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Synthesis and chemistry of selected di- and tricoordinate organosilicon compounds

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SYNTHESIS AND CHEMISTRY OF SELECTED DI- AND TRICOORDINATE ORGANOSILICON COMPOUNDS

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Synthesis and chemistry of selected di- and tricoordinate organosilicon compounds

by

William F. Goure

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

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Major: Organic Chemistry

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For the Graduate College

Iowa State University
Ames, Iowa
1982

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INTRODUCTION

Although the chemistry of silylenes - silicon analogues of carbenes - began over forty years ago with the discovery of dichlorosilylene (1,2), our current understanding of these interesting molecules is based primarily on the results of studies conducted within the last two decades. Indeed, the development of organosilylene chemistry did not begin until the early 1960s when Skell and Goldstein reported the generation of the first organosilylene (3). Even then, it was not until the pioneering work of Gilman and coworkers (4,5) and Atwell and Weyenberg (6,7) that the development of silylene chemistry began in earnest. Throughout the last twenty years, silylene chemistry has been extensively investigated, and continues today unabated.

In some aspects, the chemistry of silyl radicals is similar to that of silylenes. Thus, less than fifty years ago the first silyl radicals were discovered. Although interest in the chemistry of silyl radicals has paralleled that of silylenes, the lack of convenient methods for the clean production of silicon based radicals has retarded advancements in this field of silicon chemistry. Despite this shortcoming, the last two decades have witnessed a substantial increase in our understanding of silyl radicals.

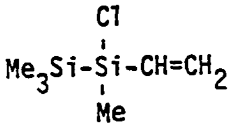
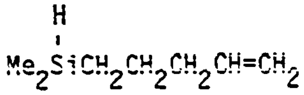
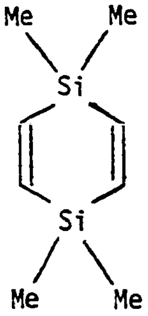
This thesis will present the results of four primary investigations: a) the attempted utilization of silylenes as synthons for silaoxetanes; b) the preparation and chemistry of selected silylenes which contained substituents and were generated under conditions such that intramolecular rearrangements would be favored; c) the thermal- and photochemistry of 7-

silanorbornadienes; and d) the preparation and chemistry of alkenyl-substituted silyl radicals. In addition to these main areas of investigation, the results obtained from a study of the addition of dimethylsilylene to cyclooctatetraene and a brief study of the addition of $Cl_3C\cdot$ to diallyldimethylsilane will be described.

NOMENCLATURE

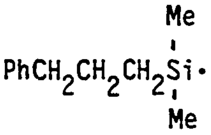
The nomenclature used in this thesis will, with the exceptions described below, follow the conventions set down by IUPAC. Simple organosilicon compounds will be named as derivatives of silane (SiH_4) while more complicated linear and cyclic systems will be named as sila-analogs of the corresponding carbon systems. Divalent silicon species will be named as derivatives of the parent silylene ($:SiH_2$).

Examples:

Me_2SiClH	dimethylchlorosilane
 $Me_3Si-\overset{Cl}{\underset{Me}{Si}}-CH=CH_2$	1-chloro-1-vinyltetramethyldisilane
 $Me_2\overset{H}{Si}CH_2CH_2CH_2CH=CH_2$	2-methyl-2-sila-6-heptene
	1,1,4,4-tetramethyl-1,4-disilin

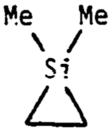
Silicon centered radicals will be named as derivatives of the parent silyl radical ($H_3Si\cdot$).

Examples:

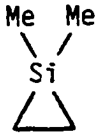
$Me_3Si\cdot$	trimethylsilyl radical
 $Me_3SiSiMe_2\cdot$	(trimethylsilyl)dimethylsilyl radical
 $PhCH_2CH_2CH_2SiMe_2\cdot$	(3-phenylpropyl)dimethylsilyl radical

Three membered rings containing a silicon and two carbon atoms will be named as derivatives of silarane or silacyclopropane and silarene or silacyclopropene. Silacyclopentadienes will be named as derivatives of silole.

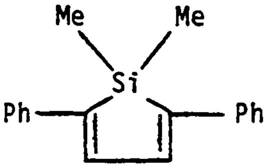
Examples:



1,1-dimethylsilarane
or 1,1-dimethylsilacyclopropane



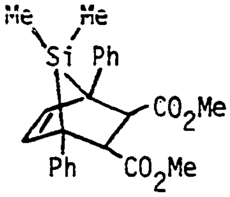
1,1-dimethylsilarene
or 1,1-dimethylsilacyclopropene



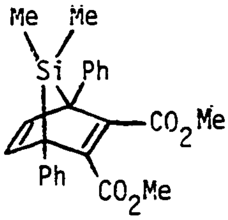
1,1-dimethyl-2,5-diphenylsilole

Finally, the [2,2,1] bicycloheptene and heptadiene ring systems, containing a silicon at the seven position, will be named as derivatives of 7-silanorbornene and 7-silanorbornadiene.

Examples:



1,4-diphenyl-2,3-dicarbomethoxy-
7,7-dimethyl-7-silanorborna-5-ene



1,4-diphenyl-2,3-dicarbomethoxy-
7,7-dimethyl-7-silanorbornadiene

HISTORICAL

Silylenes have been extensively reviewed (8-14). Thus, to prevent duplication, a complete survey of the chemistry of silylenes will not be presented. Instead, the review of the known chemistry of silylenes will concentrate on those aspects, particularly the advances made within the last two decades, that have contributed the most to our understanding of silylenes. The chemistry of difluorosilylene, which in many ways is different from the chemistry of all other silylenes, will not be presented since it has been adequately reviewed elsewhere (8-14).

Silyl radicals have also been the subject of several reviews (15-18). However, a number of significant advances have occurred in this field of silicon chemistry since the last review; thus, a more extensive survey of the known chemistry of silyl radicals will be presented.

Silylenes

The preparation and spectral observation of the first silylene, dichlorosilylene, was reported over 40 years ago (1,2). Although this discovery was contemporary to the beginnings of carbene chemistry, the development of silylene chemistry has lagged behind that of carbenes. This was due in part to a dearth of convenient methods of silylene generation prior to 1962. Indeed, the existence of the first organosilylene, dimethylsilylene, was confirmed less than two decades ago.

The electronic configuration and molecular geometry of inorganic silylenes, the dihydrides and mono- and dihalides, have been the subject of numerous studies, both theoretical and experimental. Nefedov has conveniently tabulated these data (11). The mono- and dihalides are known to have a singlet ground state electronic configuration and a bent molecular geometry (bond angle ≅ 101°).

The ground state of silylene (H_2Si:) has been experimentally determined by fixed-frequency laser photoelectron spectrometry to be a singlet; about 14 kcal/mole lower than the triplet (19). The bond angle of ground state silylene has been determined by double-flash ultraviolet spectroscopy to be 92.08° with bond lengths of 1.516 Å (20). These values are in good agreement with other theoretical and experimental results (11,21,22).

Only recently have theoreticians begun to grapple with the problem of organosilylenes. Gordon has utilized a STO-4G SCF calculation to study both the singlet and triplet states of the three isomers of $SiCH_4$; methylsilylene ($CH_3\ddot{S}iH$), silaethylene ($H_2Si{=}CH_2$), and silylmethylene ($H_3Si\ddot{C}H$) (23). The results of this study are given in Table 1.

Table 1. Relative energies calculated for methylsilylene, silaethylene and silylmethylene (kcal/mole)

		Without d-orbitals			With d-orbitals		
		no CI	2 CI	37 CI	no CI	2 CI	37 CI
$H\ddot{S}i{-}CH_3$	singlet	0	0	0	0		
	triplet	21.78	25.46		24.11	28.46	
$H_2Si{=}CH_2$	singlet	23.16	2.26	12.48	9.18	1.72	6.80
	triplet	24.00	27.68		14.36	18.71	
$H_3Si{-}\ddot{C}H$	singlet	66.98	64.64	70.06	50.28	49.60	54.63
	triplet	21.68	25.36		4.88	9.23	

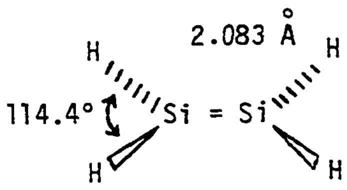
Of the three isomers, methylsilylene was predicted to be the most stable singlet ($\sphericalangle$ HSiC=92.9°, R_{SiC}=1.89 Å, R_{SiH}=1.46 Å), and to be about 22 kcal/mole lower than the triplet. The most stable triplet isomer was calculated to be silylmethylene. Thus, singlet methylsilylene and triplet silylmethylene would not be expected to isomerize to silaethylene. However, the isomerization of singlet silylmethylene to silaethylene is predicted to be thermodynamically favorable, and has been observed experimentally for substituted silylcarbenes (24,25,26,27).

Gosavi and coworkers, utilizing ab initio SCF-MO calculations, have studied the reaction surface for the lowest triplet state interconversions of $CH_3\ddot{S}iH$, $H_2Si{=}CH_2$, and $H_3Si\ddot{C}H$ (28). Methylsilylene and silylmethylene were calculated to be, respectively, 0.8 and 4.6 kcal/mole more stable than silaethylene. The energies of activation for the isomerization of triplet $CH_3\ddot{S}iH$ and $H_3Si\ddot{C}H$ to triplet $H_2Si{=}CH_2$ were calculated to be 83.0 and 92.5 kcal/mole, respectively.

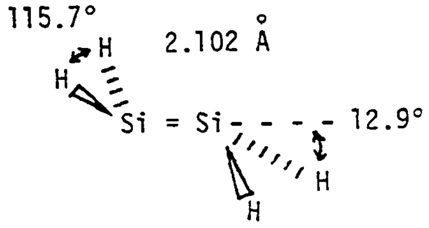
Recently, Goddard et al. have calculated the energy profile for the lowest singlet state interconversions of the three isomers of $SiCH_4$, thereby completing the theoretical picture for these isomers (29). Using double-zeta SCF-MO theory with configuration interaction, these authors predicted methylsilylene to be a ground state singlet; 19 kcal/mole below the lowest triplet and 11.6 kcal/mole below singlet silaethylene. Inclusion of d-orbital functions in the basis sets of carbon and silicon lowered this latter energy separation to 0.4 kcal/mole. Silylmethylene was calculated to be a ground state triplet; 25 kcal/mole lower than the singlet. The 1,2 hydrogen shift of singlet $H_3Si\ddot{C}H$ to $H_2Si{=}CH_2$ was found to be exothermic by

69 kcal/mole with an activation energy of less than 3 kcal/mole. For the interconversion of $H_3C\ddot{Si}H$ and $H_2Si{=}CH_2$ an activation energy of approximately 40 kcal/mole was calculated.

Snyder and Wasserman, utilizing ab initio SCF-MO calculations with a STO 4-31 G basis set, have recently reported the results of their study of the ground state structure for Si_2H_4 (30). With assumed D_{2h} point group symmetry, planar disilene (**1**) was calculated to have a Si-Si double bond length of 2.083 Å; 0.27 Å shorter than the computed Si-Si bond length of disilane. When the constraint of planarity was removed, **1** relaxed to a



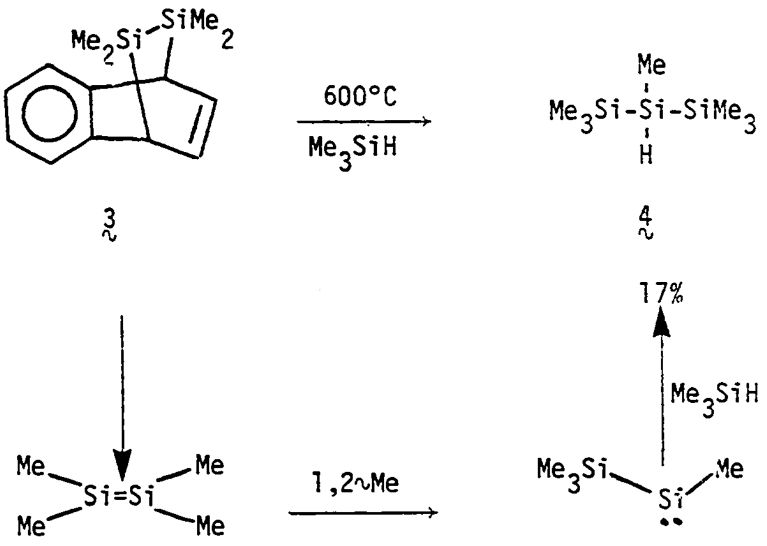
1



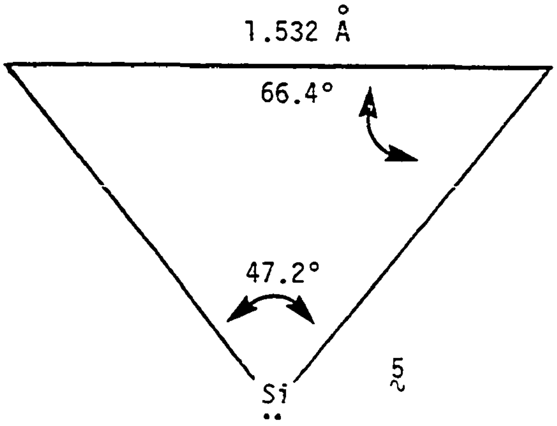
2

trans-bent form, point group S_2, with the SiH_2 groups at each end bent up and down by an angle of 12.9°. The trans-bent form of disilene (**2**) was computed to be 0.5 kcal/mole more stable than **1**. The most stable isomer of Si_2H_4 was calculated to be singlet silylsilylene; 2.5 kcal/mole lower than triplet silylsilylene and 8.6 kcal/mole lower than planar disilene (**1**). Thus, these results predict that disilene should isomerize to singlet silylsilylene, if the energy of activation for this process is not prohibitively high.

Wulff and coworkers have provided experimental support for this prediction (31). They found that copyrolysis of disilene generator **3** with excess trimethylsilane afforded 4, the expected trapping product of trimethysilylmethylsilylene.



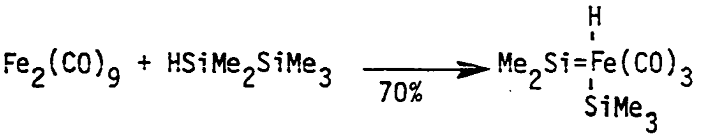
The final theoretical study of organosilylenes, that has been reported to date, is the work of Barthelot, Trinquier, and Bertrand (32). Using a double-zeta SCF-MO method, silacyclopropylidene 5 was computed to be a ground state singlet; 34.6 kcal/mole lower than the first triplet.



5

Two important conclusions regarding the properties of silylenes can be made on the basis of the physical and theoretical studies reported thus far. First, all silylenes reported are ground state singlets. Second, silylenes are more stable than their carbon analogues.

Although silylenes are more stable than carbenes, no molecule incorporating a divalent silicon atom has yet been isolated. However, Sakurai and coworkers have reported the preparation of 6, the first example of a silylene transition metal complex (33).



$$Fe_2(CO)_9 + HSiMe_2SiMe_3 \xrightarrow[70\%]{} Me_2Si{=}\overset{H}{\underset{SiMe_3}{Fe}}(CO)_3$$

6

Thermal Methods of Silylene Generation

Prior to 1962, the established methods for silylene formation were very harsh and limited to the preparation of only the inorganic silylenes. Among these processes, the reduction of tetrahalogenosilanes by silicon has been known for some time (10). The reduction of trichloro and tetrachlorosilane by hydrogen has also been found to produce silylene intermediates (8,9,10).

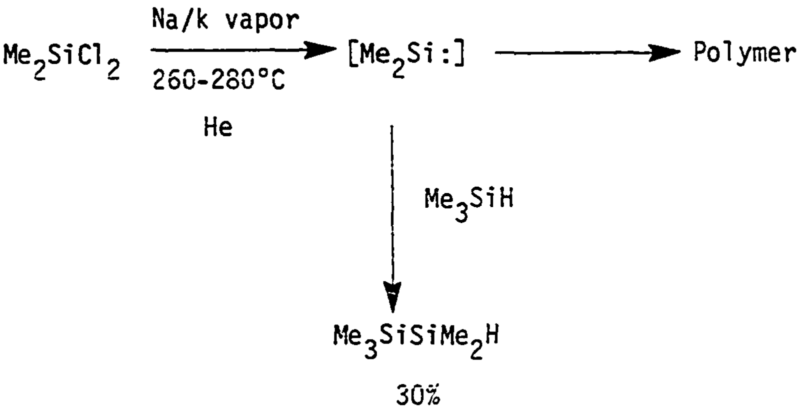
$$SiX_4\ (gas) + Si\ (solid) \xrightleftharpoons{1000\text{-}1300^\circ C} 2{:}SiX_2\ (gas)$$

X = F, Cl, Br, or I

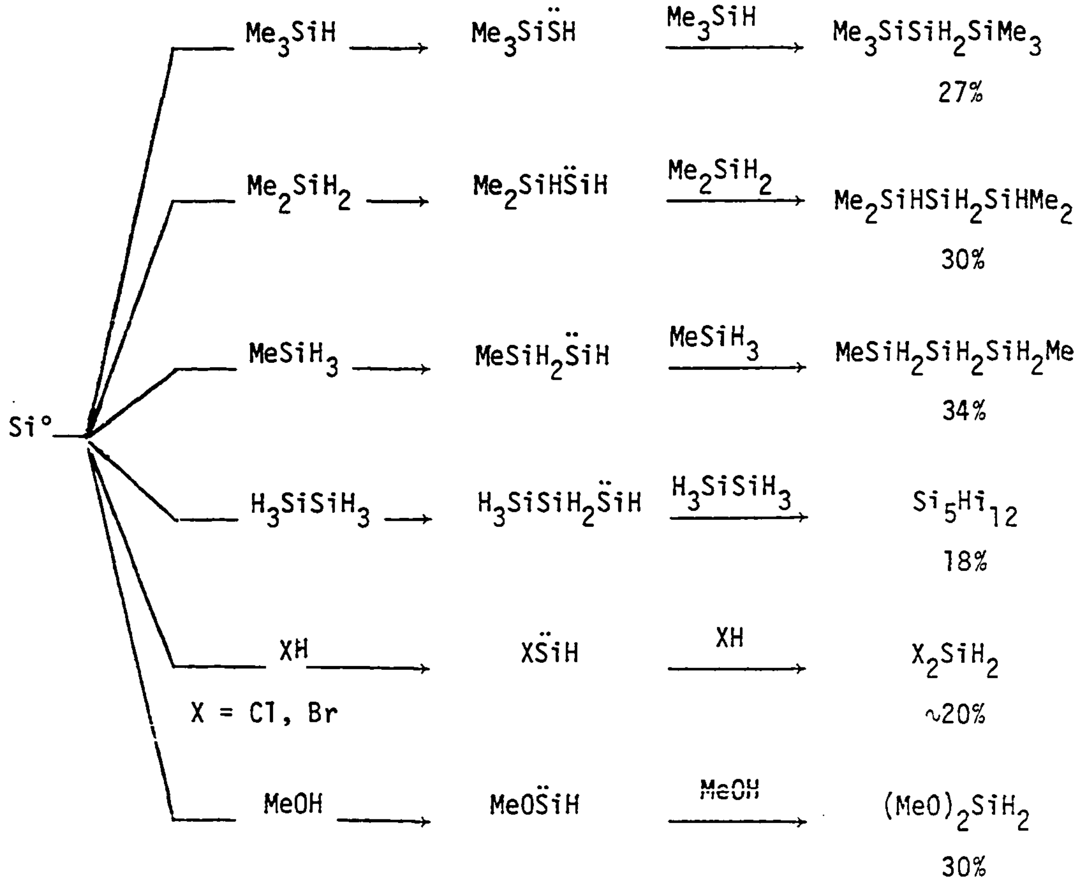
$$SiCl_4 + H_2 \xrightarrow{\sim 1000^\circ C} :SiCl_2 + 2HCl$$

By analogy with the reactions of dihalomethanes and lithium, in which carbenes are formed, dialkylsilylenes were assumed to be intermediates in the reactions of dialkyldichlorosilanes and lithium in benzene or tetrahydrofuran at temperatures of about 200°C (8). However, subsequent work has clearly demonstrated that dialkylsilylenes are not generated under these conditions (9).

In contrast, reduction of dichlorosilanes by lithium in the gas phase does lead to the production of silylenes (3). Skell and Goldstein found that reaction of dimethyldichlorosilane with Na/K vapor at 260-280°C afforded dimethylsilylene ($:SiMe_2$), thereby providing the first example of an organosilylene. Confirmation of the intermediacy of $Me_2Si:$ was provided by trapping with trimethylsilane to afford pentamethyldisilane. The lack of geminate coupling products, when trimethylsilane was present, led these authors to conclude that $Me_2Si:$ was in a singlet electronic state.



Skell and Owen have found that cocondensation of atomic silicon vapor and various silanes, methanol, and acid halides produces silylene intermediates (34,35,36). The products obtained from these reactions were suggested to arise by initial insertion of atomic silicon into the Si-H, X-H (X=Cl,Br) or O-H bond to give the corresponding silylene, which subsequently inserts into another molecule of substrate to produce the observed products.



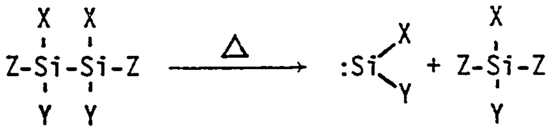
Gaspar and coworkers have reported that recoiling silicon atoms, produced by neutron bombardment of $^{31}PH_3$ react with silane to afford di- and trisilanes (37,38). It was suggested that these products arise from silylene intermediates formed by primary abstraction or insertion-dissociation processes (39).

$$^{31}PH_3 \xrightarrow{\text{neutron}} {}^{31}Si$$

$$^{31}Si + SiH_4 \longrightarrow \underset{48\%}{H_3{}^{31}SiSiH_3} + \underset{7\%}{H_3{}^{31}SiSiH_2SiH_3}$$

However, doubt was cast on the intermediacy of silylenes in these reactions when it was observed that the products which arise from the reaction of recoiling silicon atoms with butadiene, even in the presence of silane, differ from the products of thermally generated $:SiH_2$ with the same substrate (40).

The most general thermal method of silylene generation is the pyrolysis of substituted disilanes.

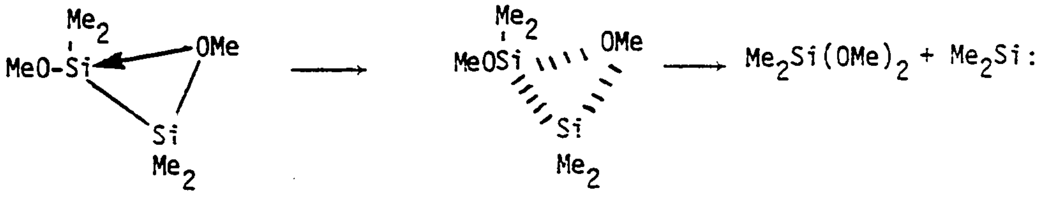


$$Z\text{-}\underset{Y}{\overset{X}{Si}}\text{-}\underset{Y}{\overset{X}{Si}}\text{-}Z \xrightarrow{\Delta} :Si{<}^{X}_{Y} + Z\text{-}\underset{Y}{\overset{X}{Si}}\text{-}Z$$

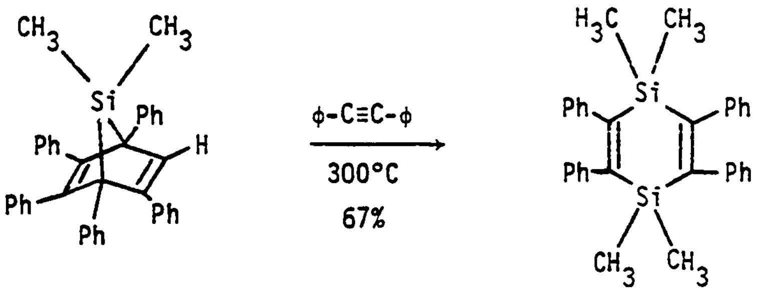
The migrating group Z can be hydrogen, halogen, or alkoxy while X and Y can be hydrogen, halogen, alkoxy, alkyl, aryl, or silyl. Although this reaction was first discovered in 1880 by Friedel and Ladenburg (41), it was not until 1962 that it was suggested to proceed by the formation of silylenes (42).

A careful study by Jenkins and coworkers established the intermediacy of silylenes in the pyrolysis of disilanes when the migrating group was hydrogen or halogen (43). In this study, it was found that the relative rate of a 1,2-hydrogen shift compared to a 1,2-chlorine shift for MeSiHClSiMeHCl was 4.4, while only 1,2-hydrogen shifts were observed for $F_2SiHSiH_3$ and $Cl_2SiHSiH_3$. In general, 1,2 chlorine shifts require temperatures of approximately 600°C with a contact time of 10 to 20 seconds in the hot zone under gas-phase conditions. Hydrogen migrations required temperatures of about 500°C under the same conditions.

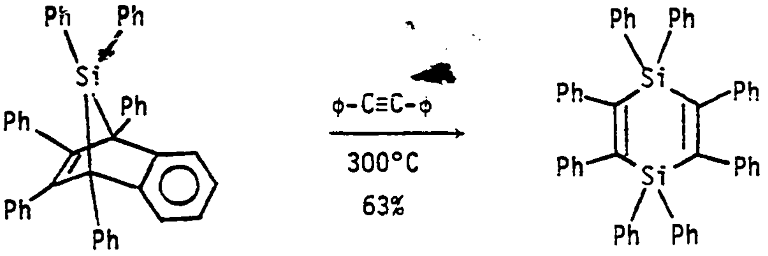
Atwell and Weyenberg have extended this methodology to alkoxy substituted disilanes and found temperatures of 325 to 350°C were necessary for silylene extrusion from 1,2-dimethoxytetramethyldisilane and 1-methoxypentamethyldisilane (6,7,44). Increasing the number of alkoxy groups attached to the disilane decreases the thermal requirements for silylene extrusion (44). Kinetic studies established a first order dependence for disilane with a rate constant of 4.7 X 10^{-5} sec^{-1} for the decomposition of 1,2-dimethoxytetramethyldisilane at 225°C (45). On the basis of these results, the decomposition of alkoxydisilanes, and by analogy the halogenodisilanes, were proposed to proceed by an α-elimination process.



Pyrolysis of 7-silanobornadienes provides still another method of silylene production. Gilman et al. reported that copyrolysis of **7** and **8** with diplenylacetylene afforded disilins **9** and **10**, the expected products of silylene trapping (4,5).

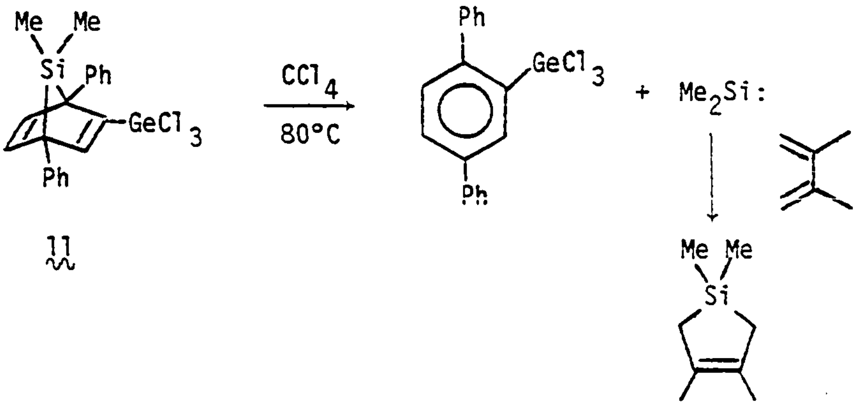


7 9



8 10

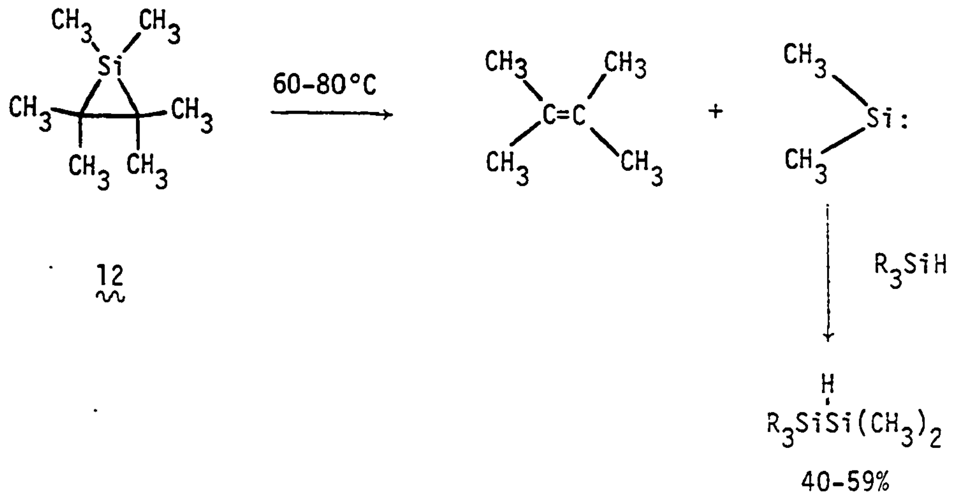
Laporterie obtained the trapping product of Me$_2$Si: and 2,3-dimethylbutadiene when 7-silanorbornadiene 11 was heated to 80°C (46). Surprisingly, this latter method has not been utilized as a general dimethylsilylene generator.



11

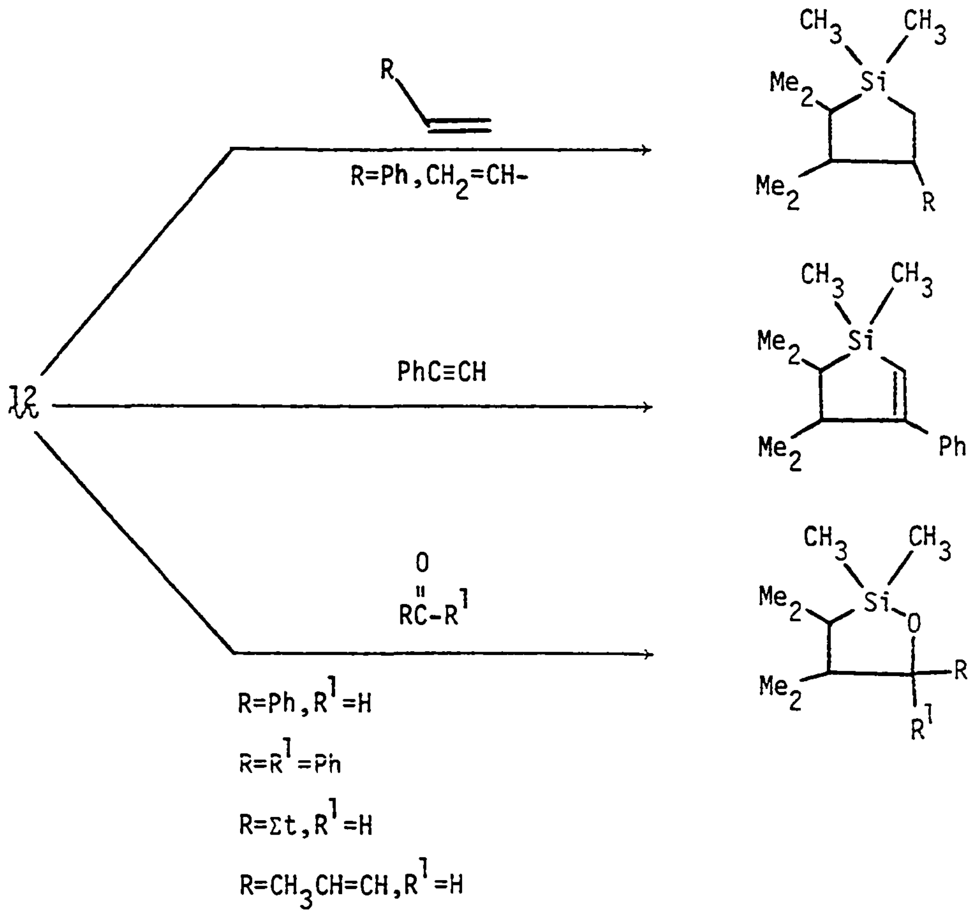
It has been suggested by Barton that 7-silanorbornadienes may decompose via a stepwise radical process (47). Recently, Mayer and Neuman (48) have provided evidence which they claim substantiates Barton's suggestion. However, as will be demonstrated in this thesis, most, if not all, of the results reported by Mayer and Neuman have been found to be incorrect. Nevertheless, the use of 7-silanorbornadienes as silylene sources must be regarded with skepticism until a more complete study of this method is reported.

The least severe method of silylene generation is the thermolysis of hexamethylsilarane (12) which was found by Seyferth and Annarelli to liberate dimethylsilylene at temperatures of 60-80°C. (49,50).

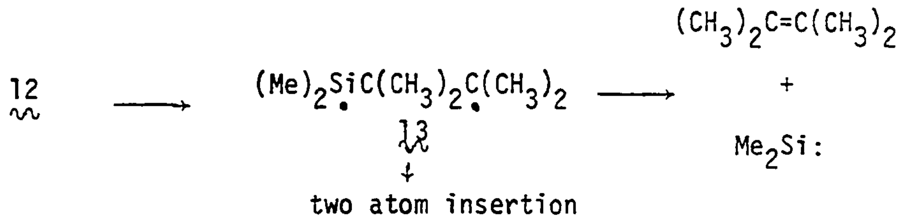


12

Although 12 is an excellent source of Me$_2$Si:, its use is not without complications. Hexamethylsilarane is itself a good trap for silylenes, and thus, competes with added traps for Me$_2$Si: (49,51). Furthermore, when 12 is allowed to react in the presence of conjugated olefins or acetylenes, or with normal α,β-unsaturated aldehydes or ketones, a novel two atom insertion reaction is observed, affording 5-membered rings (52,53).

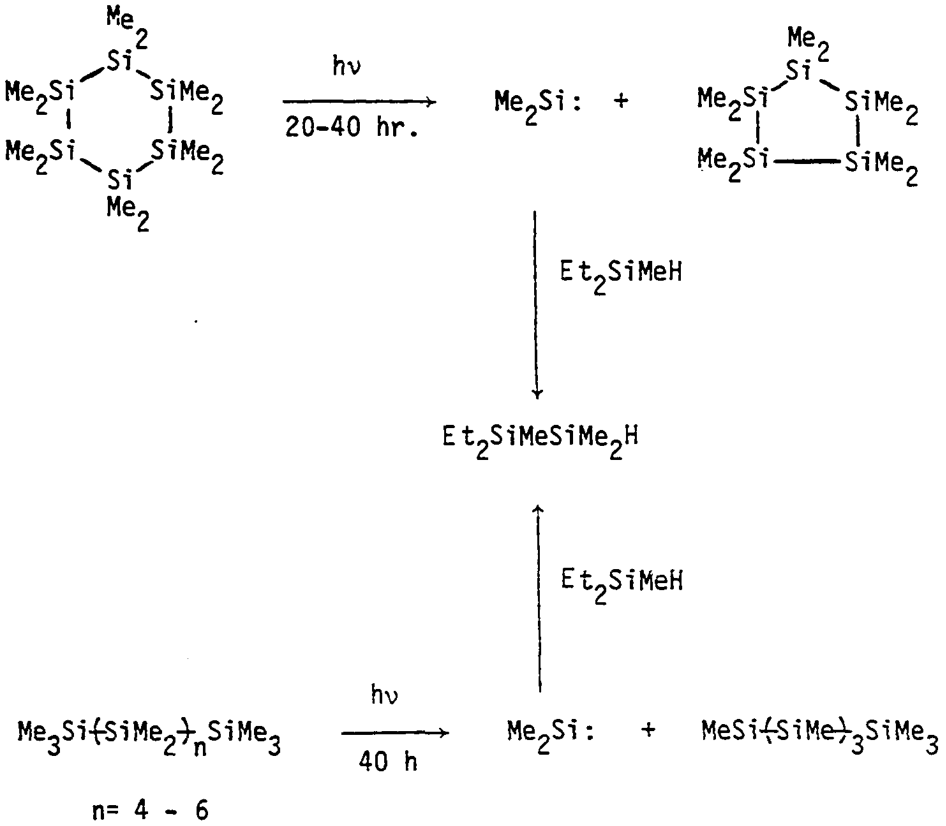


On the basis of the two atom insertion reactions, Seyferth has suggested that thermal decomposition of 12 may proceed via diradical 13.

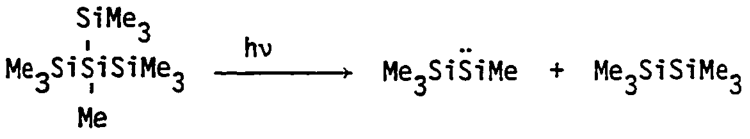


Photochemical Methods of Silylene Generation

The first example of a photochemically generated silylene appeared in 1970 when Ishikawa and Kumada reported that the photolysis of dodecamethylcyclohexasilane (14) led to ring contraction with the concomitant extrusion of dimethylsilylene (54,55). In an analogous manner (chain contraction accompanied by silylene extrusion), permethylated, linear polysilanes have been shown to produce silylenes photochemically (56,57).

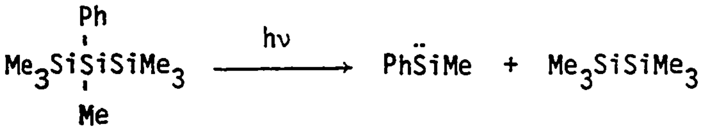


In contrast to higher homologues, irradiation of octamethyltrisilane gives Me_2Si: in about 20% only after prolonged irradiation (> 60 hours). However, photolysis of trisilanes 15 and 16 do serve as convenient sources of trimethylsilylmethylsilylene and phenylmethylsilylene, respectively (58,59). The use of **15**, **16**, and the permethylated cyclic and linear polysilanes, which are the most commonly employed substrates for photochemical silylene generation, has recently been reviewed (60,61).



$$Me_3Si\overset{SiMe_3}{\underset{Me}{Si}}SiMe_3 \xrightarrow{h\nu} Me_3Si\ddot{Si}Me + Me_3SiSiMe_3$$

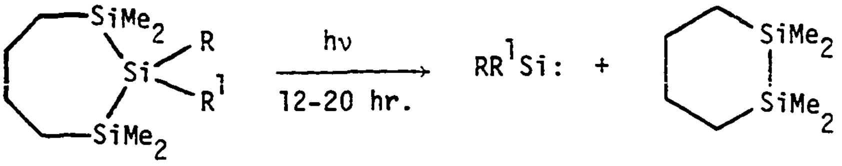
15



$$Me_3Si\overset{Ph}{\underset{Me}{Si}}SiMe_3 \xrightarrow{h\nu} Ph\ddot{Si}Me + Me_3SiSiMe_3$$

16

Tri- and tetrasilacycloalkanes are also known to decompose upon irradiation to give silylenes (62). Sakurai et al. have used this technique to develop a tailor-made organosilylene generator based on the photolysis of 1,2,3-trisilacycloheptane derivatives (63).

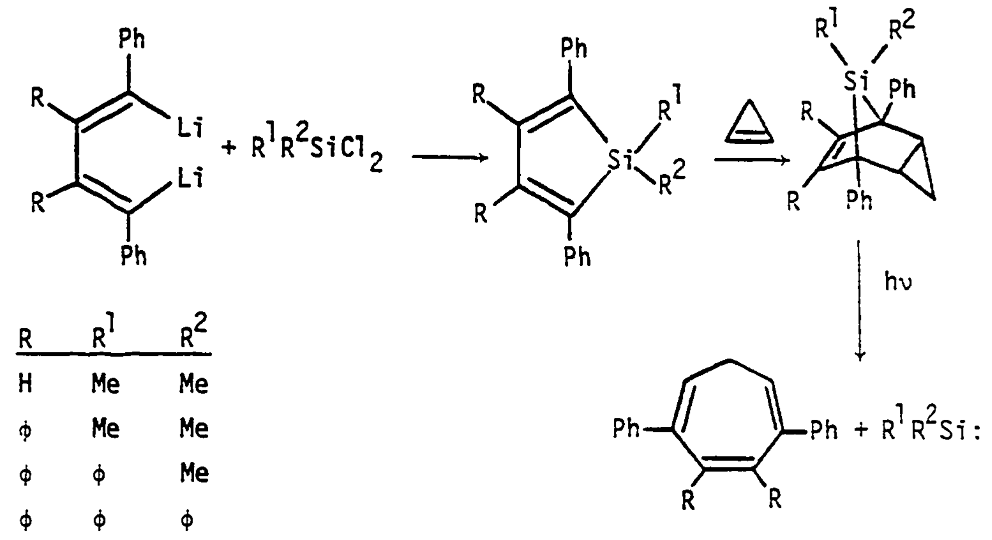


$R = Me, R^1 = \textit{i}\text{-}Pr$

$R = R^1 = -CH_2CH_2CH_2CH_2-$

$R = R^1 = Me$

More recently, Sakurai and coworkers have reported a new class of silylene generators based on the photolysis of 8-silatricyclo[3.2.1.$0^{2,4}$] octa-6-enes (64). This technique represents a three-step conversion of a dichlorosilane to a silylene, and therefore, provides a convenient method for the generation of a large number of unsymmetrically substituted organosilylenes.



R	R^1	R^2
H	Me	Me
ϕ	Me	Me
ϕ	ϕ	Me
ϕ	ϕ	ϕ

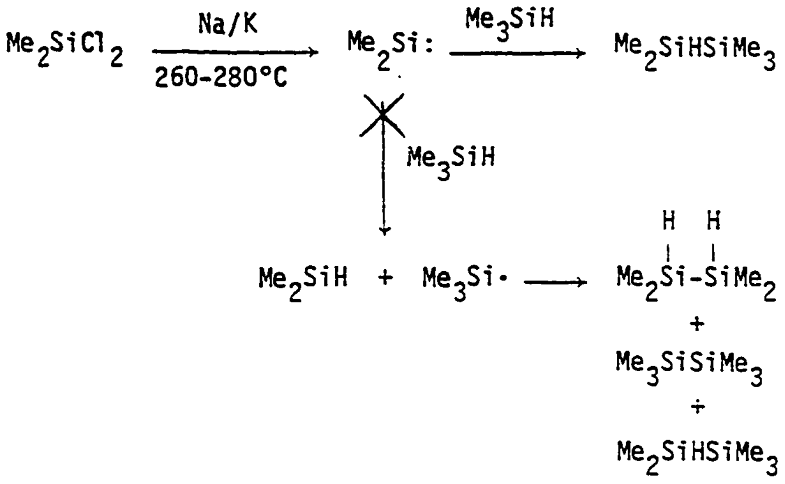
Insertion Reactions of Silylenes

A wide variety of reactions which involve insertion of silylenes into sigma bonds are known. Thus, silylenes insert into Si-Y bonds where Y=H, Cl, Br, O and Si to produce the corresponding disilanes. Insertion into Z-H bonds where Z=O or N yields silanols and silylamines.

The most extensively investigated insertion reaction of silylenes is that into Si-H bonds. With the exception of $:SiX_2$ (X=Cl or F) (43) and $:Si(OMe)_2$ (13), all silylenes prepared thus far are known to insert into Si-H bonds. This reaction is often used as a diagnostic test when the question of silylene intermediacy is at issue.

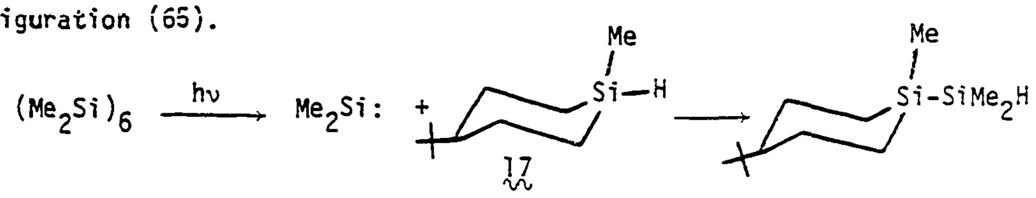
That insertion occurs, rather than hydrogen abstraction followed by radical recombination, is indicated by the absence of geminate coupling products, which would be expected for the latter process. Evidence supporting direct silylene insertion has also been obtained from numerous kinetic studies (13).

Skell and Goldstein used the occurrence of direct insertion as evidence that it is the singlet state of dimethylsilylene that takes part in these reactions (3).



$$\begin{tikzcd}
Me_2SiCl_2 \arrow[r, "Na/K", "260\text{-}280^\circ C"'] & Me_2Si: \arrow[r, "Me_3SiH"] \arrow[d, "Me_3SiH", "\times"'] & Me_2SiHSiMe_3 \\
 & Me_2SiH + Me_3Si\cdot \arrow[r] & \begin{array}{c} \overset{H}{Me_2Si}\text{-}\overset{H}{SiMe_2} \\ + \\ Me_3SiSiMe_3 \\ + \\ Me_2SiHSiMe_3 \end{array}
\end{tikzcd}$$

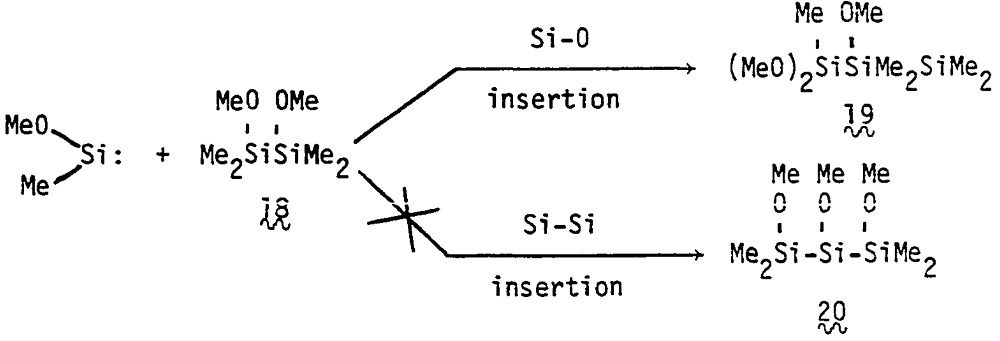
Further evidence for direct insertion by singlet silylene has been reported by Sakurai and Murakami who found that Me_2Si: inserted into the Si-H bond of configurationally stable silacyclohexane **17** with retention of configuration (65).



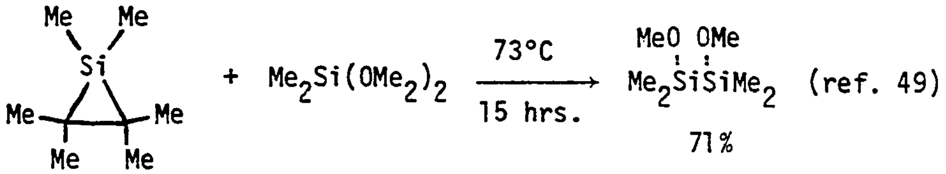
Kinetic studies of the insertion of thermally generated silylene (H_2Si:) have shown that substitution of methyl groups for the hydrogens of silane enhances the reactivity of the remaining Si-H bonds toward insertion (13). These studies also displayed non-zero energies of activation for the insertion of thermally generated H_2Si: into various Si-H bonds, although, no general agreement exists as to the exact values.

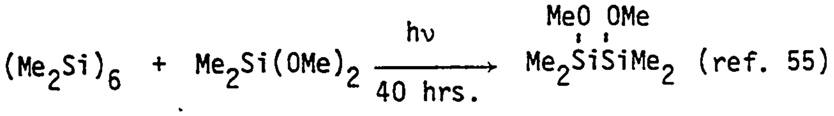
Recently, Davidson and Ostah have determined the kinetics of insertion of photochemically generated dimethylsilylene into the Si-H bonds of trimethylsilane, pentamethyldisilane, and sym-tetramethyldisilane (66). The activation energy for insertion was found to be zero for all cases in the temperature range of 140-240°C. The rate constants for insertion into Me_3SiH, $Me_3SiSiMe_2H$, and $Me_2SiHSiMe_2H$ were in the ratio of 1:3.1:4.3.

It was first suggested in 1966 that silylenes insert into the silicon-oxygen bond of alkoxy silanes (6). This suggestion was subsequently confirmed when Atwell and coworkers observed that methylmethoxysilylene inserted into disilane **18** to afford trisilane **19** (45). The finding that trisilane **19** was obtained and not **20** demonstrated that insertion occurred into a Si-O bond not a Si-Si bond.



Atwell and Weyenberg have reported that insertion of dimethylsilylene into trimethylmethoxysilane or dimethyldimethoxysilane is not competitive with related insertions into methoxypolysilanes (7). In contrast, dimethylsilylene, generated thermally from hexamethylsilarane (49), or photochemically from dodecamethylcyclohexasilane (55), inserts readily into dimethyldimethoxysilane. This discrepancy is most reasonably due to the presence of additional trapping reagents in the study by Atwell and Weyenberg rather than the inherent inability of Me_2Si: to insert into the Si-O bond of alkoxymonosilanes.

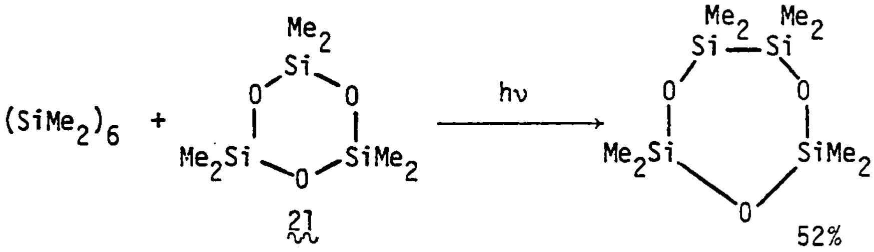




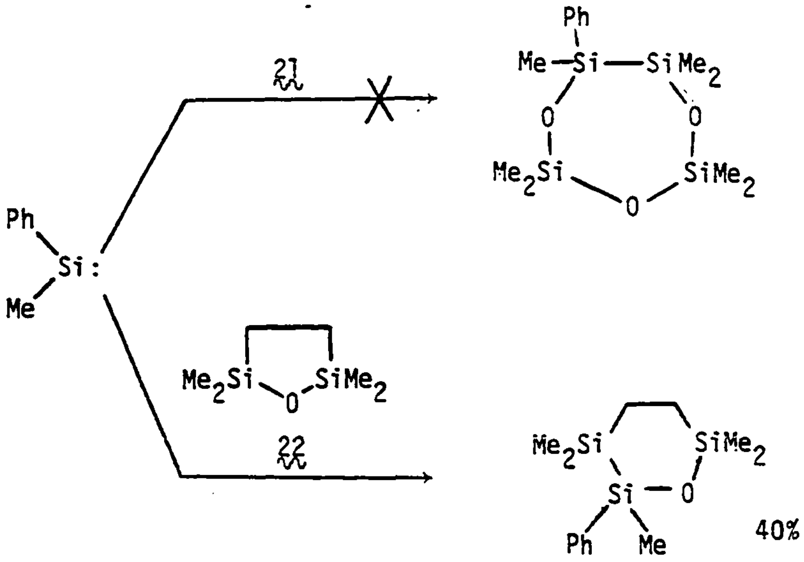
$$(Me_2Si)_6 + Me_2Si(OMe)_2 \xrightarrow[40\ hrs.]{h\nu} \overset{MeO\ \ OMe}{Me_2SiSiMe_2}$$ (ref. 55)

Gu and Weber have recently obtained experimental support for this conclusion when they demonstrated that the Si-O bonds of alkoxypolysilanes were more reactive toward silylene insertion than those of alkoxymonosilanes (67).

Soysa and coworkers have reported the insertion of Me_2Si: into hexamethylcyclotrisiloxane (**21**), thus providing the first example of a silylene insertion into the S-O bond of a polysiloxane (68).



Subsequent work by Okinoshima and Weber showed that 22 is a far better trap than 21 since phenylmethylsilylene is trapped by 22 but not by 21 (69).



Insertion of thermally generated silylenes into silicon-halogen sigma occurs in the same manner as that for silicon-oxygen bonds, and has recently been reviewed (10). The reactions of photochemically generated silylenes differ, however. When $(Me_2Si)_6$ was photolyzed in the presence of excess Me_2SiCl_2, the expected product of dimethylsilylene isertion, 23, was formed in only minor amounts (55). Instead, trisilane 24 and tetrasilane 25 were found to be the major products.

$$(Me_2Si)_6 \xrightarrow[Me_2SiCl_2]{h\nu} \underset{23}{Cl(SiMe_2)_2Cl} + \underset{25}{Cl(SiMe_2)_3Cl} + \underset{25}{Cl(Me_2Si)_4H}$$

Similar results were observed when polysilane 26 was irradiated in the presence of excess dimethyldichlorosilane.

$$\underset{26}{Me(Me_2Si)_6Me} \xrightarrow[Me_2SiCl_2]{h\nu} \underset{27}{Me_3SiSiMe_3} + \underset{24}{Cl(SiMe_2)_2Cl}$$

$$+ \underset{25}{Cl(SiMe_2)_3Cl} + \underset{28}{Me(Me_2Si)_2Cl}$$

$$\underset{29}{Me(Me_2Si)_3Cl}$$

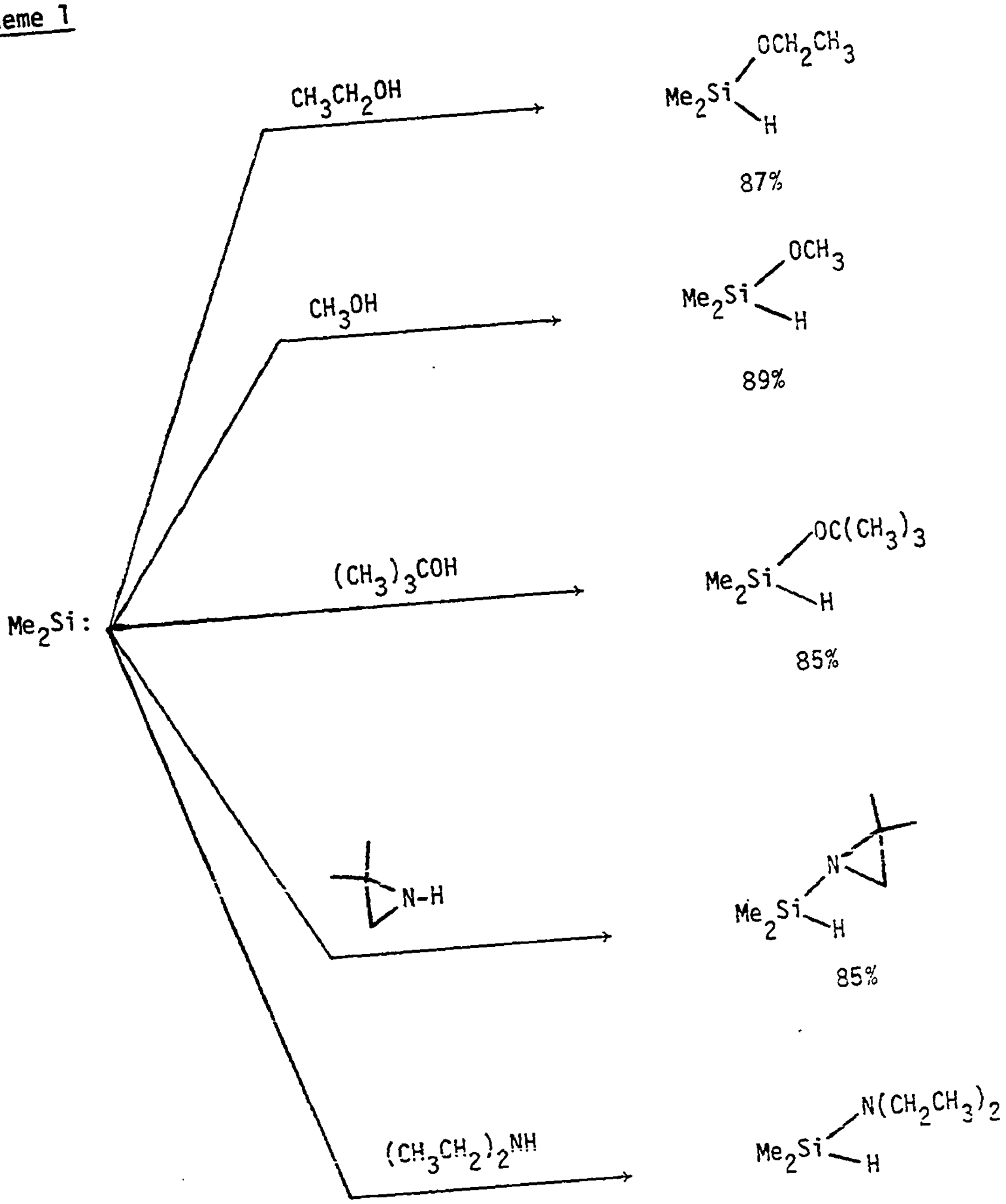
For the latter reaction, octamethyltrisilane and 24 were the expected major products. The absence of octamethyltrisilane, coupled with the presence of 27, 28, and 29, led Ishikawa and Kumada to suggest that Me_2SiCl_2 was reacting with photo-excited 26 (or $(Me_2Si)_6$ for the former reaction), and that dimethylsilylene extrusion was a minor process for these reactions (55).

More recently, Davidson and Ostah have proposed that photolysis of polysilanes in the presence of chlorosilanes leads to products via radical processes (66).

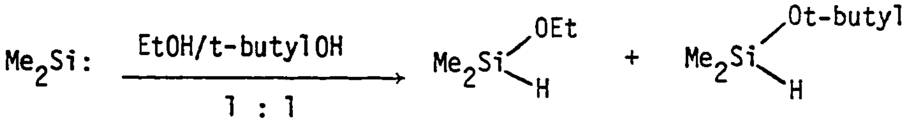
The reaction of silylenes with Z-H bonds (Z=oxygen or nitrogen) has been less extensively investigated than those involving Si-H and Si-O bonds. Atwell and Weyenberg reported the first example of silylene insertion into the O-H bond of an alcohol (7). More recently, Gu and Weber have found this reaction to be general for a variety of alcohols, as well as primary and secondary amines (70) (Scheme 1).

For the reaction with alcohols, a dramatic solvent effect has been reported (71). Steele and Weber have observed that the selectivity of dimethylsilylene for alcohols with the least substitution on the carbon

Scheme 1


Me2Si:
CH3CH2OH
CH3OH
(CH3)3COH
N-H
(CH3CH2)2NH
Me2Si(OCH2CH3)H
87%
Me2Si(OCH3)H
89%
Me2Si(OC(CH3)3)H
85%
Me2Si(N)H
85%
Me2Si(N(CH2CH3)2)H
81%

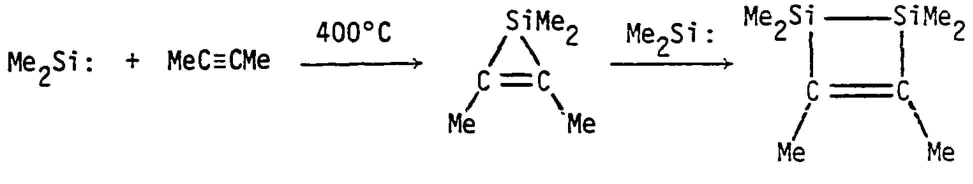
attached to oxygen increases as the solvent is changed from cyclohexane to diethylether to tetrahydrofuran. The increased selectivity in ether solvents has been rationalized to be due to coordination of the ether oxygen to the electrophilic silylene, thereby decreasing the reactivity of the silylene.



cyclohexane	1.8	:	1
diethylether	4.7	:	1
THF	9.6	:	1

To date, reports of silylene insertion into Si-C and Si-Si bonds are sparse, and limited to strained rings. Atwell and Uhlmann (72), in a study of the reaction of dimethylsilylene and 2-butyne, reported the isolation of 1,2-disilacyclobutene 30 (Scheme 2), that was proposed to arise by Me_2Si: insertion into tetramethylsilarene (31). That silylenes insert into the Si-C bond of stained silacycles was subsequently confirmed by Seyferth and Vick who reported insertion of Me_2Si: into 12 and 32 (51).

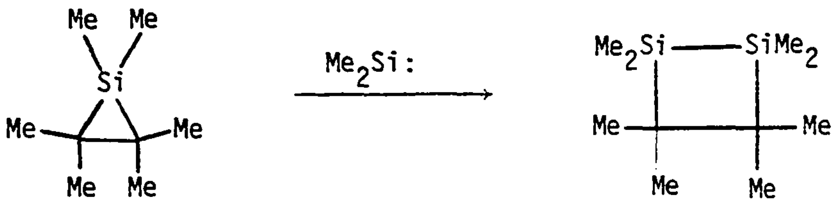
Scheme 2



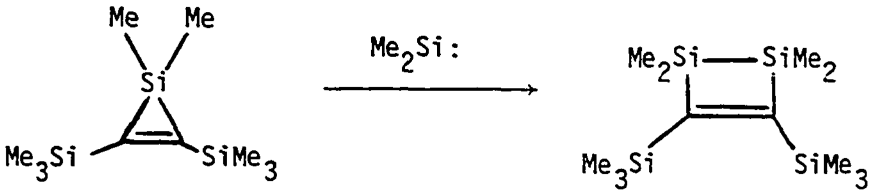
31

30

31%

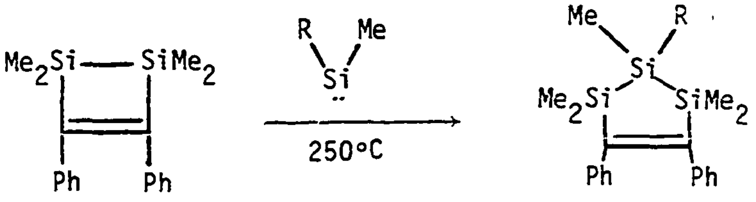


12



32

The report by Sakurai and coworkers that silylenes react with disilacyclobutene **33** to give trisilacyclopentenes **34a** and **b** constitutes the only examples of silylene insertion into a Si-Si bond (73).



33

34a, R=Ph

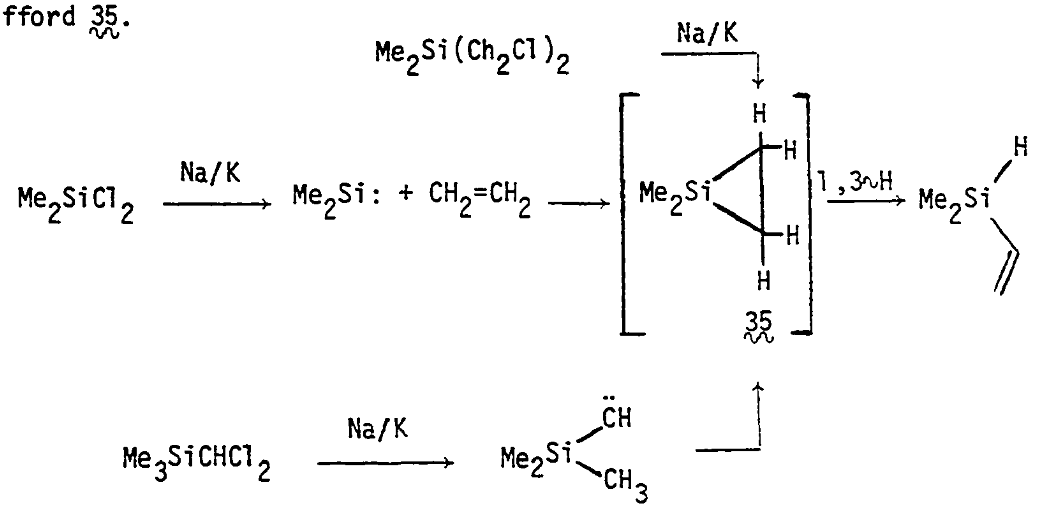
34b, R=Me

Other insertion reactions of silylenes have been discussed in a recent review (10). Among these are insertion into E-X (E=B, P, C and

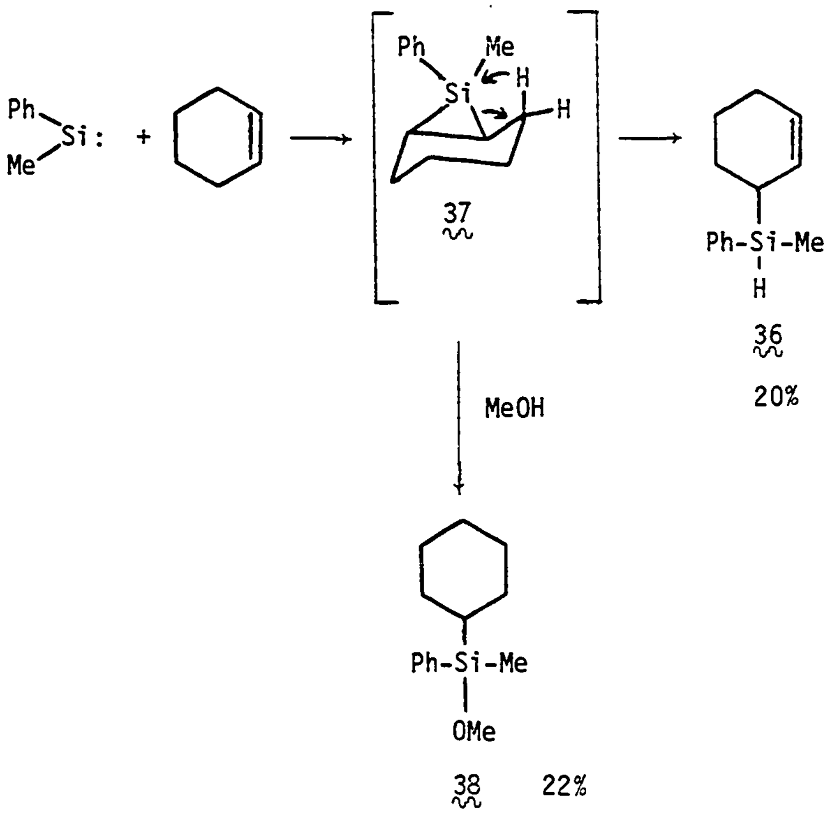
X=F, Cl), E-H (E=Ge, S, or halogen), and insertion into carbon-carbon bonds.

Addition of Silylenes to Olefins

The first demonstrable example of silylene addition to a carbon-carbon double bond (the sila analogue of the well-known carbene cyclopropanation reaction) was that of Skell and Goldstein for the reaction of dimethylsilylene and ethylene (74). Evidence for the intermediacy of silacyclopropane 35 was the formation of the same product (dimethylvinylsilane) from several other reaction systems which would reasonably be expected to afford 35.



The next report of any substance on this subject was that of Ishikawa and coworkers who found that photogenic phenylmethylsilylene reacted with cyclohexene to form mono-adduct 35 (75). Ishikawa suggested that 36 was formed from silarane 37 by a 1,3-hydrogen migration. That silylene addition to the double bond occurred to form 37 was shown by trapping of 37 with methanol to afford 38 (76). More recently, Ishikawa and coworkers have provided definitive evidence for the direct addition of silylenes to olefins by NMR observation of the resultant silacyclopropanes (77).

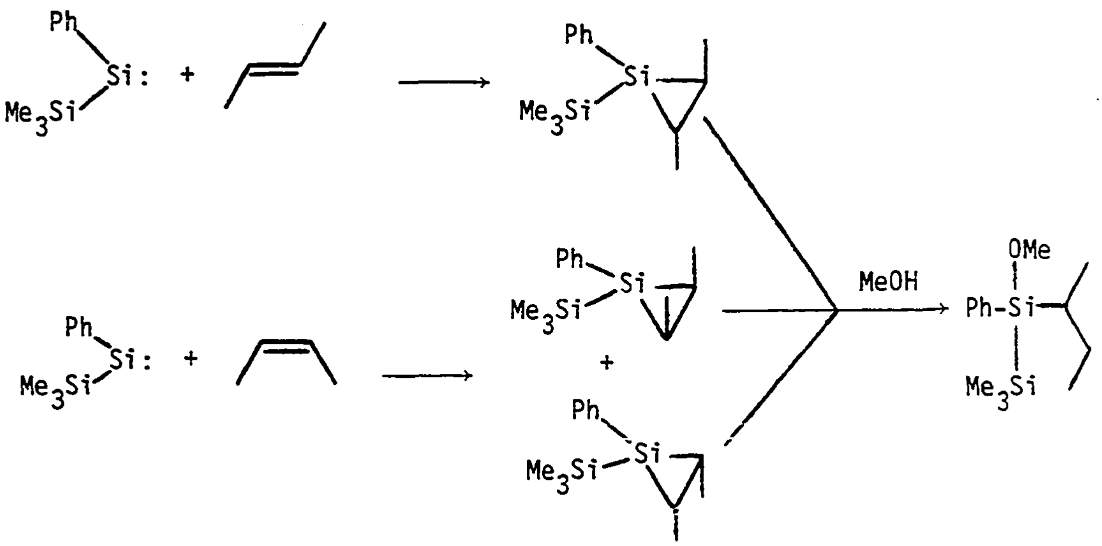


In a subsequent study, the addition of photogenic silylenes to carbon-carbon double bonds was shown to be general for a variety of acyclic and and cyclic olefins (Table 2) (78).

Seyferth and Annarelli (79) have reported that dimethylsilylene, generated thermally from hexamethylsilacyclopropane, adds readily to internal olefins to give high yields of the corresponding silacyclopropanes (Table 2), thus establishing the generality of this reaction for thermally generated silylenes.

A determination of the stereochemistry of the addition of silylenes to olefins is not as simple for silicon as for carbon since the intermediate silacyclopropanes are much less stable than cyclopropanes, and only isolable with great effort. Despite this difficulty, two reports of the stereochemistry of silylene addition to olefins have appeared.

In the first, by Ishikawa and coworkers, photogenic $Ph\ddot{S}iSiMe_3$ reacted with trans-2-butene to afford only a single silacyclopropane (78). In contrast two stereoisomeric silacyclopropanes were formed from addition to cis-2-butene. All three isomers gave the same methanolysis product. These observations are most consistent with a cis-addition mechanism.



In an analogous study, Tortorelli and Jones found that Me_2Si: added stereoselectively to cis- and trans-2-butene to form silacyclopropanes, which were in turn stereoselectively ring opened by methanol (80). Although the exact nature of addition could not be established, the stereoselectivety reported is most reasonably explained by cis- addition of Me_2Si:.

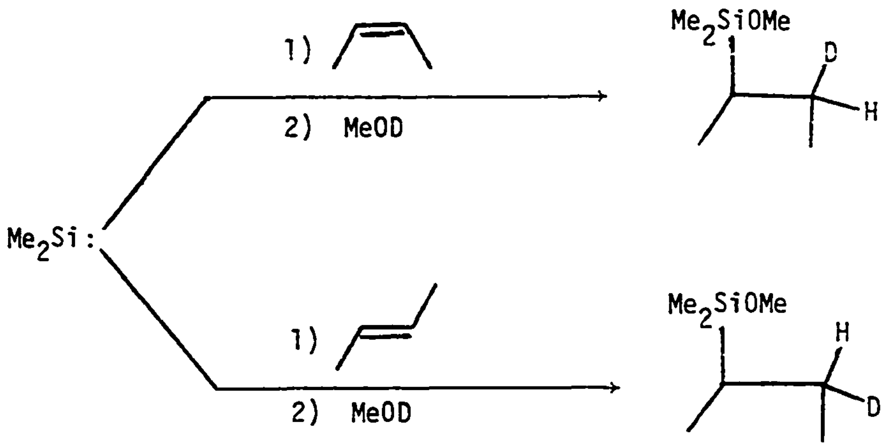


Table 2 provides a partial listing of silacyclopropanes obtained by addition of silylenes to various olefins.

The chemistry of silylene additions to 1,3-dienes began in 1968 with the report by Atwell and Weyenberg that dimethylsilylene, generated thermally from 7-silanorbornadiene 7 or *sym*-dimethoxytetramethyldisilane, reacted with 2,3-dimethylbutadiene to afford tetramethylsilacyclopentene 39 in moderate yield (7).

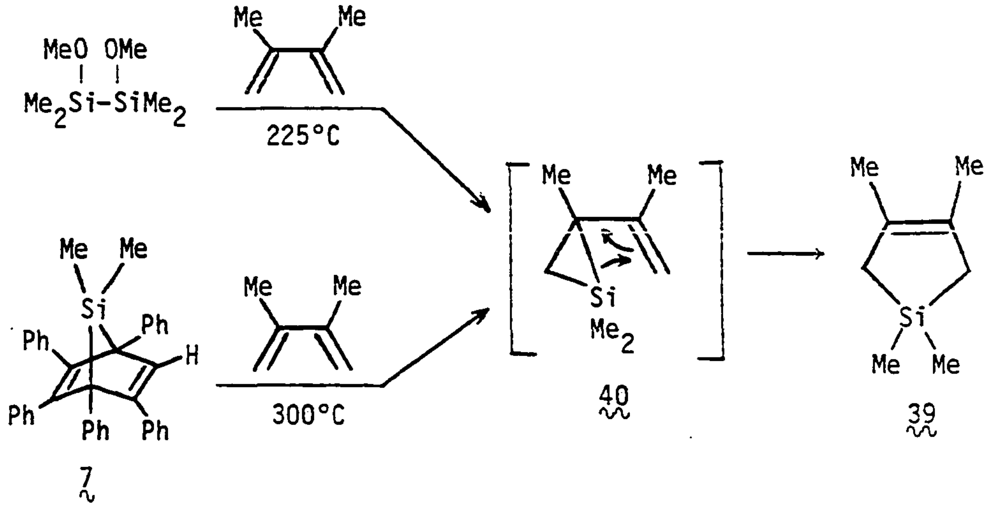


Table 2. Yields of Silacyclopropanes from Addition of Silylenes to Olefins

Silylene	Conditions[a]	Olefin	Yield of Silacyclopropane (%)[b]	Ref.
$\mathrm{Ph\ddot{S}iMe}$	hν	1-butene	27	27
$\mathrm{Ph\ddot{S}iSiMe_3}$	hν		47	78
$\mathrm{Ph\ddot{S}iMe}$	hν	isobutene	39	77
$\mathrm{Ph\ddot{S}iSiMe_3}$	hν		52	78
$\mathrm{Ph\ddot{S}iMe}$	hν	*cis*-2-butene	29	77
$\mathrm{Ph\ddot{S}iSiMe_3}$	hν		35	78
$\mathrm{Me\ddot{S}iMe}$	Δ		20-24	79

---

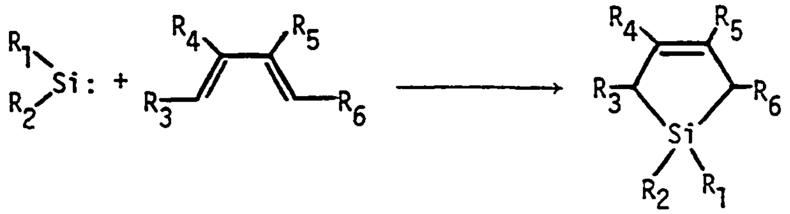
[a] Conditions refers to method of silylene generation: hν = photochemical, Δ = thermal.

[b] Yields are based on the combined yields of the methanolysis and 1,3-hydrogen shifted products.

Table 2. Cont.

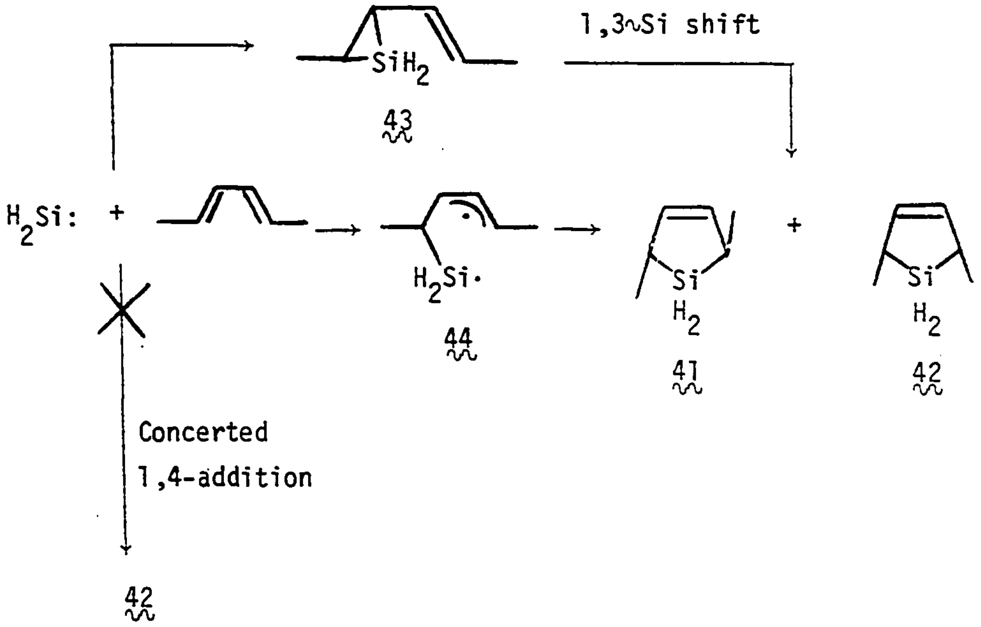
Silylene	Conditions[a]	Olefin	Yield Silacyclopropane (%)[b]	Ref.
$\mathrm{Ph\ddot{S}iSiMe_3}$	hν	*trans*-2-butene	40	78
$\mathrm{Me\ddot{S}iMe}$	Δ		20-24	79
$\mathrm{Ph\ddot{S}iMe}$	hν	1-octene	34	77
$\mathrm{Ph\ddot{S}iMe}$	hν	allyltrimethylsilane	25	77
$\mathrm{Ph\ddot{S}iMe}$	hν	isopropenyltrimethylsilane	23	77
$\mathrm{Ph\ddot{S}iMe}$	hν	tetramethylethylene	31	77
$\mathrm{Ph\ddot{S}iSiMe_3}$	hν	trimethylvinylsilane	62	78
$\mathrm{Ph\ddot{S}iMe}$	hν	cyclohexene	34	77
$\mathrm{Me\ddot{S}iMe}$	Δ		22	79
$\mathrm{Ph\ddot{S}iMe}$	hν	cyclooctene	38	77
$\mathrm{Me\ddot{S}iMe}$	Δ		35	79
$\mathrm{Me\ddot{S}iMe}$	Δ	*cis*-4-octene	69	79
$\mathrm{Me\ddot{S}iMe}$	Δ	1-trimethylsilylpropene	48	79
$\mathrm{Me\ddot{S}iMe}$	Δ	2,3-dimethyl-2-pentene	68	79

Although **39** is formally a product of 1,4-addition, it was proposed that **39** is formed by initial 1,2-addition to give vinylsilacyclopropane **40** which rearranged under the reaction conditions to **39**. Since this initial investigation, acyclic 1,3-dienes have been found to be excellent traps for thermally generated silylenes, affording in moderate to good yields the corresponding 1-silacyclopent-3-enes:

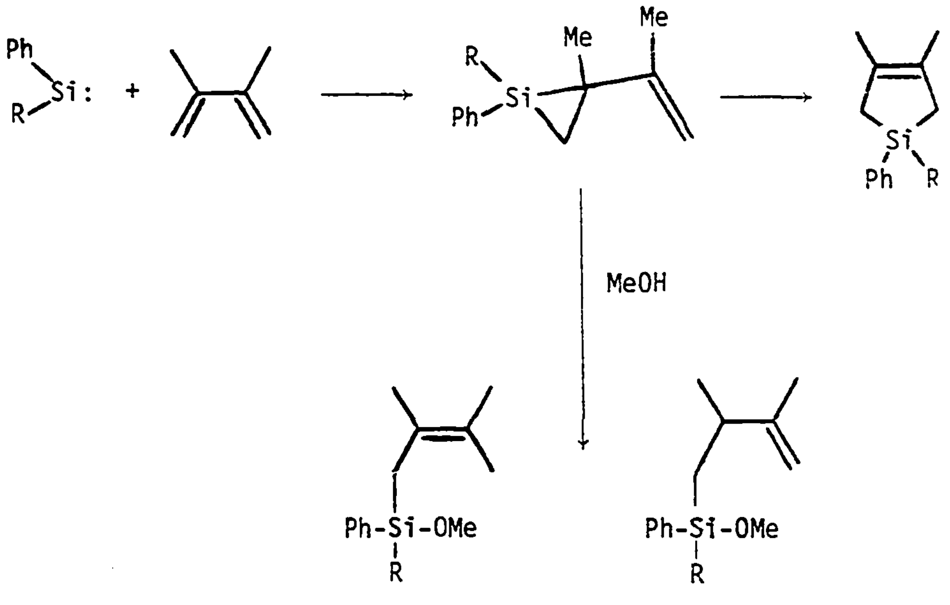


R_1	R_2	R_3	R_4	R_5	R_6	% Yield	Ref.
Me	Me	H	Me	Me	H	15-38	7,49
OMe	OMe	H	H	H	H	∿60	7,9
OMe	Me	H	Me	Me	H	∿60	7
H	H	H	H	H	H	40	39,81,82
Cl	Cl	H	H	H	H	∿90	83
Cl	Cl	H	Me	H	H	95	83
Cl	Cl	Me	H	H	H	95	83
Cl	Cl	H	Cl	H	H	∿90	83
H	H	Me	H	H	Me	20	84

That the silacyclopentenes derived from silylene addition to 1,3-dienes do not arise by concerted 1,4-addition has been convincingly shown by Gaspar and Hwang (84). When silylene was generated in the presence of excess trans-2-trans-4-hexadiene a 20% yield of approximately a one-to-one mixture of silacyclopentenes **41** and **42** was obtained. If the addition proceeded by concerted 1,4-addition, only silacyclopentene **42** would have been expected. Thus, Gaspar and Hwang postulated that the reaction occurs by initial 1,2-addition to afford **43**, or by a radical process involving intermediate **44**.



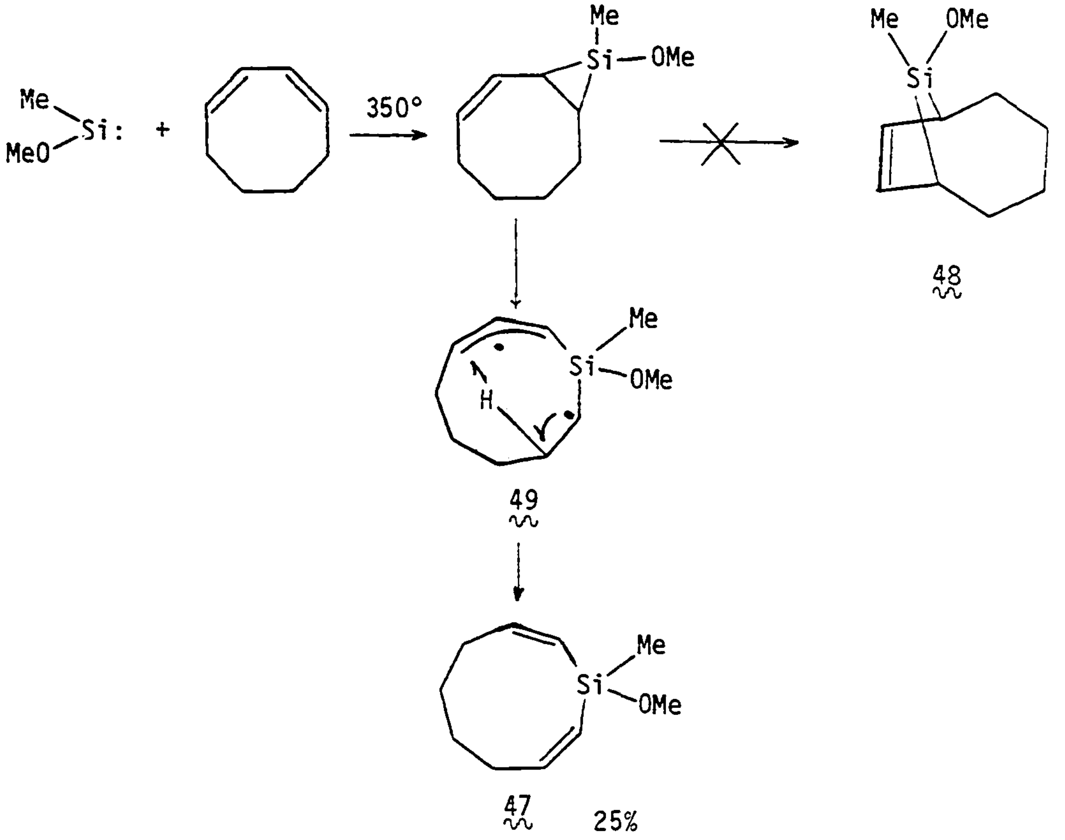
Definitive evidence that silylenes add to conjugated dienes by initial 1,2-addition has been reported by Ishikawa and coworkers who found that reaction of photogenic silylenes with 2,3-dimethylbutadiene, in the presence of methanol, afforded methoxysilanes **45** and **46** (85,86). These results, coupled with the earlier study by Gaspar and Hwang (84), firmly established 1,2-addition as the first step in the addition of silylenes to conjugated dienes.



45 46

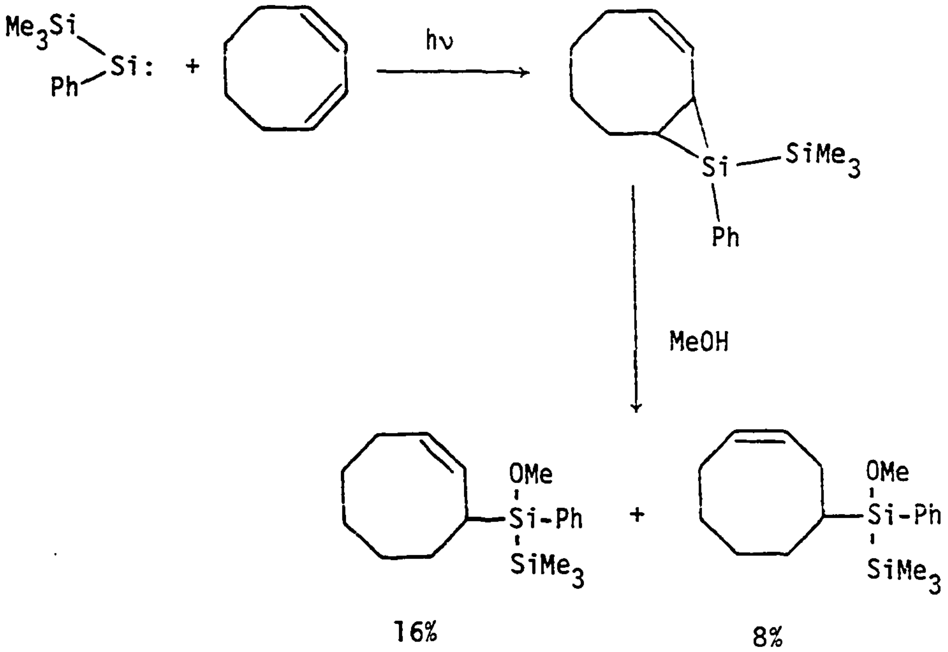
R = Me	6%	-
R = $SiMe_3$	13%	6%

The addition of silylenes to cyclic 1,3-dienes is mechanistically similar to that of acyclic 1,3-dienes; however, rather than affording products of formal 1,4-addition, the reaction with cyclic dienes yields products of formal carbon-carbon sigma bond insertion. This was first observed by Childs and Weber who found that methylmethoxysilylene reacted with 1,3-cyclooctadiene to give silacyclononadiene 47, instead of the expected bicyclo-9-sila[4.2.1]nona-7-ene 48 (87).

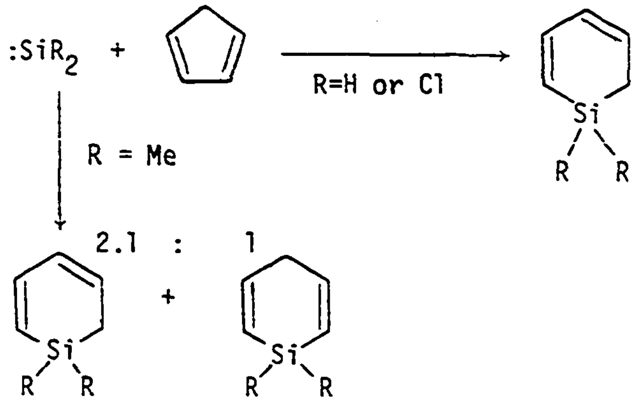


These authors postulated that 47 was formed by initial 1,2-addition followed by carbon-carbon bond homolysis to give diradical 49. Transannular hydrogen abstraction by the remote end of the allylic radical, in a 1,5 sense, yields 47.

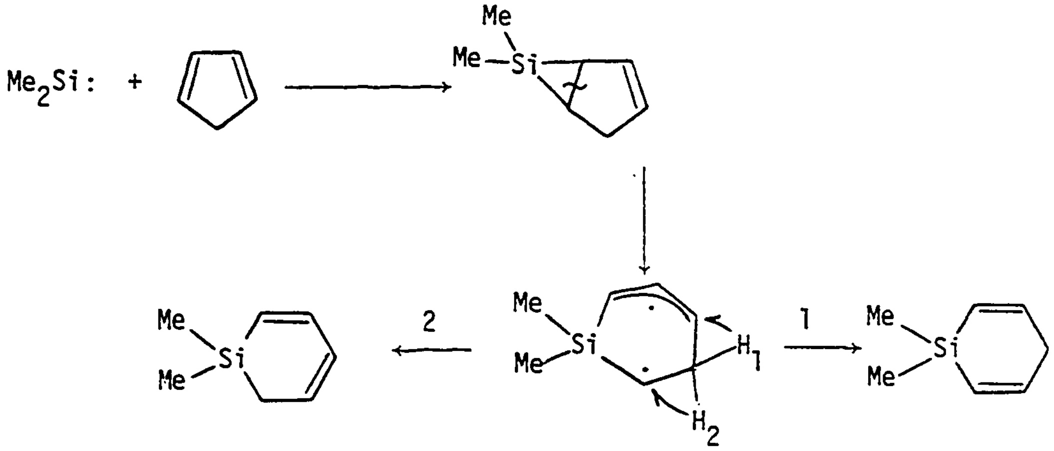
That the formation of 47 was indeed proceeding by initial 1,2-addition was confirmed by Ishikawa and coworkers by methanol trapping of the the intermediate vinylsilacyclopropane (86).



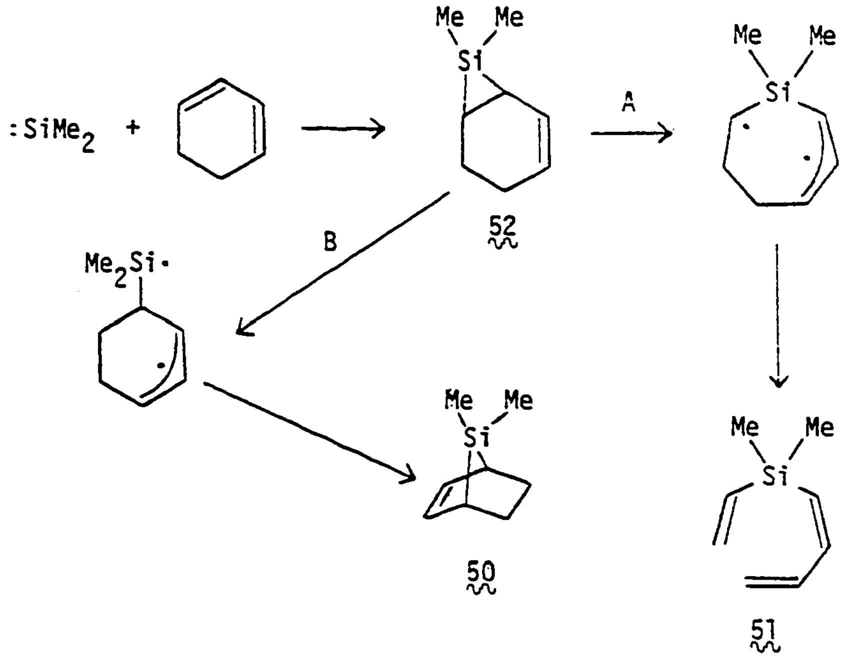
Further support for the proposal that silylenes react with cyclic 1,3-dienes by initial 1,2-addition followed by bond homolysis to give a diradical has been provided by Hwang and coworkers (88). While the addition of $:SiH_2$ and $:SiCl_2$ to cyclopentadiene was found to afford exclusively the conjugated 1-sila-2,4-cyclohexadienes, addition of $:SiMe_2$ gave both the 2,4- and 2,5-isomers.



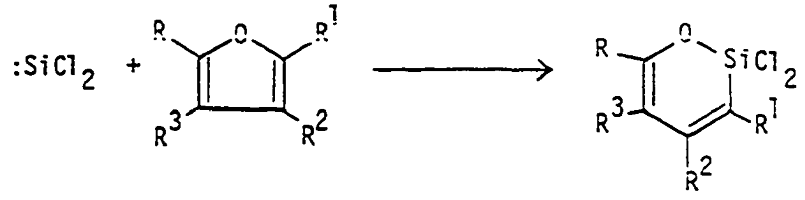
The finding that the product ratio of Me_2Si: addition remained constant over a 150°C temperature span indicated that a common intermediate was involved in the formation of both the 2,4- and 2,5-isomers. Thus, Hwang proposed the following mechanism:



Compelling evidence supporting this proposal was obtained from the reaction of dimethylsilylene and 1,3-cyclohexadiene which afforded 7,7-dimethyl-7-silanorbornene (50) and 3,3-dimethyl-3-sila-1,4,6-heptatriene (51) in yields of 10% each (88). Compounds 50 and 51 are clearly most consistent with initial 1,2-addition to give silanorcarene 52. Intermediate 52 gives 51 by carbon-carbon bond homolysis followed by β-scission, while silanorbornene 50 is formed by Si-C bond homolysis followed by radical recombination.



