed by disproportion of silyl radical 241. Based on bond energies (99), this would be a higher energy process by at least 15 kcal/mol.

Such a high yield production of dimethylsilanone from allyloxyallyldimethylsilane 236 led to the postulation of other similar precursors. One compound that was thought to be a good candidate was 1,2-diallyloxy-1,1,2,2-tetramethyldisilane 245 (195). It was rationalized that 245 might decompose to two moles each of dimethylsilanone and propene. This could occur either via initial oxygen-allyl or silicon-silicon homolysis followed by disproportionation. Although it is well-known that alkoxy disilanes undergo reductive-elimination to silylenes (147), it was believed that conditions were silyloxy radical formation would be competative could be found. When 245 was pyrolyzed at 760°C (1 X 10^{-4} mm Hg), 66% of the mass was recovered and analyzed by GC. Three major



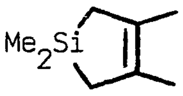
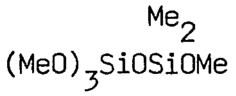
products were present. They were isolated by preparative GC and identified as diallyloxydimethylsilane 247 (20%) (196), 3-allyloxy-1-allyl-1,1,3,3-tetramethyldisiloxane 248 (25%), and 1,5-diallyl-1,1,3,3,5,5-hexamethyltrisiloxane 249 (18%) (197). All of the starting material, 245, was consumed under these conditions.



The presence of a dimethylsilanone unit ($Me_2Si{=}O$, $C_2H_6Si_1O_1$) in all of the products suggested that perhaps 245 had decomposed as predicted. However, 247 could be an α-elimination product that would be formed on extrusion of dimethylsilylene from 245. To examine these possibilities, trapping experiments for both reactive intermediates were carried out.

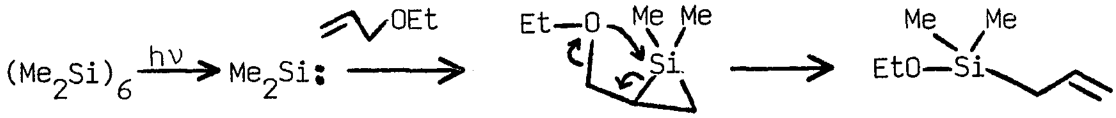
Therefore, a nitrogen-flow (35 mL/min) copyrolysis of 245 and 2,3-dimethylbutadiene (silylene trap) (147), and a copyrolysis of 241 and tetramethoxysilane (silanone trap) (188) were done at 500°C. These data are given in Table 14. From these data, not only can it be seen that addition of

Table 14. Trapping experiments of 241 at 500°C

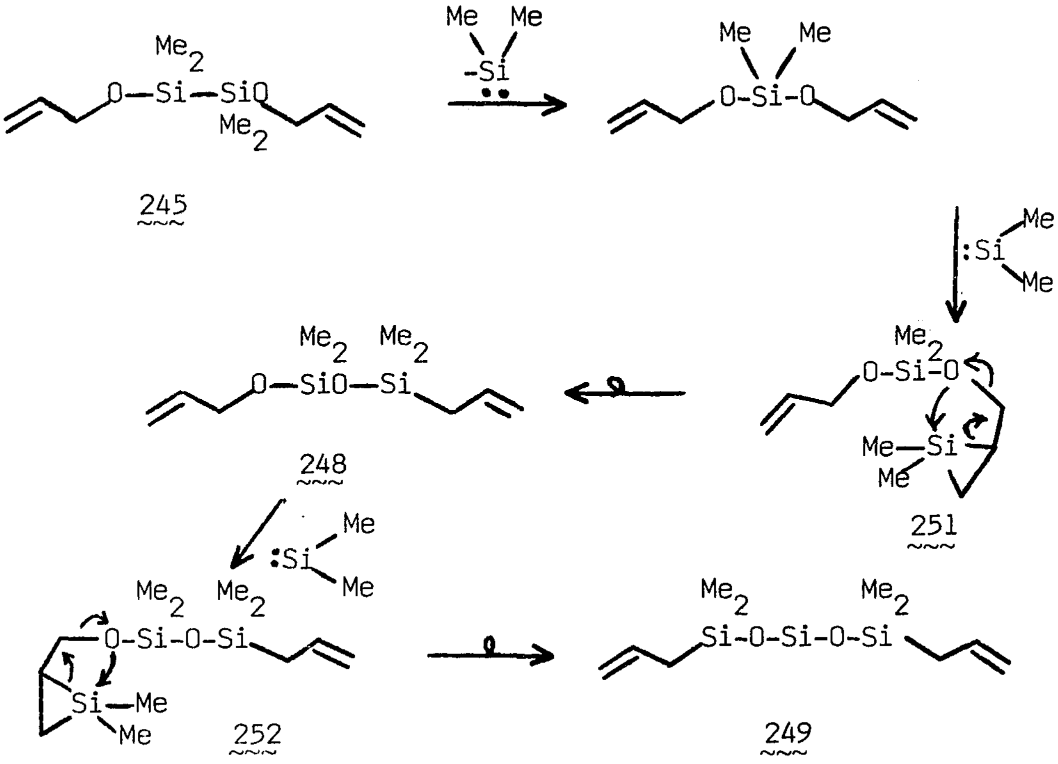
	Relative % Yield Ratio			Trap Product (% Yield)	
Trap	247	248	249		
None	1	1.25	9	-	
	1	0.29	0	 250	(11%)
$(MeO)_4Si$	1	1	trace	 $(MeO)_3SiO\overset{Me_2}{Si}OMe$ 240	(0%)

2,3-dimethylbutadiene reduces the relative yield of both 248 and 249, but the characteristic silylene trapped adduct, 250, is also formed. Thus, a silylene is certainly involved in the thermal decomposition of 245. However, there was no evidence of silanone trapping with an eight fold excess of tetramethoxysilane. Also, notice that the relative yield of 247 and 248 did not change significantly.

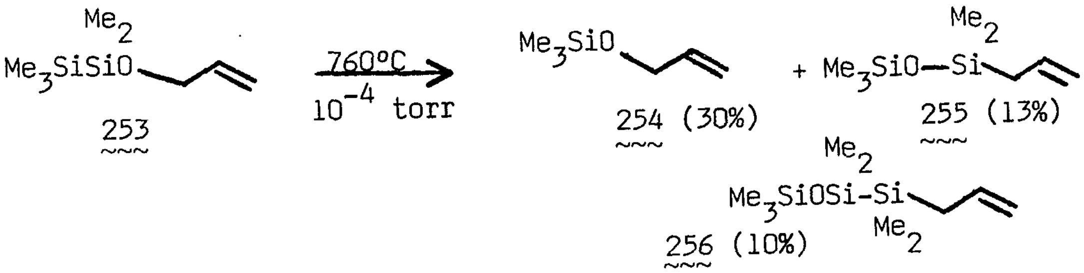
The observations summarized in Table 14 lead to the proposed mechanism outlined in Scheme 33. Reductive-elimination of dimethylsilylene from 245 would afford diallyloxydimethylsilane 247. Insertion of dimethylsilylene into the π-bond of 247 followed by a six-electron rearrangement would give 248, which could repeat the π-insertion/rearrangement process giving the third product 249. This mechanism seems to best fit all of the observations. The π-insertion/rearrangement process is not without literature precedent as Ishikawa and coworkers (198) have shown that photochemically generated silylenes add to allyl ethers affording silyl ethers in 3% to 12% yield.



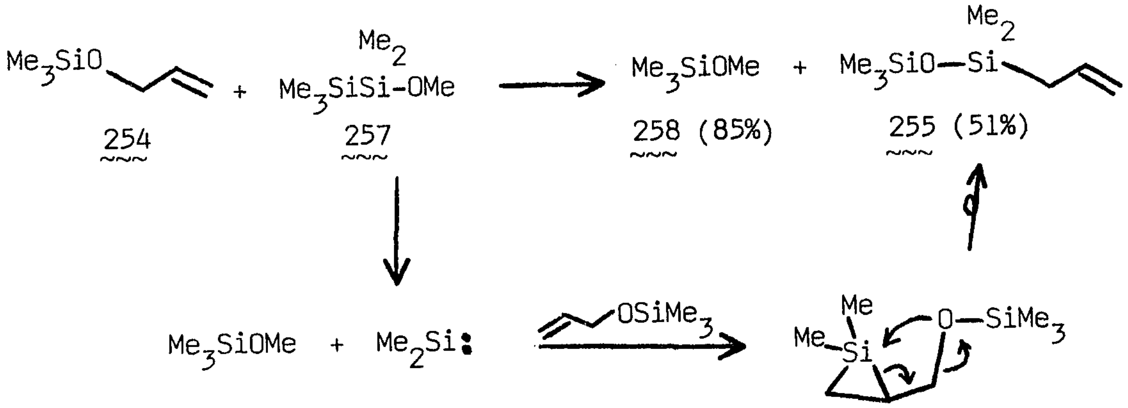
Scheme 33



To examine the scope of this allyloxydisilane rearrangement, the precursor was made simpler by replacing one of the allyloxy groups with a methyl. Thus, when 1-allyloxypentamethyldisilane 253 was pyrolyzed at 760°C in a vacuum (1 X 10^{-4} mm Hg), GC analysis of the pyrolysate (77% mass recovery) showed cleanly three major products. They were isolated by preparative GC (15 ft, 20% OV-101/Chrom W, column temperature 130°C) and identified as allyloxytrimethylsilane 254 (30%) (199), 1-allylpentamethyldisiloxane 255 (13%) (137), and 1-(trimethylsiloxy)-2-allyl-1,1,2,2-tetramethyldisilane 256 (10%). All of 253 was consumed under these conditions. These products are best rationalized as proceeding

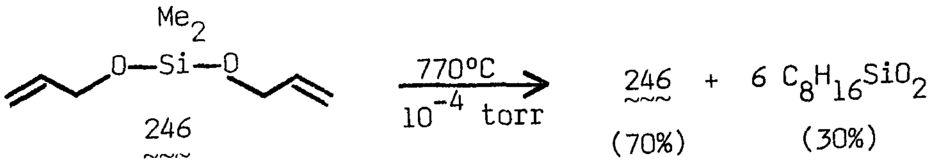


via a mechanism involving α-elimination of dimethylsilylene followed by π-insertion and subsequent rearrangement. The mechanism is analogous to that outlined for the rearrangement of 245 (Scheme 33). When a copyrolysis of 253 and a thirteen fold excess of 2,3-dimethylbutadiene was done at 500°C, trimethylallyloxysilane 254 was formed in 87% yield and the characteristic silylene adduct (147), 1,1,3,4-tetramethyl-1-silacyclopent-3-ene 250, was present in 95% yield. The yield of 255 was reduced to only 4% while no 256 was formed, thus, demonstrating the importance of dimethylsilylene to this transformation. Perhaps the best evidence for π-insertion of dimethylsilylene followed by rearrangement was found when 254 was independently pyrolyzed in the presence of another silylene generator (200). Copyrolysis of 254 and 1-methoxypentamethyldisilane 257 in a nitrogen-flow system at 500°C cleanly afforded trimethylmethoxysilane 258 (85%) and 255 (51%).



Although this chemistry of allyloxydisilanes produced some equally interesting results, it was still desired to find evidence of intramolecular cyclization of an alkenylsilyloxy radical. The problems with the precursors tried thus far were the alternative decomposition routes available to them. While (4-pentenyl)allyloxydimethylsilane 226 was shown to undergo an all-carbon retroene elimination, the next lower homolog, 3-butenylallyloxydimethylsilane 235, gave a complex mixture of products. Allyloxyallyldimethylsilane 236 appears to have given a silyloxy radical under pyrolytic conditions. However, decomposition to dimethylsilanone prevents the cyclization process. With allyloxydisilanes, reductive-elimination to silylene predominated.

One possible precursor that does not possess any of the features of those previously tried is diallyloxydimethylsilane 247. The only reasonable mode of decomposition of 247 is via initial oxygen-allyl cleavage. Therefore, 247 was thought to have the best chance of cyclizing. Thus, the flash-vacuum pyrolysis (1 X 10^{-4} mm Hg) of 247 was carried at 770°C. Analysis by GC showed no products with shorter retention times (more volatile) than starting material 247 which made up about 70% of the mixture. The other 30% of the pyrolysate (80% mass recovery) was made up of six isomers of 247. At 830°C (1 X 10^{-4} mm Hg), diallyloxydimethylsilane 247 made up only 50% of the pyrolysate with the same six $C_8H_{16}SiO_2$ isomers making up the other 50%. There were only very trace amounts (< 2%) of other volatile compounds formed. Therefore, the pyrolysis of 247 was found not to be a useful precursor to alkenylsilyloxy radicals.



In summary, unlike allylsilanes which give silyl radicals, pyrolysis of allyloxysilane as precursors to silyloxy radicals does not readily occur. However, this may not be entirely due to a reluctance of allyloxysilanes to cleave to silyloxy radicals as it is the availability of alternate, and perhaps lower energy, pathways to decomposition. Only in one case, the clean formation of dimethylsilanone from allyloxyallyldimethylsilane 236, was any evidence found for homolysis to a silyloxy radical. All the other compounds either failed to give silyloxy radicals or the products could be rationalized as having formed via alternative, but equally interesting, pathways.

CONCLUSION

When generated in dilute aromatic solvents, alkenylsilyl and alkenyldisilanyl radicals were shown to undergo intramolecular cyclization when the total chain length consisted of five and six atoms. However, no cyclic products were observed for those radicals where the total chain length was four atoms. In all cases examined, including an alkenyloxysilyl radical, the products formed were those corresponding to endo-closure of the silyl radical on to the π-unit. The regiospecificity of silyl radical cyclization (endo-closure) is, therefore, completely opposite that which would be predicted by the Beckwith rules (1) (exo-closure) of radical cyclization. The departure of silyl radicals from the Beckwith-mode of closure is due to the increased length of a silicon-carbon bond and the pyramidal geometry of the silicon radical. Therefore, it is clear that the Beckwith rules can not be extended to include silicon-centered radicals.

In the gas phase, silyl radicals were also shown to cyclize in a regiospecific endo-fashion. This was demonstrated for 1,2-diallyl and 1-allyl-2-vinyldisiloxanes, and cis-2-phenyl-1-(allyldimethylsilyl)-ethylene which afforded silyl radicals via cleavage of the silicon-allyl bond under pyrolytic conditions. Alkenyldisilanyl radicals, when generated by silicon-allyl cleavage at high temperatures, were found to undergo a facile disproportionation to silenes. The silene intermediates underwent rearrangement to 1,3-disilacyclics via a silene to silylene rearrangement. A silene to silylene rearrangement, and not the previously proposed silyl radical mechanism (3), best explains the clean, high yield (61%) conversion of 1,2-diallyl-1,1,2,2-tetramethyldisilane to 1,1,3,3-tetramethyl-1,3-disilacyclopentene. A direct concerted retroene elimination to the silenes was not ruled out in this study.

Unfortunately, hydrogen abstraction by a peroxy radical or silicon-allyl homolysis as generators of alkenylsilyl radicals were both found to be low to moderate yield processes. Therefore, these are not viewed as good synthetic routes to silacyclic compounds.

The pyrolytic decomposition of 3-butenylsilanes starts with carbon-allyl homolysis of the butenyl unit to afford α-silyl radicals. When 3-butenyldimethylsilane was pyrolysed to afford dimethylsilylcarbinyl radical, 1,2-hydrogen migration from silicon to carbon took place. This was evidenced by the formation of trimethylsilyl radical which was trapped by methyl chloride as trimethylchlorosilane. This is the first example of 1,2-hydrogen migration from silicon to a carbon-centered radical. Good evidence for the formation of these α-silyl radicals was demonstrated in the endo-closure (37%) of allyldimethylsilylcarbinyl radical to silacyclopentene products. Allyldimethylsilylcarbinyl radical was generated from the corresponding 3-butenylsilane.

Finally, allyl cleavage of allyloxysilanes was found not to be a good method of generating silyloxy radical in the gas phase. However, the pyrolysis of allyloxyallyldimethylsilane afforded sym-dimethoxytetramethyldisiloxane in very good yield (93%) when carried out in the presence of dimethoxydimethylsilane (silanone trap). This was shown to occur via homolysis of the oxygen-allyl bond to afford allyldimethylsilyloxy radical which underwent disproportionation to dimethylsilanone which was trapped. This is one of the highest yield silanone generators. All other allyloxysilanes tried decomposed via alternative pathways.

EXPERIMENTAL

Instrumentation

^{1}H NMR spectra were obtained either on a Varian model EM-360, a Nicolet model 1280 300 MHz, or a Bruker WM 300 MHz spectrometer. Decoupling experiments were done on the same spectrometers. ^{13}C NMR spectra were obtained either on a Joel model FX90Q 90 MHz or a Nicolet model 1280 300 MHz spectrometer. All chemical shifts were reported as parts-per-million (δ scale) using either TMS, benzene, chloroform or acetone as internal standards.

IR spectra were recorded on an IBM IR/90 series FTIR spectrometer. The bands were reported in reciprocal centimeters (cm^{-1}).

GCMS data were collected at 70 eV on a Finnegan model 4023 quadropole mass spectrometer, and exact mass measurements were obtained on a AEI MS-902 mass spectrometer. Gas chromatographic separations were performed on a Varian-Aerograph series 1700 instrument.