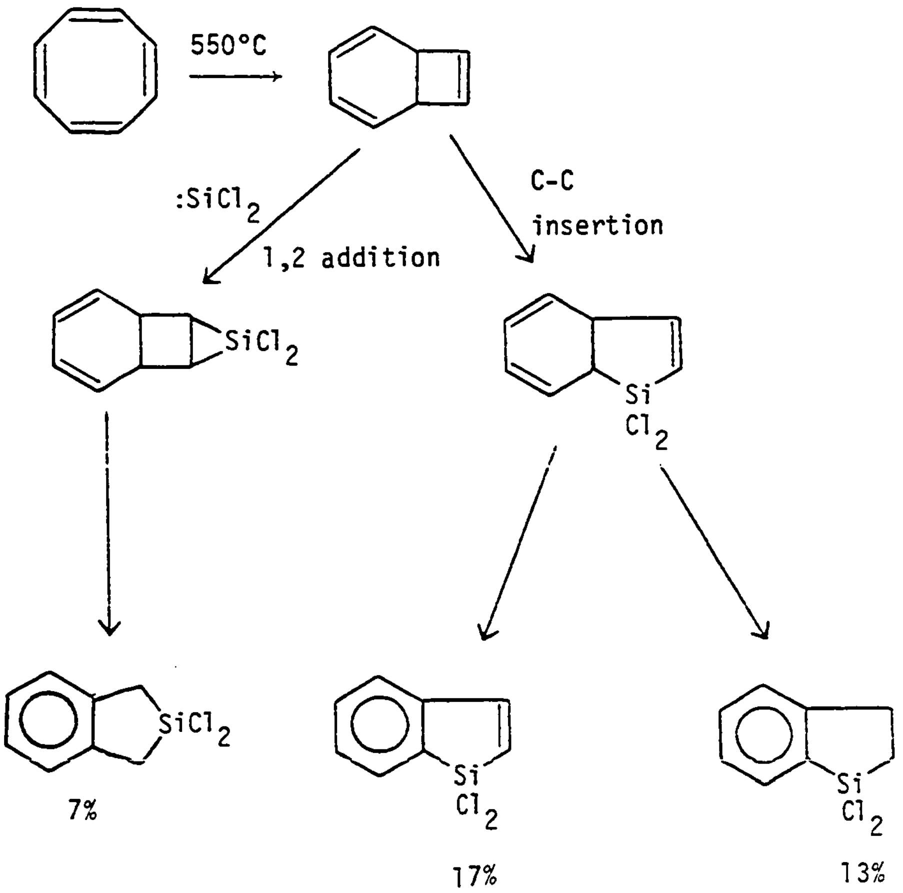
Chernyshev and coworkers have reported a similar process for the reaction of dichlorosilylene and furans (89). Thus, dichlorosilylene reacts with substituted furans to afford ring expanded products of formal C-O insertion.



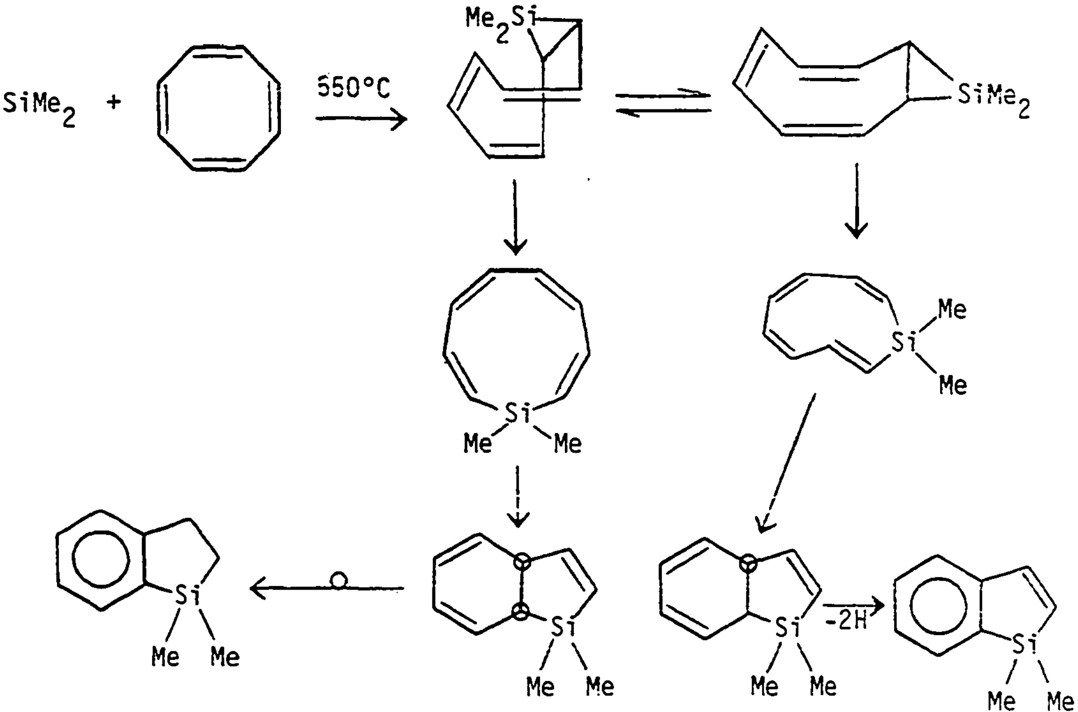
R^1	R^2	R^3	R	Yield (%)
H	H	H	H	30
H	H	H	CH_3	40
CH_3	H	H	CH_3	40
$-(CH)_4$	-	$-(CH)_4$	-	70
H	H	$-(CH)_4$	-	70

In a related study, employing methylmethoxysilylene and 2,4-dimethylfuran, Childs and Weber obtained similar results, although in much lower yields (90).

Addition of silylenes to olefins containing more than two conjugated double bonds has been reported only twice. Chernyshev and coworkers reported that dichlorosilylene adds to cyclooctatetraene to afford products of both carbon-carbon sigma bond insertion and 1,2-addition followed by rearrangement (91).



Barton and Juv'et found that dimethylsilylene reacts with cyclooctatetraene to afford 1-silaindene **53** and 1-silaindane **54** in yields of 30% and 15%, respectively, at 550°C (92). No 2-silaindane, analogous to that reported by Chernyshev, was observed. The formation of **53** and **54** was proposed to occur via an initial 1,2-addition to cyclooctatetraene followed by competing rearrangements.



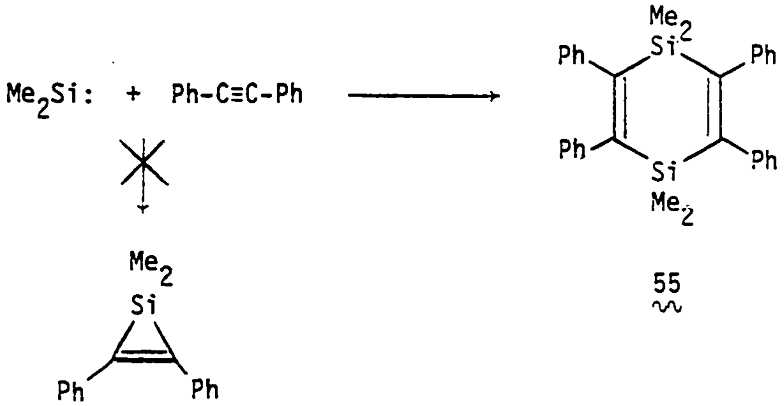
54

53

Addition of Silylenes to Acetylenes

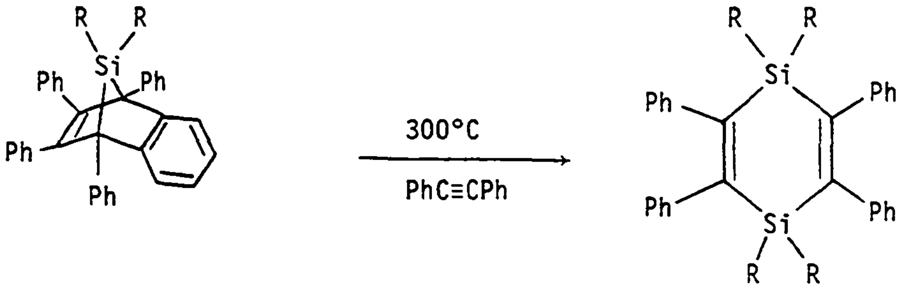
The study of silylene additions to acetylenes and the mechanism of formation of the resultant products has led to the discovery of chemistry that has had a profound influence on the development of organosilicon chemistry. Even though this reaction is almost twenty years old, it has only been within the last five years that an understanding of the complex processes involved has begun to emerge.

In 1962, Vol'pin and coworkers claimed to have isolated the first silacyclopropene from the addition of thermally generated dimethylsilylene to diphenylacetylene (93). Shortly thereafter, however, West and Bailey demonstrated that the product obtained by Vol'pin was not a silacyclopropene, but its formal dimer, disilin 55 (94).



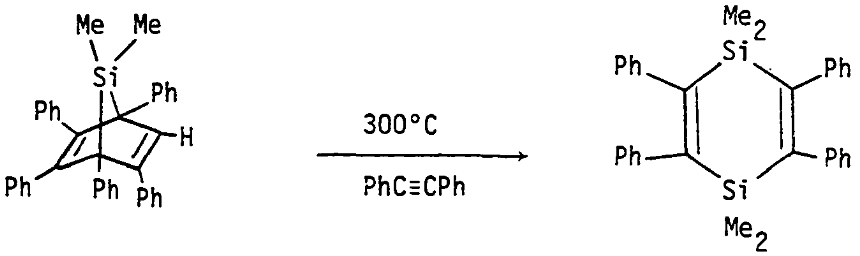
55

The addition of thermally generated silylenes to acetylenes to afford the corresponding disilins has been shown to be general for a variety of silylenes, with the exception of dimethoxysilylene (7), and acetylenes in the condensed phase at temperatures greater than 200°C. Thus, Gilman, Cottis, and Atwell have found that pyrolysis of 7-silanorbornadienes in the presence of diphenylacetylene affords disilins in good yields (4,5).



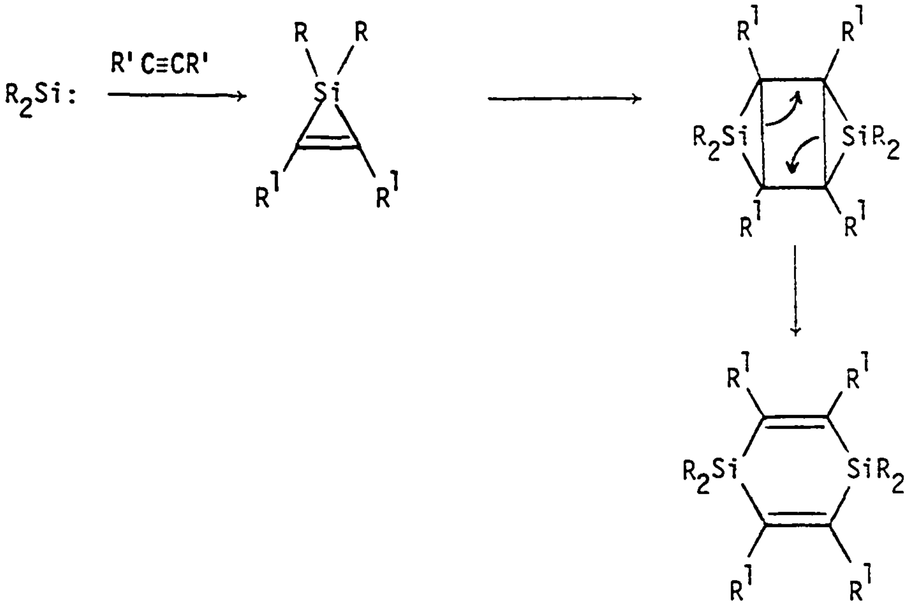
R = Me, 50%

R = Ph, 63%



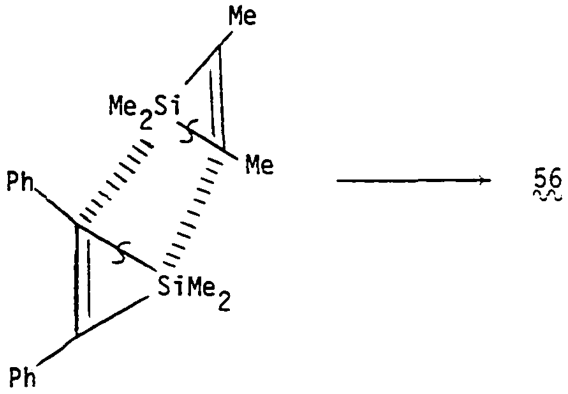
Atwell and coworkers have obtained similar results from the copyrolysis of alkoxydisilanes and acetylenes (7,9,95).

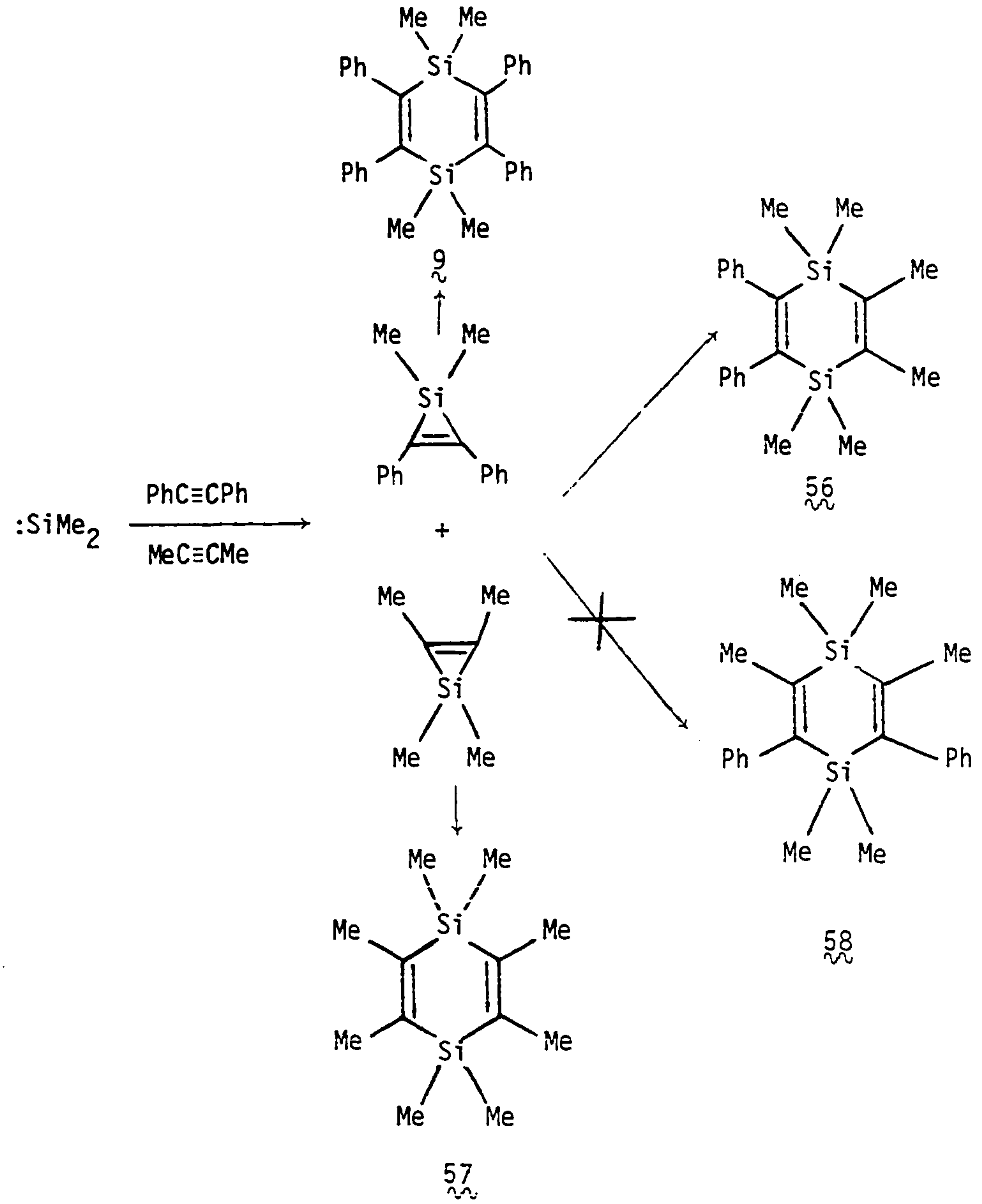
The mechanism that was initially proposed to account for the formation of 1,4-disilins was silylene addition to the acetylene to afford a silacyclopropene. Pi-dimerization of this intermediate followed by ring opening would then give the observed products (4,5).



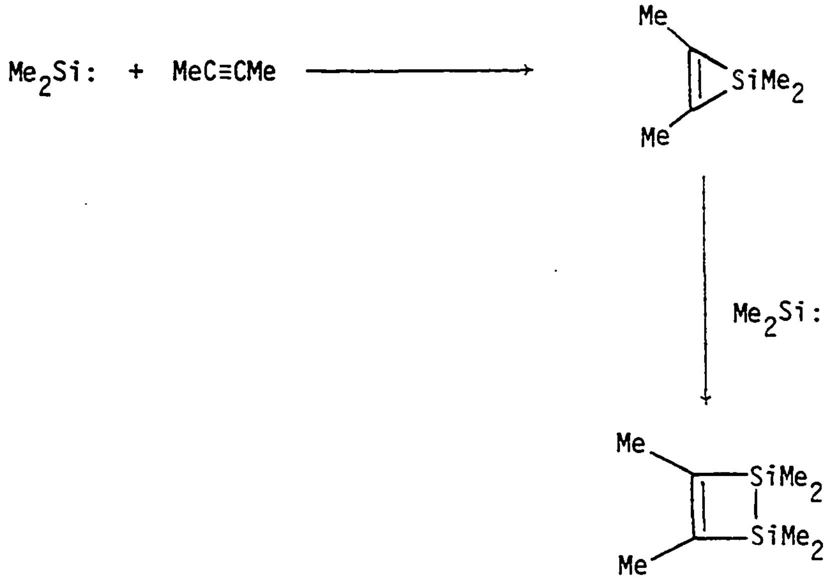
Doubt was cast on this mechanism, however, when dimethylsilylene was found to react with a 1:1 mixture of diphenylacetylene and 2-butyne to give disilins 9, 56, and 57 (6).

The absence of 58 eliminated the π-dimerization mechanism. Therefore, to account for the formation of 56, a sigma dimerization was tentatively proposed.



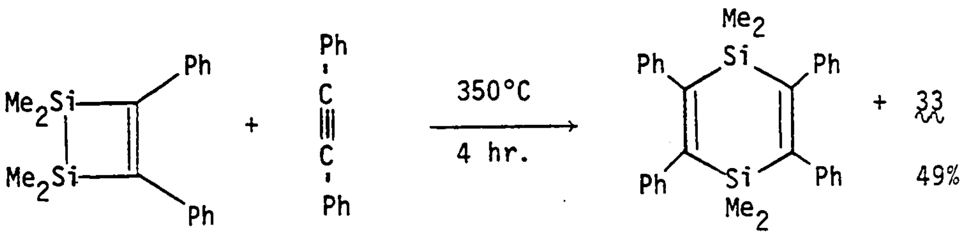


In contrast to the solution reactions, Atwell and Uhlmann found that in the gas phase dimethylsilylene adds to 2-butyne to afford only permethyl-1,2-disilacyclobutene (72). It was suggested that this product was formed by silylene addition to 2-butyne to give permethylsilacyclopropene. This intermediate, upon silicon-carbon bond insertion by dimethylsilylene, led to the disilacyclobutene.



In a study designed to delineate the role of 1,2-disilacyclobutenes in the reaction of silylenes and acetylenes, Barton and Kilgour found that copyrolysis of permethyl-1,2-disilacyclobutene and 3-hexyne provided disilin 59 as the only isomer (96,97). In addition, tetramethyldisilene was found to react with 2-butyne to give octamethyldisilin (57) under the same conditions that dimethylsilylene is known to react with 2-butyne to give 57. On the basis of this latter result, Barton and Kilgour proposed initial silylene dimerization to a disilene followed by its 2 + 2 cycloaddition to acetylene as an alternative route to 1,2-disilacyclobutenes. Moreover, by demonstrating that permethyl-1,2-disilacyclobutene reacts with acetylenes in the condensed phase to afford disilins an alternative to the sigma-dimerization mechanism was established. Scheme 3 summarizes the mechanistic proposal and results of Barton and Kilgour.

Since it is now known that silylenes dimerize in the gas phase (98) and in solution (99) to disilenes, and that disilenes cycloadd to acetylenes to give 1,2-disilacyclobutenes (73), the elementary reactions of Barton and Gilgour's mechanism have been precedented. However, the report by Sakurai and coworkers (73) that copyrolysis of 1,2-disilacyclobutene 33 and diphenylacetylene led to only a 1.2% yield of disilin 9 argued against the generality of this mechanism.



33

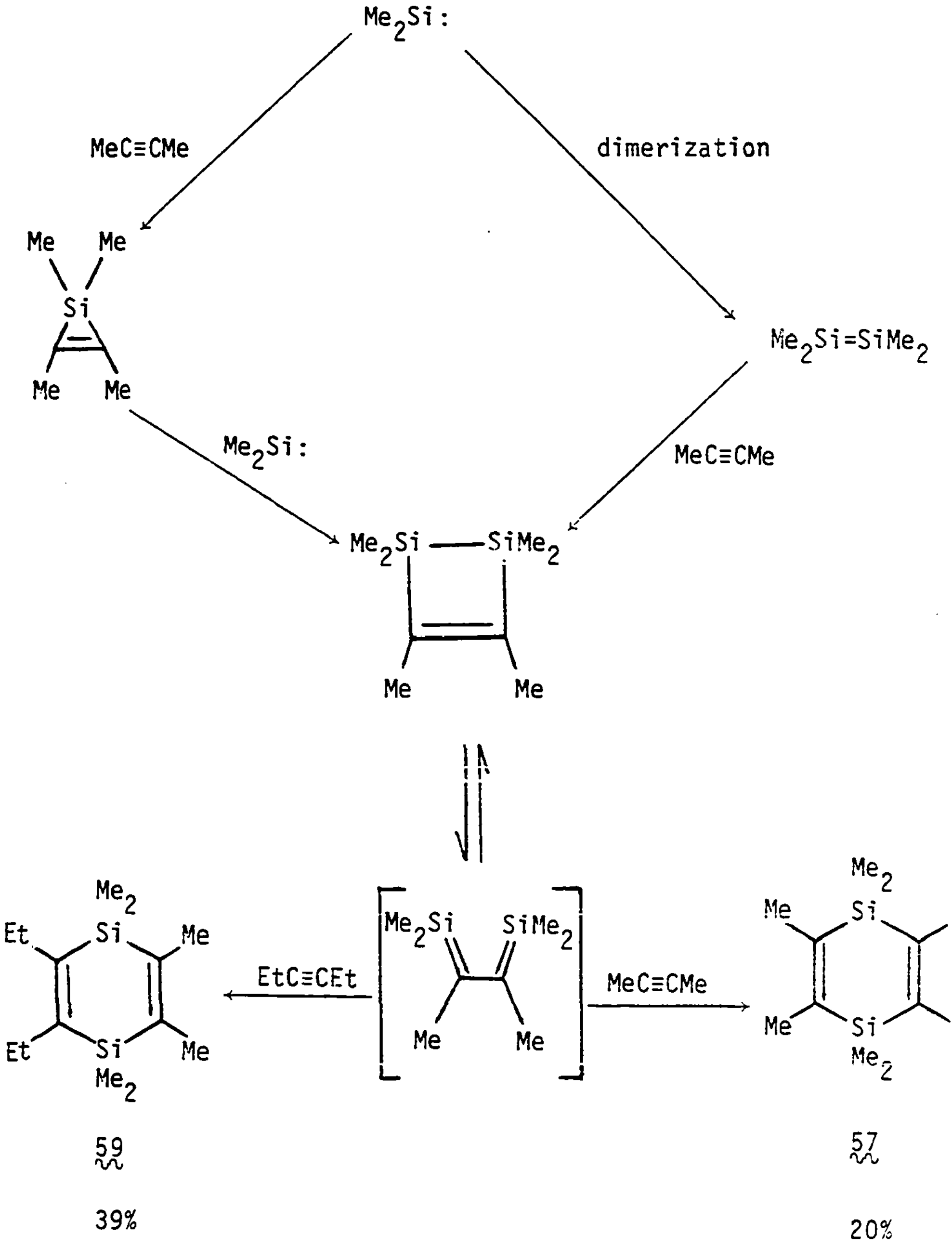
9

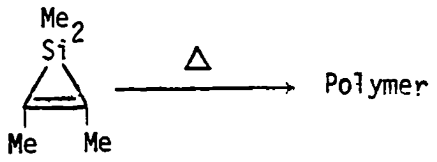
1.2%

Even more confusion has been added to this problem with the findings that tetramethylsilacyclopropene (31) thermally polymerizes (100) while the phenyltrimethysilyl analogue 60 undergoes direct thermal dimerization (101). The latter reaction was demonstrated not to involve an intermediate 1,2-disilacyclobutene, and thus, is most consistent with direct sigma-dimerization.

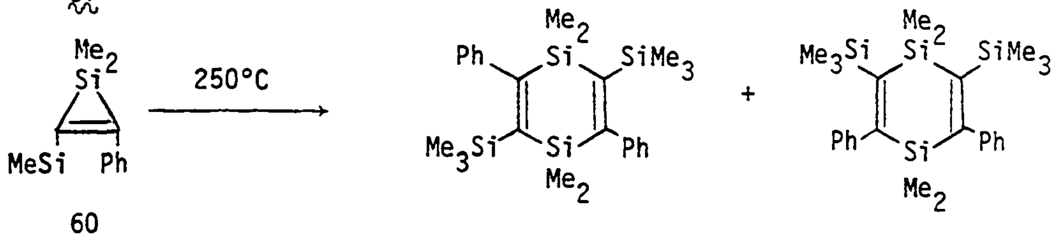
Despite the aforementioned mechanistic ambiguities, that silylenes add to acetylenes to form silacyclopropenes is an experimental fact. Both Conlin and Gaspar (100) and Seyferth and coworkers (102) have shown that

Scheme 3


Me$_2$Si:
MeC≡CMe
dimerization
Me$_2$Si=SiMe$_2$
Me$_2$Si:
MeC≡CMe
EtC≡CEt
MeC≡CMe
59
39%
57
20%



31



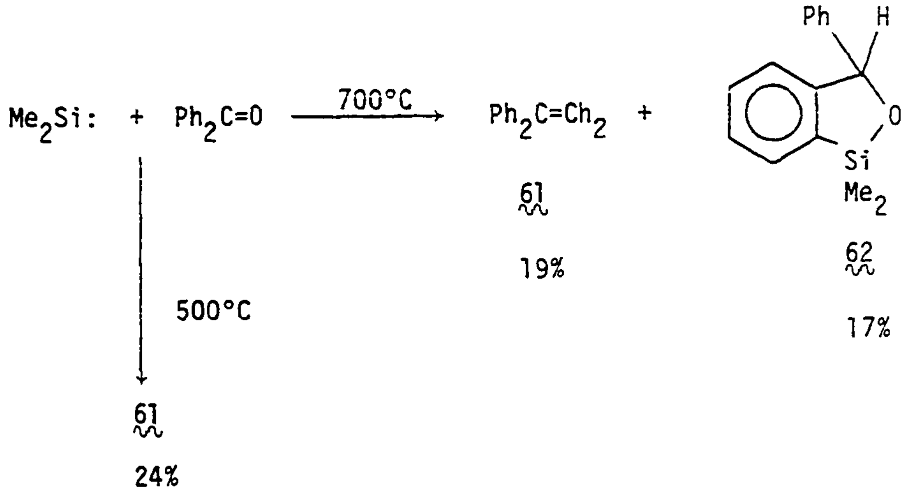
60

thermally generated dimethylsilylene adds to 2-butyne to give tetramethylsilacyclopropene. More recently, Ishikawa and coworkers have found that photogenic $\mathrm{Me_3Si\ddot{S}iPh}$ adds to terminal and internal acetylenes to afford the corresponding silacyclopropenes in moderate yield (103,104).

At the present, a number of elementary reactions from which sequences can be constructed to account for the formation of disilins from the reaction of silylenes and acetylenes are known. Despite this knowledge, it is still not possible for a given set of reaction conditions to determine which sequence or sequences are operative.

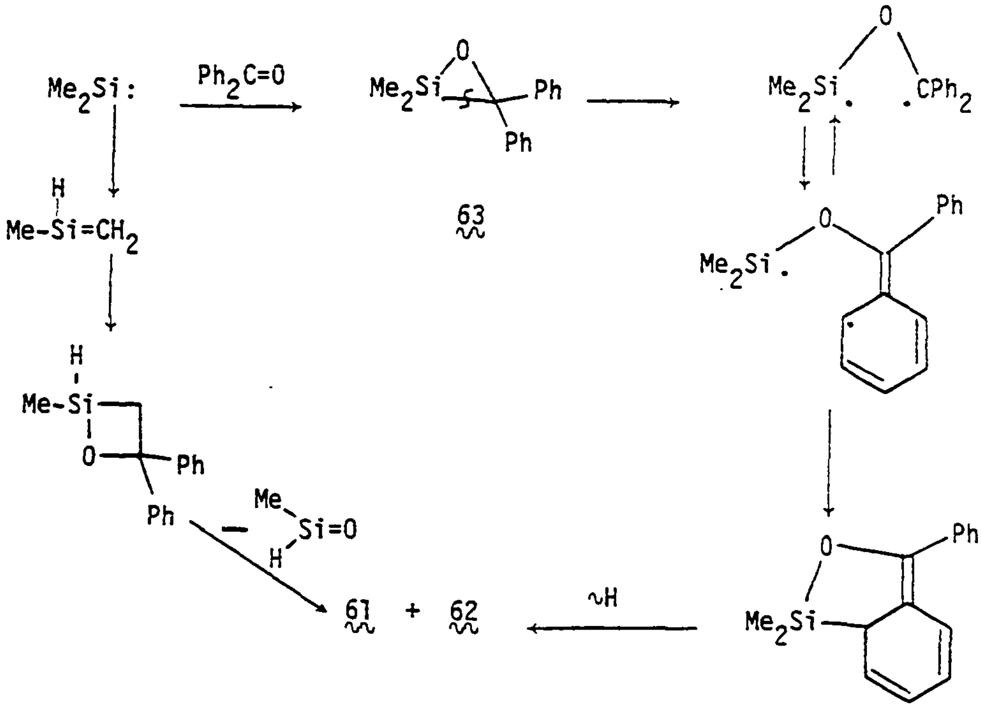
Addition of Silylenes to Carbonyls

The first report of silylene additions to carbonyls is that of Ando and coworkers (105). When dimethylsilylene was generated in the gas phase at 700°C in the presence of excess benzophenone, two major products of interest were obtained, 61 and 62. At 500°C, only 61 was obtained as a major product.



The formation of 62 was proposed to be consistent with addition of silylene to the carbon-oxygen double bond to form silaoxarane 63 (Scheme 4). Intermediate 63 leads to 62 by silicon-carbon bond homoloysis followed by rearrangement of the resulting diradical. Diphenylethylene (61) was proposed to arise by decomposition of silaoxatane 64, which could be formed by silylene isomerization to silene followed by 2 + 2 cycloaddition of silene to benzophenone (Scheme 4). Ample literature precedent exists for the addition of silenes to non-enolizable aldehydes and ketones, and for the decomposition of silaoxetanes to olefins (106). However, the isomerization of a silylene to a silene had been suggested only once prior to this report (98), and as will be presented later is still not known to occur under these reaction conditions. Therefore, the mechanistic proposal for the formation of 61 must be regarded with skepticism.

Scheme 4



An alternative mechanism (Scheme 5) that is not only consistent with the observed products but also precedented by the known ability of silyl radicals to disproportionate to silenes (*vide infra*) is a viable alternative to that proposed by Ando and coworkers (*vide supra*).

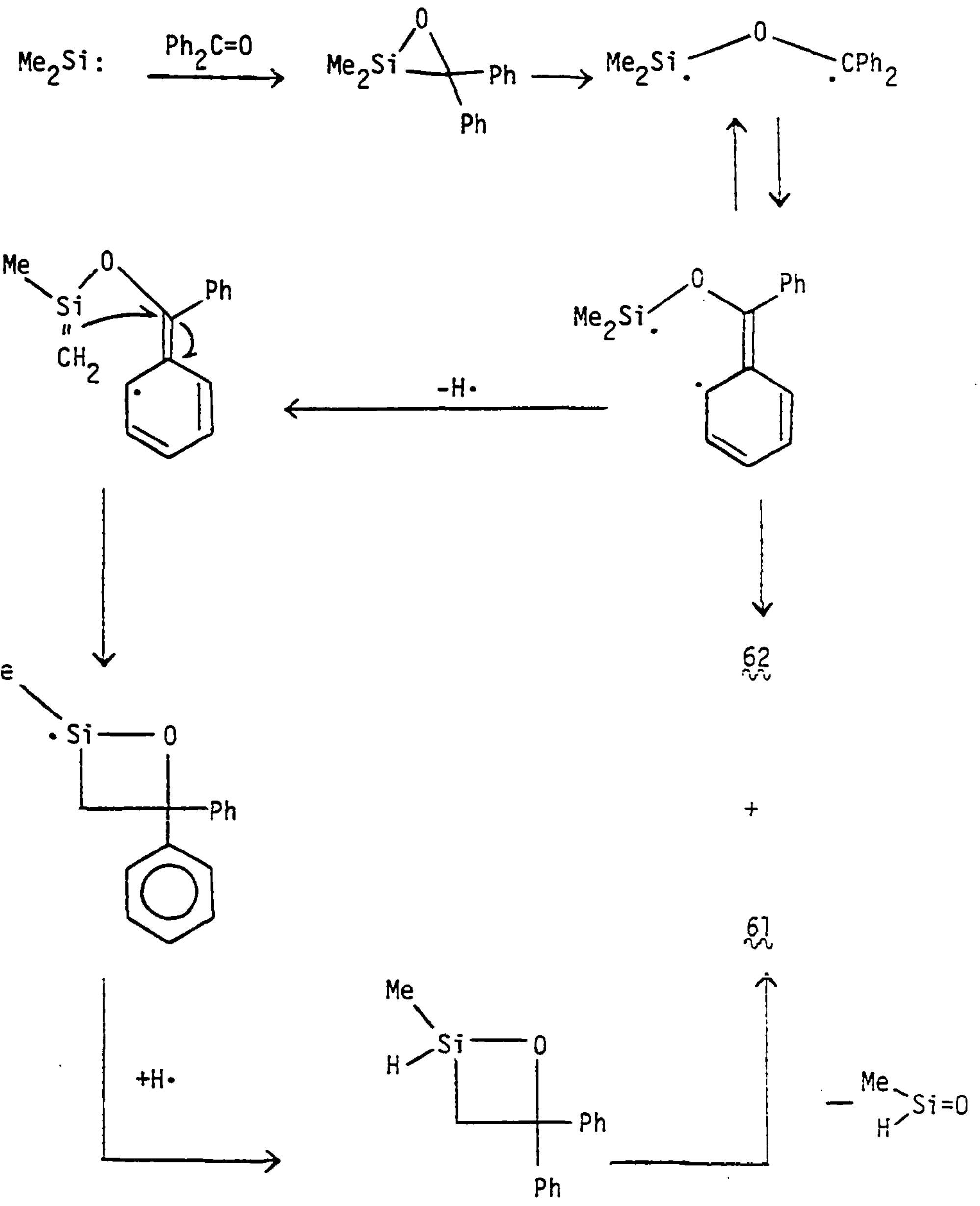
When enolizable ketones were employed as traps, Ando and coworkers (105) observed products of formal silylene insertion into the O-H bond of the enol form of the substrate ketones (Scheme 6). However, the finding that dimethylsilylene did not react with ethanol or neopentyl alcohol under the reaction conditions used was offered as evidence to eliminate from

$$Me_2Si: + ROH \not\xrightarrow{500^{\circ}C} ROSiMe_2H$$

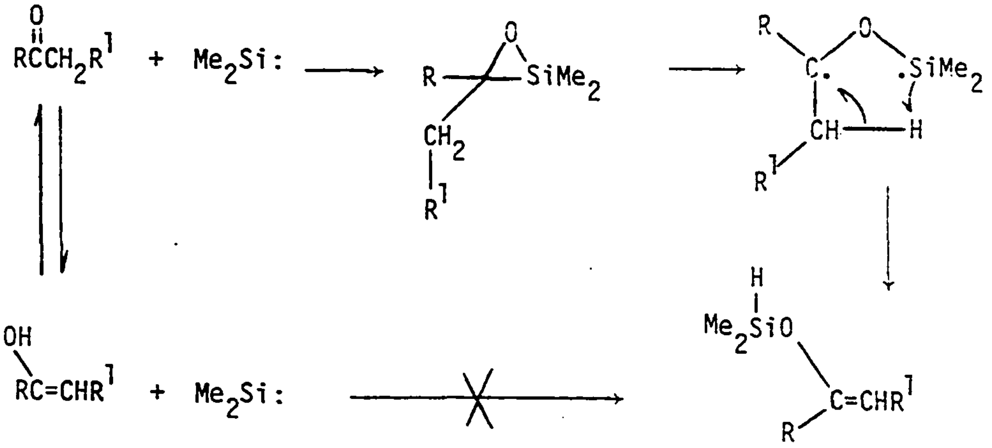
$$R = CH_3CH_2\text{-},\ Me_3CCH_2\text{-}$$

consideration direct silylene addition to the enol. Thus, the reaction of dimethylsilylene with enolizable ketones was also believed to involve the intermediate formation of a silaoxarane.

Scheme 5



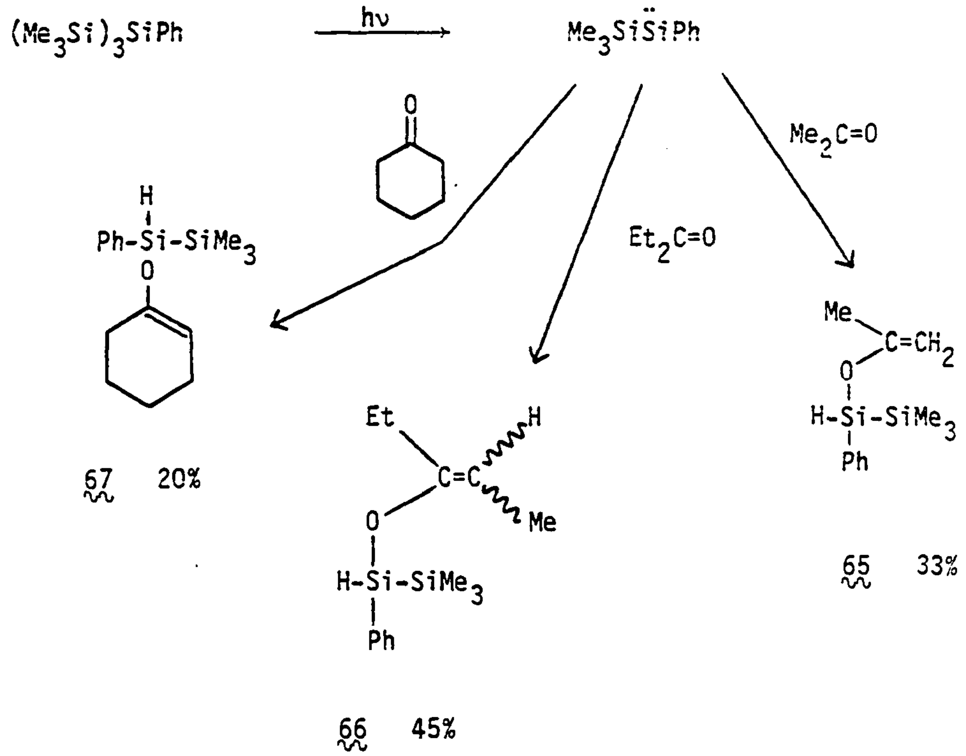
Scheme 6



Unfortunately, no control experiments designed to demonstrate that ethanol and neopentanol were stable to the reaction conditions were reported. Therefore, the contention that direct silylene addition to the enol is not operative under these conditions must be regarded as unsubstantiated, particularly in view of the known ability of silylenes to insert into the O-H bond of alcohols (vide supra).

Ishikawa, Nakagawa, and Kumada studied the reaction of photochemically generated trimethylsilylphenylsilylene with various ketones and observed similar results (107). Thus, photolysis of tris(trimethylsilyl)-phenylsilane in the presence of excess acetone, diethylketone, and cyclohexanone gave disilanyl enol ethers 65, 66, and 67, respectively.

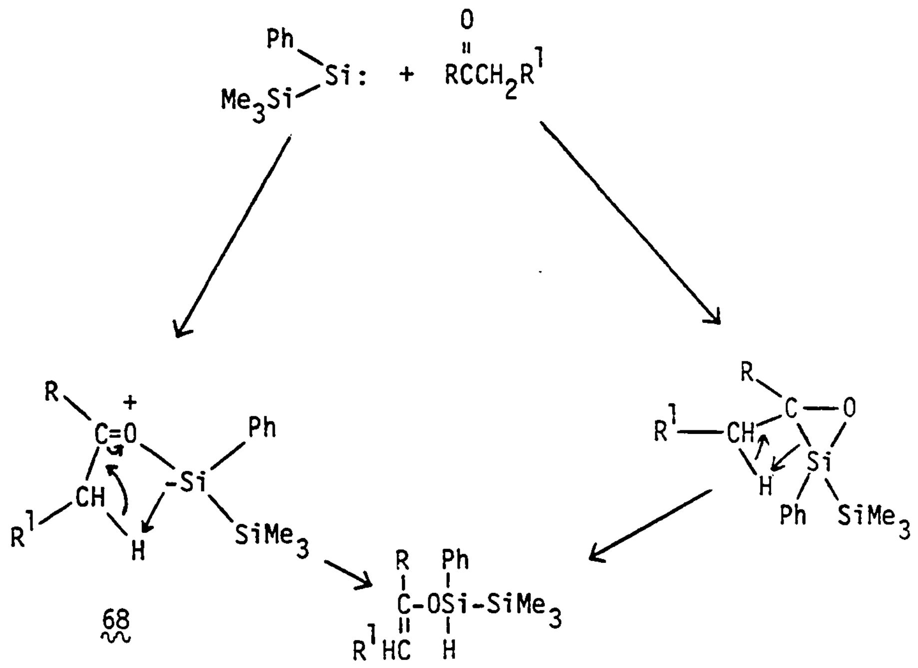
The possibility that these products were formed by silylene addition to the enol forms of the ketones was eliminated since silicon-carbon double-bonded intermediates, generated under similar conditions in the presence of enolizable ketones, did not give the products expected for reaction with the enol tautomer (60,61).



The mechanism that was favored to explain the formation of 65, 66, and 67, was a concerted process involving rearrangement of silyl ylid 68 (Scheme 7). However, a mechanism involving initial formation of a silaoxarane, followed by isomerization to the observed products, could not be excluded.

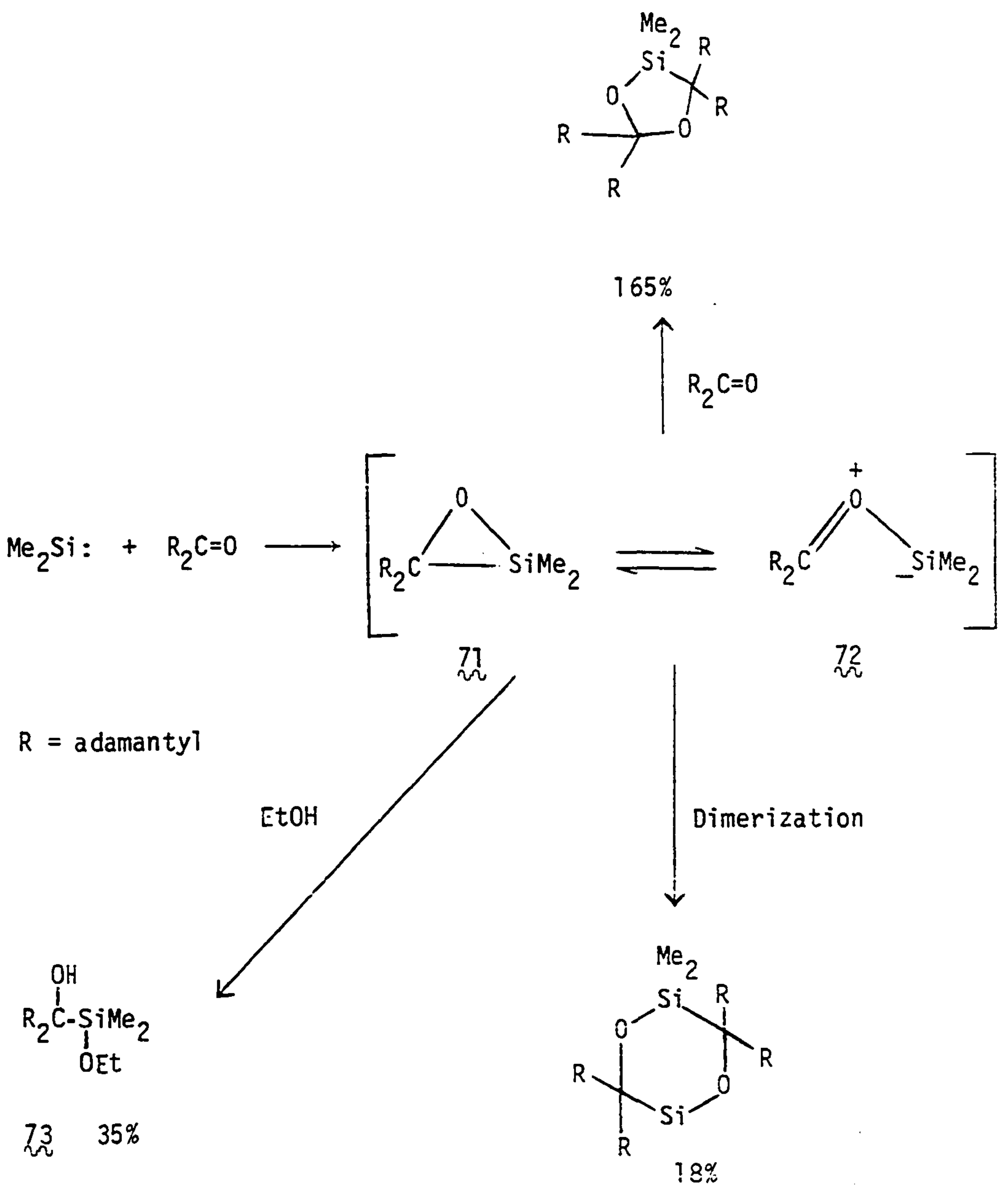
Although the mechanism of silyl enol ether formation from the reaction of silylenes and enolizable ketones has not been established, the reaction is synthetically useful. Ando and Ikeno have shown that dimethylsilylene, generated photochemically from dodecamethylcyclohexasilane, reacts with a variety of enolizable aldehydes and ketones to produce the corresponding silyl enol ethers in good to excellent yields (108).

Scheme 7

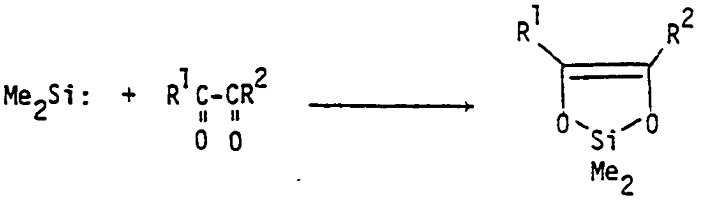


When non-enolizable ketones are used as traps for photogenic dimethylsilylene, Ando and coworkers observed the formation of dimers 69 and 70 (109). Although these products are consistent with the intermediacy of either silaoxarane 71 or silyl ylid 72, trapping experiments argued against the latter (Scheme 8). Thus, strong evidence for the intermediacy of 71 was obtained when the same reaction was carried out in the presence of ethanol and it was found (with appropriate control experiments) that 73 was a primary product of the reaction. Further support for the supposition that 71 is an intermediate in this reaction has been provided by Seyferth and Lin who have reported similar silaoxarane dimerizations (110).

Scheme 8



More recently, Ando and Ikeno found that photogenic dimethylsilylene reacted with 1,2-diketones to produce 1,3-dioxa-2-silacyclopent-4-enes (111).



$R^1 = R^2 = Me$ 41%

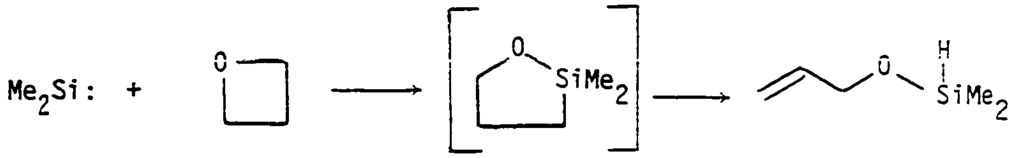
$R^1 = Et, R^2 = Me$ 38%

$R^1 = R^2 = $ n-Pr 45%

$R^1 = R^2 = $ i-Pr 67%

Reactions of Silylenes with Oxetanes, Epoxides and α-β Unsaturated Ethers

Gu and Weber have recently reported the results of a study of the reactions of photochemically generated dimethylsilylene and various oxetanes (112). When dimethylsilylene was generated in the presence of excess oxetane at 0°C, oxasilacyclopentane 74 and allyloxysilane 75 were formed as major products. Initially, 75 was believed to arise from vibrationally excited 74 by a retro-hydrosilylation reaction.

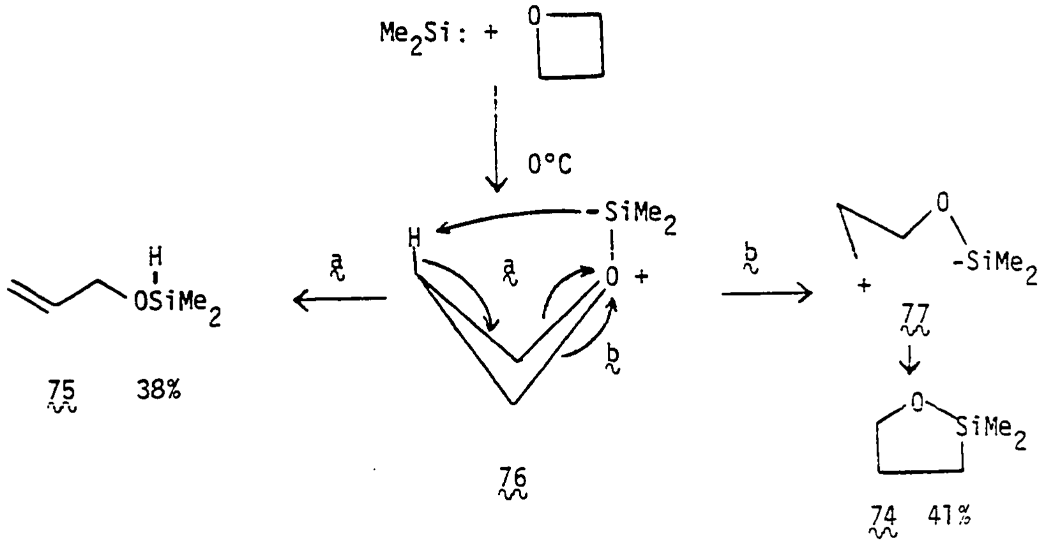


74 75

However, the finding that only 75 was produced at -98°C, under otherwise identical reaction conditions, eliminated this possibility. Thus, to explain the formation of 74 and 75 the intermediacy of silyl ylid 76 was proposed (Scheme 9). Hydrogen abstraction in a 1,4-sense by 76 with concomitant ring opening would give 75. Alternatively, 76 could ring open to zwitterion 77, which upon 1,5-ring closure would give 74 (Scheme 9).

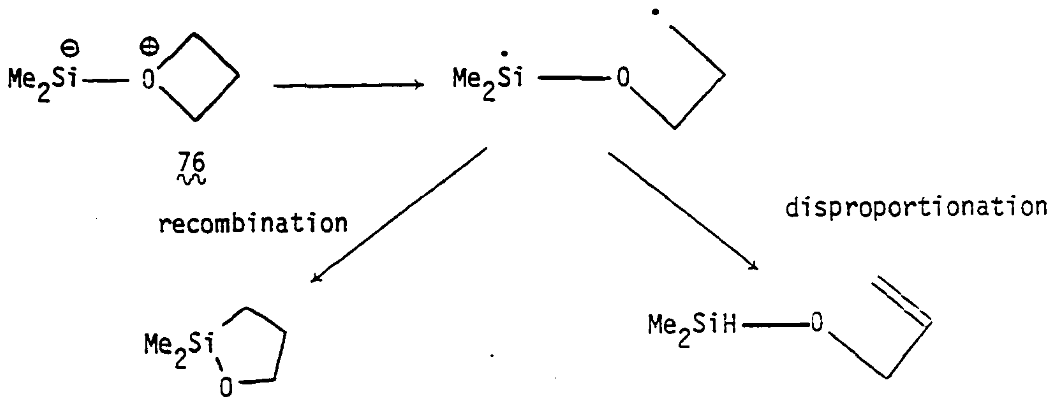
Support for this proposal was obtained from the results of reactions employing substituted oxetanes (Scheme 10). Thus, reaction of dimethylsilylene with 3,3-dimethyloxetane yields only oxasilacyclopentane 78. When 2,2-dimethyloxetane was used as the substrate, 79, 80, and 81 were obtained. Both 79 and 80 arise from 1,4-hydrogen abstractions, while 81 is consistent with ring opening of the dimethyl derivative of 76 to afford the more

Scheme 9

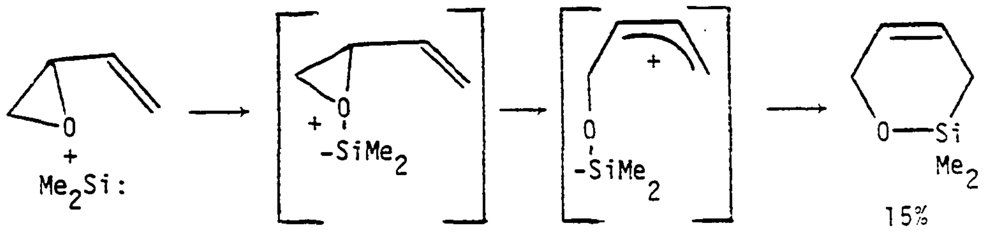


stable tertiary carbonium ion. Subsequent closure of this 1,5-zwitterion would give 81 regiospecifically. Finally, reaction of dimethylsilylene with 2-vinyloxetane yields 3-vinyloxasilacyclopentane 82 and oxasilacycloheptene 83. The formation of these products is consistent with silyl ylid fragmentation to an allylic carbonium ion-silyl anion zwitterion which closes either 1,5 or 1,7.

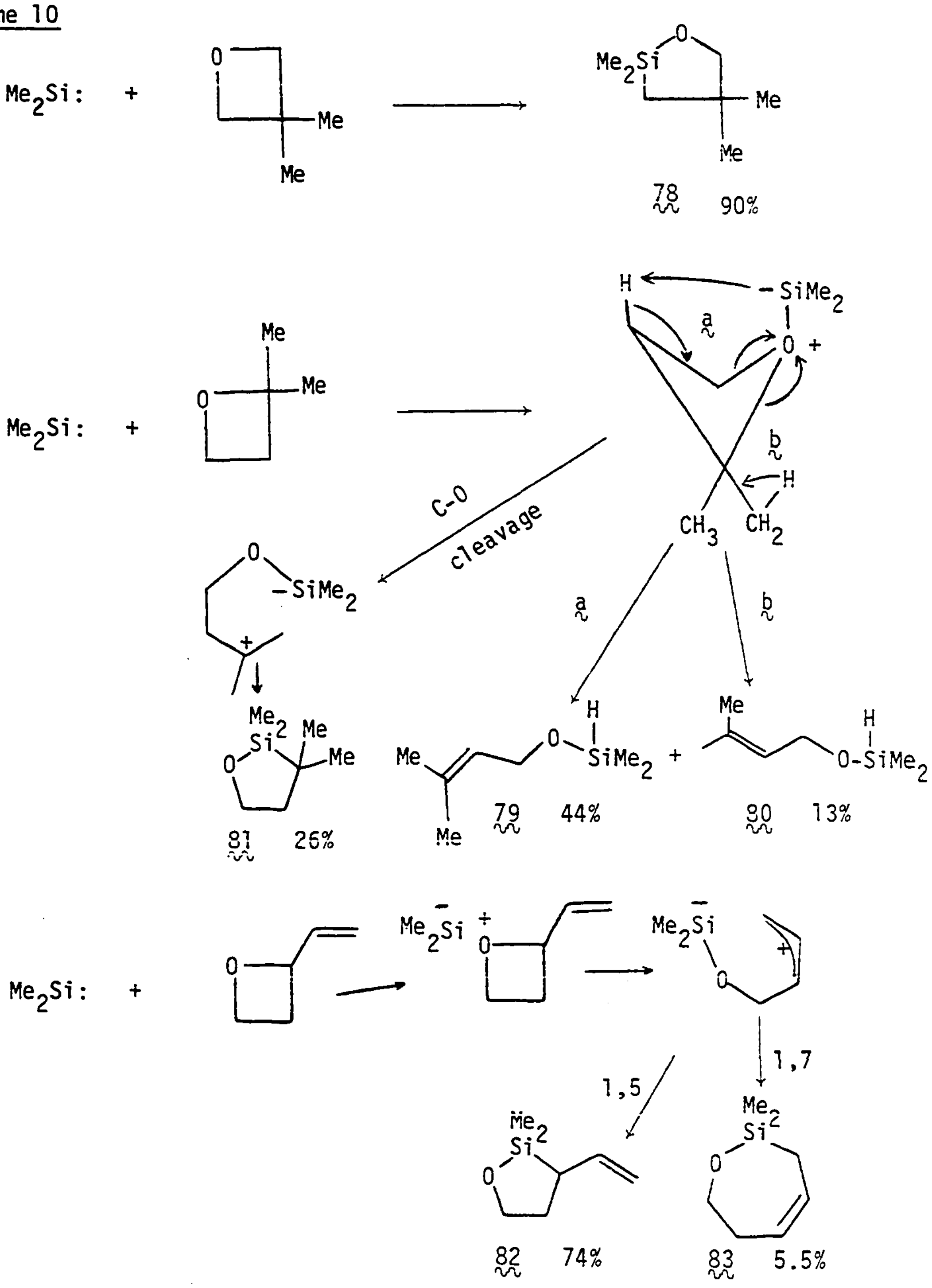
Gasper has recently pointed out that the results of Gu and Weber (112) are also consistent with decomposition of 76 to a diradical intermediate whose subsequent cyclization and disproportionation could give rise to the observed products (14). Therefore, the mechanism of the reaction of silylenes with epoxides must be regarded as unestablished.



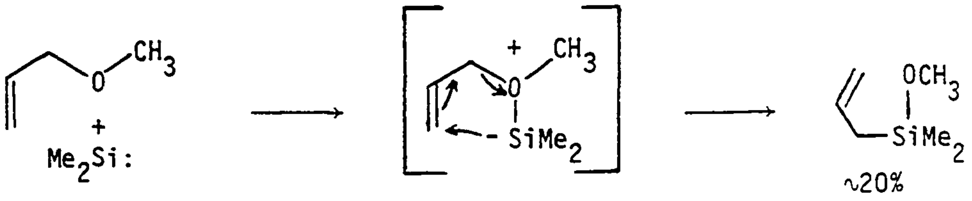
Tzeng and Weber have proposed a similar mechanism to that in Scheme 10 for the reaction of photogenic dimethylsilylene and 3,4-epoxy-1-butenes (113).



Scheme 10


Me2Si:
+
O
Me
Me2Si
78 90%
H
SiMe2
a
O +
b
CH3
CH2
C-O cleavage
+
79 44%
80 13%
81 26%
O-SiMe2
1,5
1,7
82 74%
83 5.5%

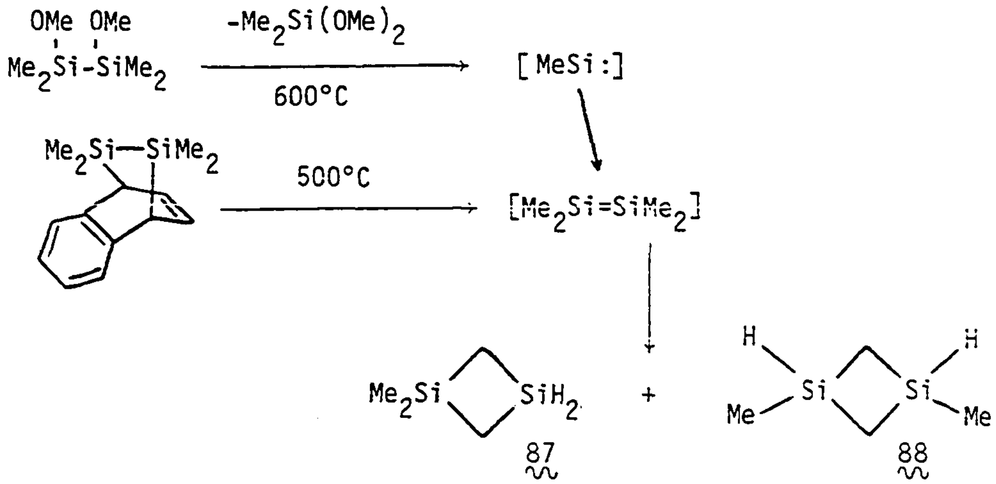
An analogous process, that involving initial formation of a silyl ylid, has also been used to explain the products of formal silylene insertion into the carbon-oxygen bond of methallylethers (114,115).



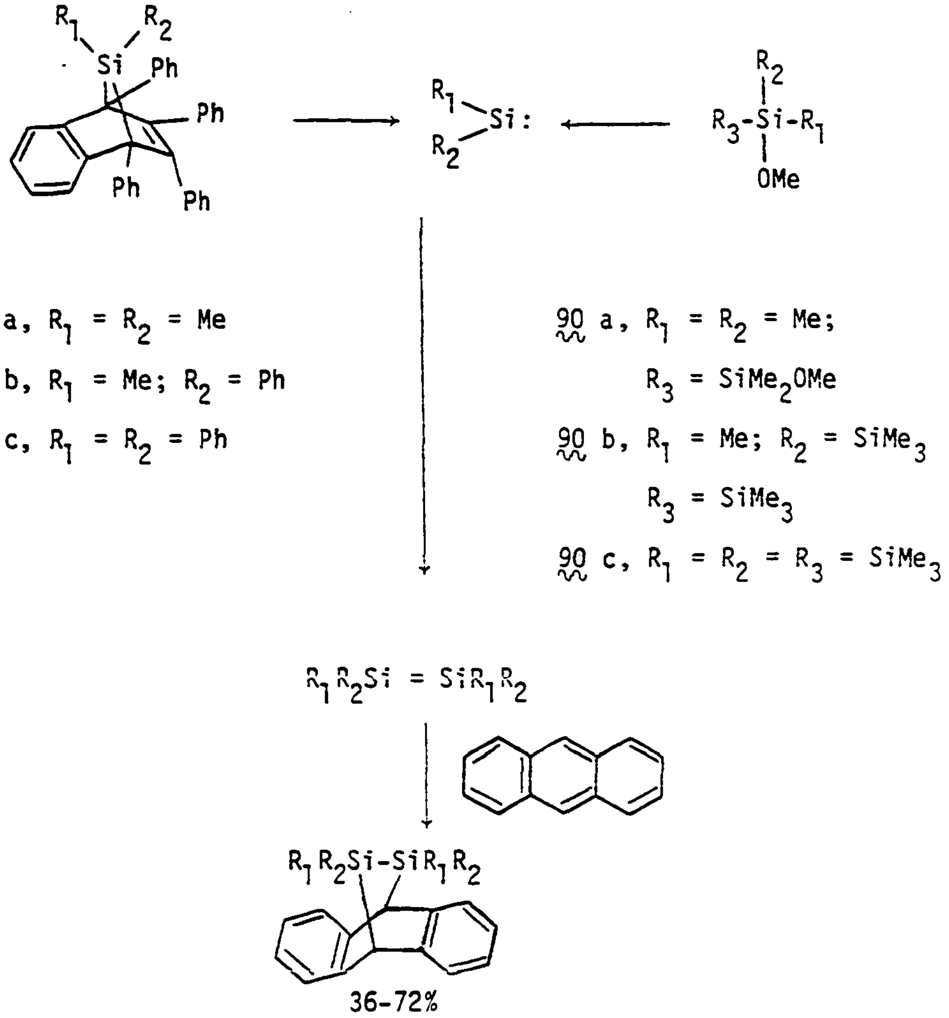
Silylene Dimerization

Conlin and Gaspar reported the first example of silylene dimerization to a disilene in 1976 (98). When dimethylsilylene was generated at 600°C in the gas-phase, 1,3-disilacyclobutanes 87 and 88 were obtained in yields of 12 and 14%, respectively (Scheme 11). It had been previously demonstrated that thermally generated tetramethyldisilene rearranged to 87 and 88 (116). Thus, strong evidence was provided for dimethylsilylene dimerization to tetramethyldisilene followed by rearrangement of this intermediate to 87 and 88.

Scheme 11



Nakadaira and coworkers have also provide exidence for silylene dimerization to disilenes (99). Thermal extrusion of various silylenes from 7-silanorbornadienes **89** a-c or alkoxydisilanes **90** a-c in the presences of excess anthracene afforded to expected anthracene Diels-Alder adducts in moderate to good yield.



89 a, $R_1 = R_2 = Me$

89 b, $R_1 = Me$; $R_2 = Ph$

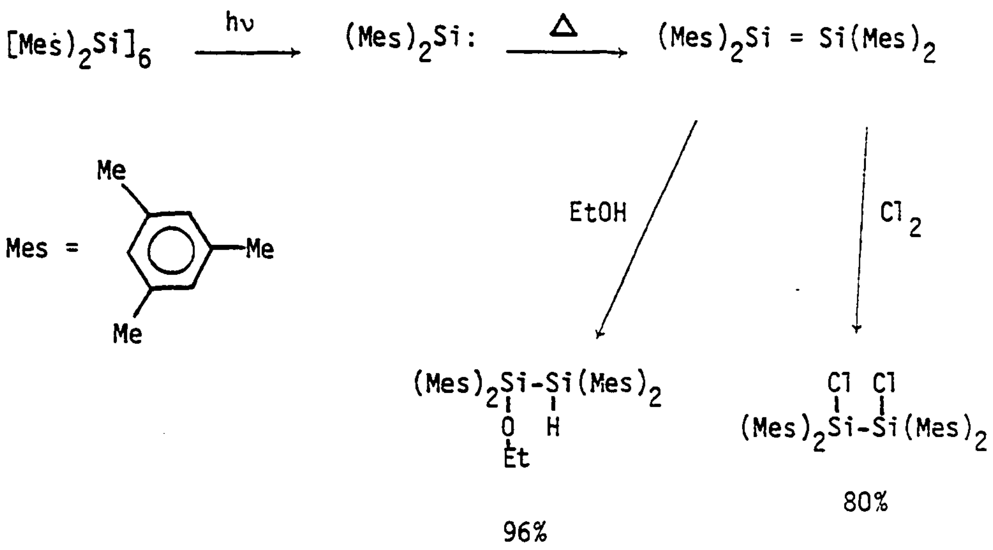
89 c, $R_1 = R_2 = Ph$

90 a, $R_1 = R_2 = Me$;
$R_3 = SiMe_2OMe$

90 b, $R_1 = Me$; $R_2 = SiMe_3$
$R_3 = SiMe_3$

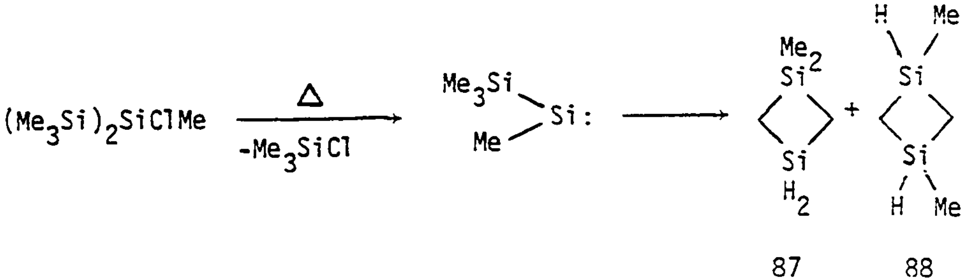
90 c, $R_1 = R_2 = R_3 = SiMe_3$

More recently, West has reported that photochemically generated dimesitylsilyene thermally dimerizes to tetramesityldisilene (117).



Silylene Rearrangements

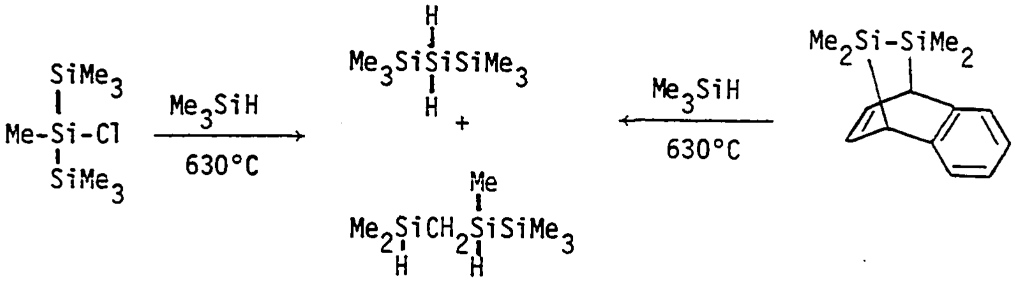
Prior to 1978, no confirmed examples of intramolecular silylene reactions existed. However, in 1978, Wulff and coworkers found that silylenes undergo rapid rearrangement in the gas phase (31). When trimethylsilylmethylsilylene was generated from the vacuum-flow gas-phase pyrolysis of 2-chloroheptamethyltrisilane, 1,3-disilacyclobutanes 87 and 88 were obtained in 28 and 15% yields, respectively.



87 88

Since these are the same products obtained from thermally generated tetramethyldisilene (116), the possibility of silysilylene isomerization to disilene was considered. However, on the basis of trapping experiments with trimethylsilane, it was found that tetramethyldisilene isomerizes to trimethylsilylsilylene (Scheme 12).

Scheme 12

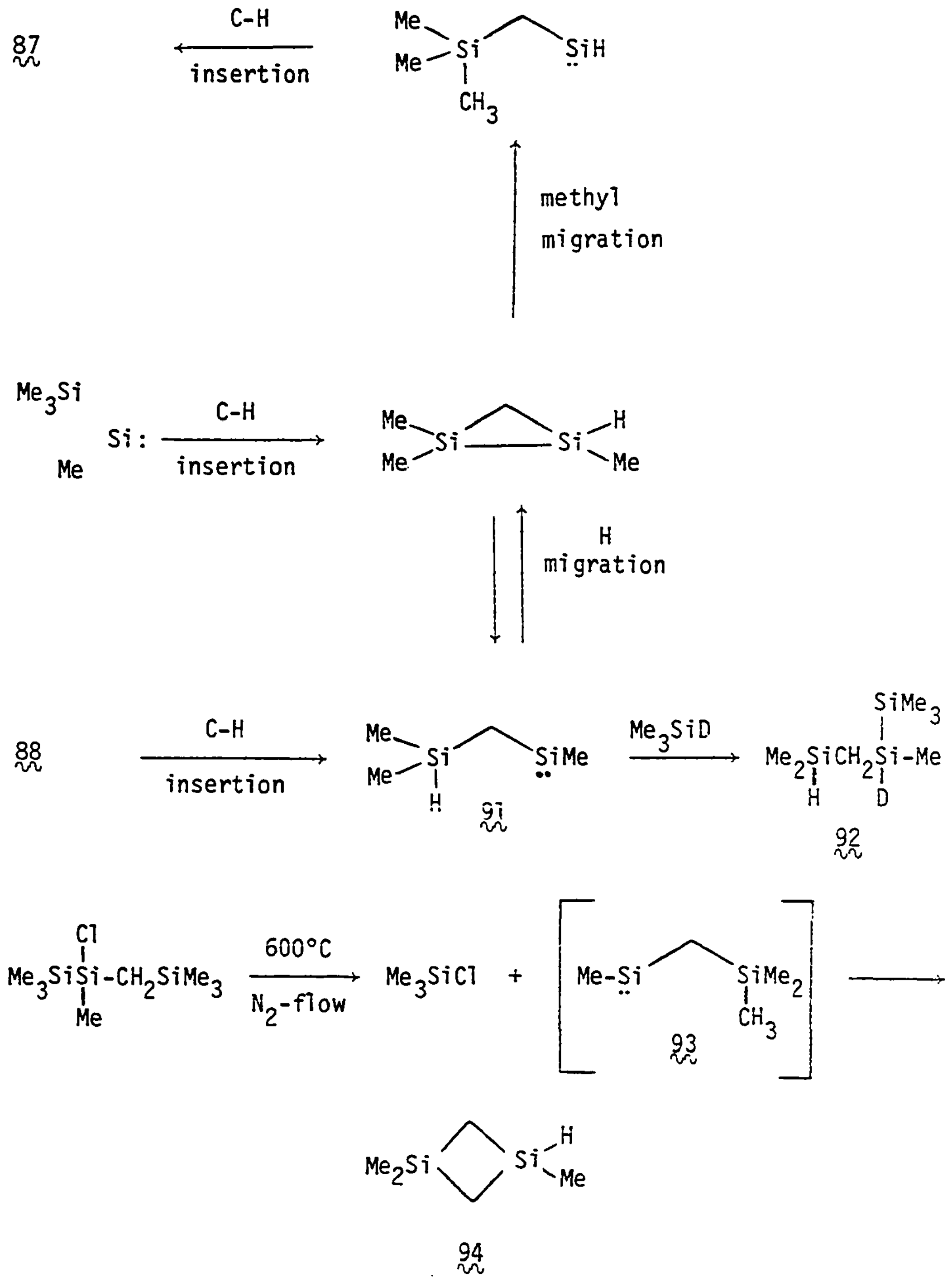


To explain the formation of 87 and 88, the following mechanism was proposed (Scheme 13). This proposal was supported by the finding that silylene 91 was trapped by Me_3SiD to afford 92. In addition, independent generation of silylene 93 led to the clean production of 1,3-disilacyclobutane 94.

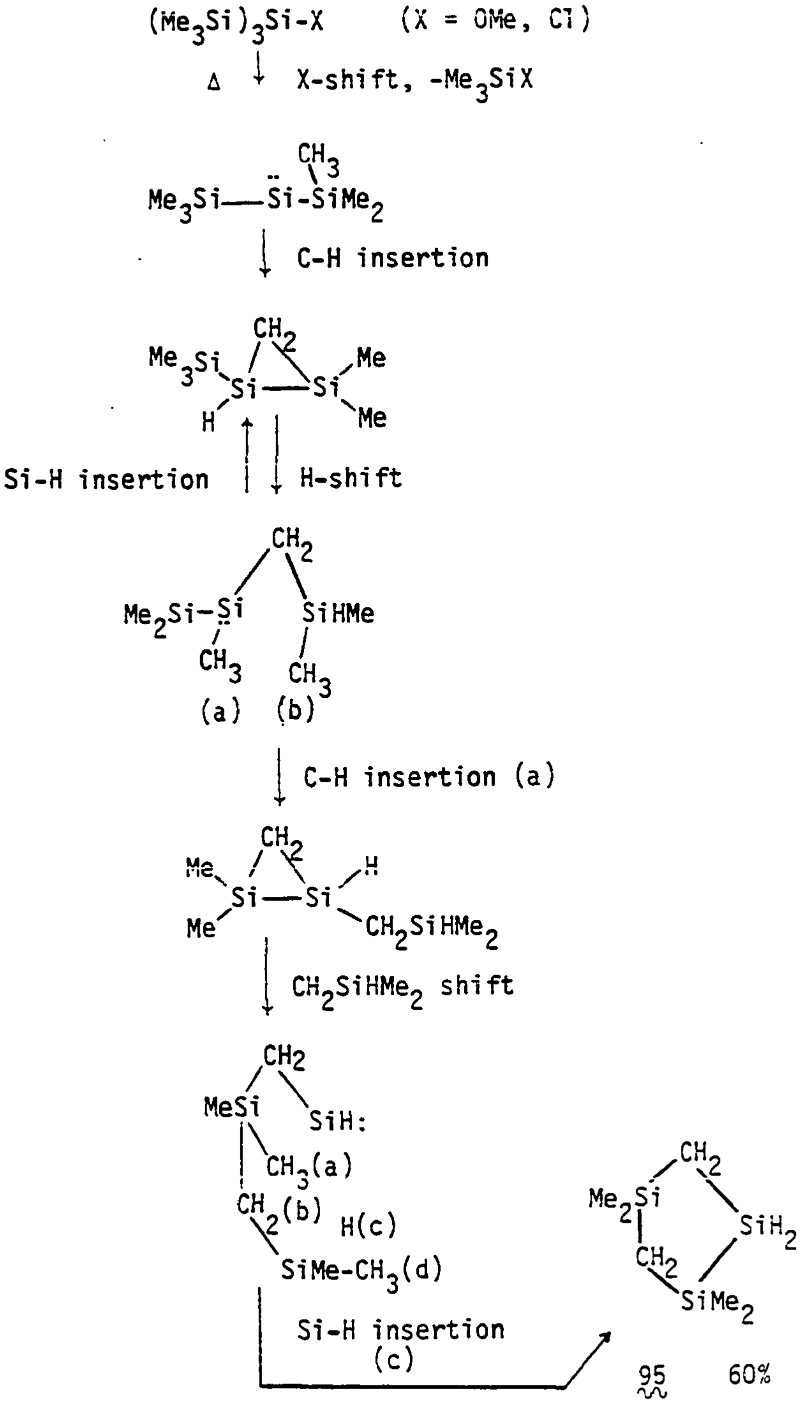
Recently, Chen, Cohen, and Gaspar have reported a similar rearrangement for bis(trimethylsilyl)silylene (118). Gas-phase vacuum-flow pyrolysis of tris(trimethylsilyl)methoxy- or chlorosilane gave 1,3-disilacyclopentane 95 in approximately 60% yield. Scheme 14 depicts the proposed mechanism for this reaction.

As discussed previously, dimethylsilylene has been suggested to isomerized to 1-methylsilaethylene twice in the intervening 19 years since its discovery (98,105). Recently, however, Conlin and Wood have obtained

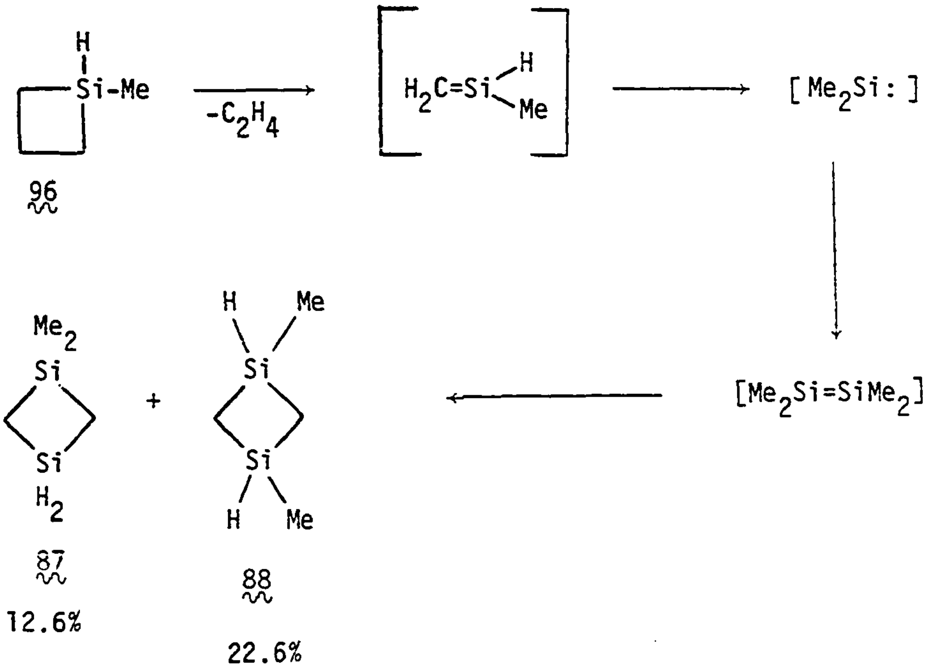
Scheme 13


87
C-H
insertion
Me
Me
Si
CH3
SiH
methyl
migration
Me3Si
Si:
Me
C-H
insertion
Me
Me
Si
Si
H
Me
H
migration
88
C-H
insertion
Me
Me
Si
H
SiMe
91
Me3SiD
SiMe3
Me2SiCH2Si-Me
H
D
92
Cl
Me3SiSi-CH2SiMe3
Me
600°C
N2-flow
Me3SiCl
+
Me-Si
SiMe2
CH3
93
Me2Si
Si
H
Me
94

Scheme 14


(Me3Si)3Si-X (X = OMe, Cl)
Δ
X-shift, -Me3SiX
C-H insertion
Si-H insertion
H-shift
(a)
(b)
C-H insertion (a)
CH2SiHMe2 shift
H(c)
Si-H insertion (c)
95
60%

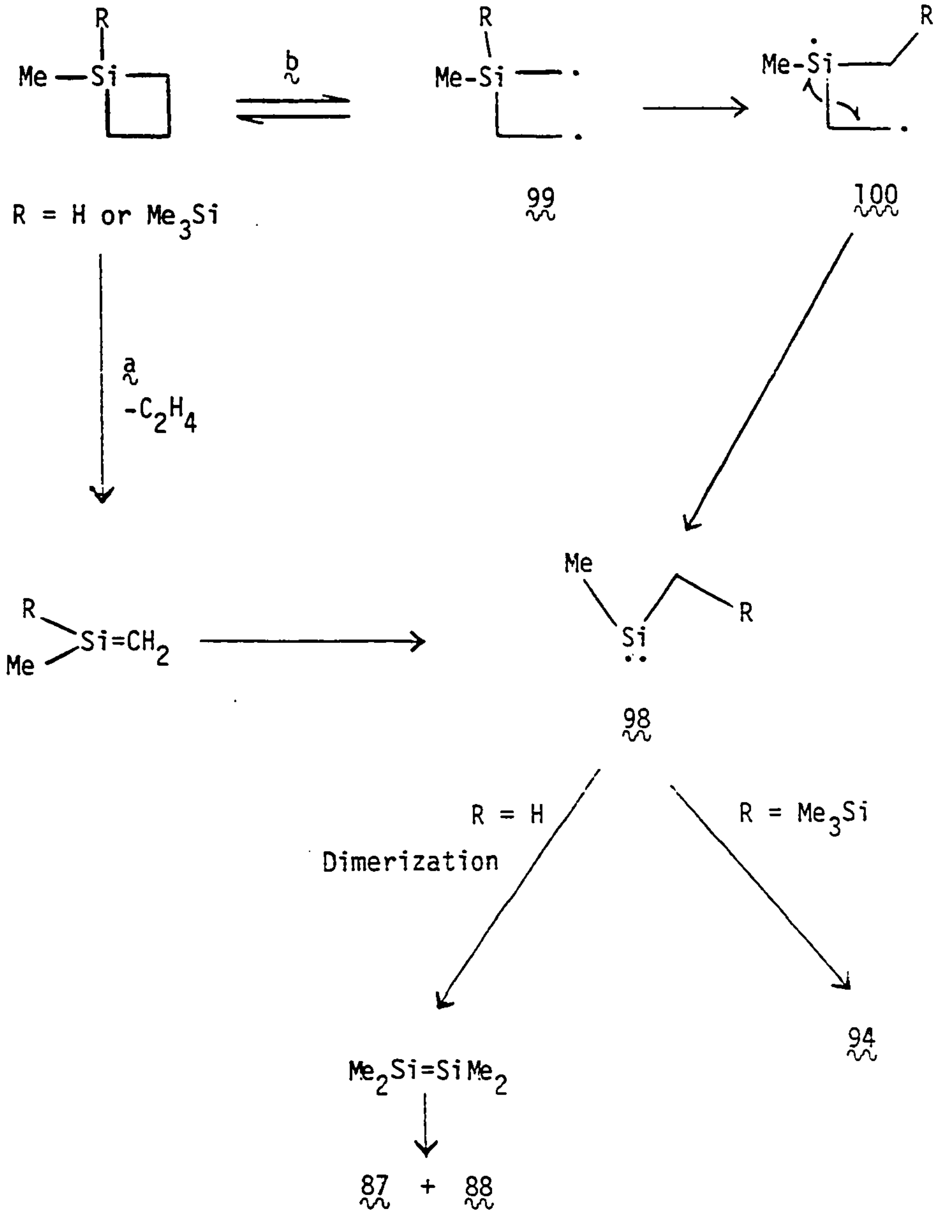
results which they interpret as evidence supporting the opposite isomerization; 1-methylsilaethylene rearranging to dimethylsilylene (119). Gas-phase flow-pyrolysis of silacyclobutane 96 led to the formation of 1,3-disilacyclobutanes 87 and 88; the same products obtained from dimethylsilylene dimerization under similar conditions (98). It was, therefore, proposed that 1-methylsilaethylene rearranges to dimethylsilylene under these conditions.



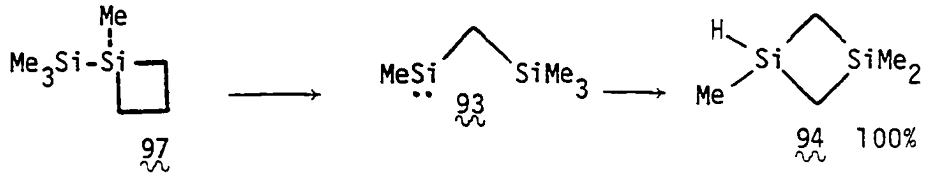
Support for this mechanistic proposal was obtained when copyrolysis of 96 in the presence of butadiene or trimethylsilane gave only products of dimethylsilylene trapping.

Similar results have been obtained by Barton and S. Burns (120). When trimethylsilylmethylsilacyclobutane (97) was flash-vacuum pyrolysed, 1,3-silacyclobutane 94 was obtained in essentially quantitative yield. The formation of 94 from 93 had been previously demonstrated (31); thus,

Scheme 15

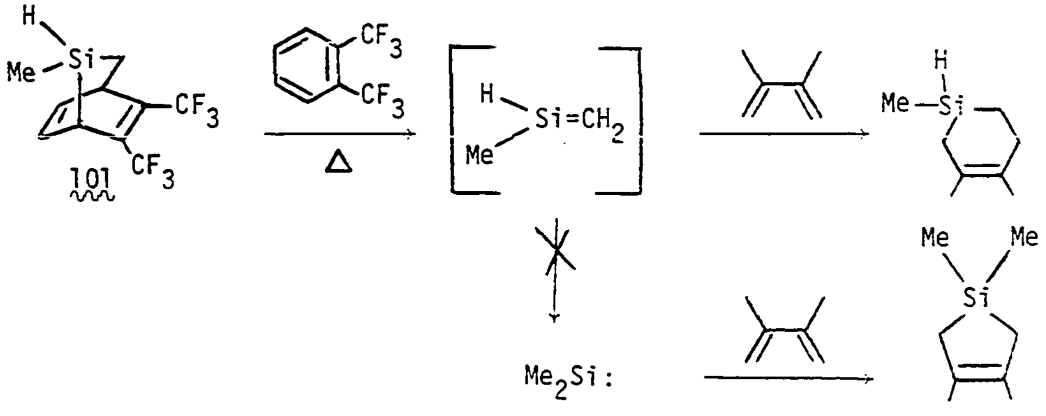

R = H or Me_3Si
b
99
100
a
$-C_2H_4$
98
R = H
Dimerization
R = Me_3Si
$Me_2Si=SiMe_2$
94
87 + 88

decomposition of 97 to 93 was strongly indicated.



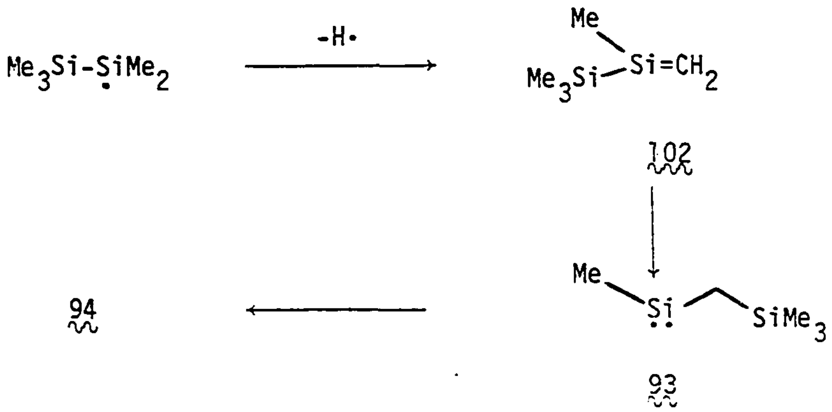
Barton and S. Burns (120) argued that two different mechanistic alternatives were consistent with the formation of 93 from 97; and by analogy Me_2Si: from 96 (Scheme 15). The first (path a), which is identical to that proposed by Conlin and Wood (119), involves silacyclobutane decomposition to a silene which rearranges to silylene 98. The second process (path b), proceeds by initial C-C bond homolysis to give diradical 99. Silacyclobutanes are known to undergo thermal decomposition largely through initial C-C, rather than Si-C, ring-bond homolysis (121). From 99 R migration from silicon to carbon gives 100 which upon loss of ethene yields 98.

That 98 (R=H) did not occur via path a was convincingly demonstrated when thermolysis of 101, a known silene generator (106), gave only 1-methylsilaethylene derived products. Thus, the claimed silene to silylene isomerization of Conlin and Wood (119) is now known to be false.

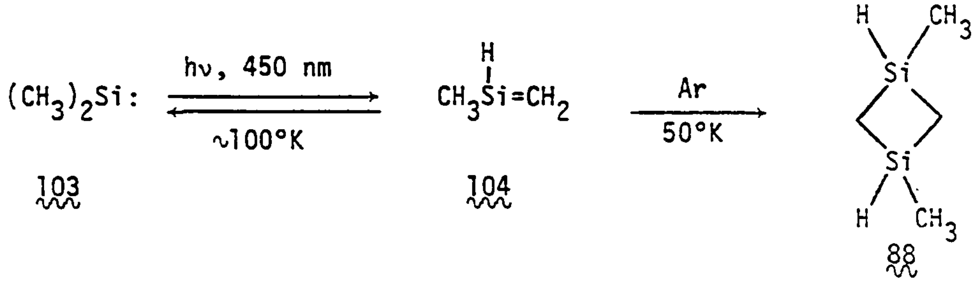


That silenes may in fact rearrange to silylenes has been suggest by Barton and coworkers for thermally generated 1-trimethylsilylsilene (122,123). When pentamethyldisilanyl radical was generated by flash-vacuum pyrolysis of allylpentamethyldisilane, octamethyltrisilane, or decamethyltetrasilane, disilacyclobutane **94** was obtained in 18, 20 and 21% yields, respectively. The key feature of the mechanism for the formation of **94** is isomerization silylsilene **102** to silylene **93** (Scheme 16). A more complete discussion of the mechanistic details of this reaction will be presented in the section on silyl radicals.

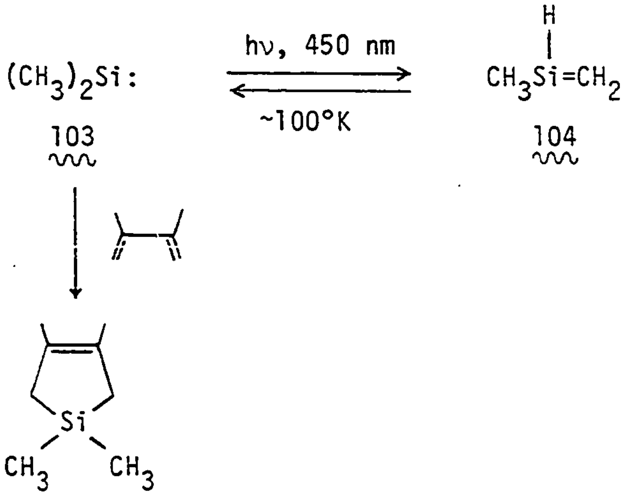
Scheme 16



In 1979, Drahnak, Michl, and West reported the first, and to date the only, direct spectroscopic observation of an organosilylene; dimethylsilylene (124). During the course of this investigation, it was observed that irradiation of the rigid solutions of dimethylsilylene caused the disappearance of the visible and I.R. absorption bands attributed to the silylene. On the basis of the appearance of a new electronic absorption band at 260 nm and a new IR band at 2186 cm^{-1}, it was suggested that dimethylsilylene was rearranging to 1-methylsilene upon irradiation.



Recently, these same authors have reported evidence to support their earlier claim (125). Irradiation at 450 nm of solid solutions of 103 produced new IR signals, which, by comparison to those reported for $Me_2Si=CHMe$ (26,27), were consistent with 104. More direct evidence for the presence of 104 was the finding that 88, the expected cyclodimer of 104, was obtained upon annealing of the irradiated matrices at 50°K. In contrast, when 104 was formed in a 3-methylpentane glass, containing 2,3-dimethyl-1,3-butadiene or methanol, and then annealed at 100°K, only products of dimethylsilylene trapping were obtained. It was, therefore, concluded that thermal reversion of 104 to 103 was likely at 100°K.



Silyl Radicals

Although the chemistry of silicon centered radicals began in the late 1930s with the generation of silyl (126) and trimethylsilyl (127) radicals, our present knowledge of these reactive intermediates is primarily based on studies that have been reported within the last two decades. In general, silyl radicals are known to undergo essentially all reactions that are typical of their carbon analogues. Thus, silyl radicals undergo recombination, disproportionation, abstraction, S_{H2}, and various rearrangement reactions. However, differences between silicon and carbon centered radicals do exist, thus, it should not be assumed that silyl radicals inevitably mimic their carbon counterparts.

In Table 3, the bond energies of various carbon and silicon compounds, as complied by Walsh (128), are shown. Many of these data are subject to considerable uncertainty, yet some general trends can be observed. The bond energies for silicon or carbon and hydrogen, methyl, and themself follow the same general pattern for both elements. In contrast, the bond energies for silicon and electronegative elements are substantially stronger than for carbon. More importantly, the silicon-silicon bond is one of the weakest bonds for M=Si.

On the basis of the data presented in Table 3, two important conclusions can be made. First, abstraction of hydrogen, rather than halogen, is favored for carbon radicals, whereas the opposite is true for silicon. Secondly, the strong bonds between silicon and electronegative atoms prevents the utilization of these compounds as sources of silyl radicals. For example, silylazo compounds of the type $R_3SiN=NSiR_3$ (129) or

Table 3. Bond-Dissociation Energies
$D(Me_3M\text{-}X)$ (kcal/mole) (128)

	M	
X	C	Si
H	92	90.3
Me	82	89.4
MMe_3	70	80.5
OH	91	128
Cl	80	113
Br	64	96
I	51	77
NHMe	80	100
SC_4H_9	77	99

$R_3SiN{=}NAr$ (130,131) do not serve as thermal sources of silyl radicals.

Other properties which lead to differences in the type and rate of free radical reactions of silicon compared to those of carbon are shown in Table 4, as compiled by Jackson (16). Examples of the effect of these properties will be given in the following sections where they are appropriate.

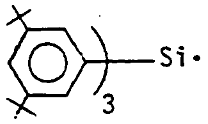
Structure and Stereochemistry of Silyl Radicals

Silyl radicals have been the subject of numerous ESR studies. The results of all the studies published to date are compiled in Table 5. Of particular interest are the large ^{29}Si isotopic hyperfine coupling

Table 5. ESR Data for Silyl Radicals

		Coupling Constants (G)			
Radical	g Value	α-H	β-H	^{29}Si	Ref.
$SiH_3\cdot$	2.006	8.1		266	132
	2.003			190	133
	2.0032	7.84			134
		7.96			135
	2.003	7.9		182	136
$SiD_3\cdot$	2.003	1.2(D)		182	136
$MeSiH_2\cdot$		11.82	7.98		135
	2.0032	12.11	8.21		134
	2.0032	11.8	8.0	181	137
$Me_2SiH\cdot$		16.99	7.19	183.05	135
	2.0031	17.29	7.30		134
Me_3Si			6.28	181.14	135
	2.0031		6.34	183	134
	2.0029		6.3	181	137
			6.32	172.5	138
			6.2	129	138
$Et_3Si\cdot$	2.0030		5.73		134
			5.69		135
$Cl_3Si\cdot$		12.4(Cl)		416	138
		13.4(Cl)		440	138
		13.1(Cl)		416	139

Table 5. (cont.)

Radical	g Value	Coupling Constants (G)			Ref.
		α-H	β-H	^{29}Si	
$Cl_2SiMe\cdot$	2.0041	13.0(Cl)		408	140
		11.4(Cl)		308	138
		10.5(Cl)		295	138
$ClSiMe_2\cdot$			5.2	215	138
			5.2	229	138
$F_3Si\cdot$	2.0003	136.6(F)		498	141
		138(F)		521	142
$F_2SiH\cdot$	2.0013	89.9(H)			141
		77.8(F)			
$FSiH_2\cdot$	2.0024	34.6(H)			141
		55.2(F)			
$FSiMe_2\cdot$	2.0022	65.26(F)	4.53		141
$F_2Si(OSiF_3)\cdot$		143.3(F)		556.7	142
$F_2Si(NMe_2)\cdot$		131.7(F)		361.7	142
$[Me_3Si)_2CH]_3Si\cdot$	2.0027		4.8	193	143
	2.0027	0.95 (*ortho*-H)	1.17 (*para*-H)		144
$Me_3SiSiMe_2\cdot$	2.0037		8.21	137	145
$(Me_3Si)_2SiMe\cdot$	2.0045		9.36	71	145
$(Me_3Si)_3Si\cdot$	2.0051			65	145

constants for all but the last two entries. The magnitude of these coupling constants indicates that the unpaired electron is occupied in an orbital of considerable 3s character. This implies that these radicals have a pyramidal structure. For the last two entries, the low value of the ^{29}Si coupling constants indicates that these species are essentially planar. It has been argued that this trend toward planarity with the substitution of a trialkylsilyl group for a hydrogen on silyl radical ($H_3Si\cdot$) is due to conjugative interactions of the unpaired electron with the β-silicon atoms and increased steric interactions (145). The electronegativity effects of the second silicon atom may also play a role in this trend toward planarity (145).

Table 4. Selected Properties of Silicon and Carbon

		Electronegativity		ΔH of Reaction (kcals/mole)	
Element	Covalent Radius (Å)	Allred-Rachow	Pauling	$H_3M\cdot$[a]	$H_2M:$[b]
C	0.77	2.50	2.55	99	94
Si	1.18	1.74	1.90	78	51

[a] For the reaction: $H_4M \longrightarrow H_3M\cdot + H\cdot$.

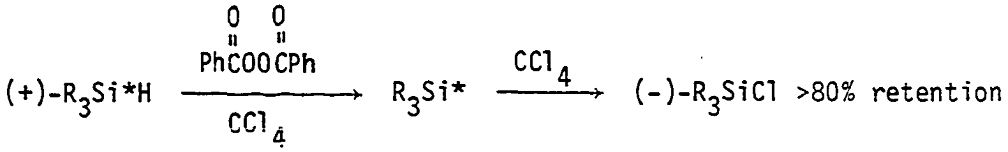
[b] For the reaction: $H_4M \longrightarrow H_3M: + H_2$.

Bennett and coworkers (134) and Krusic and Kochi (135) have suggested, on the basis of the increased α-proton coupling constants for the series $SiMe_NH_{3-N}$ (N=0-3), that replacing hydrogen atoms by methyl groups results in a flattening of the radicals. This suggestion is supported by the

CNDO-2 calculations of Réffy who found that the deviation from planarity decreases with methyl substitution on the silyl radical (146). However, the angle between the carbon-silicon bond and the plane of an assumed planar configuration was calculated to be the same for methylsilyl, dimethylsilyl, and trimethylsilyl radicals. Thus, the effect of methyl substitution does not appear to be additive.

In general, when free radicals are generated from optically active carbon atoms, such that the asymmetric carbon bears the unpaired electron, racemic products are formed. This behavior of carbon-centered radicals is in marked contrast to that of optically active silyl radicals.

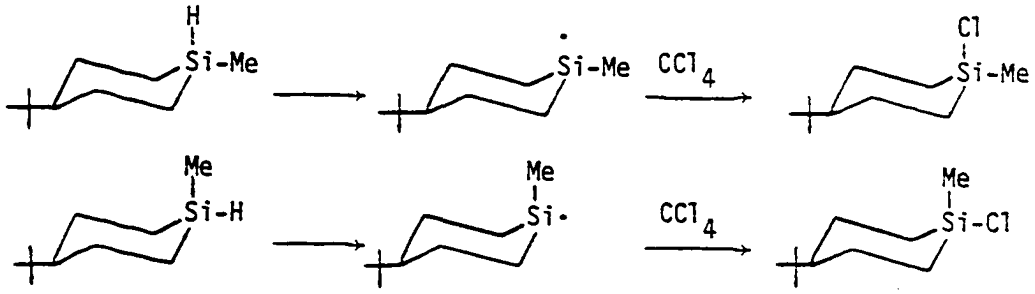
When (+)-1-naphthylphenylmethylsilane [(+)-R_3Si^*H] was heated at 80°C in a solution of carbon tetrachloride containing benzoyl peroxide, the resulting chlorosilane, (-)-1-naphthylphenylmethylchorosilane, was obtained in good yield with 80% retention of configuration (147).



$$(+)\text{-}R_3Si^*H \xrightarrow[CCl_4]{Ph\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}Ph} R_3Si^* \xrightarrow{CCl_4} (-)\text{-}R_3SiCl \;>80\%\ \text{retention}$$

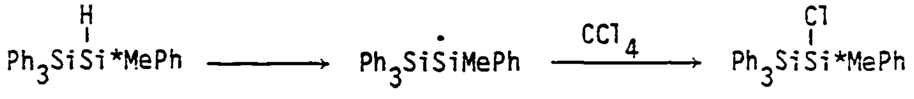
Similar results have been obtained when the 1-naphthylphenylmethylsilyl radical was generated in the presence of carbon tetrachloride, either by direct photolysis of (+)-R_3Si^*H (18) or by photolysis of the corresponding optically active acylsilane (148). For the latter reaction, 64% net retention was observed.

Silyl radicals produced by hydrogen abstraction from configurationally stable cis and trans-1-methyl-4-t-butylsilacyclohexanes also undergo chlorine abstraction from carbon tetrachloride in a stereospecific manner (18).



The results of these stereochemical studies are in good agreement with the results of ESR experiments, and provide further support for the pyramidal structure of silyl radicals.

ESR studies have shown that silyl-substituted sily radicals are more nearly planar, and thus, would be expected to lose their stereochemical integrity more rapidly than trialkylsilyl radicals. This prediction was verified when it was found that optically active disilane 105 reacted, either thermally or photochemically, with benzoyl peroxide in the presence of carbon tetrachloride to yield chlorodisilane 106 with only 10% retention (18).



$$\mathrm{Ph_3Si\overset{H}{Si}{}^{*}MePh} \longrightarrow \mathrm{Ph_3Si\overset{\bullet}{Si}MePh} \xrightarrow{CCl_4} \mathrm{Ph_3Si\overset{Cl}{Si}{}^{*}MePh}$$

105 106

Thermal Methods of Silyl Radical Generation

Based on the data compiled in Table 3, the thermolysis of disilanes should provide a convenient source of silyl radicals. This is found to be the case for hexamethyldisilane, which decomposes in the gas (149) and condensed (150,151) phase to trimethylsilyl radicals.

In marked contrast, not only to hexamethyldisilane, but to hexaarylethanes as well, hexaaryldisilanes do not decompose to the corresponding silyl radicals. For example, both hexaphenyldisilane (M.P. 361-362°C) and hexa-p-biphenyldisilane (M.P. 432-434°C) are stable, crystalline solids that do not decompose when heated above their melting points (152).

Further evidence that the thermolysis of disilanes is not generally useful for the generation of silyl radicals has been reported by Sakurai and Hosomi (153). When unsymmetrical disilanes of the type $RSiMe_2SiMe_3$ (R=n-Pr, cyclo-Pr, Ph, or $PhCH_2$) were heated at 190°C for extended periods of time, a reversible redistribution reaction was observed. That silyl radicals were not involved in this redistribution was demonstrated by the lack of phenyl-silyl exchange when R=Ph, and by the absence of chlorosilanes when the reaction was conducted in the presence of chlorobenzene, under otherwise identical conditions. Under similar conditions, hexamethyldisilane is known to decompose to $Me_3Si\cdot$ (151).

$$RSiMe_2SiMe_2 \xrightleftharpoons{\Delta} RSiMe_2SiMe_2R + Me_3SiSiMe_3$$

Another characteristic of disilanes that limits their utility as silyl radical generators is their ability to thermally α-eliminate. Thus, as discussed previously, disilanes of the type $RSiMe_2SiMe_3$ (R=H, halogen or alkoxy) thermally decompose to Me_2Si: and $RSiMe_3$. This α-elimination process is due in part to the ability of silicon to form relatively stable divalent species (see Table 4).

Although the bond-dissociation energies listed in Table 3 suggest that the Si-H bond is stronger than the Si-C bond, thermolysis of trialkylsilanes is known to yield trialkylsilyl radicals by homolysis of the Si-H bond.

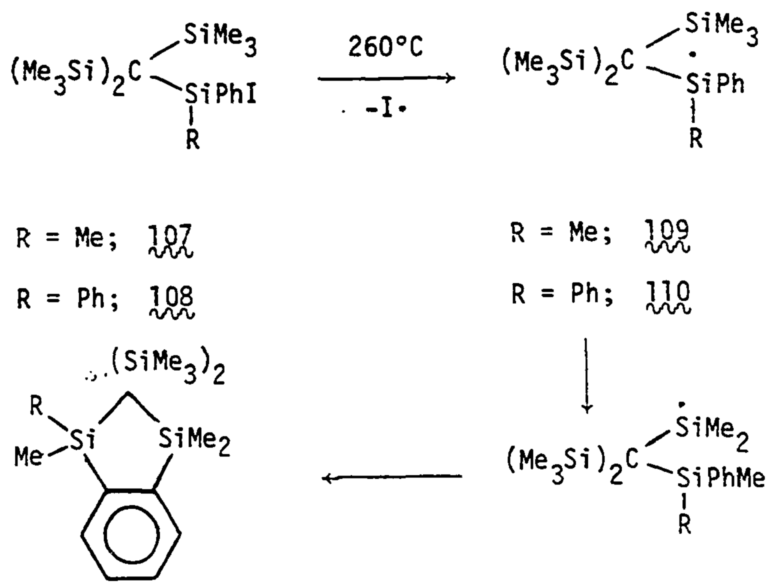
From a rate study of the pyrolysis of $MeEt_2SiH$, Et_3SiH, Pr_3Si-H, and i-Bu_3SiH, Mares and Chvalovsky concluded that the primary mode of thermal decomposition was cleavage of the Si-H bond, yielding the corresponding silyl radicals (154). The activation energies for these reactions were estimated to be 24-41 kcal/mole, and on this basis, the literature value for the bond-dissociation energy of the Si-H bond was suggested to be high. However, Sakurai has suggested that these values may imply that the decomposition proceeds via a chain mechanism or through initial silylene formation (18).

Further evidence for the thermal cleavage of Si-H bonds has been reported by Davidson and Lambert (155,156). When trimethylsilane was pyrolysed in the gas-phase in the temperature range of 670 to 758°C, the formation of $Me_2Si\cdot$ was confirmed on the basis of kinetic results and product analysis. However, a competing Si-C bond homolysis affording $MeSiH\cdot$ was also found. Due to this competition between Si-H and Si-C homolysis, this technique has been seldom used.

Recently, Eaborn and Sofa have found that pyrolysis of tetrasilylmethanes 107 and 108 (Scheme 17) afforded products that were most consistent with initial Si-I homolysis to afford radicals 109 and 110 (157). To date, however, no systematic study of the utility of this method of silyl radical production has appeared. Thus, its generality remains to be established.

Tetraalkylsilanes are known to thermally decompose to afford complicated product mixtures that involve free radicals of various types. For example, Fritz (158) obtained more than forty products from the thermolysis of tetramethylsilane at 650°C. Although all of these products have been rationalized as arising from free radicals, both silicon- and carbon-centered, the lack of selectivity in pyrolysis of this type severely limits the utility of this method.

Scheme 17



R = Me; 107

R = Ph; 108

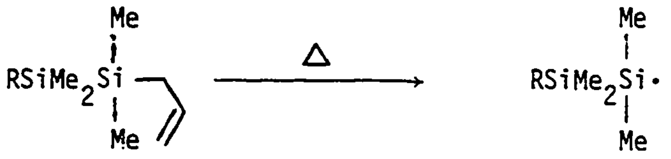
R = Me; 109

R = Ph; 110

+ other products

In contrast to the lack of selectivity observed by Fritz, recently, Davidson and Wood have found that pyrolysis of allyltrimethylsilane results in the exclusive formation of trimethylsilyl radical by rupture of the silicon-allyl bond (159). No evidence for Si-CH_3 bond rupture was found. From a kinetic analysis of this reaction, the bond dissociation energy of the silicon-allyl bond was determined to be ca. 74 kcal/mole.

Similar results have been found by Barton and Jacobi who reported clean production of disilanyl radicals by thermal cleavage of various disilanyl-allyl bonds (122).



R = Me, benzyl, or allyl

Photochemical Production of Silyl Radicals

In general, photochemical methods of silyl radical generation are more selective, and thus of greater utility, than thermal methods.

In 1966, Brook and Peddle reported that photolysis of bis(triphenylsilyl)ketone afforded hexaphenyldisilane (160). It was suggested that the product of this reaction was formed by geminate coupling of triphenylsilyl radicals that arose from starting material by a Norrish type I cleavage.

$$(Ph_3Si)_2CO \xrightarrow{h\nu} Ph_3Si\cdot + Ph_3SiCO\cdot$$

$$Ph_3SiCO\cdot \longrightarrow Ph_3Si\cdot + CO$$

$$2Ph_3Si\cdot \longrightarrow Ph_3SiSiPH_3$$

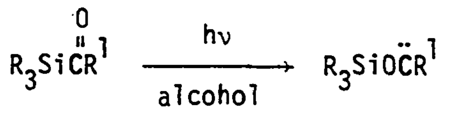
That silyl radicals are produced by photolysis of acylsilanes has been confirmed by Brook and coworkers (161). Thus, photolysis of various acylsilanes in carbon tetrachloride afforded the corresponding chlorosilanes in high yield.

$$R_3SiCOR^1 \xrightarrow[CCl_4]{h\nu} \underset{>80\%}{R_3SiCl}$$

R	R^1
Me	Et
Et	Me
n-Pr	Me
n-bu	Me
Me	Ph

Additionally, acetyltriphenylsilane and phenylacetyltriphenylsilane yield silyl radical derived products when irradiated in hexane (162).

In contrast, irradiation in alcoholic solvents leads to isomerization of the acylsilane to the corresponding siloxycarbene (163,164). This reaction, a 1,2-silyl migration from carbon to oxygen, is particularly facile for cyclic acylsilanes which yield siloxycarbene products even in hydrocarbon solvents (165).



$$R_3Si\overset{O}{\overset{\|}{C}}R^1 \xrightarrow[\text{alcohol}]{h\nu} R_3SiO\ddot{C}R^1$$

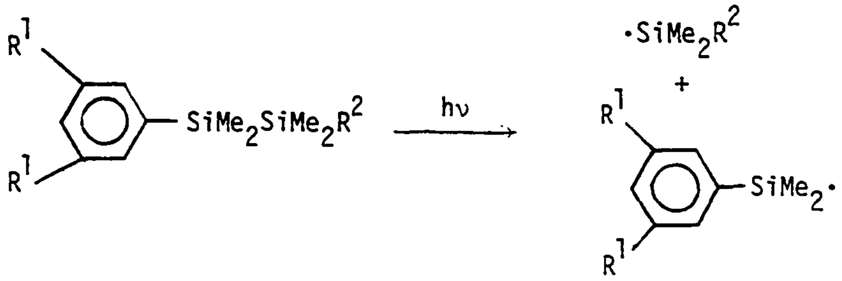
Despite the solvent limitations and the apparent utility of only acyclic acylsilanes, this method of silyl radical generation appears quite general. It is thus surprising, especially in view of the ease of preparation of acylsilanes (166,167), that this technique has been little utilized.

Another method of silyl radical generation is the photolysis of bissilylmercurials. Photolysis of bis(trimethylsilyl)mercurial has been demonstrated to produce trimethylsilyl radical by trapping with olefins (168) and aromatic compounds (169,170). The trichlorosilyl radical has also been prepared by photolysis of the corresponding mercurial (171). Although a large number of bis(triorganosilyl)mercurials are known (172), the difficulties associated with their preparation and purification have limited the utility of this method.

Direct U.V. photolysis of alkylhydrosilanes, utilizing the more common 2537Å Hg lamp as a light source, does not lead to the production of silyl radicals, due to the lack of a chromophore. When 147Å irradiation is employed (a frequency for which a suitable chromophore exists in alkylhydrosilanes), direct decomposition to a silene occurs, rather then decomposition to a silyl radical (173).

In contrast, 2537Å irradiation of arylhydrosilanes has been shown to yield silyl radicals (174). Thus, U.V. irradiation of diphenylsilane in the temperature range of 70 to 130°C was found to afford the same products in approximately the same ratio that were obtained under di-t-butyl peroxide catalyzed conditions.

More recently, Sakurai and coworkers have found that irradiation of aryldisilanes results in homolysis of the silicon-silicon bond affording the corresponding silyl radicals (175).



R^1	R^2
H	Me
t-Butyl	Me
H	F
H	O-t-butyl

The most commonly employed method of photochemical silyl radical formation is gas-phase mercury photosensitization. Nay and coworkers demonstrated the utility of this technique in a study of the sensitized photolysis of methyl-, dimethyl-, and trimethylsilane (176). In each case, only Si-H, as opposed to C-H, abstraction was found. Pollock and coworkers found this technique to be useful for the generation of the disilanyl radical when disilane was irradiated in the presence of mercury vapor (177).

$$H_3SiSiH_3 \xrightarrow[Hg]{h\nu} H_3SiSiH_2\cdot + \cdot H$$

Mercury-sensitized photodissociation of silicon-silicon bonds has also been observed (178). When a mixture of symmetrical mixed fluorodisilanes, which contained no Si-H bonds, were irradiated in the presence of mercury vapor, essentially quantitative formation of asymmetric disilanes were obtained.

$$F_3SiSiF_3 + FSiMe_2SiMe_2F \xrightarrow[Hg]{h\nu} F_3SiSiMe_2F \quad \sim 100\%$$

That this redistribution occurred via the intermediacy of silyl radicals, as opposed to a metathesis type process, was demonstrated by trapping the resulting silyl radicals with nitric oxide.

Acetone (179) and benzophenone sensitized (180,181) photolysis of hydrosilanes also afford silyl radicals. However, since carbonyls are excellent traps for silyl radicals (see below) these techniques are of limited utility.

Photodissociation of silicon-iodine bonds is a technique that may have general applicability to the generation of silyl radicals. Chen and coworkers have found that U.V. irradiation of triethylsilyl iodide in the presence of excess alkyl chlorides, or bromides, affords triethylsilyl chloride, or bromide, in good to excellent yields (182). Since triethylsilyl iodide shows significant absorption in the region 2200 to 2800Å and silyl radicals are known to abstract chlorine from alkyl chlorides (see below) the following chain mechanism was concluded to be most consistent with the experimental data.

$$Et_3SiI \xrightarrow{h\nu} Et_3Si\cdot + I\cdot$$

$$Et_3Si\cdot + RCl \longrightarrow Et_3SiCl + R\cdot$$

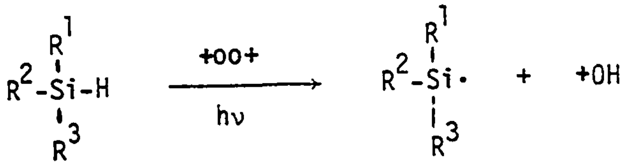
$$R\cdot + Et_3SiI \longrightarrow Et_3Si\cdot + RI$$

Silyl Radicals by Hydride Abstraction

With the possible exception of mercury photosensitized cleavage of silyl hydrides, the most commonly employed method of silyl radical generation is by treatment of the corresponding hydride with an organic initiator such as di-t-butyl peroxide. These abstractions can be promoted either photochemically or thermally.

A partial list of the silyl radicals that have been generated by U.V. irradiation of solutions of the corresponding silyl hydride and di-t-butyl peroxide is given below to illustrate the generality of this method.

Thermolysis of silyl hydrides in the presence of di-t-butyl peroxide, benzoyl peroxide, or phenylazotriphenylmethane has also been shown to afford silyl radicals (183).



$$R^2{-}\overset{R^1}{\underset{R^3}{Si}}{-}H \xrightarrow[h\nu]{+OO+} R^2{-}\overset{R^1}{\underset{R^3}{Si}}\cdot \quad + \quad +OH$$

R^1	R^2	R^3	Ref.
H	H	H	135
Me	H	H	135
Me	Me	Me	135
Et	Et	Et	182
Ph	Ph	Ph	182
OEt	OEt	OEt	182
Cl	Cl	Cl	182
Ph	Ph	H	182
Ph	H	H	182
Me	Ph	Ph	182
Me	Me	Ph	182
Me	OEt	OEt	182
Me	Me	F	182
Me	Me	Cl	182
Me	Cl	Cl	182
Me	Me	$OSiMe_2H$	182
Me	Me	$NHSiMe_2H$	182

Nelson and coworkers have studied the efficiency of various initiators in catalyzing the free radical redistribution of diphenylsilane (174). Based on the extent of redistribution of diphenylsilane, when heated at

130°C in the presence of di-t-butyl peroxide, 2,5-dimethyl-2,5-di-t-butyl peroxyhexane, 2,2-azo-bis(isobutrirylnitrile), t-butyl perbenzoate, or benzoyl peroxide, under otherwise identical conditions, it was found that di-t-butyl peroxide was the most efficient catalyst.

Di-t-butyl peroxide has been the most commonly employed catalyst under either photochemical or thermal conditions.

Two final methods of silyl radical generation, electron-transfer reactions and gama irradiation of hydrosilanes, are known. The electron-transfer technique has been adequately discussed by Sakurai (18) and therefore will not be presented here. Gama irradiation of hydrosilanes has been seldom used, with the exception of Aloni and coworkers (184,185), and will also not be discussed due to its limited utility.

Halogen Abstraction by Silyl Radicals

The first report of halogen abstraction by silyl radicals was that of Curtice and coworkers (186). When triphenylsilane and chlorobenzene were heated at 80°C in the presence of di-t-butyl peroxide, triphenylchorosilane and biphenyls were obtained.

$$Ph_3SiH + \underline{t}\text{-}BuO\cdot \longrightarrow Ph_3Si\cdot + \underline{t}\text{-}BuOH$$

$$Ph_3Si\cdot + ClC_6H_5 \longrightarrow Ph_3SiCl + \cdot C_6H_5$$

$$\cdot C_6H_5 + \cdot C_6H_5 \longrightarrow (C_6H_5)_2$$

Subsequently, Haszeldine and Young reported the photoreduction of alkyl halides to alkanes by trichlorosilane in the liquid phase (187). This reaction was proposed to occur via a free radical chain mechanism that was initiated by photodissociation of the alkyl halide. Since silicon forms stronger bonds to halogen and weaker bonds to hydrogen than carbon, the two propagation steps are exothermic and provide the driving force for this reaction.

$$\begin{array}{lll} RCl \xrightarrow{h\nu} R\cdot \ \cdot Cl & & \text{initial step} \\ R\cdot + Cl_3SiH \longrightarrow RH + Cl_3Si\cdot & & \\ & & \text{propagation steps} \\ Cl_3Si + RCl \longrightarrow Cl_4Si + R\cdot & & \end{array}$$

Kerr and coworkers (188) and Cadman and coworkers (189) have studied the photochemically initiated gas-phase reaction of alkyl chlorides and bromides with trichlorosilane, and have measured the relative rates of reactivity for various halides to that of methyl chloride. It was found that the rate of bromine abstraction was greater than that for chlorine ($k(CH_3Br)/k(CH_3Cl) = 76.3$ at 275°C), and that the order of reactivity for various alkyl halides was tertiary > secondary > primary. Similar results have been found for trimethylsilyl radical under identical conditions (190).

Nagai and coworkers have studied the relative rates of halide abstraction from various alkyl halides by triethylsilane or phenyldimethylsilane in solution at 80°C catalyzed by benzoyl peroxide (191,192). On the basis of competitive experiments, the following orders of reactivities were determined:

$$Br>Cl>F$$

$$RCCl_3>RCCl_2H>RCClH_2 \text{ (R=H, halogen, alkyl)}$$

$$\text{tertiary C-X}>\text{secondary C-X}>\text{primary C-X}$$

Similar results were obtained when triethylsilyl radical was generated photochemically from triethylsilyl iodide (193).

In addition, Nagai and coworkers (191) studied the relative rates of chlorine abstraction from the trichloromethyl group of $RCCl_3$ compounds ($R = Me, H, CH_2Cl, CHCl_2, CCl_3$ and Cl). With the exception of chloroform itself, the data obtained correlated well with Taft's σ^* constants; a ρ^* value of +0.26 was determined for $PhMe_2Si\cdot$, and a ρ^* of +0.29 was found for $Et_3Si\cdot$. The positive signs of these reaction constants indicate that the silyl radicals are nucleophilic, and are therefore in keeping with the electropositive nature of silicon.

More recently, Bowles, Hudson, and Jackson have extented this reactivity sequence to include α-carbonyl, allyl, proparagyl, benzyl, and cyanomethyl halides (194). Utilizing irradiation of a mixture of di-t-butyl peroxide, triethylsilane, and various organic halides, the following relative reactivity sequence was found:

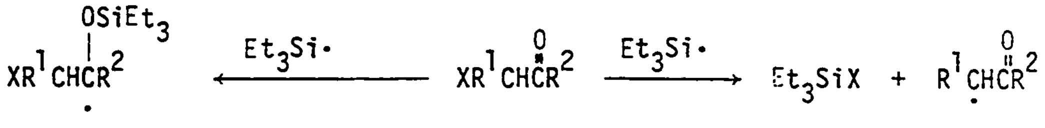
$$\begin{aligned} & \text{cyanomethyl} > \text{benzyl} \approx \text{proparagyl} \approx \text{allyl} \\ > \; & \cdot CH_2CO_2Et \approx \text{acetonyl} > \text{tertiary} > \text{secondary} \\ > \; & \text{primary} \end{aligned}$$

Of particular interest, was the finding by these authors that triethylsilyl radical abstracted bromine or chlorine from α-halocarbonyls rather than attacking the carbonyl oxygen (see Scheme 18). As will be presented later, silyl radical attack at a carbonyl oxygen is a very facile reaction.

Cooper has studied the selectivity of chlorine abstraction from n-hexyl chloride and cyclohexyl chloride by a series of silyl radicals - $Me_nCl_{3-n}Si\cdot$ (n=0 to 3) - generated by photosensitization of the corresponding silyl hydrides (195). The selectivity of the silyl radical was found to decrease with progressive substitution of methyl groups for chlorine.

This was interpreted as a progressive reduction in the reactivity of the silyl radicals; $Me_3Si\cdot > Me_2ClSi\cdot > MeCl_2Si\cdot > Cl_3Si\cdot$.

Scheme 18

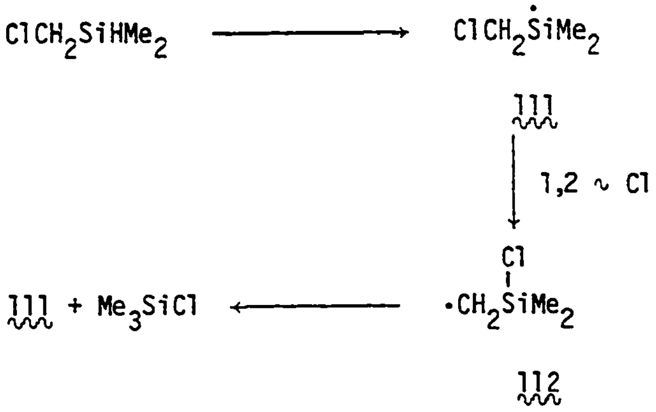


$$XR^1\underset{\bullet}{C}H\overset{OSiEt_3}{\overset{|}{C}}R^2 \xleftarrow{Et_3Si\cdot} XR^1CH\overset{O}{\overset{\|}{C}}R^2 \xrightarrow{Et_3Si\cdot} Et_3SiX + R^1\underset{\bullet}{C}H\overset{O}{\overset{\|}{C}}R^2$$

X	R^1	R^2
Cl	H	Me
Cl	H	OMe
Br	Et	OEt

Although abstraction of halogens by silyl radicals has been known for over twenty years, it has only been recently that absolute rate constants for several examples of these reactions have been determined (196). When triethylsilyl radical was generated by laser flash photolysis of solutions of triethylsilane and di-t-butyl peroxide containing benzyl bromide, benzyl chloride, n-pentyl bromide, or n-pentyl chloride, the rate constants for halogen abstraction were determined to be 1.4×10^9, 1.8×10^7, 5.5×10^8, and $2.6 \times 10^5\ M^{-1}\ sec^{-1}$ at 30°C, respectively. Additionally, the rate constant for the reaction of t-butoxy radicals and triethylsilane to yield triethylsilyl radical was found to be $6.0 \times 10^6\ M^{-1}\ sec^{-1}$ at 25°C.

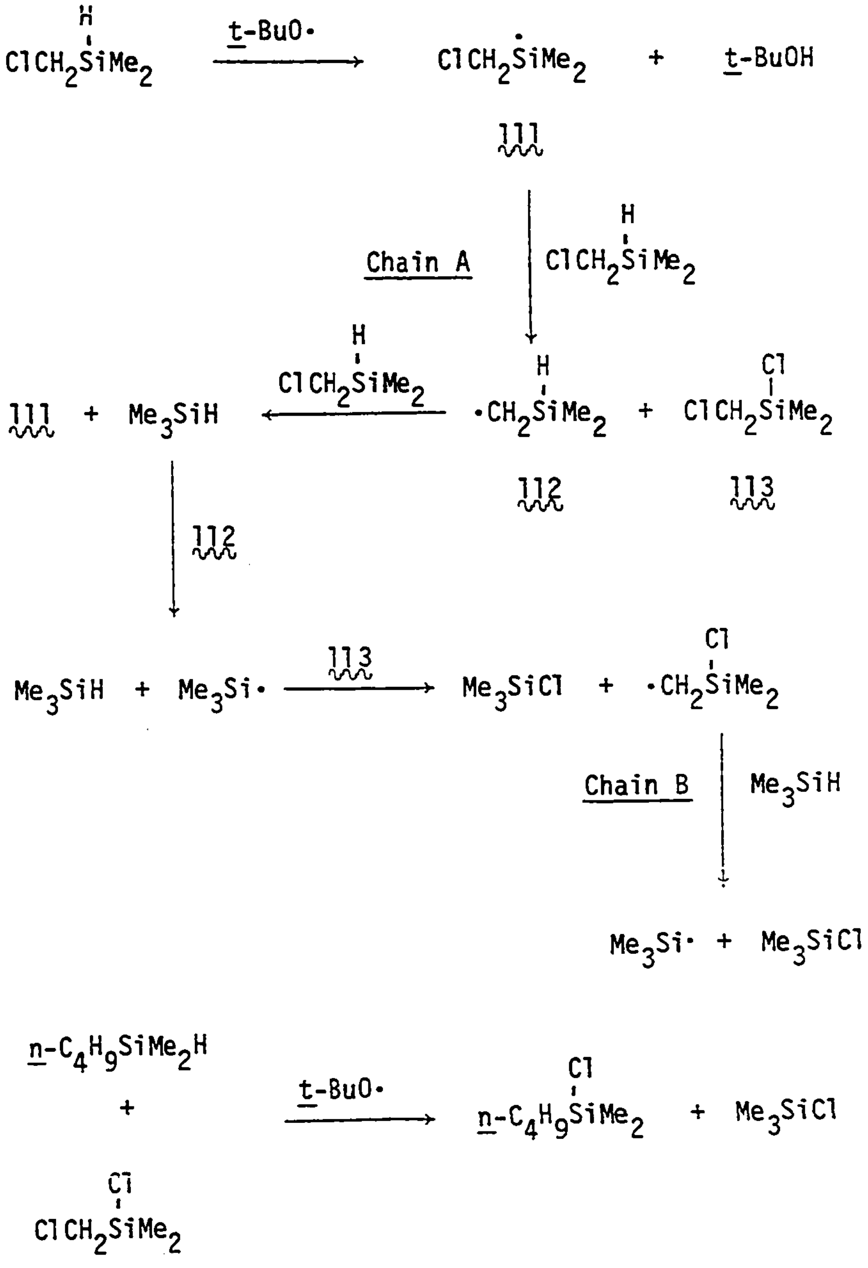
In 1972, Atton and coworkers reported that t-butoxyl abstraction of hydride from chloromethyldimethylsilane ($ClCH_2SiMe_2H$) yielded trimethylchlorosilane as the only major product (197). The mechanism that was proposed had as a key step was the novel 1,2 shift of chlorine from silyl radical 111 to give methyl radical 112.



More recently, however, Jung and Weber (198) have demonstrated that this reaction does not involve a 1,2-chlorine shift but two concurrent chain process (Scheme 19). Thus, after 20 minutes at 138°C, 40% of chloromethyldimethylsilane had reacted to give equal amounts of trimethylsilane (∿20%) and chlorosilane **113**. However, if the reaction mixture was heated for longer periods of time the amounts of trimethylsilane and chloromethyldimethylchlorosilane (**113**) decreased, while the yield of trimethylchlorosilane increased. Further evidence supporting this mechanism was provided by independent verification of the second radical chain process (chain B, Scheme 19). Thus, heating *n*-butyldimethylsilane and **113** together in the presence of a catalytic amount of di-*t*-butyl peroxide afforded equal amounts of *n*-butyldimethylchlorosilane and trimethylchlorosilane (Scheme 19).

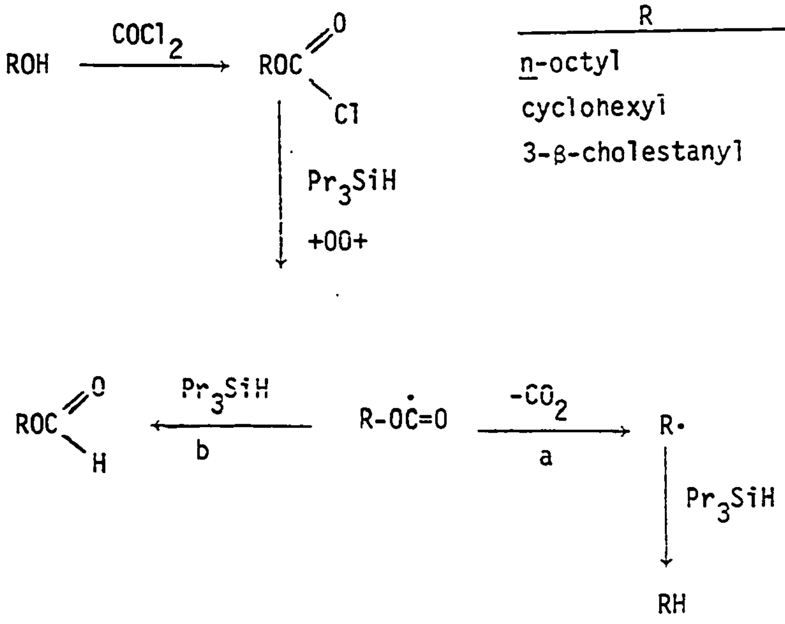
Although the reduction of alkyl halides to alkanes by silyl radicals has the potential for synthetic utility, this reaction is most often effected by trialkylstannyl radicals (18).

Scheme 19


t-BuO·
111
Chain A
112
113
Chain B
t-BuOH
Me3SiH
Me3Si·
Me3SiCl
n-C4H9SiMe2H

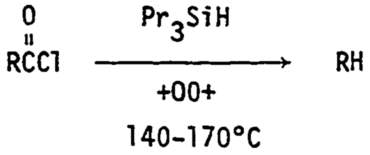
That silyl radical abstraction of halogens possesses synthetic utility has recently been demonstrated by Billingham and coworkers (199). When primary and secondary alcohols were converted to the corresponding chloroformates, by reaction with phasgene, and then heated with tri-_n_-propylsilane and di-_t_-butyl peroxide, good to excellent yields of the dehydroxylated alkanes were obtained. Based on the mechanism proposed for this reaction (Scheme 20), silyl hydrides were suggested to be preferable to the analogous tin compounds since stannyl hydrides are known to react with acyl radicals to give the corresponding aldehydes (path b) (200). This reaction was found not to be useful for the reduction of phenol or benzyl alcohol. However, the chloroformate of 1-hydroxypentan-4-one was converted to pentan-2-one in 69% yield, thereby indicating that carbonyls are tolerated by this technique.

Scheme 20



R	% Yield
_n_-octyl	92
cyclohexyl	91
3-β-cholestanyl	69

More recently, Billingham and coworkers have extended this methodology to the decarboxylation of acid chlorides (201). When various acid halides were heated at 140-170°C with tripropylsilane and di-t-butyl peroxide, reasonable yields of the corresponding alkanes were obtained. As was observed previously (199), yields were good when R was a primary or secondary alkyl group, poor when R was tertiary or benzylic, and gave only traces of benzene when R was phenyl.



$$\mathrm{R\overset{\overset{O}{\|}}{C}Cl} \xrightarrow[\substack{\mathrm{+OO+} \\ 140\text{-}170^\circ\mathrm{C}}]{\mathrm{Pr_3SiH}} \mathrm{RH}$$

R	% Yield
n-pentyl	56
β-phenethyl	55
cyclohexyl	68
1-adamantyl	13
benzyl	6
Phenyl	trace

In addition to the studies described above, numerous other examples of halogen abstraction by silyl radicals have been reported (18). One important conclusion can be drawn from these studies, namely, that without exception all silyl radicals are known to abstract halogens from RX compounds (X=Cl, Br, and I). Indeed, the generality of this reaction is such that, it is often used as a diagnostic test when the question of silyl radical intermediacy is at issue.

Aromatic Substitution of Silyl Radicals

In 1963, Nelson and coworkers reported the first example of a homolytic aromatic displacement reaction by a silyl radical (174). When diphenylsilane was exposed to U.V. irradiation at 70° to 130°C, or heated at 130°C, in the presence of a variety of peroxy or azo initiators, extensive phenyl redistribution was observed.

$$PH_2SiH_2 \rightleftharpoons Ph_4Si + Ph_3SiH + PhSiH_3 + SiH_4$$

Based on the observations that this reaction did not occur in the dark or in the absence of a radical catalyst, and that no positional isomerization occurred during the redistribution of tolyl groups, a mechanism involving direct displacement of a silyl group from the aromatic nucleus by a silyl radical was proposed.

$$\begin{array}{lrcl}
 & \text{Peroxide} & \xrightarrow{\Delta} & 2R\cdot \\
\text{initiation} & R\cdot + \equiv Si^{*}\text{-}H & \longrightarrow & \equiv Si^{*}\cdot + RH \\
 & \text{or } \equiv Si^{*}\text{-}H & \xrightarrow{h\nu} & \equiv Si^{*}\cdot \\
 & & & \\
\text{propogation} & Si^{*}\cdot + PhSi\equiv & \rightleftarrows & Ph^{*}Si\equiv + \cdot Si\equiv \\
 & & & \\
 & \cdot Si\equiv + \equiv Si^{*}H & \rightleftarrows & HSi\equiv + \equiv Si^{*}\cdot
\end{array}$$

A similar displacement of silicon from an aromatic ring by a silyl radical was also reported by Eaborn and coworkers (202). Copyrolysis of phenyltrimethylsilane and trichlorosilane at 500°C in the gas-phase gave phenyltrichlorosilane in 83% yield.

Trimethylsilyl radicals, produced by irradiation of solutions of bis(trimethylsilyl)mercury have also been found to react with aromatic substrates to afford the products of homolytic aromatic substitution (203).

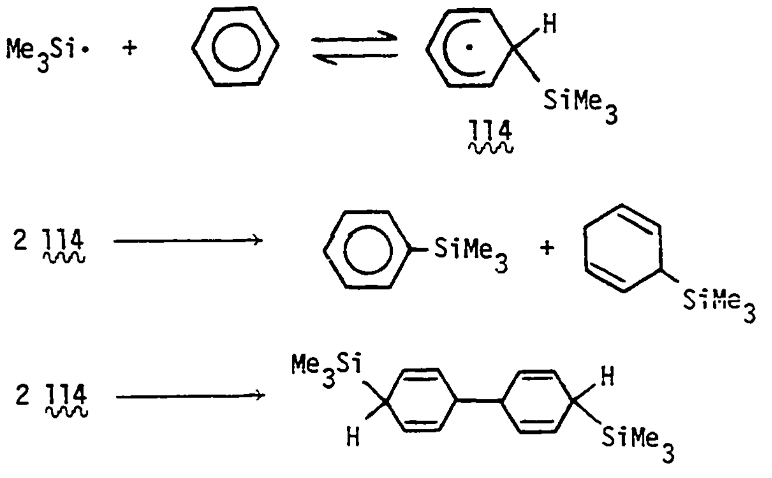
When anisole was used as the substrate, o-, m-, and *p*-trimethylsilylanisoles were obtained in approximately 8, 4, and 1% yield, respectively, in addition to hexamethyldisilane (50%). Similarly, toluene gave *o*-, *m*-, and *p*-trimethylsilyltoluene in a ratio of approximately 2:2:1.

In a subsequent study, utilizing benzene as substrate, a more complex reaction mixture was obtained (204). Thus, photolysis of bis(trimethylsilyl)mercury in benzene at 45°C gave hexamethyldisilane, phenyltrimethylsilane, 2,5-cyclohexadienyltrimethylsilane, and large amounts of products of high molecular weight. Based on the products obtained, and their relative yields as a function of initial mercurial concentration, the following mechanism was proposed.

$$Hg(SiMe_3)_2 \xrightarrow{h\nu} Hg + 2\,Me_3Si\cdot$$

$$Me_3Si\cdot + Hg(SiMe_3)_2 \longrightarrow (Me_3Si)_2 + Hg + Me_3Si\cdot$$

$$2Me_3Si\cdot \longrightarrow (Me_3Si)_2$$



(and other isomers)

The most extensive investigations of homolytic aromatic substitution reactions by silyl radicals have been those of Sakurai and coworkers (205,206,207). Table 6 gives the results obtained from the thermolysis of various hydrosilanes in benzene solutions containing di-t-butyl peroxide (205).

Table 6. Reaction of Hydrosilanes with Benzene in the Presence of di-t-butyl Peroxide at 135°C.

Hydrosilane	Phenylsilane	% Yield
Et_3SiH	Et_3SiPh	16.3
n-$PrSiMe_2$	n-$PrSiMe_2Ph$	29.5
$Me_3SiSiMe_2H$	$Me_3SiSiMe_2Ph$	19.2
$Me_3SiSiMe_2SiMe_2H$	$Me_3SiSiMe_2SiMe_2Ph$	15.0

In an elegant study designed to delineate the directive effects and relative reactivities of homolytic aromatic silylations, Sakurai and co-workers investigated the reaction of pentamethyldisilanyl radical, generated thermally in the presence of di-t-butyl peroxide, with substituted benzenes (206). From competition experiments, the relative rates of silylation of anisole, toluene, and trifluoromethylbenzene, relative to benzene, were found to be 0.45, 0.62, and 2.19, respectively. These data, coupled with the meta-para substitution ratios (4.3 for anisole, 1.9 for toluene, and 0.92 for trifluoromethylbenzene), showed that the disilanyl radical was nucleophilic in nature. This conclusion was further supported by the ρ value for silylation, which was determined to be +1.4. With the exception of the Hammett correlation, which was not determined, n-propyldimethylsilyl radical gave similar results. These results complement nicely those of Nagai and coworkers (191), and provide further evidence for the nucleophilicity of silyl and alkyl substituted silyl radicals.

Addition of Silyl Radicals to Multiple Bonds

The addition of silyl radicals to carbon-carbon double and triple bonds, the so-called free radical hydrosilation reaction, has been extensively reviewed by Lukevits and Voronkov (208), and by Sakurai (18). Therefore, rather than repeating the contents of these reviews, only a summary of the material compiled by Sakurai will be presented.

The free radical hydrosilation reaction involves the formal addition of a hydrosilane to a carbon-carbon multiple bond via a chain process as shown below.

$$\begin{aligned} R_3SiH &\xrightarrow{\text{INT.}} R_3Si\cdot \\ R_3Si\cdot + CH_2{=}CHR &\longrightarrow R_3SiCH_2\text{-}\dot{C}HR \\ R_3SiH + R_3SiCH_2\text{-}\dot{C}HR &\longrightarrow R_3Si\cdot + R_3SiCH_2CH_2R \end{aligned}$$

These reactions can be initiated by virtually all the techniques available for the generation of silyl radicals. Thus, thermal reaction at high temperatures, direct U.V. irradiation, and high energy gamma-irradiation have been utilized. Generally however, these reactions are initiated by thermal or photochemical induced decomposition of organic peroxides or azo compounds, usually in catalytic amounts.

The presence of electron-withdrawing groups on silicon facilitates the ease of reaction. This was determined by an examination of the reactivity of various hydrosilanes under fixed conditions, and which exhibited the following order of reactivity (209,210):

$$Cl_3SiH>MeCl_2SiH>Et_2SiH_2>>Et_3SiH$$

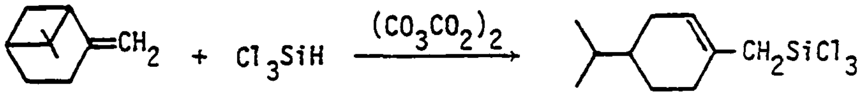
Phenyl, diphenyl, and tiphenylsilane, as well as pentamethyldisilane, react readily with olefins to give products in moderate to high yield. In contrast, trialkyl- and trialkoxysilanes react with olefins to give only low yields of hydrosilation products (211).

The nature of the olefin also affects the ease and outcome of this reaction. Dohmaru and Nagata, on the basis of competition experiments, have determined that there is a regular increase in the reactivity of an olefin toward hydrosilation by trichlorosilane with double bond substitution by an alkyl group (212). The results of this study are given in Table 7.

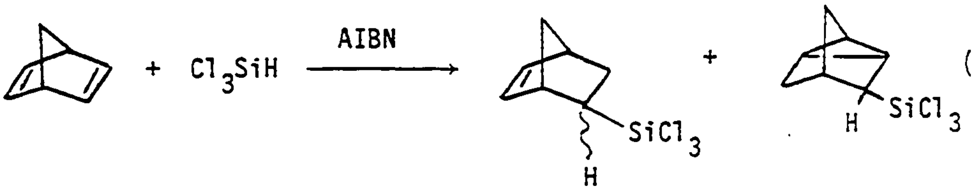
Table 7. Relative Rates of Hydrosilation of Olefins by Trichlorosilane at 250°C.

Olefin	Relative Rate Constant
$CH_2=CH_2$	1
$CH_2=CHCH_3$	3.3
$CH_2=CHCH_2CH_3$	3.7
$CH_2=CHCH_2CH_2CH_3$	4.4
$CH_2=CH(CH_3)_2$	14.5

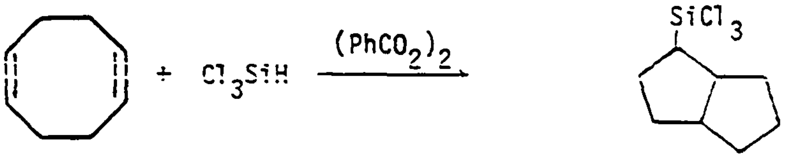
With reactive olefins, or olefins which upon addition of the silyl radical yield an alkyl radical which is strained or situated in a favorable position for intramolecular radical reactions, products other than those of simple hydrosilation are obtained. For example, with acylonitrile, methyl acrylate, and styrene only high molecular weight polymers are obtained. When pinene, norbornadiene, or 1,5-cyclooctadiene were employed as substrates, products resulting from secondary, intramolecular radical reactions were found.



(213)



(214)



(215)

With terminal olefins or acetylenes the addition of the silyl radicals is to the terminal end to afford the more highly substituted radical. Thus, the addition occurs in an anti-Markonikoff manner. With internal olefins or acetylenes, the addition can lead to a mixture of products. However, if steric and electronic factors exist which favor addition at one end of the multiple bond a single product can predominate.

For example:

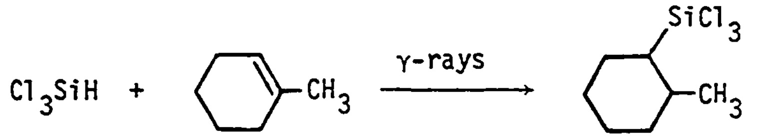
$$Cl_3SiH + H_2C{=}CHC_4H_9 \xrightarrow[h\nu]{+OO+} Cl_3SiCH_2CH_2C_4H_9 \quad 88\% \qquad (211)$$

$$Cl_3SiH + CH_2{=}CMe_2 \xrightarrow[h\nu]{(ACO)_2} Cl_3SiCH_2CHMe_2 \quad 64\% \qquad (216)$$

$$Cl_3SiH + EtCH{=}CHMe \xrightarrow[75°C]{PhCO_3CMe_3}$$

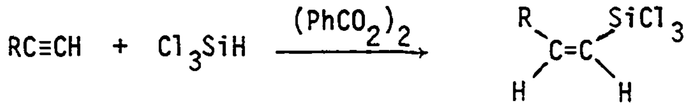
$$\underline{n}\text{-}C_3H_7CH(CH_3)SiCl_3 + C_2H_5CH(C_2H_5)SiCl_3 \qquad (217)$$

70:30 mixture



(218)

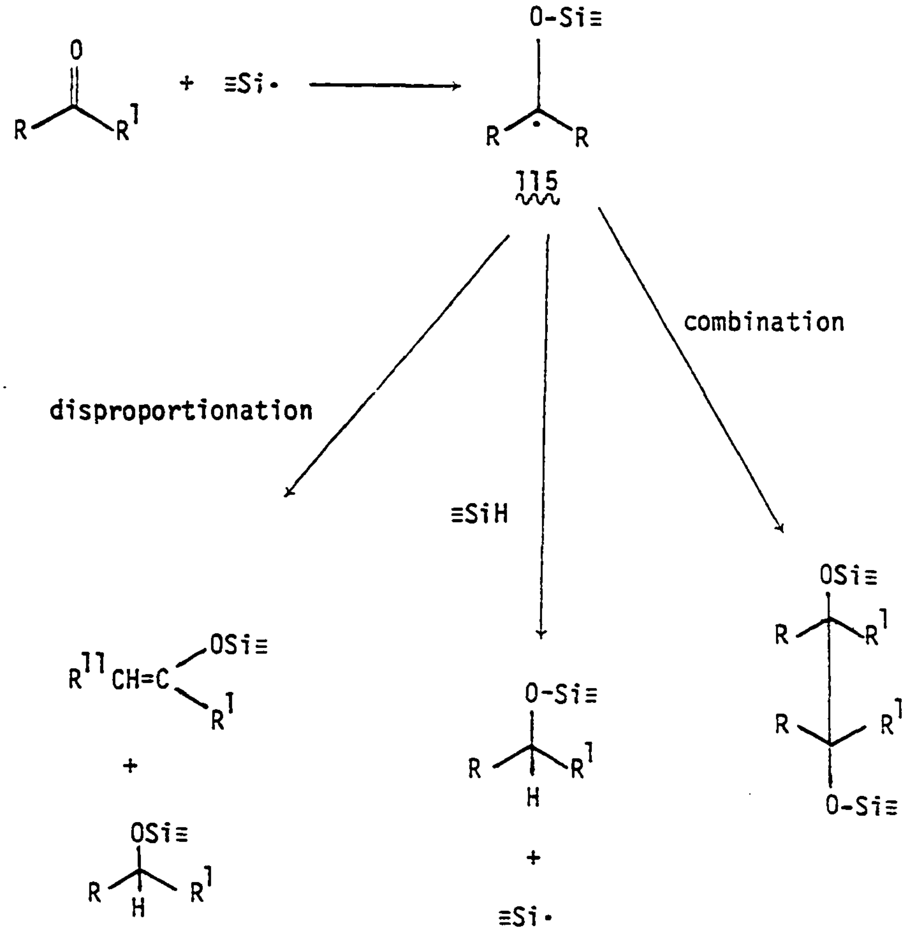
The stereochemistry of free radical hydrosilation of acetylenes has been determined by Benkeser to be trans addition, thereby, affording products with cis stereochemistry (219).



$$RC{\equiv}CH + Cl_3SiH \xrightarrow{(PhCO_2)_2} \overset{R}{\underset{H}{>}}C{=}C\overset{SiCl_3}{\underset{H}{<}}$$

For olefins, the stereochemistry of addition is less easily determined. Nonetheless, Selin and West have found that the product of trichlorosilane addition to methylcyclohexene is consistent with trans-addition (220).

Silyl radicals are also known to react with the carbon-oxygen double bond of esters, aldehydes, and ketones (16).



The intermediate alkyl radical, 115, that is formed by addition of the silyl radical to the oxygen of the carbonyl group, can proceed to stable products by three different pathways. In the absence of a chain carrying species, such as a silyl hydride, 115 leads to products by either disproportionation or combination. For example, when trimethylsilyl radical is generated from bis(trimethylsilyl)mercury in the presence of acetone or cyclohexanone, disproportionation is the major pathway (221). In contrast, when acetophenone was used as the substrate, under otherwise identical conditions, combination was the main pathway leading to products.

Although the reaction of silyl radicals with carbonyl groups has been known for over twenty-five years, it has been systematically studied only within the last decade. The most extensive study is that by Cooper and coworkers who examined the reaction of triethylsilyl radical with a variety of ketones and esters (222).

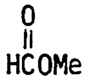
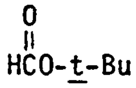
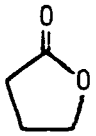
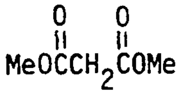
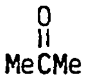
$$\mathrm{Et_3SiH} \xrightarrow[h\nu]{+\mathrm{OO}+} \mathrm{Et_3Si\cdot} \qquad \text{(Eq. 1)}$$

$$\mathrm{Et_3Si\cdot} + \mathrm{O{=}CXY} \longrightarrow \mathrm{Et_3SiO{-}CXY} \qquad \text{(Eq. 2)}$$

In the presence of a carbonyl compound, the silyl radical produced by Eq. 1 can react with the carbonyl compound to give the corresponding adduct by Eq. 2. If the rate of reaction of Eq. 2 is relatively rapid only the silyl radical-carbonyl adduct will be observed by ESR. On the other hand, if this reaction is slow or does not occur the silyl radical will be observable. Utilizing this reasoning, Cooper and coworkers were able to determine the relative reactivity of various carbonyl compounds toward triethylsilyl radical.

With formaldehyde, simple ketones, and σ-diketones only the silyl radical-carbonyl adduct was observed. In contrast, esters such as methyl acetate, methyl propionate, and γ-butyrolactone did not react with triethylsilyl radical to afford the corresponding adduct. Methyl and ethyl formates occupied an intermediate position with respect to ketones and acetates. For the formates, higher temperatures were found to favor adduct formation. This implies that there is a significant energy of activation for adduct formation even though the overall reaction is exothermic. The results of of this study are summarized in Table 8.

Table 8. Reactions of Triethylsilyl Radicals with Carbonyl Compounds

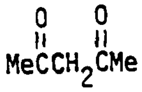
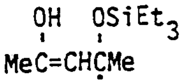
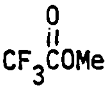
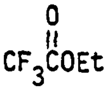
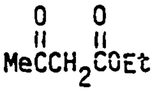
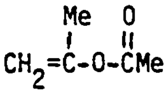
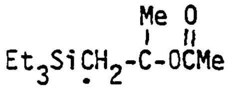
Substrate	Radical Observed[a]
 $H\overset{O}{\overset{\|}{C}}OMe$	Adduct[b] + $Et_3Si\cdot$
 $H\overset{O}{\overset{\|}{C}}OEt$	Adduct + $Et_3Si\cdot$
 $H\overset{O}{\overset{\|}{C}}O\text{-}\underline{t}\text{-}Bu$	Adduct + $Et_3Si\cdot$
 $Me\overset{O}{\overset{\|}{C}}OMe$	$Et_3Si\cdot$
 $Et\overset{O}{\overset{\|}{C}}OMe$	$Et_3Si\cdot$
	$Et_3Si\cdot$
 $MeO\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OMe$	$Et_3Si\cdot$
 $MeO\overset{O}{\overset{\|}{C}}OMe$	$Et_3Si\cdot$
CH_2O	Adduct
 $Me\overset{O}{\overset{\|}{C}}Me$	Adduct
 $Me\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Me$	Adduct

---

[a] Radicals observed by ESR.

[b] Adducts correspond to $R_3Si\dot{O}CXY$.

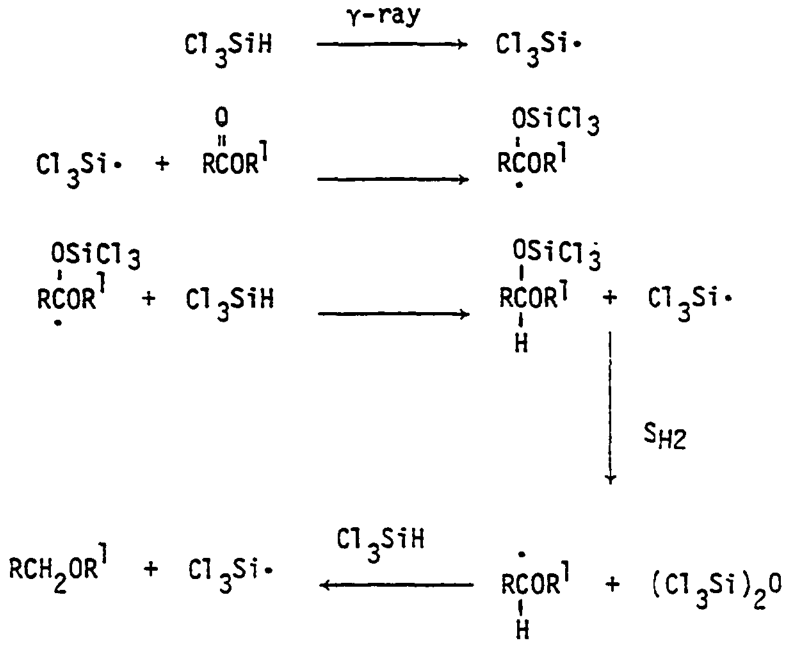
Table 8. (cont.)

Substrate	Radical Observed[a]
 $\overset{O}{\overset{\|}{C}}$: $Ph\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Ph$	Adduct
 $Me\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}Me$	 $Me\overset{OH}{\overset{\|}{C}}=CH\overset{OSiEt_3}{\overset{\|}{\underset{\bullet}{C}}}Me$
 $CF_3\overset{O}{\overset{\|}{C}}OMe$	Adduct
 $CF_3\overset{O}{\overset{\|}{C}}OEt$	Adduct
 $Me\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}Me$	Adduct
 $Me\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OEt$	Ketone Adduct
 $CH_2=\overset{Me}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}Me$	 $Et_3Si\underset{\bullet}{C}H_2-\overset{Me}{\overset{\|}{C}}-O\overset{O}{\overset{\|}{C}}Me$

The unreactivity of esters was suggested to be due in part to polar effects. That polar effects are important was demonstrated by the fact that methyl trifluoroacetate (as well as higher fluorinated esters) and anhydrides form adducts with silyl radicals.

The results obtained when bifunctional compounds were employed as substrates confirmed the relative unreactivity of the ester grouping. Thus, with isopropenyl acetate only addition to the carbon-carbon double-bond was observed, while ethyl aceto-acetate gave only the adduct of addition to the ketone carbonyl.

In contrast, Tsurugi and coworkers found that trichlorosilane reacts with aliphatic esters under the influence of gama irradiation to afford the corresponding dialkyl ethers in good to excellent yield (223). This reaction was proposed to proceed via the following mechanism.



Numerous other studies of the addition of silyl radicals to a carbonyl oxygen have been reported. Those that appeared prior to 1969 have been adequately reviewed by Jackson (16). More recently, the gas-phase addition of trichlorosilane to acetone (224) and the addition of triethyl- and triphenylsilane to benzil (225,226) have been reported. Quinones are also known to be excellent traps for silyl radicals (182,227).

Very recently, Ingold has determined the rate constants for the addition of triethylsilyl radical to a variety of ketones (228). These results are given in Table 9.

The addition of silyl radicals to various multiple bonds has become, in the last decade, a standard technique for the generation and study of a variety of carbon and heteroatom radicals. A partial listing of the silyl radicals and multiple bond substrates that have been employed is given in Table 10 to illustrate the utility of this technique.

Table 9. Rate Constants for the Addition of
$Et_3Si\cdot$ to Ketones at 25°C.

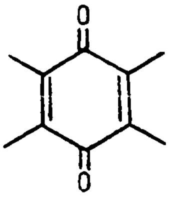
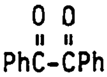
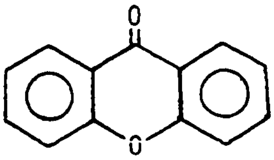
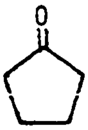
Ketone	Rate Constant ($M^{-1}sec^{-1}$)
	2.4×10^9
 $PhC(=O)-C(=O)Ph$	3.3×10^8
	2.4×10^8
 $EtC(=O)Et$	2.1×10^5
	7.0×10^5

Table 10. Reactions of Silyl Radicals with Multiple Bond Compounds.

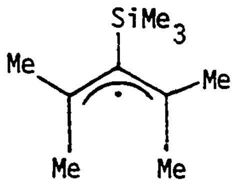
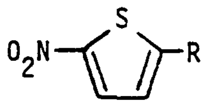
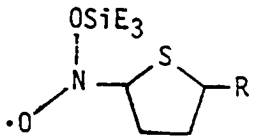
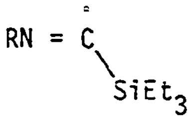
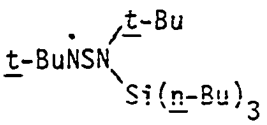
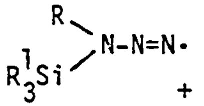
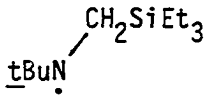
Substrate	Silyl Radical	Adduct	Ref.
$Me_2C{=}C{=}CMe_2$	$Me_3Si\cdot$		229
 R = H, alkyl, Ph, NO_2, CHO, CH, CO_2Me, SO_2Me, OAC, SMe	$Et_3Si\cdot$		230
RN=C: R=Me, t-butyl, Et	$Et_3Si\cdot$	$RN = \dot{C}{-}SiEt_3$	231
t-BuN=S=Nt-Bu	($\underline{n}$-Bu)$_3$Si·	$\underline{t}\text{-Bu}\overset{\bullet}{N}SN(\underline{t}\text{-Bu})Si(\underline{n}\text{-Bu})_3$	232

Table 10. (cont.)

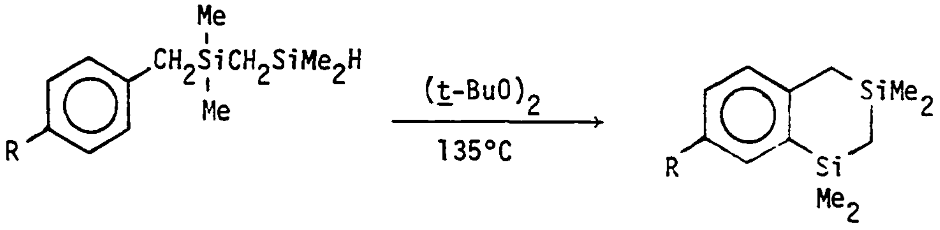
Substrate	Silyl Radical	Adduct	Ref.
$R-\ddot{N}=N=\underset{\cdot\cdot}{\dot{N}}\colon$ R = 1°,2°,3° alkyl; Me_3Si, Ph, *t*BuOC(O)	$R^1_3Si\cdot$ R^1=Me,Et, Ph	 + $RN=N-\dot{N}-SiR^1_3$	233
*t*BuN=CH_2	$Et_3Si\cdot$		234
O_2	$R_3Si\cdot$ R = Me, Et, *n*-Bu, Ph	$R_3SiOO\cdot$	235

Cyclization Reactions of Silyl Radicals

Unlike their carbon analogues, for which numerous examples of cyclization reactions exist (236,237), few examples of silyl radical cyclizations are known. Of the known examples, only those involving homolytic aromatic silylation have been well studied.

Sakurai and coworkers found that heating an equimolar mixture of (3-phenylpropyl)dimethylsilane at 135° for 15 hours afforded silatetralin 116 in 14% yield (207). Mechanistically, two pathways were considered for the formation of 116 (Scheme 21). Cyclization could occur via rearranged radical 117 (path a) or directly via path b. The finding that

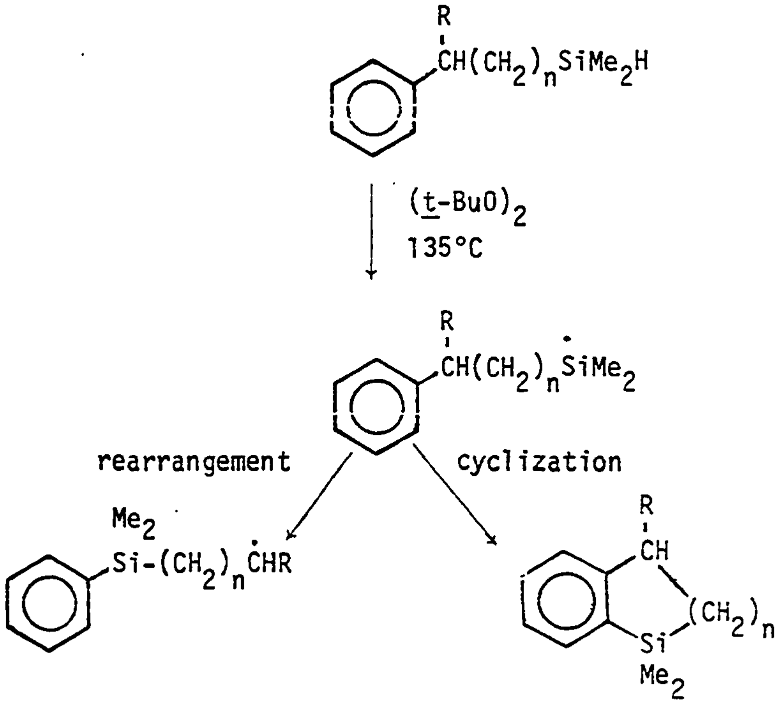
(3-*p*-tolylpropyl)dimethylsilane gave only silatetralin 118 clearly demonstrated that cyclization occurred by path b. Similar results were obtained with silanes 119 and 120.



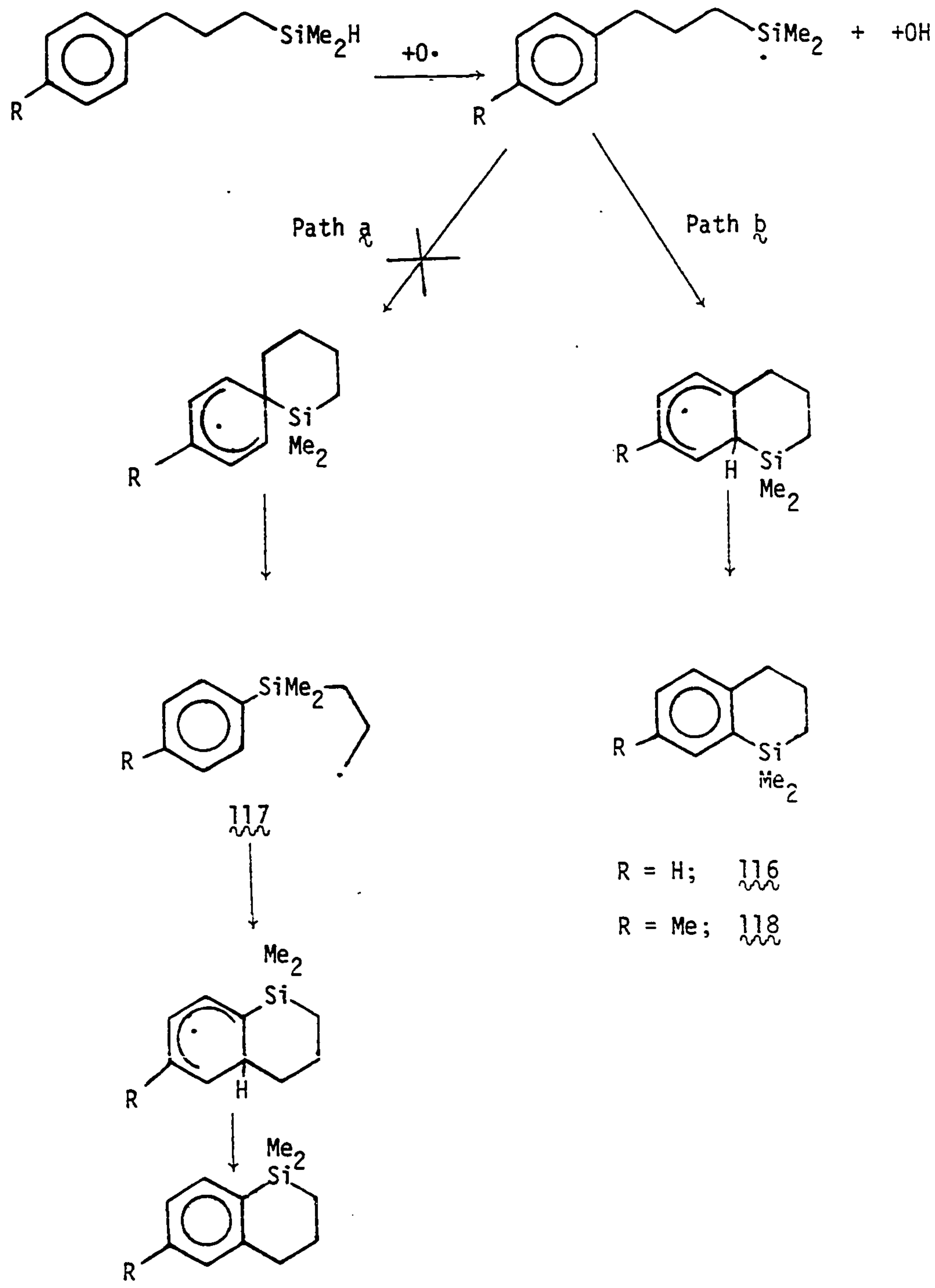
R = H; 119

R = Me; 120

In a similar study, Sakurai and Hosomi (238) examined the possible competition between rearrangement and cyclization for a number of compounds of the general formula $PhCHR(CH_2)_nSiMe_2H$ (R = H, Me, or Ph). The results of this study are given in Table 11.



Scheme 21


SiMe$_2$H
+O·
SiMe$_2$
+ +OH
R
Path a
Path b
Si
Me$_2$
H
SiMe$_2$
117
R = H; 116
R = Me; 118

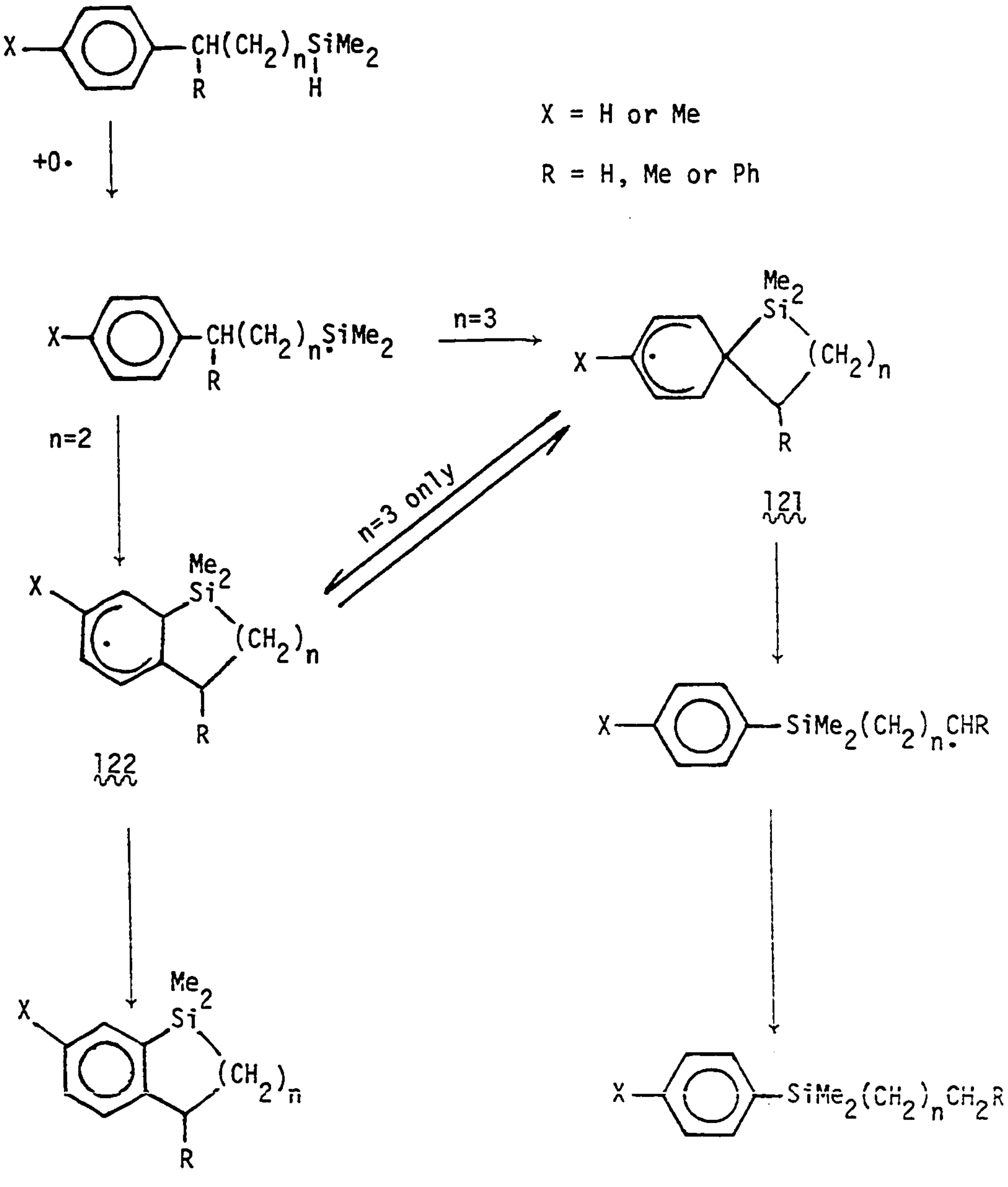
When cyclization was observed, it was clearly demonstrated to occur via the silyl radical and not the rearranged carbon radical by labeling experiments analogous to those described above. On the basis of these results, a mechanism was proposed (Scheme 22) which for n=3 involved a subtle equilibrium between spirocyclohexadienyl radical **121** and cyclohexadienyl radical **122**. When n=0, 1, 4 or 5, the silyl radical does not interact with the aromatic nucleus, while for n=2, only **122** is involved. The findings that the ratio of cyclization to rearrangement was 3 to 1 for n=3 and R=H and 1 to 3 for N=3 and R=Me provided support for the proposed equilibrium between **121** and **122**.

Table 11. Reaction of $PhCHR(CH_2)_nSiMe_2H$ with di-_t_-butyl Peroxide at 135°C.

n	R	Rearrangement	Cyclization
0	H	No	No
0	Me	No	No
0	Ph	No	No
1	H	No	No
2	H	No	Yes
2	Me	No	Yes
2	Ph	No	Yes
3	H	Yes	Yes
3	Me	Yes	Yes
4	H	No	No
5	H	No	No

Sakurai has also observed cyclized products from 4-pentenylsily radicals (18). These results are given in Table 12.

Scheme 22



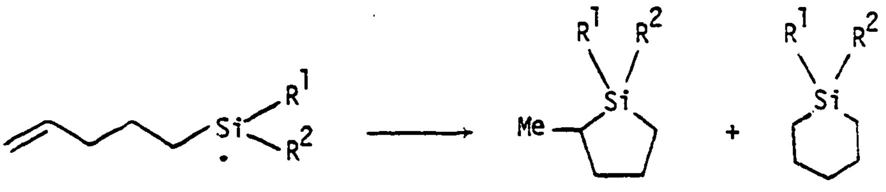
X = H or Me

R = H, Me or Ph

n=2 and 3

n=3 only

Table 12. Intramolecular Hydrosilylation of 4-Pentenylsilanes Catalyzed by di-*t*-butyl Peroxide

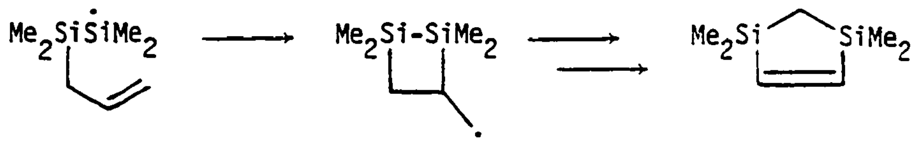


123 124

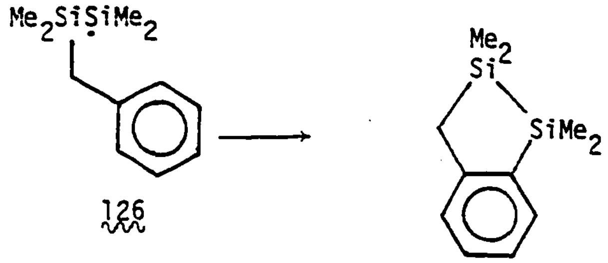
R^1	R^2	Temperature (°C)	% Yield	
			123	124
Me	Ph	135	0.65	5.46
		30	1.47	9.48
Ph	Ph	135	0.74	6.1
		30	3.1	12.6
i-Pr	Cl	135	3.94	5.47
Me	Cl	135	71.6	12.6
		30	4.8	1.7

Interestingly, when the same four silanes were cyclized by chloroplatinic acid, 123 was obtained in 94.6, 88.8, 53.6, and 89.3% yields, respectively. As of yet, no reasonable explanation for these results has been presented.

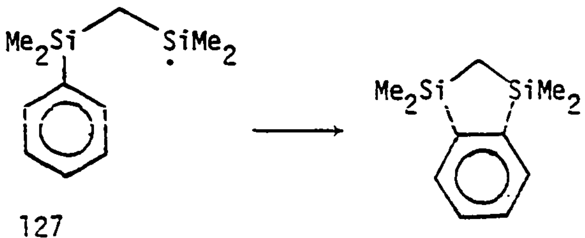
More recently, Barton and Jacobi have obtained evidence that disilanyl radicals 125 and 126 and silyl radical 127 cyclize at high temperatures (122). A more complete discussion of the chemistry associated with these reactions will be presented in the next section.



125



126



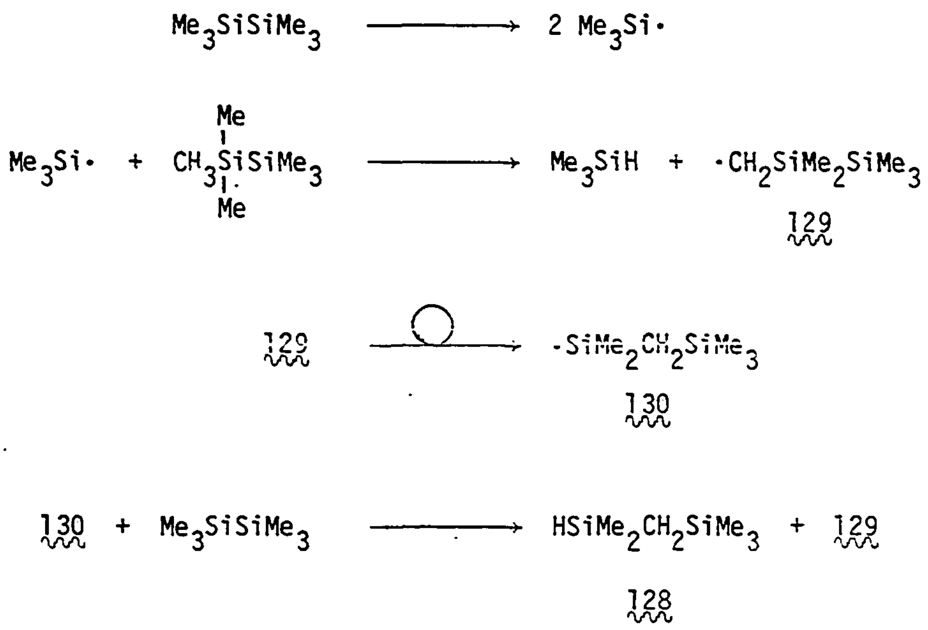
127

Rearrangement Reactions of Silyl Radicals

In general, silyl radical rearrangements were similar to those of carbon radicals. Thus, at lower temperatures (<200°C) silyl radicals are not known to rearrange, with the exception of (4-phenylbutyl)dimethylsilyl radical (see Table 11). However, at higher temperatures, in either the condensed or gas-phase, rearrangements occur.

The most extensively investigated silyl radical rearrangement is that associated with the thermolysis of hexamethyldisilane. This was first pyrolyzed at 600°C in the gas-phase by Shiina and Kumada (149), who observed the formation of 2,2,4-trimethyl-2,4-disilapentane (128) as the major product, in addition to trimethylsilane. To account for the formation of these products, a chain mechanism involving the intermediacy of trimethylsilyl radicals was proposed (Scheme 23). The key feature of this mechanism is the 1,2-silyl migration of radical 129 to afford 130.

Scheme 23



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

$$Me_3Si\cdot + CH_3\overset{Me}{\underset{Me}{Si}}SiMe_3 \longrightarrow Me_3SiH + \cdot CH_2SiMe_2SiMe_3 \ (129)$$

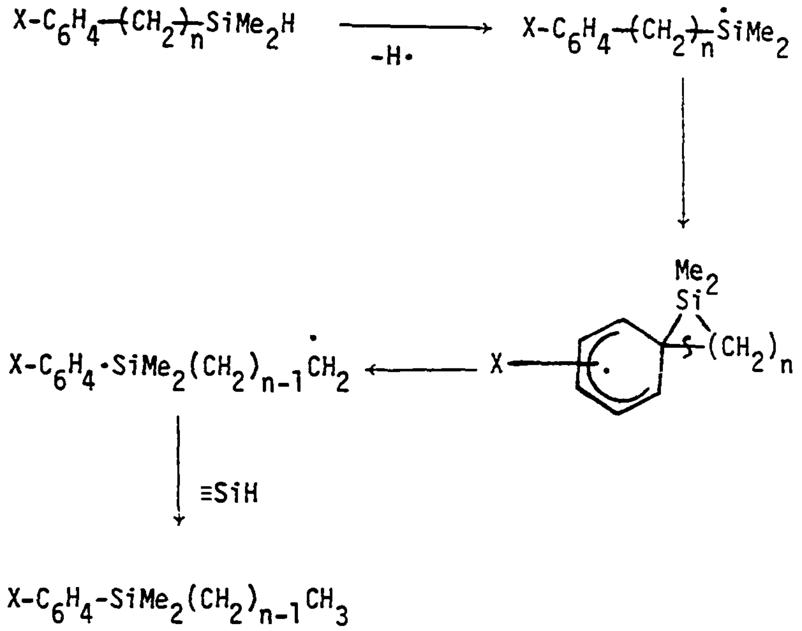
$$129 \xrightarrow{\bigcirc} \cdot SiMe_2CH_2SiMe_3 \ (130)$$

$$130 + Me_3SiSiMe_3 \longrightarrow HSiMe_2CH_2SiMe_3 \ (128) + 129$$

The ratio of 128 to trimethylsilane was found to be 4:1 under these reaction conditions, and therefore, indicated a chain length of four (239). However, at higher pressures (sealed tube, 400°C), the chain length is considerably longer (>60), and almost quantitative yields of 128 are obtained (150,151). At lower temperatures (<200°C) the isomerization of **129** to **130** does not occur (151,239). These results, coupled with the kinetic data obtained by Davidson and coworkers (240), clearly established the chain mechanism shown in Scheme 23.

At lower pressures the decomposition of hexamethyldisilane is more complex and apparently quite condition dependent. Thus, static pyrolysis of hexamethyldisilane at 523 to 550°C and 0.2 to 0.8 torr affords Me_3SiH, Me_4Si, $Me_3SiSiMe_2CH_2SiMe_3$, and $(Me_3SiSiMe_2)_2CH_2$ in the respective ratio of 5:1:4:1 (241,242). In contrast, when low concentrations of hexamethyldisilane were pyrolyzed in a stirred-flow system at temperatures of 500 to 600°C, the main product was Me_3SiH and smaller amounts of Me_4Si, $Me_3SiCH_2SiMe_2H$, and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (243,244).

As discussed previously, (phenylalkyl)dimethylsilanes of the general form $Ph\text{-}(CH_2)_n\text{-}SiMe_2H$ do not undergo rearrangement in the presence of di-*t*-butyl peroxide at 135°C, with the exception of the compound where n=4 (238). However, Sakurai and coworkers have found that benzyldimethylsilane rearranges to phenyltrimethylsilane at temperatures greater than 425°C (245). Higher homologues were found to give similar results (see Table 13). Although no mechanism was proposed for these rearrangements, the fact that the reactions were shown to be intramolecular suggests the following mechanism.



The data given in Table 13 are consistent with this mechanistic scheme. Thus, the (arylalkyl)dimethylsilanes which can cyclize to the favored 3, 5, or 6-membered spirocyclohexadienyl radicals are found to give the highest yield of rearranged products.

In the last two years, studies designed to delineate the mechanisms of product formation from the pyrolysis of allyltrimethylsilane have led to the discovery of several novel silyl radical rearrangements.

In the first of these reports, Neider and coworkers (246), on the basis of labeling experiments, proposed that formation of trimethylvinylsilane from allyltrimethylsilane occurred via rearrangement of allyldimethylsilyl radical, rather than direct loss of methylene as proposed previously by Sakurai and coworkers (247).

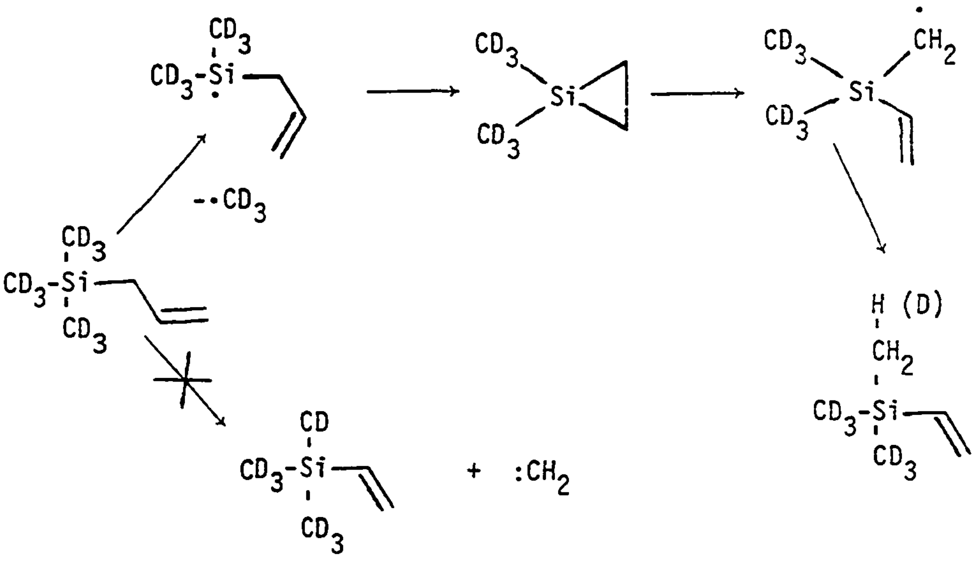


Table 13. Thermal Rearrangement of (Arylalkyl)-Dimethylsilanes

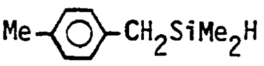
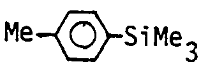
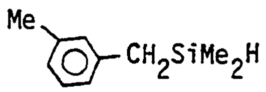
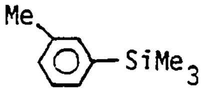
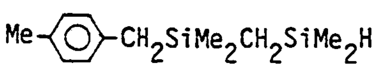
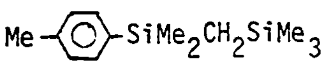
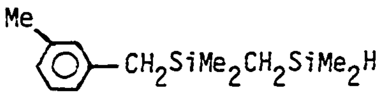
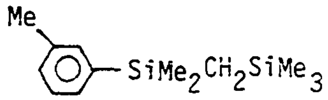
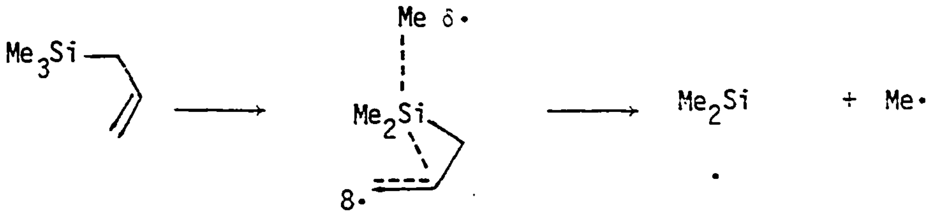
(Arylalkyl)Dimethylsilane	Temperature (°C)	Product	% Yield
$PhCH_2SiMe_2H$	440	$PhSiMe_3$	≈ 80
	440		-
	440		-
$PhCH_2SiMe_2CH_2SiMe_2H$	370	$PhSiMe_2CH_2SiMe_3$	~100
	370		-
	370		-

Table 13. (cont.)

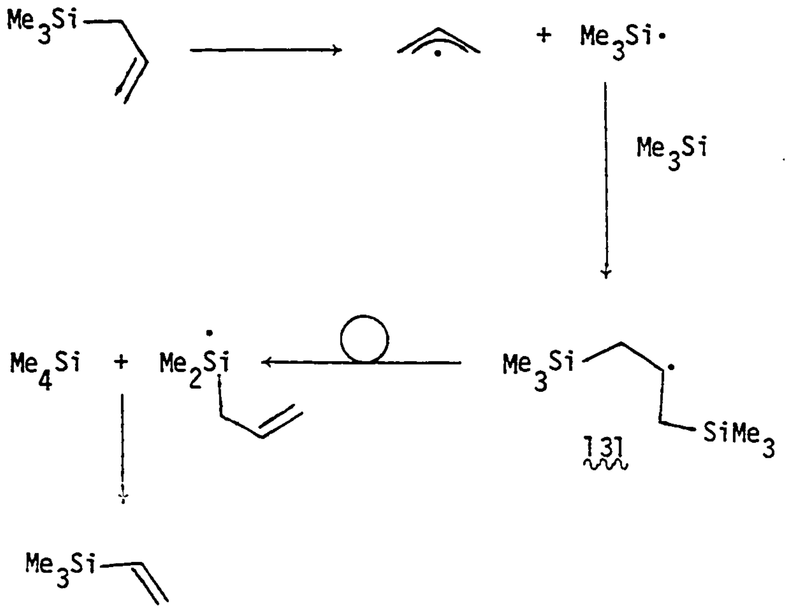
(Arylalkyl)Dimethylsilane	Temperature (°C)	Product	% Yield
$Ph(CH_2)_2SiMe_2H$	370	$PhSiMe_2Et$	0
$Ph(CH_2)_3SiMe_2H$	370	$PhSiMe_2$(*n*-Pr)	67.5
$Ph(CH_2)_4SiMe_2H$	370	$PhSiMe_2$(*n*-Bu)	38.5
$Ph(CH_2)_5SiMe_2H$	370	$PhSiMe_2$(*n*-Pent)	8.7
$Ph(CH_2)_6SiMe_2H$	370	$PhSiMe_2$(*n*-hex)	0

Barton and Jacobi (122), however, have argued that the loss of methyl radical should not be competitive with the loss of allyl radical under the conditions employed by Neider, and therefore proposed that π participation was necessary to explain the observed results.



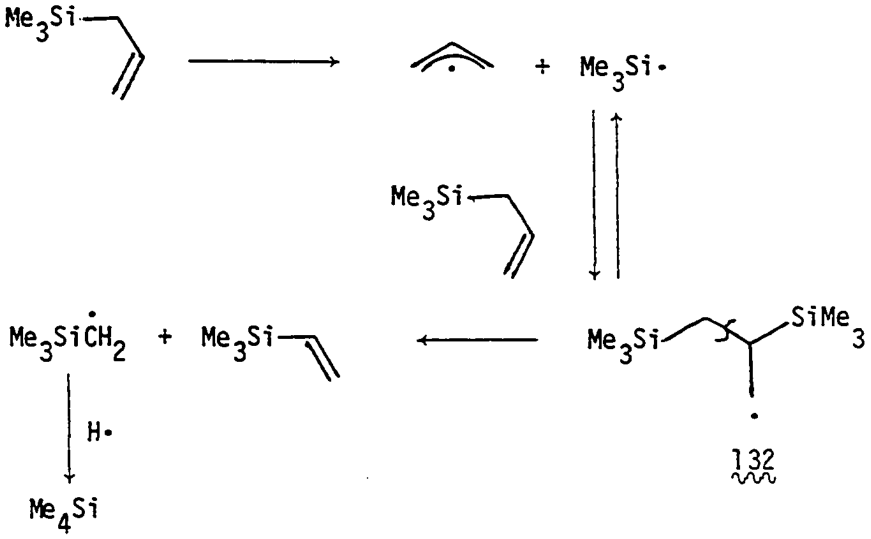
More direct evidence against the proposal of Neider has been reported by Davidson and Wood who found that the pyrolytic conversion of allyltrimethylsilane to vinyltrimethylsilane is a bimolecular reaction proceeding by initial homolysis of the Si-allyl bond (159). These authors proposed that the formation of vinyltrimethylsilane proceeded by addition of $Me_3Si\cdot$ to allyltrimethylsilane to afford radical 131, which underwent subsequent unimolecular rearrangement and elimination to afford Me_4Si and allyldimethylsilyl radical (Scheme 24). Allyldimethylsilyl radical would then afford trimethylvinylsilane by an identical route to that proposed by Neider (vide supra). An exact mechanism by which 131 rearranges and eliminates to afford Me_4Si and allyldimethylsilyl radical was not proposed.