Combustion analyses were performed on previously unreported compounds by MicAnal, Tucson, AZ.

Unless otherwise specified, the yields reported herein were determined by GC using internal standards and predetermined response factors. The peak areas and response factors were obtained using either a Varian-Aerograph series 1700 or a Hewlett Packard series 5790A gas chromatography instrument.

Procedures and Results

The solution radical cyclization reactions were carried out in degassed, evacuated, sealed pyrex ampoules in a heated oil bath. All peroxide decomposition reactions were conducted both in tert-butyl benzene and in benzene, but yields were determined in only one solvent. No effect of solvent was observed.

All GC yields are based on the amount of reacted starting material.

Synthesis of 5-bromo-1-pentene and 4-bromo-1-butene

The synthesis of 5-bromo-1-pentene and 4-bromo-1-butene were accomplished by a literature procedure (201) and were characterized by NMR spectroscopy. 4-Bromo-1-butene is also commercially available from Aldrich Chemical Company.

Synthesis of 1-chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane

The synthesis of 1-chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane were accomplished according to the method of Sakurai et al. (202).

Synthesis of 4-pentenyl-1-dimethylsilane 64 (114)

To a stirred mixture of excess Mg turnings in 125 mL of dry THF under N_2 was added dropwise a solution containing 29.6 g (0.20 mol) of 5-bromo-1-pentene and 18.9 g (0.20 mol) of dimethylchlorosilane in 125 mL of dry THF. After 8 hours, the reaction mixture was hydrolyzed with excess H_2O and transferred to a separatory funnel containing 100 mL of pentane. The pentane layer was extracted with H_2O, separated, dried over

Na_2SO_4, and filtered. Distillation (108-118°C) afforded 17.8 g (70%) of **64**: ^1H NMR ($DCCl_3$) δ 0.06 (d, J = 3.62 Hz, 6H), 0.57-0.63 (d of t, J = 3.24 Hz, J = 8.28 Hz, 2H), 1.39-1.50 (m, 2H), 2.04-2.12 (q, J = 7.1 Hz, 2H), 3.83-3.87 (m, 1H), 4.94 (d, J = 10.39 Hz, 1H), 5.00 (d, J = 19.07 Hz, 1H), 5.73-5.86 (m, 1H); ^{13}C NMR ($DCCl_3$) δ -4.41, 13.79, 23.97, 37.24, 114.55, 138.87; IR (neat) 2112 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 127 (M-1, 1%), 113 (6), 100 (7), 87 (44), 85 (18), 60 (9), 59 (100) calculated for SiC_7H_{15} m/e 127.09431, measured m/e 127.09489. Elemental analysis calculated for $C_7H_{16}Si$: C, 65.52; H, 12.59. Found: C, 65.72; H, 12.72.

Synthesis of 3-butenyldimethylsilane **59** (114)

Synthesis of **59** was accomplished by the same procedure as for **64** using 14.1 g (0.15 mol) of 4-bromo-1-butene and 20.0 g (0.15 mol) of chlorodimethylsilane dissolved in 100 mL of dry THF to provide 13.6 g (80%) of **59** after distillation (65°-75°C). The spectral properties of **59** matched those in the literature (114): ^1H NMR ($DCCl_3$) δ 0.13 (d, J = 3.69 Hz, 6H), 0.71-0.78 (m, 2H), 2.11-2.19 (m, 2H), 3.89-3.94 (m, 1H), 4.95 (d of d, J_{gem} = 1.61 Hz, J_{cis} = 10.06 Hz, 1H), 5.04 (d of d, J_{gem} = 1.61 Hz, J_{trans} = 17.06 Hz, 1H), 5.86-6.06 (m, 1H); ^{13}C NMR δ ($DCCl_3$) -4.36, 13.46, 28.52, 113.09, 141.2; IR (neat) 2116 cm^{-1} (SiH) mass spectrum m/e (% rel. int.) 113 (M-1, 1%) 99 (16), 86 (14), 72 (22), 71 (26), 59 (100), 58 (23) calculated for SiC_6H_{13} (M-1) m/e 113.07866, measured m/e 113.07872. Elemental analysis calculated for $C_6H_{14}Si$: C, 63.06; H, 12.38. Found: C, 63.41; H, 12.54.

Synthesis of allyldimethylsilane 60

To a stirred mixture of excess Mg turnings in 100 mL of THF under N_2 was added a small portion of allyl bromide for initiation. The remainder of the allyl bromide (28.8 g, 23.9 mmol total) and 22.6 g (23.9 mmol) of dimethylchlorosilane were dissolved in 100 mL of dry THF and added dropwise to the stirred solution at a rate sufficient to maintain reflux. After stirring for 12 hours, the reaction mixture was hydrolysed with excess H_2O and transferred to a seperatory funnel containing 100 mL of pentane. The pentane layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. Fractional distillation (67°-70°C) gave 15.0 g (63%) of allyldimethylsilane 60: ^{1}H NMR ($DCCl_3$) δ 0.05 (d, J = 4.0 Hz), 1.53 (broad d of d, J = 4.0 Hz, J = 8.0 Hz, 2H), 3.63-4.04 (m, 1H), 4.57-5.03 (m, 2H), 5.40-6.15 (m, 1H); IR (neat) 2120 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 100 (18), 99 (7), 85 (33), 72 (29), 61 (6), 59 (100), 58 (13), 57 (8). Compound 60 is also commercially available from Petrarch Systems Inc.

Synthesis of cyclopropyldimethylsilane 103 (61)

To a stirred clowdy suspension of 0.69 M cyclopropyl lithium in ether, freshly prepared at 0°C under N_2 by the method of Seyferth and Cohen (203) using 5.00 g (41.4 mmol) of cyclopropyl bromide (Aldrich) and 2 equivalents of finely cut lithium wire, was added 4.73 g (50.0 mmol) of dimethylchlorosilane in a dropwise fashion. The reaction mixture was stirred at 0°C for 5 minutes then allowed to warm to room temperature and stirring continued for an additional 15 minutes. The resulting slurry was then filtered through celite and washed with ether. Fractional distillation (60°-64°C) afforded 3.27 g (79% yield) of cyclopropyldimethylsilane 103: ^{1}H NMR ($DCCl_3$) δ -0.43 to -0.34 (m, 1H), 0.03 (d, J = 3.67 Hz, 6H), 0.18-0.26 (m, 2H), 0.56-0.62 (m, 2H), 3.71-3.77 (m, 1H); ^{13}C NMR ($DCCl_3$) δ -6.32, -5.03, 1.66; IR (neat) 2130 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 100 (1), 99 (7), 85 (39), 73 (7), 72 (65), 60 (8), 59 (100), 57 (11).

Synthesis of (3-butenyl)-1,1,2,2-tetramethyldisilane 62

To a stirred mixture of excess Mg turnings and 7.33 g (39.4 mmol) of 1,2-dichlorotetramethyldisilane in 25 mL of dry THF under N_2 was added a small portion of 4-bromo-1-butene for initiation. The remainder of the 4-bromo-1-butene (5.32 g, 39.4 mmol total) was dissolved in 50 mL of dry THF and added dropwise to the stirred solution. After 7 hours, the liquid phase was removed by vacuum distillation (ca. 0.05 torr) at room temperature and collected at -78°C. The distillate was then added to a stirred solution of excess $LiAlH_4$ in 200 mL of ether. The organic phase was removed by distillation (0.05 torr, 25°C), diluted with 100 mL of pentane, extracted with H_2O, separated, and dried over Na_2SO_4. Isolation of 2.0 g of pure 62 was accomplished by preparative GC on a 9 ft, 20% SE-30/Chromosorb W column at 140°C. The GC-determined yield was 30% of 62: ^{1}H NMR ($DCCl_3$) δ 0.09 (s, 6H), 0.13 (d, J = 4.63 Hz, 6H), 0.70-0.76 (m, 2H), 2.02-2.12 (m, 2H), 3.60-3.67 (m, 1H), 4.88 (d of d, J_{gem} = 1.32, J_{cis} = 10.12 Hz, 1H), 4.98 (d of d, J_{gem} = 1.32, J_{trans} = 17.06, 1H), 5.82-5.95 (m, 1H); ^{13}C NMR ($DCCl_3$) δ -6.53, -3.82, 14.55, 28.68, 112.92, 141.58; IR (neat) 2091 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 172 (1), 157 (4), 144 (15), 129 (7), 117 (18), 116 (19), 114 (7), 113 (53), 112 (8), 99 (8), 98 (10), 86 (11), 85 (74), 73 (47), 72 (7), 71 (7), 60 (10), 59 (100) calculated for $Si_2C_8H_{20}$ m/e 172.11036, measured m/e 172.11129. Elemental analysis calculated for $C_8H_{20}Si_2$: C, 55.72; H, 11.71. Found: C, 55.94; H, 11.72.

Synthesis of allyl-1,1,2,2-tetramethyldisilane 61

The synthesis of 61 was performed by the same procedure as for 62 using 7.7 g (0.1 mol) of allyl chloride and 18.6 g (0.1 mol) of 1,2-dichlorotetramethyldisilane in 150 mL of dry THF. Distillation (140°-145°C) afforded 5.0 g of 61 (32%): ^{1}H NMR ($DCCl_3$) δ 0.09 (s, 6H), 0.13 (d, J = 4.68 Hz, 6H), 1.62 (d, J = 8.09 Hz, 2H), 3.63-3.69 (m, 1H), 4.81-4.88 (m, 2H), 5.71-5.86 (m, 1H); ^{13}C NMR ($DCCl_3$) δ -6.53, -4.20, 22.94, 112.87, 135.08; IR (neat) 2093 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 158 (3), 143 (13), 127 (8), 119 (8), 118 (20), 117 (92), 116 (81), 101 (8), 99 (31), 85 (8), 83 (8), 74 (9), 72 (100), 71 (17), 59 (77) calculated for $Si_2C_7H_{18}$ m/e 158.09471, measured m/e 158.09433. Elemental analysis calculated for $C_7H_{18}Si_2$: C, 53.07; H, 11.48. Found: C, 52.78; H, 11.48.

Synthesis of 2-vinyl-1,1,2,2-tetramethyldisilane 111

A stirred solution of 10.0 g (53.8 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane in 25 mL of ether was cooled to -78°C under N_2 to which was added 24.5 mL (53.9 mmol) of 2.2 M vinyl lithium (Alfa) in THF very slowly over a 2 hour period. The liquid phase was then removed by vacuum distillation (ca. 0.05 torr) at room temperature and collected in a flask cooled to -78°C. The distillate was then added to a stirred solution of excess $LiAlH_4$ in 100 mL of ether in a dropwise fashion. After stirring 15 minutes, the liquid phase was removed by distillation at room temperature under vacuum (0.05 mm Hg) and collected in a flask cooled to -78°C. The final solution was diluted with 100 mL pentane and extracted with H_2O followed by separation and drying (Na_2SO_4) of the organic layer. After careful removal of the solvent, distillation (112°-120°C) afforded 2.2 g (29%) of 2-vinyl-1,1,2,2-tetramethyldisilane 111: ^1H NMR ($DCCl_3$) δ 0.12 (d, J = 4.52 Hz, 6H), 0.16 (s, 6H), 3.64 (heptet, J = 4.52 Hz, 1H), 5.64 (d of d, J_{gem} = 3.85 Hz, J_{trans} = 20.02 Hz, 1H), 5.95 (d of d, J_{gem} = 3.85 Hz, J_{cis} = 14.96 Hz, 1H), 6.12-6.23 (m, 1H); ^{13}C NMR ($DCCl_3$) δ -6.74, -4.04, 131.34, 138.66; IR (neat) 2097 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 144 (6), 129 (19), 117 (13), 116 (76), 86 (10), 85 (94), 83 (10), 73 (84), 60 (8), 59 (100), 58 (10) calculated for $C_6H_{16}Si_2$ m/e 144.07906, measured m/e 144.07871.

Synthesis of 4-dimethylsiloxy-1-butene 113 (199)

To a stirred solution of 5.0 g (69.4 mmol) of 3-buten-1-ol and 5.5 g (69.4 mmol) of pyridine in dry Et_2O was added one equivalent of chlorodimethylsilane in a dropwise fashion. The reaction mixture was diluted with 75 mL of pentane and then washed twice with saturated $NaHCO_3$ solution. The organic layer was separated, dried over Na_2SO_4, and distilled (98°-104°C) to afford 7.2 g (80%) of 22: ^1H NMR ($DCCl_3$) δ

0.19 (d, J = 2.85 Hz, 6H), 2.29 (q, J = 6.78 Hz, 2H), 3.66 (t, J = 6.8 Hz, 2H), 4.59-4.62 (m, 1H), 5.02 (d of d, J_{gem} = 1.11 Hz, J_{cis} = 9.77 Hz, 1H), 5.07 (d of d, J_{gem} = 1.11 Hz, J_{trans} = 6.69 Hz, 1H), 5.72-5.86 (m, 1H); ^{13}C NMR ($DCCl_3$) δ -1.49, 37.03, 63.73, 116.55, 135.19; IR (neat) 2112 cm^{-1} (SiH), 1094 (SiO); mass spectrum m/e (% rel. int.) 129 (M-1, 1%), 115 (20), 90 (9), 89 (99), 87 (15), 85 (7), 61 (13), 60 (9), 59 (100).

Synthesis of allyloxydimethylsilane 116 (122)

The lithium alkoxide of allyl alcohol was prepared under N_2 by addition of 104 mL (0.150 mol) of 1.44 M n-butyl lithium to a stirred solution of 8.7 g (0.150 mol) of allyl alcohol in 120 mL of ether cooled to -78°C. To this stirred solution was added 13.0 g (0.138 mol) of dimethylchlorosilane in a dropwise fashion. The final solution was stirred at -78°C for 15 minutes then warmed to room temperature and hydrolyzed with excess H_2O. The ether layer was extracted with H_2O, seperated, dried over Na_2SO_4, and filtered. After removal of the solvent, distillation (68°-74°C) afforded 9.0 g (56%) of allyloxydimethylsilane 116: ^1H NMR ($DCCl_3$) δ 0.19 (d, J = 3.00 Hz, 6H), 3.88-4.18 (m, 2H), 4.38-4.68 (m, 1H), 4.87-5.33 (m, 2H), 5.50-6.21 (m, 1H); IR (neat) 2110 cm^{-1} (SiH), 1100 cm^{-1} (SiOC); mass spectrum m/e (% rel. int.) 116 (2), 115 (15), 101 (64), 99 (57), 85 (16), 75 (100), 73 (14), 71 (20), 61 (32), 59 (75), 58 (9). The spectral properties matched those reported in the literature (121).

Decomposition of 4-pentenyl-1-dimethylsilane **64**

A 1% (wt) solution of **64** (48.1 mg, 0.376 mmol) in benzene containing 19.7 mg (0.135 mmol) of DTBP was heated for 4 hours. The products were separated and isolated by GC on a 9 ft, 20% OV-101/Chromosorb W column at 130°C. In addition to unreacted **64** (48%), the only major product containing silicon was 1,1-dimethyl-1-silacyclohexane **90** (114, 115) (19%): ^{1}H NMR (D_6C_6) δ 0.01 (s, 6H), 0.57 (t, J = 6.62, 4H), 1.33-1.41 (m, 4H), 1.62-1.70 (m, 2H); ^{13}C NMR (D_6C_6) δ -3.08, 14.36, 24.65, 30.29; mass spectrum m/e (% rel. int.) 128 (26), 113 (100), 85 (99), 72 (19), 59 (53). The GC retention time and spectral properties exactly matched those of an authentic sample prepared by coupling pentane-1,5-dimagnesium bromide with dichlorodimethylsilane.

Decomposition of 3-butenyldimethylsilane **59**

A 1% (wt) solution of **59** (0.140 g, 1.23 mmol) in *t*-butylbenzene containing 0.085 g (0.58 mmol) of DTBP was heated at 145°C for 12 hours. The products were analyzed and separated by GC on a 9 ft, 20% SE-30/Chromosorb W column at 80°C isothermal. Other than **59** (9), the only volatile silicon-containing product was 1,1-dimethyl-1-silacyclopetane **95** (114,115) 18%; ^{1}H NMR (D_6C_6) δ 0.04 (s, 6H), 0.50-0.55 (m, 4H), 1.54-1.62 (m, 4H); ^{13}C NMR (D_6C_6) δ -1.78, 13.17, 27.42; mass spectrum m/e (% rel. int.) 114 (18), 100 (5), 99 (44), 97 (16), 87 (11), 86 (100), 71 (26), 59 (24), 58 (54); the GC retention time and spectral properties exactly matched with an authentic sample of **95** prepared by coupling butane-1,4-dimagnesium bromide with dichlorodimethylsilane.

Attempted decomposition of 3-butenyldimethylsilane **59** with BP and AIBN

A NMR scale portion of a 1% (wt) solution of 26.8 mg (0.235 mmol) of **59** in benzene containing 10.5 mg (0.043 mmol) of BP was heated at 110°C for 30 hours. By NMR, the only silicon product presented was **59**.

A 1% (wt) solution of 19.2 mg (0.168 mmol) of **59** in benzene containing 5.4 mg (0.033 mmol) of AIBN was heated at 45°C for 16 hours. GC analysis showed only unreacted **59**.