Scheme 24



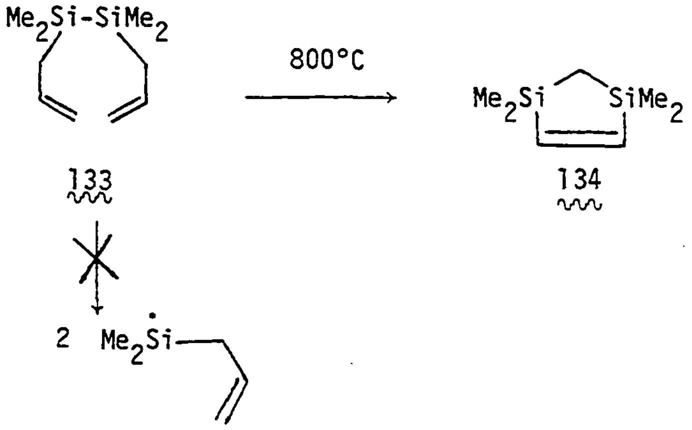
Barton (248) has argued that a more reasonable mechanism for the formation of Me_4Si and trimethylvinylsilane, based on the results obtained by Davidson and Wood, is addition of $Me_3Si\cdot$ to allyltrimethylsilane to afford radical 132 (Scheme 25). Radical 132 would lead to the observed products by β-scission and subsequent hydrogen abstraction by the resulting trimethylsilylmethyl radical.

Scheme 25

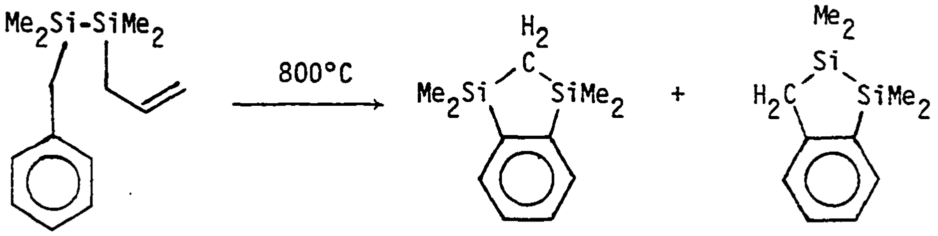


The obvious discrepancy between the results of Davidson and Wood and those of Neider and coworkers has yet to be reconciled.

Barton and Jacobi (122) attempted to examine more closely the chemistry of allyldimethylsilyl radical by pyrolysis of 1,2-diallyltetramethyldisilane (133). Rather than decomposing by Si-Si bond rupture as hoped, pyrolysis of 133 in the gas-phase at 800°C afforded 1,3-disilacyclopentene 134 in 51% yield.



In a similar experiment, pyrolysis of 1-allyl-2-benzyltetramethyldisilane (135) afforded disilaindanes 136 and 137 in respective yields of 21% and 29%. In addition, careful examination of the pyrolysate revealed the presence of 134 (<5%).



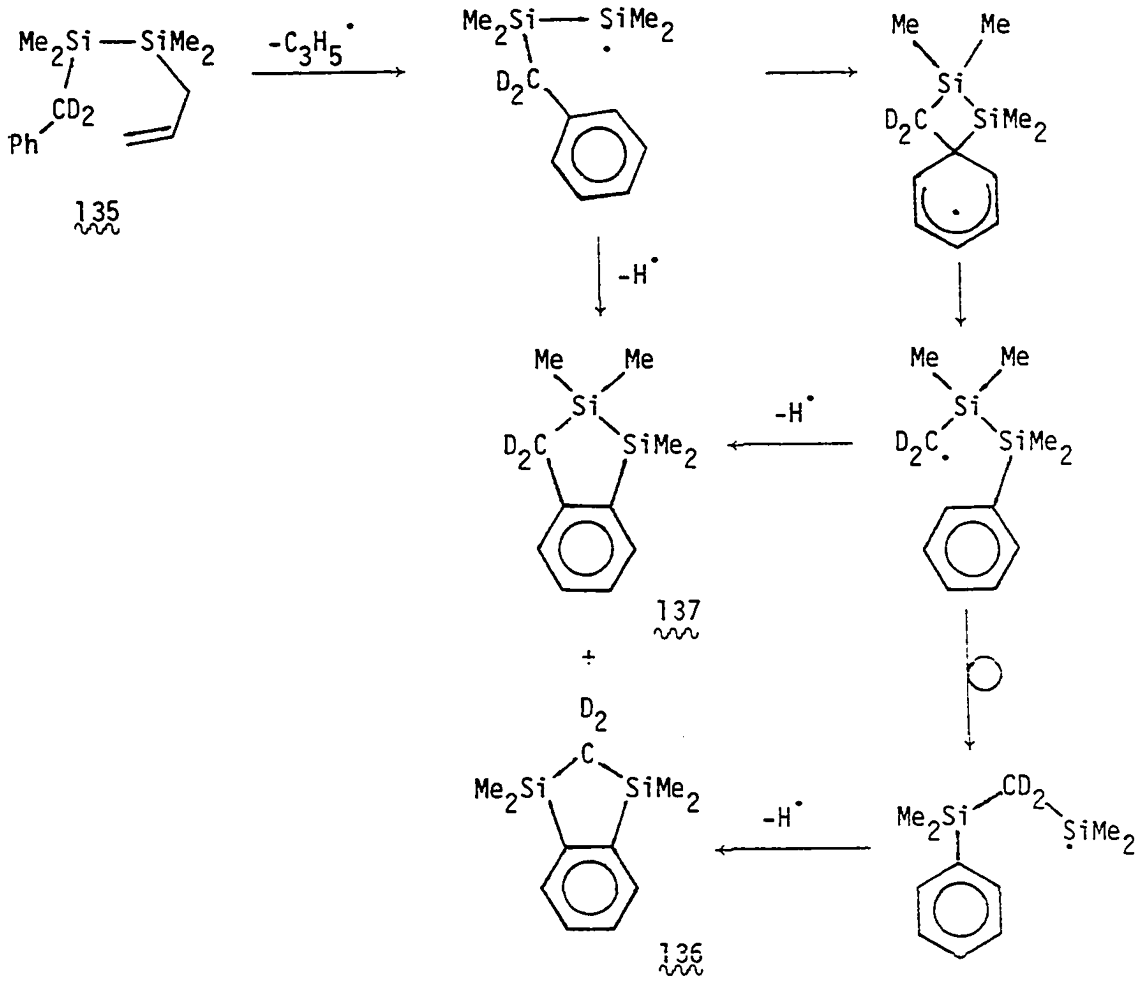
135 136 137

+ 134

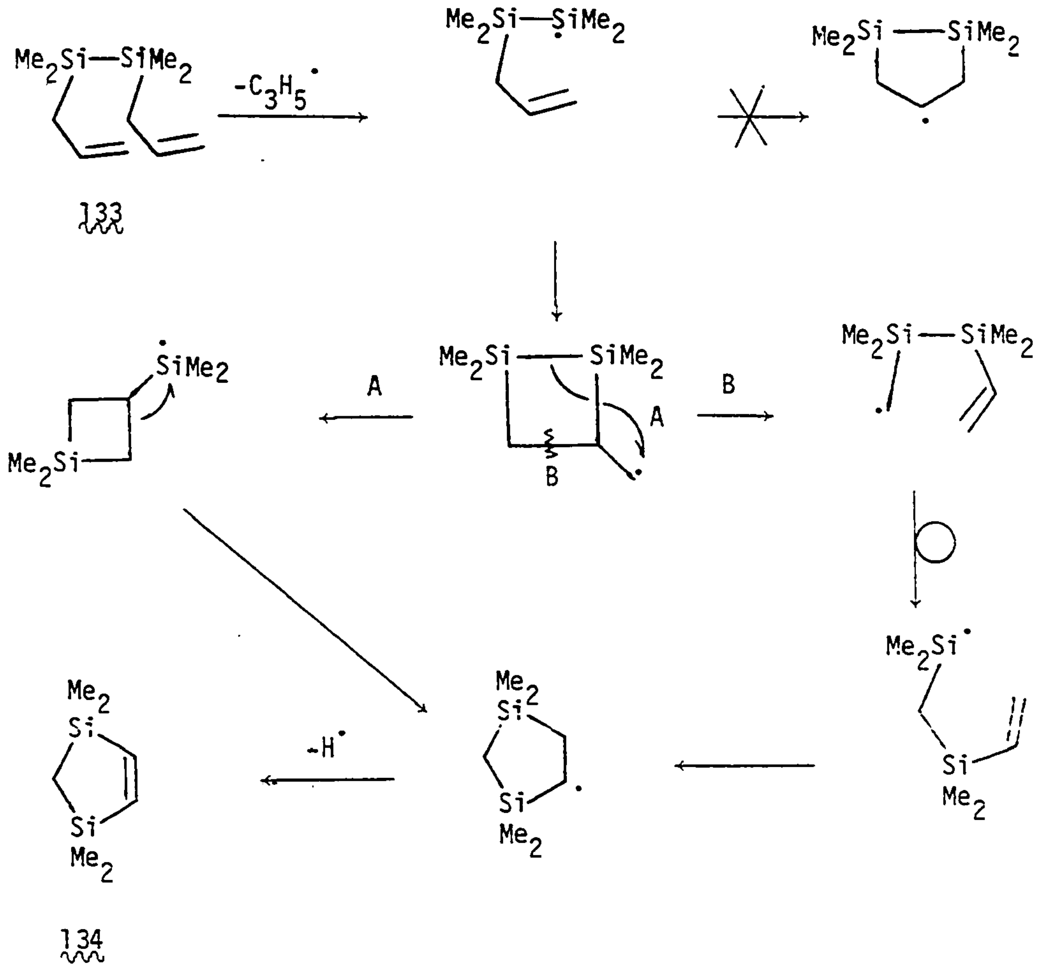
These results, plus those of a deuterium labeling experiment, suggested a mechanism involving initial Si-allyl bond homolysis and rearrangement of the resulting benzyldisilanyl radical as the origin of 136 and 137 (Scheme 26). Disilacyclopentene 134 was proposed to arise via rearrangement of allyldisilanyl radical that is formed from 133 by Si-allyl bond rupture or from 135 by Si-benzyl bond rupture (Scheme 27).

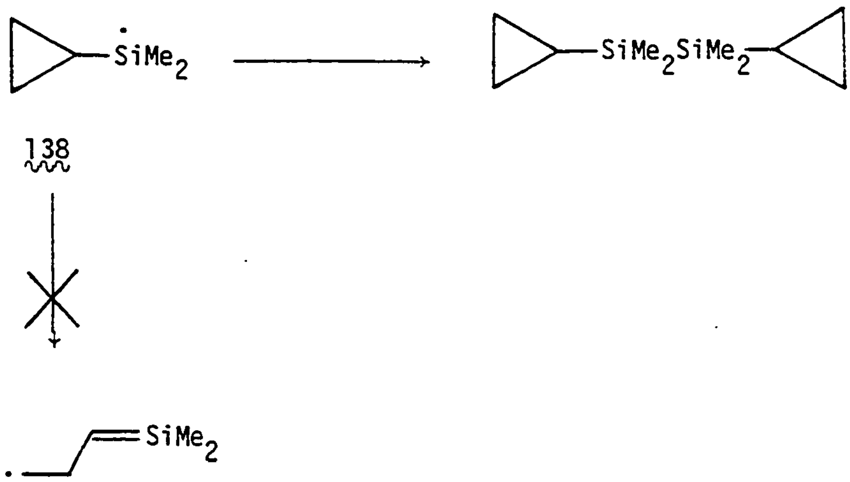
One final study pertaining to the tendency of silyl radicals to rearrange is of interest. Sakurai has found that cyclopropylsilyl radicals 138 and 139 (generated from the corresponding hydrosilane by t-butoxyl radical abstraction) do not rearrange (18). This behavior is in marked contrast to that of the carbon analogues (235).

Scheme 26

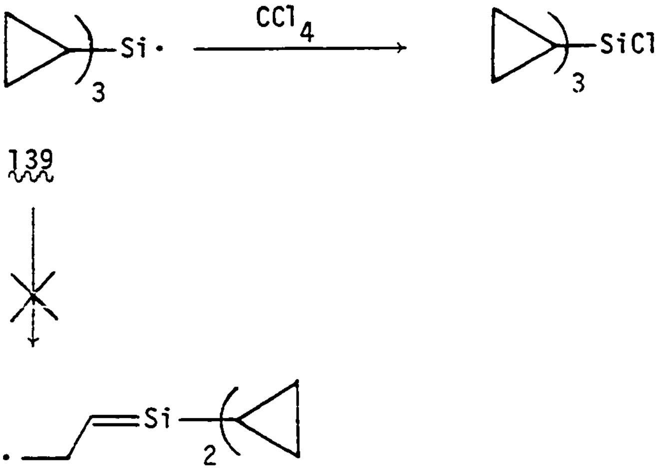

Me$_2$Si—SiMe$_2$
CD$_2$
Ph
135
-C$_3$H$_5$•
Me$_2$Si— SiMe$_2$
D$_2$C
Me
Me
Si
D$_2$C
SiMe$_2$
-H•
Me
Me
Si
D$_2$C
SiMe$_2$
137
+
D$_2$
C
Me$_2$Si
SiMe$_2$
136
-H•
Me
Me
Si
D$_2$C
SiMe$_2$
-H•
Me$_2$Si
CD$_2$
SiMe$_2$

Scheme 27


Me2Si—SiMe2
133
-C3H5•
Me2Si—SiMe2
Me2Si—SiMe2
A
B
A
B
SiMe2
Me2Si
Me2Si—SiMe2
Me2Si•
Si
Me2
-H•
Me2
Si
Si
Me2
Me2
Si
Si
Me2
134



138



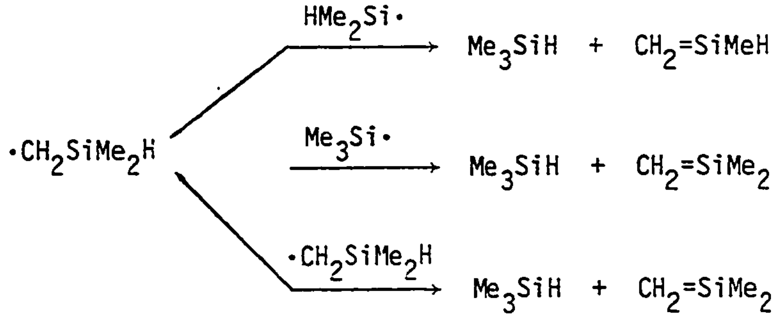
139

Disproportionation of Silyl Radicals to Silenes

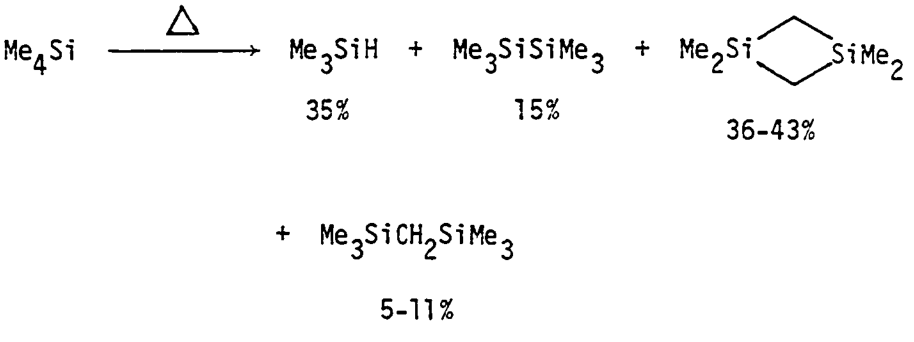
Prior to 1972, no known examples of silyl radical disproportionation to a silene existed. In fact, prior to 1972, the existence of silenes

$$CH_3\dot{S}iR_2 \xrightarrow{X\cdot} XH + CH_2{=}SiR_2$$

themselves was regarded by most as unsubstantiated, although in 1969 Davidson and Lambert, on the basis of the results of a kinetic study of the gas phase pyrolysis of trimethylsilane, had proposed that silyl substituted methyl radicals disproportionated to silenes (155,156).



In 1972, Clifford and coworkers found that the pyrolysis of tetramethylsilane in a flow system at 540 to 700°C and 0.1 to 30 torr gave trimethylsilane, hexamethyldisilane, and 1,1,3,3-tetramethyl-1,3-disilapentane as the major products in yields of 35, 15, 36-43, and 5-11%, respectively (249).



It was argued that disproportionation of $\mathrm{Me_3Si\cdot}$ to $\mathrm{Me_2Si{=}CH_2}$, which then dimerizes in a head to tail fashion to afford the 1,3-disilacyclobutane, must be occurring to explain the kinetic results and observed products. The reactions that were considered operative under these reaction conditions are:

$$\begin{aligned}
\mathrm{Me_4Si} &\xrightarrow{\quad a \quad} \mathrm{\cdot CH_3} + \mathrm{Me_3Si\cdot} \\
\mathrm{2Me_3Si\cdot} &\xrightarrow{\quad b \quad} \mathrm{Me_3SiSiMe_3} \\
\mathrm{2Me_3Si\cdot} &\xrightarrow{\quad c \quad} \mathrm{Me_3SiH} + \mathrm{Me_2Si{=}CH_2} \\
\mathrm{Me_3Si\cdot} + \mathrm{Me_4Si} &\xrightarrow{\quad d \quad} \mathrm{Me_3SiH} + \mathrm{Me_3Si\dot{C}H_2} \\
\mathrm{Me_3Si\cdot} &\xrightarrow{\quad e \quad} \mathrm{Me_2Si{=}CH_2} + \mathrm{H\cdot} \\
\mathrm{Me_3Si\cdot} + \mathrm{Me_3SiCH_2\cdot} &\xrightarrow{\quad f \quad} \mathrm{Me_3SiCH_2SiMe_3} \\
\mathrm{\cdot CH_3} + \mathrm{Me_3Si\cdot} &\xrightarrow{\quad g \quad} \mathrm{CH_4} + \mathrm{Me_2Si{=}CH_2}
\end{aligned}$$

Since under the reaction conditions employed only small amounts of hydrogen and methane were produced, processes e and g were considered to be negligible. Thus, the principal reactions for the consumption of $\mathrm{Me_3Si\cdot}$ are: b, c, d, and f. Based on the assumption that process d is negligible, due to the endothermicity of this reaction, and taking into account the amount of $\mathrm{Me_3Si\cdot}$ consumed by process f, the ratio of c to b (disproportionation to combination) was determined to be 1.2 at 627°C. Since process d is the only step that does not require two radicals to find one another, and since the endothermicity of this reaction could easily be overcome at

627°C (the energy of activation for process d was determined to be 18 kcal/mole), the validity of the assumption that process d is negligible must be questioned. Thus, the calculated ratio of c to b must be regarded with skepticism. Despite this inconsistency, the observation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane as a product in these reactions provides strong evidence supporting the proposed disproportionation of $Me_3Si\cdot$ to $Me_2Si=CH_2$.

More recently, Baldwin and coworkers reexamined the gas phase pyrolysis of tetramethylsilane (250). From a detailed product and kinetic analysis (aided by computer modelling), it was also concluded that disproportionation of trimethylsilyl radicals to 1,1-dimethylsilene is an important reaction over the temperature range 570 to 680°C.

On the basis of a detailed kinetic and product analysis, trimethylsilyl radicals, generated from hexamethyldisilane by pyrolysis at low pressures and 500 to 600°C (243,244) and from the gas-phase reaction between iodine and trimethylsilane at 250 to 350°C (251), have also been suggested to disproportionate to 1,1-dimethylsilene.

The first report which provided direct evidence that trimethylsilyl radical disproportionates to 1,1-dimethylsilene was that of Tokach and Koob (252). When tetramethylsilane was photolysed at 147 nm in the presence of methanol, the expected product of methanol trapping of 1,1-dimethylsilene, trimethylmethoxylsilane, was obtained.

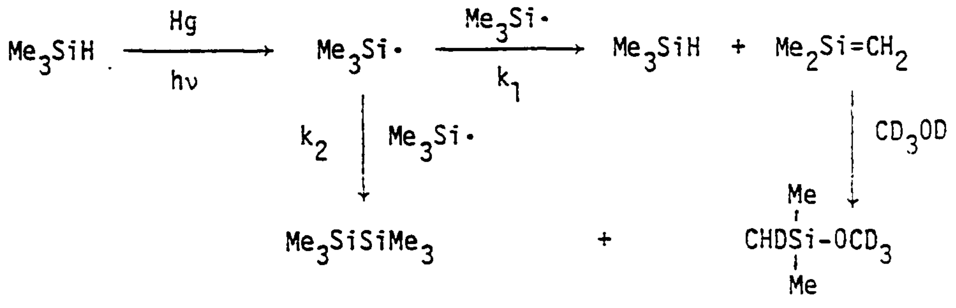
$$Me_4Si \xrightarrow{h\nu} Me_2Si=CH_2 \xrightarrow{MeOH} Me_3SiOMe$$

From the results of experiments conducted with a radical scavenger present, it was demonstrated that $Me_2Si{=}CH_2$ arose in part by a direct photoprocess. However, on the basis of the high yields of Me_3SiH and the results

$$Me_4Si \xrightarrow{h\nu} CH_4 + Me_2Si{=}CH_2$$

of the methanol trapping experiments, it was concluded that $Me_2Si{=}CH$ must also arise by disproportionation of trimethylsilyl radical. A kinetic analysis of the reaction gave a value of disproportionation to combination for $Me_3Si\cdot$ of 0.48.

Even more definitive evidence for the disproportionation of $Me_3Si\cdot$ to $Me_2Si{=}CH_2$ has been reported by Tokach and Koob (253) for the mercury photosensitized decomposition of trimethylsilane in the gas phase in the presence of perdeuteromethanol. The formation of methoxysilane 140, which it was argued could not arise from sensitization of methanol, clearly demonstrated the intermediacy of 1,1-dimethylsilene. From the ratio of the quantum yields of trimethylmethoxysilane (140) to hexamethyldisilane, the ratio of disproportionation to combination (k_1/k_2) was determined to be 0.31 ± 0.08.



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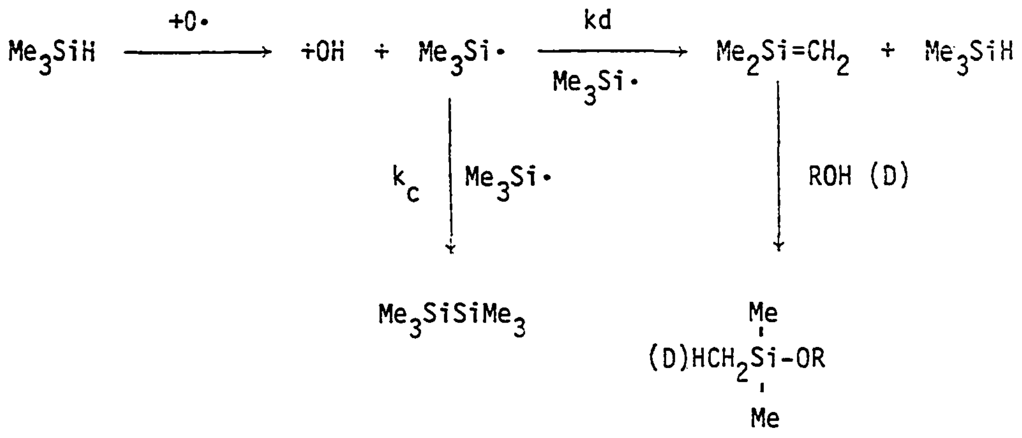
In a companion communication to that of Tokach and Koob (253), Gammie and coworkers (254) have described kinetic evidence which demonstrated that trimethylsilyl radicals, derived from the photolysis of bis-(trimethylsilyl)mercury in the gas-phase, also affords silenes by self-disproportionation, although the ratio of disproportionation to combination (0.05) was much lower than that reported by Tokach and Koob. The ratios of disproportionation to combination for a variety of other silyl radicals were also determined. These values are given in Table 14. Finally, Gammie and coworkers determined the rate constant for self-disproportionation of $Me_3Si\cdot$ to be 7.5×10^{10} cm^3 $mol.^{-1}$ $sec.^{-1}$. This value, which is more than six orders of magnitude greater than the rate constant for H abstraction from Me_3CH, is an indication of the driving force for this disproportionation reaction due to the formation of the Si-C double bond.

Table 14. Ratio of Disproportionation to Combination (kd/kc) for Various Silyl Radicals in the Gas Phase at 25°C.

Reaction	kd/kc
$Me_3Si\cdot + Me_3Si\cdot \longrightarrow Me_3SiH + CH_2{=}SiMe_2$	0.05
$Me_3Si. + Me_2SiH. \longrightarrow Me_3SiH + CH_2{=}SiMeH + Me_2Si:$	0.3
$Me_3Si. + MeSiH_2. \longrightarrow Me_3SiH + CH_2{=}SiMe_2 + Me\ddot{S}iH$	0.5^a
$Me_2SiH\cdot + Me_2SiH\cdot \longrightarrow Me_2SiH_2 + CH_2{=}SiMeH$	0.1
$MeSiD_2\cdot + MeSiD_2^{\bullet} \longrightarrow MeSiD_2H + CH_2{=}SiD_2$	0.04

[a] Sum of both the silaethylene and silylene producing disporportionations.

That disproportionation of silyl radicals is not restricted to the gas phase has been demonstrated by Cornett and coworkers (255). When trimethylsilyl radical was generated by photolysis of t-butyl peroxide in solutions of trimethylsilane containing Me_3COD or MeOH, hexamethyldisilane and the corresponding trimethylalkoxysilanes, derived from alcohol trapping of 1,1-dimethylsilene, were obtained in ratios of approximately 5 to 1. From the ratio of alkoxysilane to hexamethyldisilane the ratio of disproportionation to combination (kd/kc) was determined to be 0.2.



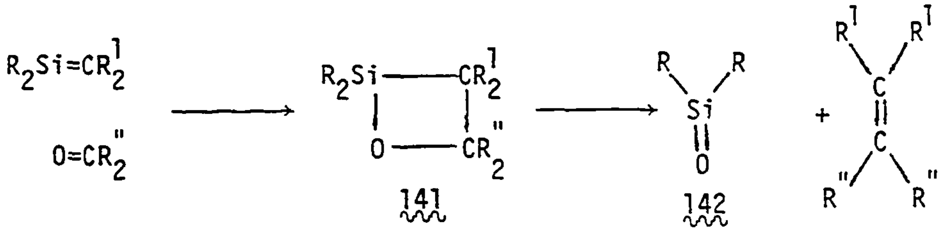
R = t-Bu, Me

RESULTS AND DISCUSSION

Attempted Preparation of Silaoxetanes Utilizing Silylene Insertion Reactions

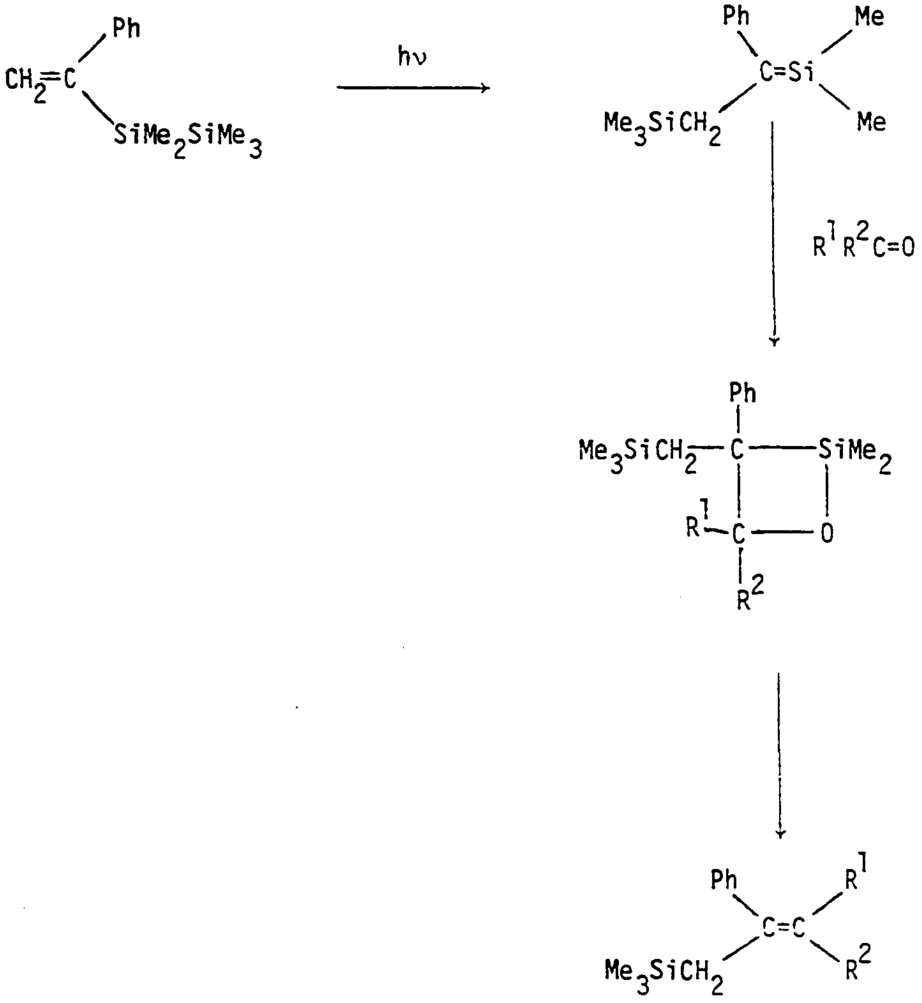
Reaction of Dimethylsilylene with Cyclooctene Oxide

Since the initial proposal by Barton and coworkers (256), and Kline (257), that silenes ($R_2Si{=}CR^1_2$) cycloadd to the carbonyl group of ketones and aldehydes to form silaoxetanes (141), which under their reaction conditions (>400°C, gas phase) underwent decomposition to a silanone (142) and an olefin, this reaction has become a standard test for silene intermediacy (106,258).



That this reaction is not restricted to silenes generated at high temperatures has been demonstrated by Ishikawa and coworkers (259,260). Thus, U.V. irradiation (low pressure Hg lamp, vycor filter) of α-disilanylstyrene in a solution of benzene and either acetone or acetophone at room temperature afforded the corresponding olefins in moderate yields as the only volatile products. These reactions were also proposed to proceed via the intermediacy of a silaoxetane (Scheme 28).

Scheme 28



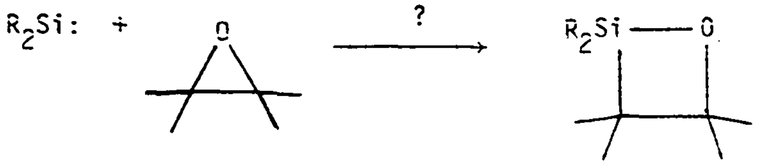
$R^1 = R^2 = Me$; 17%

$R^1 = Me$, $R^2 = Ph$; 19%

(E:Z = 1.4:1)

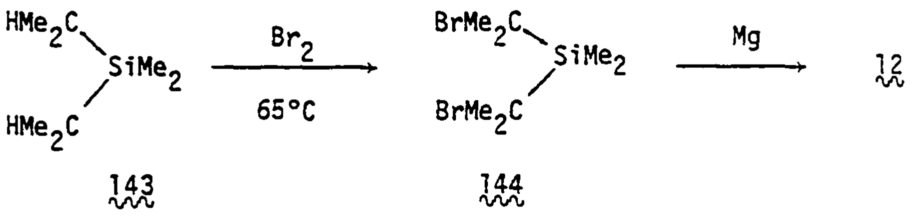
Hoekman has estimated the ΔH of reaction for the unimolecular decomposition of **141** to **142** and an olefin to be 58 kcal/mole (261). This estimate, coupled with the prediction that the strain energy of a silaoxetane is less than that of an analogous 1-silacyclobutane (261), which are known to be isolable and stable at room temperature, suggests that silaoxetanes should be stable, isolable species. Thus, although the decomposition of **141** at high temperatures is not unexpected, its facile decomposition under the much milder conditions employed by Ishikawa and coworkers (*vide supra*) is an unreasonable thermodynamic expectation.

We were, therefore, interested in obtaining a silaoxetane ring, and exposing it to a variety of thermal and photochemical conditions to elucidate the chemistry of this species. Since numerous attempts to prepare silaoxetanes by direct chemical methods had all met with failure (262), we turned our attention toward the use of silylenes as silaoxetane precursors. Both the established ability of silylenes to insert into strained rings (51,73), and the considerable strength of the silicon-oxygen bond (Table 3), suggested that insertion of silylenes into epoxides to form silaoxetanes was a reasonable expectation.



In view of the thermal instability of silaoxetanes (*vide supra*), and in an effort to maximize the chances of actually isolating a silaoxetane, the mildest known thermal generator of dimethylsilylene, hexamethylsilarane (**12**) (49,50), was chosen for the initial studies.

Prior to this investigation, the established method of preparation of **12** involved the conversion of diisopropyldimethylsilane (**143**) to dimethylbis(α-bromoisopropyl)silane (**144**), by treatment with molecular bromine, followed by Wurtz-type ring closure of **144** to **12** (49).



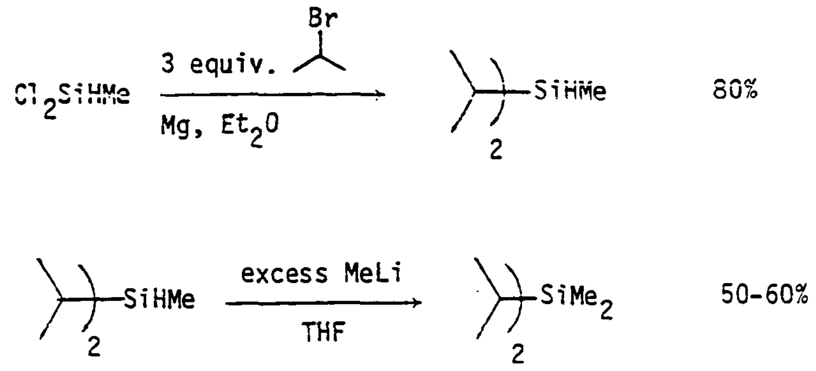
Unfortunately, the availability and utility of **12** was limited by the difficulty associated with the preparation of **143** by the established literature method. Eaborn had previously prepared **143**, although in only 22% yield, by the sequential addition of two equivalents of isopropyl Grignard and two equivalents of methyl Grignard to tetrafluorosilane (263).

Initially, this low yield was felt to be acceptable provided that **143** could be easily isolated. However, several attempts to repeat Eaborn's synthesis led in all cases to reaction mixtures which contained (by G.C.) greater than five products, none of which predominated. Clearly, a more desirable method for the preparation of **143** was needed.

Attempts to prepare **143** by the addition of two equivalents of either isopropyl Grignard or isopropyl lithium to dimethyldichlorosilane, even under forcing conditions, also failed. The failure to obtain **143** by this route was surprising since in general the displacement of halogens from silicon by Grignard reagents is a facile reaction (264). However, these results are in keeping with the report that diisopropyldichlorosilane was obtained in only 22% yield from the reaction of isopropyl Grignard with tetrachlorosilane (265).

Since Kimble (266) had previously prepared diisopropylmethylsilane in 80% yield by the reaction of excess isopropyl Grignard with methyldichlorosilane, the failure to effect the addition of two isopropyl groups to dimethyldichlorosilane was postulated to be due to steric hindrance at silicon which prevented the approach of the incoming nucleophile.

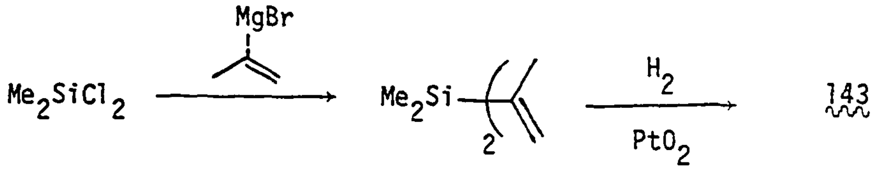
Due to the ready availability of diisopropylmethylsilane, a method for its conversion to 143 was sought. The direct displacement of silicon hydrides by organolithium reagents is a well precedented reaction (263). Therefore, reaction of methyllithium with diisopropylmethylsilane was expected to afford 143. This was indeed found. Thus, when a THF solution of diisopropylmethylsilane and excess methyllithium was refluxed for 48 hours, 143 was obtained in 56% yield. The ability to effect this transformation constitutes a two step conversion of methyldichlorosilane to 143 in an overall yield of 45%, and therefore, represents a two fold increase in the yield of 143 when compared to the previous method of preparation.



143

More recently, an improved synthesis of 143 has been reported by Seyferth and coworkers (267). It was found that conversion of dimethyldichlorosilane to dimethyldiisopropenylsilane, by reaction with isopropenyl

Grignard, followed by hydrogenation gave **143** in 61% overall yield.



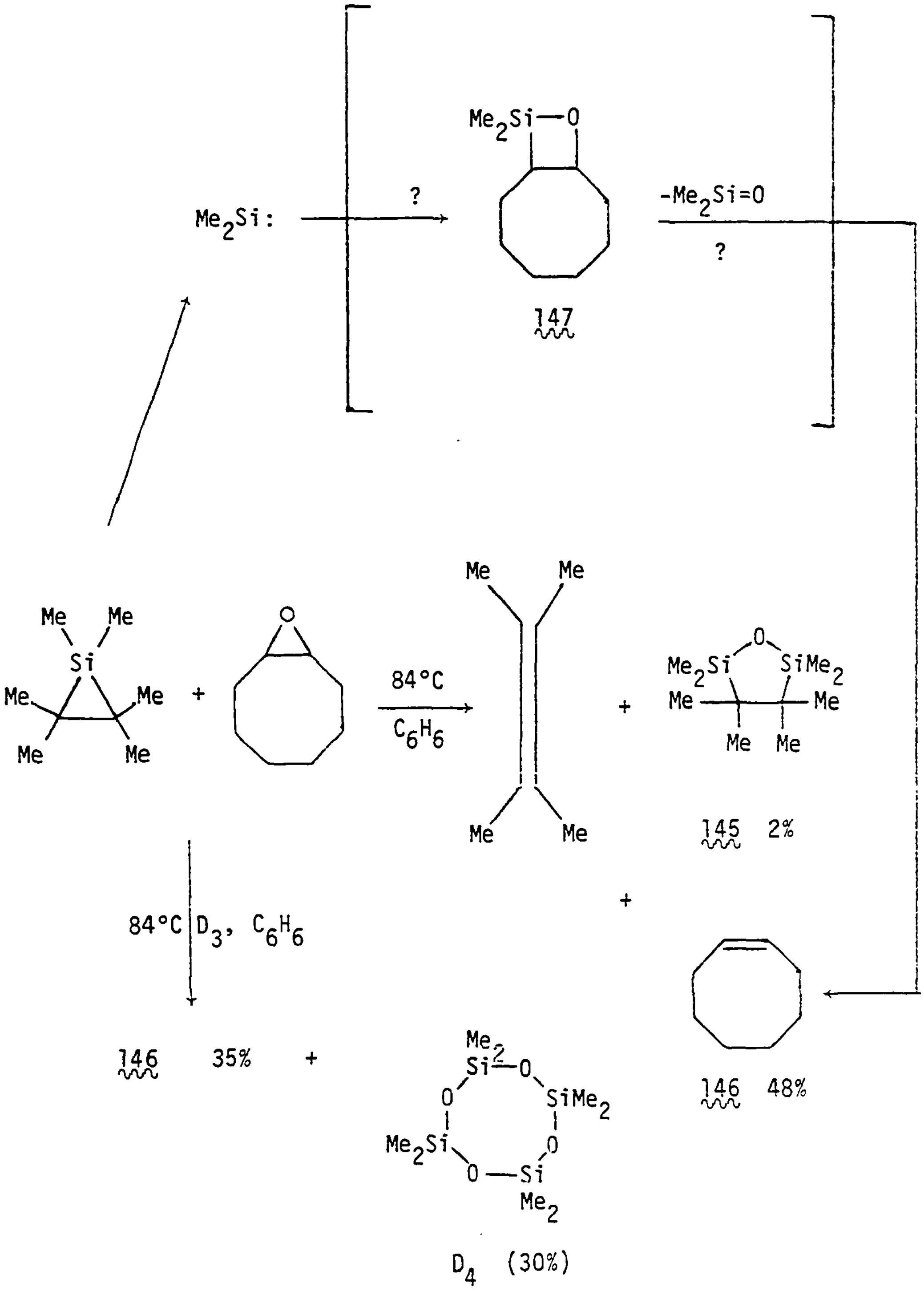
From **143** the synthesis of **12** was conducted as previously described by Seyferth and Annarelli (49).

Having succeeded in preparing **12**, we turned our attention toward its reaction with epoxides. Heating a benzene solution of **12** and an excess of cyclooctene oxide at 84°C for 12 hours led to the formation of tetramethylethylene and octamethyl-2,5-disilaoxacyclopentane **145**, the usual products from the thermolysis of **12** (49,50), along with a 48% yield of cyclooctene (Scheme 29). Cyclooctene was independently shown not to arise from the thermolysis of cyclooctene oxide under the reaction conditions.

These results are in keeping with the desired insertion of dimethylsilylene into the epoxide to form silaoxetane **147**, which extruded dimethylsilanone to afford cyclooctene under the reaction conditions employed. Evidence supporting the intermediacy of dimethylsilanone was obtained when inclusion of hexamethylcyclotrisiloxane (D_3) in the reaction mixture, under otherwise identical conditions, resulted in the formation of octamethylcyclotetrasiloxane (D_4) in a yield of 30%. Insertion of dimethylsilanone into D_3 to form D_4 has often been used as a test for silanone intermediacy (e.g., 268). Thus, if silaoxetane **147** is formed under these reaction conditions, it is either too unstable or to reactive to survive.

Therefore, to lower the thermal requirements for dimethylsilylene generation, we turned to the photolysis of dodecamethylcyclohexasilane (**14**)

Scheme 29


Me2Si:
?
Me2Si—O
-Me2Si=O
?
147
Me
Si
+
84°C
C6H6
145 2%
SiMe2
84°C
D3, C6H6
146 35%
+
D4 (30%)
146 48%

Scheme 30

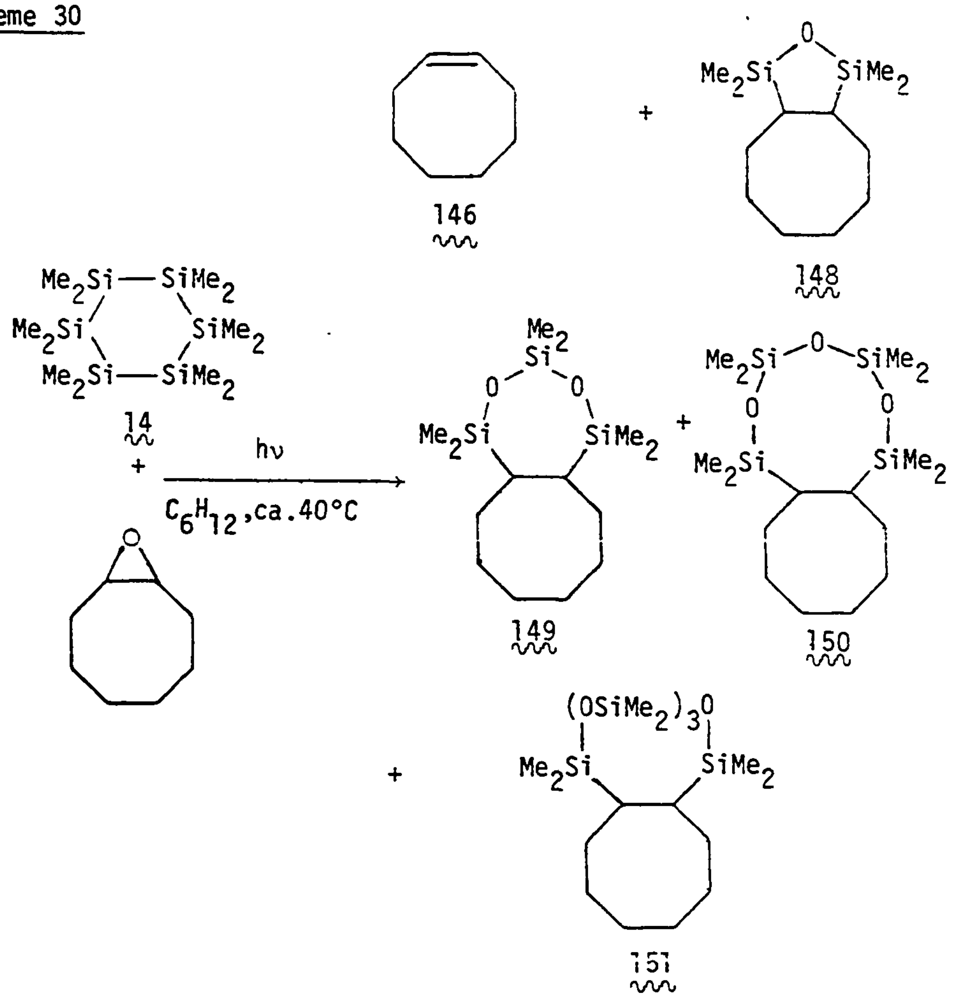


Table 15. Photolysis of 14 and Cyclooctene Oxide

Irradiation time (h)	Yield (%)[a]				
	146	148	149	150	151
2	62	-	-	-	-
12	44	<1	4	2	-
18	16	-	5	2	2

[a] Yields are obtained by calibrated GC and are based on reacted epoxide.

(54,55). Irradiation (450 W. Hanovia through quartz) of a cyclohexane solution of 14 and excess cyclooctene oxide afford a 62% yield of cyclooctene after 2 hours. Continued irradiation resulted in the gradual disappearance of cyclooctene, and the formation of cyclic siloxanes 148, 149, 150, and 151 (Scheme 30 and Table 15). The identities of 148, 149, 150, and 151, were established by the usual spectroscopic methods.

The formation of 148, 149, 150, and 151 is consistent with the intermediacy of dimethylsilanone in these reactions. The involvement of dimethylsilanone was further suggested by the observation that the addition of D_3 to the reaction mixture, under otherwise identical conditions, eliminated the secondary products 148-151, and afforded high yields of D_4 and significant amounts of decamethylpentacyclosiloxane (D_5). The only other new product observed was 152, the known adduct of dimethylsilylene and D_3 (68). Scheme 31 and Table 16 summarize these results.

Scheme 31

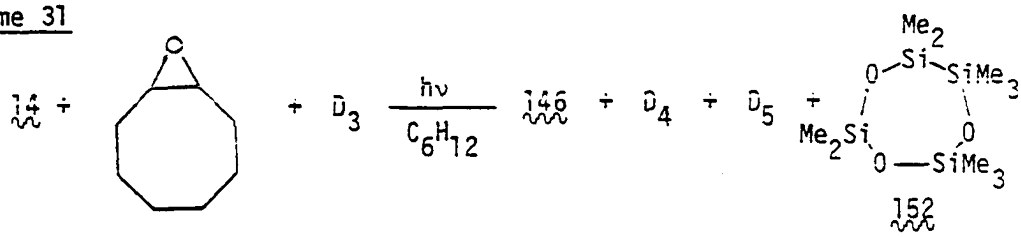


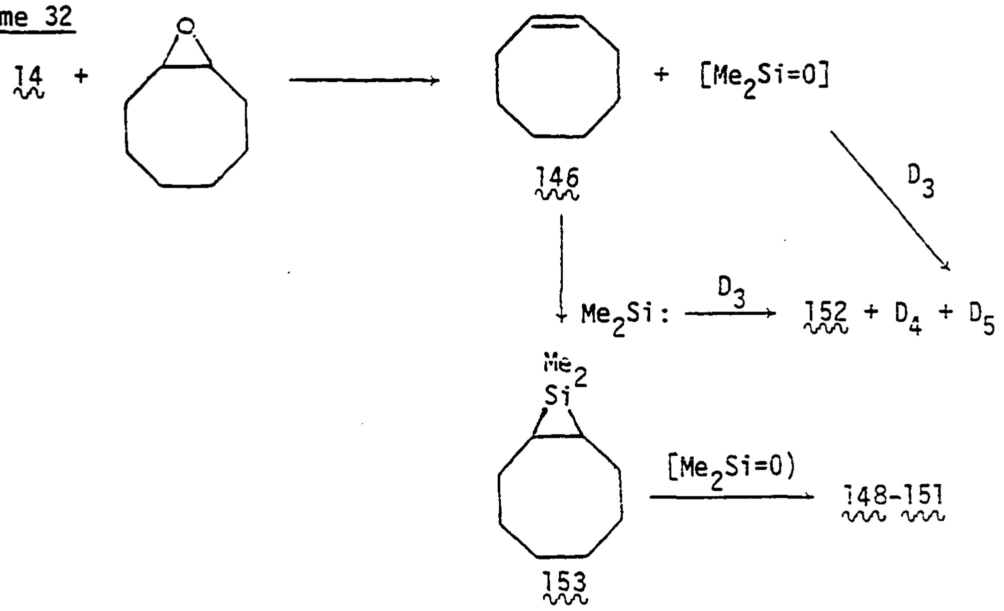
Table 16. Photolysis of 14, cyclooctene oxide, and D_3.

Irradiation time (h)	Yield (%)[a]			
	146	D_4	D_5	152
2	76	73	>2	-
12	22	60	8	9

[a] Yields (GC) of 146, D_4 and D_5 are based on reacted epoxide. The yield of 152 is based on reacted D_3.

An economical explanation for both the decrease in cyclooctene and the appearance of cyclic siloxanes 148-151, upon extended irradiation and in the absence of D_3, is the addition of dimethylsilylene to cyclooctene to afford silarane 153, which upon sequential insertions of dimethylsilanone would yield the observed products (Scheme 32). Precedent for the addition of silylenes to cyclic olefins (77) and for the insertion of dimethylsilanone into silaranes (269) has been previously reported. In the presence of D_3 both dimethylsilylene and dimethylsilanone are trapped by D_3 to afford, respectively, 152 and D_4 and D_5, thus preventing the formation of 148-151.

Scheme 32



Although the results of both the thermal and photochemical reactions of dimethylsilylene with cyclooctene oxide can be explained by initial silylene insertion into cyclooctene oxide to give silaoxetane 147, which decomposes to cyclooctene and dimethylsilanone, the intermediacy of both

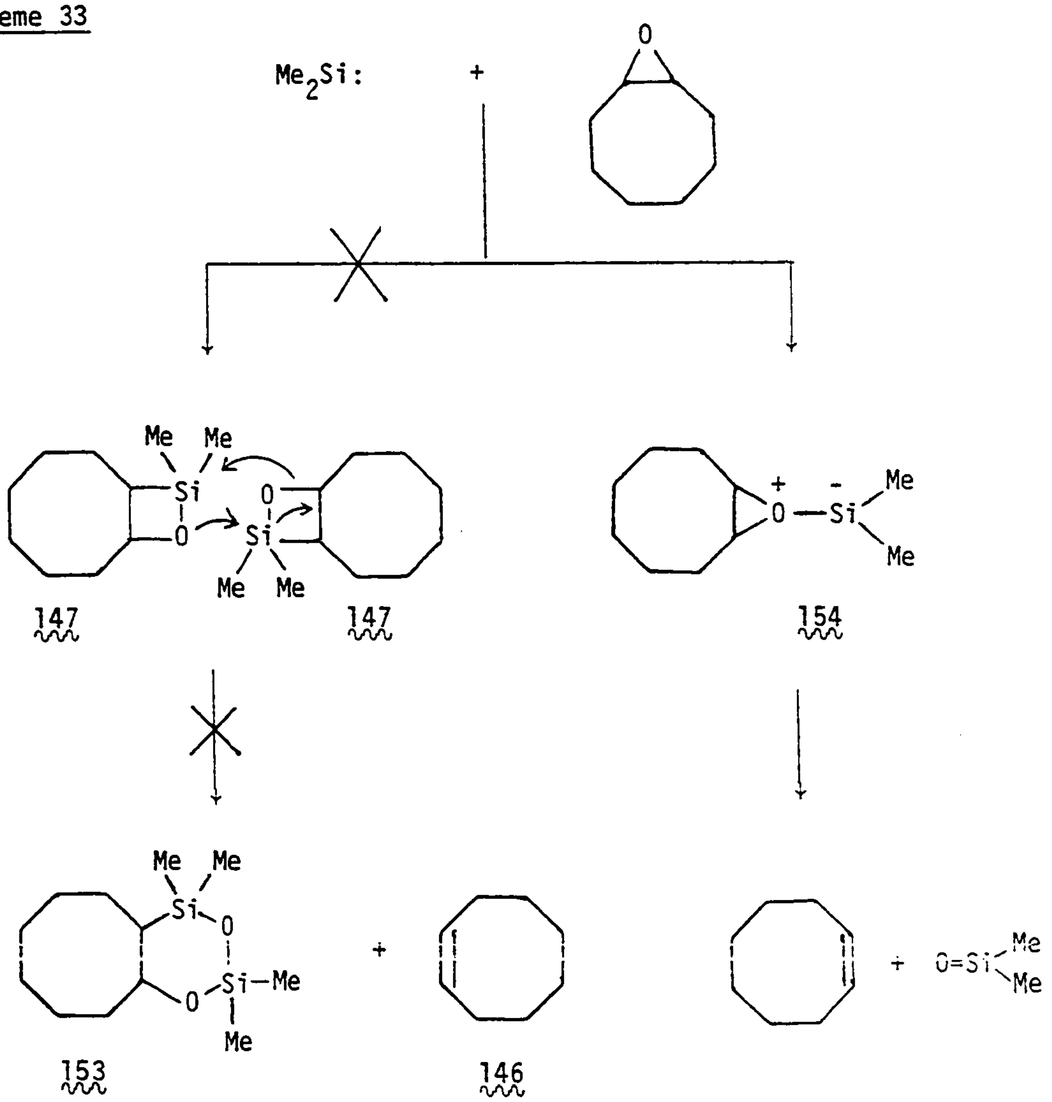
147 and dimethylsilanone must be questioned.

As discussed previously, we find it difficult to believe that **147** would be so thermally unstable as to extrude silanone under our reaction conditions. It is possible that **147** could serve as a "silanone transfer agent", as shown in Scheme 33, to produce cyclooctene. However, this process has been discarded since the other expected product, disiloxane **153**, is never observed. On the basis of these arguments, and by analogy to the reactions of nucleophilic carbenes with epoxides and oxetanes (270), silyl ylid **154** is proposed as a more reasonable intermediate for these reactions (Scheme 33).

When the proposed intermediacy of **154** was first made (271), no literature precedent for its existence was available. Now, however, several examples of the intermediacy of silyl ylids, derived from the reactions of silylenes with oxygen containing substrates, are known (see Historical on silylenes). In particular, Tzeng and Weber (113) have likewise interpreted the reaction of dimethylsilylene and vinyl epoxides to proceed through an ylid intermediate (**155**), which rearranges in a stepwise fashion to afford the observed product (**156**). This proposal is not without ambiguity, however, since the possibility of initial silylene addition to the π-bond was not considered, nor could the data obtained by these authors provide a distinction. Our data strongly suggest that indeed initial ylid formation is correct, since we find that cyclooctene does not significantly compete with cyclooctene oxide for dimethylsilylene.

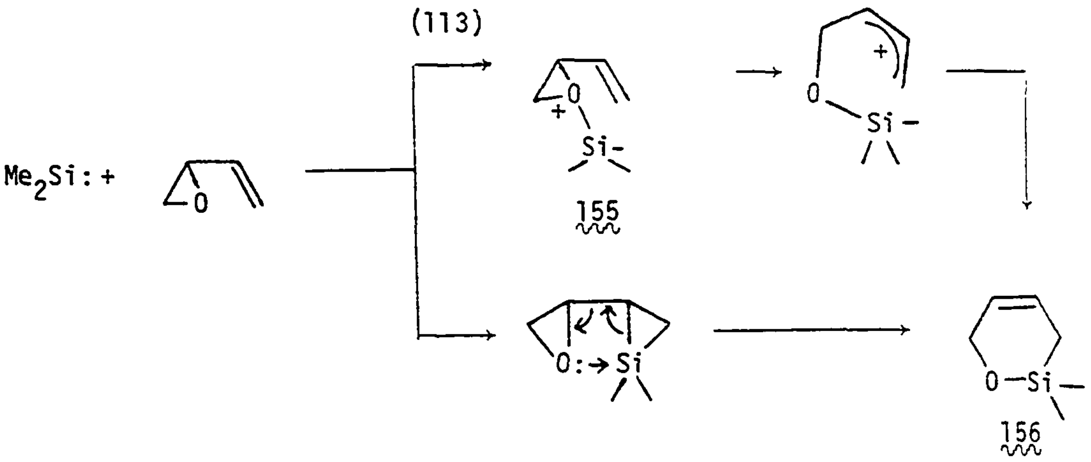
The question concerning the intermediacy of free dimethylsilanone in these reactions is less readily reconciled. Thus, while the decomposition of ylid **154** to cyclooctene and dimethylsilanone is not an unreasonable

Scheme 33

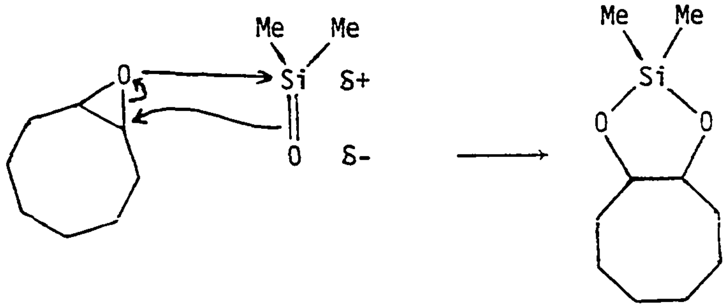


not observed

(113)

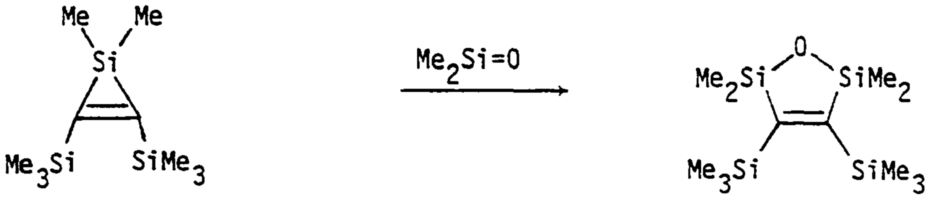


expectation, the absence of cyclic oligomers of dimethylsilanone (D_3 and D_4), when these reactions were conducted in the absence of an added trap, argues against its intermediacy. Cyclooligomerization of dimethylsilanone has been previously proposed to give D_3 and D_4 (272,273,274). A further argument against the intermediacy of dimethylsilanone in our reactions is the absence of cyclic siloxane 157, or its higher homologues.



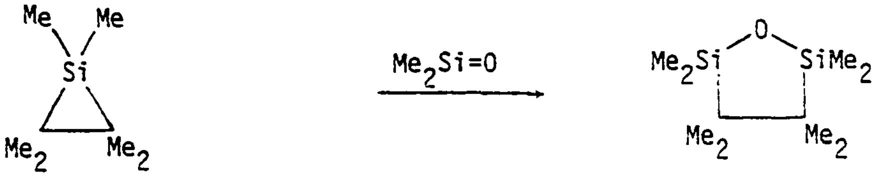
157

Ab initio calculations by Jaquet and coworkers (275), and Rudenberg and Barton (276), have demonstrated that silanone ($H_2Si=O$) is a highly polarized molecule in which the oxygen bears a partial negative charge (-0.22 to -0.99 depending upon the basis set) and silicon bears a partial positive charge (+0.51 to +1.41 depending upon the basis set). Thus, from a consideration of the polarized nature of silanone and the strength of the silicon-oxygen σ-bond the formation of 157 is expected to be a thermodynamically favored process. That silanones insert into strained rings has been previously reported by Seyferth, who proposed that dimethylsilanone inserts into 32 and 12 to afford cyclic disiloxanes 158 and 159, respectively (269).



32

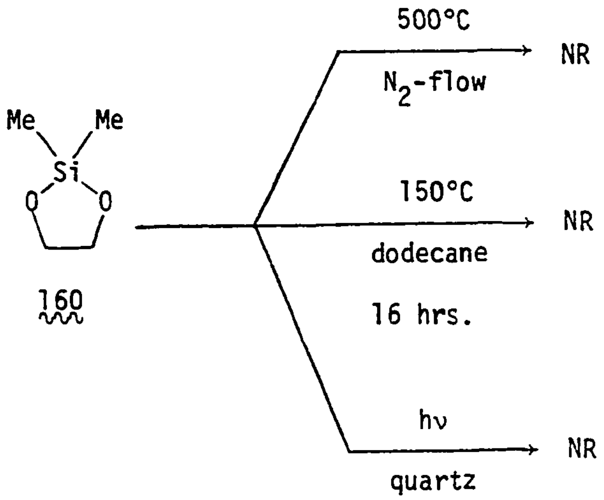
158



12

159

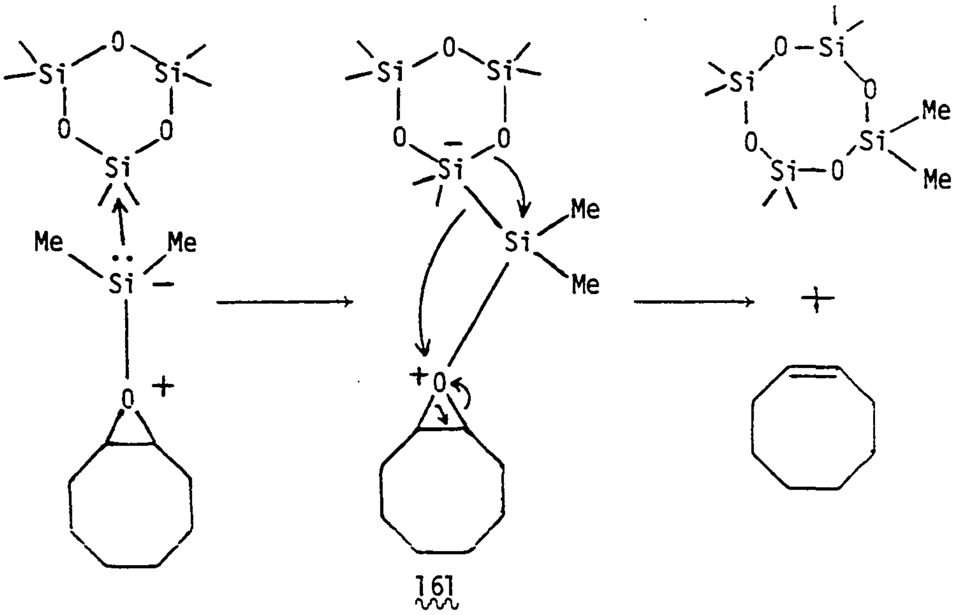
Thus, on the basis of this reasoning, and the known thermal and photochemical stability of the analogous cyclic siloxane 160 (261), the absence of 157 in our reactions is taken as evidence which argues against the intermediacy of free dimethylsilanone.



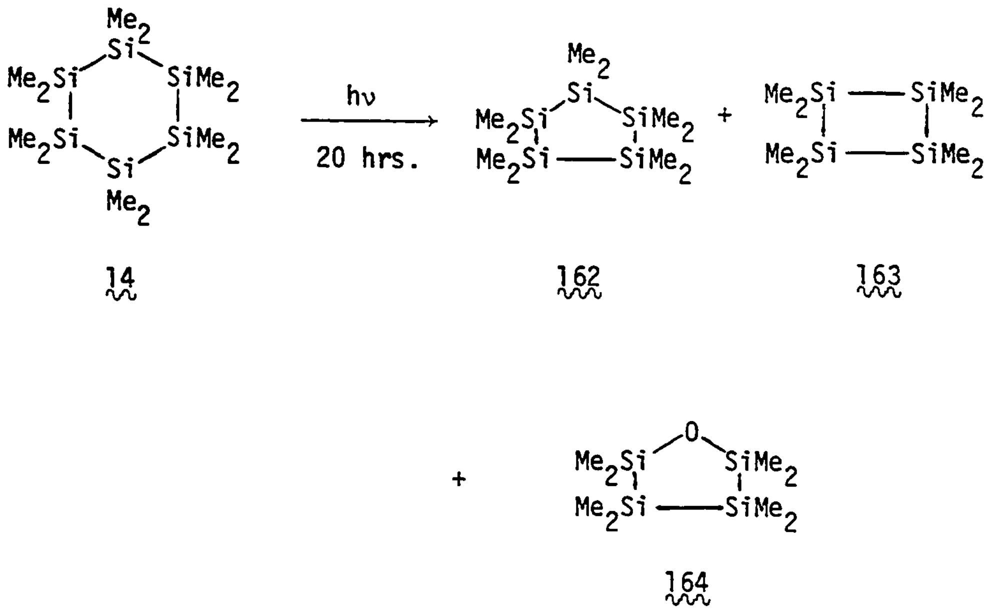
As an alternative to the intermediacy of dimethylsilanone, the possibility that ylid 154 could transfer the formal unit of dimethylsilanone was considered. Although the polarity of ylid 154 is opposite that required for a direct insertion into a Si-O bond, it is possible that 154 could act as a "silanone transfer agent". As illustrated in Scheme 34, such a transfer would be initiated by nucleophilic attack by the silyl anion of 154 on silicon in a siloxane. Decomposition of 1,3-ylid 161 in either a stepwise or concerted fashion could yield the formal product of silanone insertion and cyclooctene. Such a route has the added advantage of explaining the absence of the expected oligomers of dimethysilanone (e.g., D_3 and D_4) and 157 in the untrapped reactions. Although the data will not allow absolute distinction between extrusion of dimethylsilanone from ylid 154 and "silanone transfer", on the basis of the previous arguments, the latter process is favored.

Finally, the intermediacy of free dimethylsilylene in the photochemical reaction of 14 and cyclooctene oxide must also be questioned.

Scheme 34



In their pioneering studies on the use of 14 as a photochemical source of dimethylsilylene, Ishikawa and Kumada (54,55) found that the photochemical decomposition of cyclohexane solutions of 14 (low pressure Hg lamp, Vycon filter) required irradiation times in excess of 20 hours. For example, irradiation of 4 g of 14 in 200 ml of cyclohexane for 20 hours afford a reaction mixture which contained unreacted 14 (17%), cyclic silanes 162 and 163 (68 and 12%, respectively), and cyclic siloxane 164 (3%) as the major volatile products. Although the rate of decomposition of 14 was greater in more dilute solutions, the formation of 162, 163, and 164 in significant amounts was observed in all cases.



Thus, it was very surprising that irradiation of a cyclohexane solution of 14 containing excess cyclooctene oxide results in the complete disappearance of 14 after 2 hours. Equally surprising, was the complete absence of 162, 163, and 164, the expected decomposition products of 14. Indeed, with the exception of unreacted epoxide and D_3 (when added as a trap), the only detectable products of the reaction 14 and cyclootene oxide were those previously described (*vide supra*).

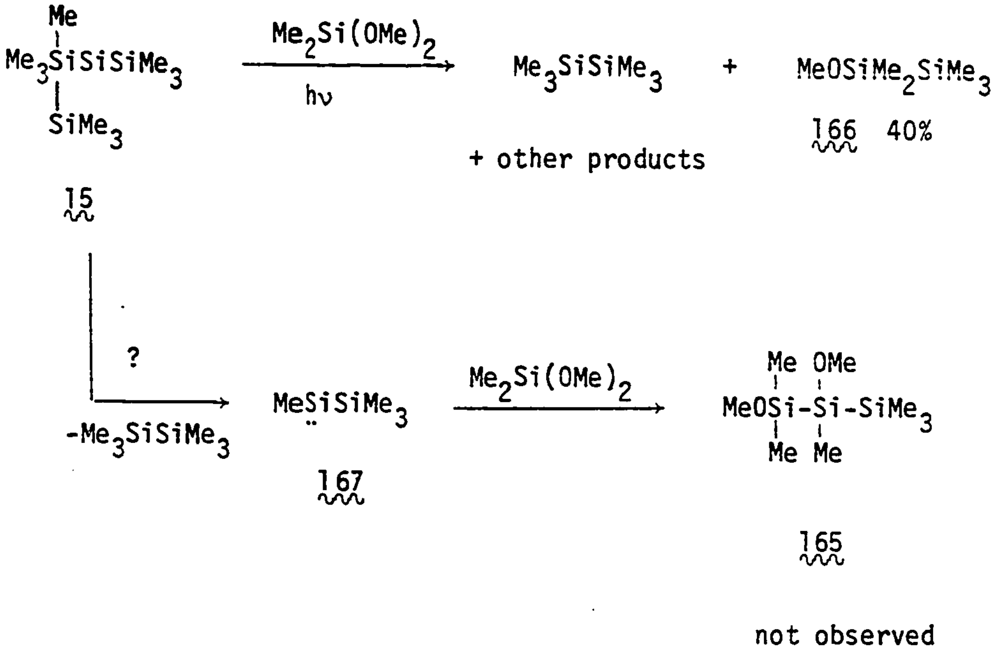
Thus, the possibility that coordination of cyclootene oxide and 14 (or photoexcited 14) may well proceed the transfer of "dimethylsilylene" must be considered.

It is interesting to note that irradiation of a cyclohexane solution of 14 and excess cyclohexene episulfide for 13.5 hours, under similar conditions to those employed for the reactions with cyclooctene oxide, afforded a complex reaction mixture that contained as major components unreacted 14 and 162. This result demonstrates that the enhanced rate of photochemical decomposition of 14 is dependent upon the presence of oxygen containing substrates.

Although this phenomenon is not understood it has also been observed for a variety of other polysilanes. For example, irradiation of tris-(trimethylsilyl)methylsilane (15) in a hydrocarbon solution with either low-pressure or medium-pressure Hg lamps (quartz filter) resulted in the slow disappearance of 15 and the appearance of hexamethyldisilane as the only observable product. Thus, after irradiation for 66 hours with a low pressure Hg lamp, approximately 75% unreacted 15 remained. When a medium pressure Hg lamp was employed, 80% unreacted 15 was still present after irradiation for 35 hours.

In contrast, when dimethyldimethoxysilane was included in the reaction mixture, photolysis for 12 hours at 45°C (medium pressure Hg lamp, quartz filter) resulted in the complete disappearance of 15 and the formation of a complex reaction mixture from which only hexamethyldisilane and methoxypentamethyldisilane (40% yield based on $Me_3SiSiMe_3$) could be isolate. Surprisingly , none of the expected silylene trapping product, 165, was found.

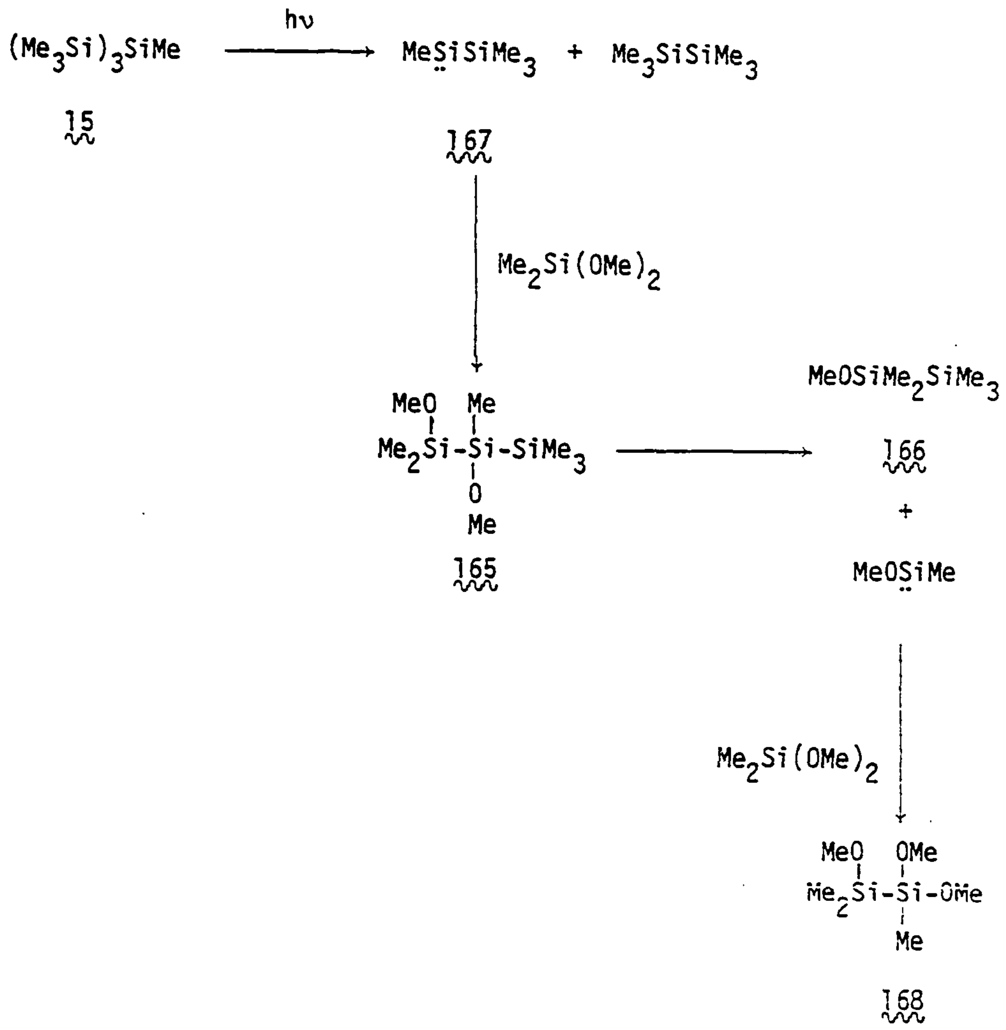
It is possible to explain the results of this reaction via the intermediacy of silylene 167 (Scheme 35). Gaspar (14) has demonstrated that 2-alkoxytrisilanes photochemically decompose by extrusion of the central silicon atom to afford the corresponding disilane and silylene. Thus,



disilane 166 can be rationalized as arising from the photochemical decomposition of 165. The methylmethoxysilylene produced by such a process would then, upon reaction with dimethyldimethoxysilane, yield disilane 168. Since it is known that alkoxypolysilanes are more efficient traps for silylenes than alkoxymonosilanes (67), the methoxydisilanes 166 and 168, as well as Trisilane 165, could compete with dimethyldimethoxysilane for the silylenes produced under these reaction conditions to afford still more products, each of which could undergo further reactions. Thus, while the complexity of this reaction was not anticipated, the results are consistent with decomposition of 15 to hexamethyldisilane and methyltrimethylsilylsilylene.

Whatever the mechanistic fate of this reaction, the finding that the rate of decomposition of 15 is greatly enhanced by dimethyldimethoxysilane

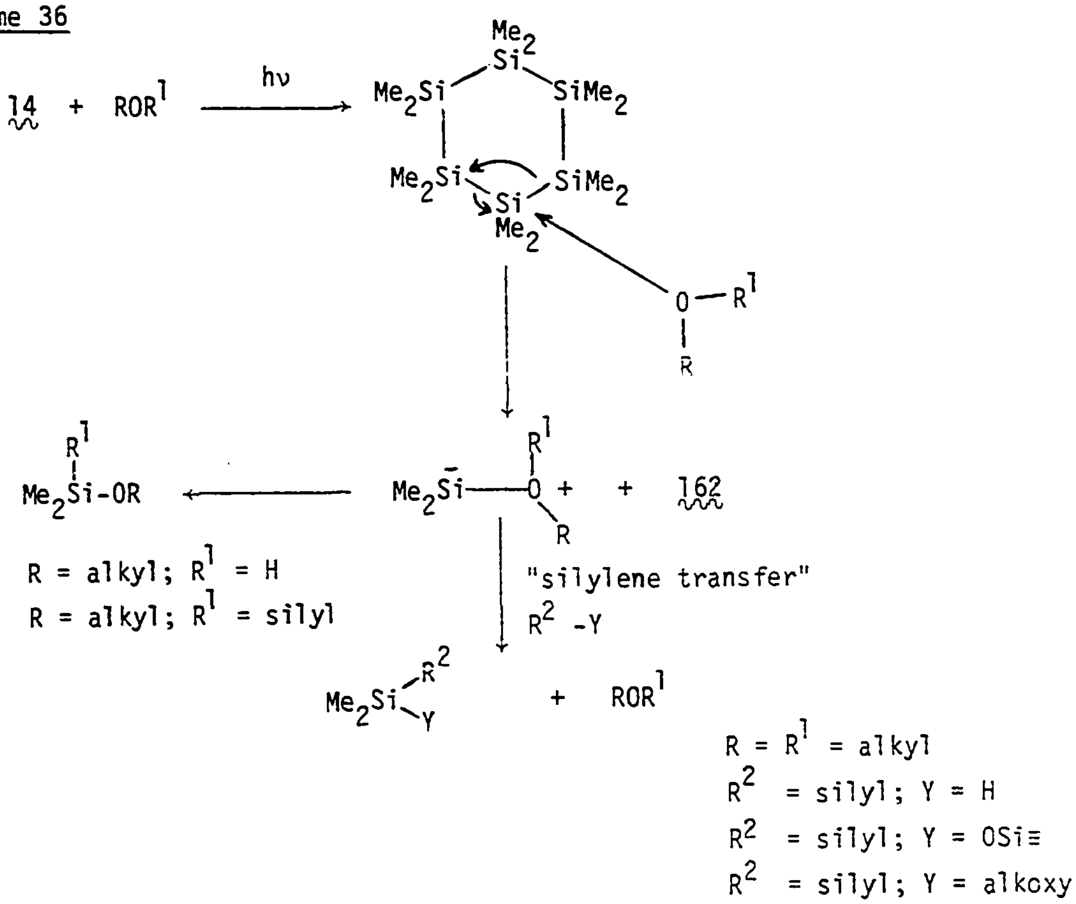
Scheme 35



suggests that an interaction between **15** (or photoexcited **15**) and dimethyldimethoxysilane - presumably through oxygen coordination - is occurring. Thus, the possibility that this reaction does not involve the intermediacy of a "free" silylene" must be considered.

It is interesting to note that Steele and Weber have likewise noted a solvent effect in the reactions of **14** with various substrates (71). These authors have interpreted their results as being consistent with initial extrusion of dimethylsilylene from **14**, followed by silylene coordination to the oxygen of either the solvent or added substrate. While this interpretation is adequate for explaining the solvent modified reactivity of photogenic dimethylsilylene, it does not explain the enhanced rate of decomposition of **14** in the presence of oxygen containing substrates. A mechanistic proposal that is more consistent with both our results and those of Steele and Weber is that oxygen coordination to **14** (or photo-excited **14**) precedes "silylene" extrusion (Scheme 36).

Scheme 36

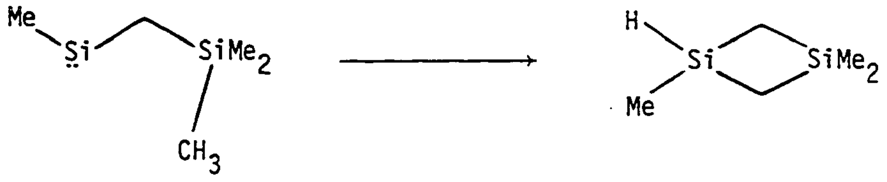


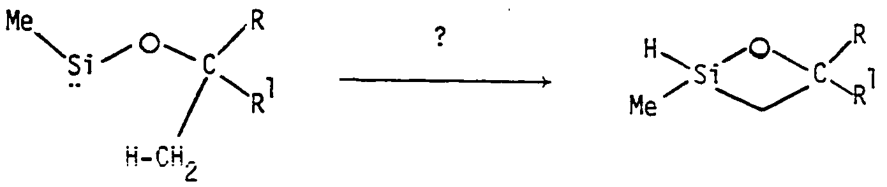
R = alkyl; R^1 = H
R = alkyl; R^1 = silyl

R = R^1 = alkyl
R^2 = silyl; Y = H
R^2 = silyl; Y = OSi≡
R^2 = silyl; Y = alkoxy

Attempted Preparation of 2-Methyl-2-Silaoxacyclobutane 173 from Methylethoxysilylene

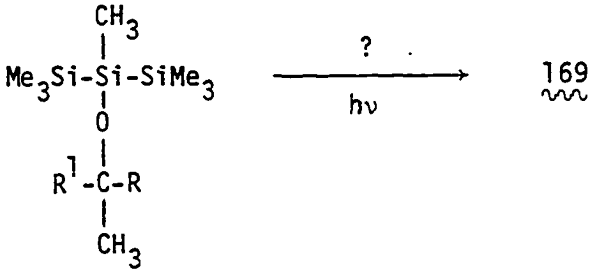
Since it had been previously demonstrated by Wulff and coworkers (31) that thermally generated silylenes would afford 4-membered rings by an intramolecular γ-C-H insertion reaction, the possibility of effecting a similar transformation with alkoxysilylenes of the general type 169 was considered as a possible synthetic route to silaoxetanes.





169

Since silaoxetanes have been proposed to decompose at higher temperatures (vide supra), we choose the use of photochemical silylene generators in an effort to maximize the chances of isolating of a silaoxetane. The general silylene generator that was chosen for the preparation of 169 was 2-alkoxytrisilane 170. Although simple trisilanes do not in general function as efficient photochemical silylene generators (see Historical section on silylenes), Gaspar has reported that 2-alkoxy-2-trimethylsilyltrisilane 171 produced trimethylsilylmethoxysilylene upon U.V. irradiation (14). Therefore, based on this report, and the ready availability of 2-chloroheptamethyltrisilane, from which 170 was expected to be readily prepared, an investigation of the synthesis and photochemistry of silanes of the general type 170 was undertaken.



$$Me_3Si\text{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\underset{\underset{R^1\text{-}\overset{|}{\underset{\underset{CH_3}{|}}{C}}\text{-}R}{|}}{O}}{|}}{Si}}\text{-}SiMe_3 \xrightarrow[h\nu]{?} 169$$

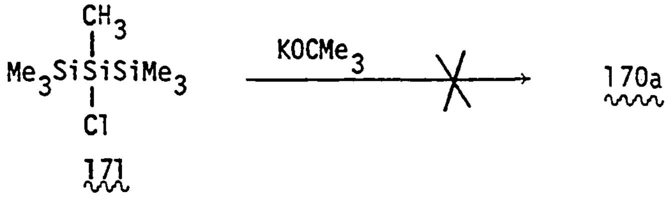
170a, $R = R^1 = Me$
170b, $R = R^1 = H$

$$\underset{171}{(Me_3Si)_3SiOMe} \longrightarrow Me_3SiSiMe_3 + Me_3S\ddot{i}SiOMe$$

In order to maximize the chances for the desired intramolecular insertion reaction the synthesis and photolysis of trisilane 170a was chosen first, since the silylene that was anticipated upon its photochemical decomposition would contain nine γ-C-H bonds.

In contrast to expectations, the preparation of 170a could not be effected. Thus, when an equal molar ratio of 2-chloroheptamethyltrisilane (171) and potassium t-butoxide were allowed to react in THF for 12 hours at room temperature, none of the desired 170a was produced. Even forcing conditions (excess potassium t-butoxide, excess t-butanol, and 60°C for

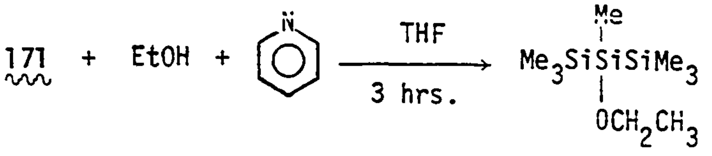
12 hours) failed to produce 170a. Apparently, the steric bulk of both 171 and t-butoxide prevents the approach of the incoming nucleophile, and thus, prevents the formation of 170a.



$$Me_3Si\overset{CH_3}{\underset{Cl}{Si}}SiMe_3 \xrightarrow{KOCMe_3} 170a$$

171

Having failed to effect the preparation of 170a, we turned to the preparation of 170b. If the preparation of 170a was thwarted by the steric bulk of both 171 and t-butoxide, substitution of ethoxide for t-butoxide would decrease the steric bulk of the incoming nucleophile, and thus, favor the production of the desired alkoxytrisilane. Indeed, reaction of 171 with excess ethanol and pyridine afforded 170b as a distillable (B.P. 80-81°C at 13 Torr) colorless liquid in 59% yield. The identity of 170b was established by the usual spectroscopic methods.



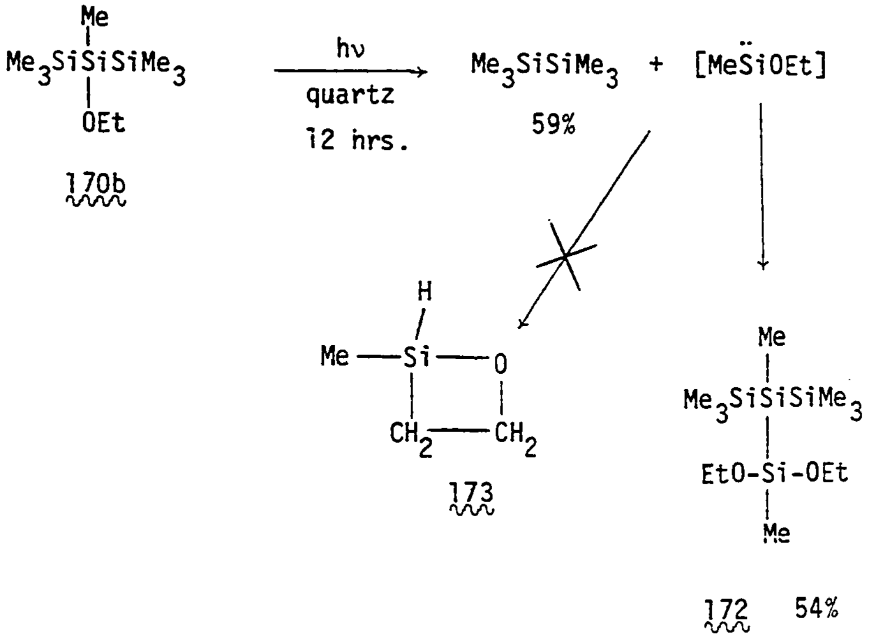
$$171 + EtOH + \text{pyridine} \xrightarrow[3\ hrs.]{THF} Me_3Si\overset{Me}{\underset{OCH_2CH_3}{Si}}SiMe_3$$

170b 59%

Having succeeded in preparing 170b, we then turned to an examination of its photochemistry. Irradiation (450 W. Hanovia, quartz) of a Et_2O solution of 170b for 12 hours at room temperature resulted in the complete disappearance of 170b, and afforded as the major products hexamethyldisilane and diethoxytetrasilane 172 in yields of 59 and 54%, respectively (Scheme 37).

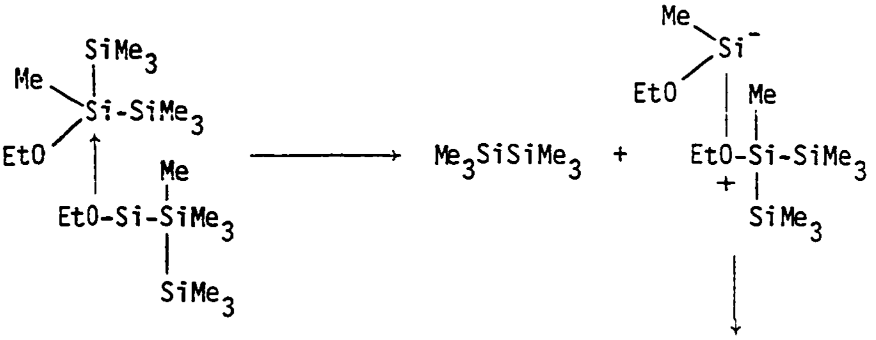
The formation of $Me_3SiSiMe_3$, the expected decomposition product of 170b, and 172, the expected product of methylethoxysilylene insertion into the Si-O bond of 170b, clearly demonstrated that 170b was decomposing to afford the desired "silylene". However, no evidence suggesting that the desired γ-insertion reaction had occurred was obtained.

Scheme 37



On the basis of the previous discussion regarding the effect of oxygen containing substrates upon the photochemical decomposition of polysilanes, the results of this reaction do not demand that a free silylene be involved. Indeed, the possibility that the products of this reaction proceed by a bimolecular coordination complex such as 174 is equally consistent with the results.

Even if free silylenes are involved in this reaction, it is clear that



174

172

they do not yield silaoxetane 173 as originally hoped. Indeed, based on the amount of hexamethyldisilane produced, the yield of 172 represents a 92% yield of silylene trapping, thus the maximum yield of 173 could be no greater than 8%.

On the basis of these results, and the ambiguity associated with the existence of free silylenes when generated photochemically in the presence of oxygen containing substrates, no further attempts were made to generate silaoxetanes by insertion reactions of photogenic silylenes.

The Addition of Dimethylsilylene to Cyclooctatetraene (COT)

In 1975, Barton and Juv'et (92), in an investigation of the addition of thermally generated dimethylsilylene to COT, reported the formation of 1,1-dimethyl-2,3-benzosilole 53 in 8% yield in the gas-phase at 450°C (Scheme 38). At 550°C, under otherwise identical reaction conditions, the yield of 53 increased to 30% concomitant with the appearance of a second major product, 1,1-dimethyl-2,3-benzo-1-silacyclopentane (54, 15% yield). The mechanism that was proposed to account for the formation of 53 and 54 involved initial 1,2-addition of dimethylsilylene to COT to afford

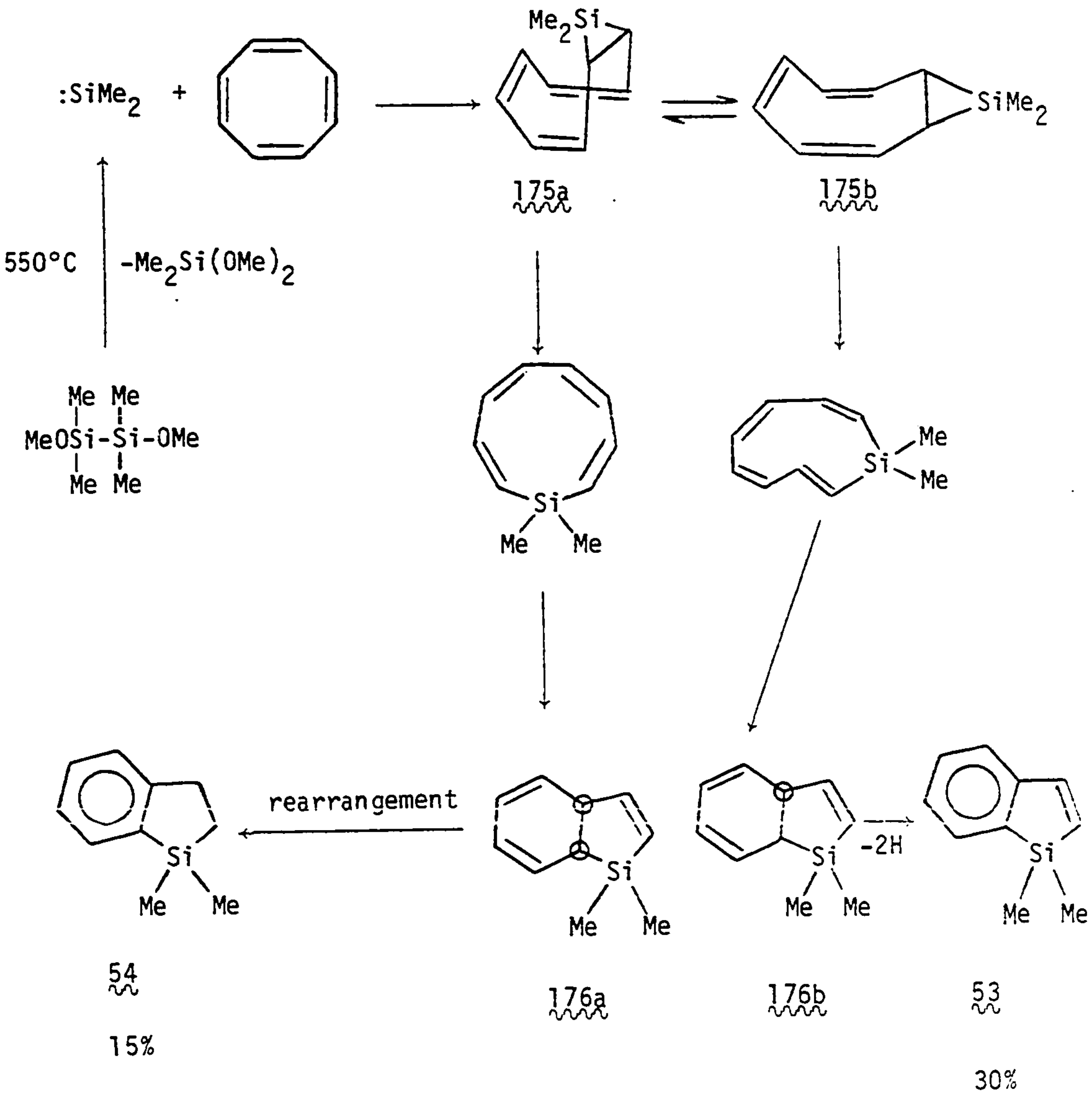
9,9-dimethyl-9-silabicyclo[6.1.0]nonatriene (as a mixture of *endo* and *exo* isomers, **175a** and **175b**) which underwent competing rearrangements to afford, respectively, *cis* and *trans* dihydrosilylindenes **176a** and **176b** (Scheme 38). Dihydrosilylindene **176b** gave **53** upon aromatization, while **176a** gave **54** by a symmetry allowed $\sigma 4s + \pi 2s$ thermal group transfer of hydrogen. However, due to the harsh reaction conditions employed, the details of this mechanism remained speculative.