Decomposition of allyldimethylsilane **60**

Diglyme solvent A solution of 0.10 g (1.00 mmol) of **60** and 0.07 g (0.48 mmol) of DTBP in 0.2 mL of diglyme was heated at 140°C for 3 hours. GC analysis on a 5 ft, 12% SE-30/Chromosorb W column at 140°C coupled with GCMS revealed one major silicon product along with unreacted **60**. Attempts to isolate a pure sample of the major product failed. By GCMS, the compound had a molecular formula equal to twice that of **60**: 200 (2), 185 (4), 157 (10), 131 (8), 129 (11), 128 (12), 127 (100), 125 (7), 117 (9), 101 (16), 100 (18), 99 (88), 98 (40), 97 (10), 85 (15), 83 (7), 73 (38), 72 (73), 71 (10), 60 (7), 59 (92), 58 (8), 57 (6).

o-Dichlorobenzene solvent The reaction was carried out using the same quantities of **60** and DTBP in 0.3 mL of *o*-dichlorobenzene for 2 hours at 140°C. Along with unreacted **60**, the major silicons products were allyldimethylchlorosilane and the same dimer of **60** (GCMS) obtained in diglyme. The mass spectrum of allyldimethylchlorosilane exactly match that of an authentic sample (see the Experimental section). Also present in the mixture was chlorobenzene (GCMS).

tert-Butylbenzene solvent   A 1% (wt) solution of **60** (76.0 mg, 0.76 mmol) in *tert*-butyl benzene containing DTBP (34.0 mg, 0.232 mmol) was reacted for 12 hours at 145°C. The major silicon products were the "**60** dimer" and unreacted **60**.

In all three solvents, the yield of the dimer product was too low to allow for isolation.

Decomposition of cyclopropyldimethylsilane **103**

A small portion (1.286 g) of a 1% (wt) solution of 68.0 g (0.680 mmol) of **103** in *tert*-butylbenzene containing 29.0 mg (0.199 mmol) of DTBP was heated at 145°C for 12 hours. By GCMS, two major silicon products along with unreacted **103** were present. One had a molecular formula equal to twice that of **103**: mass spectrum m/e (% rel. int.) 200 (6), 199 (30), 173 (27), 172 (10), 171 (66), 159 (10), 158 (14), 157 (100), 143 (16), 134 (8), 133 (62), 131 (22), 129 (8), 119 (25), 117 (32), 109 (45), 103 (16), 97 (9), 95 (10), 73 (61), 71 (13), 66 (37), 59 (57), 57 (13). The other product was assigned to cyclopropyldimethylsilanol ($C_5H_{12}SiO$) based on its mass spectrum: m/e (% rel. int.) 116 (1), 101 (49), 76 (7), 75 (100), 73 (6), 61 (50), 47 (19).

Reduction of chloromethyldimethylvinylsilane

The reduction of chloromethyldimethylchlorosilane was done using a literature procedure (204). Thus, 0.1466 g of a solution prepared from 0.1042 g (0.774 mmol) of chloromethyldimethylvinylsilane (Petrarch), 0.3574 g (1.23 mmol) of freshly prepared tri-*n*-butyl hydride (TBTH) (205) and 7.4 mg (0.045 mmol) of azobisisobutyronitrile (AIBN) dissolved in 7.0 mL of dry benzene was septum sealed in a quartz NMR tube. The NMR tube was suspended in a Rayonet and photolyzed (253 nm) for 1 hour. NMR showed a complete loss of the singlet at 2.75 ppm which corresponded to the $-CH_2-Cl$ protons. Also, the intensity of the singlet at ca. 0.1 increased. No other new signals were observed.

When the reaction was repeated, using a NMR scale solution of 27.7 mg (0.206 mmol) of chloromethyldimethylvinylsilane, 8.75 mg (0.301 mmol) of TBTH, and 5.2 mg (0.032 mmol) of AIBN, under identical conditions with pentane (2.2 mL total) as the solvent, the vinyl region was monitored by NMR. There was no significant change in the pattern for the vinyl protons. Based on these observations, the compound formed was trimethylvinylsilane.

Decomposition of (3-butenyl)-1,1,2,2-tetramethyldisilane 62

A 1% (wt) solution of 62 (51.1 mg, 0.297 mmol) in benzene containing 17.0 mg (0.116 mmol) of DTBP was heated at 145°C for 1 hour. Separation and isolation of the products by GC was performed on a 9 ft, 20% OV-101/Chromosorb W column at 130°C. In addition to unreacted 62 (11%), the only silicon-containing volatile product was 1,1,2,2-tetramethyl-1,2-disilacyclohexane 107 (118) (23%): ^1H NMR ($DCCl_3$) δ 0.05 (s, 12H), 0.68-0.72 (m, 4H), 1.54-1.59 (m, 4H); ^{13}C NMR ($DCCl_3$) δ -3.98, 17.09, 26.24; m/e (% rel. int.) 173 (12), 172 (M^+, 62), 157 (59), 144 (22), 129 (37), 116 (46), 99 (34), 98 (21), 97 (100), 85 (39), 73 (74), 59 (48).

Decomposition of allyl-1,1,2,2-tetramethyldisilane **61**

A 1% (wt) solution of **61** (25.2 mg, 0.159 mmol) in benzene containing 7.1 mg (0.049 mmol) DTBP was heated at 145°C for 1 hour. GC separation and isolation of the products was carried out on a 15 ft, 20% OV-101/Chromosorb W column at 130°C. In addition to **61** (14%), the only volatile silicon-containing product was 1,1,2,2-tetramethyl-1,2-disilacyclopentane **110** (118) (13%): ^{1}H NMR (D$_6$C$_6$) δ 0.12 (s, 12H), 0.70 (t, J = 6.77 Hz, 4H), 1.73 (pentet, J = 6.77 Hz, 2H); ^{13}C NMR (D$_6$D$_6$) δ -4.11, 18.96, 22.92; mass spectrum m/e (% rel. int.) 159 (10), 158 (57), 143 (40), 131 (10), 130 (56), 117 (43), 116 (43), 115 (100), 99 (19), 85 (26), 83 (15), 73 (87), 72 (29), 59 (75). The spectral properties matched those reported in the literature (118,206).

Decomposition of vinyl-1,1,2,2-tetramethyldisilane **111**

A 1% (wt) solution of 34.5 mg (0.240 mmol) of **111** in *tert*-butyl benzene containing DTBP (10.9 mg, 0.075 mmol) was heated at 145°C for 1 hour followed by GC analysis which revealed a complete lose of **111**. By GCMS, a compound with twice the molecular formula of **111** was formed: mass spectrum m/e (% rel. int.) 288 (2), 229 (9), 171 (15), 156 (7), 155 (40), 141 (16), 131 (7), 129 (8), 117 (27), 116 (18), 97 (20), 85 (10), 74 (8), 73 (100), 59 (31).

Decomposition of 4-dimethylsiloxy-1-butene **113**

A 1% (wt) solution of **113** (0.63 g, 4.85 mmol) in *t*-butylbenzene containing 0.20 g (1.37 mmol) of DTBP was heated at 145°C for 1 hour. GC isolation (10 ft, 15% OV-101/Chromosorb W, 120°C) afforded **113** (14%)

and 2,2-dimethyl-2-silaoxacyclohexane 113 (120,121) (21%): ^{1}H NMR (60 MHz, $DCCl_3$) δ 0.05 (s, 6H), 0.55 (broadened t, J = 8 Hz, 2H), 1.22-1.88 (m, 4H), 3.72 (broad t, J = 5.8 Hz, 2H); m/e (% rel. int.) 130 (M^+, 14), 115 (100), 87 (74), 61 (22), 59 (20), 47 (10). The NMR spectrum matched that previously reported (120).

Dibenzoylperoxide (BP) decomposition of 4-dimethylsiloxy-1-butene 113

A solution of 88.0 mg (0.677 mmol) of 113 and 38.0 mg (0.157 mmol) of BP dissolved in 352 mg of *o*-dichlorobenze was heated at 110°C for 3.5 hours and monitored by NMR. NMR showed two multiplets (δ 0.55 and δ 1.20-1.90) and a new singlet in the silicon-methyl region (*ca*. 0.05) which were assigned to 115. The ratio of 113 to 115 was approximately 5:1.

Decomposition of allyloxydimethylsilane 116

A 1% (wt) solution of 47.0 mg (0.405 mmol) of 116 in *tert*-butyl benzene containing DTBP (21.2 mg, 0.145 mmol) was heated at 145°C for 10 hours. GC analysis showed a complete loss of 116. By GCMS a trace amount (<1%) of a compound having a molecular formula (CHSiO) consistent with that of 2,2-dimethyl-2-silaoxacyclopentane was present: mass spectrum m/e (% rel. int.) 116 (11), 102 (9), 101 (100), 99 (24), 88 (38), 75 (7), 61 (11), 59 (17), 58 (37), 57 (10).

Synthesis of 1,2-diallyl-1,1,2,2-tetramethyldisilane 76

1,2-Diallyl-1,1,2,2-tetramethyldisilane 76 was prepared by the method of Barton and Jacobi (3). To a stirred mixture of excess Mg turnings in 60 mL of dry THF under N_2 was added a small portion of allyl bromide for initiation. The remainder of the allyl bromide (35.6 g, 0.294 mol total) and 21.1 g (0.113 mol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane were dissolved in 90 mL of dry THF and added dropwise to the stirred solution. After 12 hours, the reaction mixture was hydrolyzed with excess H_2O and transferred to a separatory funnel containing 250 mL of pentane. The pentane layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. After removal of the solvent, distillation (112°-118°C) afforded 20.8 g (93%) of 1,2-diallyl-1,1,2,2-tetramethyldisilane **76** (3): ^{1}H NMR ($DCCl_3$) δ 0.03 (s, 12H), 1.53 (d, J = 8.00 Hz, 4H), 4.60-5.00 (m, 4H), 5.43-6.13 (m, 2H); mass spectrum m/e (% rel. int.) 198 (2), 159 (41), 158 (90), 157 (100), 141 (40), 131 (62), 129 (100), 117 (99), 115 (52), 99 (68), 97 (42), 85 (50), 83 (50), 73 (99), 59 (99), 58 (72).

Vacuum pyrolysis of 1,2-diallyl-1,1,2,2-tetramethyldisilane **76**

Compound **76**, 9.20 g (46.5 mmol) was slowly distilled at 25°C (1×10^{-4} mm Hg) through a quartz tube packed with chips and heated to 840°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 80% mass recovery. Distillation (117°-123°C) of the pyrolysate gave 4.36 g (60%) of 1,1,3,3-tetramethyl-1,3-disilacyclopentene **76** as the only product. The spectra of **76** matched that reported by Barton and Jacobi (3): ^{1}H NMR (C_3D_6O) δ -0.33 (s, 2H), 0.16 (s, 12H), 6.98 (s, 2H); ^{13}C NMR (D_3D_6O) δ -3.68, 0.28, 156.19; mass spectrum m/e (% rel. int.) 156 (16), 143 (7), 142 (16), 141 (100), 113 (7), 99 (5), 83 (5), 73 (14), 69 (5), 63 (8), 59 (11).

Synthesis of 1-allyl-3-vinyl-1,1,3,3-tetramethyldisiloxane 133

To a stirred solution of 11.0 g (54.0 mmol) of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane (Petrarch) in ether under N_2 was added 250 mL (54.0 mmol) of 0.22 M allylmagneism bromide in ether very slowly. This mixture was stirred for 45 minutes at room temperature then cooled to -78°C. Vinyllithium (Alfa), 25 mL (60.0 mmol) of 2.4 M, was then added in a dropwise fashion. The final mixture was then allowed to warm to room temperature and was stirred for 3 hours then hydrolyzed with excess H_2O. The ether layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. After solvent removal, the residue was distilled (148°-155°C) to afford 3.0 g (28%) of 1-allyl-3-vinyl-1,1,3,3-tetramethyldisiloxane 133 (133): ^1H NMR ($DCCl_3$) δ 0.07 (s, 6H), 0.15 (s, 6H), 1.55 (d, J = 9.0 Hz, 2H), 4.67-5.08 (m, 2H), 5.40-6.30 (m, 4H); ^{13}C NMR ($DCCl_3$) δ 0.14, 0.52, 26.52, 113.39, 131.64, 134.46, 139.63; IR (neat) 1065 cm^{-2} (SiOSi); mass spectrum m/e (% rel. int.) 160 (15), 159 (100), 157 (17), 149 (37), 134 (9), 133 (69), 119 (22), 117 (12), 75 (10), 73 (29), 72 (9), 59 (37), calculated for $C_9H_{20}Si_2$ m/e 200.10528, measured m/e 200.10546.

Synthesis of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane 140

To a stirred mixture of excess Mg turnings in 75 mL of ether under N_2 was added a small portion of allyl chloride for initiation. The remainder of the allyl chloride (5.7 g, 74.3 mmol total) and 5.0 g (24.8 mmol) of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane

(Petrarch) were dissolved in 50 mL of ether and were added dropwise to the stirred solution. After having stirred for 10 hours, the reaction mixture was hydrolyzed with excess H_2O. The ether layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. After removal of the solvent, distillation (175°-180°C) of the residue afforded 3.9 g (73%) of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane **140** (135): ^{1}H NMR ($DCCl_3$) δ 0.06 (s, 12H), 1.53 (d, J = 7.8 Hz, 4H), 4.50-5.00 (m, 2H), 5.43-6.13 (m, 1H); ^{13}C NMR ($DCCl_3$) δ 0.01, 26.50, 113.37, 134.44; IR (neat) 1069 cm^{-1} (SiOSi); mass spectrum m/e (% rel. int.) 199 (M-15, 1%), 175 (10), 174 (21), 173 (100), 157 (14), 134 (14), 133 (96), 131 (21), 119 (14), 117 (11), 73 (43), 66 (29), 59 (34), calculated for $C_9H_{19}Si_2O$ m/e (M-15) 199.09745, measured m/e 199.09819.

Vacuum pyrolysis of 1-allyl-3-vinyl-1,1,3,3-tetramethyldisiloxane **133**

A slow distillation of 0.1839 g (1.14 mmol) of **133** was carried out at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 840°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 81% mass recovery. Analysis of the pyrolysate by GC revealed two major products along with unreacted **133** (34%). A trace amount (ca. 3%) of hexamethylcyclotrisiloxane (D_3) was also present (identified by GCMS). The two major products were isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 130°C. They were identified as 3,3,5,5-tetramethyl-3,5-disila-4-oxycyclopentene

134 (18%) and 4,4,6,6-tetramethyl-4,6-disila-5-oxycyclohexene 135 (15%). The spectra for both compounds are given below.

3,3,5,5-Tetramethyl-3,5-disila-4-oxycyclopentene 134 ^{1}H NMR (C_3D_6O) δ 0.15 (s, 12H), 7.17 (s, 2H); ^{13}C NMR (C_3D_6O) δ 0.60, 154.73; IR (neat) 940 cm^{-1} (SiOSi); mass spectrum m/e (% rel. int.) 158 (8), 145 (9), 144 (16), 143 (100), 117 (7), 83 (5), 73 (19), 71 (6), 59 (7), 51 (12), calculated for $C_6H_{14}SiO$ m/e 158.05833, measured m/e 158.05822. Elemental analysis calculated for $C_6H_{14}Si_2O$: C, 45.50; H, 8.93. Found: C, 45.96; H, 8.72.

4,4,6,6-Tetramethyl-4,6-disila-5-oxycyclohexene 135 ^{1}H NMR (C_6D_6) δ 0.12 (s, 6H), 0.21 (s, 6H), 1.32 (d, J = 4.99 Hz collapses to broad s with hν at 6.8, 2H), 5.64 (d, J = 14.00 Hz collapses to m with hν at 6.8, 1H), 6.75-6.83 (m, collapses to d with hν at 1.32, J = 14.00 Hz, 1H); ^{13}C NMR (C_3D_6O) δ 0.65, 1.09, 19.45, 126.97, 146.38; IR (neat) 986 cm^{-1} (SiOSi); mass spectrum m/e (% rel. int.) 172 (20), 159 (11), 158 (21), 157 (100), 131 (11), 129 (18), 117 (6), 103 (14), 73 (22), 72 (6), 71 (18), 66 (9), 59 (17), 52 (6); calculated for $C_7H_{16}Si_2O$ m/e 172.07398, measured m/e 172.07334. Elemental analysis calculated for $C_7H_{16}Si_2O$: C, 48.77; H, 9.37. Found: C, 48.67; H, 9.15.

Vacuum pyrolysis of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane 140

A slow distillation of 0.3812 g (1.78 mmol) of 140 was done at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 840°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 80% mass recovery. GC analysis revealed the presence of two major products along with unreacted **140** (26%). A third product, which was present in only a trace amount (<2%), was identified as 1,1,3,3-tetramethyl-1,3-disilacyclobutane **118** based on comparison of its mass spectrum with that of the known compound (93): m/e (% rel. int.) 144 (23), 130 (14), 129 (100), 103 (11), 85 (35), 73 (10), 59 (18). The two major products were isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 130°C and were identified as 3,3,5,5-tetramethyl-3,5-disila-4-oxycyclopentene **134** (18%) and 4,4,6,6-tetramethyl-4,6-disila-5-oxychlohexene **135** (20%). All spectra properties and GC retention times exactly matched those of **134** and **135** produced from **133**.