Since we had gained experience in the preparation and handling of hexamethylsilarane (**12**) in our study of its reaction with cyclooctene oxide (*vide supra*), and since **12** is known to extrude dimethylsilylene at temperatures of ∿100°C - conditions under which the respective formation of **54** and **53** from **176a** and **b** would not be expected - an investigation of the thermal reaction of **12** with COT was undertaken in the hopes of elucidating in more detail the mechanism of this reaction.

Thermolysis of **12** in the presence of neat COT for 15 hours at 85-90°C resulted in the complete disappearance of **12** and the formation of tetramethylethylene (TME) in a 90% yield (as determined by NMR), as the only identifiable product. Although the presence of a weak silicon methyl absorption was observed by NMR between σ 0.01 and 0.3, analysis of the reaction by gas chromatography (GC) revealed the presence of TME as the only detectable product.

While this result was initially discouraging, it is in keeping with the report by Seyferth and Annarelli (49) that the yields of addition products of dimethylsilylene (produced by thermolysis of **12**) to 1,3-dienes were dependent on both the concentration of the dienes and the

Scheme 38


:SiMe$_2$
+
550°C
-Me$_2$Si(OMe)$_2$
MeOSi-Si-OMe
Me Me
Me Me
Me$_2$Si
SiMe$_2$
175a
175b
Si
Me
Me
rearrangement
-2H
54
15%
176a
176b
53
30%

presence of an inert diluent. Thus, for the addition to 2,3-dimethyl-1,3-butadiene, the best yield of the desired trapping product, 1,1,3,4-tetramethyl-1-silacyclopent-3-ene, was obtained with a THF solution of **12** and a 5.3 molar excess of the diene. Increasing the concentration of the diene led to a decrease in the yield of the silacyclopentene, and none of this product was obtained when the reaction was performed in the absence of a diluent.

Therefore, the reaction of **12** and COT was investigated using THF and benzene as diluents. When **12** was thermolized at 65-70°C for 24 hours in a THF solution of COT, in which the molar ratio of COT to **12** was 17:1, the presence of trace amounts (<5%) of two products were found, which on the basis of their Gas Chromatographic Mass Spectra (GCMS) were consistent with the addition of dimethylsilylene to COT. Unfortunately, due to the low yields of these products, their isolation and characterization was not possible.

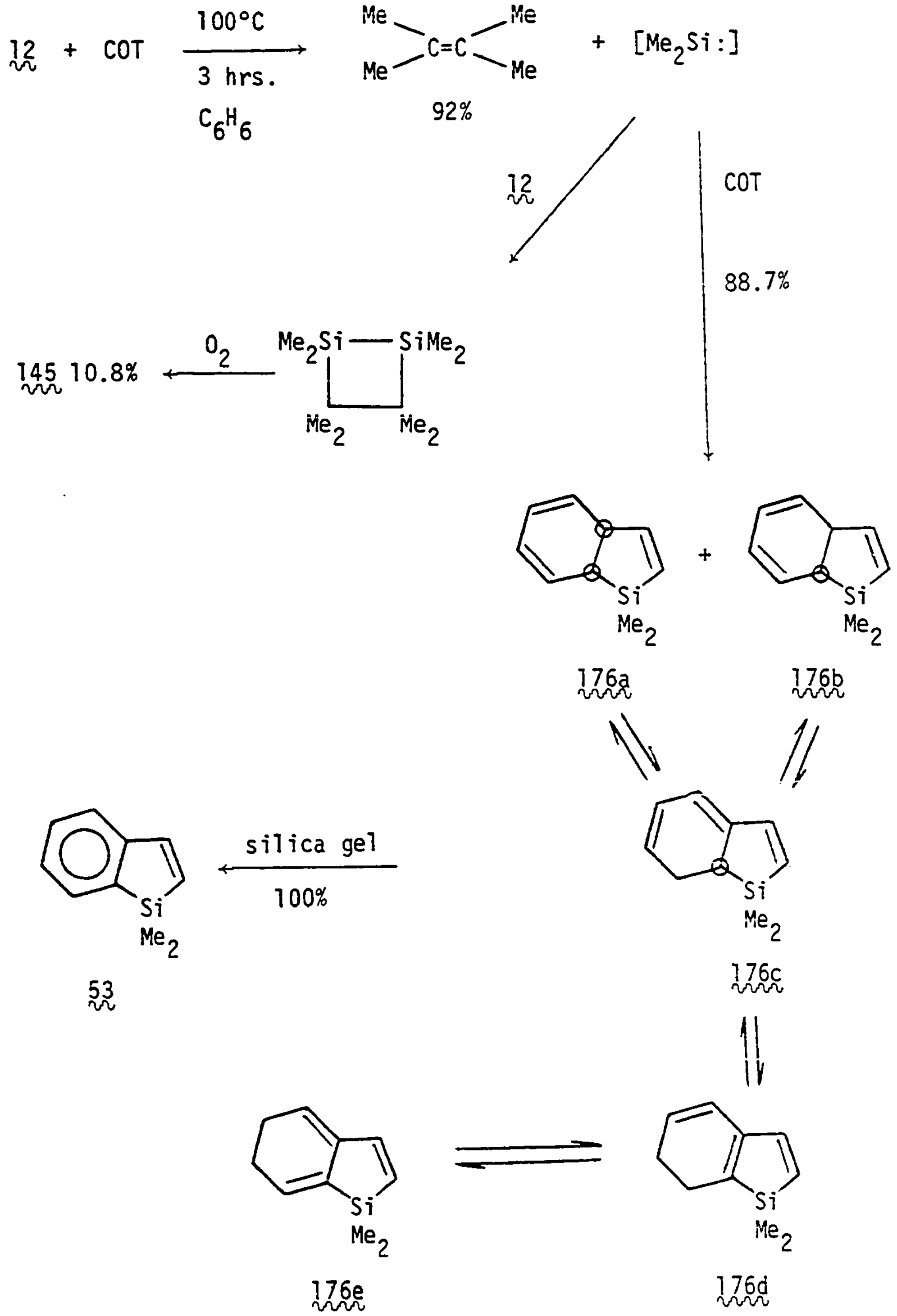
However, thermolysis of **12** (100-110°C for 3 hours) in a benzene solution of COT (molar ratio of COT to **12** was 4.5:1) resulted in a dramatic increase in the yields of these products. Mass spectrometric analysis of these products, following their isolation by preparative GC, clearly demonstrated that they were those of the addition of dimethylsilylene to COT. However, by NMR, it was found that each product was actually a mixture of isomers, none of which could be identified. That the isomerization of the desired products **176a** and **b** had not occurred during isolation was demonstrated by the finding that all of the silicon methyl NMR signals present in the isolated samples were also present in approximately the same ratio in the crude reaction mixture. Thus, the formation of these products was clearly occurring under the conditions of the reaction.

Although it was not possible to identify these products on the basis of the obtainable spectral data, two observations do allow for the proposal that these products are the isomeric, 1,5-hydrogen shifted compounds 176a-e (Scheme 39): a, upon standing in the presence of D_6-acetone for several weeks at room temperature quantitative decomposition to silylindene 53 was found; b, attempted purification of these isomers by chromatography (silica gel) also led to their quantitative decomposition to 53.

The combined yield of these isomers was determined by NMR to be 88.7%, based on the amount of TME produced, while the yield of TME was determined to be 92%, based on reacted 12. The only other product of this reaction was cyclic siloxane 145, which was obtained in 10.8% yield, based on the amount of TME produced. The results of this reaction are summarized in Scheme 39.

On the basis of these results, the principal conclusion that can be drawn is that the reaction of 12 and COT does not yield results which allow for the elucidation of the mechanism of the addition of dimethylsilylene to COT. However, if our assignment of the products of this reaction is correct, these results demonstrate that the competing rearrangements of 175a and 175b (Scheme 38) are not necessary to explain the observed products of the high temperature reaction. Thus, rearrangement of either 175a or 175b would be expected to afford the same equilibrium mixture of 176a and 176b by way of their rapid interconversion by 1,5-hydrogen shifts.

Scheme 39


12
+
COT
100°C
3 hrs.
C6H6
Me
Me
C=C
Me
Me
92%
+ [Me2Si:]
12
COT
88.7%
O2
145 10.8%
Me2Si
SiMe2
Me2
Me2
Si
Me2
+
Si
Me2
176a
176b
Si
Me2
176c
silica gel
100%
Si
Me2
53
Si
Me2
176e
Si
Me2
176d

Intramolecular Reactions of Silylenes

Prior to 1978, no known examples of intramolecular reactions of silylenes existed. In fact, prior to 1978, no attempted investigation of the intramolecular chemistry of silylenes had been reported. In view of the known similarity between the chemistry of silylenes and carbenes (see the Historical section on silylenes), the lack of any known intramolecular reactions of silylenes was most surprising. Thus, an investigation of silylenes, generated under conditions which would be expected to favor intramolecular reactions, was deemed worthy of study. Of particular interest, was our desire to prepare silylenes such that rearrangement to silenes would be favored.

At the onset of such an investigation a question which must be asked is: Why have silylene rearrangements not already been observed? a, They simply may never occur. That is, the thermodynamics are too unfavorable for the transformation $\mathrm{R\ddot{Si}CXR_2} \longrightarrow \mathrm{RXSi{=}CR_2}$. b, They may have occurred with the few silylenes which have been thus far generated, but the products were minor, and therefore ignored. c, Most previous silylene synthesis contained or generated efficient silylene traps and these may have kinetically prevented the occurrence of silylene rearrangements.

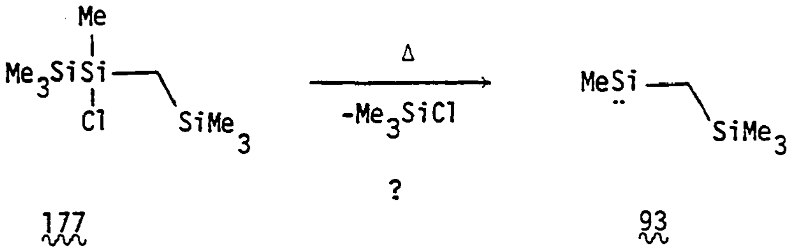
Of the three possible answers to the questions of why silylene rearrangements had not been previously observed, the latter was considered the more likely. Thus, an examination of the available literature on silylenes that existed at the onset of this study revealed that with very few exceptions silylenes had not been generated under conditions that would be expected to favor intramolecular rearrangements (high dilution or in the gas-phase in the absence of traps). Furthermore, the examination of the available literature on silylenes revealed that prior to the beginning of this study only "simple" silylenes - those containing only alkyl, aryl, alkoxy, and halogens as substituents - had been thus far generated.

Therefore, these questions, and the available literature regarding silylenes, dictated an approach whose thrust was to design and build silylenes which possessed substituents that would be expected to favor intramolecular rearrangements, and to generate these silylenes either in the gas-phase or in solution under conditions of high dilution in the absence of added traps.

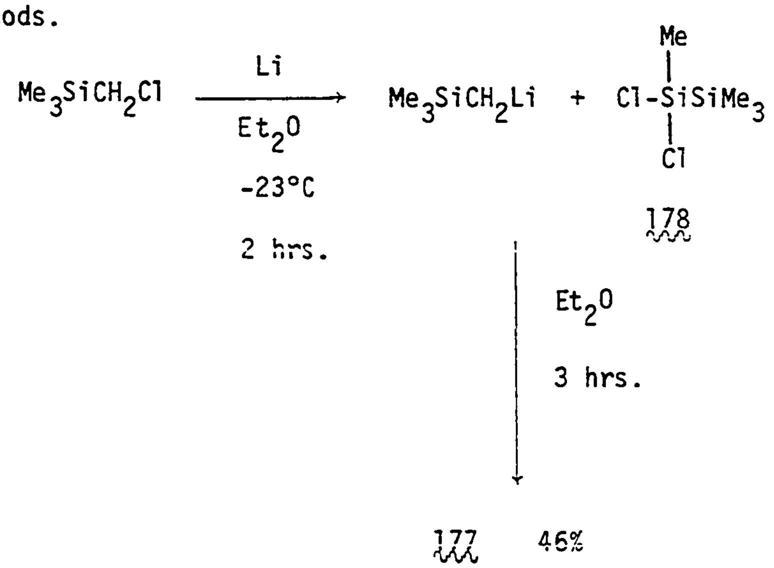
Thermal Chemistry of Methyltrimethylsilylmethylsilylene

At the onset of this project, Wulff (277) had obtained evidence for the first example of an intramolecular silylene rearrangement from a study of the thermal chemistry of methyltrimethylsilylsilylene. When 2-chloroheptamethyltrisilane was pyrolyzed in the gas-phase at 700°C, disilacyclobutanes 87 and 88 were obtained in 28 and 15% yields, respectively. The mechanism that was proposed to account for these products (Scheme 40) involved a series of unprecedented intramolecular silylene C-H insertions (see the Historical section on silylenes for a more detailed discussion of this mechanism).

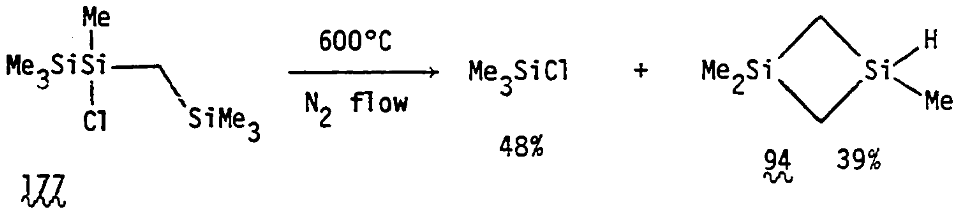
As a test of the last step of this mechanistic proposal, the gas-phase thermal chemistry of methyltrimethylsilylmethylsilylene (93) was investigated. Silylene 93 had not been previously generated thermally, thus, it was necessary to prepare a thermal generator of 93 to examine its thermal chemistry. By analogy to the preparation of methyltrimethylsilylsilylene, pyrolytic α-elimination of trimethylchlorosilane from 177 was proposed as a viable route to 93.



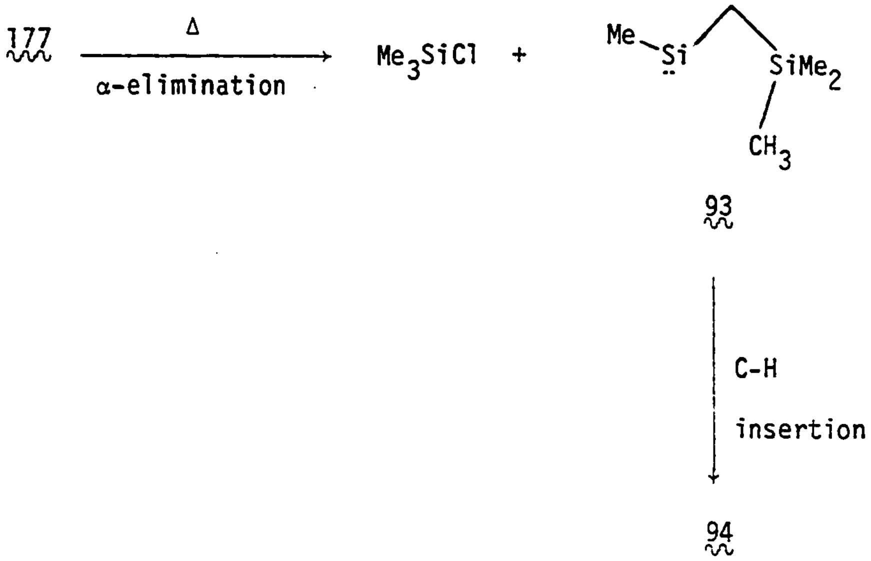
Chlorotrisilane 177 was conveniently prepared in 46% yield by the reaction of trimethylsilylmethyllithium and 1,1-dichlorotetramethyldisilane (178). The identity of 177 was established by the usual spectroscopic methods.



Pyrolysis of 177 (gas-phase flow, 600°C) resulted in the complete disappearance of 177, and afforded trimethylchlorosilane and the desired 1,3-disilacyclobutane 94 in 48 and 39% yields, respectively.

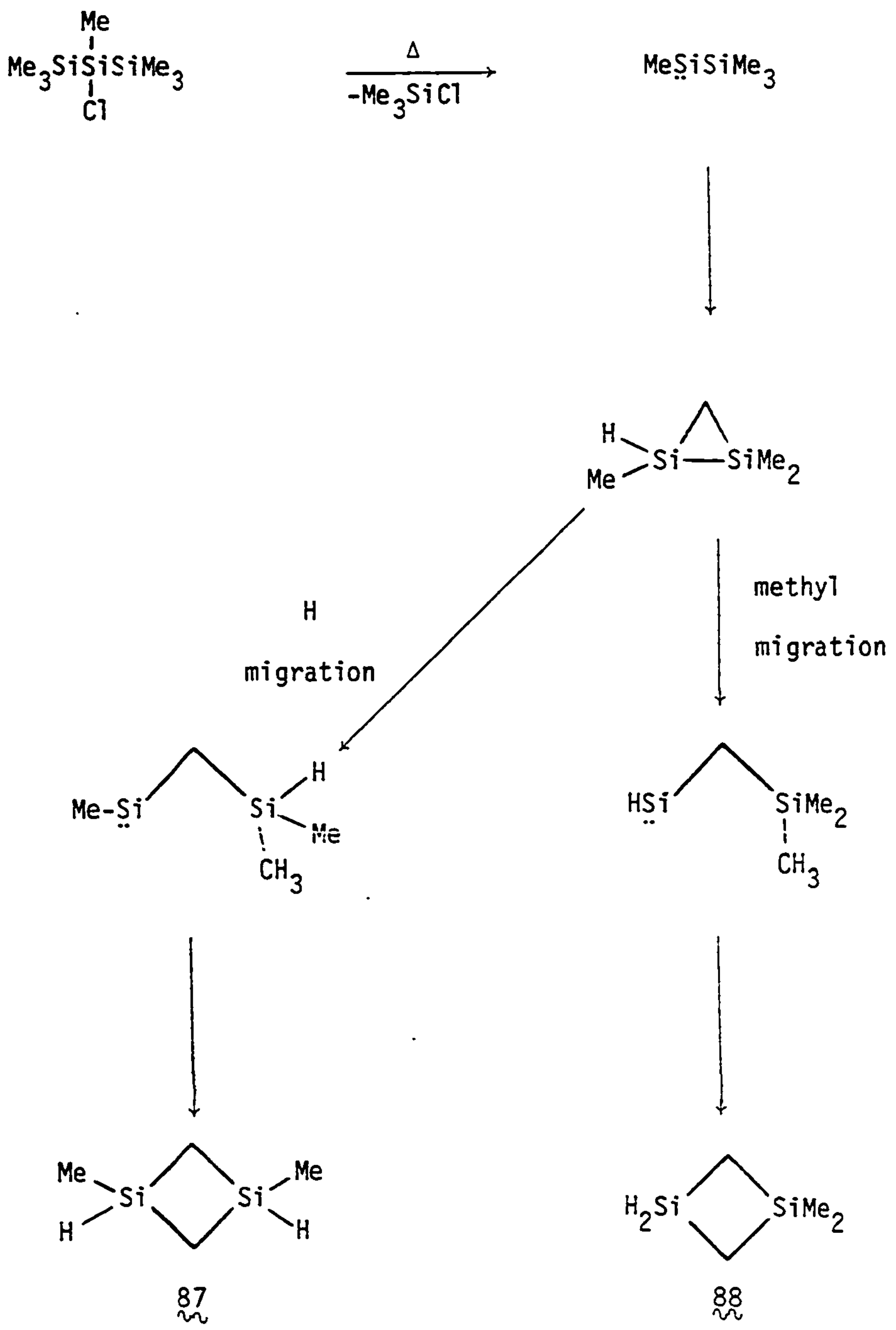


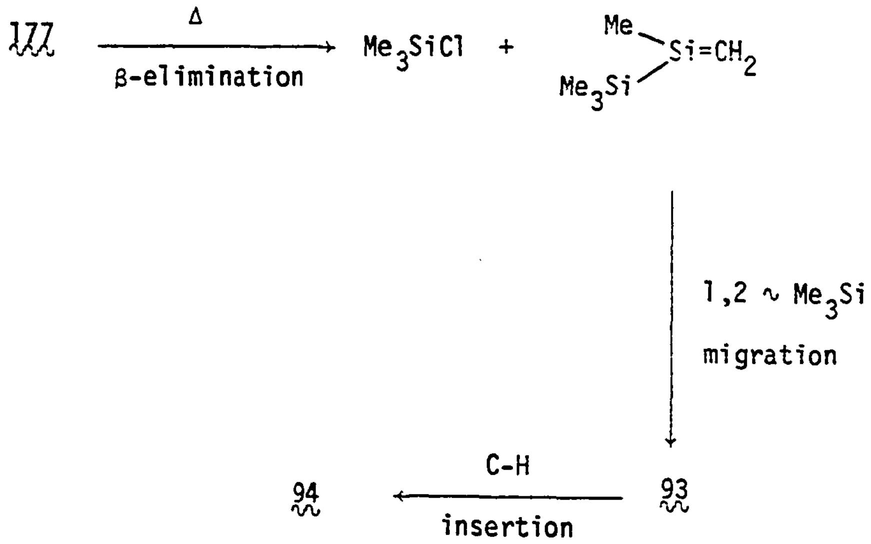
At the time that this work was conducted, these results were interpreted as being consistent with the desired α-elimination of trimethylchlorosilane from 177 to afford silylene 93, which upon intramolecular γ-C-H insertion afforded 94.



More recently, however, Barton and coworkers (278,279) have demonstrated that β-elimination of disilylmethanes of the type $RMe_2Si\text{-}CR_2SiMe_2OMe$ occurs to afford silenes under pyrolytic conditions in the gas phase. These results, coupled with the proposal by Barton and coworkers (122,123) that 1-silylsilenes undergo a 1,2-silyl migration to afford silylenes (see the Historical section on silylenes) suggested an alternative route to 93.

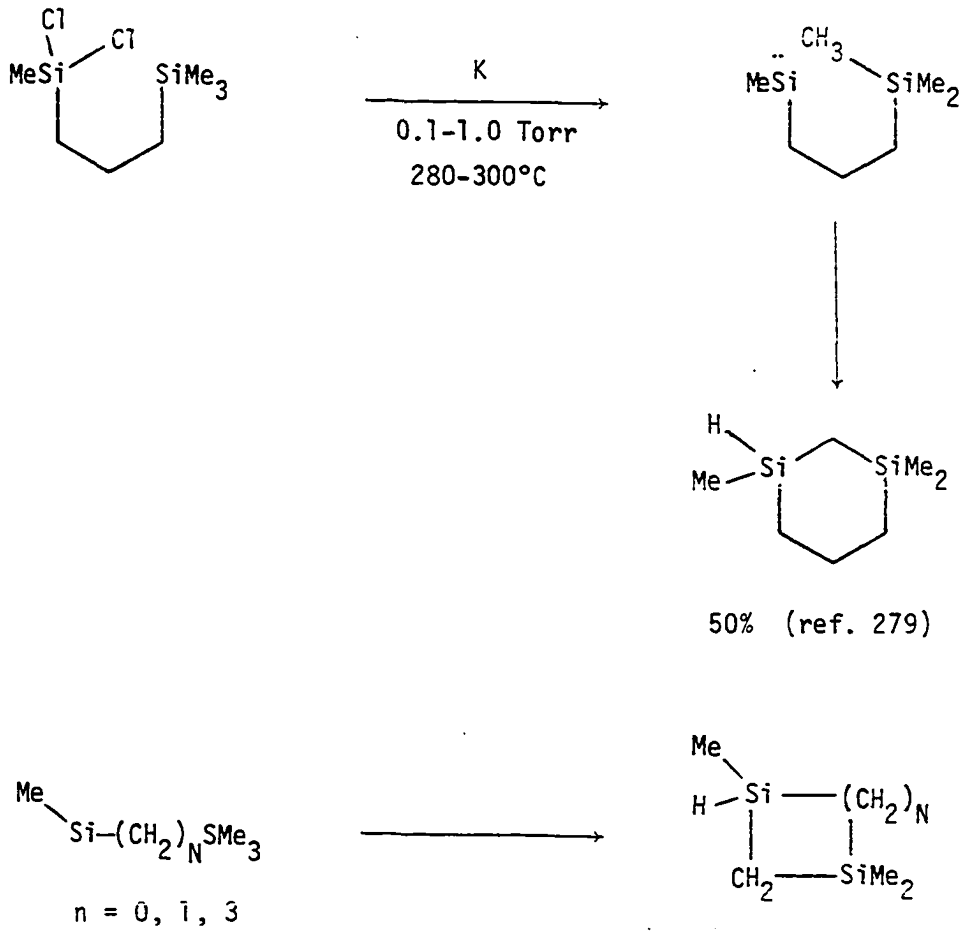
Scheme 40


Me
Me3SiSiSiMe3
Cl
Δ
-Me3SiCl
MeSiSiMe3
H
Me
Si
SiMe2
H
migration
methyl
migration
Me-Si
Si
H
Me
CH3
HSi
SiMe2
CH3
Me
Si
H
Si
Me
H
H2Si
SiMe2
87
88



Although the exact mechanistic origin of 93 cannot be determined on the basis of the data presented, since both mechanisms predict the formation of the same products, that silylenes undergo γ-C-H insertion reactions at high temperatures in the gas-phase is unambiguous. More recently, Gusel'nikov and coworkers (280) have also observed intramolecular silylene C-H insertion in the gas phase, although in this report the insertion occurred at the methyl group of a γ-silicon (Scheme 41). Therefore, from the data presented in this thesis, the previous work of Wulff (277), and the recent report of Gusel'nikov (280), insertions of thermally generated silylenes into the C-H bond of methyl groups attached to α, β, and γ silicons are now established.

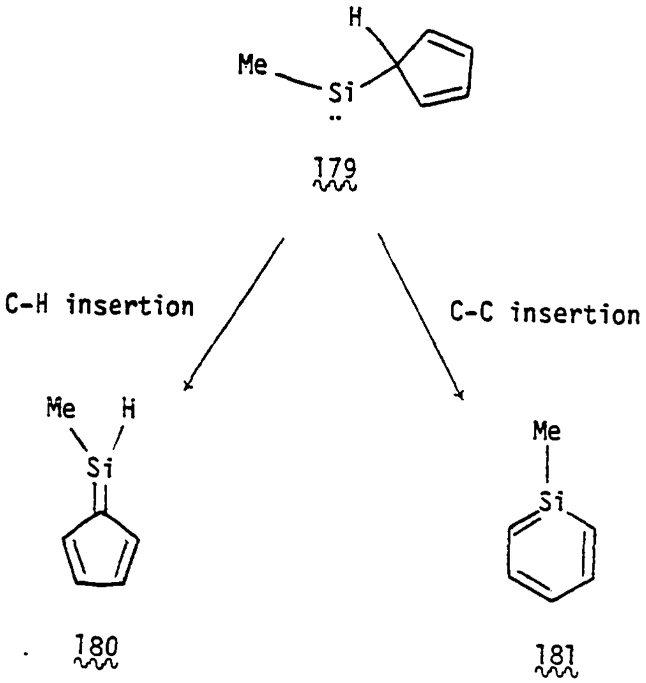
Scheme 41



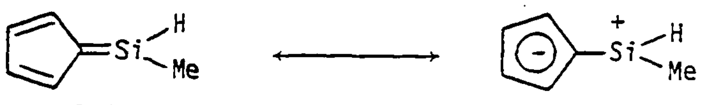
Investigation of the Thermal- and Photochemistry of Cyclopentadienylmethylsilylene (179)

Since it was our general goal to develop silylenes that were appropriately substituted such that an intramolecular rearrangement to a silene would be favored, we chose as a starting point for this project an investigation of cyclopentadienylmethylsilylene (179). As illustrated in Scheme 42, 179 has two possible rearrangement pathways available, both of which afford silenes.

Scheme 42



Although at the onset of this project silafulvenes (molecules analogous to 180) had not yet been prepared, they had been suggested as a molecule containing a silicon-carbon double bond which could be a stable compound (106). This suggestion was based on the belief that the known polarization of silenes would favor resonance structure 180b, thereby stabilizing the silafulvene.



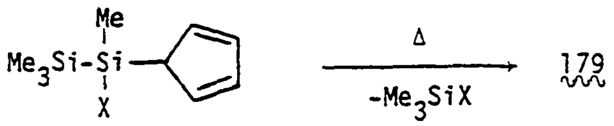
180a

180b

However, it has been our belief that the lack of "stability" of silenes is, to a large extent, due to enhanced reactivity because of this bond polarity, thus, if 180 was formed from 179 it was not expected to be isolable. Indeed, Barton and coworkers have provided definitive evidence demonstrating that 6,6-dimethyl-6-silafulvene is not a stable, isolable species (281). Although 180b undoubtedly leads to an increased reactivity for 180 due to the bond polarity, the possibility that this resonance would stabilize 180 relative to 179 and thus favor the isomerization of 179 to 180 was still considered.

The second rearrangement pathway that was considered likely for 179 was insertion into a carbon-carbon bond (formally a vinyl migration) to afford silabenzene 181. Silabenzene 181 is now a well-established species (282,283,284), and thus its formation under these reaction conditions was believed to be feasible. In particular, qualitative observations by Burns (285) suggested that 181 is more stable than typical silenes. Therefore, a driving force for the isomerization of 179 to 181 was qualitatively predicted.

Silylene 179 had not been previously reported; thus, it was necessary to generate this silylene to examine its chemistry. Since it was our desire to examine the chemistry of 179 at high temperatures in the gas-phase, thermolytic α-elimination of 179 from either 182 or 183 was chosen.

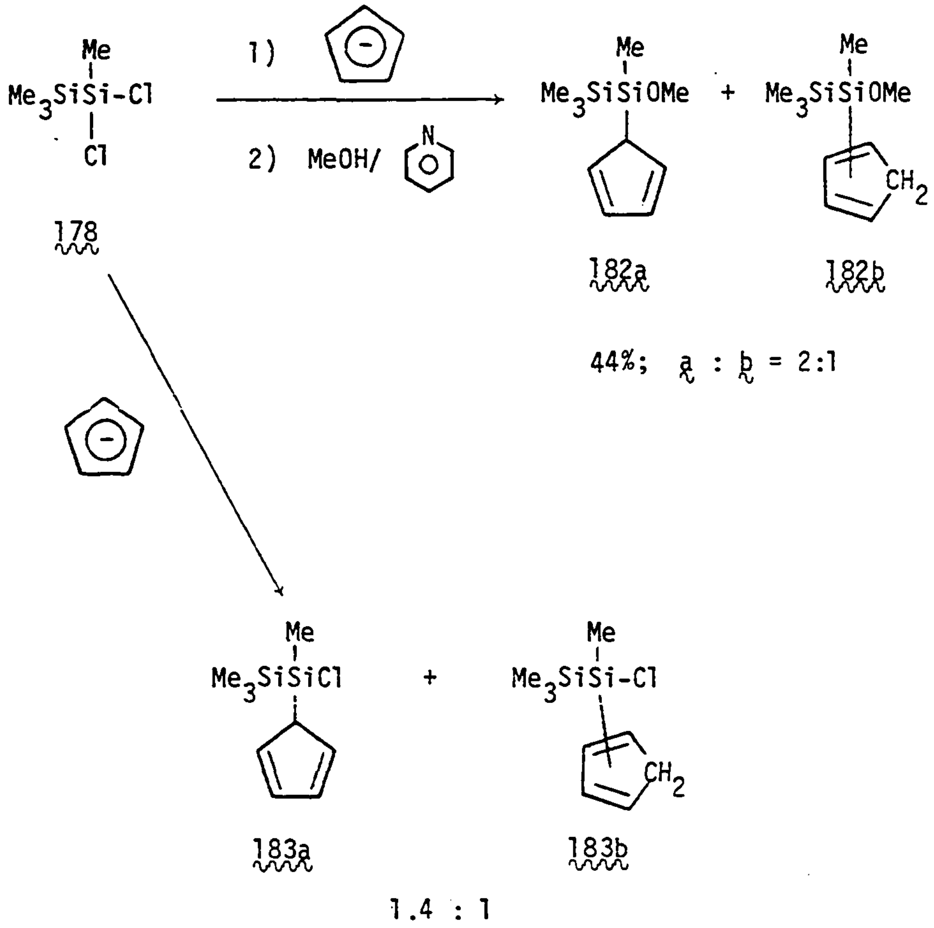


182; X = OMe

183; X = Cl

Disilane 182, as a mixture of isomers 182a and b, was prepared in a 44% overall yield by the sequential addition of cyclopentadienyllithium and methanol/pyridine to dichlorodisilane 178. Disilane 183 was prepared in an analogous fashion, also as a mixture of isomers 183a and b, by omitting the methanol/pyridine step (Scheme 43). Since at the high temperatures needed to effect the α-elimination reaction, rapid isomerization of 182 and 183 would be expected to occur, no attempt was made to separate the individual isomers obtained in the synthesis of 182 and 183.

Scheme 43

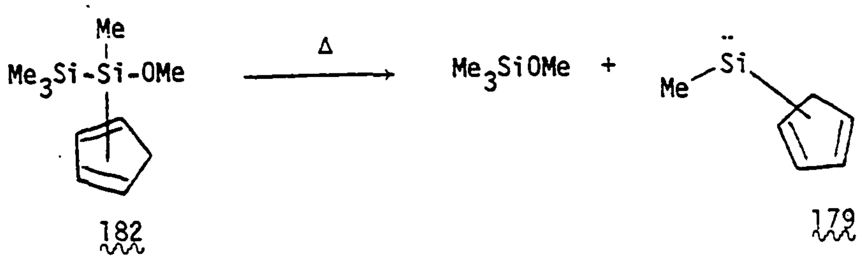


Atwell and Weyenberg (6,7) had previously demonstrated that alkoxydisilanes decompose to afford silylenes at lower temperatures than analogous chlorodisilanes, thus the thermal chemistry of 182 was chosen for our initial investigations. Gas-phase flow pyrolysis of 182 (as a mixture of isomers) at 580°C resulted in the complete disappearance of 182. Analysis of the crude pyrolysate by NMR revealed the presence of trimethylmethoxysilane as the only observable product. On the basis of NMR integration, Me_3SiOMe accounted for greater than 90% of the pyrolysate. After *en vacuo* removal of the volatiles from the pyrolysate, analysis of the resulting residue by GC revealed the presence of greater than 20 compounds, none of which were major, and none of which could be isolated and identified.

$$\text{182a and b} \xrightarrow[N_2 \text{ flow}]{580^\circ C} Me_3SiOMe \; + \; > 20 \text{ other products}$$

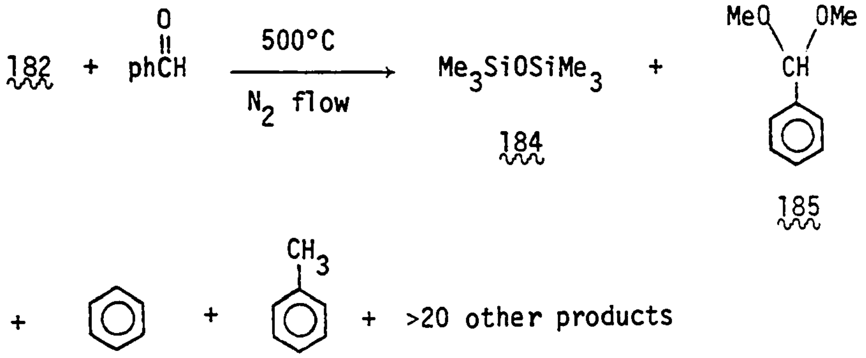
Although, based on a consideration of the two possible modes of rearrangement available to 179 (see Scheme 42), this reaction was not expected to be "clean", the plethora of products obtained was unexpected. The production of Me_3SiOMe in this reaction is in keeping with the desired α-elimination of 182 to afford 179. Therefore, the formation of such a complex reaction mixture was postulated to be due to a large number of secondary, bimolecular reactions of 179 and/or its rearrangement products. In an effort to decrease the likelihood of these secondary reactions the vacuum flow pyrolysis of 182 was investigated. Despite the anticipated reduction in complexity, pyrolysis of 182 at 780°C and 1×10^{-4} Torr afforded a reaction mixture that was virtually identical to that previously obtained.

Since in both these pyrolysis the only major product obtained was Me_3SiOMe (in both cases it accounted for >90% of the pyrolysate), decomposition of 182 to 179 was strongly implied.



Based on this assumption, the complex product mixture obtained from these pyrolysis was postulated to be due to secondary thermal reactions of either 179 or its rearrangement products 180 and 181, or a combination of these three isomers. Therefore, to establish the intermediacy of these isomers, the pyrolysis of 182 was conducted in the presence of a variety of trapping reagents.

The first trapping reagent that was chosen for study was benzaldehyde, since it is a well-known silene trap (286). Copyrolysis of 182 (as a mixture of isomers) at 500°C in the presence of a 4.4 molar excess of benzaldehyde afforded a complex reaction mixture containing greater than 20 products from which only unreacted benzaldehyde, hexamethyldisiloxane (184), phenyldimethoxymethane (185), benzene, and toluene could be identified by GCMS.



The absence of Me_3SiOMe, coupled with the presence of 184 and 185 as the major products of the reaction (but whose yields were not determined due to the complexity of the reaction), suggests that in the presence of benzaldehyde 182 was decomposing by pathways other than α-elimination to afford 179.

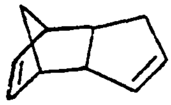
Copyrolysis of 182 and a 2.7 molar excess of triethylsilane at 480°C afforded a somewhat cleaner reaction mixture. However, again no Me_3SiOMe was found in the pyrolysate. Analysis of the pyrolysate by GCMS revealed, in addition to unreacted triethylsilane, the presence of 184, octamethyltrisiloxane (186), and dicyclopentadiene (187) as the only identifiable products (Scheme 44). To our surprise, none of the expected silylene trapping product 188 was produced.

Although the mechanistic origin of these products is unkown, the absence of Me_3SiOMe and 188 suggests that in the presence of triethylsilane 182 is not decomposing to afford silylene 179. Indeed, the presence of 187 is consistent with the decomposition of 182 to afford cyclopentadienyl radical which upon hydrogen abstraction from triethylsilane yields cyclopentadiene. Upon its subsequent dimerization cyclopentadiene would yield 187 (Scheme 45). While this mechanism will explain the formation of 187, the expected coupling and abstraction products of silyl radicals 189 and 190 were not observed. Thus, this process remains speculative.

Scheme 44

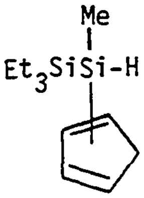
$$182 + Et_3SiH \xrightarrow[N_2\ \text{flow}]{550°C} 184 + \underset{186}{Me_3SiOSiMe_2OSiMe_3}$$

+



187

+ other products

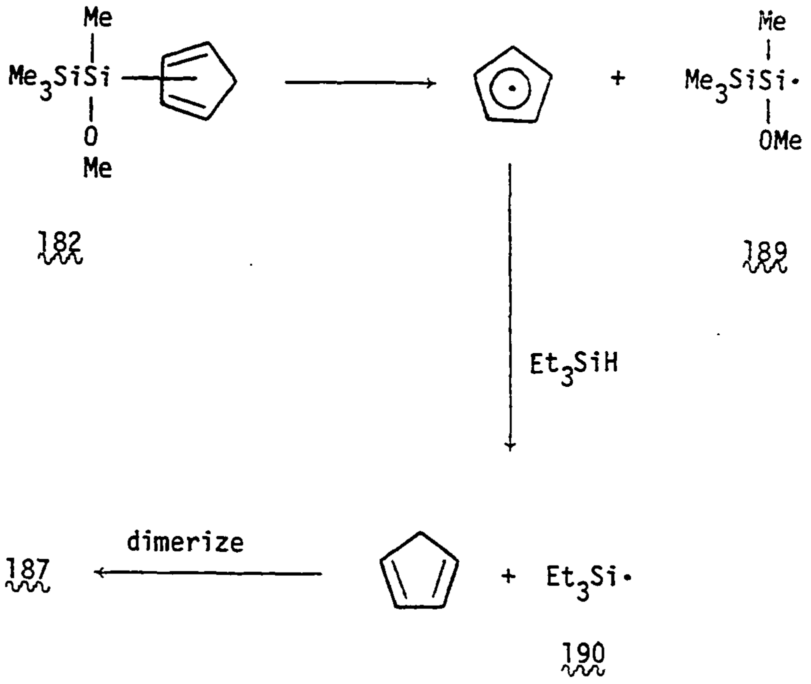


188

not observed

Despite the discouraging results obtained upon copyrolysis of 182 and benzaldehyde and triethlsilane, one further attempt was made to detect the intermediacy of 179. Since acetylenes are known to be excellent traps for silylenes in the gas-phase (see Historical section on silylenes), the pyrolysis of 182 in the presence of excess acetylene was investigated. Pyrolysis of 182 at 500°C in a flow system using purified acetylene as a carrier gas did not afford silylacetylene 191, as hoped. Instead, the

Scheme 45

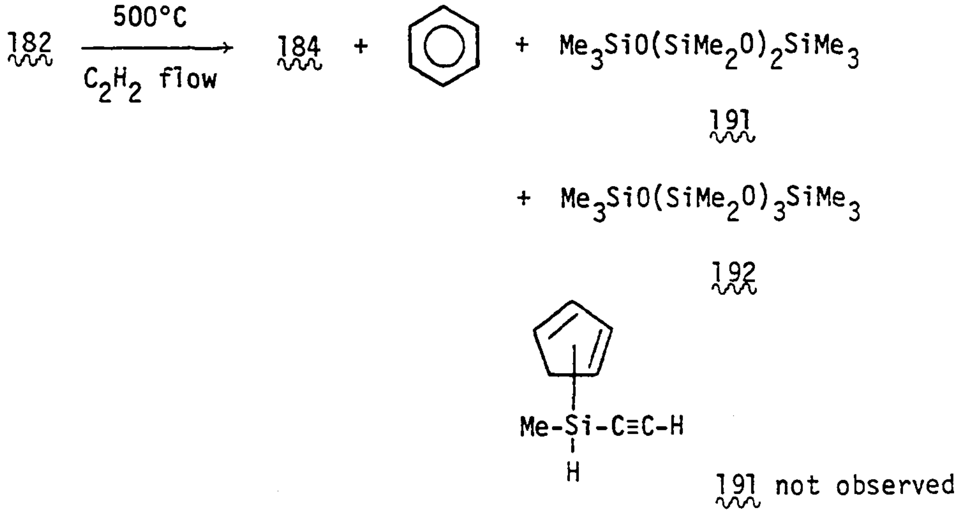


pyrolysate was found to contain as major products hexamethyldisiloxane (184) and benzene (together accounting for >85% of the pyrolysate), and minor amounts of polysiloxanes 191 and 192 (Scheme 46). In addition, greater than 10 other unidentified products were found to be present by GCMS analysis. The absence of Me_3SiOMe and the expected product of silylene trapping, 191, again suggests that under these reaction conditions 182 was not decomposing to afford silylene 179.

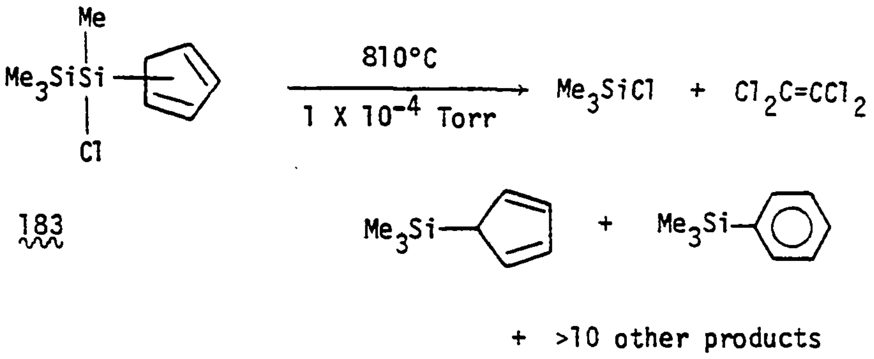
It is interesting to note, that in the absence of added traps, 182 thermally decomposes to afford Me_3SiOMe as the only identifiable product, while in the presence of added traps only linear siloxanes are obtained (vide supra). Although the effect of the added traps is not understood, these results would suggest that the added traps change the decomposition pathway of 182.

During the course of these investigations, Hoekman (261) had discovered that alkoxysilanes undergo an unprecedented carbon-oxygen homolysis reaction at high temperatures to afford alkyl- and siloxy-radicals. Although the decomposition of methoxysilanes was found to be slight under the conditions employed for the thermolysis of 182, the possibility that such a process was occurring in our reactions was considered feasible, particularly in the presence of added traps which could serve as chain-carrying species. To alleviate this possibility, the pyrolysis of chlorodisilane 183 was investigated. Pyrolysis of 183 (as a mixture of isomers) at 810°C and 1 X 10^{-4} Torr afforded trimethylchlorosilane, the expected product of α-elimination, as the only major product (Me$_3$SiCl accounted for about 80% of the pyrolysate as determined by NMR and GC). In addition, the presence of minor amounts of tetrachloroethane, trimethylsilylcyclopentadiene, phenyltrimethylsilane, and greater than 10 other unidentified products were detected by GCMS analysis (Scheme 47).

Scheme 46

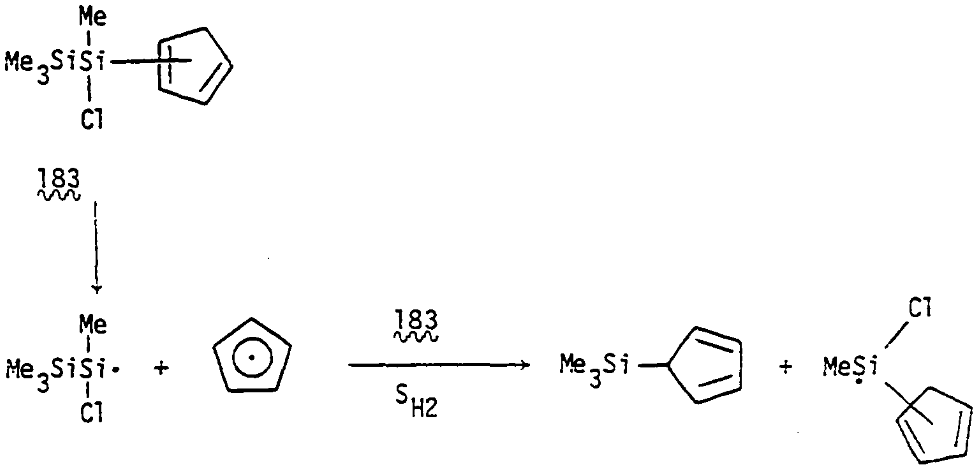


Scheme 47



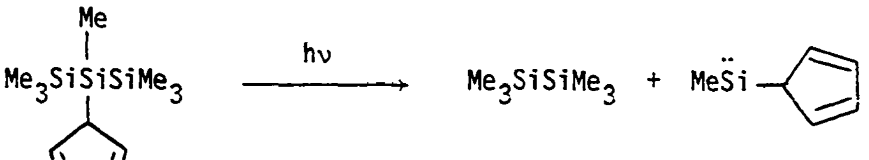
The formation of trimethylchlorosilane upon pyrolysis of 183 is consistent with, though not demanding of, the decomposition of 183 by an α-elimination pathway to afford silylene 179. However, if 179 is produced in this reaction it is clearly not undergoing, at least to any great extent, the desired rearrangement to silenes 180 and 181. While it is possible to rationalize the origin of trimethylsilylcyclopentadiene (Scheme 48), the mechanistic origin of the other products of this reaction (excluding Me_3SiCl) are unknown.

Scheme 48



Since **181** (283,284,285) and the 6,6-dimethyl analogue of **180** (28) have been generated, and their respective trapping products and dimers identified, employing identical techniques to those used for the pyrolysis of **182** and **183**, it is obvious from the results presented that **181** and **180** are not formed in detectable amounts from **182** and **183**. The formation of Me_3SiOMe from the pyrolysis of **182** in the absence of traps, and the formation of Me_3SiCl from the pyrolysis of **183**, are consistent with, though not demanding of, the intermediacy of silylene **179**. If **179** is formed in these reactions, the results obtained do not comment on its rearrangement to **180** and/or **182**, since these species could be undergoing a plethora of secondary reactions under the conditions employed to afford the complex reaction mixtures observed. More bothersome are the results obtained by the pyrolysis of **182** in the presence of traps (*vide supra*), for which no reasonable explanation can be seen.

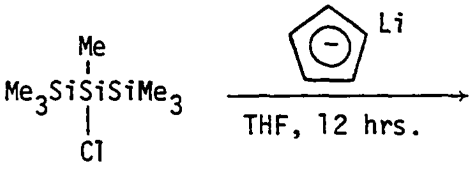
It is interesting to note that our pyrolysis of **182** and **183** represents, to our knowledge, the first reported example of the attempted generation of a silylene from a disilane precursor in which the silylene bears groups other than alkyl, halogen, alkoxy, silyl, or aryl. In view of the complex nature of our results, it is quite possible that the decomposition of disilanes containing groups other than those above proceeds in a manner that does not involve the intermediacy of silylenes. Thus, the generation of **179** by an alternative, and less harsh route, was examined. Since trisilanes are known to photochemically extrude the central silicon atom as a silylene (see Historical section on silylenes), the photolysis of trisilane **193** was investigated.



193

179

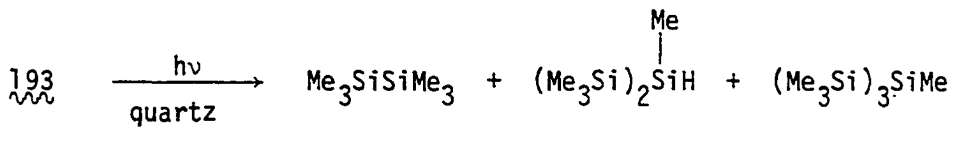
Trisilane 193 was prepared in 75% yield by the reaction of cyclopentadienyllithium and 2-chlorotrisilane 171. The identity of 193 was established by the usual spectroscopic methods. It is interesting to note that in contrast to the preparation of 182 and 183, which afforded a mixture of isomers (*vide supra*), by NMR, 193 was demonstrated to be the only isomer formed.



193 75%

If the formation of complex reaction mixtures can be considered typical for this project, the photolysis of 193 was typical. Thus, irradiation of a cyclohexane solution of 193 (450 W. Hanovia, quartz) for 20 hours at approximately 45°C afforded a reaction mixture that contained greater than 10 products. Of this plethora of products, the only identifiable compounds were: hexamethyldislane (the expected product of the photodecomposition of 193), unreacted 193, and polysilanes 194 and 195 (Scheme 49). Due to the complexity of this reaction, no attempt was made to obtain yields, however, by GC analysis hexamethyldisilane was determined to be the major product. Of particular significance, is the fact that the dimers of either 180 and 181 were shown by GCMS not to be products of this reaction. Since Burns (285) had previously detected these dimers by GCMS, this result demonstrates that 193 does not photochemically yield 180 and 181.

Scheme 49



$$193 \xrightarrow[\text{quartz}\atop\text{20 hrs.}]{h\nu} Me_3SiSiMe_3 + (Me_3Si)_2\overset{\overset{Me}{|}}{Si}H + (Me_3Si)_3SiMe$$

194 195

+ 193 + >10 other products

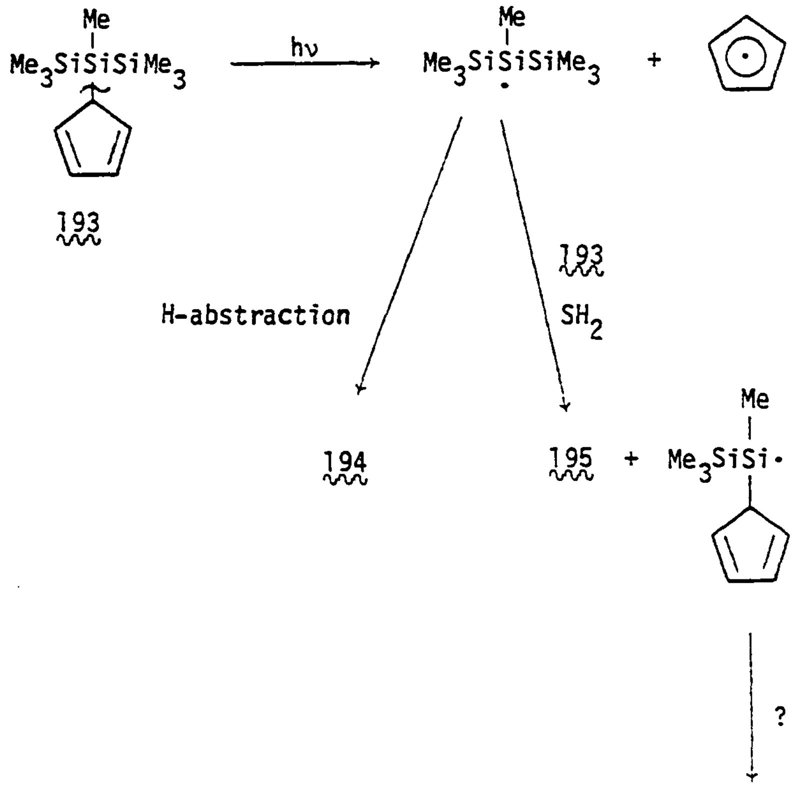
Although the formation of $Me_3SiSiMe_3$ as the major product of this reaction is consistent with the extrusion of 179 from 193, the mechanistic origin of 194 and 195 is most easily rationalized via a radical pathway (Scheme 50), thus the intermediacy of 179 in this reaction is questionable.

As a result of our total inability to obtain evidence for the isomerization of 179 to 180 and/or 181 from these photochemical and thermal studies, no further effort was expended on this project.

Investigation of the Thermal Chemistry of Methylvinylsilylene (196)

One of the more extensively studied reactions of carbenes is that involving rearrangement of α-β unsaturated carbenes (270). Although the mechanism of these reactions has not been unambiguously established, Class and coworkers (287), in a study of the thermal reactions of tosylhydrazones of α-β unsaturated aldehydes and ketones, favored the sequence shown in Scheme 51.

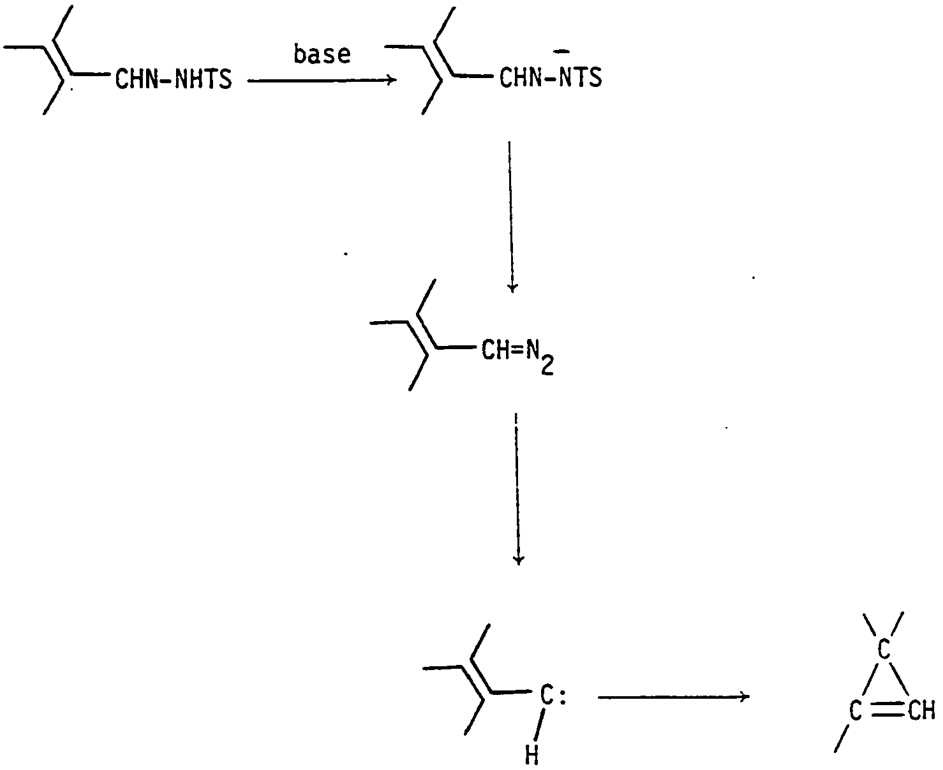
Scheme 50



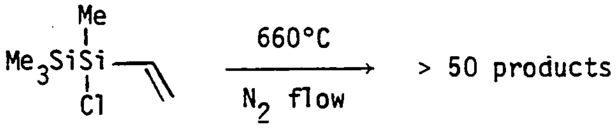
Since the chemistry of vinylsilylenes had not been previously reported, an investigation of the thermal chemistry of methylvinylsilylene (196) was undertaken.

Analysis of the possible rearrangement pathways available to 196, and the possible products which would be expected from these rearrangements, suggested that such an investigation would involve the analysis of a very complex reaction mixture (Scheme 52). A complex reaction mixture was also predicted from the results of our investigation of methylcyclopentadienylsilylene, which suggested that "functionalized" disilanes

Scheme 51



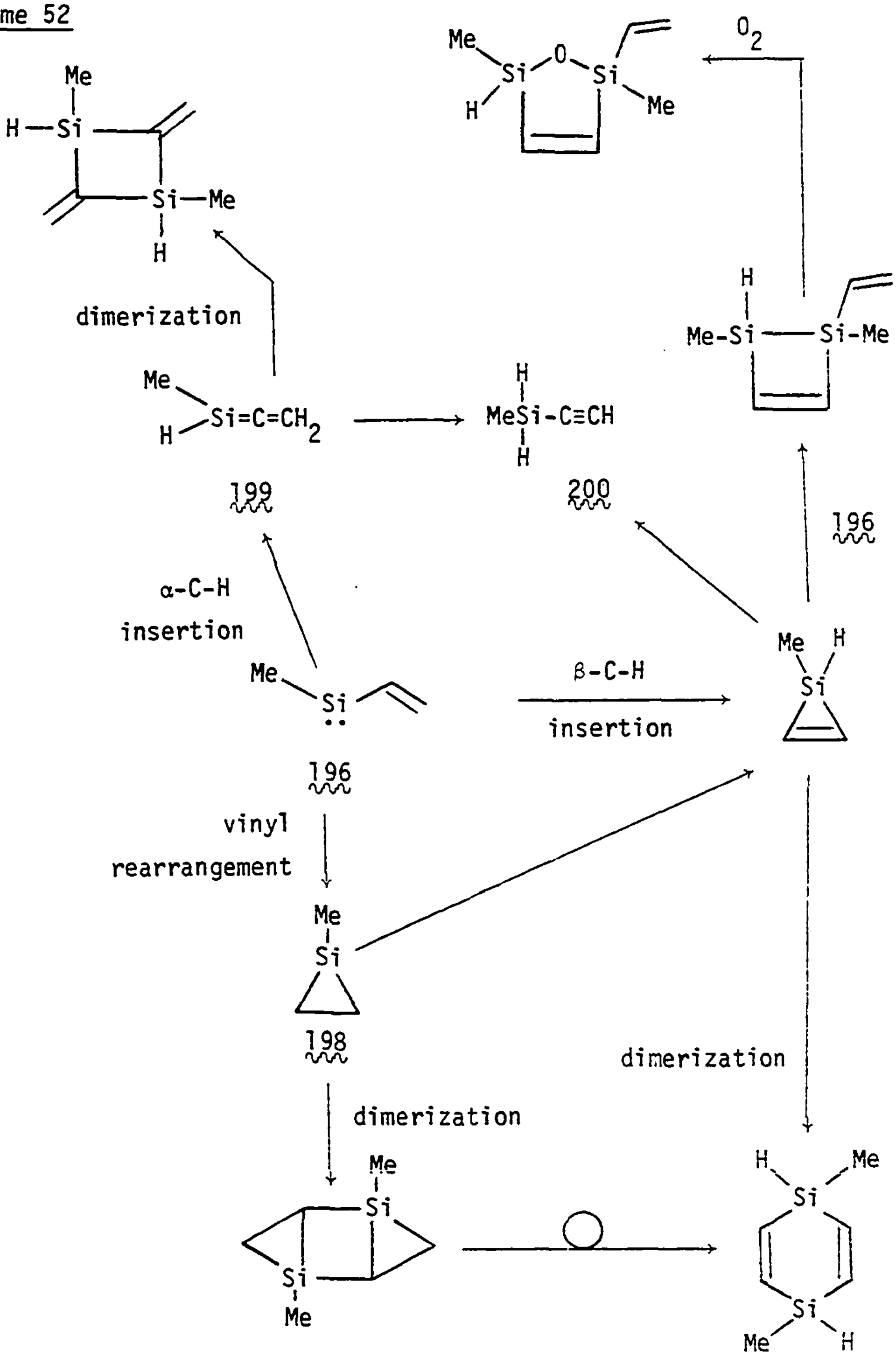
decompose by processes other than α-elimination. Therefore, it was not surprising that pyrolysis of disilane 201, the expected thermal precursor of 196, at 660°C in the gas-phase afforded a reaction mixture which contained greater than 50 products, none of which were major.



201

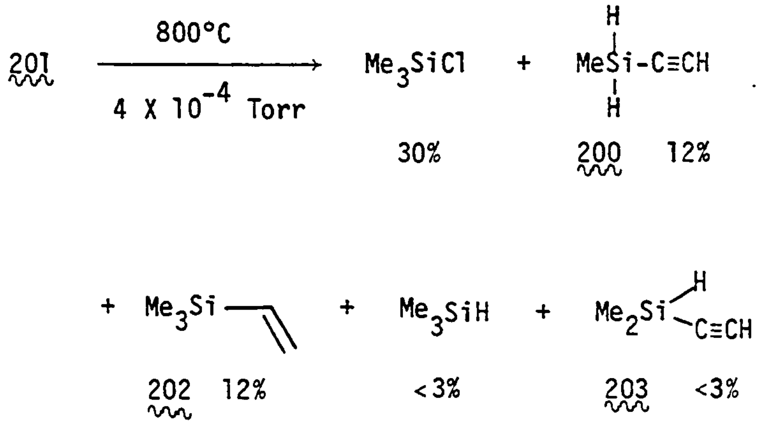
However, flash-vacuum-pyrolysis (FVP) of 201 at 800°C and 4 X 10^{-4} Torr afforded a pyrolysate which contained trimethylchlorosilane (30%

Scheme 52


Me
H—Si
Si—Me
H
dimerization
Me
H
Si=C=CH2
199
MeSi-C≡CH
H
H
200
Me
Si
O
Si
H
Me
O2
H
Me-Si
Si-Me
196
α-C-H
insertion
Me
Si
196
β-C-H
insertion
Me
H
Si
vinyl
rearrangement
Me
Si
198
dimerization
dimerization
Me
Si
Si
Me
H
Me
Si
Si
Me
H

yield based on reacted 201), trimethylvinylsilane (202, 12% yield), and methylethynylsilane (200, 12% yield) as the major products, in addition to trace amounts (<3%) of trimethylsilane and dimethylethynylsilane (203). The results of this pyrolysis are summarized in Scheme 53.

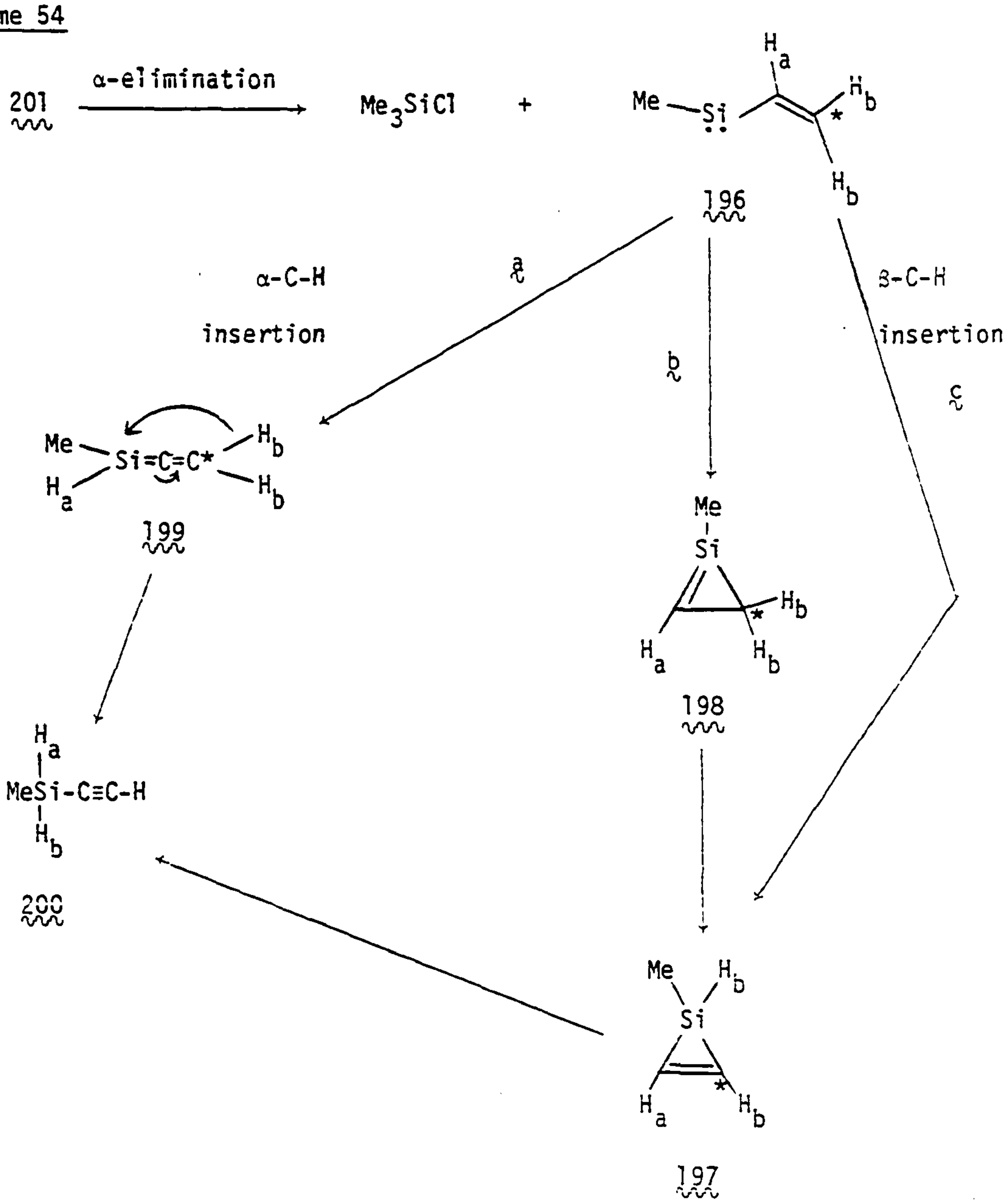
Scheme 53



Mechanistically, 202 is most reasonably formed from 201 by a direct α-elimination process. The fate of the methylchlorosilylene formed as a result of such a process remains unknown. Precedent for the α-elimination of vinylsilanes from vinyldisilanes has previously been reported by Barton and Wulff (288).

The mechanism of formation of 200 is less straight forward (Scheme 54). Since 200 is isomeric with methylvinylsilylene, its formation is proposed to occur by rearrangement of this silylene. Thus, by way of hydrogen migrations both 1-silapropadiene 199 and silacyclopropene 197 would yield 200. Precedent for the thermal isomerization of silacyclopropenes to silylacetylenes has been previously reported (98,100,289). Silylpropadienes, although well-known intermediates in the photolysis of

Scheme 54

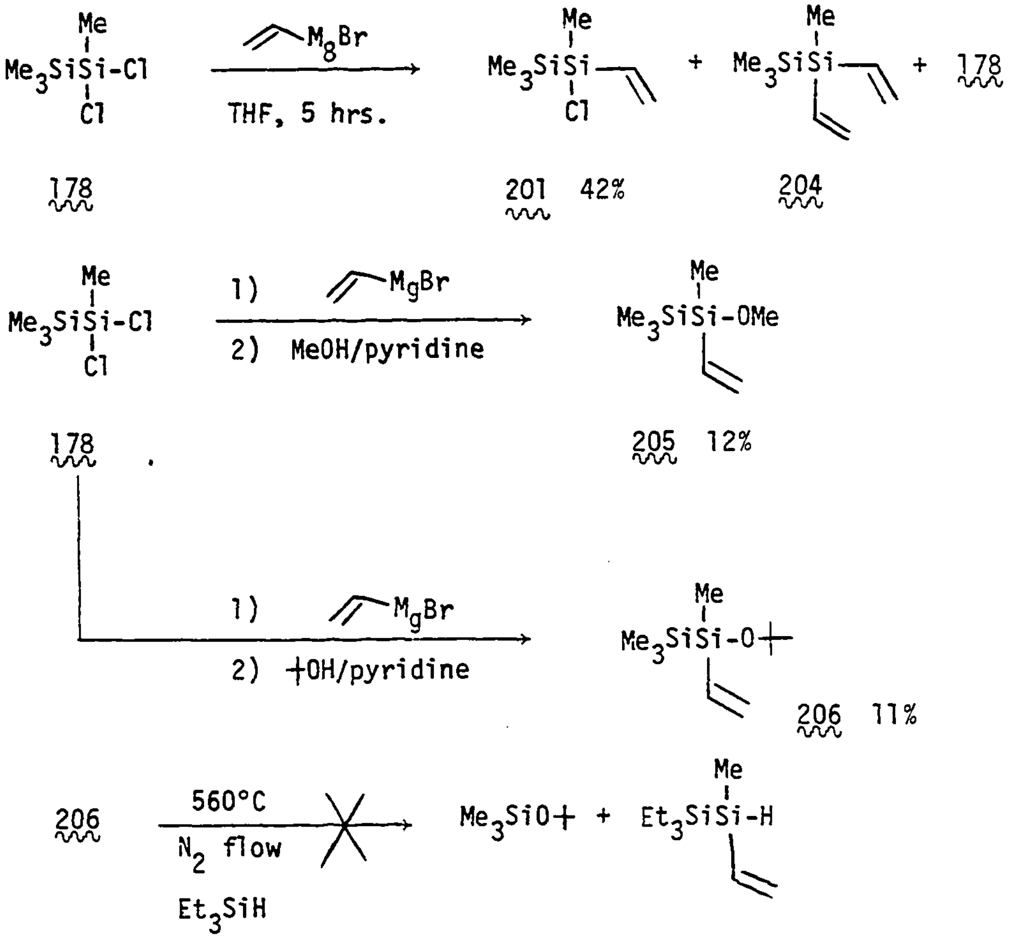


alkyldisilanes (60,61), have not been generated under thermal conditions, thus the rearrangement of 199 to 200 is unprecedented. The formation of 199 is visualized as occurring from 196 by a direct α-carbon-hydrogen insertion. For silacyclopropene 197, two mechanistic pathways for its formation are possible: a, direct β-carbon-hydrogen insertion of silylene **196**; and b, vinyl rearrangement of **196** to afford **198**, which affords **197** by a hydrogen migration process. Although it is not possible to distinguish between the mechanistic alternatives on the basis of the data obtained, these results do provide evidence of the unprecedented rearrangement of a vinylsilylene.

It is obvious from a consideration of Scheme 54 that a mechanistic distinction between the alternative pathways cannot be made by a deuterium labeling experiment. However, a distinction between **197** and **199** as precursors to **200** would be possible from the results of a ^{13}C labeling experiment. Thus, were **200** formed exclusively from **199**, a ^{13}C label at either the α- or β-carbon of **196** would afford **200** containing a ^{13}C at only one of the acetylenic carbons (either α or β depending upon the location of the label in **196**). Alternatively, if **200** arises from **197** the ^{13}C label will be distributed equally between the α- and β-acetylenic carbons.

Although disilane **201** was prepared in a yield of 42% as shown in Scheme 55, it was always contaminated by varying amounts of unreacted **178** and 1,1-divinyltetramethyldisilane (**204**). Due to the similarity in the boiling points of **178**, **204**, and **201**, **201** could only be isolated by preparative GC in typical yields of about 10%. Thus, this route to a selectively labeled precursor to **196** is clearly unacceptable in view of the expense of ^{13}C labeled compounds. We thus sought to functionalize **201** such that its separation from **178** and **204** could be effected by distillation or chromatography.

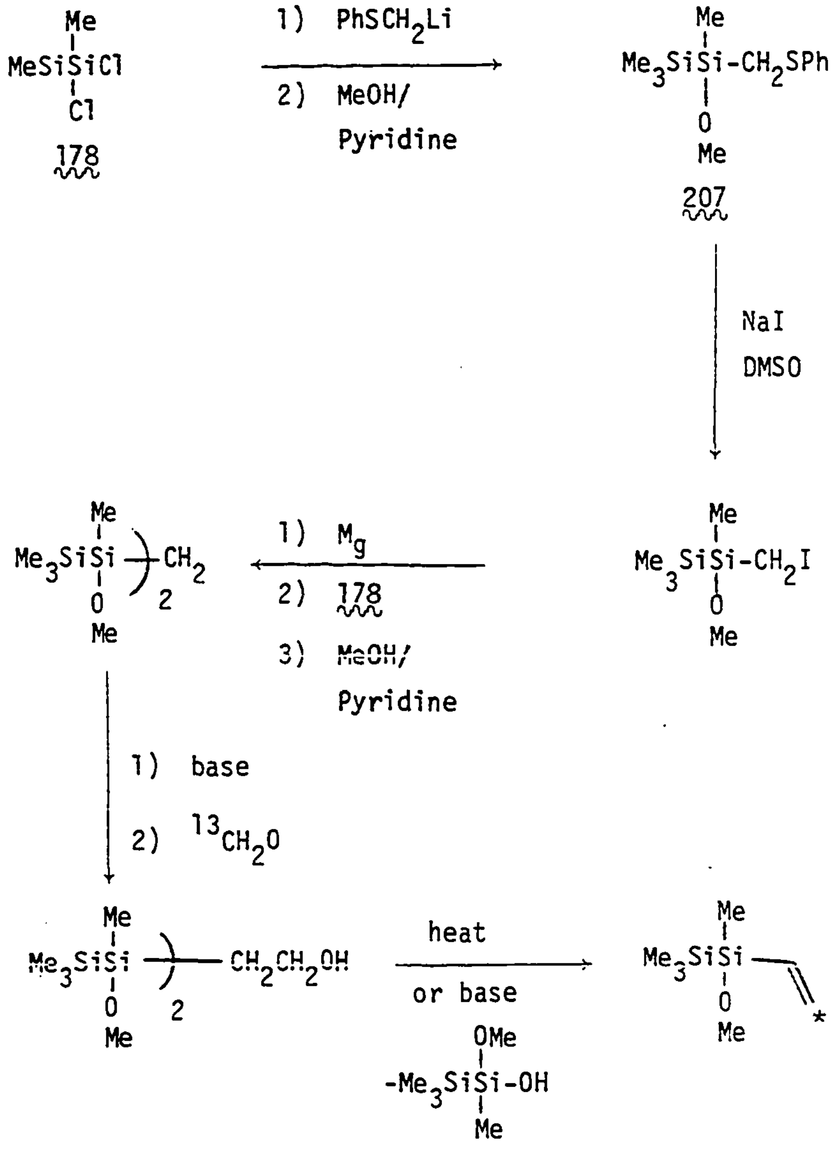
Scheme 55



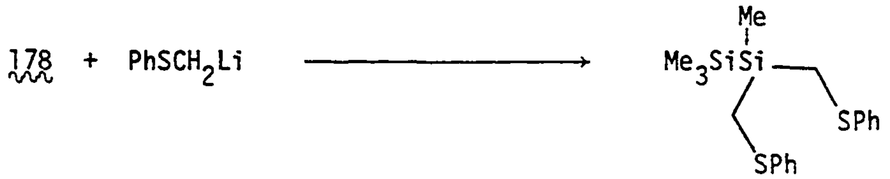
The methoxyl derivative of 201, 205, proved no easier to separate from 178 and 204 than 201. We, therefore, turned to the *t*-butoxyl derivative, 206. Contrary to expectations, the synthesis of 206, which was effected in a manner analogous to that for 205, preceded in a yield of only 11% (Scheme 55). This low yield, coupled with the finding that 206 did not thermally decompose to afford methylvinylsilylene, demonstrated that this route was not a viable solution to our problem.

As a result of these failures, an alternative route for the preparation of a disilane precursor to 196 was examined. Our general synthetic strategy is shown in Scheme 56.

Scheme 56



However, contrary to expectations, either normal or inverse addition of the anion of thioanisol to 178 failed to afford 207. Instead, these reactions afford complex mixtures from which only the diadduct 208 was isolated. No further work was done on this reaction.



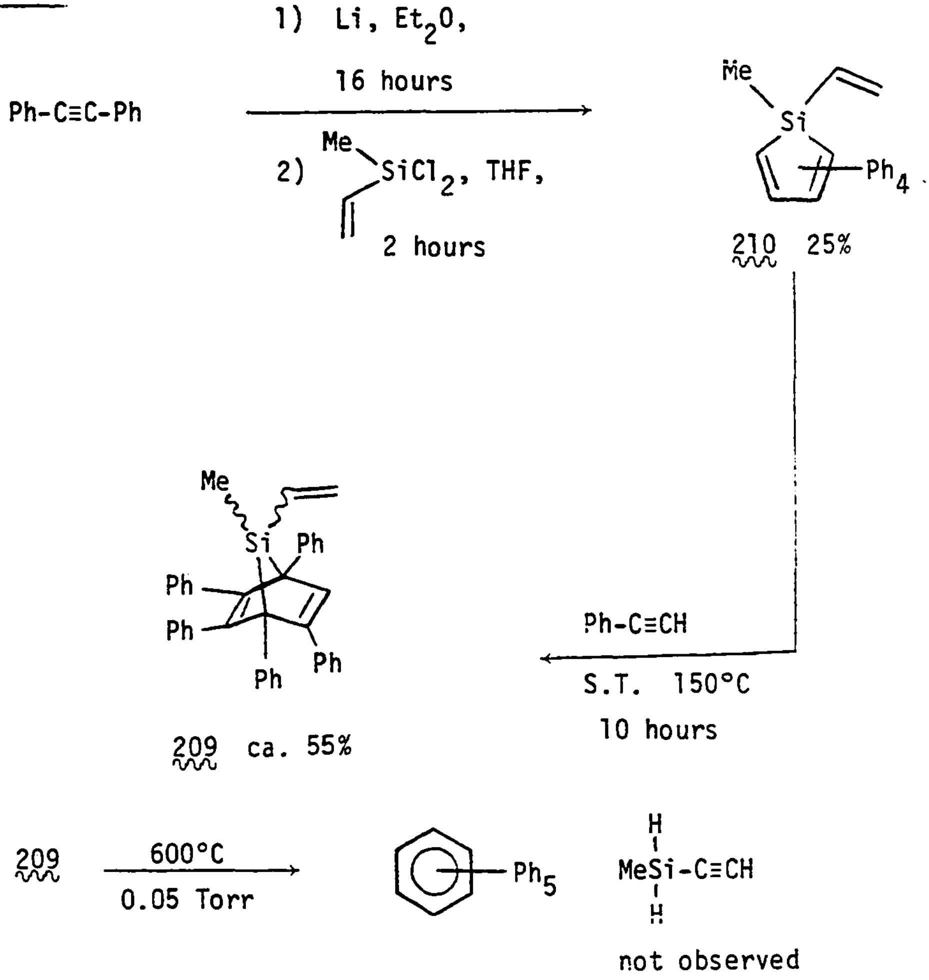
208

normal addition	53%
inverse addition	42%

Due to the failure to effect a convenient synthesis and isolation of a disilane precursor to 196 which would allow for the convenient incorporation of a ^{13}C label, an alternative method of preparation of 196 was investigated. Since 7-silanorbornadienes have been proposed to thermally extrude the bridging silicon as a silylene (see Historical section on silylenes), the synthesis and pyrolysis of 7-methyl-7-vinyl-7-silanorbornadiene 209 was undertaken. The synthesis of 209, as a mixture of diastereoisomers, was readily effected by a Diels-Alder reaction of tolan and silole 210, prepared by the method of Balasubramanian and George (290) (Scheme 56). However, vacuum pyrolysis of 209 (vertical flow, 600°C, 0.05 Torr) failed to afford 200, although pentaphenylbenzene, the expected product of silylene extrusion from 209, was obtained.

Due to this succession of failures in our attempts to develop a synthesis of a precursor to 196, such that the incorporation of a ^{13}C label would be feasible, the desired labeling experiment has not been performed.

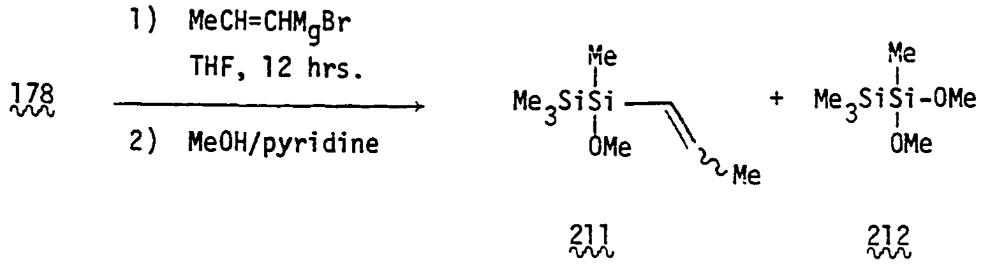
Scheme 56



Therefore, the details of the mechanism of formation of **200** (Scheme 54) remain ambiguous.

In an attempt to establish the generality of the rearrangement of vinylsilylenes, the synthesis and pyrolysis of disilane **211** was examined. Disilane **211** was prepared as shown in Scheme 57 as a mixture of *cis* and *trans* isomers in a 31% yield. Unfortunately, due to the formation of approximately an equal amount of dimethoxydisilane **212**, **211** could only be isolated by preparative GC.

Scheme 57



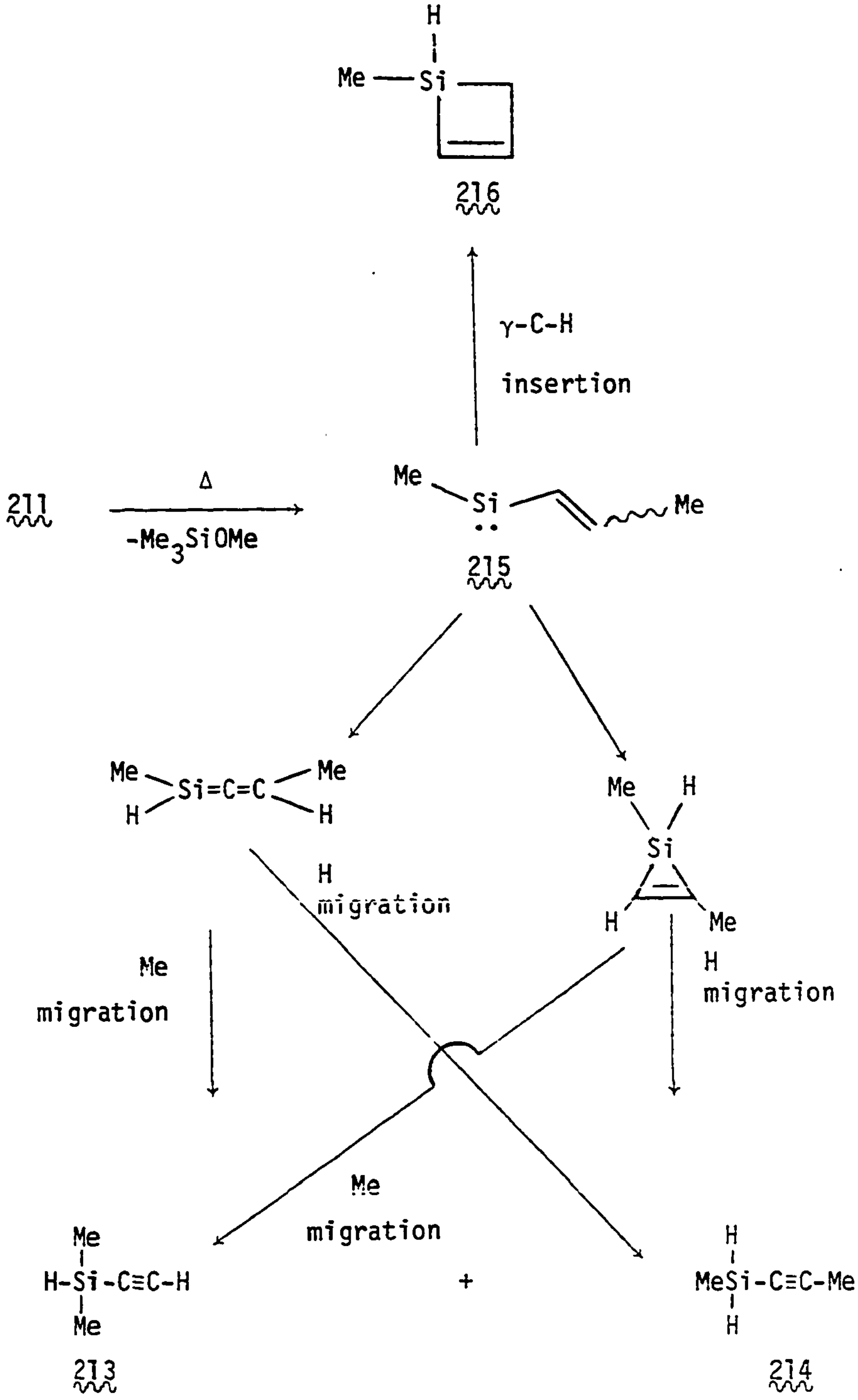
If 211 thermally decomposed in a manner analogous to that of 201, the anticipated products would be trimethylmethoxysilane, and silylacetylenes 213 and 214 (Scheme 58). Additionally, the cis isomer of silylene 215 could afford silete 216 by a γ-C-H insertion.

In contrast to expectations, pyrolysis of 211 (780°C, 1 x 10^{-4} Torr) afforded a complicated pyrolysate containing at least 13 compounds, of which trimethylmethoxysilane was the only major product. Analysis of the minor products by GCMS failed to reveal the presence of any products that were isomeric with 215, although the presence of trace amounts (>5%) of trimethylsilane, 217, and silylacetylene 218 were found (Scheme 59).

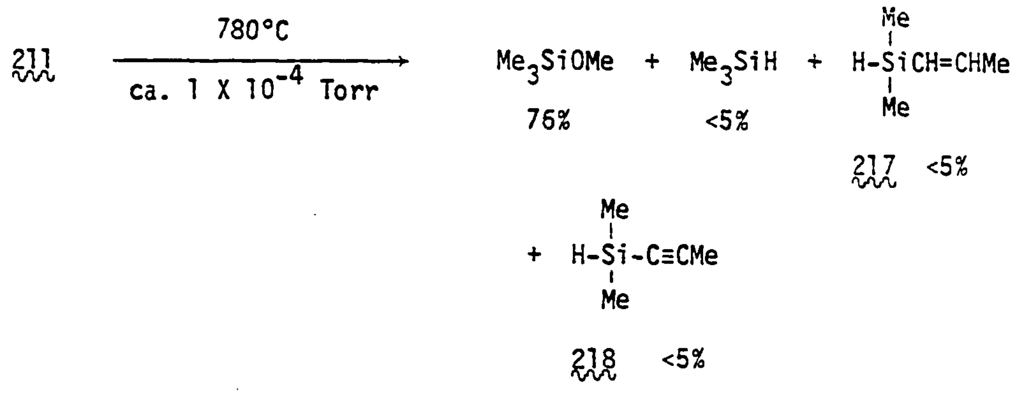
In contrast to our results, a recent reexamination by Burns (285) of the pyrolysis of 211, under conditions similar to those reported here, afforded silacyclobutene 216 in approximately 40% yield. The discrepancy between the results reported in this thesis and those found by Burns is not known.

One final attempt was made to provide a second example of a vinylsilylene rearrangement. Thus, an investigation of the synthesis and

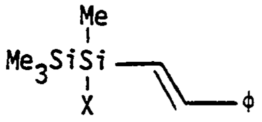
Scheme 58


216
γ-C-H
insertion
211
Δ
-Me$_3$SiOMe
215
H
migration
Me
migration
H
migration
Me
migration
+
213
214

Scheme 59



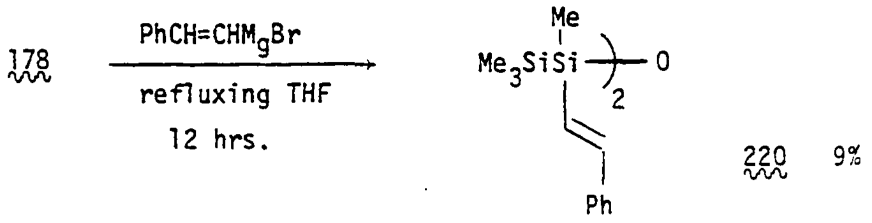
thermal chemistry of styryldisilane **219** was undertaken.



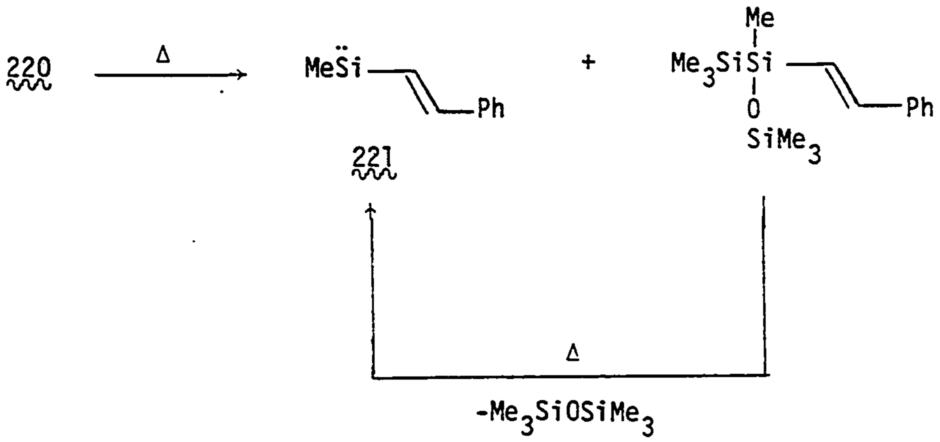
219

X = Cl or OMe

Following the general method used for the preparation of **201** and **211** (*vide supra*), the addition of the Grignard of β-bromostyrene to **178** was expected to afford **219** (X-Cl) in moderate yield. However, numerous attempts to effect the synthesis of **219** by this route led, in all cases, to the formation of complex reaction mixtures from which only disiloxane **220**, the hydrolysis product of **219**, could be obtained in low yields.

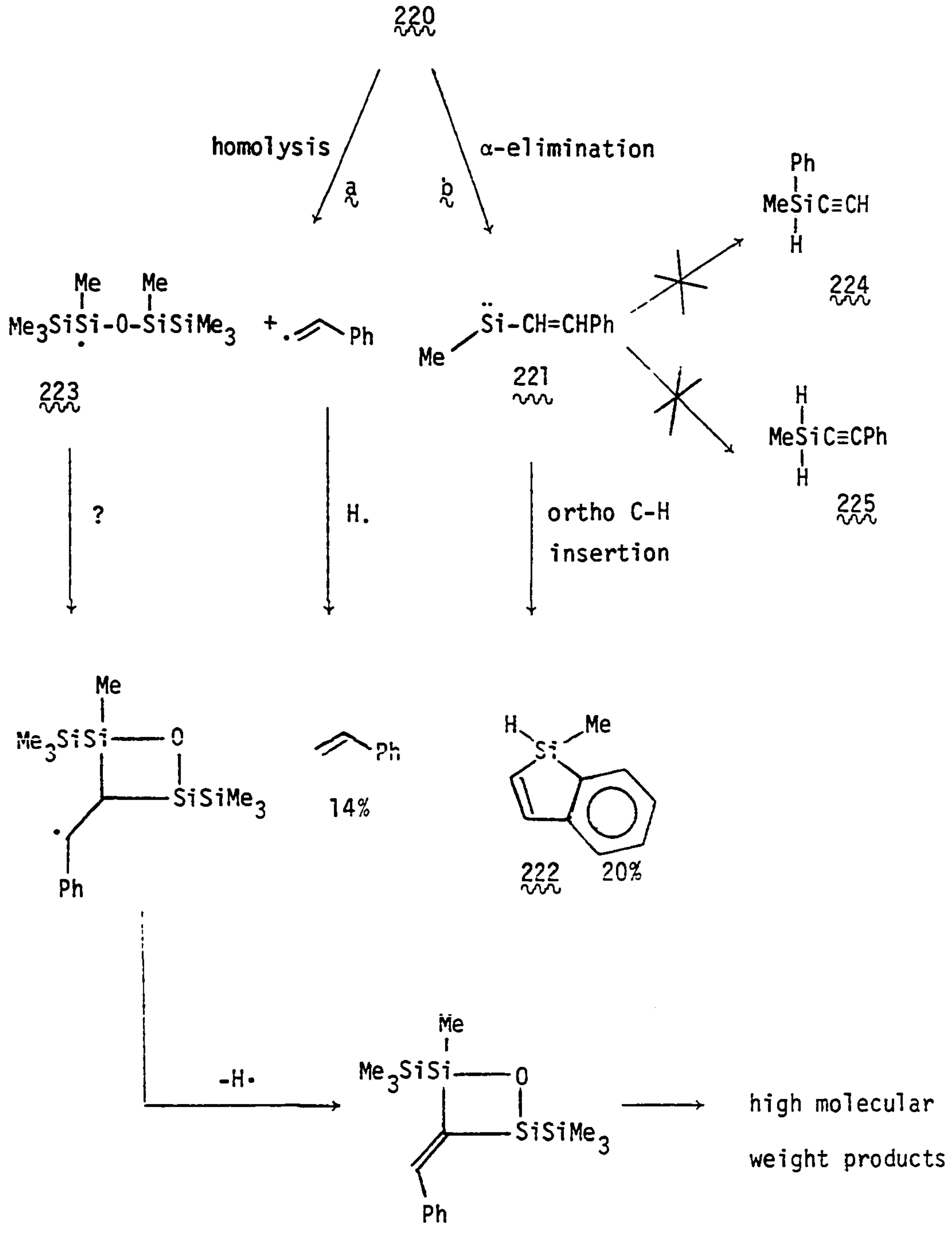


Although we were unable to prepare the desired silylene generator, Weyenberg and Atwell (44) had previously found that siloxydisilanes thermally α-eliminate to afford silylenes, thus pyrolysis of **220** was expected to afford 2 molecules of the desired β-stryrylsilylene, **221**.