Vacuum pyrolysis of 1,2-divinyl-tetramethyldisiloxane **138**

A slow distillation of 0.1021 g (0.549 mmol) of **138** (Petrarch) was carried out at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 840°C. The pyrolysate, represented by an 85% mass recovery, was collected in a trap cooled by liquid nitrogen. Analysis by GC showed quantitative recovery of **138**.

Synthesis of 1-allyl-2-(3-butenyl)-1,1,2,2-tetramethyldisilane **142**

To a stirred solution of 10.0 g (53.8 mmol) of 1,2-dichloro-1,1,3,3-tetramethyldisilane in 15 mL of dry THF under N_2 was added 200 mL (55.0 mmol) of 0.66 M 3-butenylmagnesium bromide in dry THF very slowly. This mixture was stirred for 20 minutes after which time 200 mL (55.0 mmol) of 0.66 M allylmagnesium bromide in THF was added in a dropwise fashion. The final reaction mixture was stirred for 8 hours then hydrolyzed with excess H_2O and transferred to a separatory funnel containing 100 mL of pentane. The pentane layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. After removal of the solvent, distillation of the residue afforded a fraction between 105°-125°C/30 mm Hg that contained 3.0 g (26% yield by GC) of 1-allyl-2-(3-butenyl)-1,1,2,2-tetramethyldisilane **142**. Pure **142** could be isolated by preparative GC on a 9 ft, 20% SE-30/Chromosorb W column between 130°-150°C: ^1H NMR ($DCCl_3$) δ 0.06 (s, 6H), 0.07 (s, 6H), 0.68-0.73 (m, 2H), 1.60 (d, J = 8.11 Hz, 2H), 2.03-2.10 (m, 2H), 4.80-5.03 (m, 4H), 5.71-5.95 (m, 2H); ^{13}C NMR ($DCCl_3$) δ -4.11, -3.76, 14.50, 22.98, 28.73, 112.71, 112.85, 135.30, 141.73; mass spectrum m/e (% rel. int.) 171 (M-41, 44%), 131 (9), 129 (15), 117 (27), 99 (14), 97 (55), 85 (39), 73 (98), 71 (9), 59 (100), calculated for $C_8H_{19}Si$ m/e (M-15) 171.10253, measured m/e 171.10237. Elemental analysis calculated for $C_{11}H_{24}Si_2$: C, 62.17; H, 11.41. Found: C, 61.12; H, 11.33.

Synthesis of 1-allyl-2-vinyl-1,1,2,2-tetramethyldisilane **168**

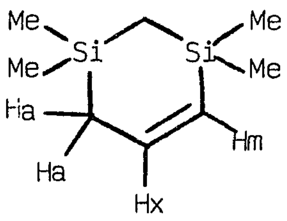
To a stirred mixture of excess Mg turnings and 10.0 g (54.0 mmol) of 1,2-dichlorodisilane in 60 mL of dry THF under N_2 was added a small portion of allyl bromide for initiation. The remainder of the allyl bromide (6.5 g, 54.0 mmol total) was dissolved in 100 mL of dry THF and added dropwise to the stirred solution. After 12 hours, 11.6 g (108.0 mmol) of vinyl bromide dissolved in 40 mL of dry THF was added and stirring continued for 3 hours. The mixture was hydrolyzed with H_2O then transferred to a separatory funnel containing 150 mL of pentane. The pentane layer was extracted with H_2O, seperated, dried over Na_2SO_4, and filtered. After solvent removal, the residue was distilled (102°-109°C/100 mm Hg) to afford 3.0 g (30%) 1-allyl-2-vinyl-1,1,2,2-tetramethyldisilane 168 (141): ^1H NMR ($DCCl_3$) δ 0.05 (s, 6H), 0.11 (s, 6H), 1.60 (d, J = 7.40 Hz, 2H), 4.80-4.87 (m, 2H), 5.63 (d of d, J_{gem} = 3.91 Hz, J_{trans} = 20.01 Hz, 1H), 5.70-5.85 (m, 1H), 5.94 (d of d, J_{gem} = 3.91 Hz, J_{cis} = 14.59, 1H), 6.12-6.23 (m, 1H); ^{13}C NMR ($DCCl_3$) δ -4.46, -4.08, 22.73, 112.75, 131.06, 135.28, 138.92; mass spectrum m/e (% rel. int.) 184 (1), 169 (16), 143 (28), 99 (9), 85 (17), 83 (37), 74 (9), 73 (100), 71 (10), 59 (84), calculated for $C_9H_{20}Si_2$ m/e 184.11036, measured m/e 184.11041.

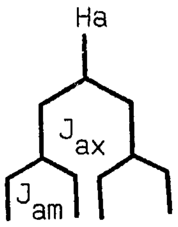
Vacuum pyrolysis of 1-allyl-2-(3-butenyl)-1,1,2,2-tetramethyldisilane 142

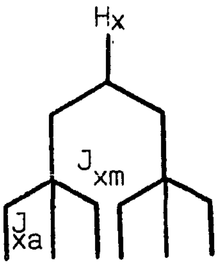
A slow distillation of 0.1230 g (0.580 mmol) of 142 was carried out at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysated was collected in a trap cooled with liquid nitrogen and represented a 61% mass recovery. Four products along with unreacted 142 (22%) could be isolated by preparative GC on a 9 ft, 20% SE-30/Chromosorb W column at 130°C. The compounds were identified as 1,1,3,3-tetramethyl-

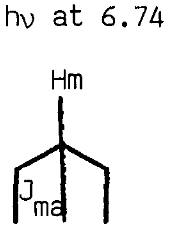
1,3-disilacyclohexene 143 (26%) (137), 1,1,3,3-tetramethyl-1,3-disilacyclopentene 78 (27%) (3), 1,3-trimethyl-1,3-disilacyclopentene 144 (8%), and 1,1,3,3,5-pentamethyl-1,3-disilacyclopentene 145 (4%). All spectra properties of 78 matched those of this compound produced from 76. The spectra of 143, 144, and 145 are given below.

1,1,3,3-Tetramethyl-1,3-disilacyclohexene 143 The spectra of 143 matched that reported by Barton and Wulff (137). ^{1}H NMR (C_3D_6O) δ -0.16 (s, 2H), 0.04 (s, 6H), 0.05 (s, 6H), 1.38 (d of d, J_{am} = 1.46 Hz, J_{ax} = 5.40 Hz collapses to broad s with hν at 6.74, 2H), 5.50 (broad d, J = 14.0 Hz collapses to broad t with hν at 6.74, J_{am} = 1.46 Hz, 1H), 6.72 (d of t, J_{ax} = 5.40 Hz, J = 14.0 Hz, 1H); ^{13}C NMR δ -0.92, -0.43, 0.82, 19.13, 130.18, 146.22; mass spectrum m/e (% rel. int.) 170 (23), 157 (7), 156 (17), 155 (100), 129 (9), 127 (26), 115 (7), 113 (9), 95 (21), 85 (8), 83 (8), 73 (25), 71 (8), 59 (30), 55 (8).



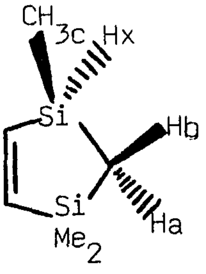


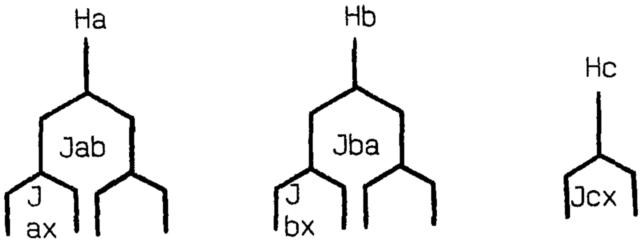




$J_{ax} = J_{xa}$ $J_{am} = J_{ma}$

1,3,3-Trimethyl-1,3-disilacyclopentene 144 ^{1}H NMR (C_3D_6O) δ -0.41 (d of d, J_{ax} = 3.00 Hz, J_{ab} = 14.54 Hz collapses to d with hν at 4.40, 1H), -0.10 (d of d, J_{bx} = 4.05 Hz, J_{ab} = 14.54 Hz collapses to d with hν at 4.40, 1H), 0.13 (s, 3H), 0.15 (s, 3H), 0.19 (d, J_{cx} = 3.5 Hz, 3H), 4.38-4.44 (m, 1H), 7.04 (d, J = 15.10 Hz, 1H), 7.14 (d, J = 15.10 Hz, 1H); ^{13}C NMR (C_3D_6O) δ -7.09, -2.38, -0.21, 0.38, 153.10, 158.14; IR (neat) 2116 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 142 (30), 129 (8), 128 (15), 127 (100), 99 (10), 85 (10), 69 (8), 59 (10), calculated for $C_6H_{14}Si_2$ m/e 142.06341, measured m/e 142.06392. Elemental analysis for $C_6H_{14}Si_2$ calculated: C, 50.62; H, 9.93. Found: C, 50.63; H, 9.96.





Jab = Jba

1,1,3,3,4-Pentamethyl-1,3-disilacyclopentene 145 ^{1}H NMR (C_3D_6O) δ -0.29 (s, 2H), 0.08 (s, 6H), 0.11 (s, 6H), 1.91 (d, J = 1.70 Hz, 3H), 6.40 (broad unresolved d, 1H); mass spectrum m/e (% rel. int.) 170 (11), 157 (8), 156 (18), 155 (100), 127 (5), 115 (5), 95 (5), 73 (14), 70 (5), 69 (5), 57 (5).

Vacuum pyrolysis of 1-allyl-2-vinyl-1,1,2,2-tetramethyldisilane 168

A vacuum pyrolysis of 168 was done by slowly distilling 0.3165 g (1.72 mmol) of the compound at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented 77% mass recovery. Three products, along with unreacted 168 (14%), could be isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 130°C. The compounds were identified as 1,1,3,3-tetramethyl-1,3-disilacyclopentene 78 (3%) (3), 1,1,3-trimethyl-1,3-silacyclopentene 144 (5%), and allylvinyldimethylsilane 172 (1%). All spectra properties of 78 and 144 matched those of these compounds produced from 76 and 142, respectively. Compound 172 was identified based on its spectra: ^1H NMR (C_3D_6O) δ 0.00 (s, 6H), 1.53 (d, J = 8.0 Hz, 2H), 4.53-5.02 (m, 2H), 5.22-6.25 (m, 4H); mass spectrum m/e (% rel. int.) 126 (2), 111 (4), 98 (6), 87 (4), 86 (9), 85 (100), 60 (5), 59 (76).

Vacuum pyrolysis of 1,2-divinyl-1,1,2,2-tetramethyldisilane 174

A slow distillation of 0.3446 g (2.03 mmol) of 174 was done at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 800°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 84% mass recovery. Along with unreacted 174 (33%), GC analysis showed a complex mixture of products. One of the products was isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 130°C and was identified as 1,1,3-trimethyl-1,3-disilacyclopentene **144** (5%). All of the spectral properties were identical to that of **144** produced from **142**. Another compound was isolated and identified as divinyldimethylsilane (11%) (207): ^{1}H NMR (C_3D_6O) δ 0.14 (s, 6H), 5.40-6.34 (m, 6H); mass spectrum m/e (% rel. int.) 98 (10), 97 (P-15, 100), 85 (10), 71 (45), 59 (28), 55 (10). Two other compounds, for which yields were obtained, were identified by GCMS as being trimethylvinylsilane (5%) (207): m/e (% rel. int.) 100 (10), 86 (9), 85 (100), 73 (13), 72 (8), 59 (83), 55 (6) and dimethylvinylsilane (6%): m/e (% rel. int.) 86 (12), 85 (6), 71 (35), 69 (13), 59 (28), 58 (100), 55 (11), 53 (13). Other compounds present in the mixture that were identifiable by GCMS were 1,1,3,3-tetramethyl-1,3-disilacyclobutane **118** and 1,1,3,3-tetramethyl-1,3-disilacyclopentene **78**.

Vacuum pyrolysis of trimethylvinylsilane

A slow distillation of 0.1071 g (1.071 mmol) of trimethylvinylsilane was carried out at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a trap cooled by liquid nitrogen and represented an 84% mass recovery. Analysis by GC showed quantitative recovery of trimethylvinylsilane.

Vacuum pyrolysis of dimethyldivinylsilane

A slow distillation (25°C, 1 X 10^{-4} mm Hg) of 90.7 mg (0.810 mmol) of dimethyldivinylsilane was done through a quartz tube heated to 760°C and the pyrolysate collected in a trap cooled by liquid nitrogen. Analysis of the pyrolysate (83% mass recovery) by GC revealed quantitative recovery of unreacted dimethyldivinylsilane.

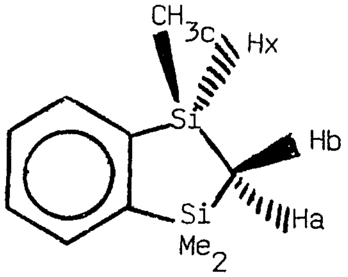
Synthesis of 1-allyl-2-phenyl-1,1,2,2-tetramethyldisilane 175

To a stirred suspension of excess Mg turnings and 10.0 g (53.8 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane in 125 mL of dry THF under N_2 was added a small portion of bromobenzene for initiation. The remainder of the bromobenzene (8.4 g, 53.8 mmol total) was dissolved in dry 20 mL THF and added dropwise to the stirred solution. After 12 hours, 6.5 g (53.8 mmol) of allyl bromide was dissolved in 20 mL of dry THF and added dropwise to the solution. The final mixture was stirred for 4 hours then hydrolysed with excess H_2O and transferred to a separatory funnel containing 100 mL of pentane. The pentane layer was extracted with H_2O, separated, dried with Na_2SO_4, and filtered. Removal of the solvent followed by distillation (138°-145°C/0.5 mm Hg) of the residue gave 6.1 g (48%) of 1-allyl-2-phenyl-1,1,2,2-tetramethyldisilane 175: ^{1}H NMR ($DCCl_3$) δ 0.07 (s, 6H), 0.37 (s, 6H), 1.50 (d, J = 7.9 Hz, 2H), 4.53-4.97 (m, 2H), 5.33-5.97 (m, 1H), 7.20-7.50 (m, 5H); ^{13}C NMR ($DCCl_3$) δ -4.36, -3.51, 22.63, 112.89, 127.85, 128.43, 133.83, 135.07, 139.36; mass spectrum m/e (% rel. int.) 234 (3), 194 (16), 193 (74), 135 (100), 136 (13), 107 (8), 105 (11), 73 (18), 59 (16), calculated for $C_{13}H_{22}Si_2$ m/e 234.12601, measured m/e 234.12668. Elemental analysis calculated for $C_{13}H_{22}Si$: C, 66.58; H, 9.48. Found: C, 65.85; H, 9.52.

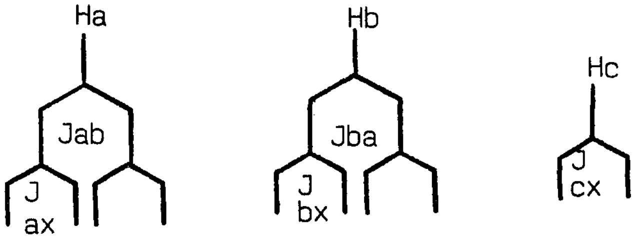
Vacuum pyrolysis of 1-allyl-2-phenyl-1,1,2,2-tetramethyldisilane 175

Compound 175, 0.3354 (1.43 mmol) was slowly distilled at 350°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 770°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 80% mass recovery. GC analysis showed one major product along with unreacted 175 (35%). Based on GCMS, one of the minor products (<3%) was identified as dimethylphenylsilane (184): m/e (% rel. int.) 136 (43), 135 (26), 122 (12), 121 (100), 105 (18), 59 (10), 58 (93), 53 (17). The major product was isolated by preparative GC on a 5 ft, 12% Se-30/Chromosorb W column at 150°C and identified as 1,1,3-trimethyl-1,3-disilaindane 176 (57%). The spectra of 176 is given below.

1,1,3-Trimethyl-1,3-disilaindane 176 ^{1}H NMR (DCCl$_3$) δ -0.04 (d of d, J_{ax} = 3.30 Hz, J_{ab} = 14.50 Hz, 1H), 0.30 (d of d, J_{bx} = 3.90, J_{ab} = 14.50 Hz, 1H), 0.37 (s, 3H), 0.40 (s, 3H), 0.48 (d, J_{cx} = 3.80 Hz, 3H), 4.80 (sixtet, J = 3.70 Hz, 1H), 7.44-7.71 (m, 4H); ^{13}C NMR (DCCl$_3$) δ -5.31, -2.27, 0.24, 0.72, 128.67, 128.85, 131.93, 132.64, 147.27, 150.95; IR (neat) 2112 cm^{-1} (SiH); mass spectrum me/ (% rel. int.) 192 (17), 179 (8), 178 (19), 177 (100), 175 (11), 161 (5), 145 (6), 105 (8), 88 (15), 81 (7), 59 (4), calculated for $C_{10}H_{16}Si_2$ m/e 192.07906, measured m/e 192.07950. Elemental analysis calculated for $C_{10}H_{16}Si_2$: C, 62.42; H, 8.40. Found: C, 62.10; H, 8.20.



176



Jab = Jba

Butadiene-flow pyrolysis of 1-allyl-2-phenyl-1,1,2,2-tetramethyldisilane **175**

A flow pyrolysis was done by dripping 50 ml of **175** through a vertical quartz tube packed with quartz chips and heated to 550°C. Butadiene (35 mL/min) was used as the carrier gas. The pyrolysate was collected in a trap and cooled to -78°C. Analysis by GC showed a very complex mixture of products of which none were isolable.

Butadiene-flow pyrolysis of 1-allyl-2-vinyl-1,1,2,2-tetramethyldisilane **168**

A flow pyrolysis was performed by dripping 60 ml of **168** through a vertical quartz tube packed with quartz chips and heated to 600°C. Butadiene was used as the carrier gas at a flow-rate of 35 mL/min. The pyrolysate was collected in a trap cooled to -78°C and GC analysis revealed a complex mixture of non-isolable products.

Synthesis of dimethylsilylphenylacetylene 181

The procedure used to prepare dimethylsilylphenylacetylene was similar to the method used by Eaborn and Walton (149) to prepare trimethylsilylphenylacetylene. A solution of 30.0 g (0.294 mol) of phenylacetylene (Aldrich) was dissolved in 150 mL of ether under N_2 and cooled to -78°C. To this stirred solution was added 140 mL (0.294 mol) of 2.1 M n-butyl lithium in hexane in a dropwise fashion. The solution was allowed to warm to room temperature then heated to reflux for 15 minutes after which time 37.8 g (0.400 mol) of dimethylchlorosilane was added dropwise. Refluxing was continued for 4 hours. The reaction mixture was then cooled to room temperature and hydrolyzed with excess H_2O. The organic layer was extracted with H_2O, dried over Na_2SO_4, and filtered. The solvent was removed and the residue distilled (120°-123°C/15 mm Hg) to afford 40.0 g (85%) of dimethylsilylphenylacetylene 181: ^1H NMR ($DCCl_3$) δ 0.33 (d, J = 4.0 Hz, 6H), 4.30 (heptet, J = 4.0 hz, 1H), 7.13-7.56 (m, 5H); ^{13}C NMR ($DCCl_3$) δ -2.87, 91.16, 106.60, 123.07, 128.26, 128.70, 132.04; IR (neat) 2162 cm^{-1} (C≡C), 2141 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 160 (36), 146 (14), 145 (100), 129 (12), 105 (11), 58 (10), 53 (10), calculated for $C_{10}H_{12}Si$ m/e 160.07083, measured m/e 160.07086. Elemental analysis calculated for $C_{10}H_{12}Si$: C, 74.91; H, 7.56. Found: C, 73.61; H, 7.54.

Synthesis of *cis*-2-phenyl-1-dimethylsilylethylene 182

The reduction of dimethylsilylphenylacetylene to *cis*-2-phenyl-1-dimethylsilylethylene was accomplished using the procedure of Eisch and Foxton (150). To a stirred solution of 125 mL (0.125 mol) of 1.0 M diisobutylaluminum hydride in heptane and 10.7 g (0.125 mol) of N-methylpyrrolidine under N_2 was added 20.0 g (0.125 mol) of dimethylsilylphenylacetylene 181 in a dropwise fashion. The final solution was heated to 70°C for 12 hours then 100°C for 10 additional hours. After cooling to room temperature, the reaction mixture was poured into a flask containing 200 mL of ice-water and then diluted with 100 mL of hexane. This slurry mixture was stirred vigorously with a mechanical stirrer then filtered through celite and washed with hexane. The organic layer was separated, dried over Na_2SO_4, and filtered. Distillation (116°-120°C/10 mm Hg) of the residue, after solvent removal, gave 19.3 g (95%) *cis*-2-phenyl-1-dimethylsilylethylene 182: ^{1}H NMR ($DCCl_3$) δ 0.20 (d, J = 3.79 Hz, 6H), 4.39-4.45 (m, 1H), 5.85 (d of d, J = 4.77 Hz, J = 15.10 Hz, 1H), 7.27-7.43 (m, 6H); ^{13}C NMR ($DCCl_3$) δ -3.09, 127.60, 128.08, 129.38, 139.63, 147.60; IR (neat) 2116 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 162 (23), 148 (14), 147 (100), 146 (8), 145 (46), 121 (27), 105 (16), 59 (17), 58 (41), 53 (12), 51 (8), calculated for $C_{10}H_{14}Si$, measured m/e 162.08621. Elemental analysis calculated for $C_{10}H_{14}Si$: C, 73.99; H, 8.71. Found: C, 73.64; H, 8.87.

Synthesis of *cis*-2-phenyl-1-dimethylchlorosilylethylene **183**

To a stirred slurry of 15.4 g (74.1 mmol) of phosphorus pentachloride in 25 mL of hexane under N_2 was added a solution of 5.0 g (25.5 mmol) of *cis*-2-phenyl-1-dimethylsilylethylene **182** in 30 mL of hexane in a dropwise fashion. After having stirred for 1 hour, the reaction mixture was filtered through celite and washed with hexane. The hexane and phosphorus trichloride were removed by distillation at atmospheric pressure. Vacuum distillation (132°-137°C/5 mm Hg) of the residue from CaH_2 afforded 11.5 g (77%) of *cis*-2-phenyl-1-dimethylchlorosilylethylene **183**: ^1H NMR ($DCCl_3$) δ 0.41 (s, 6H), 5.93 (d, J = 14.90 Hz, 1H), 7.33-7.38 (m, 5H), 7.49 (d, J = 14.90 Hz, 1H); ^{13}C NMR ($DCCl_3$) δ 3.43, 128.18, 128.24, 128.92, 139.05, 149.30; mass spectrum m/e (% rel. int.) 198 (M+2, 6%), 196 (M^+, 17%), 183 (11), 181 (31), 146 (14), 145 (100), 93 (12), 65 (15), 63 (18), calculated for $C_{10}H_{13}SiCl$ m/e 196.04751, measured m/e 196.04718. Compound **183** was too reactive to obtain a satisfactory combustion analysis.

Synthesis of *cis*-2-phenyl-1-(allyldimethylsilyl)ethylene **184**

To a stirred mixture of Mg turnings in 60 mL of dry THf under N_2 was added a small portion of allyl bromide for initiation. The remainder of the allyl bromide (3.6 g, 30.0 mmol total) and 5.0 g (25.5 mmol) of *cis*-2-phenyl-1-dimethylchlorosilylethylene **183** were dissolved in 20 mL of THF and added dropwise to the stirred solution. After having refluxed for 12 hours, the reaction mixture was cooled to room temperature, hydrolyzed with excess H_2O, then transferred to a separatory funnel containing 100 mL of pentane. The pentane layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. Removal of the solvent, followed by distillation (128°-133°C/4 mm Hg) of the residue afforded 4.1 g (80%) of cis-2-phenyl-1-(allyldimethylsilyl)ethylene 184: ^1H NMR ($DCCl_3$) δ 0.13 (s, 6H), 1.64 (d, J = 8.11 Hz, 2H), 4.87-4.92 (m, 2H), 5.74-5.90 (m, 1H), 5.90 (d, J = 15.1 Hz, 1H), 7.25-7.46 (m, 5H), 7.50 (d, J = 15.1 Hz, 1H); ^{13}C NMR ($DCCl_3$) δ -1.77, 24.56, 113.16, 127.47, 127.96, 128.11, 130.99, 134.78, 140.24, 147.56; mass spectrum m/e (% rel. int.) 202 (1), 162 (15), 161 (100), 146 (9), 145 (62), 135 (29), 105 (9), 59 (55), calculated for $C_{13}H_{18}Si$ m/e 202.11778, measured m/e 202.11851. Elemental analysis calculated for $C_{13}H_{18}Si$: C, 77.41; H, 8.98. Found: C, 77.35; H, 9.25.

Vacuum pyrolysis of cis-2-phenyl-1-allyldimethylsilylethylene 184

A slow distillation of 0.1879 g (0.93 mmol) of 184 was done at 35°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 780°C. The pyrolysated was collected in a trap cooled with liquid nitrogen and represented a 65% mass recovery. Analysis by GC showed three major products along with unreacted 184 (5%). Isolation of the three compounds were done by preparative GC on a 5 ft, 12% SE-30/Chromosorb W column at 150°C. One of the compounds was identified as styrene (4%): ^1H NMR ($DCCl_3$) δ 5.20 (d of d, J_{gem} = 2.0 Hz, J_{cis} = 11.0 Hz, 1H), 5.70 (d of d, J_{gem} = 2.0 H, J_{trans} = 20.0 Hz, 1H), 6.40-7.50 (m, 6H). The other two were identified as 1,1-dimethyl-1-

silaindene 185 (14%) (151) and *trans*-2-phenyl-1-allyldimethylsilylethylene 186 (37%). The spectra of each of these compounds is given below.

1,1-Dimethyl-1-silaindene 185 The NMR of 185 matched that reported by Juvet and Barton (151). ^{1}H NMR (DCCl$_3$) δ 0.38 (s, 6H), 6.32 (d, J = 10.35, 1H), 7.24-7.39 (m, 3H), 7.39 (d, J = 10.35 Hz, 1H), 7.57 (d, J = 6.84 Hz, 1H); ^{13}C NMR (DCCl$_3$) δ -4.01, 124.10, 126.94, 129.71, 131.65, 132.42, 138.54, 149.24, 149.38; mass spectrum m/e (% rel. int.) 160 (40), 146 (14), 145 (100), 143 (12), 119 (8), 117 (5), 105 (6), 93 (5), 53 (11); calculated for $C_{10}H_{12}Si$ m/e 160.07083, measured m/e 160.07108.

trans-2-Phenyl-1-allyldimethylsilylethylene 186 ^{1}H NMR (DCCl$_3$) δ 0.20 (s, 6H), 1.69 (d, J = 8.10 Hz, 2H), 4.65-5.10 (m, 2H), 5.43-6.20 (m, 1H), 6.42 (d, J = 20.0 Hz, 1H), 6.95 (d, J = 20.0 Hz, 1H), 7.15-7.60 (m, 5H); mass spectrum m/e (% rel. int.) 202 (9), 162 (16), 161 (100), 159 (8), 146 (9), 145 (56), 135 (31), 105 (9), 59 (71).

Vacuum pyrolysis of 186

A slow distillation of 55.8 mg (0.276 mmol) of 186 was done (25°C, 1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 780°C. The pyrolysate was collected in a liquid nitrogen cooled trap and represented a 43% mass recovery. GC analysis showed 184, 185, and 186 in a ratio of 1:2.5:5.4, respectively.

When the pyrolysis of 184 was repeated under exactly the same condition, the ratio of 184 to 185 to 186 was 1:4:5.3 by GC.

Synthesis of (o-vinylphenyl)allyldimethylsilane 189

To a stirred mixture of excess Mg turnings in 15 mL ether under N_2 was added a solution of 1.5 g (8.2 mmol) of *o*-bromostyrene (Aldrich) and 1.1 g (8.17 mmol) of allyldimethylchlorosilane dissolved in 30 mL of ether. The final mixture was refluxed for 14 hours. After cooling to room temperature, the mixture was hydrolyzed with excess H_2O then transferred to a separatory funnel containing 100 mL of pentane. The pentane layer was extracted with H_2O, seperated, dried over Na_2SO_4, and filtered. After removal of the solvent, 0.150 g (9%) (*o*-vinylphenyl)allyldimethylsilane 189 was isolated by preparative GC on a 5 ft, 12% SE-30/Chromosorb W column at 180°C: ^1H NMR ($DCCl_3$) δ 0.30 (s, 6H), 1.78 (d, 7.8 Hz, 2H), 4.63-6.20 (m, 5H), 6.75-7.67 (m, 5H); mass spectrum m/e (% rel. int.) 202 (4), 162 (18), 161 (100), 159 (34), 145 (95), 133 (25), 105 (20), 59 (27), calculated for $C_{13}H_{18}Si$ m/e 202.11778, measured m/e 202.11751.

Vacuum pyrolysis of (*o*-vinylphenyl)allyldimethylsilane 189

A slow distillation of 0.1300 g (0.64 mmol) of 189 was carried out at 35°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 780°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 68% mass recovery. The pyrolysate was a viscous yellow oil. GC analysis however, showed a product with a retention time that exactly matched that of 1,1-dimethyl-1-silaindene 185 produced from 184.

Decomposition of cis-(dimethylsilyl)phenylethylene 182

A 1% (wt) solution of 53.2 mg (0.328 mmol) of 182 in benzene containing 15.5 mg (0.106 mmol) of DTBP was heated at 145°C for 24 hours but was checked after 3 hours and 8 hours. Analysis of the pyrolysate revealed that ca. 95% of 182 remained after 24 hours. A minor product (ca. 5%) was assigned to cis-β-styrenyldimethylsilanol (cis-$PhCH{=}CHSiMe_2OH$) based on GCMS: m/e (% rel. int.) 178 (12), 147 (27), 145 (13), 136 (13), 135 (26), 121 (32), 119 (11), 118 (46), 117 (23), 109 (9), 100 (39), 91 (34), 85 (10), 65 (8), 59 (100), 58 (33). However, it was not clear where it was a mixture. No other products were observed.

Synthesis of 3-butenyltrimethylsilane 190

The synthesis of 3-butenyltrimethylsilane was accomplished by the method of Rowley and Jarvie (153). To a stirred mixture of excess Mg turnings in 10 mL of dry THF under N_2 was added a small portion of 1-bromo-3-butene for initiation. The remainder of the 1-bromo-3-butene (2.0 g, 14.8 mmol total) and 1.6 g (14.8 mmol) of trimethylchlorosilane was dissolved in 20 mL of dry THF and added dropwise to the solution. After 10 hours, the reaction mixture was hydrolyzed with excess H_2O then transferred to a separatory funnel containing 50 mL of pentane. The pentane layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. After removal of the solvent, 1.0 g (53%) of 3-butenyltrimethylsilane was isolated by preparative gas chromatography on 9 ft, 20% OV-101/Chromosorb W column at 130°C 190.

The NMR of 190 exactly matched that reported by Rowley and Jarvie (153): ^{1}H NMR ($DCCl_3$) δ 0.00 (s, 9H), 0.57-0.62 (m, 2H), 2.01-2.09 (m, 2H), 4.86-5.02 (m, 2H), 5.81-5.95 (m, 1H); ^{13}C NMR ($DCCl_3$) δ -1.60, 15.90, 28.09, 112.65, 141.80; mass spectrum m/e (% rel. int.) 113 (M-15, 28%), 85 (20), 74 (8), 74 (100), 59 (56), 58 (8), 55 (5).

Vacuum pyrolysis of 3-butenyltrimethylsilane 190

A slow distillation of 0.1054 g (0.823 mmol) of 190 was carried out at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a trap cooled with liquid nitrogen. At 760°C, only ca. 10% decomposition of 190 was observed by GC. Four compounds could be identified by GCMS to be the major components of the pyrolysate. The compounds were tetramethylsilane (TMS): m/e (% rel. int.) 88 (3), 74 (18), 73 (100), 59 (4), 57 (4), 55 (5); vinyltrimethylsilane (207): m/e (% rel. int.) 100 (9), 86 (8), 85 (100), 73 (12), 72 (9), 60 (5), 59 (70); ethyltrimethylsilane: m/e (% rel. int.) 102 (2), 87 (11), 81 (8), 73 (57), 67 (100), 59 (35), 55 (6), 54 (52), 53 (10); and 1,1,3,3-tetramethyl-1,3-disilacyclobutane 118 (93): m/e (% rel. int.) 144 (29), 130 (15), 129 (100), 113 (5), 101 (16), 73 (9), 59 (14), 57 (5).

Vacuum pyrolysis of (3-butenyl)dimethylsilane 59

A slow distillation of 0.1407 g (1.23 mmol) of 59 was done at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 840°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 56% mass recovery. Analysis of the pyrolysate by GC showed two major products along with unreacted 59 (25%). A trace amount (<2%) of 1,1,3,3-tetramethyl-1,3-disilacyclobutane 118 was also identified by GCMS to be present in the pyrolysate. The two major products were isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 130°C. One of the products was identified as allyltrimethylsilane 120 (17%) (77,185). The NMR of 120 matched that published by Fleming and Laugley (185): ^{1}H NMR ($DCCl_3$) δ 0.03 (s, 9H), 1.52 (d, J = 8.0 Hz, 2H), 4.60-5.01 (m, 2H), 5.43-6.05 (m, 1H); mass spectrum m/e (% rel. int.) 114 (10), 99 (20), 77 (18), 73 (100), 71 (9), 59 (25). The other compound was identified as allyldimethylsilane 60 (4%). The NMR, mass spectrum and GC retention time of 60 exactly matched that of an authentic sample.

Vacuum pyrolysis of 2-(3-butenyl)-1,1,2,2-tetramethyldisilane 62

Compound 62, 0.2041 g (1.19 mmol) was slowly distilled at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a trap, cooled with liquid nitrogen and represented a 73% mass recovery. Only one new product, along with unreacted 62 (6%), was present in the pyrolysate according to GC analysis. The product was isolated by preparative GC on a 9 ft, 20% OV-101/Chromosorb W column at 130°C and was identified as 4-butenyldimethylsilane 59 (96%). All spectra properties and the GC retention time of 59 exactly matched that of an authentic sample. (See the Experimental section of this dissertation.)