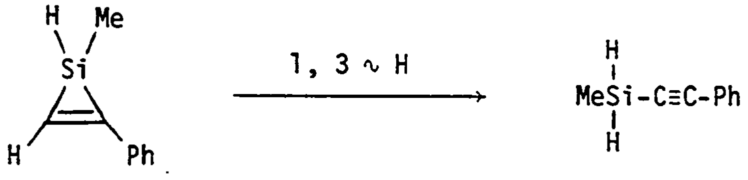


Pyrolysis of **220** at 800°C and 8 X 10^{-5} Torr afforded as major products styrene and 1-methyl-1-silaindene (**222**) in 14 and 20% yields, respectively (Scheme 60). No evidence for the formation of the desired silylacetylenes **224** and **225** was found. Mechanistically, these products are most consistent with competitive decomposition pathways for **220**. Path **a**, involves homolytic cleavage of a Si-C bond to give a styryl radical and silyl radical **223**. Hydrogen abstraction by the styryl radical gives styrene. Although the mechanistic fate of **223** is unknown, it could conceivably afford higher molecular weight products by the process shown in Scheme 60. Silylindene **222** is most reasonably formed by ortho-C-H insertion by silylene **221** (path **b**). This process, if true, would be the first example of a silylene insertion into an aromatic C-H bond. However, **222** could conceivably arise via a sequence of rearrangements (Scheme 61) involving an initial rearrangement analogous to that for the formation of **200** from **201** (Scheme 54).

Scheme 60


220
homolysis
a
b
α-elimination
Me
Me
Me3SiSi-O-SiSiMe3
223
+ Ph
Me
Si-CH=CHPh
221
Ph
MeSiC≡CH
H
224
H
MeSiC≡CPh
H
225
?
H.
ortho C-H
insertion
Me
Me3SiSi
O
SiSiMe3
Ph
Ph
14%
H
Si
Me
222
20%
-H·
Me
Me3SiSi
O
SiSiMe3
Ph
high molecular
weight products

Although this latter mechanism is not favored, since the intermediate silacyclopropene would be expected to rearrange to phenyl-3-silabutyne, it cannot be excluded.



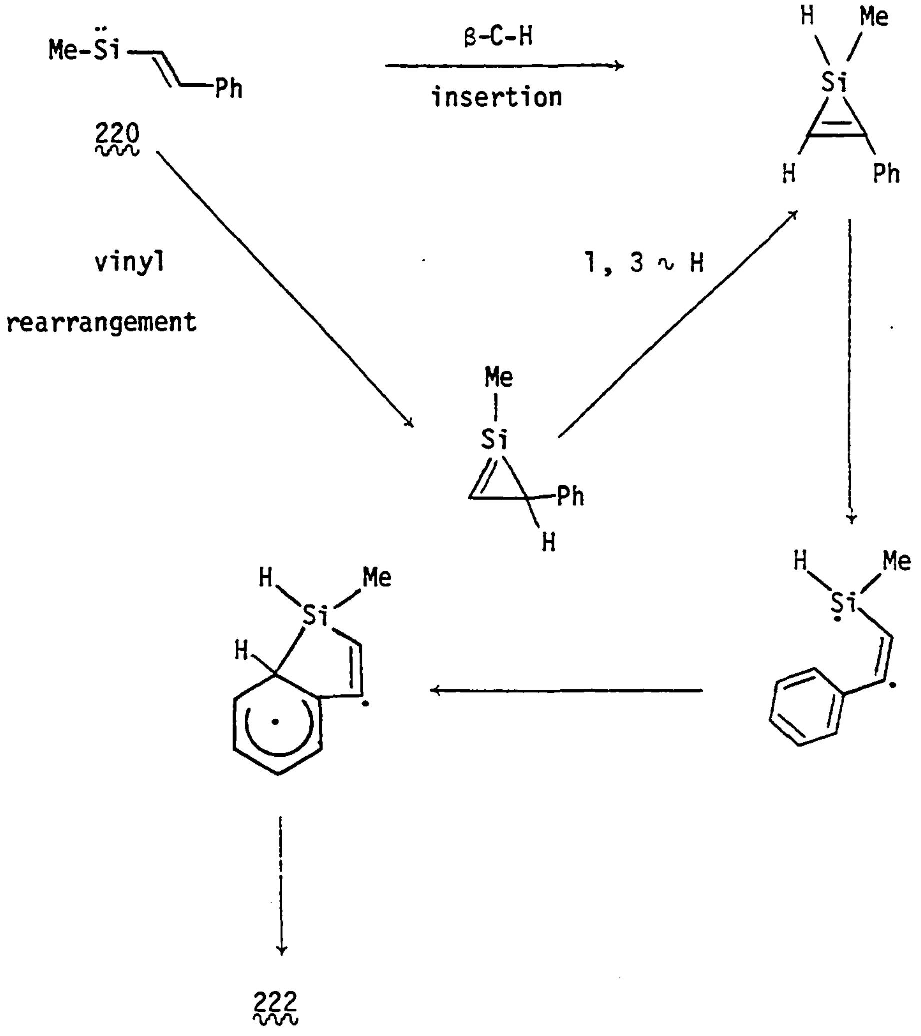
Although Schemes 60 and 61 contain several interesting mechanistic possibilities, particularly the possible intramolecular cyclization of radical 223, due to the difficulty and low yields associated with the preparation of 220, this reaction was not pursued further.

While the pyrolysis of 211 (Scheme 58) and 220 (Scheme 60) do not exhaust the possibilities for the generation of various vinylsilylenes, the results of these studies do demonstrate that the vinylsilylene rearrangement is not general.

Gas-Phase Thermal Chemistry of Methylmethoxysilylene

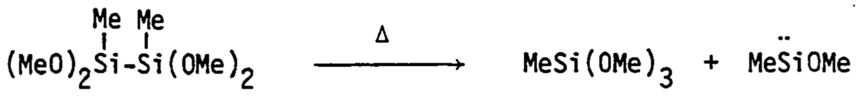
Although methylmethoxysilylene has been known as a reactive intermediate for over 10 years, its generation in the gas-phase in the absence of traps has never been reported. In view of the report by Conlin and Gaspar (98) that in the gas-phase dimethylsilylene dimerizes to tetramethyldisilene which then undergoes of series of rearrangements involving the intermediacy of silylenes, as demonstrated by Wulff and coworkers (31), the possibility that methylmethoxysilene could undergo similar chemistry was investigated.

Scheme 61



Consideration of the possible mechanistic pathways for this reaction (assume only methoxy migration) reveals that the hoped for disilene 226, upon rearrangement, would afford silylenes 227 and 228, which in turn, could lead to intermediates 229 - 232 (Scheme 62). These latter intermediates upon subsequent rearrangements would be expected to afford stable products (Schemes 63 and 64). Although this analysis would predict a plethora of products, Chen and coworkers (118) have found that the gas-phase rearrangement of bis(trimethylsilyl)silylene afforded one major product in 60% yield, even though, the reaction could conceivably produce greater than eight products. It was therefore hoped, that our reaction would proceed in a similarly clean manner.

The established method of thermal generation of methylmethoxysilylenes is pyrolysis of tetramethoxydisilane 233 (7). However, since methoxy-polysilanes are known to be excellent traps for silylenes (see Historical section on silylenes), we chose to utilize disilane 234 as our silylene source. This choice was based on the assumption that reducing the number of methoxy-groups in the starting disilane would decrease the rate of silylene trapping.



$$(MeO)_2\overset{Me}{\overset{|}{Si}}-\overset{Me}{\overset{|}{Si}}(OMe)_2 \xrightarrow{\Delta} MeSi(OMe)_3 + Me\ddot{Si}OMe$$

233

$$Me_3SiSiMe_2(OMe)_2 \xrightarrow{\Delta} Me_3SiOMe + Me\ddot{Si}OMe$$

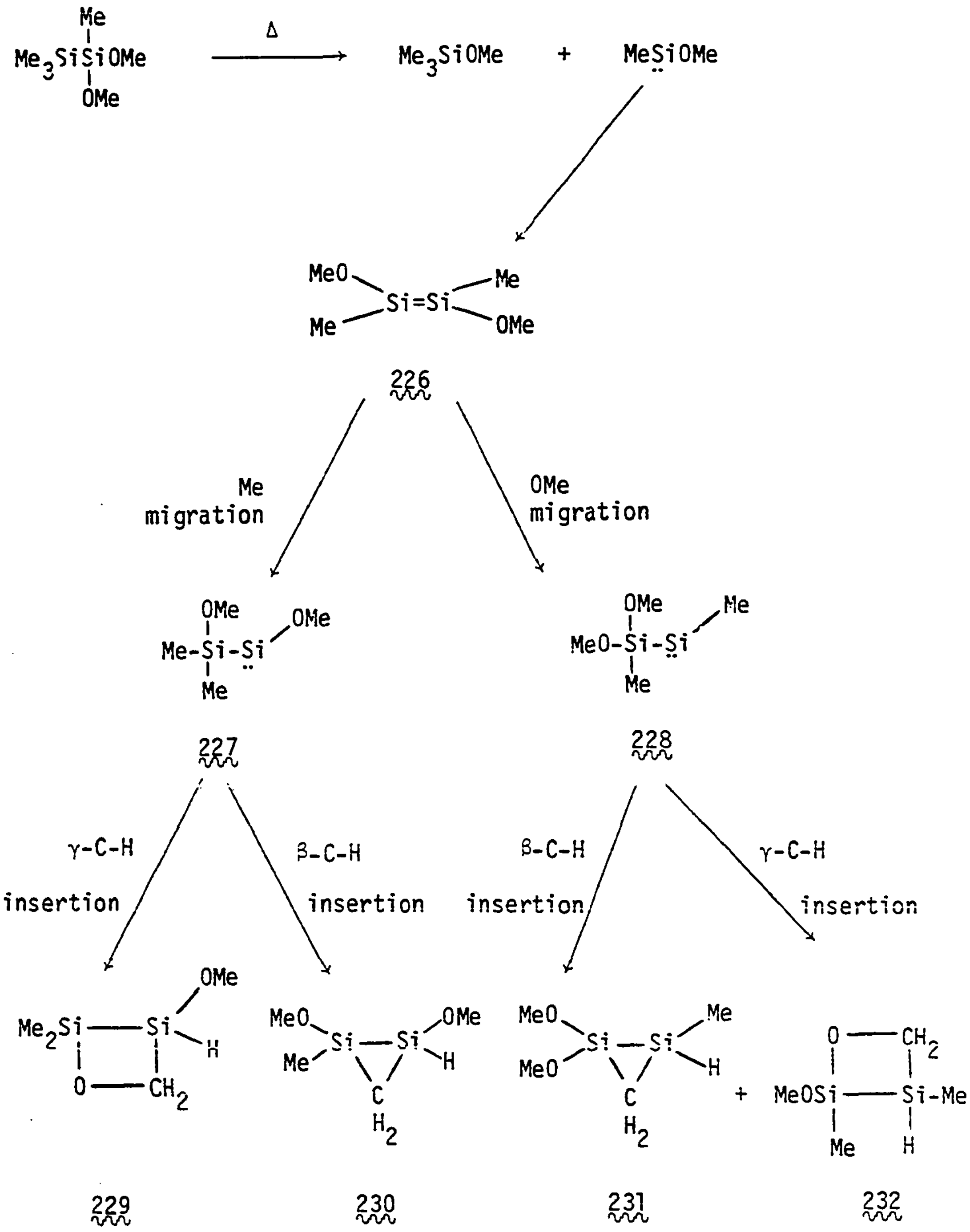
234

Disilane 234 was prepared as a distillable liquid, B.P. 61-64°C at 60 Torr, in 49% yield by the reaction of dichlorodisilane 178 with excess methanol and pyridine.

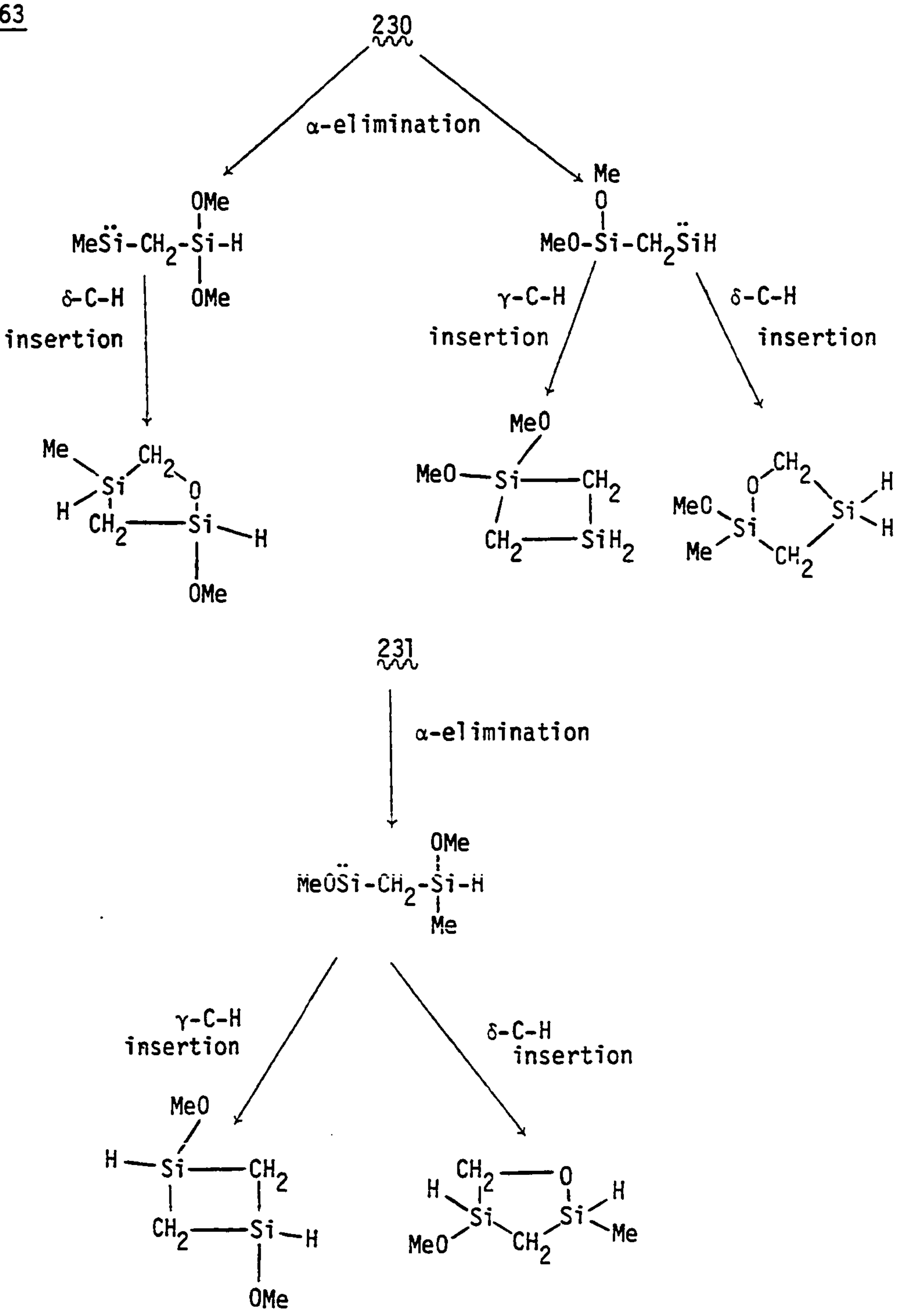
$$Me_3SiSiMeCl_2 \xrightarrow[\text{24 hrs.}]{\text{MeOH/pyridine}} \text{234} \quad 49\%$$

178

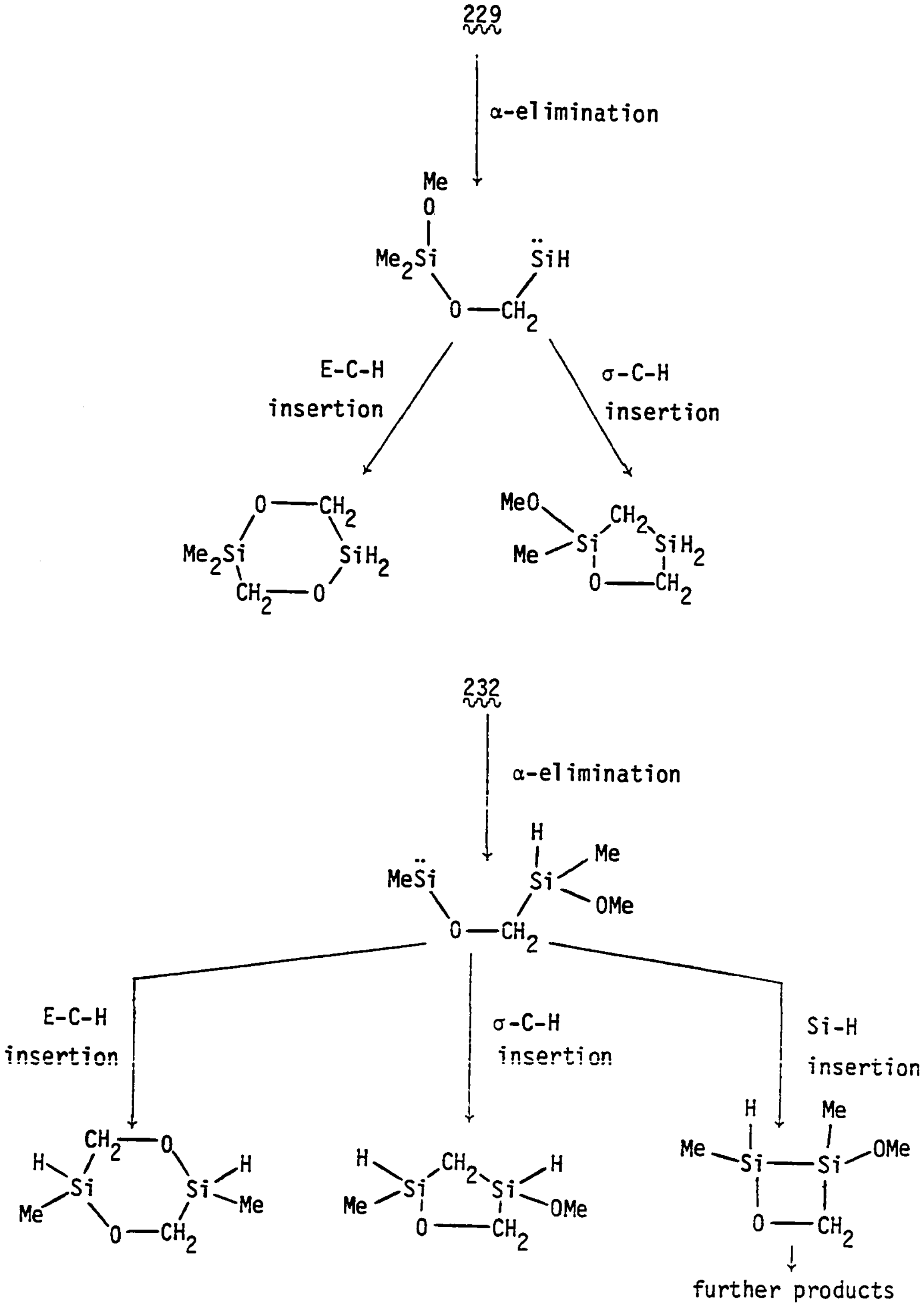
Scheme 62


Me₃SiSi(Me)(OMe)OMe
Δ
Me₃SiOMe + MeSiOMe
226
Me migration
OMe migration
227
228
γ-C-H insertion
β-C-H insertion
β-C-H insertion
γ-C-H insertion
229
230
231
232

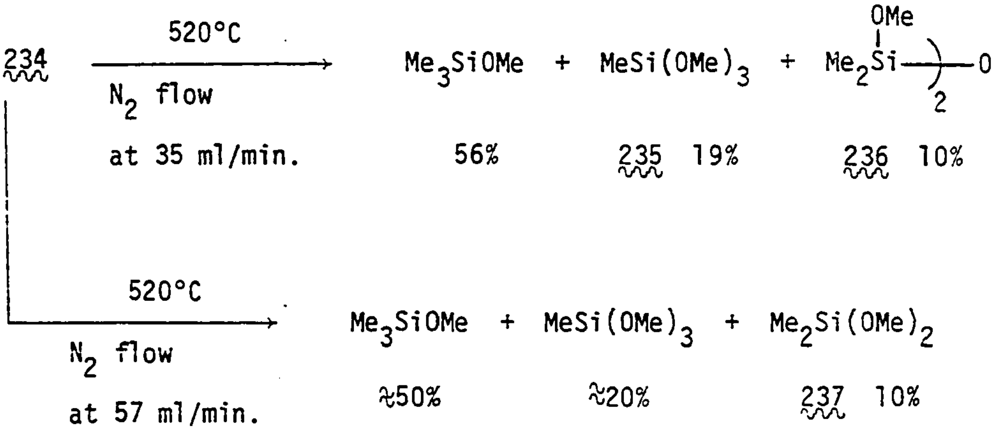
Scheme 63


230
α-elimination
MeS̈i-CH2-Si(OMe)2-H
MeO-Si(OMe)-CH2S̈iH
δ-C-H insertion
γ-C-H insertion
δ-C-H insertion
231
α-elimination
MeOS̈i-CH2-Si(OMe)(Me)-H
γ-C-H insertion
δ-C-H insertion

Scheme 64


229
α-elimination
E-C-H insertion
σ-C-H insertion
232
α-elimination
E-C-H insertion
σ-C-H insertion
Si-H insertion
further products

Pyrolysis of 234 (gas-phase, nitrogen flow, 520°C) afforded as major products trimethylmethoxysilane, methyltrimethoxysilane (235), and *sym*-methyldimethoxydisiloxane (236) in yields of 56, 19, and 10%, respectively, as the only major products. No evidence for the formation of the desired rearrangement products of disilene 226 was found. In a repeat of this reaction with a 64% increase in the rate of nitrogen flow, similar results were obtained, with the exception that the 236 was not found. Instead, dimethyldimethoxysilane (237) was obtained in approximately a 10% yield. This latter finding suggests that 236 is a secondary thermal product derived from dimethyldimethoxysilane. Indeed, Hoekman has previously demonstrated that the major product of the thermolysis of dimethyldimethoxysilane is 236 (261).

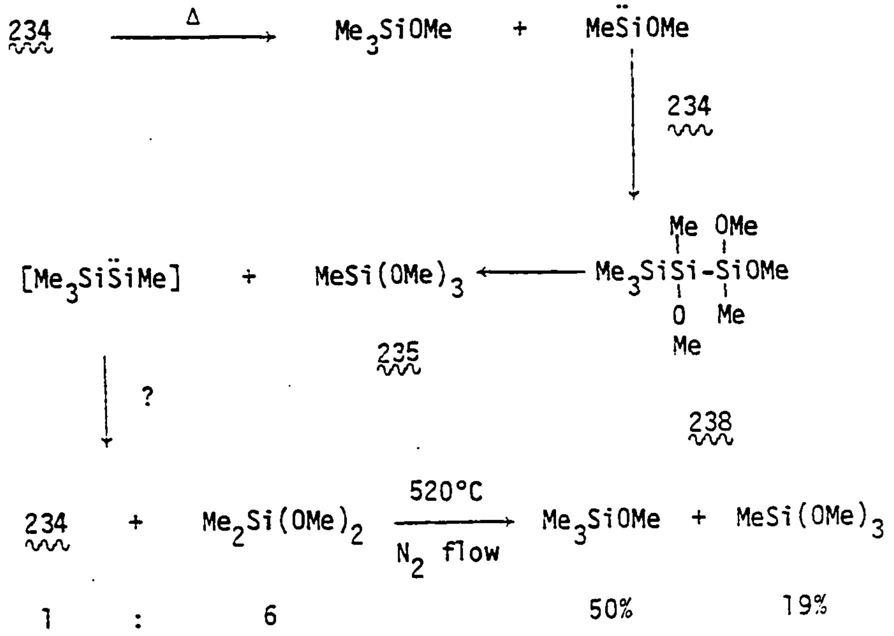


$$\mathbf{234}\ \xrightarrow[\text{N}_2\text{ flow at 35 ml/min.}]{520°\text{C}}\ \underset{56\%}{Me_3SiOMe} + \underset{\mathbf{235}\ 19\%}{MeSi(OMe)_3} + \underset{\mathbf{236}\ 10\%}{(Me_2\overset{OMe}{Si})_2O}$$

$$\mathbf{234}\ \xrightarrow[\text{N}_2\text{ flow at 57 ml/min.}]{520°\text{C}}\ \underset{\approx 50\%}{Me_3SiOMe} + \underset{\approx 20\%}{MeSi(OMe)_3} + \underset{\mathbf{237}\ 10\%}{Me_2Si(OMe)_2}$$

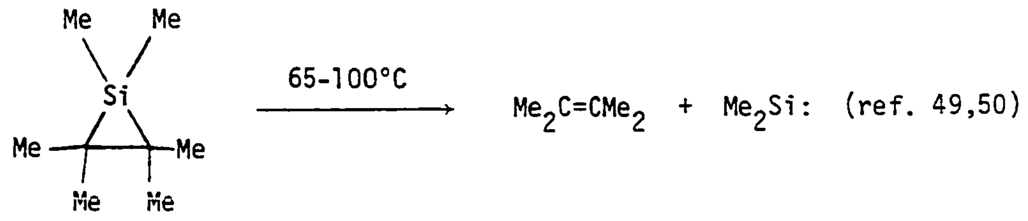
The mechanism of formation of 237, which affords 236 as previously described by Hoekman (261), is unknown. However, the formation of Me_3SiOMe and 235 is easily rationalized by the process shown in Scheme 65. Thus, insertion of methylmethoxysilylene into the Si-O bond of the starting material yields 238. By α-elimination, 238 extrudes methyltrimethylsilylsilylene and yields 235. The fate of methyltrimethylsilylsilylene under these reaction conditions is unknown. Weyenberg and Atwell (44) have previously found that increasing the number of alkoxy-groups attacked to a disilane results in more facile thermal decomposition. Thus, the proposed decomposition of 238 to afford 235 is not unreasonable. It should be noted, that based on this proposal, disilane 234, contrary to expectations, does function as an efficient silylene trap. That 234 is an efficient silylene trap was demonstrated by the finding that copyrolysis of 234 and a 6 fold molar excess of dimethyldimethoxysilane afforded Me_3SiOMe and 235 in essentially the same yields as those obtained in the absence of a trap. The efficiency of silylene trapping by 234 thus prevents the possible occurrence of the desired silylene rearrangements.

Scheme 65

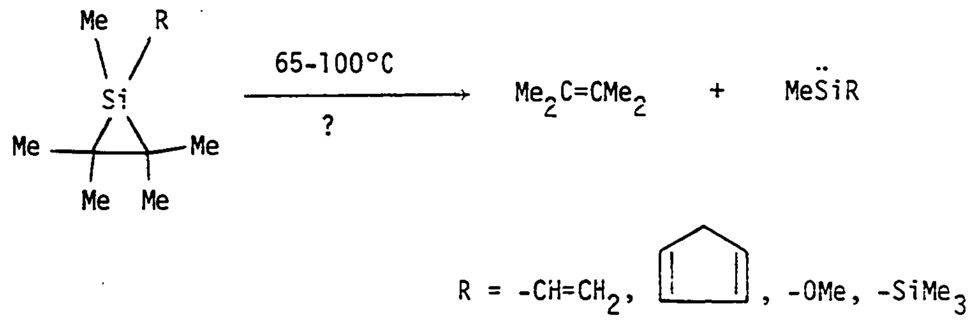


Attempted Generation of Functionalized Silacyclopropanes.

Since we had previously gained experience in the preparation and handling of hexamethylsilarane (12) in our study of the addition of dimethylsilylene to cyclooctene oxide (vide supra), the preparation of a silarane in which one of the silicon-methyls was replaced by a vinyl-, cyclopentadienyl-, or methoxyl-group was examined as an alternative route to the previously studied vinyl-, cyclopentadienyl- and methoxylsilylenes. This route was considered attractive since the mild conditions at which silylene extrusion was anticipated would hopefully reduce or eliminate the undesirable side reactions that lead to the complicated reaction mixtures previously obtained.

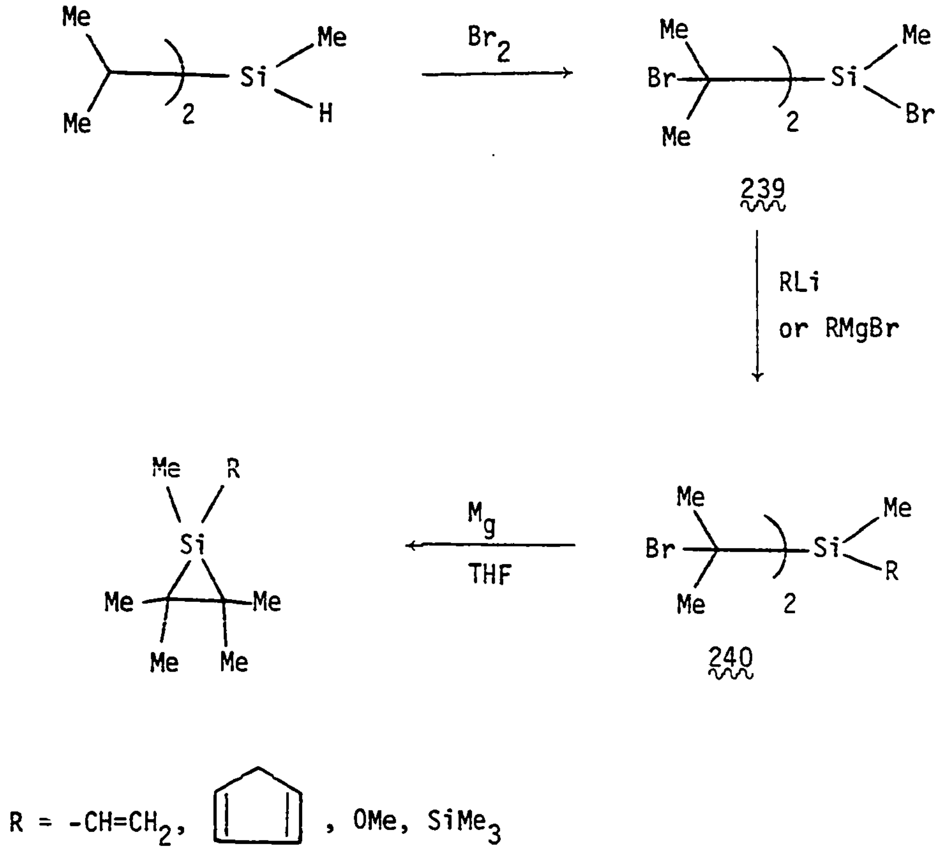


12



Scheme 66, which is a modification of our synthesis of **12**, summarizes the synthetic strategy for the synthesis of functionalized silacyclopropanes. The key step in this proposed synthesis is the transformation of **239** to **240**. Due to the nature of the desired substituents, which would not survive reaction with molecular bromine, appending the substituents prior to bromination would not be a practical alternative.

Scheme 66



Tribromide 239 was prepared in 82% yield as a waxy solid (M.P. 68-70°C) by the addition of 3 equivalents of bromine to diisopropylmethylsilane. However, reaction of 239 with either trimethylsilyllithium, cyclopentadienyllithium, or vinyl Grignard, failed to afford the desired silarane precursor. In all cases, complex reaction mixtures were obtained, and which for the latter case was demonstrated by GCMS not to contain the desired product. Furthermore, the finding that methanol and pyridine reacted with 239 to afford a major product that was identical to the major product of the reaction of 239 with vinyl Grignard suggested that the major process in these reactions was decomposition of 239.

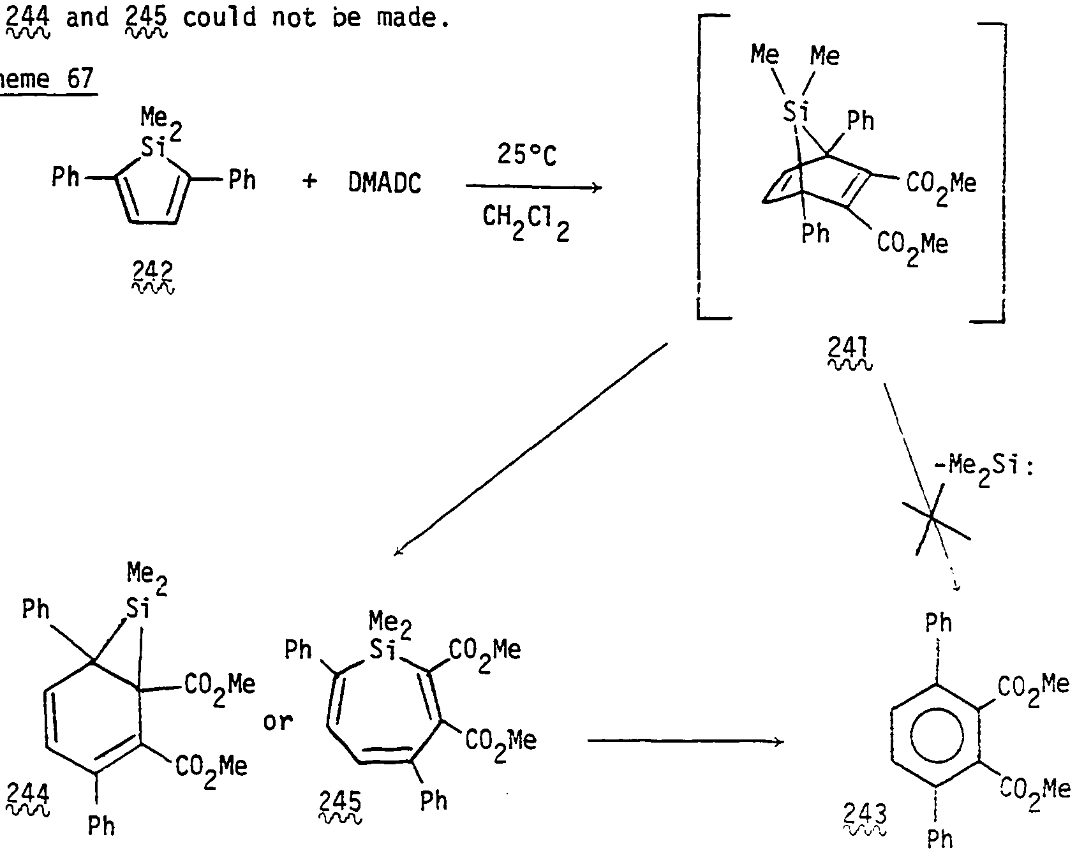
Due to our inability to effect the transformation of 239 to 240, plus our inability to develop an alternative synthetic strategy to a substituted silarane, this method of silylene generation was abandoned.

Investigation of the Thermal- and Photochemistry of 7-Silanorbornadienes

In 1972, as a result of an investigation of the synthesis of 7-silanorbornadienes that could function as low-temperature silylene generators, Witiak reported the attempted preparation of 241 (291). Contrary to expectations, it was found that the addition of dimethyl acetylenedicarboxylate (DMADC) to a CH_2Cl_2 solution of silole 242 did not afford the desired 241. Instead, the rapid formation of a deep red-colored solution was observed, from which only dimethyl 2,5-diphenylphthalate (243) was obtained in a yield of approximately 50% (Scheme 67).

Initially, the formation of 243 was postulated to occur via the intermediacy of 241, which under the reaction conditions extruded dimethylsilylene to afford 243. However, on the basis of trapping experiments, which failed to afford products of silylene trapping, and on the basis of an examination of the course of the reaction by low-temperature NMR, it was demonstrated that the extrusion of dimethylsilylene from 241 was not occurring. Instead, on the basis of the NMR studies, it was proposed that the reaction of DMADC and 242 proceeded by the initial formation of 241 which rearranged to either silanorcaradiene 244 or silapin 245 (Scheme 67). Unfortunately, due to the inability to isolate any of these compounds (with the exception of 243) a distinction between the formation of 244 and 245 could not be made.

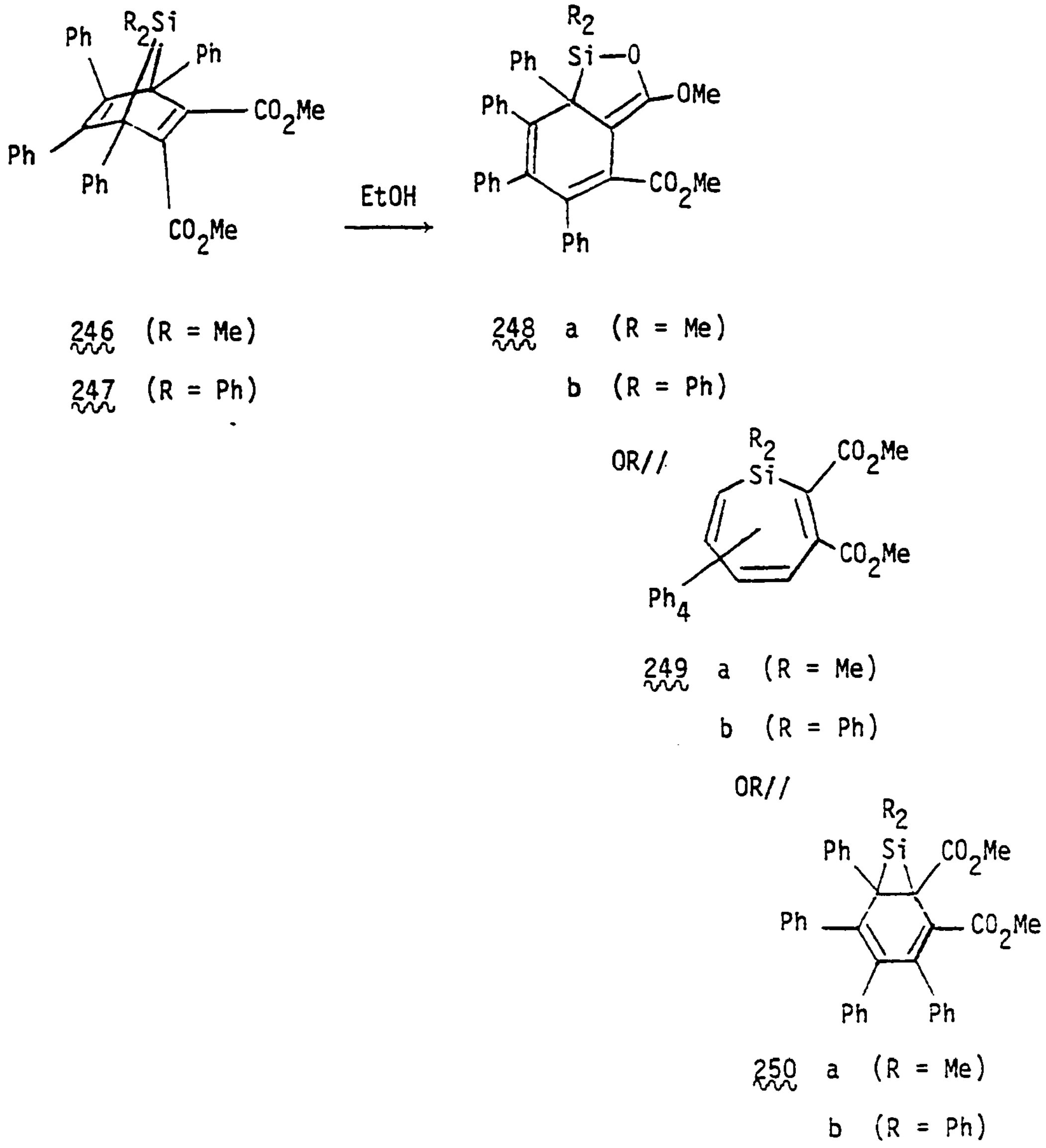
Scheme 67



Rearrangement of Diels-Alder adducts of siloles and DMADC finds precedent in the work of Gilman and coworkers (4,5). Thus, in 1964, these authors reported that both 7-silanorbornadienes 246 and 247 rearranged upon treatment with ethanol. Three stuctures were considered for the rearranged adducts: 248, 249, and 250. Siloxane 248 was eliminated from further consideration due to the absence of an absorption uniquely assignable to an Si-O-C stretch in the 1100-850 cm^{-1} region of the IR spectra (although several bands were present in this region). Thus, based on the observation that the isomerized materials showed two strong bands attributed to carbonyl stretching of two different methyl carboxylate groups (R = Me, 1727 and 1626 cm^{-1}; R = Ph, 1724 and 1618 cm^{-1}), it was felt that the products were either silapins 249 or silanorcaradienes 250, but a conclusive distinction could not be made.

It is now known that silacyclopropanes rapidly decompose in the presence of alcohols, halogenated hydrocarbons, and upon exposure to air (49,267), thus we tentatively proposed that the results of Witiak and Gilman and coworkers were more consistent with isomerization to silapins 245 and 249. Since it was possible that identification of the product from the isomerization of 241 would allow comment on this longstanding problem, a reinvestigation of the reaction of silole 242 with DMADC was undertaken.

In contrast to the results obtained in CH_2Cl_2 (*vide supra*), addition of DMADC to a CCl_4 solution of 242 resulted in the formation of 241 in high yields (approximately 85% by NMR). In addition, under these conditions the complete isomerization of 241 required approximately 3 hours



246 (R = Me)

247 (R = Ph)

248 a (R = Me)

b (R = Ph)

249 a (R = Me)

b (R = Ph)

250 a (R = Me)

b (R = Ph)

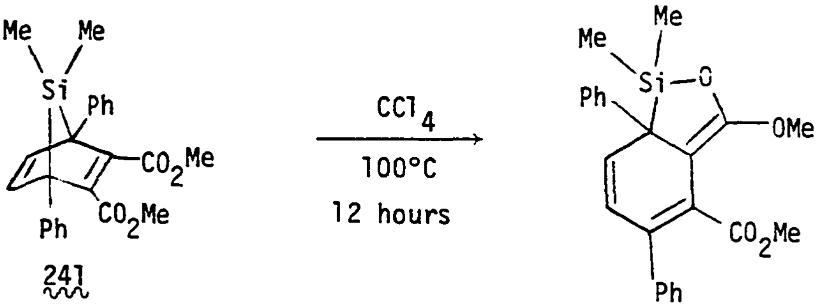
at room temperature. Further study demonstrated that the stability of 241 was oxygen dependent. Thus, when deoxygenated DMADC was added to a deoxygenated CCl_4 solution of 242, nearly quantitative formation of 241 was observed by NMR. Furthermore, under these conditions complete rearrangement of 241 occurred only after 16 to 24 hours at room temperature.

Based on these findings, it was postulated that the isolation of 241 could be effected if care was taken to exclude oxygen. This has been found to be the case. Addition of an excess of degassed DMADC to a degassed solution of 242 and hexane, followed by cooling and careful collection of the resulting crystals, afforded 241 in 20% yield. The identity of 241 was established by the usual spectroscopic methods.

With the synthesis and isolation of 241 firmly established, the attempted isolation and characterization of the rearrangement product was undertaken. Heating a CCl_4 solution of 241 for 12 hours at 100°C resulted in essentially quantitative formation of the rearranged adduct, as determined by NMR. This adduct, which was stable in solution under vacuum at 0°C, resisted all isolation attempts. Chromatography on silica gel or neutral alumina, with hexane elution, afforded only dimethyl 2,5-diphenylphthalate (243). Furthermore, attempts to crystallize the rearranged adduct under deoxygenated conditions, with hexane or benzene, resulted only in the formation of a deep red oil, which gave 243 on standing.

Despite the failure to isolate this product, it was possible to obtain important structural information for it from its IR spectrum. The infrared spectrum of the rearranged adduct showed strong, broad absorptions at 1728 and 1621 cm^{-1}. These bands are most consistent with the presence of a carbonyl and an enol ether functional group (292). Thus, a more reasonable structure for the rearrangement product of 241 is 251, not 244 or 245 as originally proposed.

The formal similarity between the IR spectrum of 251 and those reported for the rearrangement products of 246 and 247 is of interest.



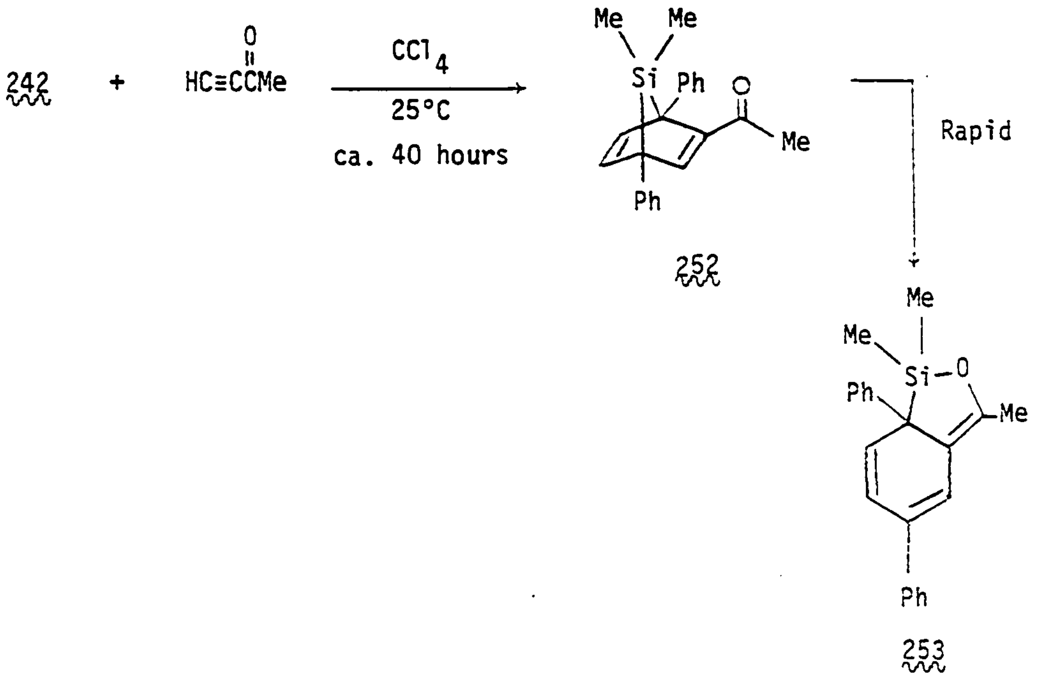
241

251

While the two strong IR bands at 1727 and 1724 cm^{-1} for the respective rearrangement products of 246 and 247 (*vide supra*) are consistent with the C=O stretching absorption of conjugated esters, the respective bands at 1626 and 1618 cm^{-1} are at much lower frequencies than those normally expected for C=O absorptions of esters. The bands at 1626 and 1618 cm^{-1} are, however, consistent with the C=C stretch of an enol ether (292). Thus, based on the IR spectra, the rearrangement adducts of 246 and 247 are clearly most consistent with 248. Precedent for this interpretation can be found in the work of Lutsenko and coworkers, who found similar bands in the IR spectra for a number of O-silyl-O-alkylketeneacetals (293).

Since 248 and 251 are O-silyl-O-alkylketeneacetals, the observed lability of these compounds is not unexpected (293). If our structural assignment for these compounds is correct, substitution of a methyl for the methoxyl attached to the carbon-carbon double bond would be predicted to decrease the lability of these systems.

As a test of this hypothesis, the synthesis and chemistry of acetyl-7-silanorbornadiene 252 was investigated. When a two fold excess of butyn-3-one was added to a solution of 242, the gradual appearance of new signals in the NMR was observed: two silicon methyl singlets at $\delta = -0.08$ and 0.35, a methyl singlet at $\delta = 2.10$, and an unsymmetrical multiplet centered at $\delta = 6.40$, that was attributed to the hydrogens on the norbornadiene ring. After 40 hours at 25°C, only these new signals, and those due to unreacted acetylene, were found. *En vacuo* removal of the solvent and unreacted acetylene afforded an moderately air stable red-brown oil which was consistent with Diels-Alder adduct 252 on the basis of its NMR and mass spectra. However, the IR spectrum of this residue showed an enol ether absorption at 1630 cm^{-1}. Thus, under these reaction conditions the 7-silanorbornadiene 252, that presumably is formed as an intermediate, rapidly rearranges to keteneacetal 253.



In contrast to **251**, which rapidly decomposes on exposure to the atmosphere or heating, **253** was found to be unchanged after heating for 8 hours in the presence of excess silole **242**, and to only partially decompose after exposure to the atmosphere for 12 hours. Although **253** was more stable than **251**, as predicted, it also decomposed to the corresponding aromatic nucleus upon attempted purification by chromatography.

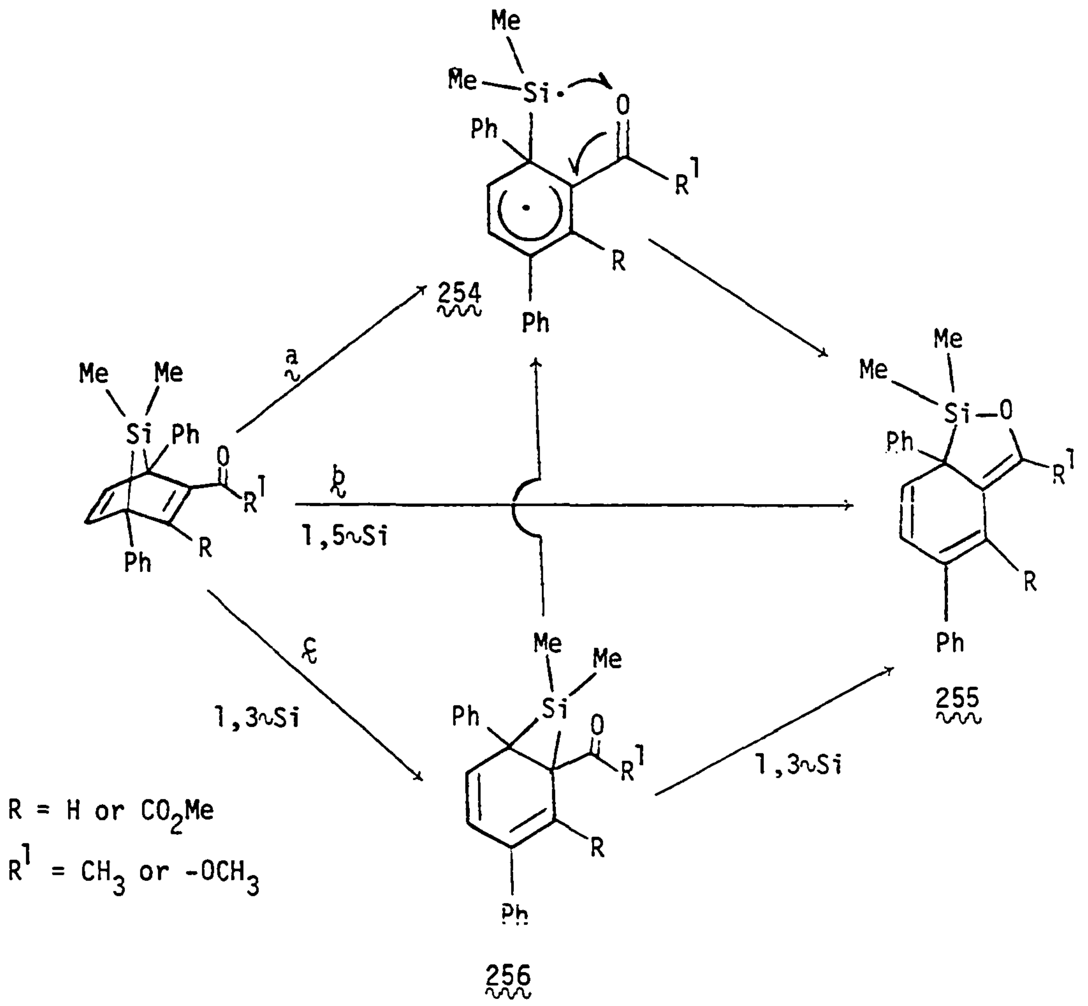
Based on the evidence presented, 7-silanorbornadienes which contain a carbonyl on at least one of the nonbridging basal ring carbons rearrange thermally, or in the presence of alcohols (4,5), to give the isomeric bicycloketeneacetals, not a silapin or silanorcaradiene as previously proposed.

In the absence of alcohols, for which the mechanism of rearrangement has been previously discussed (4), three distinct, nonionic mechanistic alternatives for this rearrangement can be visualized (Scheme 68).

Path **a** proceeds by initial silicon-carbon bond homolysis to produce hexadienyl radical **254**, which after attack at oxygen by the silyl-radical would afford **255**. Precedent for the second step of this process has been previously presented in the Historical section on silyl radicals.

Path **b** is a one step, symmetry allowed, migration of silicon from carbon to oxygen. While to date no precedent exists for a 1,5-Si migration from carbon to oxygen, the facile manner with which silicon is known to migrate in a 1,5 fashion in other systems makes this process reasonable (294,295,296). Furthermore, for the compounds examined, a 1,5-Si migration would be thermodynamically favorable since both a relief in ring strain and formation of a strong Si-O bond would occur upon

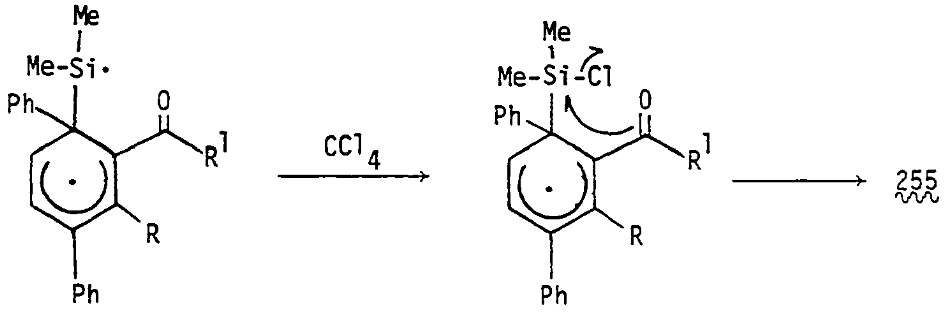
Scheme 68



rearrangement.

The third mechanistic possibility, path c, involves initial 1,3-Si migration from carbon to carbon to afford silanorcaradiene 256. From 256, two possible routes to 255 are possible. The first proceeds by Si-C bond homolysis to produce 254, which then collapses to 255. Alternatively, 256 could undergo a second 1,3-Si migration, this time from carbon to oxygen, to give 255 directly. One-three migrations of silicon from carbon to oxygen have been previously observed, thus, precedent exists for this later step (297).

The absence of geminate coupling products of 254, plus the lack of reaction between 254 and CCl_4, a known silyl-radical trap (18), argues against the involvement of a radical in this rearrangement. It is possible, however, that the rate of intramolecular trapping of the silyl-radical by the adjacent carbonyl is much greater than the rate of intermolecular trapping by another molecule of 254 or CCl_4, thus preventing the observation of radical coupling products. Moreover, the intermediate expected by reaction of CCl_4 with 254 could itself collapse to 255.



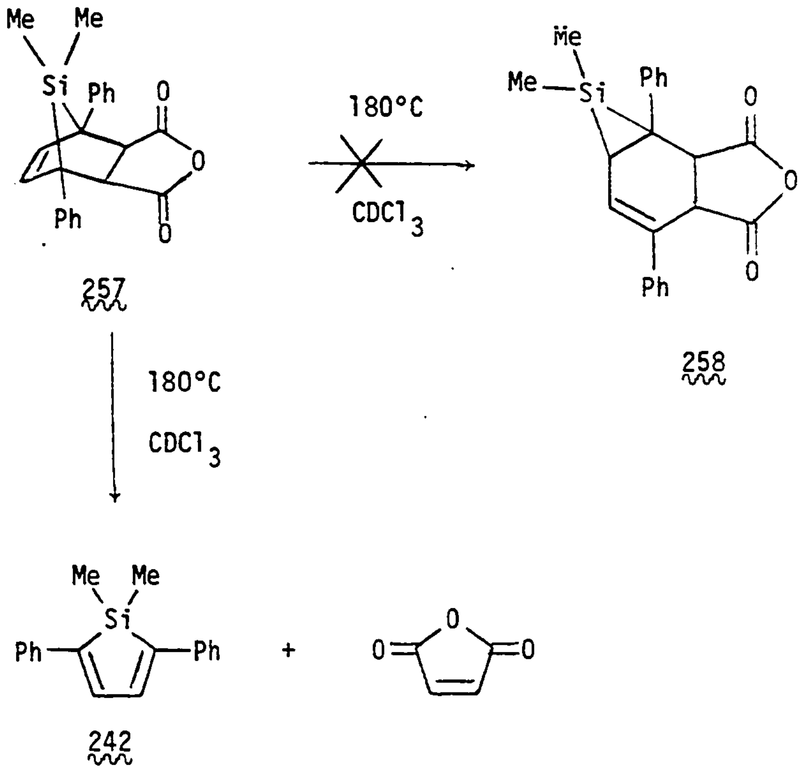
254

A more convincing argument against the involvement of a radical is the observation that oxygen greatly accelerates the isomerization of 241 to 251. Since oxygen is a known radical inhibitor, this rate enhancement by oxygen, though not understood, is exactly opposite the effect that would be expected were radicals involved. Thus, we have excluded path a as a viable route for this isomerization.

Although we are unable to rigorously exclude path c (Scheme 68) on the basis of our results, we find it also to be an unreasonable alternative. Since it has been previously reported that silacyclopropanes rapidly decompose in halogenated solvents (49,50), the near quantitative formation of **251** and **253** via the intermediacy of **256** is unlikely under the reaction conditions employed. Furthermore, the effect of oxygen on the isomerization of **241** is not in keeping with the intermediacy of **256** since silacyclopropanes are known to rapidly decompose in the presence of oxygen (267). Since no apparent steric constraints are present in **256** that would prevent its reaction with oxygen or CCl_4, its intermediacy is unlikely.

Though unlikely, the intermediacy of **256** cannot be rigorously excluded. Thus, to obtain more definitive evidence concerning the intermediacy of **256**, the thermolysis of 7-silanorbornene **257** was investigated. If **241** and **252** were rearranging by an initial 1,3-Si migration to give **256**, it would be expected that **257** would rearrange in an analogous manner to form silanorcarene **258**.

Compound **257**, prepared in 80% yield by reaction of maleic anhydride with silole **242**, was found on heating at 180°C in $DCCl_3$ to undergo a retro Diels-Alder reaction, not a 1,3-Si migration. This result has precedent in the work of Balasubramanian and George (298) who found similar results for the thermolysis of the 1,2,3,4-tetraphenyl and hexaphenyl analogues of **257**. Since a 1,3-Si migration does not occur in 7-silanorbornenes, there is no compelling reason to expect the same migration to occur in 7-silanorbornadienes. Thus, based on these results, and the previous arguments, path **c** (Scheme 68) has been excluded as a viable mechanism for these rearrangements.



Therefore, of the three mechanisms considered possible, we find the direct 1,5-migration of silicon form carbon to oxygen (path **b**, Scheme 68) to be the most favorable.

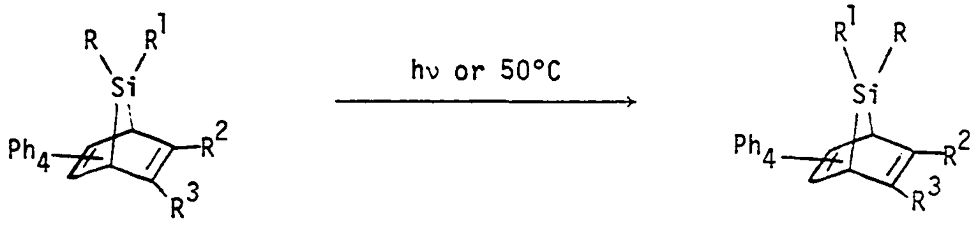
Recently, Mayer and Neuman (48) reported a variety of data ostensibly demanding initial, reversible Si-C bond homolysis in the thermolysis of 7-silanorbornadienes. In particular, our attention was captured by the disclosure that 7-silanorbornadiene **241** decomposed "rapidly even at 28°C in CCl_4 or toluene" and produced an ESR spectrum consisting of "a doublet split into a quintet". Since we had found **241** to be quite stable to decomposition under these conditions, these results were most perplexing.

To gain insight into this apparent contradiction, we also monitored the rearrangement of 241 by ESR. When 241, isolated as previously described, was dissolved in deoxygenated CCl_4 or D_6-benzene, no ESR signal was found, even though slow rearrangement to 251 was observed by NMR. However, an ESR signal, which was different from that reported by Mayer and Neuman (48), and which could not be identified, was found when degassed DMADC was allowed to react with 242 in degassed CCl_4. These data indicate that the Diels-Alder reaction leading to 241 proceeds by a radical pathway, but, that the rearrangement of 241 to 251 does not involve a radical.

Another interesting observation reported by Mayer and Neuman (48) was that 7-silanorbornadienes with two different substituents on silicon (259) underwent both thermally- and photochemically induced epimerization at silicon (Scheme 69, entries a-d). These authors proposed that 7-silanorbornadienes undergo epimerization (e.g., 259a to 260a) by homolysis of a Si-C bond to form diradical 261a, which proceeds to product by bond rotation and reclosure (Scheme 70).

The complete photochemical isomerization of 259a to 260a was most amazing since Balasubramanian and George (298) found that photolysis of the 7,7-dimethyl analogue of 259a resulted in rapid extrusion of the bridging silicon, giving dimethyl tetraphenylphthalate in 88% yield. Balasubramanian and George (298) were also unable to detect a radical when their photolysis was conducted in the presence of known radical traps. This dramatic difference in chemical behavior when a methyl on silicon is replace by a chlorine is most surprising. Equally surprising, was the report by Mayer and Neuman that 259b, prepared stereoselectively in 80% yield by a

Scheme 69

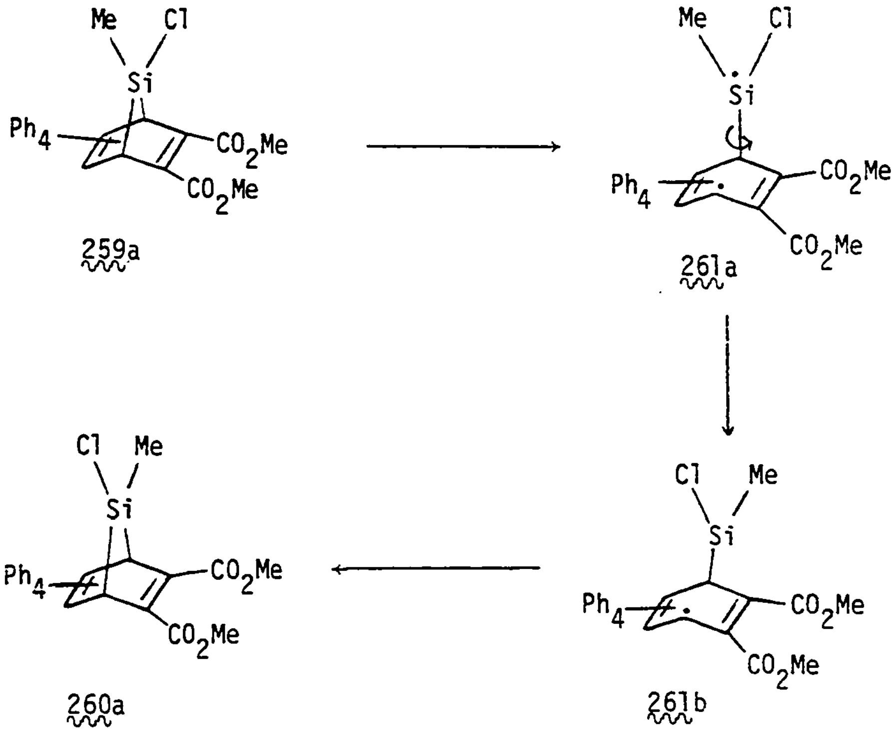


259 260

	R	R^1	R^2	R^3
a	CH_3	Cl	CO_2Me	CO_2Me
b	CH_3	Cl	Ph	H
c	Ph	CH_3	CO_2Me	CO_2Me
d	Ph	CH_3	Ph	H
e	CH_3	CH_3	Ph	H

Diels-Alder synthesis, isomerized completely to 260b at 50°C. This result, if true, is remarkable since the synthesis of 259b from phenylacetylene and 1-chloro-1-methyltetraphenylsilacyclopentadiene would be expected to require temperatures of approximately 100°C (299). For 259b to be synthesized stereoselectively in 80% yield at approximately 100°C and then isomerize completely to 260b at 50°C requires a violation of basic thermodynamics, and therefore must be questioned. Also questionable, is that while Meyer and Neuman argue that "CCl_4 enhances the thermolysis of 241 presumably by trapping biradical 254 . . . thus preventing the back

Scheme 70



reaction", we are then asked to believe that thermal epimerization of 259 a-d can take place in CCl_4 via this diradical without trapping. Coupling the above facts with the extreme unlikelihood of quantitative epimerization to a single diastereomer when the groups on silicon are sterically similar (e.g., 259 a) led us to reinvestigate these isomerizations.

In contrast to the report of Mayer and Neuman (48), photolysis of 259 c, d, or e in benzene did not afford isomerized products. Instead, the rapid extrusion of the bridging silicon and the formation of the corresponding aromatic compound was found (Table 17). Isomerization was clearly shown not to be occurring when photolysis of 259 c, d, or e in benzene was found, by NMR analysis, to cause the disappearance of the Si-CH_3 signal(s) of the starting material and the simultaneous appearance of a broad, unidentifiable Si-CH_3 resonance between δ=-0.2 and 1.5. For the photolysis of 259 d and e, chromatography of the photolysate (Neutral alumina, CCl_4) afforded only pentaphenylbenzene. In the case of 259c, photolysis resulted in the formation of a precipitate which, following isolation by filtration, was identified as dimethyl tetraphenylphthalate.

We are also unable to reproduce the results reported by Mayer and Neuman (48) for photolysis conducted in CCl_4. Photolysis of 259e should result in no apparent reaction, since the photochemical isomerization proposed by these author would be degenerate for this molecule. However, photolysis of 259e in CCl_4 was found by NMR to result in the disappearance of the two Si-CH_3 signals of the starting material and the concomitant appearance of a sharp singlet at δ = 0.78 ppm. After photolysis for 6 hours at 0°C , all of 259e had decomposed. The new Si-CH_3 signal observed in the photolysate was found not to be 1,1-dimethyltetraphenylsilole, which could arise by a retro Diels-Alder reaction, since the Si-CH_3 resonance of the silole absorbs at δ = 0.49. Moreover, en vacuo removal of the volatiles from the photolysate resulted in almost complete disappearance of the signal at δ = 0.78. Based on NMR chemical shifts, the new signal was postulated to be dimethyldichlorosilane. This was confirmed by gas-chromotagraphic-mass-spectrometric (GCMS) analysis, which revealed the presence of Me_2SiCl_2 and $Cl_3CSiCl_2Me_2$ in the photolysate.

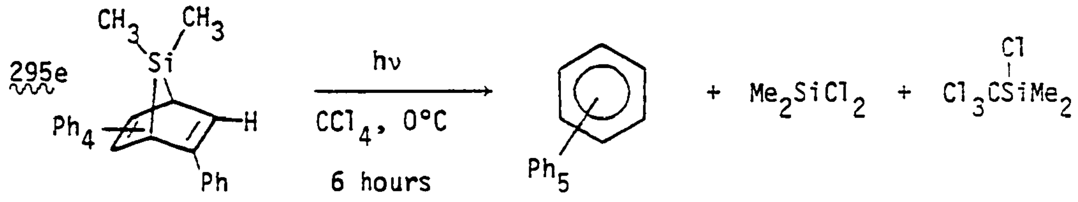
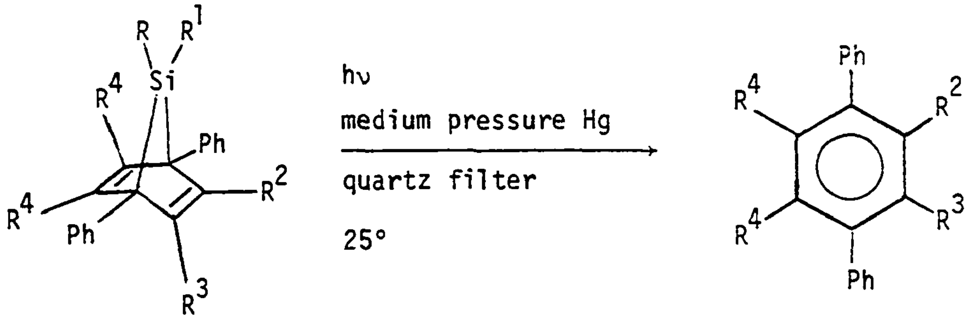


Table 17. Photolysis of 7-Silanorbornadienes



	Conditions[a]	R^2	R^3	R^4
259c	CCl_4, 210 m C_6D_6, 220 m	CO_2Me		Ph
259d	CCl_4, 100 m C_6D_6, 190 m	H	Ph	Ph
259e	CCl_4, 6 h[b] C_6D_6, 180 m	H	Ph	Ph
241c	CCl_4, 120 m	CO_2Me		

[a] All solutions deoxygenated with argon.

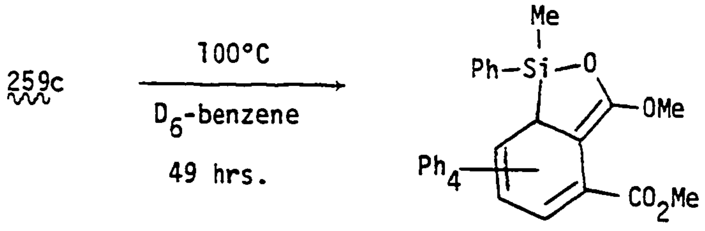
[b] 0°C.

Analysis of the residue, obtained after *en vacuo* removal of the volatiles, showed it to have a NMR spectrum identical to that of authentic pentaphenylbenzene, and indeed, chromatography of this residue (neutral alumina, CCl_4) gave only pentaphenylbenzene. Thus, photolysis of **259e** does not lead to a degenerate isomerization, but instead, leads to the extrusion of the bridging silicon and the formation of pentaphenylbenzene. Similar results were found for the photolysis of **259** c and d in CCl_4, which gave dimethyl tetraphenylphthalate and pentaphenylbenzene, respectively.

Based on the results of our photochemical investigations (Table 17), and the results of previous workers (299), extrusion of the bridging silicon upon photolysis of 7-silanorbornadienes is a general phenomenon. The lack of experimental detail in the report of Mayer and Neuman (48), which prevented us from duplicating exactly their experimental conditions, may be the source of discrepancy between their results and ours. However, a more reasonable explanation for this difference is that these authors misinterpreted their results.

Based on the belief that 7-silanorbornadienes are unable to violate thermodynamic principles, we anticipated that reexamination of the thermal-chemistry reported by Mayer and Neuman (48) would lead to different results than those observed by these authors. This anticipated difference has indeed been found. Mayer and Neuman (48) reported that thermolysis of **259c**, at 50°C in CCl_4 or benzene, resulted in disappearance of the $Si\text{-}CH_3$ signal ($\delta = 0.71$) of **259c**, and the appearance of a new signal at $\delta = 1.06$ that was assigned to **260c**. In our laboratory, thermolysis of **259c** at 100°C in deoxygenated D_6-benzene for 49 hours resulted in essentially no change.

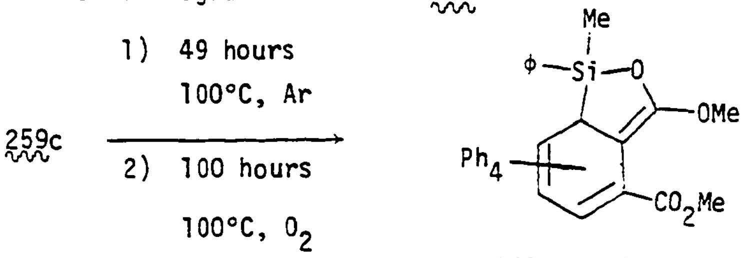
New signals, which based on relative peak areas would account for <5% isomerization of 259c, were observed at δ = 0.00, 3.31, and 3.59. These new signals, which are different from those reported by Mayer and Neuman (48), were found to be consistent with rearranged adduct 262.



262

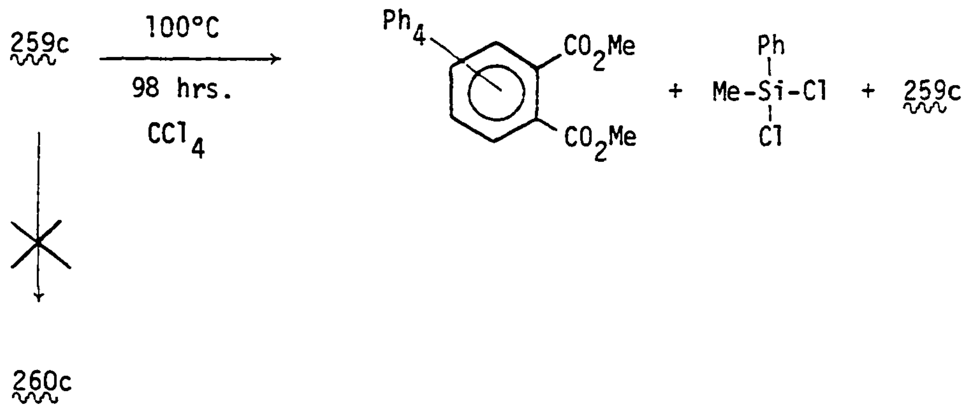
<5%

Because we had previously found rate enhancements for isomerizations of this type by oxygen, oxygen was bubbled through the reaction and heating was continued. After heating at 100°C for 29 hours, with O_2 added, about 50% of 259c had isomerized to 262. Continued heating for another 71 hours resulted in about 90% rearrangement of 259c. Although no attempt was made to isolate the product of this reaction, the presence of a strong enol ether, C=C stretch at 1620 cm^{-1} in the IR spectrum of the pyrolysate, coupled with the NMR date (vide supra), supports our structural assignment. Thus, in benzene 259c is clearly not epimerizing to 260c, but is instead isomerizing in a fashion analogous to that of 241.



262 90%

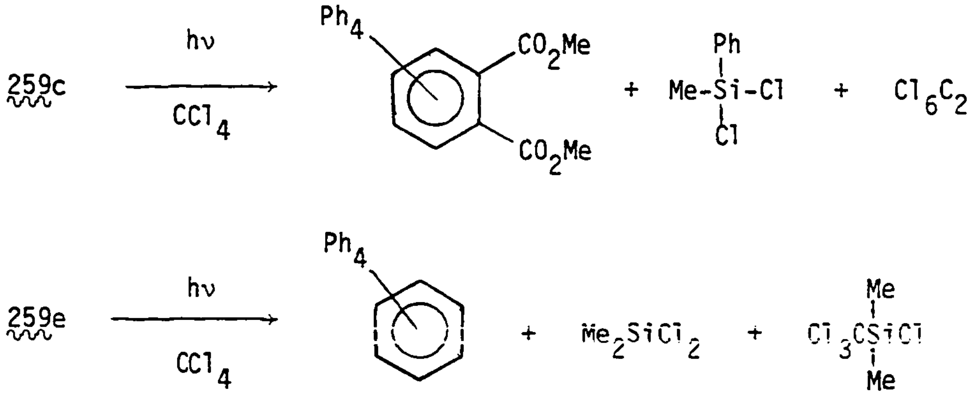
Thermolysis of 259c in CCl_4, using the same conditions as employed with benzene, initially gave the same results. Thus, heating 259c in deoxygenated CCl_4 at 100°C for 12 hours was found, by NMR analysis, to give three new signals at $\delta = 0.15$, 3.42, and 3.96. These new signals were found to be consistent with rearranged adduct 262, and on this basis indicated that about 5% of 259c had rearranged. In contrast to the reaction in benzene, these signals did not increase with continued heating. Instead, after heating for 24 hours at 100°C the signals at $\delta = -0.15$ and 3.96 decreased in intensity while the signal at $\delta = 3.42$ increased. In addition, a new signal at $\delta = 1.02$ was observed. After thermolysis for 50 hours only the signals at $\delta = 3.42$ and 1.02 were found. Based on the relative peak areas of the silicon-methyl absorbance for 259c and the new signal at $\delta = 1.02$, approximately 20% of 259c had decomposed. After thermolysis for another 48 hours, the reaction was stopped. At this time, 45% of 259c was found to have decomposed. The chemical shift of the new signals at $\delta = 1.02$ and 3.42 are similar to those reported by Mayer and Neuman (48), and thus the possibility of isomerization as proposed by these authors was considered. However, this was shown not to be the case when en vacuo removal of the volatiles resulted in complete disappearance of the peak at $\delta = 1.02$. Clearly, this result is not in keeping of the presence of 260c. Although no definitive identification of the products from this reaction was made, based on chemical shifts, the signal at $\delta = 3.42$ was found to be consistent with the carbomethoxymethyls of dimethyl tetraphenylphthalate, and the signal at $\delta = 1.02$ consistent with methylphenyldichlorosilane.



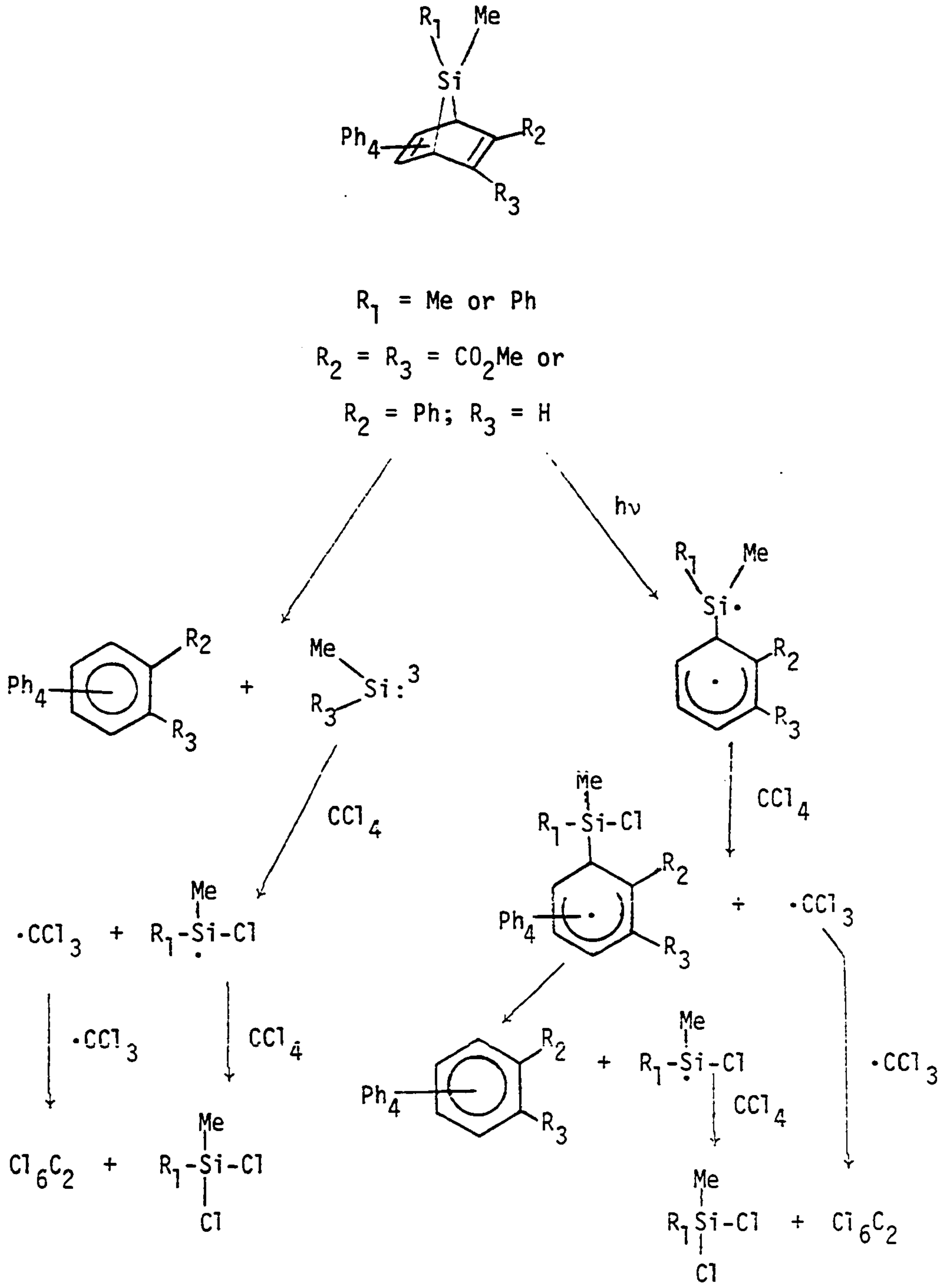
From the results of our investigation of the photo- and thermalchemistry of 7-silanorbornadienes, it can only be concluded that the analogous work of Mayer and Neuman (48) contains a multitude of incorrect data. As a result, it must be concluded that no evidence exists in their work to substantiate their mechanistic proposal for silylene extrusion from 7-silanorbornadienes. Although our results demonstrate that the reported photochemical and thermal isomerizations of 7-silanorbornadienes reported by Mayer and Neuman are incorrect, they do not comment on the mechanism of silylene extrusion from these systems. It is still possible that all 7-silanorbornadienes extrude silylenes through a stepwise, radical process, although the mechanism employed may be quite dependent on the nature of the substituents.

In particular, the volatile products obtained upon irradiation of 259c or 259e in CCl_4 are consistent with either a step wise, radical process or a concerted extrusion of a triplet silylene (Scheme 71). Thus, the formation of phenylmethyldichlorosilane and hexachloroethane (from the photolysis of 259c) and dimethyldichlorosilane (from the photolysis of 259e) are most easily rationalized as occurring by a sequence of radical abstraction recombination processes (Scheme 72). Trichloromethyldimethylchlorosilane could also arise by a stepwise, radical process by combination of the initially formed dialkylchlorosilyl and trichloromethyl radicals. However, this species could also arise by direct insertion of a singlet silylene into a C-Cl bond of CCl_4 (10), thus, the photolysis of 259e may involve the intermediacy of both silyl radicals and silylenes.

Scheme 71



Scheme 72



R_1 = Me or Ph

$R_2 = R_3 = CO_2Me$ or

R_2 = Ph; R_3 = H

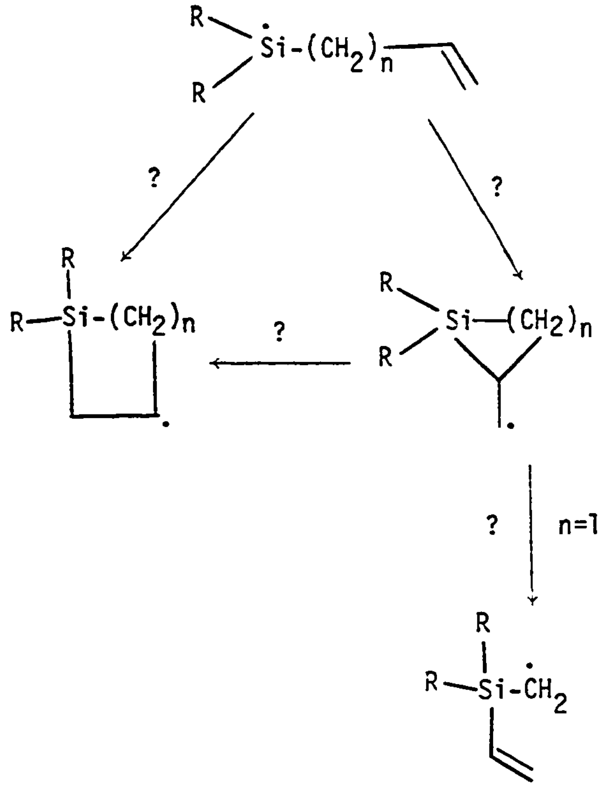
The Preparation and Chemistry of Alkenyl-Substituted Silyl Radicals

Although the chemistry of silyl radicals has not received as much attention as that of other silicon centered reactive intermediates, the dearth of reports regarding the intramolecular chemistry of alkenyl-substituted silyl radicals is surprising when one considers the extensive research that has been directed toward the analogous carbon radicals (e.g., 236,237). With the exception of the brief report of Sakurai (18) regarding the cyclization of 4-pentenylsilyl radicals and the more recent work of Barton and Jacobi (122) and Neider and coworkers (246), the ability of alkenyl-substituted silyl radicals to undergo intramolecular cyclizations remains unexamined. Thus, in an effort to alleviate this lack of knowledge regarding silyl radicals the generation and chemistry of the allyl-, 3-butenyl-, and 4-pentenyldialkylsilyl radicals were undertaken.

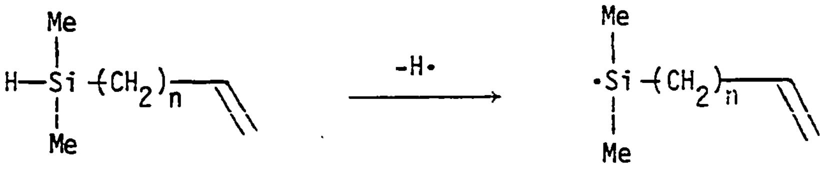
It was hoped that this study would answer several important questions dealing with the chemistry of alkenyl-substituted silyl radicals (Scheme 73): a, do silyl radicals undergo exo-addition as has been found for the analogous carbon radicals thus far studied (237); b, if so, will the intermediate silacyclomethyl radicals undergo rapid ring expansion to the more thermodynamically stable silacycloalkyl radicals; and c, does the dimethylallylsilyl radical rearrange as proposed by Neider and coworkers?

It was anticipated at the onset of this investigation that silylhydrides **263**, **264**, and **265** would function as precursors for the aforementioned radicals by homolysis of the Si-H bond by pyrolysis, abstraction

Scheme 73



by radical initiators, or mercury-sensitized photolysis. Thus, it was felt that the utilization of these techniques would allow for the study of alkenyl-substituted silyl radicals under a variety of conditions, both in the condensed and gas phase.

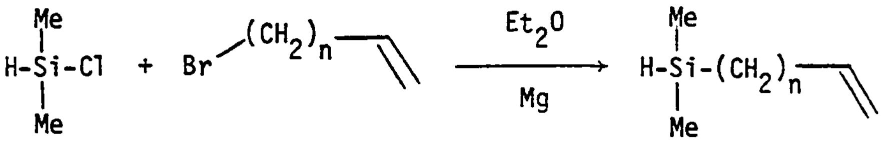


n=1 ; 263

n=2; 264

n=3; 265

Silyl hydrides 263-265 were conveniently prepared in yields of 40-60% by the addition of the corresponding alkenyl-Grignard to dimethylchlorosilane.

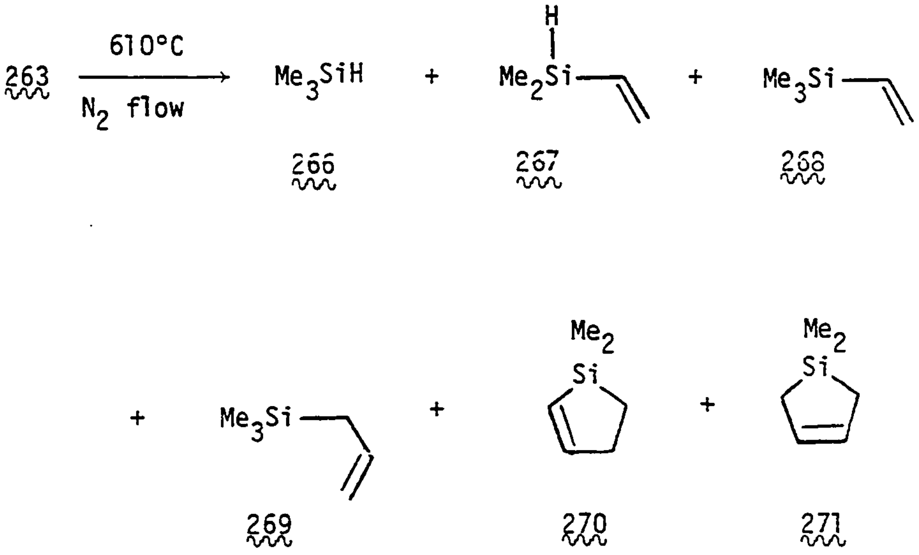


n=1,2,3

Pyrolysis of 263, 264, and 265

The gas-phase, flow pyrolysis of 263 (610-615°C) afforded 6 major products in addition to unreacted 263 (32% recovery), along with greater than 10 minor, unidentified products (Scheme 74 and Table 18).

Scheme 74



It is interesting to note that these products are formally analogous to those obtained by Sakurai and coworkers from the pyrolysis of 269 under similar conditions (247). Thus, the pyrolysis of 263 was initially believed to proceed by the extrusion of methylene followed by insertion into the Si-H bonds of 267 and unreacted 263 (Scheme 75). However, the finding that the copyrolysis of 263 and a large excess of Me_3SiH, a known methylene trap (300,301), resulted in no detectable change argued against this mechanism. Moreover, the observation that pyrolysis of 264 and 265, under similar conditions as that employed for 263, led to almost identical reaction mixtures (Table 18) suggests that a more complex process is occurring. Of more importance, is the fact that these results clearly demonstrate that pyrolysis of 263-265 did not afford the desired alkenyldialkylsilyl radicals.

Scheme 75

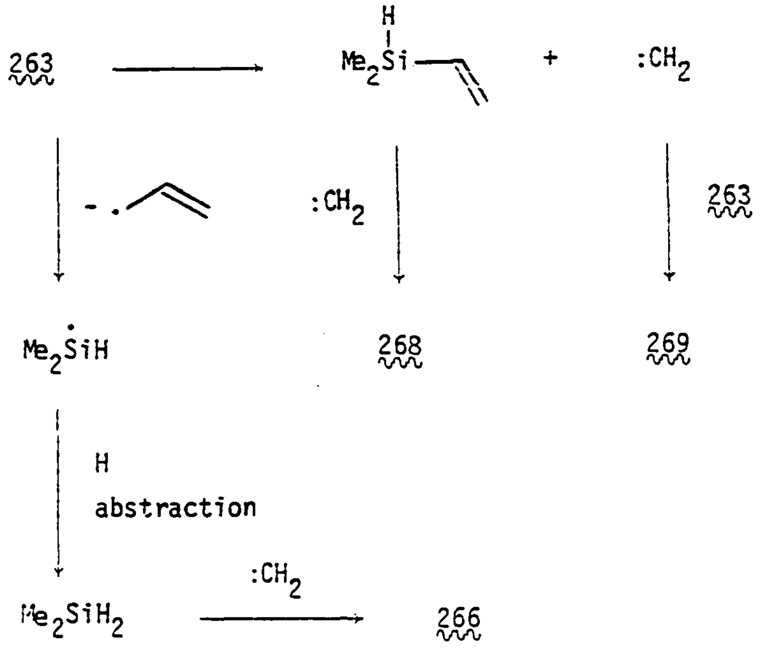


Table 18 Pyrolysis of Alkenyl-Substituted Dimethylsilanes.[a]

Starting Silane	% Yield of Products[b]							
	266	267	268	269	270	271	263	S.M.[c]
263	5	4	6	9	2.5	2.5	---	32
264	9.6	2.2	5	8.5	6.5	6.5	6.2	10
265	5	4.4	4	4	3	3	4.3	8.3

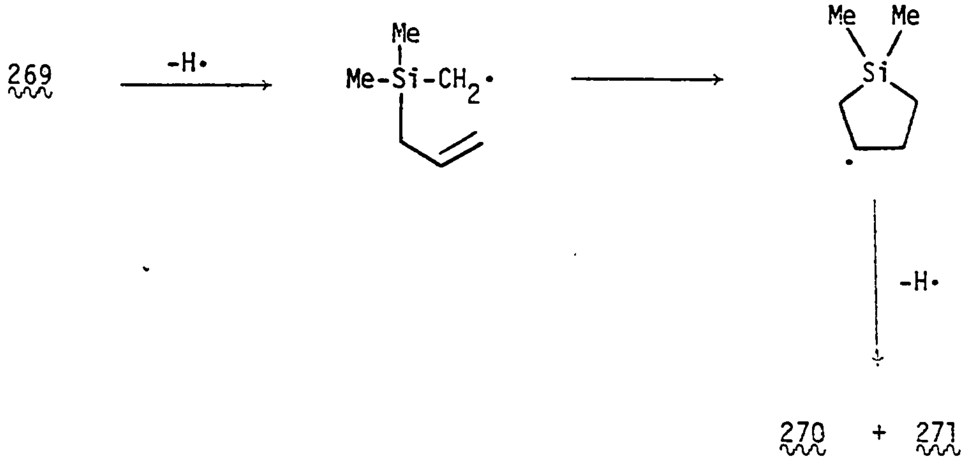
[a] Vertical, N_2 flow pyrolysis at 610-615°C.

[b] % Yields were determined by calibrated G.C. and are based on reacted starting silane.

[c] % Recovery of unreacted starting material.

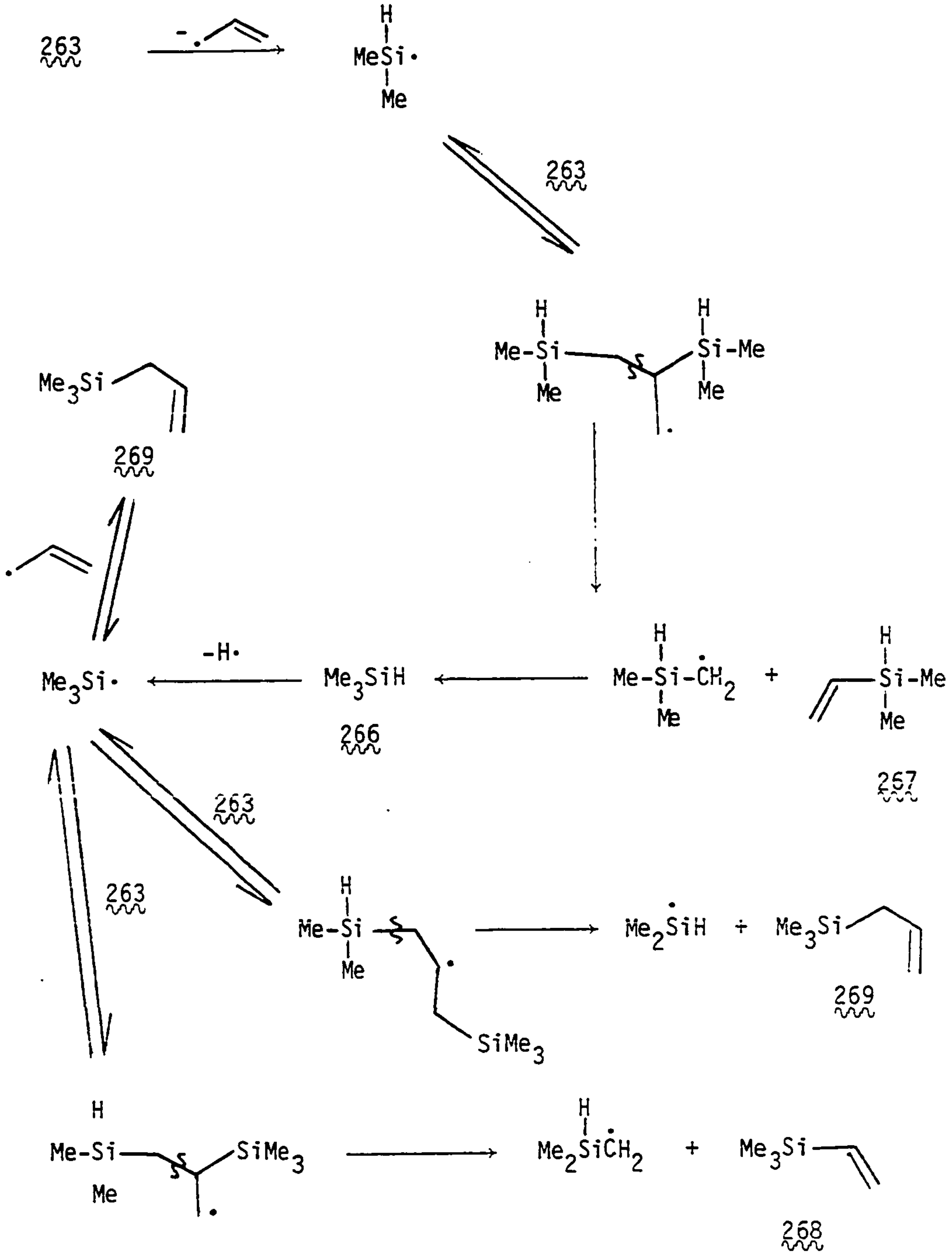
Although the mechanism of product formation in these reactions remains speculative, the similarity in both the products and yields implies that 263-265 thermally decompose to afford the same intermediates. Schemes 76 through 78 depict mechanistic proposals that are consistent with these results.