Synthesis of di-(3-butenyl)methylsilane 214

To a stirred mixture of excess Mg turnings in 50 mL dry THF undre N_2 was added first a small portion of 4-bromo-1-butene for initiation. The remainder of 6.0 g (44.8 mmol) of 4-bromo-1-butene for and 2.6 g (22.4 mmol) of methyldichlorosilane was dissolved in 20 mL of THF and added to the solution in a dropwise fashion. The final reaction mixture was stirred at room temperature for 15 hours then hydrolyzed with excess H_2O and diluted with 50 mL of pentane. The pentane layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. After removal of the solvent, distillation (78°-87°C/30 mm Hg) afforded 2.3 g (68%) di-(3-butenyl)methylsilane 214. ^1H NMR ($DCCl_3$) δ 0.08 (d, J = 3.79 Hz collapses to s with hν at 3.82, 3H), 0.67-0.75 (m, collapses to broad t with hν at 2.11, J = 3.3 Hz, 4H), 2.07-2.15 (m, collapses to broad d with hν at 0.71, J = 6.0 Hz, 4H), 3.80-3.84 (m, collapses to broad pentet with hν at 0.08, J = 2.8 Hz, 1H), 4.88-5.04 (m, 4H), 5.81-5.94 (m, 2H); ^{13}C NMR ($DCCl_3$) δ -6.15, 12.05, 28.63, 113.14, 141.15; IR (neat) 2110 cm^{-1}; mass spectrum m/e (% rel. int.) 139 (M-15, 6%), 126 (8), 111 (11), 100 (11), 99 (100), 98 (21), 97 (65), 85 (9), 84 (10), 83 (14), 72 (8), 71 (65), 59 (26), 55 (7), calculated for $C_8H_{15}Si$ (M-15) m/e 139.09430, measured m/e 139.09470.

Vacuum pyrolysis of di-(3-butenyl)methylsilane 214

A slow distillation of 214 was done at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to the desired temperature (below). The pyrolysate was collected in a liquid nitrogen cooled trap and was analyzed by GC.

730°C Compound 214, 0.1128 g (0.732 mmol), was pyrolysed affording a 37% mass recovery. GC analysis showed a complex mixture of products from which allyldimethylsilane 60 was isolable by preparative GC on a 9 ft, 20% SE-30/Chromosorb W column at 100°C. The NMR, GC retention time, and mass spectrum of 60 exactly matched that of an authentic sample. Compound 198 and 199 were also present as well as two other isomeric compounds by GCMS. The identity of 198 and 199 is based on comparison with that of the known compounds (137) (see the vacuum pyrolysis of 218).

650°C Compound 214, 0.1205 g (0.782 mmol), was pyrolyzed giving a 79% mass recovery. Only about 5% to 10% decomposition of 214 occurred at this temperature. However, the complexity of the mixture did not change.

Synthesis of di-(3-butenyl)dimethylsilane 218

To a stirred mixture of excess Mg turning in 50 mL of dry THF under N_2 was added first a small portion of 12.2 g (90.0 mmol) of 4-bromo-1-butene for initiation. The remainder of the 4-bromo-1-butene was dissolved in 60 mL of dry THF and added to the stirred mixture in a dropwise manner. Stirring at room temperature was continued for 7 hours followed by dropwise addition of 3.9 g (3.6 mmol) of dimethyldichlorosilane dissolved in 15 mL of dry THF. The final solution was refluxed for 14 hours, cooled to room temperature, hydrolyzed with excess H_2O, then diluted with 75 mL of pentane. The pentane layer was extracted with H_2O, seperated, dried over Na_2SO_4, and filtered. After removal of the pentane, distillation (85°-88°C/14 mm Hg) of the residue afforded 3.2 g (63%) of 218: ^1H NMR ($DCCl_3$) δ 0.00 (s, 6H), 0.57-0.68 (m, 4H), 2.01-2.10 (m, 4H), 4.86-5.02 (m, 4H), 5.81-5.94 (m, 2H); ^{13}C NMR ($DCCl_3$) δ -3.22, 14.49, 28.03, 112.76, 141.80; mass spectrum m/e (% rel. int.) 153 (M-15, 2%), 114 (13), 113 (100), 99 (9), 97 (12), 86 (6), 85 (53), 71 (8), 59 (69), 58 (6), calculated for $C_9H_{17}Si$ m/e (M-15) 153.10995, measured m/e 153.10972.

Synthesis of 3-butenylallyldimethylsilane 222

To a stirred solution of excess allylmagnenisum bromide, prepared from 1.59 g (13.2 mmol) of allyl bromide and excess Mg turnings in 50 mL of dry THF under N_2, was added 1.00 g (6.76 mmol) of 3-butenyldimethylchlorosilane in one portion. The final mixture was stirred under N_2 for 8 hours. The reaction mixture was then hydrolyzed with excess H_2O and diluted with 75 ml of pentane. The pentane layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. All of the pentane and other volatiles was removed by rotavapor. Pure 3-butenylallyldimethylsilane (70%) (181) was isolated by preparative GC on a 9 ft, 20% OV-101/Chromosorb W column at 120°C: ^1H NMR ($DCCl_3$) δ 0.01 (s, 6H), 0.62-0.67 (m, 2H), 1.54 (d, J = 8.07 Hz, 2H), 2.04-2.09 (m, 2H), 4.81-5.02 (m, 4H), 5.71-5.94 (m, 2H); ^{13}C NMR ($DCCl_3$) δ -3.66, 14.11, 23.32, 27.98, 112.87, 135.03, 141.58; mass spectrum m/e (% rel. int.) 154 (1), 114 (11), 113 (87), 111 (7), 99 (7), 85

(62), 71 (7), 60 (8), 59 (100), calculated for $C_9H_{18}Si$ m/e 154.11778, measured m/e 154.11792.

Vacuum pyrolysis of di-(3-butenyl)dimethylsilane 218

A slow distillation of 0.2967 g (1.77 mmol) of 218 was done at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a trap cooled by liquid nitrogen and represented a 64% mass recovery. GC analysis of the pyrolysate showed one major product and greater than six minor products along with 14% unreacted 218. The major compounds were isolated by preparative GC on a 9 ft, 20% OV-101/Chromosorb W column at 100°C and was identified as trimethylsilane 120 (32%). The NMR, mass spectrum, and GC retention time exactly matched that of 120 formed on pyrolysing 59 as well as that of an authentic sample. The NMR of 120 also matched that reported by Fleming and Langley (185).

Vacuum pyrolysis of 3-butenylallyldimethylsilane 222

A slow distillation of 0.2148 g (1.39 mmol) of 222 was done at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a liquid nitrogen cooled trap and represented a 77% mass recovery. GC analysis showed three new major products in about equal amounts. The three compounds were separated by only about 0.15 minutes on an 8½ ft, 10% OV-101/Chromosorb W column with a temperature program of 70°C to 200°C at 15°C per minute. Therefore, they were isolated as a mixture by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 100°C. They were identified as 1,1-dimethyl-1-silacyclopent-3-ene **198** (17%), 1,1-dimethyl-1-silacyclopent-2-ene **199** (21%) (137), and allylvinyldimethylsilane **172** (20%) along with 25% unreacted **222**. The NMR and GCMS of **172** exactly matched that of **172** produced in the pyrolysis of **168**. The spectra for **198** and **199** are given below.

1,1-Dimethyl-1-silacyclopent-3-ene ***198*** The NMR and mass spectrum of **198** matched that reported by Barton and Wulff (137). ^{1}H NMR ($DCCl_3$) δ 0.14 (2, 6H), 1.27 (broad d, J ≈ 1.1 Hz, 4H), 5.85 (broad s, 2H); mass spectrum m/e (% rel. int.) 112 (34), 98 (11), 97 (100), 95 (25), 71 (11), 69 (8), 59 (12), 58 (24), 53 (7).

1,1-Dimethyl-1-silacyclopent-2-ene ***199*** The NMR and mass spectrum of **199** matched that reported by Barton and Wulff (137). ^{1}H NMR ($DCCl_3$) δ 0.17 (s, 6H), 0.67-0.72 (m, 2H), 2.45-2.51 (m, 2H), 5.92 (d of t, J_{ab} = 11.22 Hz, J_{ac} = 2.20 Hz, 1H_a α to Si), 6.78 (d of t, J_{ab} = 11.22 Hz, J_{bc} = 2.64 Hz, 1H_b β to Si); mass spectrum m/e (% rel. int.) 112 (10), 98 (10), 97 (100), 95 (25), 71 (9), 69 (11), 59 (7), 58 (9), 55 (9), 53 (7).

Flow pyrolysis of (3-butenyl)allyldimethylsilane ***218***

A flow pyrolysis of **218** (30 μl) was done by dripping **218** through a vertical quartz tube packed with quartz chips and heated to 540°C. Methyl chloride was used as the carrier gas at a flow rate of 35 mL/min. The pyrolysate was collected in a trap cooled to -78°C and was analyzed by GC. By GC, there were no peaks that had the same retention time as 3-butenyldimethylchloridesilane 225. In fact, on a 8½ ft, 10% OV-101/Chromosorb W column with a temperature program of 70°-150°C at 10°/minute, there were no peaks within 15 seconds of the retention time of 225. About 60° of the mixture was unreacted 218, while the other consisted of silacyclopentenes 198 and 199 and other minor products.

Synthesis of (4-pentenyl)dimethylchlorosilane (208)

To a stirred slurry of 8.1 g (39.1 mmol) of phosphorus pentachloride in 25 mL of pentane under N_2 was added 5.0 g (39.1 mmol) of (4-pentenyl)dimethylsilane 64. The final mixture was stirred for 30 minutes. The liquid phase was distilled at room temperature under vacuum (ca. 0.05 mm Hg) and collected in a flask cooled to -78°C. After removal of the solvent, distillation (136°-140°C) gave 3.5 g (56%) of (4-pentenyl)dimethylchlorosilane: ^1H NMR ($DCCl_3$) δ 0.40 (s, 6H), 0.76-0.90 (m, 2H), 1.46-1.53 (m, 2H), 2.02-2.13 (m, 2H), 4.92-5.04 (m, 2H), 5.70-5.84 (m, 1H).

Synthesis of (4-pentenyl)allyloxydimethylsilane 226

To a stirred solution of 0.72 g (12.3 mmol) of allyl alcohol and 0.97 g (12.3 mmol) of pyridine in 15 mL of ether under N_2 was added 2.0 g (12.3 mmol) of (4-pentenyl)dimethylchlorosilane in a dropwise fashion. The cloudy mixture was then dilute with 100 ml of pentane and transferred to a separatory funnel. The pentane layer was extracted with saturated $NaHCO_3$ solution, separated, dried over Na_2SO_4, and filtered. After removal of the solvent, distillation (87°-95°C/5 mm

Hg) afforded 1.5 g (66%) of (4-pentenyl)allyloxydimethylsilane 226: ^{1}H NMR ($DCCl_3$) δ 0.10 (s, 6H), 0.57-0.64 (m, 2H), 1.40-1.50 (m, 2H), 2.03-2.10 (m, 2H), 4.10-4.13 (m, 2H), 4.91-5.27 (m, 4H), 5.71-5.96 (m, 2H); ^{13}C NMR ($DCCl_3$) δ -2.03, 16.01, 22.67, 37.35, 63.73, 114.33, 114.49, 137.41, 138.71; mass spectrum m/e (% rel. int.) 169 (M-15, 2%), 143 (5), 117 (5), 116 (8), 115 (100), 113 (12), 99 (26), 87 (5), 85 (17), 75 (10), 61 (9), 59 (32), calculated for $C_9H_{17}OSi$ m/e (M-15) 169.10487, measured m/e 169.10523. Elemental analysis calculated for $C_{10}H_{20}SiO$: C, 65.14; H, 10.96. Found: C, 65.26; H, 11.14.

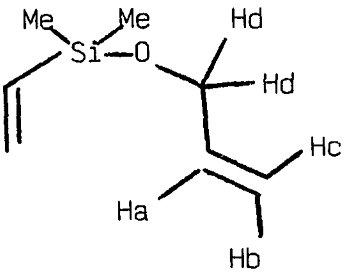
Synthesis of (4-pentenyl)dimethylphenylsilane 233

To a stirred mixture of excess Mg turnings in 50 mL of dry THF under N_2 was added a small portion of 5-bromo-1-pentene for initiation. The remainder of the 5-bromo-1-pentene (5.0 g, 33.7 mmol total) and 5.7 g (33.7 mmol) of dimethylphenylchlorosilane were dissolved in 50 mL of dry THF and added dropwise to the stirred solution. After stirring for 12 hours, the reaction mixture was hydrolyzed with excess H_2O and transferred to a separatory funnel containing 150 mL of pentane. The pentane layer was extracted with H_2O, separated, dried over Na_2SO_4, and filtered. After solvent removal, distillation (110°-115°C/2 mm Hg) of the residue afforded 4.4 g (65%) of (4-pentenyl)dimethylphenylsilane 233: ^{1}H NMR ($DCCl_3$) δ 0.27 (s, 6H), 0.74-0.81 (m, 2H), 1.37-1.50 (m, 2H), 2.04-2.13 (m, 2H), 4.92-5.04 (m, 2H), 5.71-5.85 (m, 1H), 7.31-7.61 (m, 5H); ^{13}C NMR ($DCCl_3$) δ -0.89, 17.47, 25.53, 39.68, 114.56, 127.75, 128.83, 133.58, 138.84, 139.54; mass spectrum m/e (% rel. int.) 204 (1), 154 (17), 136 (13), 135 (100), 126 (20), 121 (11), 105 (9), 98 (8), calculated for $C_{13}H_{20}Si$ m/e 204.13343, measured m/e 204.13411. Elemental analysis calculated for $C_{13}H_{20}Si$: C, 76.38; H, 9.88. Found: C, 75.58; H, 10.15.

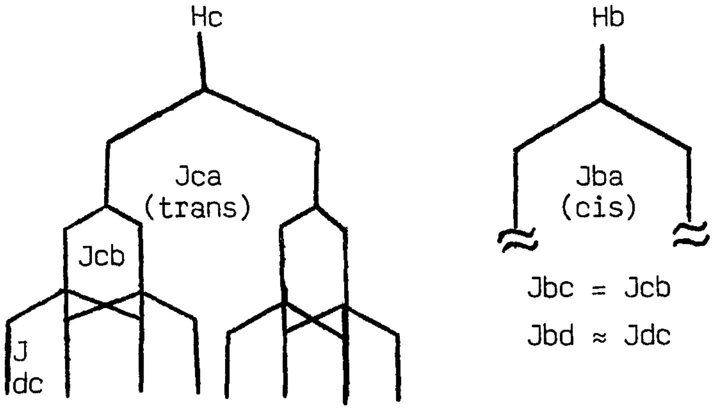
Vacuum pyrolysis of (4-pentenyl)allyloxydimethylsilane **226**

The pyrolysis of **226** was carried out by slowly distilling 0.4338 g (2.36 mmol) of **226** at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 780°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 65% mass recovery. GC analysis of the pyrolysate showed one major product along with unreacted **226** (22%). The compound was isolated by preparative GC on a 9 ft, 20% OV-101/Chromosorb W column at 120°C and identified as vinylallyloxydimethylsilane **227** (12%). When the pyrolysis was done at 700°C, the yield of unreacted **226** and compound **227** was 77% and 25%, respectively. The mass recovery at 700°C was 85%. The spectra of **227** is given below.

Vinylallyloxydimethylsilane **227** ^1H NMR ($DCCl_3$) δ 0.15 (s, 6H), 4.02-4.04 (m, 2H), 5.01 (d of q, J = 1.90 Hz, J_{cis} = 10.29 Hz, 1H), 5.30 (d of q, J = 1.94 Hz, J_{trans} = 17.09 Hz, 1H), 5.70-6.18 (m, 4H); IR (neat) 1095 cm^{-1} (SiOC); mass spectrum m/e (% rel. int.) 142 (1), 128 (8), 127 (74), 115 (9), 101 (18), 100 (12), 99 (100), 97 (18), 87 (10), 85 (45), 75 (39), 71 (37), 61 (27), 59 (60), 55 (10), 47 (11); calculated for C_4H_9Si m/e 101.04227, measured m/e 101.04218.



227



Vacuum pyrolysis of (4-pentenyl)dimethylphenylsilane 233

A slow distillation of 0.3220 g (1.58 mmol) of 233 was done at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 780°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 69% mass recovery. The pyrolysate was analyzed by GC which showed three major products and a 12% yield of unreacted 233. The compounds were isolated by preparative GC on a 5 ft, 12% OV-101/Chromosorb W column at 130°C. They were identified according to their spectral properties, given below, as dimethylphenylsilane (10%) (184), allyldimethylphenylsilane (6%) (185), and vinyldimethylphenylsilane 234 (19%) (183). When the pyrolysis of 233 was carried out at 700°C, unreacted 233 was recovered in 38% yield along with 32% yield of vinyldimethylphenylsilane 234. Only trace amounts of dimethylphenylsilane and allyldimethylsilane were detectable by GC. The mass recovery at 700°C was 83%.

Dimethylphenylsilane ^{1}H NMR (DCCl$_3$) δ 0.33 (d, J = 4.0 Hz, 6H), 4.27-4.67 (m, 1H), 7.25-7.70 (m, 5H); IR (neat) 2135 cm^{-1} (SiH); mass spectrum m/e (% rel. int.) 136 (38), 135 (25), 122 (12), 121 (100), 119 (6), 105 (21), 95 (5), 93 (6), 91 (5), 79 (7), 77 (5), 69 (5), 67 (8), 60 (6), 59 (10), 58 (87), 55 (5), 53 (20), 51 (6).