The two products that are not accounted for in Schemes 76-78 are 270 and 271. These products were obtained by Sakurai and coworkers (247) upon pyrolysis of 269, and proposed to arise by homolysis of a C-H bond to afford an allyldimethylsilylmethyl radical, which upon cyclization and loss of hydride gave 270 and 271.

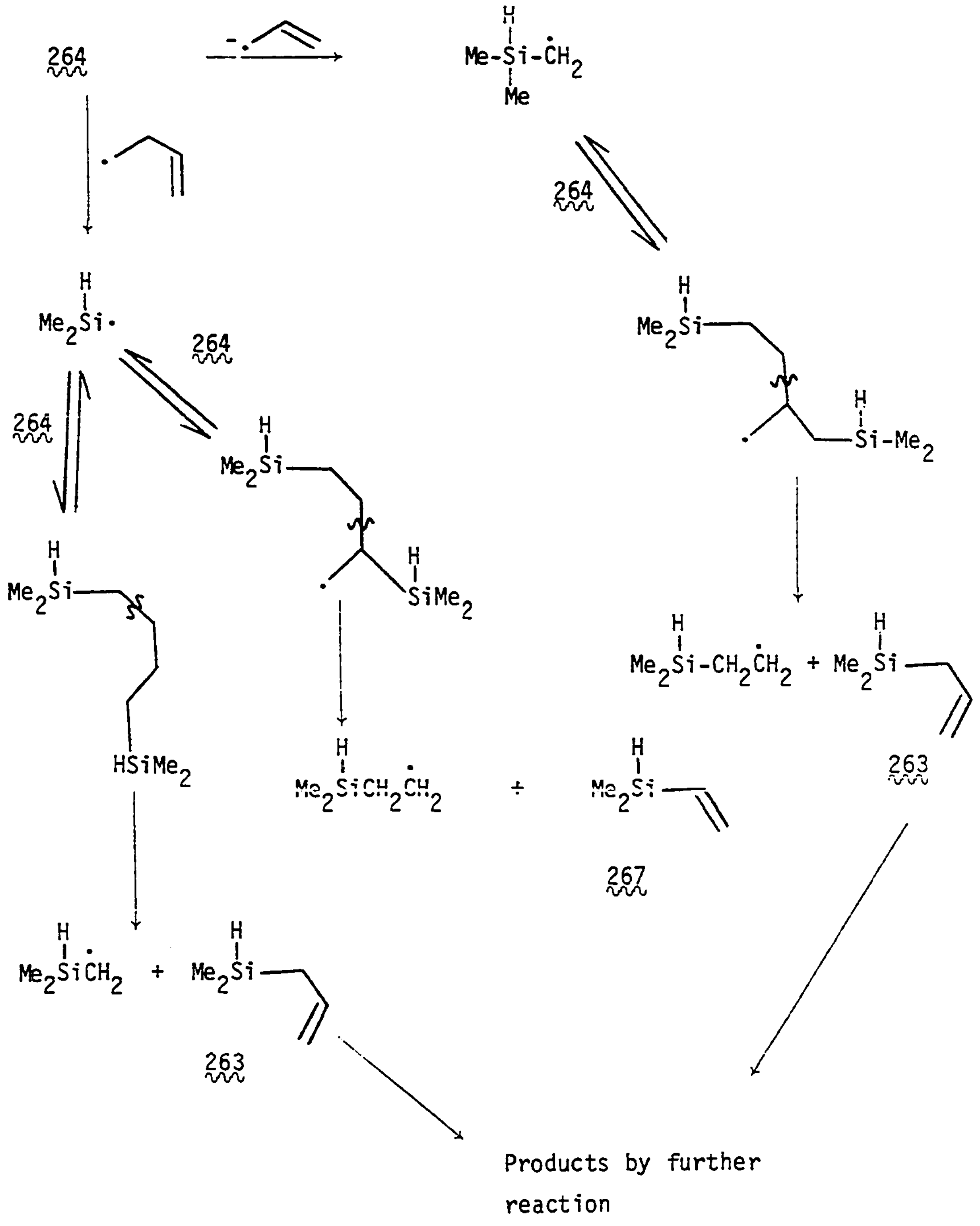


It is interesting to note that the yields of 270 and 271 obtained from the pyrolysis of 264 were greater than those found in the pyrolysis of 263 and 265 (Table 18). This observation may indicate that 264 affords 270 and 271, at least in part, by cyclization of the desired 3-butenyldimethylsilyl radical. However, due to the harsh reaction conditions and the number of products obtained, definite evidence for this process cannot be claimed.

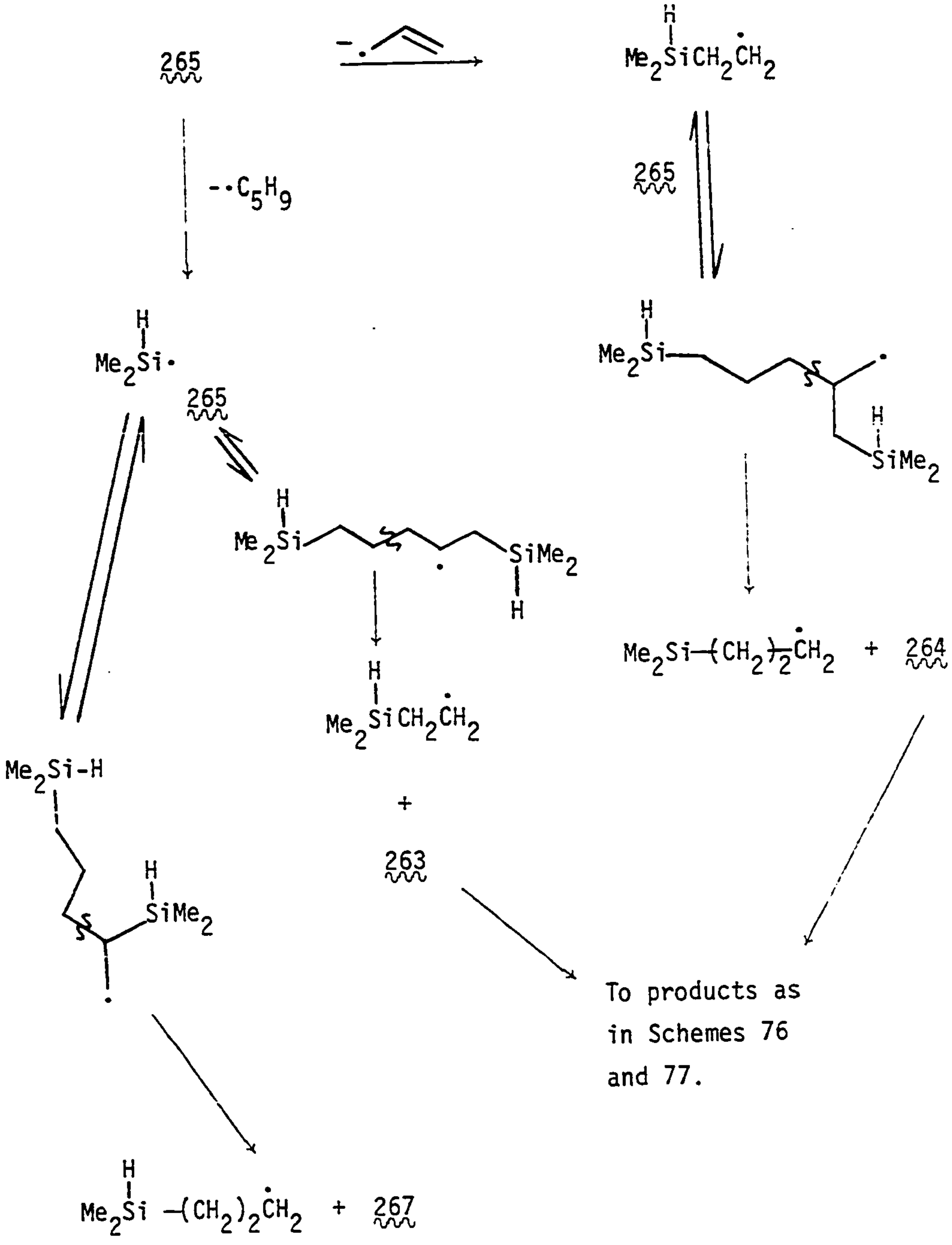
Scheme 76

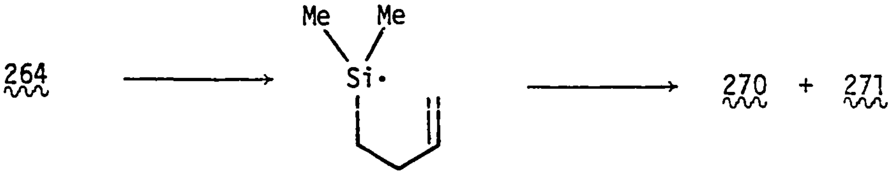

263
MeSi·
Me
H
263
H
Me-Si
Me
H
Si-Me
Me
Me3Si
269
Me3Si·
-H·
Me3SiH
266
H
Me-Si-CH2
Me
+
H
Si-Me
Me
267
263
263
H
Me-Si
Me
SiMe3
Me2SiH
+
Me3Si
269
H
Me-Si
Me
SiMe3
H
Me2SiCH2
+
Me3Si
268

Scheme 77


264
H
Me-Si-CH2
Me
264
H
Me2Si·
264
264
H
Me2Si
H
SiMe2
H
Me2Si
H
Si-Me2
H
Me2Si
HSiMe2
H
Me2SiCH2CH2
+
H
Me2Si
267
H
Me2Si-CH2CH2
+
H
Me2Si
263
H
Me2SiCH2
+
H
Me2Si
263
Products by further reaction

Scheme 78


265
$-\cdot C_5H_9$
$Me_2\overset{H}{Si}\cdot$
265
$Me_2\overset{H}{Si}CH_2\dot{C}H_2$
265
$Me_2Si-(CH_2)_2\dot{C}H_2$ + 264
$Me_2\overset{H}{Si}CH_2\dot{C}H_2$
+
263
To products as in Schemes 76 and 77.
Me_2Si-H
$\overset{H}{Si}Me_2$
$Me_2\overset{H}{Si}-(CH_2)_2\dot{C}H_2$ + 267

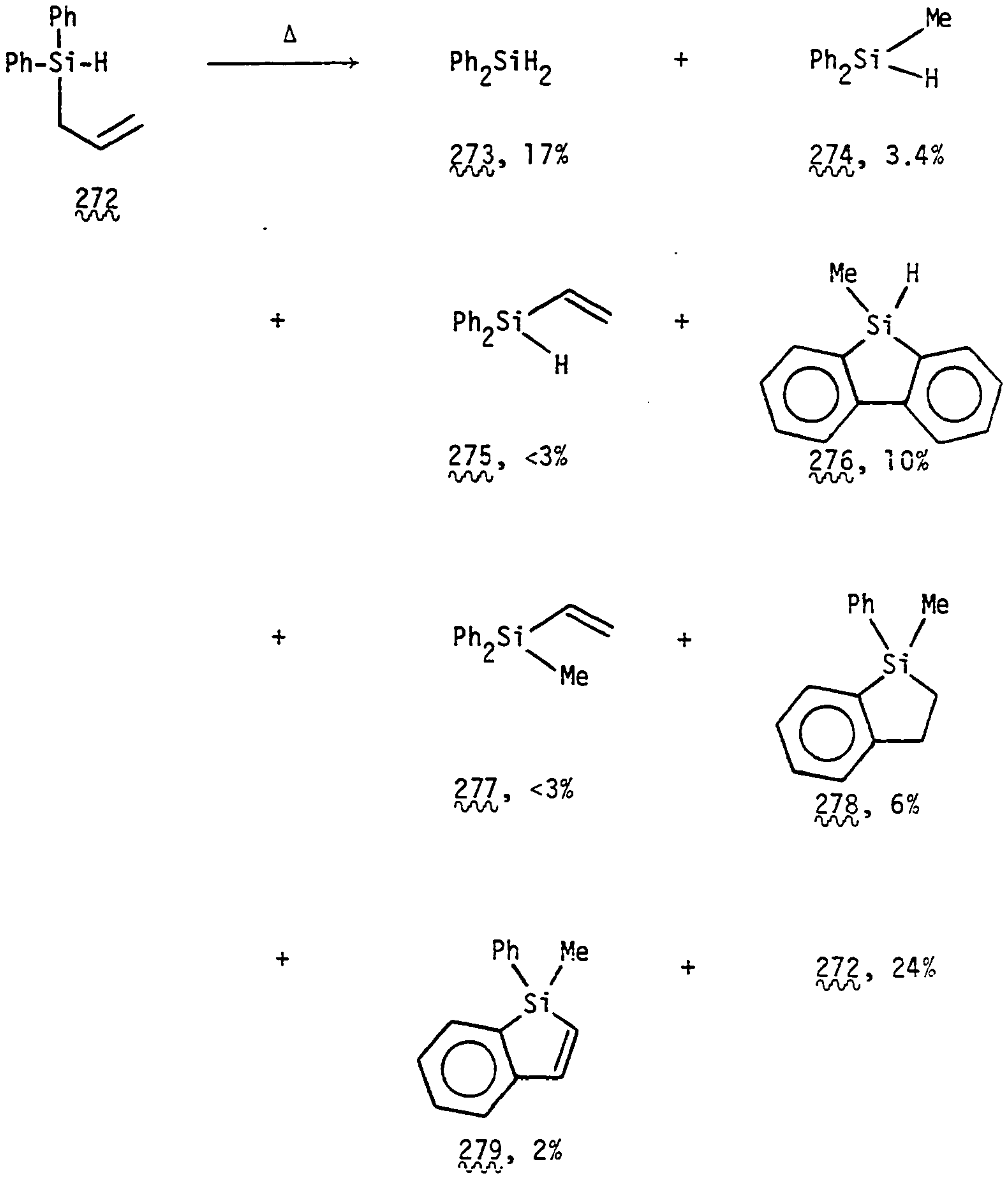


Pyrolysis of Allyldiphenylsilane (272)

Prior to the investigation of the thermal decomposition and isomerization of 264 and 265, an examination of the pyrolysis of 272 was undertaken. The purpose of this investigation was twofold: a, substitution of phenyls for the methyls of 263 would render the subsequent products less volatile and therefore make their isolation easier; b, replacement of the methyls in 263 by phenyls was expected to result in cleaner product mixtures by eliminating the possibility of α-silyl radical formation, by preventing C-H bond homolysis α to silicon.

Allyldiphenylsilane (272), prepared in 49% yield by the addition of allylmagnesium chloride to an Et_2O solution of diphenylchlorosilane, was found upon verticle flow pyrolysis (580°C, He flow) or vacuum flow pyrolysis (800°C, 1×10^{-5} Torr) to afford a complicated reaction mixture from which 273-279, in addition to unreacted 272, were isolated by preparative gas-chromatography and identified by the usual spectroscopic methods (Scheme 79). Copyrolysis of 272 and Me_3SiH (610°C, verticle flow), conducted to test for the intermediacy of methylene, afforded the same product mixture as that found in the absence of Me_3SiH, with the exception that trace amounts of triphenylsilane (<3%) were found. The results obtained from copyrolysis of 272 and Me_3SiH demonstrates that extrusion of methylene is not involved in the thermal decomposition of 272.

Scheme 79


Ph
Ph-Si-H
272
Δ
Ph_2SiH_2
273, 17%
+
Ph_2Si
Me
H
274, 3.4%
+
Ph_2Si
H
275, <3%
+
Me
H
Si
276, 10%
+
Ph_2Si
Me
277, <3%
+
Ph
Me
Si
278, 6%
+
Ph
Me
Si
279, 2%
+
272, 24%

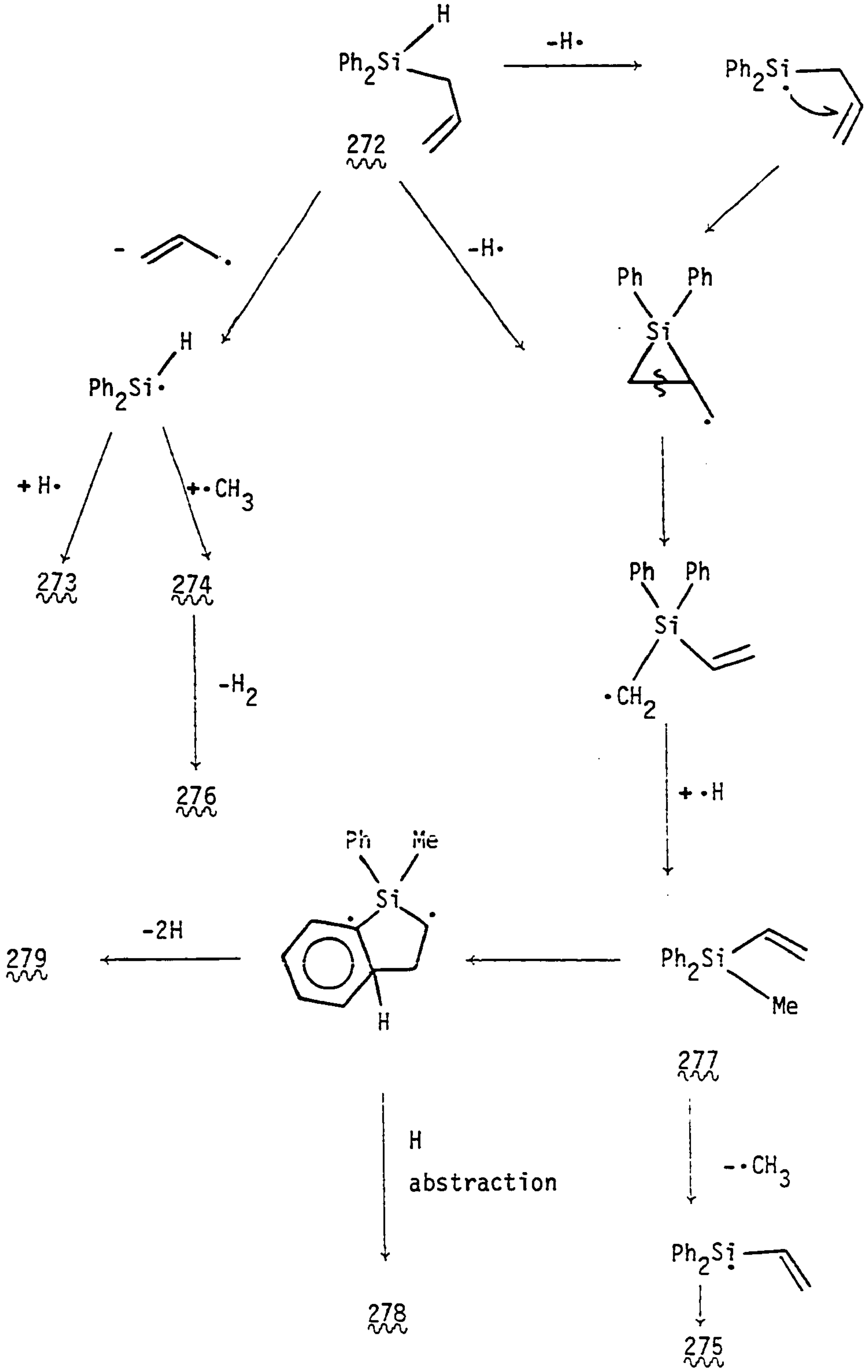
Mechanistically, the products obtained by pyrolysis of 272 can be accounted for as shown in Scheme 80. Evidence supporting the proposed conversion of 277 to 278 and 279 was obtained by pyrolysis of 277 under the same conditions as those employed for 272, affording unreacted 277, and 278 and 279, in approximately equal amounts, although in very low yields (less than 1% each). Diphenylmethylsilane was also produced in this reaction, as the only other major identifiable product, in 1% yield. Presumably, the remainder of the pyrolysate was polymeric material since 274, 277, 278, and 279 were the only major, detectable constituents of the pyrolysate.

$$\begin{array}{ccccccccc} 277 & \xrightarrow[\text{n}_2\text{ flow}]{650^\circ\text{C}} & 274 & + & 278 & + & 279 & + & 277 \\ & & 1\% & & \multicolumn{3}{c}{1\%\text{ combined}} & & 0.7\% \end{array}$$

Pyrolysis of Allylbenzyldimethylsilane (280)

Despite the plethora of products formed upon pyrolysis of 263-265, and 272, which demonstrated that these compounds did not thermally undergo clean decomposition to the desired alkenyl-substituted silyl radicals, one further attempt was made to generate allyldimethylsilyl radical under gas-phase, thermal conditions. Allylbenzyldimethylsilane (280), prepared in 37% overall yield from dimethyldichlorosilane by the sequential addition of benzylmagnesium chloride and allylmagnesium bromide, was chosen as the starting material for this final attempt, since benzyl loss would be thermodynamically more favorable than hydrogen loss. Thus, it was hoped that benzyl loss would compete favorably with allyl loss to

Scheme 80


Ph2Si
H
272
-H•
Ph2Si
- ⁄⁄\•
-H•
Ph Ph
Si
H
Ph2Si•
+H•
+•CH3
273
274
-H2
276
Ph Ph
Si
•CH2
+•H
Ph Me
Si
H
-2H
279
Ph2Si
Me
277
H
abstraction
278
-•CH3
Ph2Si
275

afford a higher percentage of products derived from allyldimethylsilyl radical.

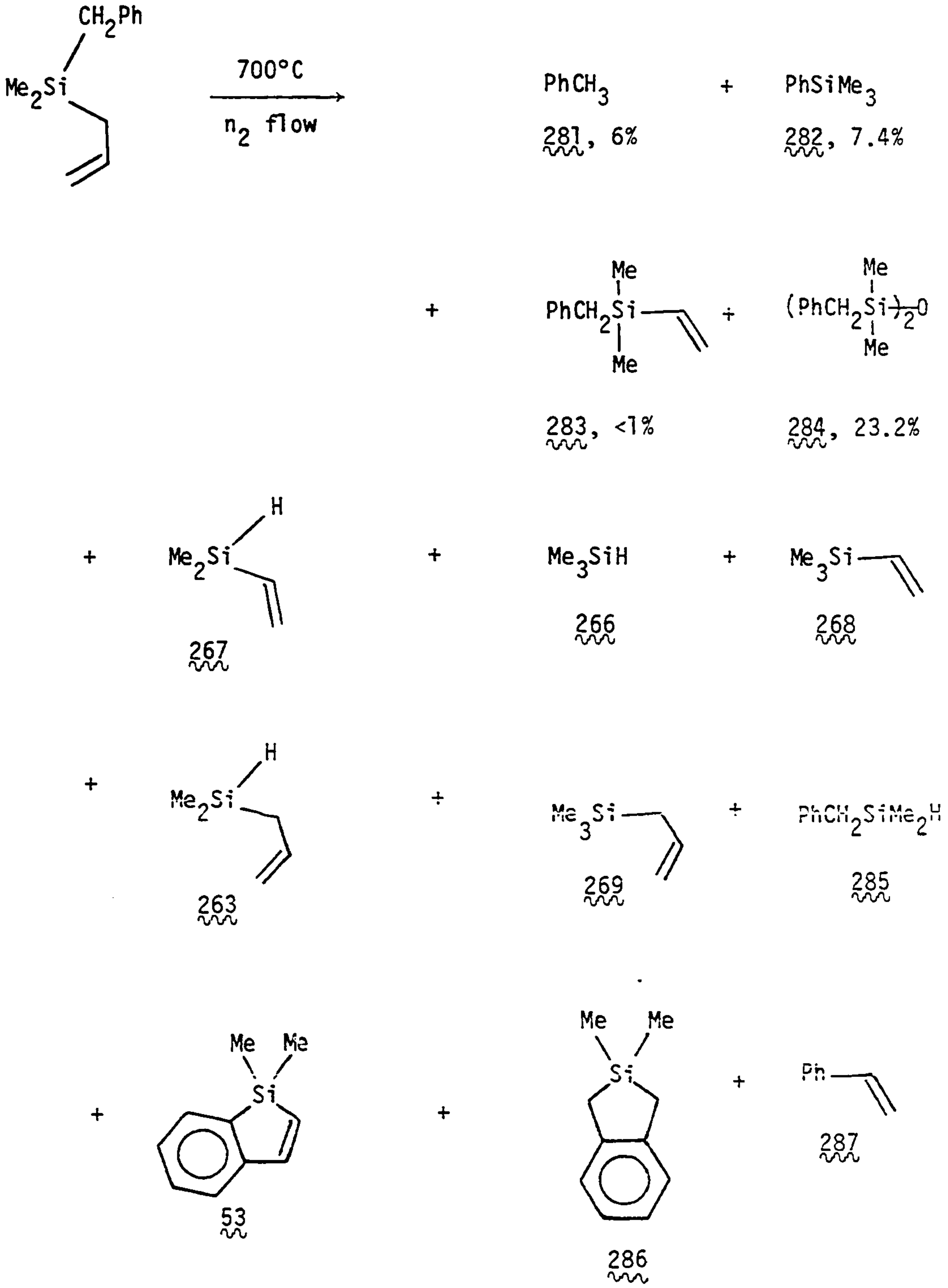
Pyrolysis of 280 proved to afford a more complicated pyrolysate than expected. Pyrolysis at 620°C (verticle, N_2 flow) afforded a pyrolysate which contained 75% unreacted 280. At 700°C, under otherwise identical conditions, 280 was recovered in 9% yield. In addition to 280, greater than 18 other products were found, of which four (281, 282, 283, and 284) were isolated by preparative gas chromatography and identified on the basis of their spectral data (Scheme 81). Nine other products, all formed in less than 1% yield, with the exception of 53 and 286 (8% combined yield), were tentatively identified by GCMS (Scheme 81).

Flash vacuum pyrolysis of 280 (860°C, 1.4 X 10^{-4} Torr) afforded a somewhat cleaner pyrolysate, although more than fifteen products were found to be present in addition to unreacted 280 (27% recovery).

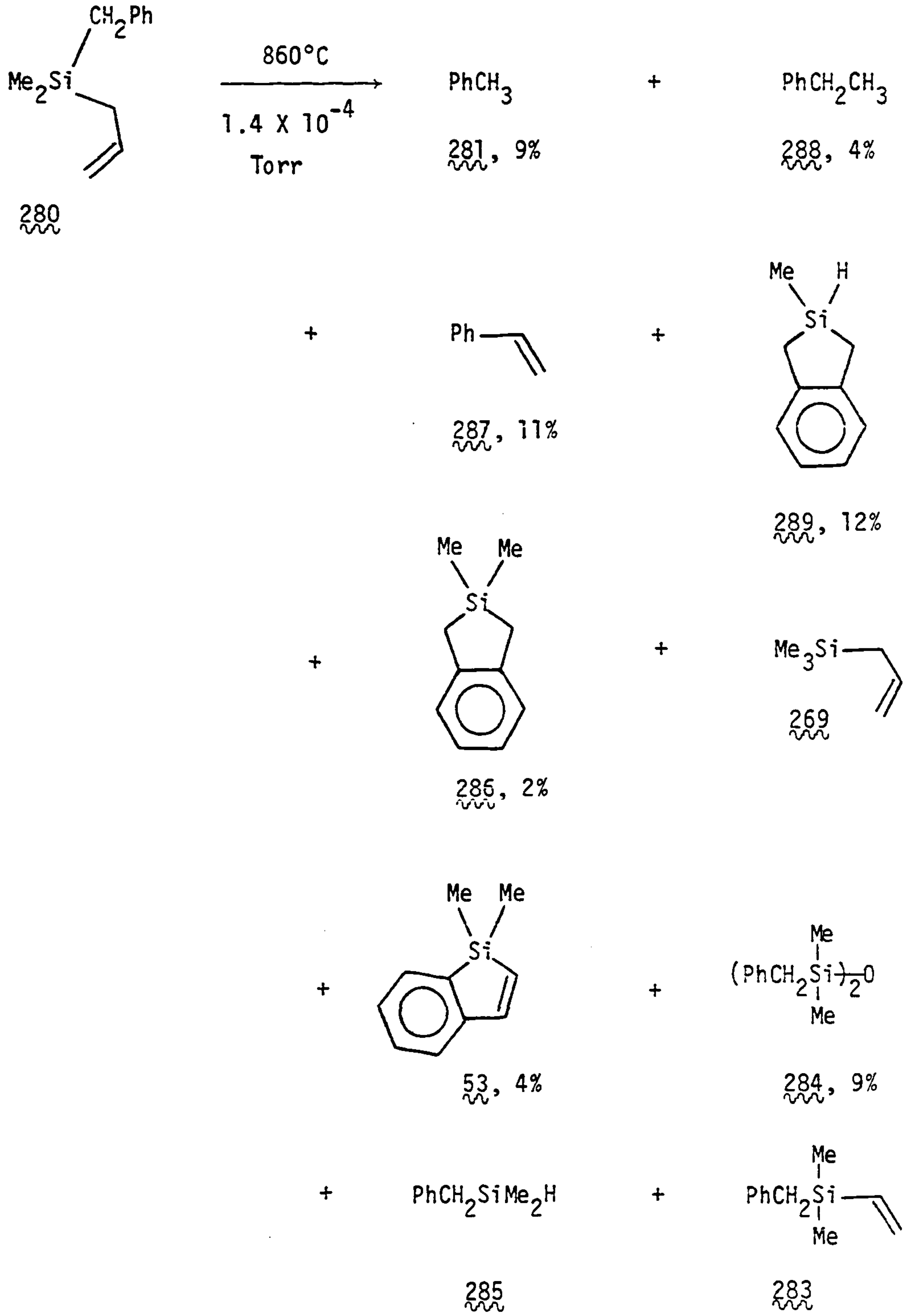
The major products of this reaction, excluding 269, 283, and 285, were isolated and identified as shown in Scheme 82. The identities of 269, 283, and 285 (all formed in less than 2% yield) were determined solely by GCMS.

Due to the large number of products produced upon verticle flow pyrolysis of 280, mechanistic speculation as to their origin is fruitless. However, for the flash vacuum pyrolysis of 280 the mechanism of formation of the major product, 289, is of interest. In Scheme 83, four mechanistic proposals for the formation of 289 are presented. Path a was eliminated from consideration since 290 was not detected, even in trace amounts.

Scheme 81

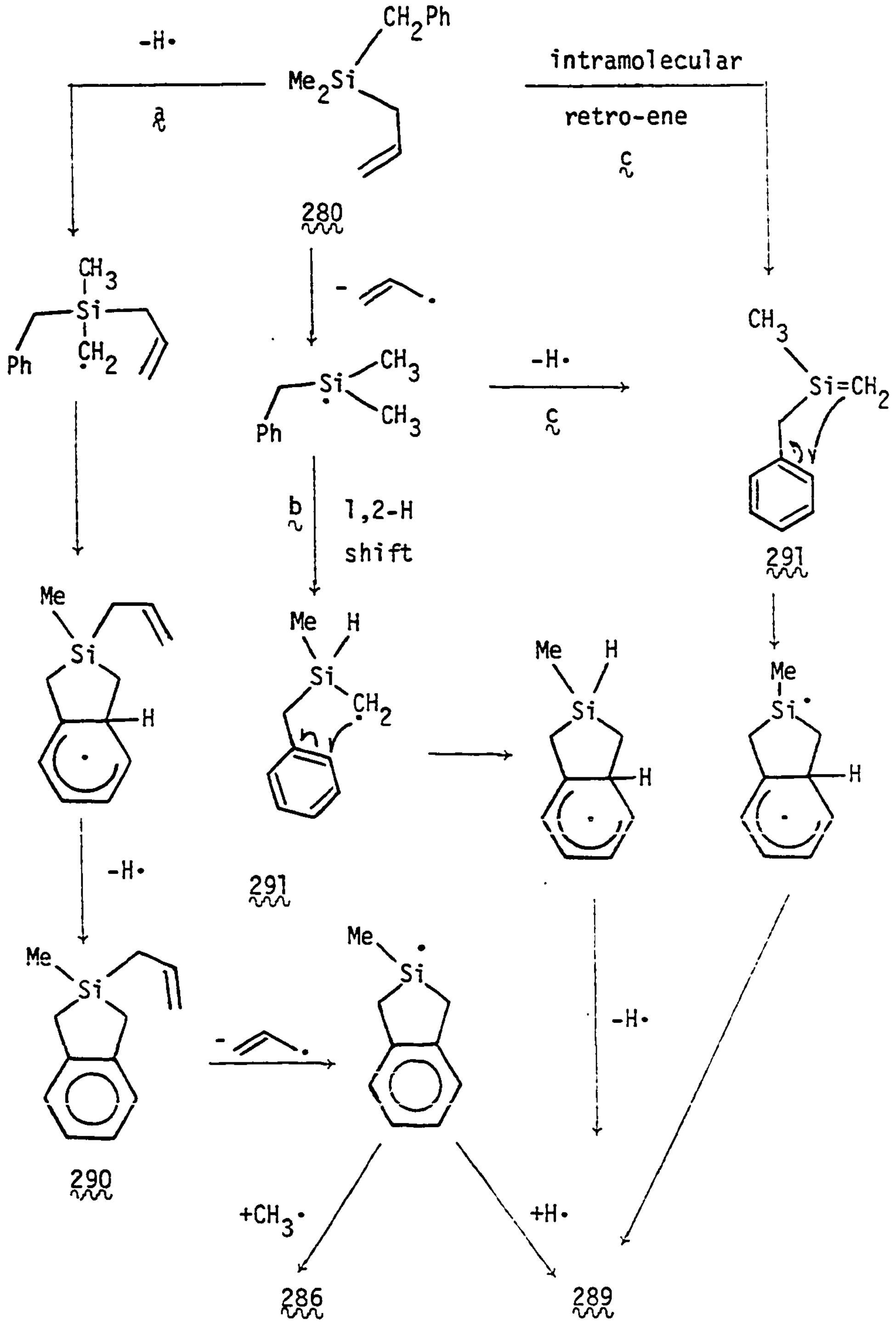

CH2Ph
Me2Si
700°C
n2 flow
PhCH3
281, 6%
PhSiMe3
282, 7.4%
PhCH2Si(Me)(Me)–CH=CH2
283, <1%
(PhCH2SiMe2)2O
284, 23.2%
Me2SiH
267
Me3SiH
266
Me3Si
268
Me2SiH
263
Me3Si
269
PhCH2SiMe2H
285
Me Me Si
53
Me Me Si
286
Ph
287

Scheme 82



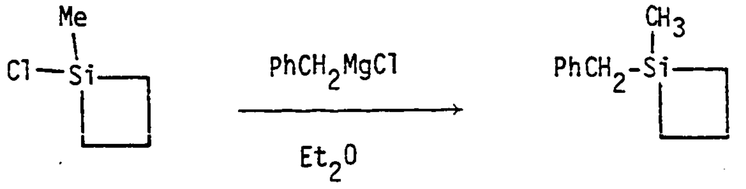
Me_2Si
CH_2Ph
280
860°C
1.4 X 10^{-4} Torr
$PhCH_3$
281, 9%
$PhCH_2CH_3$
288, 4%
Ph
287, 11%
Me
H
Si
289, 12%
Me
Me
Si
286, 2%
Me_3Si
269
Me
Me
Si
53, 4%
$(PhCH_2SiMe_2)_2O$
284, 9%
$PhCH_2SiMe_2H$
285
$PhCH_2SiMe_2$
283

Scheme 83


-H•
a
Me2Si
CH2Ph
intramolecular
retro-ene
c
280
CH3
Si
Ph
CH2
- allyl•
CH3
CH3
Ph
-H•
c
Si=CH2
291
b
1,2-H
shift
Me
H
Si
CH2
291
Me
Si
H
-H•
290
Me
Si
+CH3•
+H•
286
289

Path b was also considered unlikely since α-silyl radicals are known to rearrange to silyl radicals (18), which is opposite the rearrangement necessary to form 291. Further evidence arguing against this rearrangement is the finding by Sakurai and coworkers that benzyldimethylsilyl radical, obtained by pyrolysis of benzyldimethylsilane (285), rearranges to afford phenyltrimethylsilane, not 291 or products derived therefrom (245). In contrast, under our reaction conditions (800°C, 3 X 10^{-4} Torr) 285 was found to be recovered unreacted. Even at 860°C, pyrolysis of 285 led to the recovery of unreacted starting material as the only detectable species present in the pyrolysate.

In an attempt to provide evidence in support of path c (Scheme 83), the synthesis and thermal chemistry of benzylsilacyclobutane 292 were examined. Silacyclobutane 292 was prepared in 85% yield by the addition of benzylmagnesium chloride to 1-chloro-1-methyl-1-silacyclobutane. The identity of 292 was established by the usual spectroscopic methods.

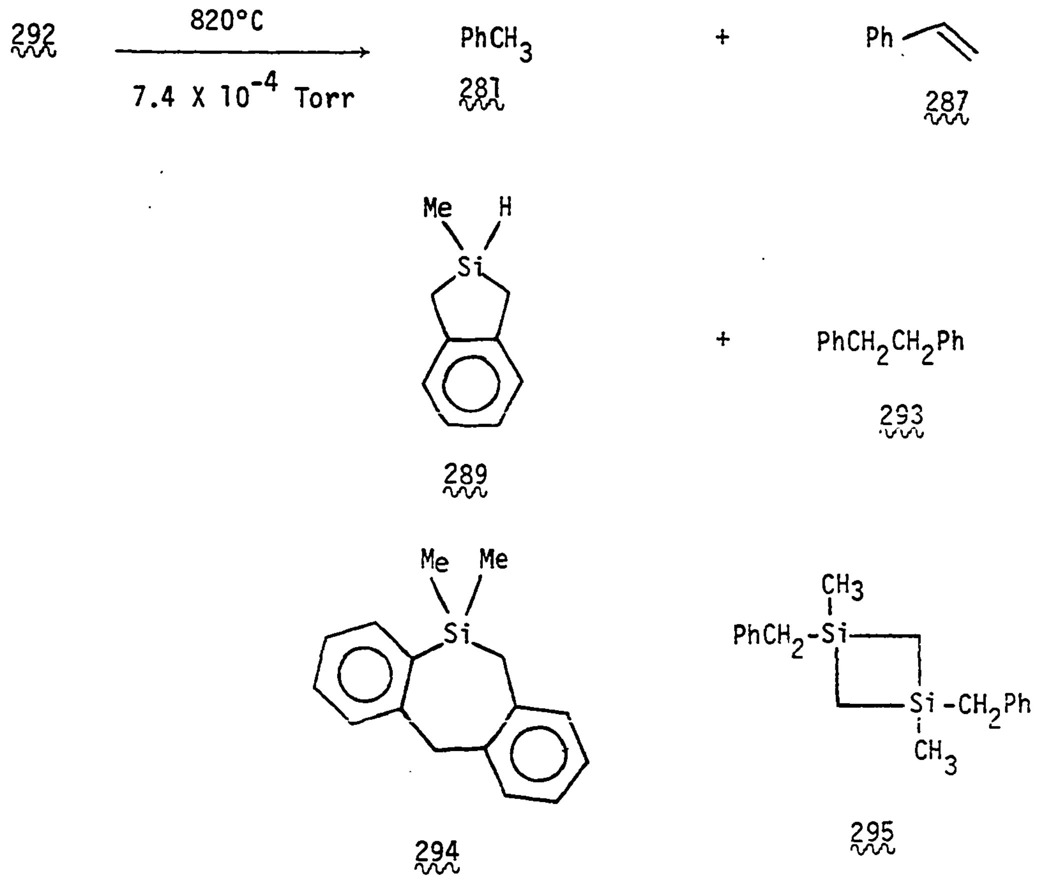


292 85%

Since silacyclobutanes are known to undergo thermal decomposition to afford ethylene and silenes (106), pyrolysis of 292 was expected to afford 291. Pyrolysis of 292 (820°C, 7.4 X 10^{-4} Torr) afforded a complex pyrolysate containing greater than 12 products, of which six were major

(Scheme 84). Although no attempt was made to determine the absolute yields of the major products of this reaction, analysis of the relative GC peak areas and NMR spectra of the crude pyrolysate revealed that 287 and 289 were the major products. That 289 was a major product in the pyrolysis of 292 provides evidence supporting our mechanistic proposal (Scheme 83, path c) for the origin of 289 in the pyrolysis of allylsilane 280.

Scheme 84

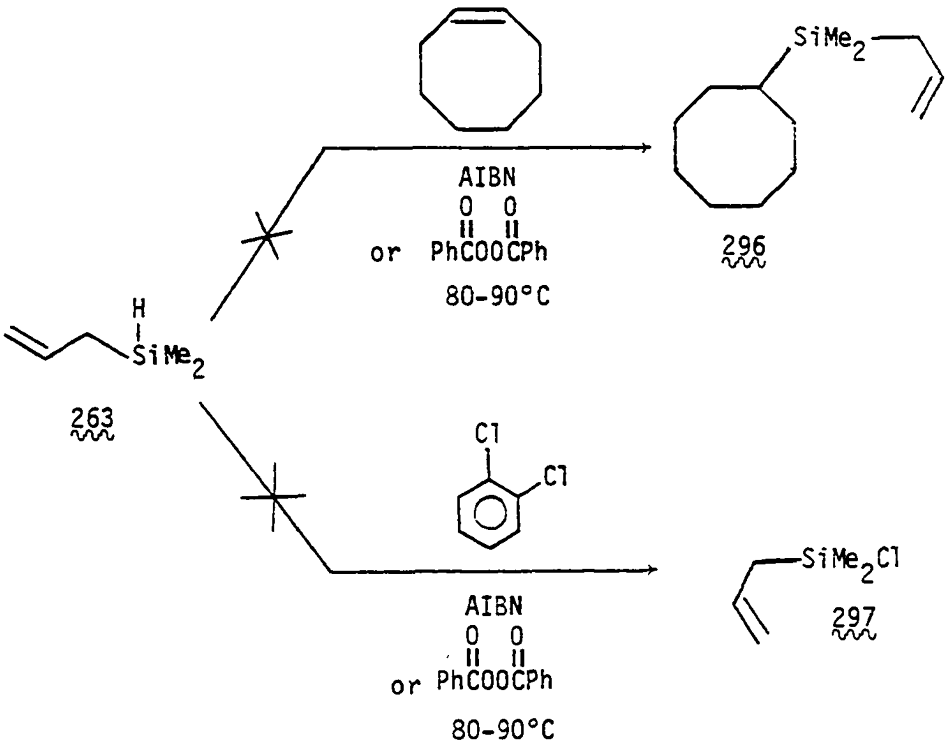


The most important conclusion that can be made on the basis of the data obtained from the pyrolysis of 263-265, 272 and 280, is that under gas-phase pyrolysis conditions these molecules do not cleanly decompose to afford the desired alkenylsilyl radicals. Indeed, for all of these reactions, the products formed indicate that the dominant mode of thermal decomposition is loss of an allyl radical and not the homolysis of the Si-H or Si-CH_2Ph bonds as desired. At the onset of this research, the homolysis of a Si-H bond in 263 and 272, and the homolysis of a Si-CH_2Ph bond, in the case of 280, was expected to compete favorably with allyl radical loss. However, the report by Davidson and Wood (159), which appeared while this work was in progress, that silicon-allyl bond homolysis was a lower energy process then Si-H bond homolysis, clearly demonstrates that such an expectation was unreasonable. Thus, as a result of our inability to cleanly generate the desired silyl radicals thermally in the gas-phase, we were forced to consider alternate methods of silyl radical generation.

Abstraction of Silyl Hydrides by Radical Initiators

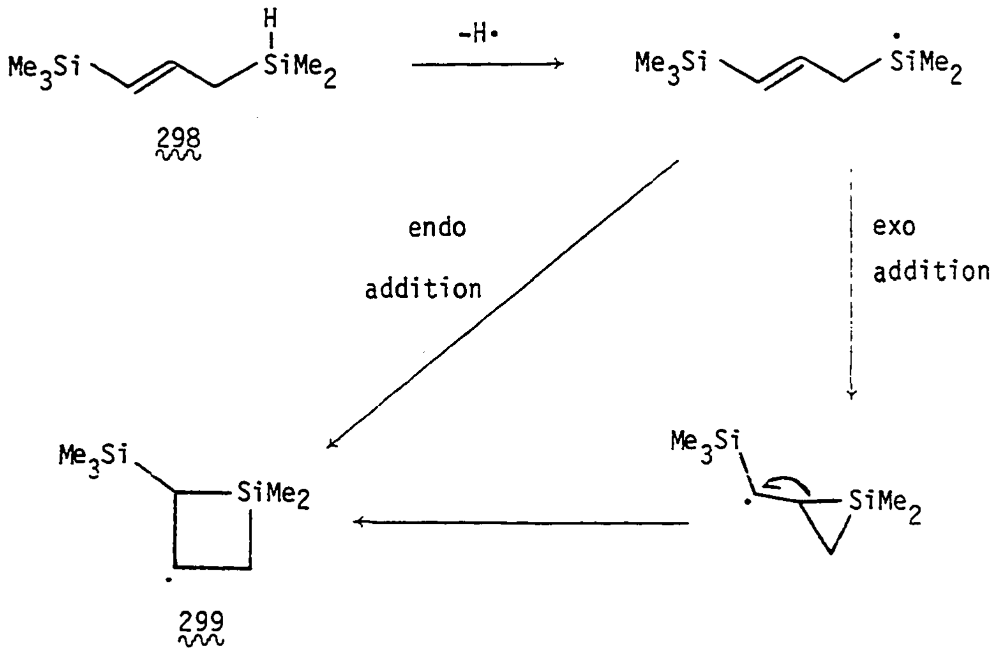
Numerous examples of silyl radical generation by hydrogen abstraction of silyl hydrides, employing typical carbon radical initiators, have been reported (see the Historical section on silyl radicals for pertinent references). We sought to take advantage of this method of silyl radical generation to examine the chemistry of alkenyl-substituted silyl radicals.

Initial experiments employing allydimethylsilane (263) and either azo-bis(isobutyryl)nitrile (AIBN) or benzoyl peroxide, as initiators, failed to afford the desired allyldimethylsilyl radical. Thus, thermolysis (90-100°C) of degassed solutions of 263, AIBN or benzoyl peroxide, and cyclooctene or ortho-dichlorobenzene, both known silyl radical traps (18), failed to afford either trapping product 296 or 297.



Although alkenes are not efficient traps for trialkylsilyl radicals (18, 208), alkyl- and aromatic-halides are very efficient silyl radical traps (e.g., 18, 191, 192), thus, the absence of 297, in those reactions employing ortho-dichlorobenzene, demonstrated that under these reactions conditions allyldimethylsilyl radical was not being formed.

These initial experiments also brought to light an experimental difficulty associated with these solution reactions. Due to the volatility of 263, and the necessity of conducting these reaction at high dilution such that intramolecular reactions would be favored, it was difficult to isolate 263, or products, should they be formed, from the reaction mixtures. Thus, in an effort to alleviate this problem, allylsilane 298 was chosen for the subsequent studies. The decision to use 298 was based on two points: a, it is relatively nonvolatile (B.P. = 73-78°C at 31 Torr compared to 52-55°C at 760 Torr for 263), and thus isolation of 298, or products derived from its radical, would be facilitated; b, cyclization of the silyl radical derived from 298 could afford 299 which would be expected to be stabilized by virtue of two silicons β to the radical center. Sakurai and coworkers (302) have obtained experimental evidence suggesting that β-silyl radicals are stabilized in a manner analogous to that of β-silyl carbonium ions.

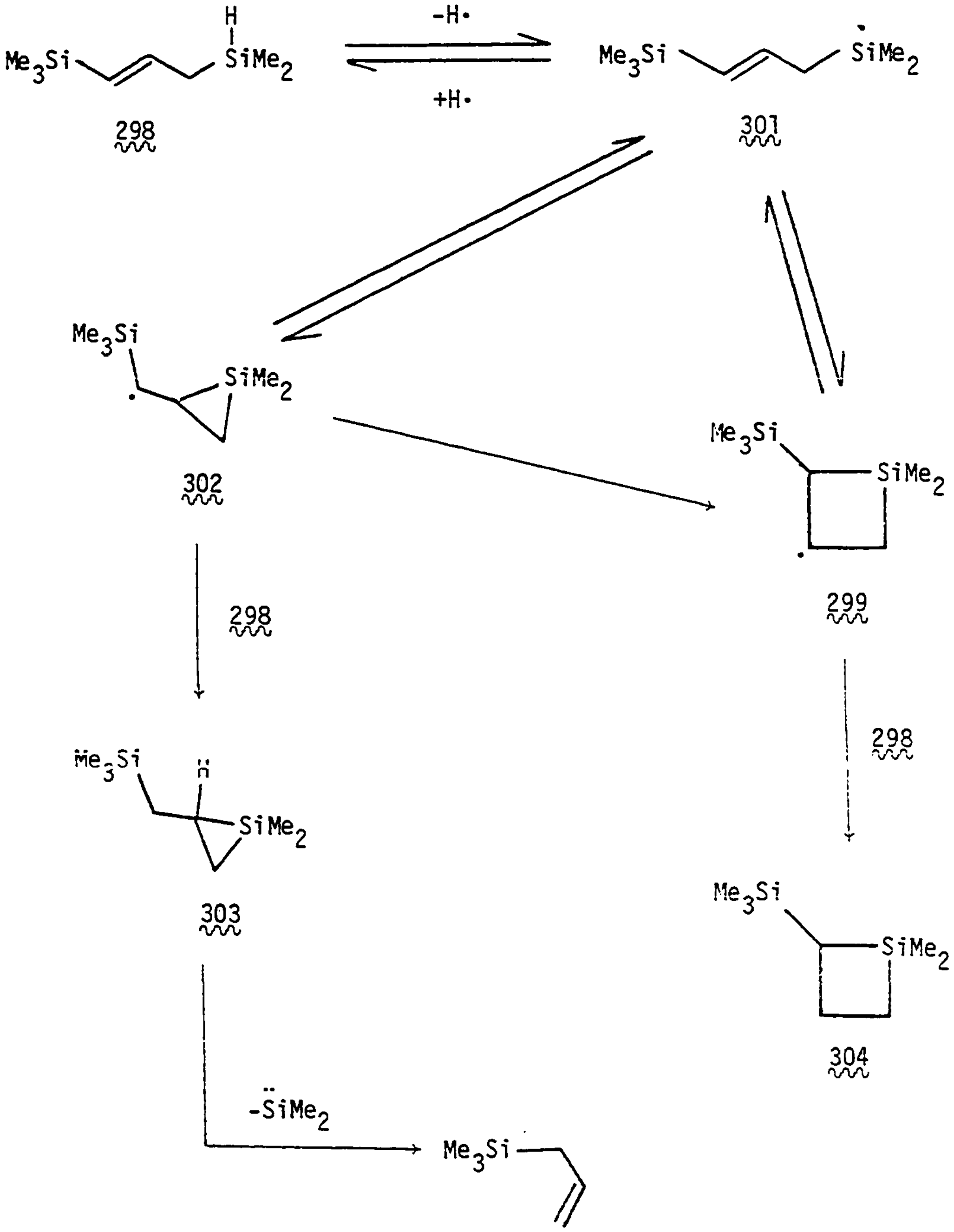


Thermolysis of **298** at temperatures ranging from 110-140°C in the presence of t-butylbenzoyl peroxide (**300**, 0.17 to 0.25 molar equivalents) neat, in benzene, or in bromocyclohexane, in all cases, failed to afford evidence for the formation of the desired silyl radical, **301**.

In the absence of a trap, cyclization of **301** to **302** followed by hydrogen abstraction from **298** would afford silarane **303** (Scheme 85). Under the reaction conditions employed, **303** would be expected to lose dimethylsilylene affording allyltrimethylsilane. Alternatively, **301** could cyclize to **299** (Scheme 85) which upon H-abstraction from **298** would afford **304**. Thus, the absence of allyltrimethylsilane and/or **304** demonstrated that if **301** was formed it was not undergoing intramolecular cyclization. However, in the absence of cyclization only unreacted **298** would be expected (excluding biomolecular reactions). Thus, the presence of unreacted **298** as the only observable species in the neat reaction did not provide evidence concerning the chemistry of **301**, since only **298** would be present if the anticipated abstraction reaction had not occurred. Indeed, when the reaction was conducted in the presence of benzene and bromocyclohexane, both known silyl radical traps (18), the presence of unreacted **298**, as the only detectable compound, demonstrated that under these reaction conditions **301** was not being formed.

As previously discussed in the Historical section on silyl radicals, the most commonly employed initiator in silyl radical chemistry is di-t-butyl peroxide (**305**). Due to our inability to effect silyl radical formation using AIBN, benzoyl peroxide, or t-butylbenzoyl peroxide, we turned our attention to **305**.

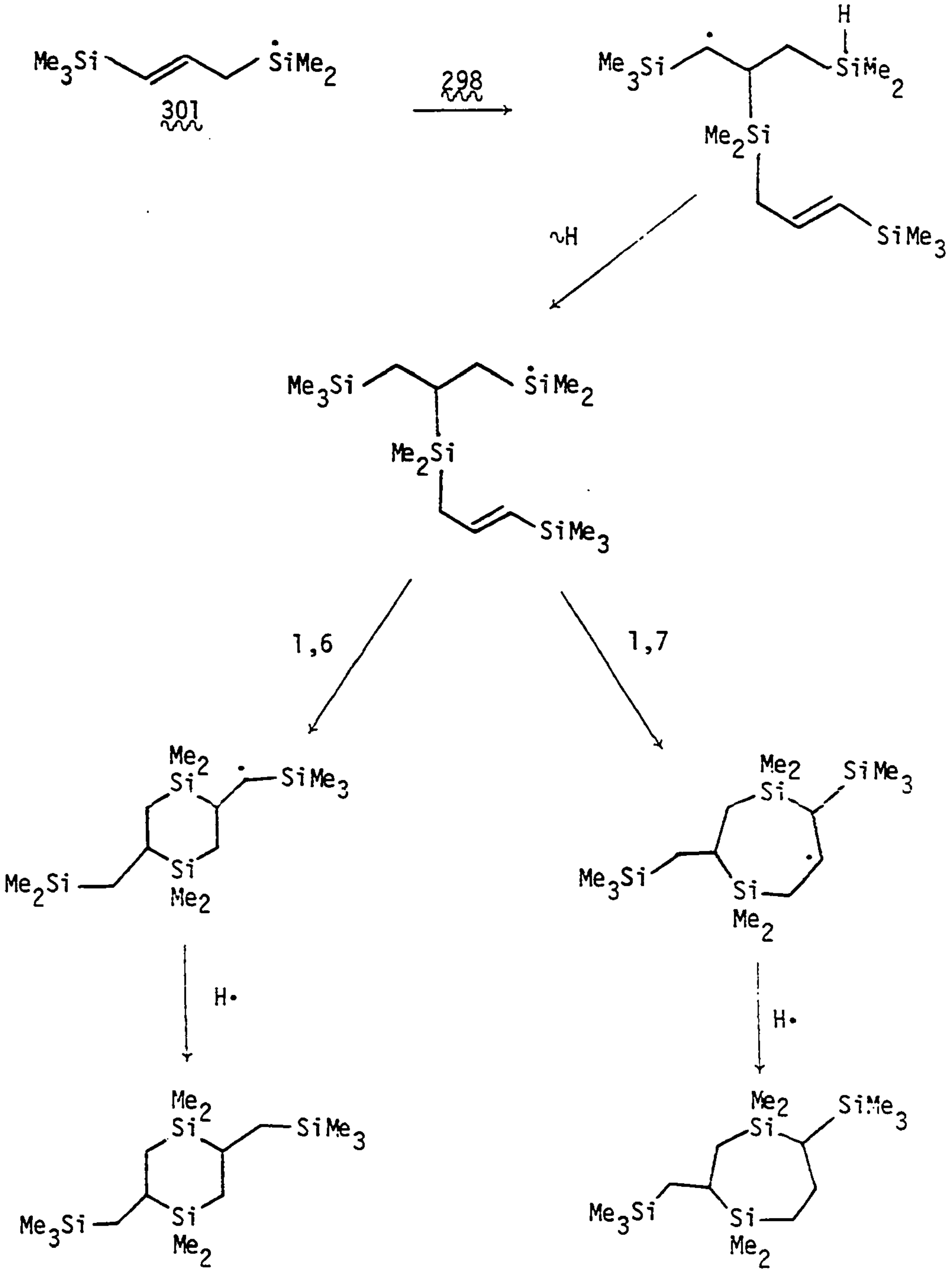
Scheme 85



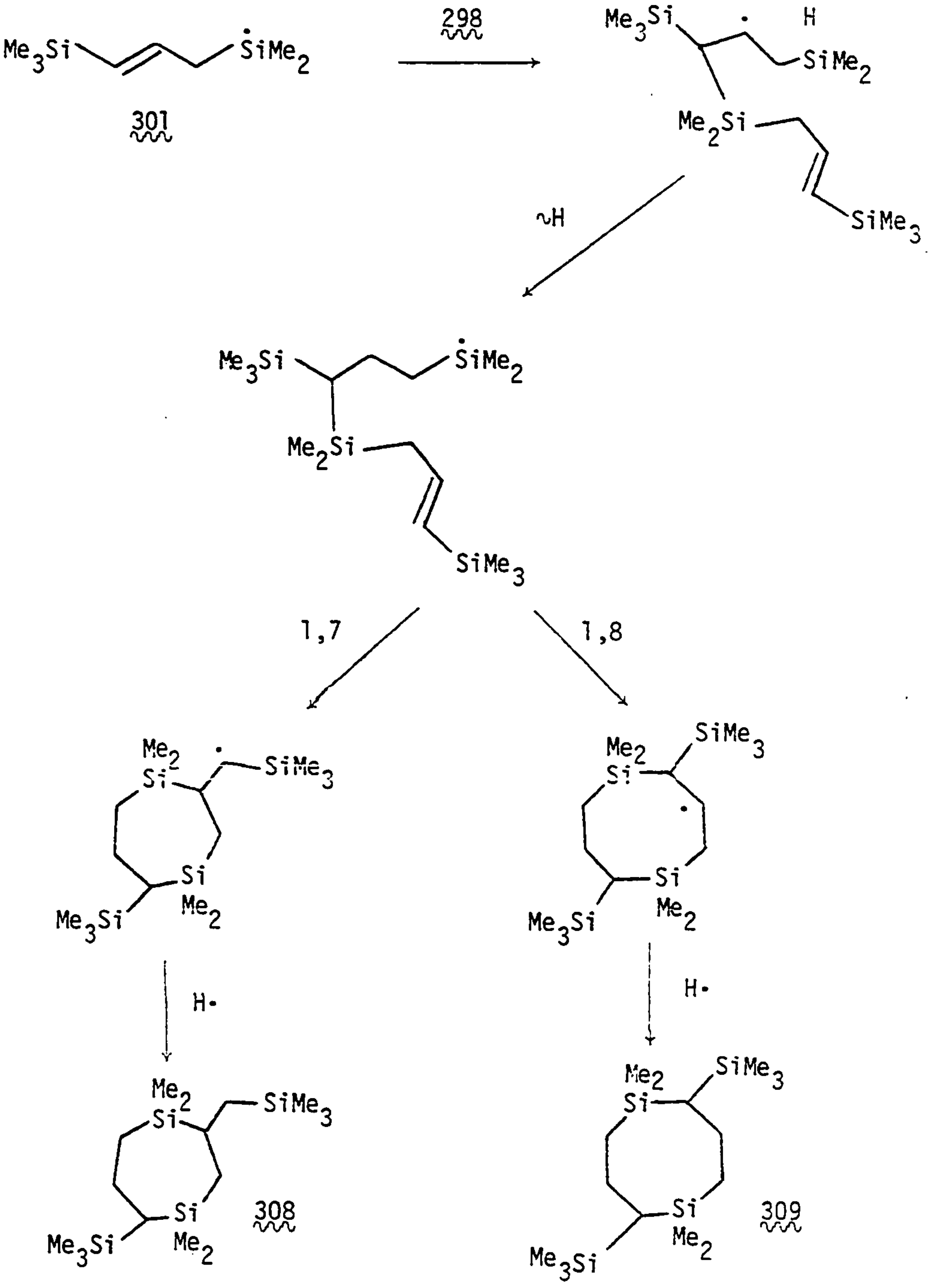
Thermolysis of a cyclohexane solution of 298 (ca. 0.7 molar), containing 0.53 molar equivalents of 305, at 135-140°C for 17 hours afforded a reaction mixture which contained *t*-butyl alcohol and unreacted 298 as the only detectable products by gas-chromatography. In contrast, thermolysis of a dilute cyclohexane solution of 298 (0.069 molar), containing 0.50 molar equivalents of 305, at 130°C for 14 hours resulted in the complete consumption of 298. With the exception of *t*-butyl alcohol, no volatile products were detectable by gas-chromatography. However, *en vacuo* removal of the solvent followed by chromatography of the resulting residue afforded two compounds which accounted for 70.6 and 8.2% mass recovery, respectively. Although the two products were shown to be pure by thin-layer-chromatography, and to contain silicon on the basis of their NMR and IR spectra, it was not found possible to identify the compounds on the basis of the obtainable spectral data. Despite the inability to identify these products, several conclusions regarding their composition can be made. First, the inability to detect these products by GC demonstrated that these compounds were of high molecular weight, and therefore, oligomeric. Secondly, both compounds contained Si-H and C=C stretching frequencies in their IR spectra (*vide infra*), demonstrating that neither was the dimeric cyclization products 306 and 307 (Scheme 86), or 308 and 309 (Scheme 87). Whatever the exact identity of the products of this reaction, the results clearly demonstrate that silyl radical 301, if formed, does not undergo clean intramolecular cyclization.

In a repeat of this reaction, employing a catalytic amount of 305 (6.6×10^{-3} molar equivalents), no comsumption of 298 was found. This

Scheme 86

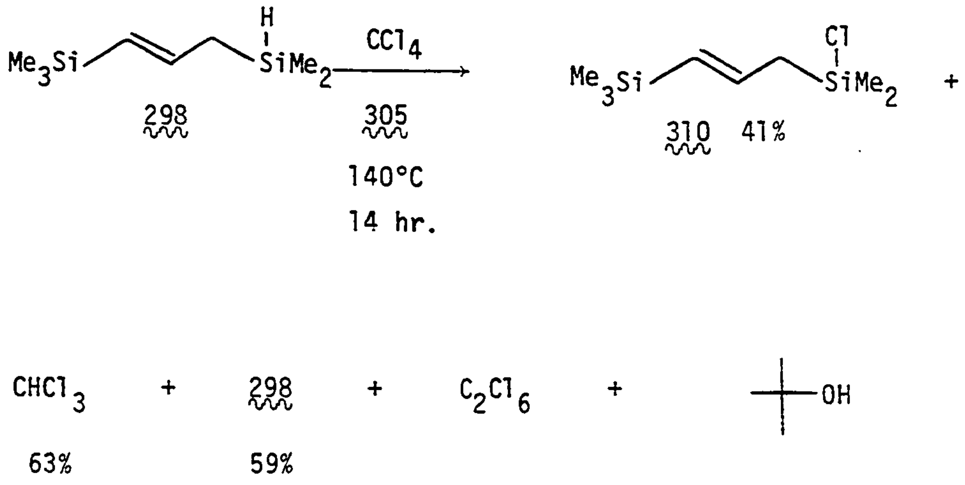


Scheme 87



result demonstrated that 301, or radicals derived from its subsequent reactions, were not serving as a radical chain carrying species.

That 301 was indeed being produced in these reactions was demonstrated by conducting the reaction in the presence of CCl_4, a known silyl radical trap (18). Thus, cothermolysis of 298, 0.49 molar equivalents of 305, and excess CCl_4 afforded 310 (the expected product of radical trapping), $HCCl_3$, and C_2Cl_6 (the expected products of reaction of $\cdot CCl_3$). Again, no reaction was observed when catalytic amounts (0.039 molar equivalents) of 305 were used under otherwise identical conditions.



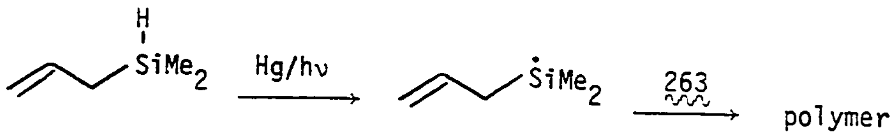
In view of the discouraging results obtained in the solution reactions of 263 and 298 with radical initiators, and the difficulty associated with product isolation when reactions were conducted under conditions of high dilution, further attempts to generate alkenyl-substituted silyl radicals in solution were abandoned. Further reasons for abandoning these solutions reactions were the findings by Krusic and Kochi that activated methylene hydrogens and hydrocarbon solvents compete favorably with silyl hydrides with respect to t-butoxyl abstraction of hydrogen (135). Thus, due to the presence of allylic methylene protons in our alkenyl-substituted silyl radical precursors, and the necessity of employing dilute hydrocarbon solutions so that intramolecular reactions would be favored, the possibility of cleanly generating the desired silyl radicals was considered improbable.

Mercury-Photosensitized Reactions of Alkenyl- and Alkenyloxy-Substituted Silyl Hydrides

As discussed previously in the Historical section on silyl radicals, mercury-sensitized photolysis of silyl hydrides is a convenient and clean method for the generation of silyl radicals. This method of silyl radical generation possesses the additional advantage of being conducted in the gas-phase, conditions which would favor intramolecular reactions. This method of silyl radical generation was, therefore, expected to be ideally suited for our study of alkenyl-substituted silyl radicals.

Mercury-sensitized photolysis of 263 (Rayonette, 2537 Å lamps, quartz filter) for 16 hours at approximately 45°C resulted in the formation of a colorless, crystalline solid, in addition to unreacted 263. That the crystalline solid was not soluble in either boiling CCl_4 or benzene demonstrated that allyldimethylsilyl radical, which was presumably formed, was polymerizing. Although the composition of the polymer could not be determined, it is most reasonably accounted for by a radical chain reaction as shown in Scheme 88.

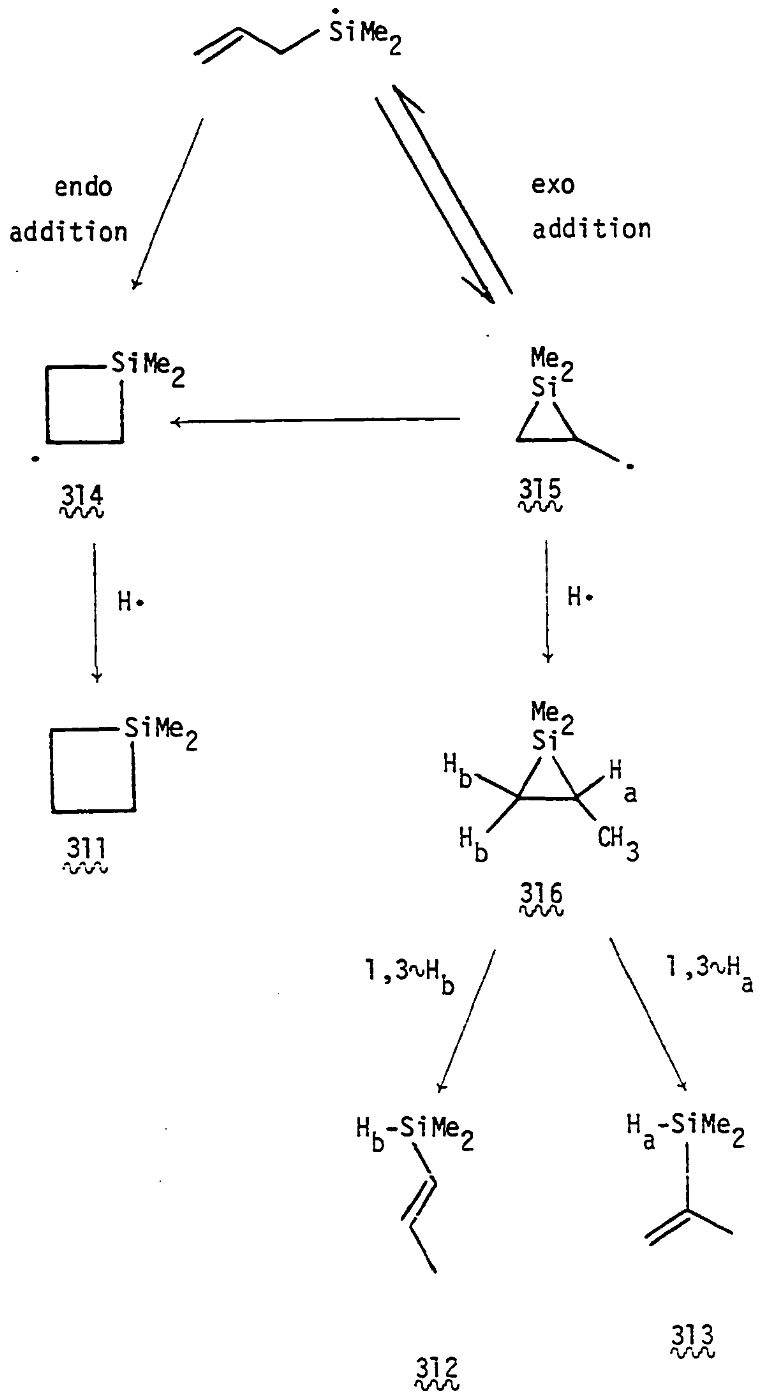
Scheme 88



Consideration of the possible intramolecular reactions of allyldimethylsilyl radical and the reasonable products expected from such reactions (Scheme 89) reveals that the polymeric product obtained was not unexpected. Thus, formation of 311 or 312 and 313 would require the formation of carbon radicals 314 and 315, respectively. Cyclobutyl radical 314 could be formed directly by endo-cyclization or by ring expansion of cyclopropylcarbinyl radical 315. Direct formation of 314 by endo-cyclization would not be expected by analogy to the chemistry of carbon radicals (237), thus, if 314 was present as an intermediate in this reaction it would most reasonably arise via ring expansion of 315. Therefore, on the basis of this reasoning, and by consideration of Scheme 89, the formation of 311 or 312 and 313, which would arise from 316 via the precedented photochemical isomerization of silaranes (60, 61), would require the intermediacy of 315. By analogy to carbon chemistry (236,237) the equilibrium between allyldimethylsilyl radical and 315 would be expected to lie strongly in favor of the former, and thus, polymerization of allyldimethylsilyl radical is not unreasonable.

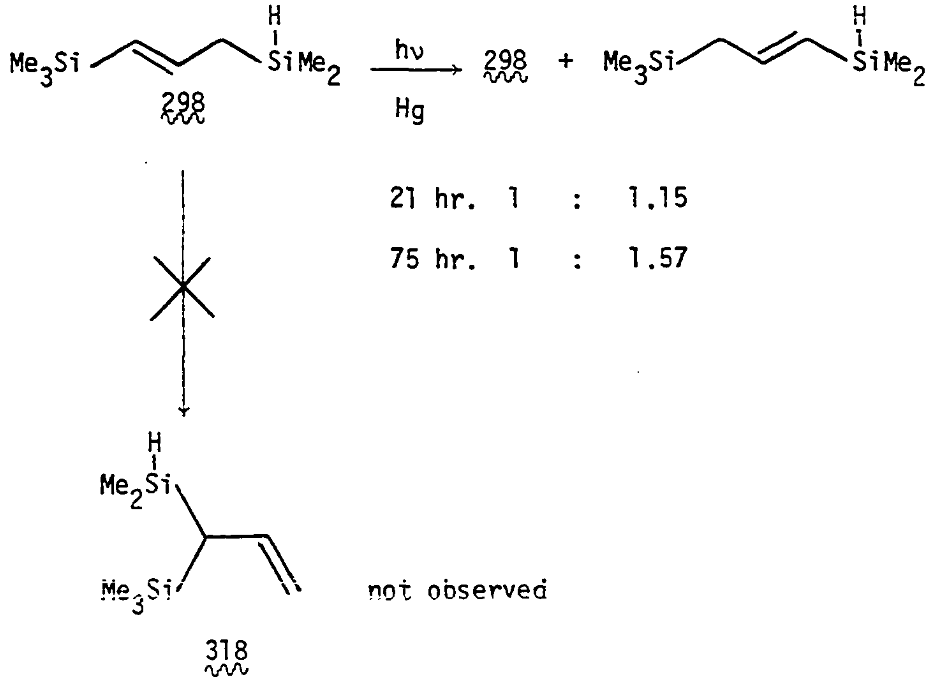
In contrast to the results obtained with 263, mercury-sensitized photolysis of 298 resulted in double bond isomerization, as determined by the isolation of 298 and 317 in 88% combined yield after 75 hours. No evidence for the formation of silyl radical 301 was found. The inability

Scheme 89


$\dot{Si}Me_2$
endo addition
exo addition
$SiMe_2$
314
Me_2Si
315
H•
H•
$SiMe_2$
311
Me_2Si
H_b
H_b
H_a
CH_3
316
1,3~H_b
1,3~H_a
H_b-$SiMe_2$
H_a-$SiMe_2$
312
313

to photochemically produce 301 from 298 is probably due to the inability to obtain a high concentration of 298 in the gas-phase under the reaction conditions employed. Since 298 undergoes photochemical isomerization, no attempt was made to increase the gas-phase concentration of 298 by conducting the reaction at higher temperatures.

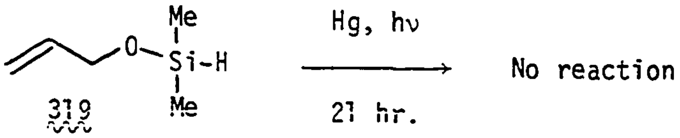
Scheme 90

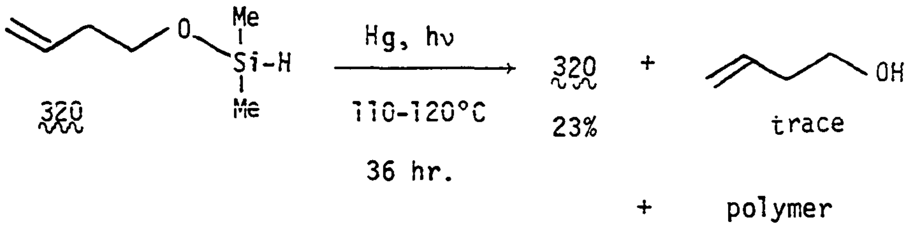


It is interesting to note, that the expected photochemical isomerization product 318 (303) was not found. It is possible, if not probable, that 318 was formed in this reaction, but under the equilibrating conditions isomerized to either 317 or back to 298 to relieve the steric strain imposed by the vicinal di- and trialkylsilyl groups. Additional driving force for the isomerization of 318 to 317 and 298 is the presence of a more thermodynamically stable double bond in the latter two compounds.

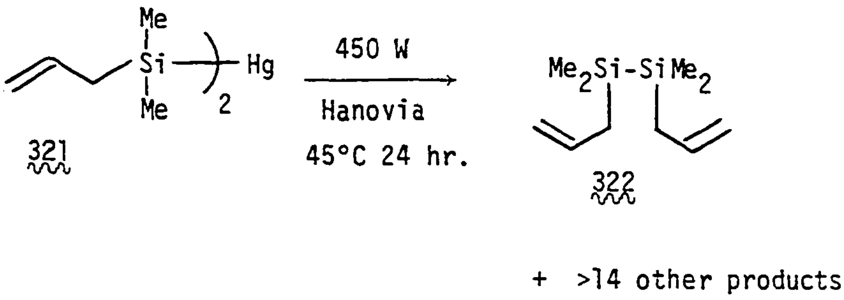
Two final attempts were made to effect the intramolecular cyclization of a silyl radical employing mercury-sensitized photolysis using alkenloxysilanes 319 and 320 as the radical precursors. The choice to use 319 and 320 as substrates rather than 264 and 265 was based on the relative ease of synthesis and purification of the former two compounds.

Mercury-sensitized photolysis of 319 (450 w hanovia, 45°C) for 21 hours resulted in no detectable consumption of 319. Under similar conditions 320 also failed to react. In contrast, irradiation of 320 in the presence of mercury and heated at 110-120°C, to insure that 320 was in the gas-phase, afforded only a 23% recovery of unreacted 320. However, with the exception of a small amount of butene-4-ol, only an unidentifiable, high molecular weight (MW of >300) residue, which was assumed to be polymeric, was obtained.





Finally, as a last attempt to obtain evidence for an intramolecular silyl radical cyclization, the photolysis of bis(allyldimethylsilyl)-mercury (321) was investigated. While the photochemical decomposition of bis-silylmecurials to silyl radicals has been investigated by a number of workers (see the Historical section on silyl radicals), the irradiation of bis(alkenylsilyl)mercurials had not been previously reported. Irradiation of 321, prepared according to the procedure of Hovland and coworkers (304), afforded 1,2-diallyltetramethyldisilane (322) as the only major product, in addition to greater than 14 minor products. Due to the presence of these latter products in only trace quantities, no attempt was made to effect their isolation and characterization.



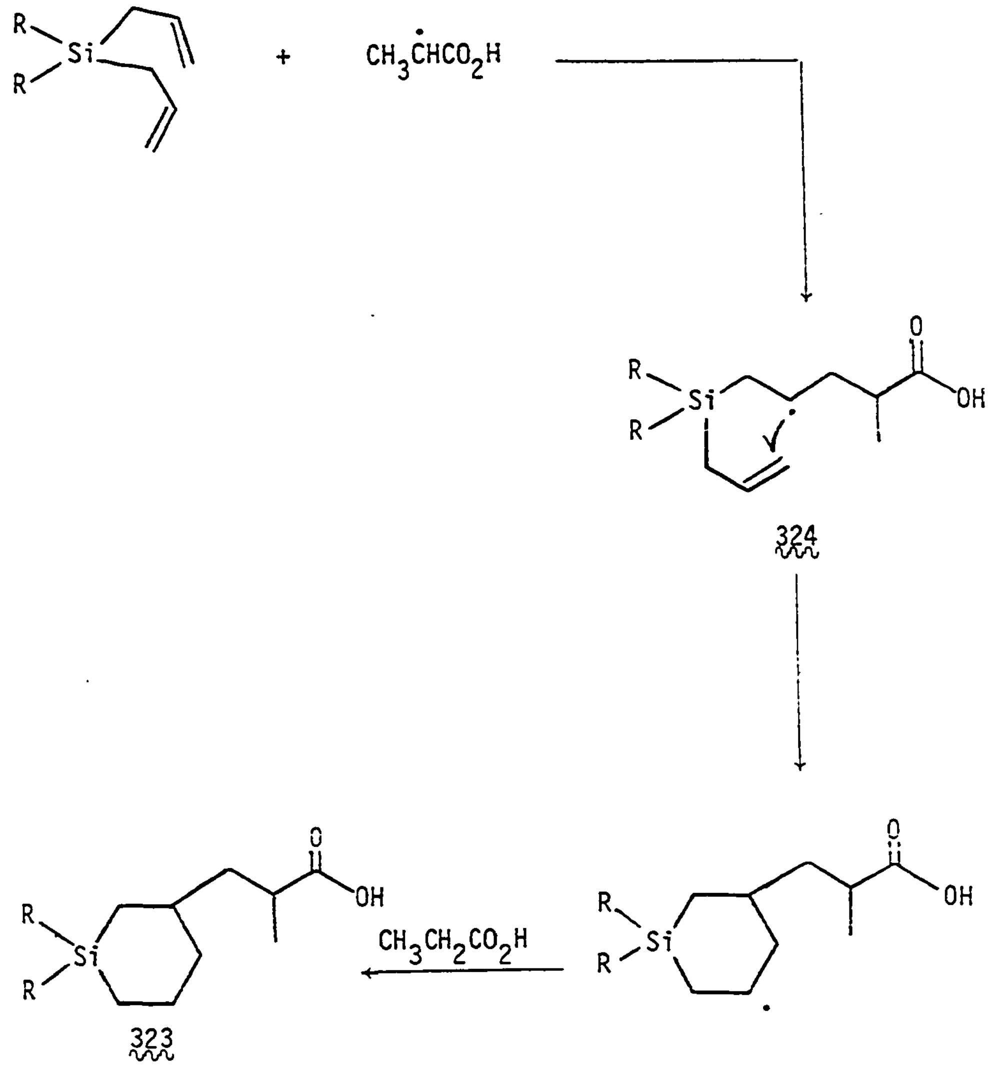
In all, our attempts to effect intramolecular cyclization of silyl radicals were disappointing. The gas-phase pyrolysis of silyl hydrides did not cleanly afford the desired silyl radicals. In contrast, trapping experiments conduted when silyl radicals were generated by hydrogen abstraction from silyl hydrides by t-butoxyl radicals did demonstrate that the desired silyl radicals were being generated. However, rather than intramolecularly cyclizing the available data (*vide supra*) showed that intermolecular oligomerization occurred instead. Similar results were observed in the mercury-sensitized photolysis experiments, i.e., oligomerization occurred rather than cyclization. The lack of oligomerization in the photolysis of 321 may indicate that 321 decomposes directly to 322, rather than homolysis to allyldimethylsilyl radicals followed by their geninate coupling. Indeed, this interpretation has previously been used to explain the products obtained in the photolysis reactions of bis-silylmecurials (18).

While these results indicate that intramolecular cyclization of silyl radicals is not as facile as that for the analogous carbon radicals, they do not comment on the mode of silyl radical cyclizations. In view of the large number of examples of intramolecular carbon radical cyclizations (236), it is unreasonable to conclude, on the basis of these results, that silyl radicals do not undergo intramolecular cyclization reactions. Rather, the major conclusion that can be drawn from this work is that the reaction conditions employed did not favor intramolecular cyclization.

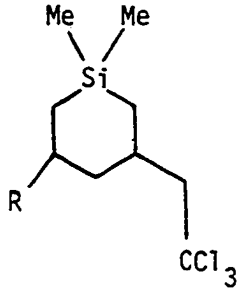
The Reaction of Diallyldimethylsilane with Trichloromethyl Radical

In 1963, Ogibin and coworkers reported that reaction of various diallylsilanes with proprionic acid in the presence of di-*t*-butyl peroxide at 132-138°C afforded silacyclohexanes 323 as the only observable cyclization products (305). The mechanism proposed for the formation of 323 involved as a key step the endo cyclization of radical 324 (Scheme 91). Since endo cyclization of carbon radicals is a violation of Beckwith's rules (237), and since the identity of 323 (R=CH_3) was based solely on IR spectroscopy, a reinvestigation of the reaction of diallyldimethylsilane (325) with carbon radicals was undertaken.

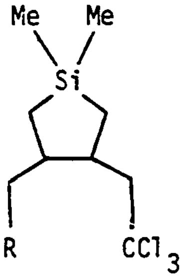
Scheme 91



Rather than using the radical derived by hydrogen abstraction from proprionic acid, the trichloromethyl radical was chosen, since the ^1H and ^{13}C NMR spectra of the two possible cyclization products (326 and 327) would be less complex than those for R=$CH(CH_3)CO_2H$.



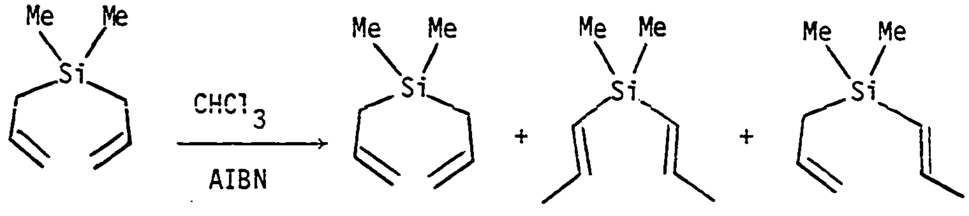
326



327

R=H or Cl

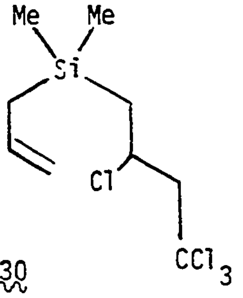
Following the general procedure of Brace (306), heating a solution of 325, $CHCl_3$, and a catalytic amount of azo-bis(isobutyryl)nitrile (AIBN) at 142-143°C for 18 hours afforded a 4:2:1 mixture (97% combined yield) of bis(propenyl)dimethylsilanes 325, 328, and 329.



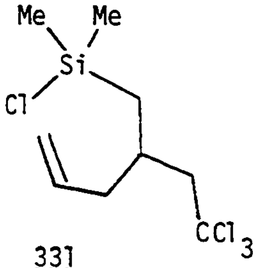
325 328 329

4:2:1

In contrast, reaction of 325, CCl_4, and a catalytic amount of AIBN at 85-90°C for 24 hours afforded a single product in approximately 80% yield. Analysis of this product by high resolution mass spectrometry revealed the highest ion signal to be 251 MU (neglecting chlorine isotope signals), and which was assigned to the loss of allyl from the 1:1 adduct of 325 and CCl_4. NMR and IR analysis of this product revealed signals consistent with a C=C moiety, and thus allylsilane 330 was found to be most consistent with the spectral data. However, chlorosilane 331, which could be formed as shown in Scheme 92, was also consistent with the spectral data.



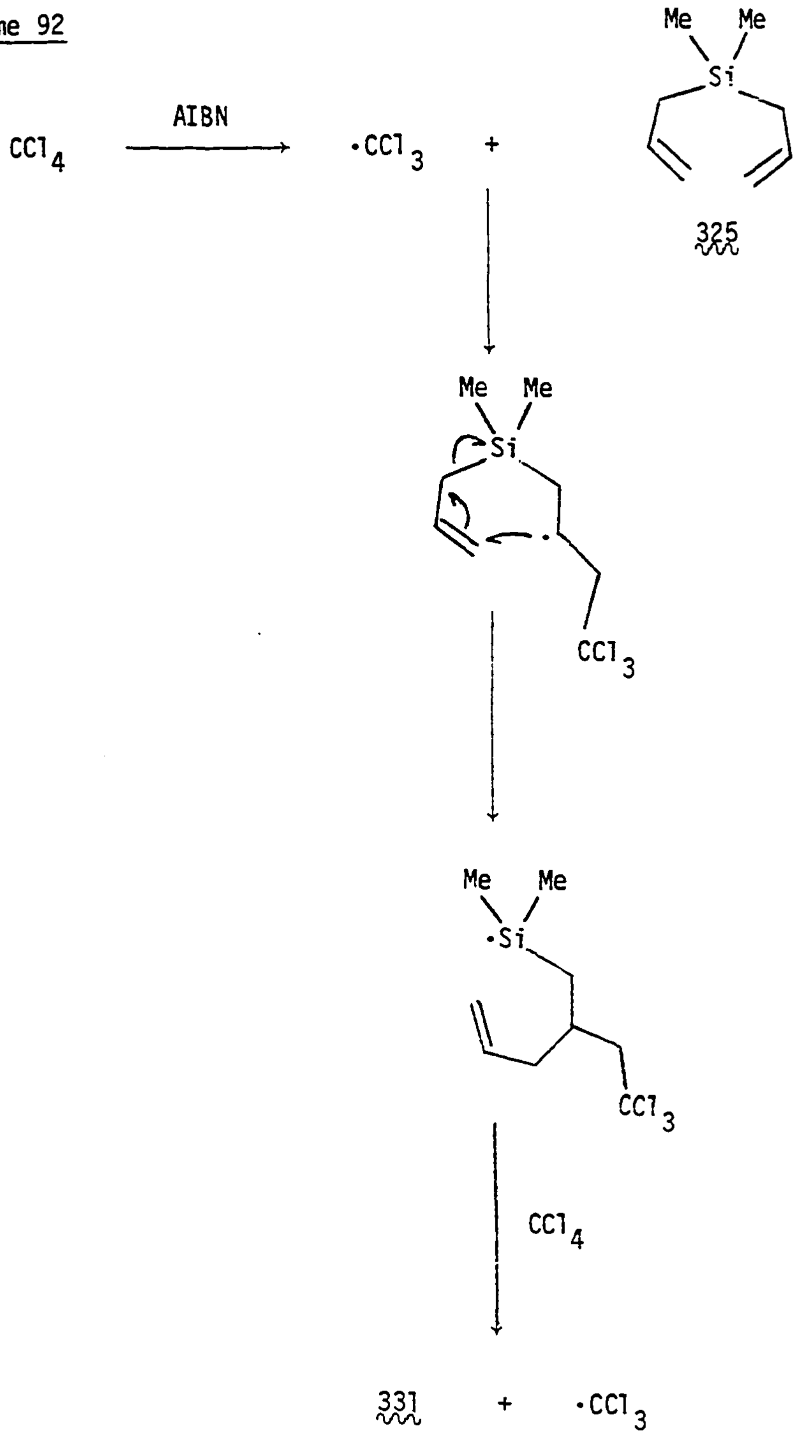
330



331

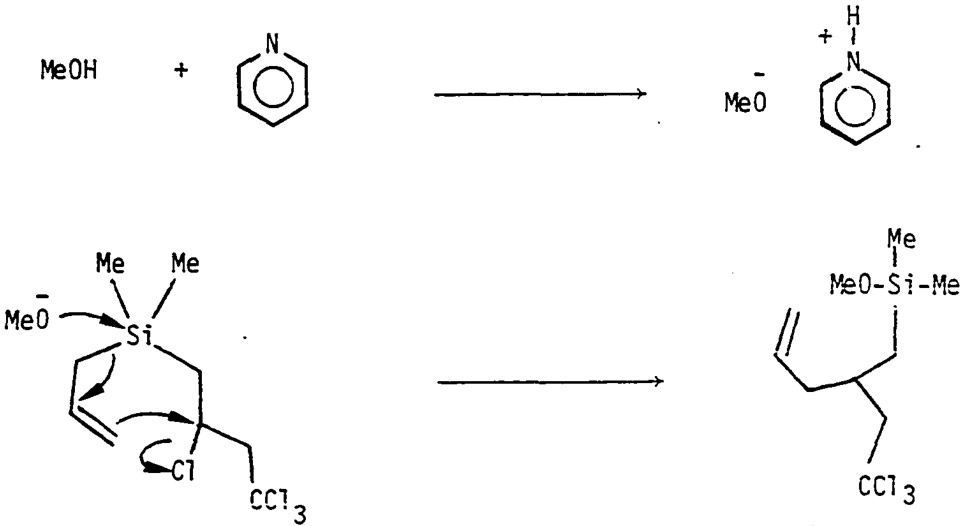
In an effort to distinguish between 330 and 331, the product of this reaction was treated with excess MeOH/pyridine. Treatment of 331 with MeOH/pyridine would afford methoxylsilane 332, while 330 would not be expected to react. Surprisingly, the reaction with excess MeOH/pyridine afforded two products, both unreacted 330 and 332. Since the product of the reaction of 325 and CCl_4 was demonstrated by GC and TLC to be pure, the presence of both 332 and 330 in the methanolysis reaction was unexpected. Although unexpected, it is possible to rationalize the formation of 332 from 330 upon reaction with MeOH and pyridine as shown

Scheme 92


CCl4
AIBN
·CCl3
+
Me
Me
Si
325
Me
Me
Si
CCl3
Me
Me
·Si
CCl3
CCl4
331
+
·CCl3

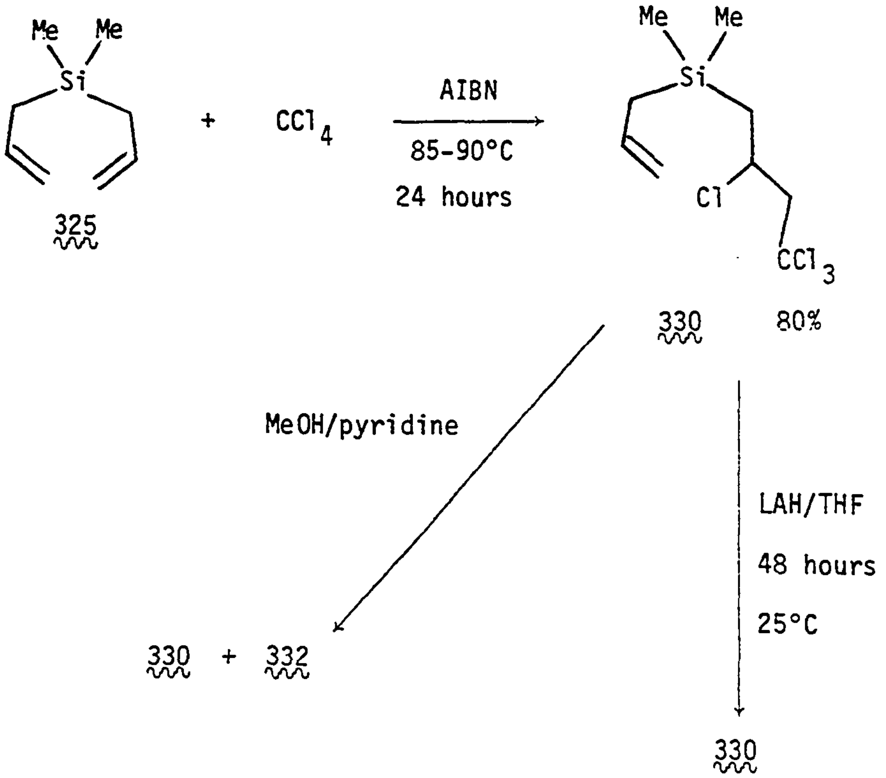
in Scheme 93. Moreover, reaction of the product of the reaction of 325 and CCl_4 with excess LAH for 48 hours followed by aqueous workup afforded only unreacted starting material. Since LAH is known to reduce chlorosilanes to the corresponding hydrosilanes (264), the presence of unreacted starting material as the only observable species in the LAH reaction, coupled with the results of the MeOH/pyridine reaction, was taken as evidence demonstrating that the identity of the product obtained from the reaction of 325 with CCl_4 was allylsilane 330. Scheme 94 schematically summarizes these results.