Allyldimethylphenylsilane The NMR matched that published by Fleming and Langley (185). ^{1}H NMR (DCCl$_3$) δ 0.27 (s, 6H), 1.75 (d, 8.0 Hz), 4.63-5.10 (m, 2H), 5.37-6.20 (m, 1H), 7.20-7.68 (m, 5H); mass spectrum m/e (% rel. int.) 176 (1), 136 (13), 135 (100), 107 (6), 105 (9), 53 (5).

Vinyldimethylphenylsilane **234** ^{1}H NMR (DCCl$_3$) δ 0.41 (s, 6H), 5.82 (d of d, J_{gem} = 3.87 Hz, J_{trans} = 20.16 Hz, 1H), 6.12 (d of d, J_{gem} = 3.87 Hz, J_{cis} = 14.58 Hz, 1H), 6.30-6.41 (m, 1H), 7.39-7.60 (m, 5H); mass spectrum m/e (% rel. int.) 162 (23), 148 (13), 147 (100), 145 (7), 135 (23), 122 (9), 121 (79), 107 (8), 105 (20), 93 (6), 79 (6), 67 (6), 59 (10), 58 (8), 55 (7), 53 (17), calculated for $C_{10}H_{14}Si$ m/e 162.08702, measured m/e 162.08648.

Synthesis of (3-butenyl)dimethylchlorosilane **225**

To a stirred slurry of 1.83 g (8.77 mmol) of anhydrous phosphorus pentachloride in 15 mL of dry pentane under N_2 was added 1.00 g (8.77 mmol) of 3-butenyldimethylsilane **59** in a dropwise fashion. The final mixture was stirred for *ca.* 15 minutes then distilled at 25°C/0.05 mm Hg and collected in a flask cooled to -78°C. The distillate was filtered through celite and washed with dry pentane. Fractional distillation, after removal of excess pentane, afforded 225 (209) (123°-126°C) in 77% yield (1.00 g): ^{1}H NMR (DCCl$_3$) δ 0.30 (s, 6H), 0.63-1.00 (m, 2H), 1.83-2.30 (m, 2H), 4.67-5.17 (m, 2H), 5.43-6.10 (m, 1H); mass spectrum m/e (% rel. int.) 148 (2), 115 (6), 97 (15), 95 (11), 93 (28), 87 (8), 76 (7), 75 (100), 61 (23), 47 (12).

Synthesis of (3-butenyl)allyloxydimethylsilane 226

To a stirred solution of 0.79 g (13.5 mmol) of allyl alcohol and an equivalent amount of pyridine in 25 mL of dry ether under N$_2$ was added 2.00 g (13.5 mmol) of (3-butenyl)dimethylchlorosilane 225 in a dropwise fashion. The final cloudy mixture was stirred for 10 minutes then filtered through celite. All of the volatiles were then carefully removed by distillation between 35° and 100°C. The remaining residue was distilled at 25°C/0.05 mm Hg and collected in a flask cooled to -78°C. GC analysis of the distillate showed one product which was identified as (3-butenyl)allyloxydimethylsilane 226 (92%): ^{1}H NMR δ 0.12 (s, 6H), 0.68-0.74 (m, 2H), 2.06-2.14 (m, 2H), 4.12-4.14 (m, 2H), 4.87-5.28 (m, 4H), 5.80-5.97 (m, 2H); ^{13}C NMR δ -1.98, 15.58, 27.27, 63.73, 112.87, 114.44, 137.30, 141.26; IR (neat) 1100 cm^{-1} (SiOC); mass spectrum m/e (% rel. int.) 155 (M-15, 11%), 128 (8), 127 (7), 117 (21), 116 (12), 115 (100), 101 (10), 99 (17), 85 (13), 75 (15), 59 (8), calculated for C$_8$H$_{15}$SiO m/e (M-15) 155.08922, measured m/e 155.08871.

Vacuum pyrolysis of (3-butenyl)allyloxydimethylsilane 226

Run 1 A slow distillation of 0.1524 g (0.90 mmol) of 226 was done at 25°C (1 X 10^{-5} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a liquid nitrogen cooled trap and represented a 69% mass recovery. About 80% of the pyrolysate was unreacted 226 and the remaining 20% consisted of about thirteen volatile components.

Run 2 0.1395 g (0.820 mmol) Of 226 was pyrolyzed affording a mass recovery of 44%. About eighteen volatile products along with 226 were observable by GC.

Synthesis of allyldimethylchlorosilane

A modified technique of hydrogen-halogen exchange between a silane and triphenylmethyl chloride (210) was used to prepare allyldimethylchlorosilane. Thus, 22.24 g (80.0 mmol) of triphenylmethyl chloride (used directly as purchased) was dissolved in 100 mL of chloroform to which was added 4.00 g (40.0 mmol) of allyldimethylchlorosilane in one portion. The final solution was stirred at room temperature under N_2 for 25 hours. The liquid phase was then removed by distillation at room temperature (0.05 mm Hg) and collected in a flask cooled to -78°C (isopropanol/dry ice). Fractional distillation (94°-97°C) afforded 3.88 g (72%) yield of allyldimethylchlorosilane. When the reaction was done on a NMR scale using 0.0353 g (0.353 mmol) of allyldimethylsilane and 0.1013 g (0.364 mmol) of triphenylmethyl chloride (95% purity) dissolved in 0.4192 g of dueterio chloroform, the yield of allyldimethylchlorosilane was 95% by NMR.

Allyldimethylchlorosilane The NMR and GC retention time of allyldimethylchlorosilane exactly matched that of an authentic sample which is commercially available (Petrarch): ^{1}H NMR ($DCCl_3$) δ 0.45 (s, 6H), 1.83 (d, J = 8.0 Hz, 2H), 4.73-5.25 (m, 2H), 5.34-6.08 (m, 1H); mass spectrum m/e (% rel. int.) 134 (7), 119 (4), 99 (7), 95 (45), 94 (10), 93 (100), 83 (6), 81 (4), 79 (11), 67 (7), 65 (24), 63 (22), 59 (6).

Synthesis of allyloxyallyldimethylsilane 236

Method 1 The lithium alkoxide of allyl alcohol was prepared under N_2 by addition of 38.7 mL (55.7 mmol) of 1.44 M n-buthyl lithium to a stirred solution of 3.2 g (55.7 mmol) of allyl alcohol in 40 mL of ether cooled to -78°C. To this stirred solution was added 5.0 g (37.1 mmol) of allyldimethylchlorosilane in a dropwise fashion. The final solution was stirred at -78°C for 15 minutes then allowed to warm to room temperature for 30 minutes. The reaction mixture was then hydrolysed with excess saturated $NaHCO_3$. The ether layer was extracted with saturated $NaHCO_3$, seperated, dried over Na_2SO_4, and filtered. Solvent removal was followed by distillation (130°-133°C) which gave 3.7 g (64%) of allyloxyallyldimethylsilane 236.

Method 2 To a stirred solution of 0.86 g (14.8 mmol) of allyl alcohol and an equivalent amount of pyridine dissolved in dry pentane under N_2 was added 2.00 g (14.8 mmol) of allyldimethylchlorosilane in a dropwise fashion. The final cloudy solution was stirred for 15 minutes then filtered through celite and washed with dry pentane.

After removal of the solvent, distillation (130°-134°C) of the residue afforded 1.46 g (63%) of allyloxyallyldimethylsilane **236**.

Allyloxyallyldimethylsilane **236** ^{1}H NMR (DCCl$_3$) δ 0.13 (s, 6H), 1.64 (d, J = 8.08 Hz, 2H), 4.14-4.17 (m, 2H), 4.84-4.93 (m, 2H), 5.09-5.28 (m, 2H), 5.72-5.97 (m, 2H); ^{13}C NMR (DCCl$_3$) δ -2.41, 24.51, 63.95, 113.74, 114.55, 133.94, 137.19; IR (neat) 1086 cm^{-1} (SiOC); mass spectrum m/e (% rel. int.) 156 (1), 116 (12), 115 (100), 114 (10), 113 (9), 99 (24), 87 (12), 85 (65), 75 (29), 61 (19), 60 (9), 59 (89), calculated for $C_8H_{16}Si$ m/e 156.09705, measured m/e 156.09730. Elemental analysis calculated for $C_8H_{16}Si$: C, 61.46; H, 10.34. Found: C, 61.30; H, 10.58.

Vacuum pyrolysis of allyloxyallyldimethylsilane **236**

A slow distillation of **236** was done at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to various temperatures. The pyrolysate was collected in a trap cooled with liquid nitrogen and was analyzed by GC.

At 810°C Compound **236**, 0.356 g (2.28 mmol), was pyrolyzed giving an 84% mass recovery of pyrolysate. GC analysis showed very little decomposition of **236**.

At 860°C Compound **236**, 0.242 g (1.55 mmol), was pyrolyzed giving a 76% mass recovery of pyrolysate. GC analysis still showed very little decomposition of **236**, but new volatile peaks had appeared.

At 900°C Compound **236**, 0.170 g (1.09 mmol), was pyrolyzed giving a 54% mass recovery of pyrolysate. GC analysis showed a complex mixture of more than ten products. By GCMS, some of the compounds present in the mixture were: 1-propenyldimethylvinylsilane 126 (21), 112 (11), 111(100), 85 (15), 55 (5); hexamethylcyclotrisiloxane (D_3) 209 (12), 208 (20), 207 (P-15, 100), 191 (11), 133 (11), 96 (27); another $C_6H_{18}O_3Si_3$ isomer, recovered starting material 236, two isomers of 236, and a compound with the molecular formula $C_{10}H_{22}Si_2O_2$ (236 + $Me_2Si{=}O$). The mass spectrum of D_3 exactly matched that of an authentic sample (Petrarch). None of the products were isolable.

Copyrolysis of 236 and dimethyldimethoxysilane 239

A solution consisting of 0.0458 g (0.294 mmol) of 236 and 0.3592 g (2.27 mmol) of dimethyldimethoxysilane was slowly dripped into a verticle quartz tube packed with quartz chips and heated to 650°C. A flow of nitrogen (35 mL/min) was used as a carrier gas. The pyrolysate was collected in a trap cooled to -78°C and represented a 53% mass recovery. GC analysis showed one new major peak along with dimethyldimethoxysilane 239. The compound was isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 120°C and was identified as sym-dimethoxytetramethyldisiloxane 240 (190) (93%). ^1H NMR (C_6D_6) δ 0.14 (s, 12H), 3.39 (s, 6H); IR (neat) 1107 cm^{-1} (SiOC), 1072 cm^{-1} (SiOSi); mass spectrum m/e (% rel. int.) 181 (8), 180 (15), 179 (P-15, 90), 163 (6), 151 (9), 150 (17), 149 (100), 133 (21), 119 (35), 105 (11), 103 (10), 89 (13), 82 (27), 75 (13), 74 (9), 73 (13), 67 (13), 59 (33).

Flow pyrolysis of dimethoxydimethylsilane **239**

A N_2-flow (35 mL) pyrolysis was carried out by dripping 96.3 mg (0.802 mmol) of **239** through a vertical quartz tube packed with quartz chips and heated to 650°C. The pyrolysate, represented by a 40% mass recovery (no attempt to optimize), was collected in a trap cooled to -78°C. Along with unreacted **239**, *sym*-dimethoxytetramethyldisiloxane **240** (190) was formed in 2% yield. Compound **240** was isolated by preparative GC and its spectral properties and GC retention time matched that of **240** obtained from the copyrolysis of allyoxyallyldimethylsilane **236** and **239**.

Flow pyrolysis of allyloxyallyldimethylsilane **236**

Nitrogen-flow A nitrogen-flow pyrolysis (35 mL/min) was done by slowly dripping **236** (50 µl) through a vertical quartz tube packed with quartz chips and heated to 500°C and 560°C. The pyrolysate was collected in a trap cooled to -78°C (isopropanol/dry ice) and was analyzed by GC. The major product at both temperatures, 70% at 500°C and 50% at 560°C, was unreacted **236**. However, a complex mixture of other products were also formed from which D_3 was identifiable by GCMS comparison with an authentic sample. The relative ratio of products presence in greater than 1% GC area was obtained.

Methyl chloride-flow A methyl chloride-flow pyrolysis of **236** (50 µl) was done as described above at the same temperatures. GC analysis showed that the relative ratios of the products were the same as in the nitrogen-flow experiment. Furthermore, no significant amount of a compound with a $C_5H_{11}SiClO$ molecular formula could be found in the GCMS. D_3 (GCMS) was also formed in this pyrolysis.

Flow pyrolysis of allyloxydimethylsilane 116

A flow pyrolysis of 0.2836 g (2.74 mmol) of 116 was done by dripping 116 through a vertical quartz tube packed with quartz chips and heated to 650°C. A flow of nitrogen (35 mL/min) was used as a carrier gas. The pyrolysate was collected in a trap cooled to -78°C and represented a 38% mass recovery. GC analysis showed a trace amount (<2%) of D_3 (GCMS identification) along with one major compound that was isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 120°C. The compound was identified as 1-allyloxy-1,1,3,3-tetramethyldisiloxane 242 (193) (11%): ^1H NMR (C_6D_6) δ 0.12 (s, 6H), 0.15 (d, J = 2.77 Hz, 6H), 4.12-4.14 (m, 2H), 4.96-5.05 (m, collapses to s at 4.98 and m 4.99-5.05 with hν at 0.15, 2H), 5.24-5.34 (m, 1H), 5.79-5.91 (m, 1H); ^{13}C NMR (C_6D_6) δ -1.24, 0.55, 63.12, 113.82, 137.28; IR (neat) 1072 (SiOSiOC); mass spectrum m/e (% rel. int.) 190 (1), 189 (2), 175 (8), 149 (14), 135 (10), 134 (13), 133 (100), 75 (8), 73 (10), 59 (11).

Copyrolysis of 116 and dimethyldimethoxysilane 239

A solution of 0.0440 g (0.404 mmol) of 116 and 0.4143 g (3.30 mmol) of dimethyldimethoxysilane was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 650°C. A flow of nitrogen (35 mL/min) was used as a carrier gas. A 52% mass recovery of pyrolysate was collected in a trap cooled to -78°C (isopropanol/dry ice). GC analysis showed three new major products along with dimethyldimethoxysilane 239. The compounds were isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 120°C and were identified as 1-methoxy-1,1,3,3-tetramethyldisiloxane 243 (4%), allyloxymethoxyldimethylsilane 244 (5%), and *sym*-dimethoxytetramethyldisiloxane 240 (190) (15%). All spectra properties and GC retention times of 240 exactly matched that of 240 obtained from the copyrolysis of 239 with allyloxyallyldimethylsilane 236. The spectra of 243 and 244 are given below.

1-Methoxy-1,1,3,3-tetramethyldisilane 243 ^{1}H NMR (C_6D_6) δ 0.12 (s, 6H), 0.17 (d, J = 3.5 Hz, 6H), 3.35 (s, 3H), 4.80-5.15 (m, 1H); IR (neat) 2137 cm^{-1} (SiH), 1072 cm^{-1} broad (SiOSiOC); mass spectrum m/e (% rel. int.) 164 (1), 163 (8), 151 (7), 150 (13), 149 (100), 133 (I8), 120 (10), 119 (79), 103 (8), 89 (9), 74 (10), 73 (16), 59 (43).

Allyloxymethoxydimethylsilane 244 ^{1}H NMR (C_6D_6) δ 0.09 (s, 6H), 3.33 (s, 3H), 4.09-4.12 (m, 2H), 4.77-5.04 (m, 1H), 5.27-5.34 (m, 1H), 5.79-5.91 (m, 1H); IR (neat) 1120 cm^{-1}, 1057 cm^{-1} (SiOC); mass spectrum m/e (% rel. int.) 146 (5), 132 (11), 131 (100), 118 (5), 117 (49), 115 (5), 114 (12), 103 (6), 102 (10), 100 (6), 90 (8).

Synthesis of 1,2-diallyloxy-1,1,2,2-tetramethyldisilane 245

The method of Hosomi and coworkers (195) was used to prepare 245. The lithium alkoxide of allyl alcohol was prepared under N_2 by adding 25.7 mL (54.0 mmol) of 2.1 M n-butyl lithium to a solution of 3.1 g (54.0 mmol) of allyl alcohol in 30 mL of ether cooled to

-78°C (isopropanol/dry ice). To this stirred solution was added 5.0 g (26.9 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane in a dropwise fashion. The liquid phase was then removed by distillation (50°C pot temperature/0.05 mm Hg) and collected in a flask cooled to -78°C. The volatile components were removed by distillation leaving 5.5 g of a residue which was 95% 1,2-diallyloxy-1,1,2,2-tetramethyldisilane 245 (195) (89%) by GC: ^{1}H NMR ($DCCl_3$) δ 0.23 (s, 12H), 4.05-4.25 (m, 4H), 4.93-5.45 (m, 4H), 5.62-6.28 (m, 2H); IR (neat) 1028 cm^{-1} (SiOC); mass spectrum m/e (% rel. int.) 189 (M-41, 9%), 135 (10), 134 (16), 133 (100), 119 (8), 117 (10), 115 (17), 85 (20), 75 (17), 73 (24), 59 (42).

Vacuum pyrolysis of 1,2-diallyloxy-1,1,2,2-tetramethyldisilane 245

A slow distillation of 0.1560 g (0.678 mmol) of 245 was carried out at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 66% mass recovery. GC analysis of the pyrolysate showed four major products that were isolated by preparative GC on a 9 ft, 20% SE-30/Chromosorb W column at 130°C. Three of the compounds were identified as diallyloxydimethylsilane 247 (20%) (196), 1-allyloxy-3-allyl-hexamethyltrisiloxane 249 (18%) (195). The spectra and GC retention time of 247 exactly matched that of an authentic sample (see the Experimental section of this dissertation). The fourth product was isolated as a mixture of $C_8H_{16}O$ isomers (8%) based on GCMS and NMR. The isomers could not be separated using preparative GC. The spectra for 249 is given below.

1,5-Diallyl-1,1,3,3,5,5-hexamethyltrisiloxane **249** ^{1}H NMR (C_3D_6O) δ 0.02 (s, 6H), 0.07 (s, 12H), 1.53 (d, J = 8.0 Hz, 4H), 4.60-5.00 (m, 4H), 5.41-6.14 (m, 2H); ^{13}C NMR (C_3D_6O) δ -0.10, 1.41, 26.77, 113.77, 135.12; IR (neat) 1055 cm^{-1} (SiOSiOSi); mass spectrum m/e (% rel. int.) 273 (M-15, 1%), 248 (12), 247 (56), 231 (10), 207 (9), 206 (7), 205 (35), 191 (9), 189 (9), 104 (10), 103 (60), 99 (68), 96 (12), 95 (13), 88 (9), 74 (9), 73 (100), 59 (43), calculated for $C_{11}H_{25}Si_3O_2$ m/e (M-15) 273.11624, measured m/e 273.11662.

Synthesis of 1-allyloxy-3-allyl-1,1,3,3-tetramethyldisiloxane **248**

To a stirred solution of 11.0 g (54.0 mmol) of 1,3-dichlorotetramethyldisilane (Petrarch) in 15 mL of dry ether under N_2 was added 200 mL (55.0 mmol) of 0.26 M allylmagnesium bromide in ether dropwise for 1.5 hours. This solution was then cooled to -78°C and 150 mL (55.0 mmol) of the lithium alkoxide (0.37 M) of allyl alcohol in ether was added in a dropwise fashion. The reaction mixture was allowed to warm to room temperature then filtered through celite and washed with pentane. After solvent removal, a pure sample of 1-allyloxy-3-allyl-1,1,3,3-tetramethyldisiloxane **248** was obtained by preparative GC on a 5 ft, 12% OV-101/Chromosorb W column at 140°C. Also formed in the reaction was 1,3-diallyloxy-1,1,3,3-tetramethyldisiloxane: ^{1}H NMR ($DCCl_3$) 0.12 (s, 12H), 4.12-4.34 (m, 4H), 4.95-5.48 (m, 4H), 5.68-6.30 (m, 2H).

1-Allyloxy-3-allyl-1,1,3,3-tetramethyldisiloxane 248 ^{1}H NMR (C_3D_6O) δ 0.03 (s, 6H), 0.05 (s, 6H), 1.55 (d, J = 8.0 Hz, 2H), 3.95-4.15 (m, 2H), 4.59-6.24 (m, 6H); ^{13}C NMR (C_3D_6O) δ -0.81, -0.21, 26.66, 63.55, 113.77, 114.10, 135.01, 138.31; IR (neat) 1065 cm^{-1} (SiOSi), 1140 cm^{-1}, 1157 cm^{-1} (SiOC); mass spectrum m/e (% rel. int.) 215 (M-15, 1%), 189 (47), 149 (10), 135 (11), 134 (13), 133 (100), 119 (11), 103 (5), 94 (9), 73 (19), 66 (14), 59 (11), calculated for $C_9H_{19}Si_2O_2$ m/e (M-15) 215.09236, measured m/e 215.09292. Elemental analysis calculated for $C_{10}H_{22}Si_2O_2$: C, 52.11; H, 9.64. Found: C, 51.85, H, 9.85.

Copyrolysis of 1,2-diallyl-1,1,2,2-tetramethyldisilane 245 and 2,3-dimethylbutadiene

A solution of 0.1352 g (0.588 mmol) of 245 and a 4.4 fold excess of 2,3-dimethylbutadiene was dripped through a vertical quartz tube packed with quartz chips and heated to 500°C. A flow of N_2 (35 mL/min) was used as a carrier gas and the pyrolysate was collected in a trap cooled to -78°C. The mass recovery was 52% (no attempts to optimize). GC analysis revealed three major products along with unreacted 245 (3%) and excess 2,3-dimethylbutadiene. The compounds were isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 120°C and were identified as diallyloxydimethylsilane 247 (7%) (196), 1-allyloxy-3-allyl-1,1,3,3-tetramethyldisiloxane 248 (1%), and 1,1,3,4-tetramethyl-1-silacyclopent-3-ene 250 (11%) (211). All spectral properties and GC retention times of 247 and 248 exactly matched those of the compounds produced in the vacuum pyrolysis of **245**. The proton NMR of **250** matched that reported in the literature (210): ^{1}H NMR δ (C_3D_6O) 0.10 (s, 6H), 1.27 (m, 4H), 1.63 (m, 6H); ^{13}C NMR (C_3D_6O) δ -1.87, 19.40, 25.96, 130.99; mass spectrum m/e (% rel. int.) 140 (54), 126 (12), 125 (100), 123 (21), 109 (10), 98 (8), 97 (24), 85 (23), 83 (22), 73 (13), 69 (9), 67 (10), 59 (75), 58 (14), 55 (11), 53 (9).

Copyrolysis of **245** and tetramethoxysilane

A N_2-flow (35 mL/min) pyrolysis of 0.2681 g (1.17 mmol) of **245** dissolved in an eight fold excess of tetramethoxysilane was done by dripping the solution through a quartz tube packed with quartz chips and heated to 500°C. The pyrolysate, represented by a 78% mass recovery, was collected in a trap cooled to -78°C. GCMS analysis showed as the only major products diallyloxydimethylsilane **247**, 1-allyloxy-3-allyl-1,1,3,3-tetramethyldisiloxane **248**, and allyloxymethoxydimethylsilane **244**. The ratio of these products was approximately 2:4:1, respectively.

Synthesis of 1-allyloxypentamethyldisilane **253**

The synthesis of 1-allyloxypentamethyldisilane was accomplished by using the method of Hosomi and coworkers (195). The lithium alkoxide of allyl alcohol was prepared under N_2 by adding 15 mL (31.0 mmol) of 2.1 M n-butyl lithium to a stirred solution of 1.9 g (33.0 mmol) of allyl alcohol in 100 mL of ether cooled to -78°C. To this stirred solution was added 5.0 g (30.0 mmol) of 1-chloropentamethyldisilane in a dropwise fashion. The final reaction mixture was allowed to warm to room temperature then distilled (25°C/0.05 mm Hg) and collected in a flask cooled to -78°C. After removal of the solvent, distillation (146°-155°C) of the residue gave 4.3 g (76%) of 1-allyloxypentamethyldisilane 253 (195): ^{1}H NMR ($DCCl_3$) δ 0.07 (s, 9H), 0.17 (s, 6H), 4.00-4.18 (m, 2H), 4.92-5.46 (m, 2H), 5.53-6.17 (m, 1H); ^{13}C NMR ($DCCl_3$) δ -2.03, -0.73, 64.49, 114.33, 137.4; IR (neat) 1072 (SiOC); mass spectrum m/e (% rel. int.) 173 (M-15, 1%), 149 (8), 148 (15), 147 (M-41, 100%), 133 (23), 131 (13), 117 (11), 115 (13), 85 (17), 75 (9), 73 (60), 59 (27).

Synthesis of allyloxytrimethylsilane 254

The synthesis of allyloxytrimethylsilane was accomplished using the method of Ghose (199). To a stirred solution of 2.7 g (46.0 mmol) of allyl alcohol and 3.6 g (46.0 mmol) of pyridine in 75 mL of ether under N_2 was added 5.0 g (46.0 mmol) of trimethylchlorosilane in a dropwise fashion. After stirring 10 minutes, the reaction mixture was transferred to a separatory funnel and the ether layer extracted with saturated $NaHCO_3$ solution. The ether layer was separated, dried over Na_2SO_4, and filtered. After removal of the solvent, distillation (90°-95°C) of the residue gave 5.1 g (85%) of allyloxytrimethylsilane 254 (195,199): ^{1}H NMR ($DCCl_3$) δ 0.20 (s, 9H), 4.07-4.27 (m, 2H), 4.94-5.48 (m, 2H), 5.48-6.33 (m, 1H); IR (neat) 1069 cm^{-1} (SiOC); mass spectrum m/e (% rel. int.) 130 (21), 116 (10), 115 (100), 99 (9), 87 (10), 85 (56), 75 (20), 73 (46), 61 (14), 59 (68), 59 (68), 57 (12).

Vacuum pyrolysis of 1-allyloxypentamethyldisilane 253

Compound 253, 0.1832 g (0.974 mmol), was slowly distilled at 25°C (1 X 10^{-4} mm Hg) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 77% mass recovery. The pyrolysate was analyzed by GC which showed three major products. The products were isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 130°C. They were identified as allyloxytrimethylsilane 254 (30%) (195,199), 1-allylpentamethyldisiloxane 255 (13%) (133), and 1-(trimethylsiloxy)-2-allyl-1,1,2,2-tetramethyldisilane 256 (10%). All spectral properties and GC retention time for allyloxytrimethylsilane 254 exactly matched that of an authentic sample. The spectra of 255 and 256 are given below.

1-Allylpentamethyldisiloxane 255 ^{1}H NMR (C_3D_6O) δ 0.14 (s, 15H), 1.64 (d, J = 8.0 Hz, 2H), 4.73-5.12 (m, 2H), 5.54-6.33 (m, 1H); ^{13}C NMR (C_3D_6O) δ 0.00, 2.01, 26.93, 113.61, 135.22; IR (neat) 1099 cm^{-1} (SiOSi); mass spectrum m/e (% rel. int.) 173 (M-15, 9%), 149 (8), 148 (15), 147 (100), 133 (12), 131 (7), 73 (24), 66 (11), 59 (12).

1-(Trimethylsiloxy)-2-allyl-1,1,2,2-tetramethyldisilane 256

^{1}H NMR (C_3D_6O) 0.10(s, 15H), 0.20 (s, 6H), 1.57 (d, J = 8.0 Hz, 2H), 4.67-5.17 (m, 2H), 5.45-6.23 (m, 1H); ^{13}C NMR (C_3D_6O) δ -2.27, 0.22, 2.12, 27.04, 113.61, 135.22; IR (neat) 1066 cm^{-1} (SiOSi); mass spectrum m/e (% rel. int.) 246 (1), 205 (12), 174 (14), 173 (82), 157 (7), 147 (23), 133 (38), 131 (13), 117 (15), 85 (7), 74 (8), 73 (100), 59 (26).

Copyrolysis of 253 and 2,3-dimethylbutadiene

A solution of 0.1295 g (0.687 mmol) of 253 in a ten fold excess of 2,3-dimethylbutadiene was dripped through a vertical quartz tube packed with quartz chips and heated to 500°C under a flow of N_2 (35 mL/min). The pyrolysate was collected in a trap cooled to -78°C and represented an 86% mass recovery. Analysis by GC revealed three products in addition to unreacted 253 (12%) and excess 2,3-dimethylbutadiene. The compounds were identified as 1,1,2,4-tetramethyl-1-silacyclopent-3-ene 250 (95%) (210), allyloxytrimethylsilane 254 (87%) (195,199), and 1-allylpentamethyldisiloxane 255 (4%) (133) based on comparison of GCMS data and GC retention time with that of 250 produced from the copyrolysis of 245 with 2,3-dimethylbutadiene, that of 254 and 255 formed in the pyrolysis of 253, and that of an authentic sample of 254 (see the Experimental section of this dissertation).

Copyrolysis of allyloxytrimethylsilane 254 and 1-methoxypentamethyldisilane 257

A solution of 0.185 g (1.43 mmol) of 254 and 0.241 g (1.49 mmol) of 257, prepared in 92% yield by the method of Ghose (199), was dripped through a quartz tube packed with quartz chips and heated to 500°C. The tube was swept with a N_2-flow at 35 mL/min and the pyrolysate collected in a trap cooled to -78°C. GC analysis of the pyrolysate (82% mass recovery) revealed two new major products along with unreacted 254

(4%) and **257** (2%). The compounds were isolated by preparative GC on a 9 ft, 20% OV-101/Chromosorb W column and were identified as 1-allylpentamethyldisiloxane **255** (51%) (133) (spectra exactly matched that of **255** obtained from **253**) and trimethylmethoxysilane **258** (85%) (200): ^{1}H NMR (DCCl$_3$) δ 0.12 (s, 9H), 3.4 (s, 3H). The GC retention time and NMR of **258** matched that of an authentic sample prepared by the method of Ghose (199).

Synthesis of diallyloxydimethylsilane **247** (196)

To a stirred solution of 6.98 (120.0 mmol) of allyl alcohol and an equivalent amount of pyridine in 150 mL of dry ether under N_2 was added 7.74 (60.0 mmol) of dimethyldichlorosilane in a dropwise fashion. The final cloudy solution was stirred for 15 minutes then filtered through celite and washed with dry ether. Excess ether was then removed by rotavapor, the residue diluted with 75 mL of pentane and filtered again thru celite. After removal of the pentane, distillation of the residue (65°-68°C/12 mm Hg) afforded 9.3 g (91%) of **247** (196): ^{1}H NMR (DCCl$_3$) δ 0.12 (s, 6H), 4.07-4.27 (m, 4H), 4.90-5.45 (m, 4H), 5.60-6.24 (m, 2H); ^{13}C NMR (C_3D_6O) δ -3.08, 63.77, 114.20, 138.20; IR (neat) 1136, 1082, 1036 cm^{-1} (COSiOC); mass spectrum 172 (1), 157 (15), 143 (13), 131 (16), 130 (29), 129 (40), 117 (8), 116 (17), 115 (45), 114 (50), 102 (8), 101 (100), 99 (71), 87 (13), 85 (47), 77 (35), 75 (56), 61 (27), 59 (66), 47 (17).

Vacuum pyrolysis of diallyloxydimethylsilane **247**

A slow distillation of 0.2146 g (1.24 mmol) of **247** was carried out at 25°C (1 X 10^{-5} mm Hg) through a quartz tube packed with quartz chips and heated to 770°C. The pyrolysate, which represented an 80% mass recovery, was collected in a liquid nitrogen cooled trap. Analysis of the pyrolysate by GC revealed no products with shorter retention times than that of **247** which made up about 70% of the mixture. The other major components were isomeric to **247** of which there were a total of six by GCMS: m/e (% rel. int.) 171 (M-1, 2%), 157 (23), 143 (23), 131 (25), 130 (53), 129 (61), 127 (9), 117 (10), 116 (28), 115 (68), 114 (72), 102 (9), 101 (95), 100 (12), 99 (100), 87 (17), 85 (60), 77 (35), 74 (64), 61 (27), 60 (9), 59 (74), 47 (18); m/e (% rel. int.) 171 (M-1, 1%), 157 (11), 143 (23), 131 (13), 130 (49), 129 (41), 117 (10), 116 (62), 115 (72), 114 (62), 113 (11), 101 (18), 100 (10), 87 (14), 85 (56), 77 (21), 75 (47), 61 (21), 59 (74), 47 (17); m/e (% rel. int.) 172 (32), 157 (40), 143 (30), 131 (11), 130 (46), 129 (43), 127 (16), 117 (10), 116 (13), 115 (33), 114 (36), 113 (18), 101 (24), 99 (70), 85 (11), 77 (19), 75 (100), 61 (15), 59(22), 47 (13); m/e (% rel. int.) 172 (24), 157 (44), 144 (21), 143 (25), 131 (10), 130 (34), 129(45), 127 (12), 117 (10), 115 (24), 114 (19), 113 (14), 101 (59), 99 (62), 88 (15), 85 (10), 79 (14), 77 (72), 75 (100), 61 (23), 59 (28), 58 (15), 57 (12), 55 (11), 47 (21); m/e (% rel. int.) 172 (39), 157 (39), 143 (21), 131 (11), 130 (52), 129 (45), 127 (12), 117 (12), 116 (11), 115 (29), 114 (30), 113 (18), 101 (21), 99 (61), 85 (12), 77 (23), 75 (100), 61 (13), 59 (27), 58 (11), 55 (11), 47 (16); m/e (% rel. int.) 172 (38), 171 (13), 157 (73), 144 (24), 143 (29), 131 (37), 130 (94), 129 (100), 117 (10), 115 (19), 113 (11), 101 (69), 99 (63), 91 (12), 88 (18), 85 (10), 79 (19), 77 (67), 75 (91), 61 (21), 59 (30), 58 (16), 57 (10), 47 (20).

At 830°C (1 X 10^{-5} mm Hg), the mass recovery was 61%. GC analysis revealed no significant (<5%) amount of products with retention times shorter than **247**. Compound **247** was the major product (*ca*. 50% of the mixture) along with the six isomeric compounds.

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