Scheme 93



332

Scheme 94



In contrast to the results obtained upon heating a solution of 325, CCl_4, and AIBN at 85-90°C for 24 hours, when the reaction was allowed to go for 48 hours, under otherwise identical conditions, a 2:1 ratio of a product which could not be distinguished between 326 or 327 (R=Cl) and 330 were obtained in a combined yield of greater than 90%.

The identity of the major product of this reaction as either 326 or 327 (R=Cl) was based on the following observations. Both the ^1H and ^{13}C NMR spectra revealed the presence of two different silicon-methyls and the absence of any olefinic protons and carbons. The lack of an olefinic moiety in this product was further supported by the absence of olefinic C-H and C=C stretching bands in the IR spectrum. However, the inability to obtain interpretable mass spectra and the inability to fully resolve the ^1H NMR spectrum prevented the distinction between **326** and **327** (R=Cl) from being made. While it is most reasonable to assign the identity of this product to **327**, by analogy to the known cyclization chemistry of carbon radicals (236, 237), an unambiguous assignment cannot be made from the results reported. Thus, the question regarding the intramolecular cyclization of 3-silahexa-5-enyl radicals remains unanswered.

CONCLUSIONS

The addition of dimethylsilylene to cyclooctene oxide was found to proceed by initial formation of a silyl ylid rather than insertion into a C-O bond to form a silaoxetane. Although the exact process by which the silyl ylid decomposed to afford products could not be established, a bimolecular "silanone" transfer mechanism was favored over a unimolecular decomposition to dimethylsilanone and cyclooctene. When photogenic dimethylsilyene generators were employed, coordination of cyclooctene oxide to the silylene generator and subsequent silylene transfer to afford the silyl ylid directly was favored over the intermediacy of free dimethylsilylene. Attempted silaoxetane formation via intramolecular C-H insertion by alkoxysilylenes failed.

Cyclopentadienylmethylsilylene did not rearrange to silafulvene or silatoluene, instead complex reaction mixtures were obtained under a variety of conditions. In contrast, vinylmethylsilylene rearranged to afford methylsilylacetylene in moderate yield, although it was not possible to establish the exact mechanism of this rearrangement.

The addition of dimethyl acetylenedicarboxylate to 1,1-dimethyl-2,5-diphenylsilole was found to afford the expected 7-silanorbornadiene, which isomerized in the presence of oxygen or upon heating in the absence of oxygen by a formal 1,5 migration of silicon from carbon to oxygen to afford a bicyclic o-silyl-o-alkylketeneacetal, not a silapin or silanorcaradiene. This isomerization was found to be most consistent with a direct

1,5-silyl migration. Additionally, the previously reported thermal and photochemical epimerization of 7-silanorbornadienes was shown to be in error.

Attempts to determine the course of intramolecular cyclization of alkenyl-substituted silyl radicals failed, principally due to our failure to cleanly produce the desired silyl radicals.

Suggestions for Future Work

Two major areas of future study can be proposed on the basis of the results presented in this thesis. Perhaps the most important area of study would be the effect of oxygen containing substrates upon the decomposition of photochemical silylene generators. As previously discussed, oxygen containing substrates have been found to dramatically enhance the rate of decomposition of photochemical silylene generators. This rate enhancement was postulated to occur via coordination of the oxygen containing substrate to the silylene generator (in either the ground or photo-excited state) followed by "silylene" transfer, rather than silylene extrusion followed by coordination. A kinetic study of the rate of decomposition of the silylene generator in solutions containing varying concentrations of an oxygen containing substrate would afford data supporting or negating this postulate. If, as expected, the rate of decomposition of silylene generator was dependent upon the concentration of an oxygen containing substrate, further understanding of this phenomenon could be obtained by varying the nucleophilicity of the added substrate (e.g., Et_2O versus THF). Additionally, the steric bulk of the oxygen containing substrate could be varied.

The second major area of future study deals with the chemistry of alkenyl-substituted silyl radicals. In view of the work presented in this thesis, to effectively study these radicals a cleaner method for their generation is needed. The pyrolysis of silyl iodides is a promising method of selective silyl radical generation under gas-phase pyrolytic conditions. Although this reaction has been reported only once (157), bond-dissociation data (see Table 3) suggest that this technique may be general. Thus, flash-vacuum-pyrolysis of alkenyl-substituted silyl iodides would be expected to afford selectively the desired alkenyl-substituted silyl radicals.

EXPERIMENTAL

General Information

Routine proton NMR spectra were recorded either on a Varian model A-60, EM-360, HA-100, Hitachi R20-B, or on a JOEL FX-90 FT-NMR spectrometer. Decoupling experiments were performed either on a Varian EM-360, HA-100, or JOEL FX-90 FT-NMR spectrometer. All chemical shifts are reported as parts-per-million (δ scale) using either tetramethylsilane, benzene, or chloroform as internal standards.

^{13}C NMR spectra were recorded on a JOEL FX-90 FT-NMR spectrometer with either $DCCl_3$ or D_6-acetone as internal standards.

Infrared (IR) spectra were recorded on either a Beckman IR-4250, IR-18A, or Acculab-2 spectrometer, and were calibrated with the 2000 cm^{-1} grating change.

Routine mass spectra and Gas Chromatographic Mass Spectra (GCMS) were obtained on a Finnegan model 4023 Mass Spectrometer. Exact mass measurements were obtained on a MS-902 Mass Spectrometer.

ESR spectra were recorded on a Varian E-3 spectrometer with a field set of 3360 and a scan range of ± 50 gauss.

Melting points were measured with a Thomas Hoover capillary melting point apparatus and are uncorrected. Gas Chromatographic (GC) data were obtained on a Varian-Aerograph Series 1700, 3700, or 920 Gas Chromatograph. Column size and packing will be reported as used. Unless otherwise specified, all GC yields were determined with internal standards after determination of the relevant response factors.

For those reactions involving hydrogen abstraction from silyl hydrides, the solvents utilized (vide infra) were purified by passage through a column of alumina prior to use. Additionally, for those reactions using di-*t*-butyl peroxide as an initiator, the initiator was also passed through a column of alumina prior to use.

Procedures and Results

Attempted Synthesis of Diisopropyldifluorosilane

A modification of the procedure of Eaborn (263) was utilized. A solution of 50 ml (38 g, 0.31 mol) of isopropyl bromide and 100 ml of dry THF was added dropwise over 1 hour to a stirred suspension of 13 g (0.53 mol) of magnesium chips in 100 ml of dry THF. After the addition was complete, the solution was stirred for 2 hours at room temperature. Gaseous SiF_4 was then slowly bubbled through the solution for 6 hours at room temperature and for an additional 3 hours at reflux. After cooling to room temperature, the solution was hydrolyzed with sat. aqueous NH_4Cl and extracted thrice with Et_2O. The organic fractions were combined, dried over $MgSO_4$, and the solvent removed en vacuo to afford 23 g of a viscous yellow solution that by gas chromatographic analysis was a mixture of greater than six products. Due to the complexity of the reaction mixture, no attempt was made to purify the products.

Attempted Synthesis of Diisopropyldimethylsilane from Silicon Tetrachloride

A solution of 50 ml (38 g, 0.31 mol) of isopropyl bromide in 100 ml of dry THF was added dropwise over 1 hour to a stirred suspension of 13 g

(0.53 mol) of magnesium chips in 100 ml of dry THF. After the addition was complete, the resulting solution was stirred for 2 hours at room temperature. This Grignard solution was then added dropwise over 3 hours to a stirred solution of 25 g (0.15 mol) of $SiCl_4$ and 100 ml of dry THF at room temperature. After the addition of the isopropyl Grignard was complete, 180 ml of a 3M solution of methylmagnesium iodide (0.54 mol) in Et_2O was added dropwise over 2 hours to the stirred reaction mixture. After this addition was complete, the reaction was stirred for 1 hour at room temperature. After cooling to 0°C, the reaction was hydrolyzed with sat. aqueous NH_4Cl and extracted twice with Et_2O. The organic fractions were combined and dried over $MgSO_4$. After <u>en vacuo</u> removal of the solvent, attempted fractionation of the resulting solution did not afford diisopropyldimethylsilane. Instead, a compound with a boiling point of 62-68°C/94 Torr was obtained, which was tentatively identified as isopropyldimethyldisiloxane: NMR (CCl_4) δ 0.11 (S, 6H), 1.03 (broad S, 7H); IR (neat) 2950, 2890, 2860, 1460, 1250, 1070, 879, 833 and 775 cm^{-1}.

Attempted Synthesis of Diisopropyldimethylsilane from Dimethyldichlorosilane

a) A solution of 11 g (0.093 mol) of isopropyl bromide in 25 ml of dry THF was added dropwise over 2 hours to a stirred suspension of 2.4 g (0.1 mol) of magnesium chips in 25 ml of dry THF. After the addition was complete, the solution was brought to reflux and maintained at reflux for 2 hours. Dimethyldichlorosilane (6.4 g, 0.05 mol) was then added dropwise with stirring over 45 minutes. After the addition was complete, the reaction mixture was maintained at reflux for another 30 minutes. After cooling to 0°C, the reaction was hydrolyzed with dilute H_2SO_4, which resulted in a vigorous exothermic reaction, and then extracted twice with Et_2O. The organic fractions were combined and dried over $MgSO_4$. Attempted fraction did not yield any products (other than solvent) with a boiling point of less than 180°C/760 Torr. Since the desired product has a boiling point of 141-142°C/760 Torr (263), no further work was done on this reaction.

b) To a stirred solution of 58 ml (0.5 mol) of dimethyldichlorosilane and 250 ml of dry THF, containing 15 g (2.16 mol) of lithium pellets, was added a solution of 123 g (1.0 mol) of isopropyl bromide in an equal volumn of dry THF, over a period of 6 hours. During the addition of about the first 50% of the isopropyl bromide, spontaneous refluxing of the reaction mixture occurred. Beyond this point, refluxing was maintained by the application of heat. After the addition was complete, the reaction was maintained at reflux for 48 hours. After cooling to 0°C, the reaction mixture was diluted with 300 ml of Et_2O and then hydrolyzed with sat., aqueous NH_4Cl. The organic phase was collected and dried over $MgSO_4$. After *en vacuo* removal of the solvent, attempted fractionation of the resulting solution did not afford any products with a boiling point of less than 180°C/760 Torr. Therefore, no further work was done on this reaction.

Synthesis of Diisopropylmethylsilane (265)

A solution of 115 g (1.0 mol) of methyldichlorosilane and 369 g (3.0 mol) of isopropyl bromide, in an equal volume of dry THF, was added dropwise over 1 hour to a stirred suspension of 72 g (3.0 mol) of magnesium chips in 300 ml of dry THF. After the addition was complete, the solution was refluxed for 24 hours. The reaction mixture was hydrolyzed with dilute aqueous acid and extracted thrice with Et_2O. The organic fractions were combined, dried over $MgSO_4$, and distilled to yield 74 g (0.57 mol, 57% yield) of diisopropylmethylsilane (b.p. 120-122°C/760 Torr): NMR (CCl_4) δ -0.05 (d, 3H, J = 4Hz), 0.95 (broad S, 14H), 3.5 (broad m, 1H), irradiation at δ 0.95 collapses the multiplet at δ 3.5 to a quartet, J = 4Hz, irradiation at δ -0.05 collapses the multiplet at δ 3.5 to a broad singlet; I.R. (neat) 2962, 2950, 2900, 2875, 2105, 1468, 1256, 1008, 885, 878, 827, and 730 cm^{-1}; mass spectrum m/e (% rel. int.) (18 ev) 130 (37), 87 (100), 59 (87); exact mass calculated for $C_7H_{18}Si$, m/e 130.11778, measured 130.1177.

Synthesis of Diisopropyldimethylsilane 143

A solution of methyllithium (110 ml, 1.6M, 0.176 mol) in Et_2O was added rapidly to a stirred solution of 14.69 g (0.113 mol) of diisopropylmethylsilane in 200 ml of dry THF. The reaction mixture was then refluxed for 48 hours. After hydrolysis with dilute aqueous acid, the reaction mixture was extracted three times with Et_2O. The organic fractions were combined, dried over $MgSO_4$, and distilled to yield 9.22 g (0.064 mol, 56%) of diisopropyldimethylsilane (b.p. 140-144°C/760 Torr): NMR (CCl_4) δ -0.1 (S, 6H), 0.95 (S, 14H); I.R. (neat) 2940, 2889, 2860, 1460, 1248, 991, 875, 819, 800, 752, and 673 cm^{-1}; mass spectrum m/e (% rel. int.) 144 (7), 101 (58), 73 (100), 59 (69); exact mass calculated for $C_8H_{20}Si$, m/e 144.13343, measured 144.13220.

Synthesis of Bis(α-bromoisopropyl)dimethylsilane 144

To 4 g (0.028 mol) of neat diisopropyldimethylsilane, maintained at 65-75°C, was added 8.8 g (0.06 mol) of bromine. The bromine was added at such a rate as to just maintain a slight red color. If the bromine was added too fast the reaction became dark in color and low yields of product were obtained. On the other hand, if the rate of addition of bromine was too slow the reaction ceased. Throughout the addition of bromine a gentle stream of nitrogen was bubbled through the reaction. After the addition was complete, the resulting residue, which solidified upon cooling, was sublined at 0.05 Torr and 25°C to afford 3.66 g (0.012 mol, 44%) of 144, m.p. 84-86°C (lit. (49) 84-86°C); NMR (CCl_4) δ 0.3 (S, 6H), 1.82 (S, 12H); IR (neat) 2960, 2920, 2870, 1457, 1440, 1410, 1379, 1363, 1252, 1080, 890, 820, 775, and 670 cm^{-1}; mass spectrum m/e (% rel. int.) (70 ev) 180 (13), 139 (99), 137 (100), 125 (26), 99 (30), 73 (47), 59 (31), 58 (22); (20 ev) 181 (11), 180 (23), 179 (12), 178 (14), 139 (100), 137 (98), 125 (37), 121 (12), 99 (31), 82 (14), 73 (18), 58 (15). The yields obtained in this bromination reaction were variable and ranged from a low of 23% to a high of 84%. In general, yields of 50-60% were typical.

Reaction of Bis(α-bromoisopropyl)dimethylsilane (144) with Magnesium to Afford Hexamethylsilacyclopropane (12)

In a typical preparation, a 25 ml 2 neck round bottom flask, equipped with a magnetic stirring bar and having one neck connected to a vacuum-stopcock and the other neck sealed with a rubber septum, was charged with

3 g (0.01 mol) of **144** and 0.5 g (0.02 mol) magnesium powder (magnesium chips could also be used). Approximately 10 ml of freshly dried THF was then added and argon was bubbled through the reaction for approximately 10 minutes. The argon bubbling was then discontinued and the reaction was stirred gently at room temperature. After approximately 30 minutes, the reaction became hot and the formation of precipitated salts was noted. After the onset of reaction, the mixture was stirred for 2 hours. The flask was then attached to a vacuum line and the contents were trap-to-trap distilled at 25°C and 0.05 Torr to a previously degassed receiver, cooled to -196°C. The THF was then removed from **12** by distillation at 25°C and 70 Torr. Hexamethylsilacyclopropane was identified by comparison of its NMR spectrum with that previously reported by Seyferth and Annarelli (49). NMR (C_6H_6) δ 0.13 (S, 6H), 1.28 (S, 12H).

Cothermolysis of Hexamethylsilacyclopropane (**12**) and Cyclooctene Oxide

A solution of 0.1773 g (0.0014 mol) of cyclooctene oxide and 0.1098 g of undecane (as an internal standard) in 3 ml of benzene was degassed by the freeze-thaw method. Silarane **12** was then trap-to-trap distilled (25°C, 0.05 Torr) into the reaction vessel (cooled to -196°C). The sealed reaction vessel was heated at 84°C for 12 hours. Analysis of the reaction mixture by GC and GCMS revealed the presence of tetramethylethylene, cyclooctene (**146**) and permethyl-1,3-disila-2-oxacyclopentane (**145**) as the only observable products, in addition to unreacted cyclooctene oxide. The identities of tetramethylethylene and **146** were established by comparing their GC retention times and GCMS spectra with those of authentic samples.

The identity of 145 was established solely on the basis of it GCMS spectrum: mass spectrum, m/e (% rel. int.) 216 (7), 201 (4), 147 (7), 133 (100), 117 (61), 73 (37), 59 (14). The yields of 145 (2%) and 146 (48%), relative to tetramethylethylene, were determined by calibrated GC using undecane as an internal standard. Thermolysis of cyclooctene oxide in the absence of 12, under otherwise identical conditions, afforded quantitatively unreacted epoxide.

Cothermolysis of Hexamethylsilacyclopropane (12), Cyclooctene Oxide, and Hexamethylcyclotrisiloxane (D_3)

A solution of 0.1158 g (9.19×10^{-3} mol) of cyclooctene oxide, 0.2351 g (0.0011 mol) of D_3, and 0.0986 g of undecane (as an internal standard) in 3 ml of benzene was degassed by freeze-thaw method. The methods of addition of 12, thermolysis, product analysis, and determination of the yields were identical to that described for the copyrolysis of 12 and cyclooctene oxide. The products obtained from this reaction were: tetramethylethylene, 146 (35%), and octamethylcyclotetrasiloxane (D_4) (30%).

Photolysis of Dodecamethylcyclohexasilane (14) and Cyclooctene Oxide

A typical experiment for the photolyses of dodecamethylcyclohexasilane (14) in the presence of cyclooctene oxide is as follows: A solution of 0.1115 g of cyclooctene oxide, 0.3058 g of 14, and 0.1182 g of undecane (as an internal standard) in 2 ml of dry cyclohexane was placed in a quartz NMR tube. The tube was sealed with a rubber septum and degassed by bubbling argon through the solution for approximately 15 minutes. The sample was irradiated for 12 hours with a 450 W Hanovia lamp at approximately 40°C. Analysis of the reaction mixture and product identification (see Table 15) for the 2, 12 and 18 hour reactions were conducted by GC and GCMS. Additionally, for the 12 and 18 hour photolyses, preparative scale reactions were performed which allowed for product isolation via preparative gas chromatography on a 6 ft x 1/4 inch, 30% SE-30/chrom W column at an initial temperature of 110°C followed by manual temperature programming to 250°C. Compounds **146**, **148**, **149**, and **150** were isolated. The low yields of **151** precluded any attempts of isolation. The identity of **146** was established by comparing its GC retention time, and GCMS and NMR spectra with those of an authentic sample. The identities of **148**-**151** were established on the basis of the following spectral data.

Disiloxane **148** NMR (CCl_4) δ 0.05 (broad S, 14H), 1.5 (broad S, 12H); mass spectrum, m/e (% rel. int.) 242 (4), 227 (2), 133 (100), 119 (12), 117 (33), 73 (23), 59 (10).

Trisiloxane **149** NMR (CCl_4) δ 0.05 (broad hump, 20H), 1.55 (broad S, 12H); IR (CCl_4) 2960, 2920, 2850, 1470, 1447, 1410, 1257, 1058, and 1015 cm^{-1}; mass spectrum, m/e (% rel. int.) 316 (3), 301 (4), 207 (100), 193 (20), 192 (11), 191 (54), 147 (11), 133 (12), 103 (11), 73 (49), 59 (11), exact mass calculated for $C_{14}H_{32}O_2Si_3$, m/e 316.17102, measured 316.17118.

Tetrasiloxane **150** NMR (CCl_4) δ 0.06 (broad hump, 26H), 1.56 (broad S, 12H); IR (CCl_4) 2960, 2920, 2850, 1470, 1445, 1410, 1258, 1070, and 1015 cm^{-1}; mass spectrum, m/e (% rel. int.) 375 (8) (parent $-CH_3$), 281 (13), 280 (12), 265 (32), 208 (15), 207 (75), 168 (44), 153 (21), 73 (100), 59 (24), exact mass calculated for $C_{16}H_{38}O_3Si_4$ (parent ion), m/e 390.189814, measured 390.189011, exact mass calculated for $C_{15}H_{35}O_3Si_4$ (parent $-CH_3$), m/e 375.166334, measured 375.166717.

Pentasiloxane 151 GCMS, m/e (% rel. int.) 499 (7) (parent $-CH_3$), 282 (20), 281 (76), 267 (12), 265 (11), 207 (9), 168 (26), 147 (26), 133 (34), 117 (11), 73 (100), 59 (21).

The yields (see Table 15) for all products of these reactions were determined by calibrated GC, using undecane as an internal standard, and are based on reacted epoxide.

Photolysis of 14, Cyclooctene Oxide, and D_3

A typical experiment for the photolysis of dodecamethylcyclohexasilane (14) in the presence of cyclooctene oxide and D_3 is as follows. A solution of 0.1334 g of 14, 0.1135 g of cyclooctene oxide, 0.2543 g of D_3 and approximately 2 ml of dry cyclohexane was placed in a quartz NMR tube. The tube was sealed with a rubber septum and degassed by bubbling argon through the tube for approximately 15 min. The sample was irradiated with a 450 W Hanovia lamp at approximately 40°C. Analysis of the reaction mixture and product identification were conducted via GC and GCMS. Additionally, one reaction was performed on a preparative scale to allow for the isolation of all products by preparative gas chromatography. The GC-retention times, GCMS, and NMR spectrum of each product was found to be identical with that of an authentic sample. The yields (see Table 16) for all products of these reactions were determined by calibrated GC, using undecane as an internal standard, and are based on reacted epoxide, with the exception of 152 whose yield is based on reacted D_3.

Photolysis of Dodecamethylcyclohexasilane (**14**) and Cyclohexene Episulfide.

A solution of 2.64 g (0.0076 mol) of **14**, 2.00 g (0.0175 mol) of cyclohexene episulfide, and 40 ml of dry methylcyclohexane was placed in a septum sealed quartz tube and deoxygenated by bubbling argon through the solution for 15 minutes. The sample was then irradiated with a 450 W, 679 A Hanovia lamp (quartz filter) at approximately 40°C. Analysis of the reaction mixture by GC, after photolysis for approximately 2.5 hours, revealed that no reaction had occurred. Analysis following irradiation for an additional 8 hours again revealed the presence of substantial amounts of unreacted **14** (estimated to be >75%) and cyclohexene. Additionally, the presence of >10 products, present in trace amounts, were detected by GCMS. Irradiation for another 3.5 hours resulted in a further increase in the amounts of reaction products and a decrease in **14**. The three major components of the reaction, cyclohexene, decamethylcyclopentasilane (**162**), and **14** were isolated by preparative gas chromatography on a 6 ft X 1/4 inch, 10% OV-101/chrom W column at an initial temperature of 60°C followed by temperature programing to 200°C at a rate of 10°/minute. The identities of cyclohexene and **14** were established by comparison of their GC retention times, and GCMS and NMR spectra with those of authentic samples. The identity of **162** was established on the basis of the spectral data presented below.

Decamethylcyclopentasilane (**162**) NMR (CCl_4) δ 0.11 (S); GCMS, m/e (% rel. int.) 290 (43) 275 (2), 217 (14), 216 (13), 215 (16), 201 (27), 171 (26), 157 (36), 143 (15), 129 (10), 115 (10), 113 (10), 99 (13), 73 (100), 59 (20).

Photolysis of **15**

A solution of 0.2155 g (8.23 X 10^{-4} mol) of **15** and 0.5 ml of hexadecane was placed in a septum sealed quartz NMR tube and degassed by bubbling argon through the solution for 15 minutes. The tube was then placed in a Rayonet photochemical reactor equipped with 2537 Å lamps and irradiated at approximately 45°C. Analysis of the photolysate by GC, after irradiation for 19 hours, revealed the presence of very small amounts of Me$_3$SiSiMe$_3$ and approximately 95% unreacted **15**. After irradiation for 66 hours, the amount of Me$_3$SiSiMe$_3$ had increased (based on GC analysis), but, large amounts (ca. 75%) of unreacted **15** still remained.

Similar results were observed when a hexadecane solution of **15** (1.3401 g, 5.1 X 10^{-3} mol of **176** and 7 ml of hexadecane) was irradiated with a 450 W, 679 A Hanovia lamp under otherwise identical conditions. Thus, after irradiation for 28 hours, 86% of unreacted **15** was present. After 35 hours, 80% of unreacted **15** remained. The yields for this latter reaction were determined by GC using the solvent as a standard.

For both of these reactions, the only observable product was Me$_6$Si$_2$.

Cophotolysis of **15** and Dimethyldimethoxysilane

A solution of 0.143 g (5.4 X 10^{-4} mol) of **15**, 1.04 g (7.0 X 10^{-3} mol) of dimethyldimethoxysilane and 1 ml of cyclohexane was placed in a septum sealed quartz NMR tube and deoxygenated by bubbling argon through the tube for 15 minutes. After irradiation for 12 hours at approximately 45°C with a 450 W, 679 A Hanovia lamp, analysis of the photolysate by GC revealed the presence of two major products and 6 minor products. The two major products were isolated by preparative gas chromatography on a 12 ft X 1/4 inch, 20% SE-30/chrom W column at 100°C. The major product of the reaction was shown to be $Me_3SiSiMe_3$ by comparison of its NMR and GCMS data with those of authentic sample. The other major product, whose yield was determined to be 40% (based on the amount of $Me_3SiSiMe_3$) by assuming that its response factor was the same as that for $Me_3SiSiMe_3$, was identified as methoxypentamethyldisilane: NMR (CCl_4) δ 0.09 (S, 9H, $SiMe_3$), 0.16 (S, 6H, $SiMe_2$), 3.4 (S, 3H, OMe); GCMS, m/e (% rel. int.) 162 (1), 147 (100) (parent-Me), 117 (30), 89 (73), 73 (93), 59 (84), 45 (26).

None of the minor products were present in sufficient concentrations to allow for their isolation and characterization.

Attempted Synthesis of 2-*t*-Butoxyheptamethyltrisilane (170a)

To a stirred suspension of 1.5 g (0.0134 mol) of potassium *t*-butoxide in 30 ml of dry THF was added 3.0 g (0.0134 mol) of 2-chloroheptamethyltrisilane. Following the addition, the reaction was stirred for 12 hours at room temperature. The reaction was then hydrolyzed with H_2O and extracted twice with Et_2O. The organic fractions were combined, dried over $MgSO_4$, and concentrated *en vacuo* to afford 2.694 g of a clear, yellow oil. Analysis of the oil by NMR showed that no *t*-butoxide had been incorporated.

In a modification of the above reaction, 3.0 g (0.0134 mol) of 2-chloroheptamethyltrisilane was added to a stirred suspension of 2 g (0.0178 mol) of potassium *t*-butoxide in 25 ml of dry THF containing 3.93 g (0.053 mol) of dry *t*-butanol. When the addition was complete, the reaction was brought to reflux and maintained at reflux for 12 hours. After cooling to room temperature, the reaction was worked up as described above. Again, NMR analysis of the resulting oil failed to reveal the presence of any t-butoxyl groups.

Synthesis of 2-Ethoxyheptamethyltrisilane (170b)

To a stirred solution of 4.26 g (0.0189 mol) of 2-chloroheptamethyltrisilane and 30 ml of dry THF was added 9.78 g (0.124 mol) of dry pyridine followed by 7.893 g (0.17 mol) of absolute EtOH. When the additions were complete, the reaction was stirred at room temperature for 3 hours. After hydrolysis with H_2O and extraction with hexanes, the resulting organic phase was washed thrice with H_2O, dried over $MgSO_4$, and concentrated en vacuo to afford 4.178 g of a clear, pale yellow liquid. Analysis of this liquid by NMR and GC showed it to be greater than 80% 170b. Purification by distillation gave 2.6 g (0.0111 mol, 59% yield) of 170b, B.P. 80-81°C at 13 Torr, which was identified on the basis of the following spectral data: NMR (CCl_4) 0.1 (S, 18H), 0.29 (S, 3H), 0.83 (t, 3H, J = 7.9 Hz, collapses to a singlet with hν at δ 3.23), 3.23 (q, 2H, J = 7.9 Hz, collapses to a singlet with hν at δ 0.83); IR (CCl_4) 2950, 2890, 1437 (W), 1385 (W), 1240, 1099, 1070, 930, and 830 cm^{-1}; mass spectrum, m/e (% rel. int.) 219 (0.2) (parent -Me), 205 (15), (parent -Et), 147 (14), 119 (28), 117 (69), 103 (11), 75 (95), 73 (100), 59 (19), 48 (28), 49 (48), exact mass calculated for $C_9H_{26}Si_3O$, m/e 234.12916, measured 234.12910.

Photolysis of **170b**

A solution of 0.9 g (0.00385 mol) of **170b** and 25 ml of dry Et_2O in a septum sealed quartz tube was deoxygenated by bubbling argon through the solution for approximately 15 minutes. The tube was then suspended next to a quartz immersion-well surrounding a 450 W, 679 A, Hanovia U.V. lamp and irradiated for 12 hours at approximately 45°C. After irradiation, the solvent was carefully removed by distillation to afford 0.725 g of a clear, pale yellow liquid. Analysis of the liquid by GC revealed the presence of 5 compounds, two of which were present in major amounts. Of the 5 compounds only the two major ones were present in sufficient amounts to allow for their isolation by preparative gas chromatography on a 6 ft X 1/4 inch, 30% SE-30/chrom W column at an initial temperature of 150°C followed by manual temperature programing to 200°C. These two products were identified as **172** and hexamethydisilane on the basis of the spectral data given below. The yields of these two products were determined by GC using *t*-butylbenzene as a standard. The yields are determined relative to the amount of **170b** that decomposed to afford silylene products, which was calculated by subtracting the molar amount of **172** obtained from the molar amount of starting trisilane. Thus from this calculation, 65% of **170b** was determined to have decomposed via silylene formation.

2,2-diethoxy-3,3-bis(trimethylsilyl)-2,3-disilabutane (**172**) NMR (CCl_4) δ 0.15 (S, broadened at the base line, 24H), 1.14 (t, 6H, J = 7.5Hz), 3.69 (q, 4H, J = 7.5Hz); GCMS, m/e (% rel. int.) 322 (3), 307 (6), 293 (4), 263 (3), 249 (9), 205 (17), 204 (31), 191 (10), 175 (81), 159 (11), 133 (38), 131 (28), 117 (24), 77 (18), 75 (12), 73 (100), 59 (16); 54% yield, 90%

yield based on the amount of $Me_3SiSiMe_3$ obtained.

Hexamethyldisilane NMR (CCl_4) 0.03 (S); GCMS, m/e (% rel. int.) 146 (7), 131 (16), 73 (100), matched with that of authentic sample, 59%.

Reactions of Hexamethylsilarane (**12**) with Cyclooctatetraene (COT)

For all of the following reactions, **12** was trap-to-trap distilled at room temperature and 0.01 Torr into a NMR tube containing an appropriate solution of COT and cooled to -196°C. The contents of the NMR tube were degassed by the freeze-thaw method prior to addition of **12**. Following the addition of **12**, the tube was sealed and then heated at 80-100°C until the presence of **12** was no longer observable by NMR. For all reactions, the identity of tetramethylethylene was established by comparison of its GC retention time and NMR and GCMS spectra with those of authentic sample.

Reaction with neat COT Silarane **12** was added to a solution of 0.137 g of toluene (used as an internal standard) and 0.403 g (3.875×10^{-3} mol) of COT. Relative integration (by NMR) of the methyl signal of toluene to the CMe_2 signal of **12** demonstrated that 0.04066 g (2.86×10^{-4} mol) of **12** had been added. After thermolysis for 15 hours at 85-90°C, analysis by NMR revealed that **12** had completely disappeared. The only identifiable product that was observed by NMR was tetramethylethylene (TME), which by integration relative to the methyl signal of toluene was determined to have been produced in a 90% yield. The NMR also revealed the presence of a weak, broad SiMe absorption between δ 0.01 and 0.3. However, analysis of the reaction by GC revealed the presence of TME as the only observable product. Identical results were obtained when the ratio of COT to **12** was 4:1 rather than 13.5:1 as used above.

*Reaction of **12** with 1/1 (V/V) COT/THF* Silarane **12** was trap-to-trap distilled into an NMR tube containing a solution of 0.3 ml (0.46125 g, 4.44 X 10^{-3} mol) of COT and 0.3 ml of dry THF. The amount of **12** added was determined to be 0.0368 g (2.59 X 10^{-4} mol) by comparison of the NMR integrated peak areas of COT and **12**. After thermolysis at 65-70°C for 24 hours, analysis of the reaction by NMR revealed the presence of TME (partially hidden under THF) as the only identifiable product. With the exception of TME, the only new signals observed by NMR were weak absorptions between δ 0.02 and 0.3. Analysis of the reaction by GC revealed, in addition to TME, the presence of two minor products. By GCMS these compounds were found to be isomeric and consistent with the products expected by addition of Me_2Si: to COT. Thus, both compounds were found by GCMS to have a molecular weight of 162. However, due to the minute quantities of these products (estimated to be present in yields of less than 5% each) it was not found possible to effect their isolation.

*Reaction of **12** with 1/1 (V/V) COT/benzene* Silarane **12** was added to a solution of 0.3844 g (0.25 ml, 3.7 X 10^{-3} mol) of COT and 0.25 ml of freshly distilled benzene. The amount of **12** added was determined to be 0.1166 g (8.21 X 10^{-4} mol) by consideration of the relative NMR peak areas of **12** to benzene. After thermolysis for three hours at 100 to 110°C, analysis of the reaction by NMR revealed that **12** had completely disappeared. By NMR, TME was found to be present in a 92% yield, based on reacted **12**. The NMR also revealed the presence of a number of $SiCH_3$ absorbances (4 singlets and one multiplet) between δ 0.00 and 0.4. By GC and GCMS the reaction mixture was found to contain three products, in addition to TME. These products were isolated by preparative gas chromatography on a 6 ft X 1/4 inch, 30% SE-30/chrom W column at 150°C. The identity of octamethyl-2,5-disilaoxacyclopentane (**145**) was established by comparison of its NMR and GCMS spectra with those previously reported (266). The yield of **145** was determined by NMR by consideration of the relative area of its CMe_2 absorption to that of TME.

Octamethyl-2,5-disilaoxacyclopentane (**145**) NMR (CCl_4) δ 0.05 (S, 12H, $SiMe_2$), 0.82 (S, 12H, CMe_2); GCMS, m/e (% rel. int.) 216 (8), 201 (3), 160 (11), 147 (19), 145 (34), 133 (100), 116 (50), 73 (47), 59 (17), 58 (12); 10.8% yield relative to the amount of TME produced.

The establishment of the identity of the other two products was less straightforward. The spectral data for these products, compound **A** for the one possessing the shorter GC retention time, and compound **B** for the one with the longer GC retention time, (both of which were found to be a mixture of isomers) are presented below.

Compound **A** NMR (CCl_4/D_6-acetone) δ 0.12 (S), 0.16 (S), 0.24 (S), 0.3 (S), all four of these signals had a total relative integration of 6H, 1.35 (m), 1.55 (m), 1.69 (m), 1.85 (m), 2.27 (m), 2.99 (d of m), the total relative integration for the signals at δ 1.35, 1.55, 1.69, 1.85, 2.27, and 2.99 is 2H, 6.0 (m), 6.71 (m), 7.17 (m), the total relative integration for the signals at δ 6.0, 6.71, and 7.17 is 5H; mass spectrum, m/e (% rel. int.) 162 (17), 161 (3), 147 (100), 145 (41), 135 (12), 131 (6), 121 (26), 105 (11), 77 (10), 69 (6), 67 (7), 59 (21), 58 (47), 53 (16), exact mass calculated for $C_{10}H_{14}Si$, m/e 162.08647, measured 162.08653.

Compound **B** NMR (CCl_4) δ 0.03 (S), 0.2 (S), 0.25 (S), 1.23 to 2.35 (overlapping multiplets with a singlet at 2.04), 5.91 (m), 6.13 (d, J = 10Hz), 6.99 (d, J = 10Hz), due to the presence of **145** as a contaminant this sample was not integrated; mass spectrum, m/e (% rel. int.). 162 (47), 147 (100), 145 (53), 135 (19), 133 (13), 121 (21), 105 (13), 77 (12), 59 (28), 58 (28), 53 (16), 51 (10), exact mass calculated for $C_{10}H_{14}Si$, m/e 162.08647, measured 162.08665.

For both compounds, which clearly consist of several isomers, attempts to obtain structural information by double irradiation on either the HA-100 or FX-90 NMRs resulted in no observable clean decoupling.

Attempts to purify compounds **A** and **B** by column chromatography on silica gel resulted in their quantitative decomposition to 1,1-dimethyl-1-sila-2,3-benzosilole (**53**): NMR (CCl_4) δ 0.3 (S, 6H), 6.15 (d, J = 10Hz, 1H), 7.2 (m, 5H); GCMS, m/e (% rel. int.) 160 (33), 147 (24), 145 (100), 143 (13), 119 (12), 117 (10), 105 (10), 77 (12), 73 (12), 59 (11), 58 (19), 53 (26), these spectra matched those previously obtained by Juvet for the same compound (307). It was also found that compound **A** quantitatively decomposed to **53** after standing for two weeks at room temperature in the presence of CCl_4 and D_6-acetone.

Since all of the SiMe NMR signals of **A** and **B** were observable in the NMR of the crude reaction mixture, the combined yields for these compounds relative to TME was determined to be 88.7% by comparison of the weighted NMR peak areas of the SiMe absorptions to that for TME. The relative area of the GC peaks of compound **A** to compound **B** was 3.76:1. Using these values, the combined yield of the isomeric compounds labeled **A** is 70% and those labeled **B** are 18.6%.

Synthesis of Tris(Trimethylsilyl)Methylsilane (15), 2-Chloroheptamethyltrisilane (171), and 1,1-Dichlorotetramethyldisilane (178).

The synthesis of 15 was effected by following the procedure previously described by Smith (308). For the synthesis of 171 and 178, a modification of the procedure of Harrell (309) was employed.

To a vigorously, mechanically stirred suspension of 106 g (15.3 mol) of lithium shot in a solution of 697.5 g (6.4 moles) of trimethylchlorosilane and 2000 ml of dry THF was added 25 ml of 317 g (2.14 mol) of methyltrichlorosilane. After about one hour, the reaction became exothermic. The remainder of the methyltrichlorosilane (diluted with an equal volume of dry THF) was then added dropwise over approximately 5 hours. When the addition was complete, the reaction was stirred at room temperature for 3 days. After the precipitated salts had been allowed to settle, the solution was decanted, hydrolyzed with H_2O, and extracted thrice with hexanes. The organic fractions were combined, dried over Na_2SO_4, and concentrated to afford 354.6 g of a cloudy, yellow oil. Fractionation of the resulting oil gave 184.43 g (0.7 mol, 33% yield) of 15, B.P. 85-87°C at 2.5 Torr, that was found to have identical physical properties (NMR, IR, B.P.) to that previously described by Smith.

From the residue remaining, after distillation of 15, was obtained 136.2 g (0.36 mol, 34% yield) of 1,1,2,2-tetrakis(trimethylsilyl)-1,2-dimethyldisilane by crystallization from 95% EtOH, and which was found to have identical physical properties to that previously prepared by Smith.

Previously, Harrell (309) had prepared 2-chloroheptamethyltrisilane and 1,1-dichlorotetramethyldisilane by reacting previously purified 15 or 1,1,2,2-tetrakis(trimethylsilyl)-1,2-dimethylsilane with either Cl_2 at -23°C or PCl_5 in refluxing CCl_4. However, a more convenient preparation of 171 and 178 involves reacting the previously described and unpurified oil with 456 g (2.20 mol) of PCl_5 in 2000 ml of CCl_4 at 65°C for 12 hours. Distillation of this reaction mixture afforded 111 g (0.6 mol, 28% yield based on starting methyltrichlorosilane) of 178, B.P. 55-60°C at 20-27 Torr, and 79.8 g (0.36 mol, 17% yield based on starting methyltrichlorosilane) of 171, B.P. 80 to 85°C at ca. 0.1 Torr. Both 171 and 178 were found to possess physical properties that were identical to those previously reported by Harrell.

Synthesis of 3-Chloro-2,2,3,5,5-Pentamethyl-2,3,5-Trisilahexane (177)

To a mechanically stirred suspension of 0.45 g (0.065 mol) of lithium dispersion (which was washed thrice with dry Et_2O under an atmosphere of argon prior to use) in 50 ml of dry Et_2O cooled to -23°C under an atmosphere of nitrogen was added rapidly 7.97 g (0.065 mol) of chloromethyltrimethylsilane. When the addition was complete, the reaction was stirred at -23°C for 2 hours. To the reaction mixture was added 10.01 g (0.053 mol) of 1,1-dichlorotetramethyldisilane (178) over a period of approximately 10 minutes. When the addition was complete, the reaction was warmed to room temperature and stirred at room temperature for 3 hours. The solvent was then replaced with hexanes, filtered through celite, and concentrated _en vacuo_. GC analysis of the resulting oil revealed a 1:1

mixture of 177 and unreacted 1,1-dichlorotetramethyldisilane. Trisilane 177, the yield of which was estimated to be 46%, was isolated by preparative gas chromatography on a 10 ft X 1/4 inch, 15% DC550/chrom W column at 140°C and identified on the basis of the following spectral data.

3-chloro-2,2,3,5,5-pentamethyl-2,3,5-trisilahexane NMR (CCl_4) δ 0.1 (d, 20H, both $SiMe_3$ groups and methylene protons), 0.49 (S, 3H); mass spectrum, m/e (% rel. int.) 238 (2), 223 (18), 165 (15), 145 (19), 130 (100), 115 (58), 73 (68), 44 (19), exact mass calculated for $C_8H_{23}Si_2Cl$, m/e 238.07962, measured 238.07821.

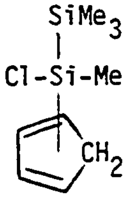
Vertical Flow Pyrolysis of 177

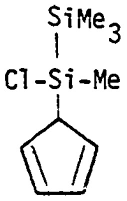
The pyrolysis of 0.97 grams of 177 is carried out by dropping it through a vertical quartz tube that is packed with quartz chips and heated to 600°C and through which a nitrogen carrier gas is passed at 30 ml/minute. The pyrolysate was collected in a liquid nitrogen trap and represented a 54% mass recovery. GC analysis indicated that all starting material was gone and that only two products were cleanly formed. These were isolated by preparative GC on a 10' X 1/4" 15% DC-550 on Chromsorb W column at 70°C. The more volatile product was identified as trimethylchlorosilane (48% GC yield) by comparison of its spectra with those from an authentic sample. The other product was identified as 1,1,3-trimethyl-1,3-disilacyclobutane 94 (39% GC yield) on the basis of its spectra: NMR (CCl_4) δ = -0.12 (m, 4H), δ = 0.06 (s, 6H), δ = 0.12 (d, 3H, J = 4.0 Hz, collapses to singlet upon hν at δ = 4.43), δ = 4.43 (m, 1H, J = 4.0 Hz, collapses to quartet upon hν at δ = -0.12); the GC mass spectrum is identical to that in the literature (98).

Synthesis of 1-Cyclopentadienyl-1-Methoxytetramethyldisilane (182)

To a stirred solution 3.5 g (0.0529 mol) of freshly cracked cyclopentadiene and 25 ml of dry THF cooled to -78°C and under an atmosphere of nitrogen was added rapidly a solution of *n*-butyllithium (33 ml, 1.6 M, 0.0528 mol) in hexane. When the addition was complete, the reaction was warmed to room temperature and stirred at room temperature for one hour. The flask was then cooled to -78°C, after which 10 g (0.0534 mol) of 1,1-dichlorotetramethyldisilane was added rapidly by syringe. When the addition was complete, the reaction was warmed to room temperature and stirred at room temperature for about 12 hours. The solvent was then removed *en vacuo* and the resulting residue was taken up in hexane. The procedure of *en vacuo* removal of the volatiles followed by uptake of the resulting residue in hexane was repeated twice more to assure complete removal of the THF. The resulting hexane solution, which contained a large amount of salts, was then filtered through a cake of celite. A small portion of filtrate was then taken and the solvent was removed *en vacuo*. From the resulting residue was isolated, by preparative gas chromatography on a 12 ft X 1/4 inch, 15% SE-30/chrom W column at 150°C, 1-chloro-1-cyclopentadienyltetramethyldisilane (183) as a mixture of isomers:

183b





183a

NMR (CCl_4) (**183b**) δ 0.11 (S, 9H, $SiMe_3$), 0.54 (S, 3H, SiMe), 3.09 (m, 2H, cyclopentadienyl methylene protons), 6.13 (m, cyclopentadienyl vinylic protons, overlapped with those of **183a**); (**183a**) δ 0.05 (S, 9H, $SiMe_3$), 0.26 (S, 3H, SiMe), 6.13 (m, cyclopentadienyl vinylic protons, overlapped with those of **183b**). The methine H of **a** could not be observed due to overlapping Si-CH_3 resonances. Based on the relative areas of the signals at δ 0.05 and 0.26 to those at δ 0.11 and 0.54, the ratio of **a** to **b** was determined to be 1.4:1. From this value the relative area of the signals at δ 3.09 and 6.31 to the Si-CH_3 signals (assuming also a contribution from the methine proton of **a**) was calculated to be 1 to 2.849, found 1 to 2.857. Mass spectrum: isomer **b**, m/e (% rel. int.) 218 (8) (parent +2), 216 (14), 203 (3), 201 (8), 181 (7), 153 (8), 151 (17), 143 (9), 123 (49), 122 (21), 108 (31), 93 (100), 73 (90), 65 (9), 63 (10); isomer **a**, m/e (% rel. int.) 218 (1.9) (parent +2), 216 (3.4), 203 (10), 201 (25), 181 (100), 153 (15), 151 (40), 123 (18), 93 (12), 73 (6).

To the remainder of the hexane solution of **183** was added equal molar amounts of excess dry pyridine and excess dry methanol. The resulting mixture was stirred for 3 hours at room temperature, filtered through celite, wash trice with H_2O, and dried over $MgSO_4$. Fractional distillation of the resulting solution afforded 5.0 g (0.023 mol, 44% yield) of **182** as a clear colorless liquid, B.P. 73-76°C at 24 Torr, which was identified on the basis of the following spectral data, again as a mixture of isomers: NMR (CCl_4) δ 0.02 (unsymmetrical d, overlapping $SiMe_3$ signals of both isomers and SiMe signal of major isomer), 0.3 (S, SiMe of minor isomer), 3.1 (m, cyclopentadienyl methylene protons of minor isomers), 3.41 and 3.51

(S, OMe signals of minor and major isomers, respectively, relative integration equals 1:1.9), 6.4 (broad m, cyclopentadienyl vinylic protons). By consideration of the relative area of the methylene signal at δ 3.1 to those of the methoxyl signals at δ 3.41 and 3.51 (relative area of δ 3.1 to 3.41 = 2:3; relative area of δ 3.1 to 3.51 = 2:6) the minor isomer was determined to be that with the disilanyl group connected to a vinyl cyclopentadiene carbon. From the relative area of the two methoxyl signals the isomer ratio was found to be 1.9:1. Using this value, the relative area of the signals at δ 6.4 and 3.1 (cyclopentadienyl protons) to those at δ 3.51 and 3.41 (methoxyl protons) to those at δ 0.3 and 0.02 ($Si-CH_3$ protons plus methine proton of major isomer) was calculated to be 1.45:1:4.22, found 1.76:1:4.26. Mass spectrum, m/e (% rel. int.) 212 (7.5), 197 (36), 147 (78), 139 (40), 117 (50), 109 (22), 93 (63), 89 (30), 73 (97), 59 (100), exact mass calculated for $C_{10}H_{20}Si_2O$, m/e 212.10526, measured 212.10535.

Vertical Flow Pyrolysis of **182**

The pyrolysis was conducted by adding **182** mechanically at a rate of 2.2 ml/hour to a vertical one foot quartz tube filled with quartz chips and enclosed in a tube furnace. The pyrolysate was swept through the tube with a nitrogen flow of approximately 30 ml/min. into a cold trap cooled to -196°C. At 300°C, the pyrolysate was found by NMR and GC to be identical to **182**, thus demonstrating that no decomposition occurred at this temperature. At 580°C, all of the starting disilane was found to have decomposed. Analysis of this pyrolysate by NMR revealed the presence of Me_3SiOMe as the only observable product in addition to small signals at δ 0.98 (m), 6.55 (m), and 7.36 (s). On the basis of relative integration of the observable signals, Me_3SiOMe accounted for greater than 90% of the pyrolysate. The identity of Me_3SiOMe was established on the basis of the following spectral data: NMR (CCl_4) 0.06 (S, 9H), 3.4 (S, 3H), identical to that of an authentic sample; GCMS, m/e (% rel. int.) 104 (2.7), 90 (37), 89 (100), 60 (30), 59 (84), 58 (27), 45 (36). After en vacuo removal of the volatiles, NMR analysis of the residue revealed broad, unidentifiable absorptions between δ -0.5 and 1.5 and 6.45 and 7.7 in addition to a broad multiplet centered at δ 3.49. Analysis of this residue by GCMS revealed the presence of greater than 20 compounds, none of which were major. Due to the plethora of products, no attempt was made to effect their isolation and characterization. Based on the assumption that this plethora of products was due to secondary thermal reactions, the pyrolysis was repeated at 380°C under otherwise identical conditions. Analysis of this pyrolysate by GC and NMR revealed the presence of Me_3SiOMe and unreacted **182** (10%) as the only observable products.

Copyrolysis of **182** with Benzaldehyde

A solution of 0.26 g (0.00123 mol) of **182** and 0.57 g (0.00538 mol) of benzaldehyde (molar ratio of 1:4.4) was pyrolyzed under otherwise identical conditions as described above at 500°C with the exception that following pyrolysis the quartz tube was cooled to room temperature and washed with CCl_4. Thus, two separate pyrolysates were obtained: A, the pyrolysate condensed in a cold trap at -196°C, and B, the pyrolysate obtained from the CCl_4 washing of the tube followed by en vacuo removal of the CCl_4. Analysis of the NMR spectrum of pyrolysate A revealed benzaldehyde to be the major component by comparison with a NMR of authentic material. In addition, major signals at δ 7.23 (S, overlapped by benzaldehyde and broadened at the base line), 3.13 (S, OCH_3), -0.05 (S, broadened at the base line, $Si-CH_3$), and smaller signals at δ 5.29 (s), and 3.27 (s) were found. Initially, the signals at δ 3.13 and -0.05 were attributed to Me_3SiOMe. However, from GCMS analysis of the pyrolysate it was determined that the major components of the pyrolysate were, in addition to benzaldehyde, hexamethyldisiloxane, and the dimethylacetal of benzaldehyde. No attempts were made to isolate any of the compounds in pyrolysate A. However, from the NMR and GCMS data obtained the identities of benzaldehyde, hexamethyldisiloxane and phenyldimethoxymethane were established.

Benzaldehyde NMR (CCl_4) δ 7.5 and 7.79 (m, aromatic protons), 9.97 (S, aldehydic proton), identical to spectrum of an authentic sample; GCMS, m/e (% rel. int.) 106 (100), 105 (98), 77 (98), 51 (50), matched with spectrum of authentic sample.

Hexamethyldisiloxane NMR (CCl_4) δ -0.05 (S); GCMS, m/e (% rel. int.) 162 (0.02) (parent ion), 147 (100) (parent $-CH_3$), 131 (15), 73 (40), 66 (30), 59 (26), 52 (13), 45 (25), matched with that of an authenic sample.

Phenyldimethoxymethane NMR (CCl_4) δ 3.13 (S, 6H), 5.29 (S, 1H, methine proton), 7.23 (S, broadened at base line, was not integrated due to partial overlap with benzaldehyde); GCMS, m/e (% rel. int.) 152 (3), 151 (2), 121 (100) (parent $-OCH_3$), 105 (17), 91 (35), 77 (49), 75 (25), 51 (27).

In addition to the previous two major products, greater than 16 other minor compounds were observed by GCMS. Of these, only benzene and toluene could be identified.

Analysis of pyrolysate B by NMR also revealed the presence of benzaldehyde. Additionally, broad signals at δ 0.01 and 7.11 were observed. From the GCMS of pyrolysate B, greater than 12 compounds were found to be present, none of which were major and many of which (on the basis of their mass spectrum) did not contain silicon. Due to the number of products present, no attempt was made to effect their isolation and characterization.

Copyrolysis of 182 and Triethylsilane

Copyrolysis of 0.4 g (0.0019 mol) of 182 and 0.6 g (0.0052 mol) of triethylsilane at 400°C, utilizing the same procedure as employed above, afforded a pyrolysate containing approximately 80% unreacted 182. At 480°C, copyrolysis of 0.12 g (5.7×10^{-4} mol) of 182 and 0.38 g (3.28×10^{-3} mol) of triethylsilane led to the complete decomposition of the starting disilane. By GC, the pyrolysate was found to contain (in addition to Et_3SiH) three main products that were identified as hexamethyldisiloxane, octamethyltrisiloxane, and the Diels-Alder dimer of cyclopentadiene solely on the basis of their GCMS spectra.

Hexamethyldisiloxane GCMS, m/e (% rel. int.) 147 (100) (parent - Me), 73 (30), 66 (18), 59 (17).

Octamethyltrisiloxane GCMS, m/e (% rel. int.) 221 (23) (parent - Me), 191 (7), 147 (6), 117 (4), 73 (100), 59 (5), matched with spectrum of authentic sample.

Dicyclopentadiene GCMS, m/e (% rel. int.) 132 (4.4), 117 (1.2), 91 (1.7), 78 (1.8), 77 (2.5), 66 (100), 51 (5).

Copyrolysis of 182 and Acetylene

Disilane 182 was added mechanically to a one foot quartz tube filled with quartz chips as described above with the exception that acetylene, at a flow rate of 60 ml/minute, was used as the carrier gas, rather than nitrogen. Prior to its entry into the pyrolysis tube the acetylene was purified by first passing through a one foot X 2 cm tube filled with basic alumina, then through concentrated H_2SO_4, and finally through a two foot X 5 cm tube filled with alternating layers of Drierite and NaOH pellets. The pyrolysis tube was preconditioned for at least 15 minutes at the requisite temperature with a N_2 flow at 100 ml/minute prior to the admission of acetylene to the tube. Acetylene was allowed to pass through the tube for about 3 minutes before the addition of 182 was begun. At a temperature of 400°C, essentially no decomposition of 182 occurred. At 500°C, 182 was found to completely decompose. Analysis of this latter pyrolysate by gas chromatography and GCMS revealed the presence of two major products, hexamethyldisiloxane and benzene, which together accounted for about 85% of the pyrolysate. The presence of more than 10 other products, none of which were major, was observed by GCMS. Of these, decamethyltetrasiloxane and dodecamethylpentasiloxane were identified on the basis of their mass spectra.

Decamethyltetrasiloxane GCMS, m/e (% rel. int.) 295 (10) (parent -

Me), 207 (56), 73 (100).

Dodecamethylpentasiloxane GCMS, m/e (% rel. int.) 369 (1.4) (parent - Me), 221 (40), 147 (24), 73 (100).

Due to the low yield of these two products (estimated to be less than 5% each), no effort was made to effect their isolation and unambiguous characterization.

The most important result of this reaction is that none of the products were found by GCMS to be consistent with acetylene **191**, the expected product of the reaction of cyclopentadienylmethylsilylene with acetylene.

Vacuum Flow Pyrolysis of 182

Disilane **182** was distilled at room temperature and 1 X 10^{-4} Torr into a one foot quartz tube filled with quartz chips and enclosed in a tube furnace heated at 780°C. The pyrolysate was condensed into a cold trap cooled to -196°C. Analysis of the crude pyrolysate by NMR revealed the presence of Me_3SiOMe (estimated to account for >90% of the pyrolysate) as the only observable product. *En vacuo* removal of Me_3SiOMe from the pyrolysate and analysis of the resulting residue by NMR disclosed broad, unidentifiable absorptions between δ -0.1 and 0.9, 3.1 and 3.8, and 5.5 and 7.8. Due to the similarity of these results to those of the vertical flow pyrolysis of **181** at 580°C (*vide supra*) no further effort was expended on this reaction.

Vacuum Flow Pyrolysis of 183

Disilane **183** was pyrolyzed at 810°C under otherwise identical conditions to those employed for the vacuum flow pyrolysis of **182** (see preceding paragraph). The NMR spectrum of the pyrolysate displayed a strong singlet at δ 0.37 which was identified as Me_3SiCl by comparison to the NMR spectrum of an authentic sample. Further conformation of this assignment was provided by the observation that the GC retention time of the major product of the reaction matched that of authentic Me_3SiCl. This assignment was further confirmed by GCMS analysis. In addition to Me_3SiCl, the NMR spectrum of the pyrolysate also revealed the following weak signals: δ 1.22 (m), 2.9 (m), 5.8 (m), 6.5 (m), 7.3 (S). Consideration of the areas of these signals to that of Me_3SiCl indicated that Me_3SiCl accounted for approximately 80% of the pyrolysate. This estimate was also found to agree with the relative peak areas observed upon GC analysis of the pyrolysate.

Analysis of the pyrolysate by GCMS revealed, in addition to Me_3SiCl, the presence of a number of other products (greater than 10) of which three were identified on the basis of their mass spectrum. Due to the low yields of these other products (estimated to be no greater than 5% each), no attempt was made to effect their isolation. These compounds and their mass spectral data are given below.

Tetrachloroethene GCMS, m/e (% rel. int.) 170 (10) (parent +6), 168 (48) (parent +4), 166 (100) (parent +2), 164 (80) (parent), 133 (25), 131 (78), 129 (82) (parent - Cl), 96 (28), 94 (43), matched with that of authentic sample.

Trimethylsilylcyclopentadiene GCMS, m/e (% rel. int.) 138 (14), 123 (23), 95 (17), 73 (100).

Phenyltrimethylsilane GCMS, m/e (% rel. int.) 150 (10), 135 (100), 105 (7), matched with that of authentic sample.

Synthesis of 2-Cyclopentadienylheptamethyltrisilane (193)

To a stirred solution of 0.963 g (0.0146 mol) of freshly cracked cyclopentadiene and 50 ml of dry THF, cooled to -78°C and under an atmosphere of nitrogen, was added a solution of n-butyllithium (9.11 ml, 1.6 M, 0.0146 mol) in hexane. After stirring for 15 minutes, 2.41 g (0.0095 mol) of 2-chloroheptamethyltrisilane was added with stirring to the resulting suspension. When the addition was complete, the reaction was allowed to warm to room temperature and was maintained at room temperature for 12 hours. The reaction mixture was then hydrolyzed with H_2O and extracted twice with hexanes. The organic fractions were combined, dried over Na_2SO_4, and concentrated en vacuo (0.01 Torr at 25°C for 12 hours) to afford 2.41 g of a clear, pale yellow oil that by G.C. and NMR was greater than 75% 193. Preparative gas chromatography on a 5 ft X 1/4 inch, 20% SE-30/chrom W column at 175°C afford pure 193: NMR (CCl_4) δ 0.01 (d, 21H) 2.9 (m, 1H), 5.51 to 6.75 (m, 4H); IR (film) 3061 (W), 2942, 2890, 1235, 1040 (W), 1040 (W), 820, and 767 cm^{-1}; mass spectrum, m/e (% rel. int.) 254 (12), 195 (19), 181 (47), 180 (15), 166 (12), 165 (63), 131 (17), 123 (12), 116 (12), 93 (11), 73 (100), exact mass calculated for $C_{12}H_{12}Si_3$, m/e 254.134242, measured 254.134241.

Photolysis of 193

A solution of 0.252 g (9.9×10^{-4} mol) of 193 and 5 ml of cyclohexane was placed in a septum sealed quartz tube and deoxygenated by bubbling argon through the tube for 15 minutes. After irradiation for 20 hours at approximately 45°C with a 450 W, 679 A Hanovia lamp, analysis of the photolysate by GC and GCMS revealed the presence of $Me_3SiSiMe_3$, unreacted **193**, and greater than 10 other minor products. Of the minor products, 1,1,1,2,3,3,3-heptamethyltrisilane and 2-trimethylsilylheptamethyltrisilane were identified by GCMS.

1,1,1,2,3,3,3-heptamethyltrisilane GCMS, m/e (% rel. int.) 190 (19), 175 (13), 117 (11), 116 (40), 102 (41), 101 (18), 73 (100), 59 (13), 45 (20), 43 (13).

2-trimethylsilylheptamethyltrisilane GCMS, m/e (% rel. int.) 262 (11), 189 (15), 174 (38), 173 (13), 159 (13), 131 (17), 129 (14), 115 (10), 73 (100), 45 (18), matched that of authentic sample.

With the exception of $Me_3SiSiMe_3$, $(Me_3Si)_2SiMeH$, $(Me_3Si)_3SiMe$, and **193**, none of the other products of this reaction could be identified. Of particular significance is the fact that the dimers of either **180** or **181** were shown by GCMS not to be products of this reaction.

Synthesis of 3-Chloro-3,4,4-Trimethyl-3,4-Disila-1-Pentene (**201**) and its Methoxyl Derivative (**205**)

To a stirred solution of 4.04 g (0.0216 mol) of 1,1-dichlorotetramethyldisilane and 10 ml of dry THF, under an atmosphere of nitrogen and cooled to 0°C, was added over 5 minutes a solution of vinylmagnesium chloride (18 ml, 1.2 M, 0.0216 mol) in THF. When the addition was complete, the reaction was allowed to warm to room temperature, after which it was stirred at room temperature for 5 hours. The solvent was then removed *en vacuo* and the resulting residue, which contained a substantial amount of precipitated salts, was taken up in hexane. The procedure of *en vacuo* removal of solvent followed by uptake of the residue in hexane was repeated twice more to assure complete removal of the THF. Finally, the hexane solution of 201 and suspended magnesium salts was filtered through a cake of celite. The solvent was then removed *en vacuo* to afford 2.33 g of a clear, pale yellow-green reaction mixture. Analysis by GCMS revealed the presence of small amounts of the unreacted starting disilane (178) and 1,1-divinyltetramethyldisilane in addition to the desired product, 201. By GC, using *t*-butylbenzene as a standard, the yield of 201 was determined to be 42%. It was not possible to purify 201 by fractional distillation due to the similarity of the boiling points of 201, 1,1-dichlorotetramethyldisilane, and 1,1-divinyltetramethyldisilane. However, 201 could be isolated by preparative gas chromatography on a 12 ft X 1/4 inch, 20% SE-30/chrom W column at 150°C, although in yields of only about 17%. In repetitive synthesis the isolated yield of 201 varied from a low of 1.5% to a high of 25%. The identity of 201 was established on the basis of the following spectral data: NMR (CCl_4) δ 0.17 (S, 9H), 0.5 (S, 3H), 6.08 (m, 3H); IR (CCl_4) 3050, 2945, 2890, 1395, 1237, 1050, 990, 948, 850, 825, and 710 cm^{-1}; mass spectrum, m/e (% rel. int.) 180 (0.9), 178 (2.4) (parent ion), 165 (2.2), 163 (4.6), 155 (38), 85 (69), 73 (100); exact mass calculated for $C_6H_{15}Si_2Cl$, m/e 178.04007, measured 178.04013; exact mass calculated for $C_5H_{12}Si_2Cl$ (Parent minus methyl), m/e 163.01661, measured 163.01654.

1,1-divinyltetramethyldisilane (204) NMR (CCl_4) δ 0.11 (S, 9H), 0.21 (S, 3H), 6.17 (m, 6H); GCMS, m/e (% rel. int.) 170 (0.2), 155 (100), 129 (13), 127 (22), 116 (15), 97 (25), 95 (29), 85 (59), 83 (13), 73 (97), 71 (48), 69 (11), 59 (68), 55 (17), 45 (52).

The methoxyl derivative of 201 was prepared by treating the initially obtained hexane solution of 201 (after removal of the magnesium salts) with excess trimethyl orthoformate, followed by stirring the resulting solution for 3 days at room temperature. The hexane solution was then washed trice with H_2O and dried over $MgSO_4$. After removal of the solvent en vacuo, 205 was isolated (12% yield) by preparative gas chromatography on a 5 ft X 1/4 inch, 20% FX-1150/chrom W Column at 80°C.

3-Methoxy-3,4,4-trimethyl-3,4-disila-1-pentene (205) NMR (CCl_4) δ 0.1 (S, 9H), 0.22 (S, 3H), 3.35 (S, 3H), 5.99 (m, 3H); GCMS, m/e (% rel. int.) 174 (20), 173 (26), 159 (86), 146 (16), 133 (60), 133 (60), 131 (49), 129 (23), 119 (32), 117 (22), 101 (66), 99 (18), 89 (66), 85 (33), 75 (51), 73 (87), 71 (32), 59 (100), 45 (58).

Vertical Flow Pyrolysis of 201

The pyrolysis was conducted in a vertical one foot quartz tube filled with quartz chips and enclosed in a tube furnace thermostated at 600°C. Disilane 201 (0.396 g, 0.0022 mol) was mechanically added at a rate of 2.2 ml/hour concomitant with a nitrogen flow of 30 ml/minute. The pyrolysate was collected in a liquid nitrogen trap and represented a 49% mass recovery. Analysis of the pyrolysate by GC revealed the presence of two major compounds. The compounds were isolated by preparative gas chromatography on a 12 ft X 1/4 inch, 20% SE-30/chrom W column at 140°C and identified as trimethylchlorosilane and unreacted **201** on the basis of their NMR spectra and comparison of their GC retention times with those of authentic samples. Unreacted **201** accounted for approximately 80% of the pyrolysate. At 660°C, under otherwise identical reaction conditions, all of the starting disilane was found by GCMS to have decomposed. However, the pyrolysate was found to contain greater than 50 compounds, from which only trimethylsilane and trimethylvinylsilane could be identified on the basis of GCMS. Due to the plethora of compounds in the pyrolysate, no effort was made to effect their isolation and characterization.

Vacuum Flow Pyrolysis of **201**

Disilane **201** was distilled at room temperature and 4 X 10^{-4} Torr into a horizontal quartz tube filled with quartz chips and enclosed in a tube furnace. The pyrolysate was collected in a cold trap cooled to -196°C. Typically, the pyrolysate represented 45-55% mass recovery. With the temperature at 660°C, unreacted **201** accounted for greater than 85% of the pyrolysate as estimated by NMR. At a temperature of 800°C, the presence of **201** was no longer observed by NMR. However, GC analysis of the pyrolysate showed **201** to be present in about a 5% yield. Since by GC the major products of the reaction were volatiles, the volatiles were separated from the rest of the pyrolysate by trap-to-trap distillation at room temperature and 0.05 Torr into an NMR tube cooled to -196°C. Analysis of the volatiles by GCMS revealed the presence of 5 compounds: trimethylsilane, methylethynylsilane (**200**), dimethylethynylsilane (**203**), trimethylvinylsilane (**202**), and trimethylchlorosilane. The yields of **200**, **202** and Me_3SiCl were determined by relative integration of the vinyl protons of **202**, the Si-H and acetylenic protons of **200**, and the methyl protons of Me_3SiCl to the methylene protons of a known amount of added bibenzyl. For all four compounds, the requisite signals were separated from one another and were not contaminated by signals due to the other two products. Since trimethylsilane and dimethylethynylsilane were only observable by GCMS their yields were estimated to be less than 3%.

Trimethylsilane GCMS, m/e (% rel. int.) 74 (4), 73 (39), 59 (78), matched with a spectrum of authentic sample.

Dimethylethynylsilane GCMS, m/e (% rel. int.) 84 (27), 83 (26), 69 (91), 58 (100), 53 (38).

Methylethynylsilane (**200**) NMR (CCl_4) $Si-CH_3$ is hidden under the silicon methyls of the other products, δ 2.27 (t, 1H, J = 1Hz, collapses to a singlet upon $h\nu$ at δ 3.97), 3.97 (quartet of doublets, 2H, J = 4.5Hz, J = 1Hz, collapses to a quartet upon $h\nu$ at δ 2.27), spectrum identical to that of an authentic sample; mass spectrum, m/e (% rel. int.) 70 (27), 69 (24), 68 (7), 55 (100), 54 (17), 53 (42), matched with a spectrum of authentic sample; 11.9% yield based on reacted **201**, 39.3% yield based on Me_3SiCl formed.

Trimethylchlorosilane NMR (CCl_4) δ 0.43 (S); GCMS, m/e (% rel. int.) 110 (1.6), 108 (4.6) (parent ion), 95 (51), 93 (100), 85 (18), 73 (46), 65 (24), 63 (20), 59 (14), matched with spectrum of authentic sample; 30.3% yield based on reacted **201**.

Trimethylvinylsilane (**202**) NMR (CCl_4) δ 0.05 (S, 6H), 5.98 (m, 3H), spectrum identical to that of an authentic sample; mass spectrum, m/e (% rel. int.) 100 (7), 85 (100), 73 (14), 59 (87), matched with spectrum of authentic sample; 11.6% yield based on reacted 201.

Analysis of the pyrolysate, after *en vacuo* removal of the volatiles, revealed the presence of greater than 10 compounds, from which only unreacted 201 could be isolated.

Synthesis of Ethynylmethylsilane (200)

To 100 ml of THF at 0°C that was saturated with acetylene was added 0.216 moles of ethylmagnesium bromide in THF. Acetylene was bubbled through the solution during addition and the resulting ethynyl Grignard solution was added to a solution of 0.60 moles of $MeSiCl_3$ in 200 ml of THF at 0°C. The solution was stirred for a few hours at room temperature, then 150 ml of toluene was added and all of the volatiles collected up to 110°C. These volatiles were redistilled through a 25 cm column packed with glass helices and a fraction collected from 75-85°C that by NMR was a mixture of 4.4 grams (15%) of methyldichloroethynylsilane and 1.8 grams of THF. This fraction had the following spectral absorptions due to methyldichloroethynylsilanes: NMR (CCl_4) $\delta = 0.93$ (s, 3H), $\delta = 2.90$ (s, 1H); IR (CCl_4) 3280, 3190 and 2040 cm^{-1}.

A solution of 1.45 grams of the fraction, 3 ml of THF and 0.27 grams of lithium aluminum hydride was mixed at 0°C in a flask that was connected via a closed system to an NMR tube containing CCl_4 at -78°C. After 2 hours, 0.5 ml of water was added via septum, and after the pressure was released, the flask was warmed to 40°C. Ethynylmethylsilane was collected in the NMR tube over a period of 4 hours and the following spectra obtained: NMR (CCl_4) δ = 0.35 (t, 3H, J = 4.5 Hz, collapses to a singlet upon $h\nu$ at δ = 4.05), δ = 2.35 (t, 1H, J = 1 Hz, collapses to a singlet upon $h\nu$ at δ = 4.05), δ = 4.05 (quartet of doublets, 2H, J = 4.5 Hz, J = 1 Hz, collapses to quartet upon $h\nu$ at δ = 2.35); IR (CCl_4) 3295, 2970, 2155, 2025 (weak), 1250, 1060, 940, 890, 700, 670 and 600 cm^{-1}; GC mass spectrum (70 eV) m/e (% rel. int.) 70 (38), 69 (33), 68 (10), 55 (100), 54 (25), 53 (60), 45 (27), 44 (54), 43 (40).

Synthesis of 3-*t*-Butoxy-3,4,4-Trimethyl-3,4-Disila-1-Pentene **206**

To a stirred solution of 10.01 g (0.0538 mol) of 1,1-dichlorotetramethyldisilane and 30 ml of dry THF at 0°C and under an atmosphere of N_2 was added over approximately 5 minutes a solution of vinylmagnesium bromide (49 ml, 1.1 *M*, 0.0538 mol) in THF. When the addition was complete, the reaction was allowed to warm to room temperature and was stirred at room temperature for 5 hours. The THF solvent was then replaced with hexane and the resulting hexane solution, which contained large amounts of precipitated salts, was filtered through celite. To the resulting filtrate was added, with stirring, 4.3 g (0.0538 mol) of dry pyridine followed by 4.0 g (0.0538 mol) of dry *t*-butanol. When the additions were complete, the reaction was stirred at room temperature for 24 hours. The reaction mixture was then hydrolysed with H_2O. The organic phase was collected by extraction, washed twice with H_2O, once with sat. aqueous NaCl, and dried over Na_2SO_4. *En vacuo* removal of the solvent afforded 6.9 g of a clear, yellow liquid which by GC (using *t*-butylbenzene as a standard) was found to contain 1.23 g (0.0057 mol, 11% yield) of 206. Disilane 206 was isolated by preparative gas chromatography on a 10 ft X 1/4 inch, 20% SE-30/chrom W column at 150°C. The identity of 206 was established on the basis of the following spectral data: NMR (CCl_4) δ 0.11 (S, 9H, $SiMe_3$), 0.32 (S, 3H, SiMe), 1.31 (S, 9H, CMe_3), 6.12 (m, 3H); GCMS, m/e (% rel. int.) 201 (5.4) (parent - Me), 160 (60) (parent - $Me_2C{=}CH_2$), 159 (74) (parent - CMe_3), 145 (49), 143 (29), 133 (19), 132 (22), 131 (28), 129 (22), 119 (28), 117 (14), 87 (100), 85 (41), 75 (44), 73 (60), 61 (55), 59 (48), 57 (57), 45 (45).

The major product of this reaction was determined by NMR and GCMS to be 1,1-divinyltetramethyldisilane, whose yield was not determined.

Copyrolysis of 206 and Triethylsilane

A solution of 0.157 g (7.24 X 10^{-4} mol) of disilane 206 and 0.503 g (4.34 X 10^{-3} mol) of triethylsilane was added mechanically at the rate of 2.2 ml/hour concomitant with a nitrogen flow of 30 ml/minute to a one foot quartz tube filled with quartz chips and enclosed in a tube furnace thermostated at 560°C. The pyrolysate was condensed in a cold trap cooled to -196°C and represented a 56% mass recovery. On the basis of GC analysis, Et_3SiH was estimated to accounted for greater than 85% of the pyrolysate. Analysis of the pyrolysate by GCMS revealed the presence of three silicon containing compounds, trimethylvinylsilane, hexamethyldisiloxane, and unreacted disilane 206, all of which were identified by comparison of the mass spectral data with those of authentic samples.

Attempted Synthesis of 1-Phenyl-3-Methoxy-3-(Trimethylsilyl)-3-Sila-1-Thiabutane (207)

a) Following the method of Corey and Seeback (310), the anion of thioanisole was prepared by the addition of a solution of *n*-butyllithium (17 ml, 2.4 M, 4.08 X 10^{-2} mol) in hexanes to a stirred solution of 4.80 g (0.0387 mol) of thioanisole, 4.34 g (0.0387 mol) of DABCO, and 150 ml of dry THF under an atmosphere of argon and cooled at 0°C. When the addition was complete, the reaction was stirred at 0°C for 2 hours. Disilane 178, 7.60 g (0.041 mol), was then added rapidly by syringe. When this addition was complete, the stirred reaction was warmed to room temperature and maintained at room temperature for 18 hours. To this mixture was then added 4 ml (0.05 mol) of dry pyridine followed by 2 ml (0.05 mol) of dry methanol. This mixture was then stirred for 14 hours at room temperature. The solvent was then replaced with hexanes and the resulting solution was filtered through a cake of celite to remove the precipitated salts. After *en vacuo* removal of the solvent, chromatography of the resulting residue afforded 3.9876 g (0.01 mol, 53% yield based on starting thioanisole) of 1,5-diphenyl-3-methyl-3-(trimethylsilyl)-3-sila-1,5-dithiapentane as the only isolable product: NMR (CCl_4) δ 0.22 (S, 9H, $SiMe_3$), 0.30 (S, 3H, SiMe), 2.32 (S, 4H, SCH_2), 7.1 (S, broadened at the base line, 10H).

b) In a modification of the above reaction, the THF solution of the anion of thioanisole at 0°C and under an atmosphere of argon was added over 2 hours to a stirred solution of 7.5 g (4.0 X 10^{-2} mol) of 178 and 15 ml of dry THF at 0°C and under an atmosphere of argon. When the addition was complete, the reaction was warmed to room temperature and stirred at room temperature for 18 hours. Following treatment with pyridine and methanol as described above, workup as before afforded 11.6 g of a viscous yellow oil. Vacuum distillation of this residue afford two fractions, B.P. 35-40°C at 0.2 Torr (1.853 g), and B.P. 73-97°C at 0.2 Torr (1.676 g), that were not identified, but, which by NMR were deomonstrated not to be the desired **207**. Chromatography of the residue, following distillation, on silica gel afforded 3.003 g (8.3×10^{-3} mol, 42% yield based on starting thioanisole) of **208** as the only isolable product.

Synthesis of 1-Methyl-1-Vinyl-2,3,4,5-Tetraphenylsilacyclopenta-2,4-Diene (**210**)

A modification of the method of Balasubramanian and George (290) was used for this reaction. To a stirred suspension of 0.2438 g (0.0351 mol) of lithium shot in 200 ml of dry Et_2O under an atmosphere of argon was added rapidly 6.256 g (0.0351 mol) of tolan. After stirring for one hour at room temperature, the reaction began to take on a red color. The reaction was stirred for 15 hours at room temperature following the first observation of the red color. A solution of 2.475 g (0.0176 mol) of methylvinyldichlorosilane and 150 ml of dry THF was then added over 10 minutes to the stirred reaction solution. When the addition was complete, the reaction was stirred at room temperature for approximately 2 hours. The resulting yellow-green solution was then poured onto crushed ice and the organic phase was extracted, washed twice with H_2O, and dried over $MgSO_4$. After en vacuo removal of the solvent, the residue was crystallized from CH_2Cl_2/hexane to afford impure **210** (M.P. 98-110°C). The resulting crystals were then chromatographed on florasil with hexane elution followed by $CHCl_3$ elution to afford 1.90 g (0.00445 mol, 25% yield) of crystalline 210, M.P. 172-174°C (lit. (290) 177-178°C): NMR (CCl_4) δ 0.55 (S, 3H), 6.25 (m, 3H), 7.04 (m, 20H); IR (CCl_4) 3080, 3060, 3021, 2950, 1595, 1485, 1440, 1402, 1295, 1250, 1085, 1072, 1025, 1000, 952, 935, 910, 860, and 690 cm^{-1}; mass spectrum, m/e (% rel. int.) 426 (100), 358 (19), 268 (16), 249 (18), 248 (71), 247 (13), 233 (25), 199 (24), 179 (16), 167 (30), 166 (22), 165 (20), 105 (26), 57 (41), 56 (30), 41 (28), exact mass calculated for $C_{31}H_{26}Si$, m/e 426.18038, measured 426.17984.

Synthesis of 7-Methyl-7-Vinyl-1,2,3,4,5-Pentaphenyl-7-Silanorbornadiene (209)

Silole 210 (1.90 g, 4.45 X 10^{-3} mol) and 0.93 g (9.11 X 10^{-3} mol) of phenylacetylene were placed in an evacuated sealed tube and heated at 150°C for 10 hours. The resulting residue was then placed in a flask attached to a vacuum line and evacuated at 0.05 Torr and room temperature for about three hours to remove the excess phenylacetylene. Attempts to recrystallize the resulting residue from CH_2Cl_2/hexane or Et_2O/hexane gave only oils. Crystals were obtained from Et_2O/MeOH, however, they were found by NMR to be decomposition products. Attempts to chromatograph the residue on neutral alumina also led to decomposition. Due to the unsuccessful attempts to purify 209, the residue was evacuated at 0.1 Torr and 50°C for 3 hours to afford 1.71 g of a pale yellow, crystalline, solid (M.P. 75-82°C) that was found by NMR to be approximately 75% 209 on the basis of the area of the aromatic proton signals relative to those of the $Si-CH_3$

signals. The presence of two Si-CH_3 resonances in the NMR indicated that **209** was a mixture of diastereomeres, in a relative ratio of 1.9 to 1, with the major isomer being that with the Si-CH_3 syn to the vinyl portion of the norbornadiene ring which contained only one phenyl substituent, by analogy with the chemical shifts of the silicon methyls of the 7,7-dimethyl analogue of **209** previously prepared by Gilman and coworkers (4,5). The identity of **209** was established on the basis of the following spectral data: NMR ($CDCl_3$) δ 0.45 and 0.76 (S, 3H, relative areas 1.9:1), 6.17 (m, 3H, vinyl protons, partially overlapped by aromatic protons), broad aromatic absorption from δ 6.6 to 7.5 (m, 39H); IR ($CDCl_3$) 3080, 3060, 3025, 2955, 1597, 1490, 1440, 1401, 1245, 1212 (W), 1071, 1038, 1002, 960, 805, and 780 cm^{-1}; mass spectrum, m/e (% rel. int.) 528 (30), 457 (24), 425 (18), 102 (100), exact mass calculated for $C_{39}H_{32}Si$, m/e 528.22734, measured 528.22809.

Vacuum Flow Pyrolysis of **209**

A solution of approximately 0.855 g (0.0016 mol) of **209** and 2.5 ml of D_6-benzene was added slowly by syringe to a one foot quartz tube filled with quartz chips and enclosed in a tube furnace thermostated at 620°C and evacuated at 0.05 Torr. The pyrolysate was condensed into a cold trap cooled to -196°C. When the pyrolysis was complete, the cooled vessel containing the pyrolysate was attached to a vacuum line and the volatile components were trap-to-trap distilled at room temperature and 0.1 Torr into a NMR tube containing $CDCl_3$ and cooled to -196°C. After the NMR tube was sealed and allowed to warm to room temperature, analysis of its contents by NMR revealed only the presence of $CDCl_3$ and an unidentified singlet at δ 1.5. No 200 was observed even at high amplitude settings. Analysis of the nonvolatiles by NMR revealed the presence of pentaphenylbenzene as the major product (by comparison with the NMR of authentic pentaphenylbenzene) and a small $Si-CH_3$ resonance as a broad unidentifiable hump between δ 0.0 and 0.5.

Synthesis of 4-Methoxy-4,5,5-Trimethyl-4,5-Disila-2-Hexene (211)

To a mechanically stirred suspension of 0.56 g (0.081 mol) of lithium dispersion (washed thrice with 25 ml aliquots of dry Et_2O under an atmosphere are argon prior to use) in 2.5 ml of dry Et_2O, cooled to 0°C and under an atmosphere of nitrogen, was added rapidly 4.87 g (0.042 mol) of 1-bromopropene (mixture of cis and trans isomers, Aldrich). After the addition was complete, the reaction was stirred at 0°C for 3 hours. The reaction was then cooled to -78°C, after which 7.61 g (0.041 mol) of 1,1-dichlorotetramethyldisilane was added rapidly by syringe. When the addition was complete, the reaction was allowed to warm to room temperature and was then heated to reflux. After refluxing for 12 hours, the reaction was cooled to room temperature and then filtered through a cake of celite. To the stirred filtrate was added 3.3 ml (3.23 g, 0.041 mol) of dry pyridine followed by 1.7 ml (1.34 g, 0.042 mol) of dry methanol. The resulting reaction mixture was then stirred for 5 hours at room temperature. This mixture was filtered through celite and distilled to afford 5.0 g of a clear colorless solution that by GC analysis was found to be approximately a 1:1 mixture of 1,1-dimethoxytetramethyldisilane (212) and 211 (as a mixture of cis and trans isomers). It was not found possible to separate 212 and 211 by fractional distillation, therefore, 211 was isolated by preparative gas chromatography on a 10 ft X 1/4 inch, 10% OV-101/chrom W column at 110°C. The yield of 211 was determined by GC, using toluene as a standard, to be 31%. The identification of 211 (as a mixture of cis and trans isomers) was based on the following spectral data: NMR (CCl_4) δ 0.1 (S, 9H), 0.24 (S, 3H), 1.73 (unsymmetrical doublet of multiplets, 3H, allylic CH_3, collapses to broad multiplet with $h\nu$ at 6.33), 3.25 (S, 3H, OCH_3), 5.49 (m, 1H, vinylic proton α to silicon), 6.33 (m, 1H, vinylic proton α to methyl), irradiation at δ 1.73 collapses the signals at 5.49 and 6.33 to two AB quartets, J_{AB} for cis isomer = 13.5Hz, J_{AB} for trans isomer = 17.8Hz; GCMS m/e (% rel. int.) 188 (1.2), 187 (1.49), 173 (45), 133 (42), 115 (34), 99 (16), 89 (27), 75 (48), 73 (65), 59 (100).

Synthesis of 4-Chloro-4,5,5-Trimethyl-4,5-Disila-2-Hexene (211a)

A solution of 4.36 g (0.036 mol) of 1-bromopropene (as a mixture of cis and trans isomers, Aldrich) in 35 ml of dry THF was added over 30 minutes to a stirred suspension of 1.5 g (0.063 mol) of magnesium chips in 10 ml of dry THF under an atmosphere of nitrogen. When the addition was complete, the reaction was brought to reflux and maintained at reflux for 5 hours. After cooling to room temperature, the resulting Grignard solution was added dropwise over 30 minutes to a stirred solution of 6.7 g (0.036 mol) of 1,1-dichlorotetramethyldisilane and 15 ml of dry THF under an atmosphere of nitrogen. When the addition was complete, the resulting mixture was brought to reflux and maintained at reflux for 18 hours.

After cooling to room temperature, the solvent was removed *en vacuo* and the resulting residue, which contained a substantial amount of precipitated salts, was taken up in hexane. The procedure of *en vacuo* removal of the solvent followed by uptake of the residue in hexane was repeated twice to assure complete removal of the THF. Finally, the hexane solution of **211a** and suspended magnesium salts was filtered through a cake of celite. After *en vacuo* removal of the solvent, 5.5 g of a clear yellow solution was obtained. Analysis by GC revealed the presence of **211a** in 29% yield (toluene was used as a standard). Isolation of **211a** was effected by preparative gas chromatography on a 10 ft X 1/4 inch, 15% SE-30/chrom W column at 150°C. The identity of **211a** (as a mixture of cis and trans isomers) was established on the basis of the following spectral data: NMR (CCl_4) δ 0.15 and 0.16 (S, 9H), 0.45 and 0.55 (S, 3H), 1.87 (m, 3H, allylic CH_3, collapses to a broad singlet with $h\nu$ at δ 6.5), 5.76 (unsymmetrical m, 1H, vinylic proton α to Si), 6.5 (m, 1H, vinylic proton α to CH_3), irradiation at δ 1.87 collapses both signals at 5.76 and 6.5 to a multiplet overlapped by an AB quartet, J_{AB} = 14 Hz; IR (CCl_4) 3000 (weak), 2965, 1615, 1440, 1403, 1250, 977, 861, and 837 cm^{-1}; GCMS, m/e (% rel. int.) 177 (2.8), 175 (3.7), 159 (16), 133 (16), 117 (14), 101 (19), 99 (26), 77 (16), 75 (100), 73 (66), 61 (35), 59 (31), 47 (30).

Vacuum Flow Pyrolysis of **211**

Disilane **211** (0.7174 g, 0.0038 mol) was distilled at room temperature and 1 X 10^{-4} Torr into a one foot quartz tube filled with quartz chips in a tube furnace thermostated at 780°C. The pyrolysate, which represented a 69.8% mass recovery, was condensed into a cold trap cooled to -196°C. Analysis of the pyrolysate by NMR revealed that Me_3SiOMe was the major component of the reaction (76% yield). In fact, with the NMR amplitude set such that the $Si\text{-}CH_3$ signal of Me_3SiOMe was about 65% of the maximum pen deflection, only Me_3SiOMe was observable by NMR. Analysis of the pyrolysate by GCMS revealed the presence of 12 compounds, in addition to Me_3SiOMe, none of which could be cleanly separated from one another by GC. Due to the low yields and number of products present, no attempt was made to effect their isolation and characterization, with the exception of Me_3SiOMe, which was identified by comparison of its NMR and GC retention time with those of an authentic sample. The presence of Me_3SiH, $Me_3SiCH{=}CHMe$, and $Me_3SiC{\equiv}CMe$ (all formed in yields estimated to be <5% by comparison of their GC peak areas with that of Me_3SiOMe) was established solely on the basis of GCMS.

Trimethylsilane GCMS, m/e (% rel. int.) 74 (4), 73 (50), 59 (100), 58 (24), matched with a spectrum of authentic sample.

4-methyl-4-sila-2-pentene GCMS, m/e (% rel. int.) 114 (16), 101 (19), 100 (12), 99 (100), 89 (19), 83 (61), 78 (11), 75 (16), 74 (13), 73 (94), 59 (95), 58 (25), 55 (21), 53 (22).

4-methyl-4-sila-2-pentyne GCMS, m/e (% rel. int.) 112 (13), 99 (9), 98 (15), 97 (100), 69 (14), 67 (11), 59 (16), 52 (10).

Synthesis of 3,5-Dimethyl-3,5-Bis(Trimethylsilyl)-1,7-Diphenyl-4-Oxa-3,5-Disila-Hepta-1,6-Diene (220)

To a stirred suspension of 0.57 g (0.0234 mol) of magnesium in 10 ml of dry THF was added over a period of 30 min a solution of 2.9 g (0.0158 mol) of β-bromostyrene and 25 ml of dry THF. After the addition was complete, the reaction was stirred at room temperature for 12 hours. The resulting Grignard solution was then added rapidly to a stirred solution of 3.003 g (0.0016 mol) of 1,1-dichlorodisilane and 10 ml of dry THF. When the addition was complete, the reaction was stirred at room temperature for 3 hours and then heated at reflux for 12 hours. After cooling to room temperature, the solvent was removed *en vacuo* and the resulting residue, which contained a substantial amount of precipitated salts, was taken up in hexane. The procedure of *en vacuo* removal of the solvent followed by uptake of the residue in hexane was repeated twice to assure complete removal of the THF. Finally, this hexane solution, which contained suspended magnesium salts, was filtered through a cake of celite. After *en vacuo* removal of the solvent from the filtrate, 3.39 g of a clear, pale yellow liquid was obtained from which **220** (0.3085 g, 6.8 X 10^{-4} mol, 8.6% yield) was isolated by preparative gas chromatography on a 5 ft X 1/4 inch, 20% SE-30/chrom W column at 200°C. The identity of **220** was established on the basis of the following spectral data: NMR (CCl_4) 0.2 (S, 18H), 0.59 (S, 6H), 6.8 (AB quartet, 4H, J = 19.8Hz), 7.4 (m, 10H); IR (CCl_4) 3060 (W), 3010 (W), 2950, 2895, 1594, 1565, 1484, 1439, 1395, 1323 (W), 1240, 1020 (broad, W), and 970 cm^{-1}; mass spectrum, m/e (% rel. int.) 454 (58), 323 (28), 309 (28), 249 (25), 233 (41), 147 (20), 131 (69), 105 (23), 104 (84), 103 (45), 78 (36), 77 (25), 73 (100), 44 (31). It should be noted that this mass spectrum also contained ions of m/e (% rel. int.) 456 (22) and 455 (30), which suggested that this sample contains an impurity, the identity of which is unknown. By NMR, **220** was found to be at least 90% pure.

This synthesis was originally attempted to prepare 1-phenyl-3-chloro-3-(trimethylsilyl)-3-sila-1-butene, however during the workup the intended chlorodisilane was inadvertently hydrolyzed to the disiloxane. Several attempts were made to prepare the chlorodisilane with great care being taken to prevent contact of the reaction mixture with moisture, however, in all cases, work-up afforded complex reaction mixtures from which only the disiloxane was obtained. The susceptibility of this chlorodisilane to hydrolysis is not understood since under identical reaction conditions using solvents and 1,1-dichlorotetramethyldisilane obtained from the same reagent vessels, in addition to identical work-up procedures, chlorodisilane **211a** was obtained in a reasonable yield (*vide supra*). Distillation of β-bromostyrene prior to use was also found not to effect the course of the reaction.

Vacuum Flow Pyrolysis of **220**

Disiloxane **220** (0.3085 g, 6.8 X 10^{-4} mol) was distilled at 100°C and 8 X 10^{-5} Torr into a one foot quartz tube filled with quartz chips and placed in a tube furnace thermostated at 800°C. The pyrolysate, which represented a 33.8% mass recovery, was condensed into a cold trap cooled to -196°C. Analysis of the pyrolysate by GC revealed the presence of two major components which were isolated by preparative gas chromatography on a 12 ft X 1/4 inch, 20% SE-30/chrom W column at 180°C and identified as styrene and 1-methyl-1-silaindene **222**. The identity of styrene (obtained in 14% yield) was established by comparison of its NMR and mass spectral data with those of an authentic sample. The identity of 222 was established on the basis of the following spectral data. The yields of 222 and styrene were determined by GC using *t*-butylbenzene as a standard and are based on the amount of starting 220.

1-methyl-1-silaindene (222) NMR (CCl_4) δ 0.12 (d, 2H, J = 4Hz, collapses to a singlet with hν at δ 4.4), 4.4 (q, 1H, J = 4Hz, collapses to a singlet with hν at δ 0.12), 6.0 (d, 1H, J = 10.2Hz, vinylic proton α to silicon), 7.02 (m, 5H, aromatic and one vinylic proton); IR (CCl_4) 3060, 3000, 2963, 2130, 1529, 1441, 1249, 1125, 1072, 887, and 849 cm^{-1}; GCMS, m/e (% rel. int.) 146 (100), 145 (78), 131 (59), 105 (53), 53 (36), 20% yield based on reacted 220.

Synthesis of 1,1-Dimethoxytetramethyldisilane (234)

To a stirred solution of 10.01 g (0.0535 mol) of 1,1-dichlorotetramethyldisilane and 100 ml of hexane was added 8.47 g (0.1071 mol) of dry pyridine followed by 3.43 g (0.10 mol) of dry methanol. When the additions were complete, the reaction was stirred at room temperature for 24 hours. The resulting mixture was then filtered through celite, concentrated *en vacuo*, and distilled to afford 4.7 g (0.0264 mol, 49% yield) of 234, B.P. 61-64°C at 60 Torr: NMR (CCl_4) δ 0.00 (d, overlapped $SiMe_3$ and SiMe, 12H), 3.31 (S, 6H, OMe), IR (CCl_4) 2961, 2901 (W), 2840, 1249, 1186, 1075 (S), 865 (W), and 833 cm^{-1}; mass spectrum, m/e (% rel. int.) 178 (2), 163 (48), 133 (76), 105 (36), 89 (19), 75 (35), 73 (67), 59 (100), 45 (33), exact mass calculated for $C_6H_{18}Si_2O_2$, m/e 178.08454, measured 178.08472.

Vertical Flow Pyrolysis of **234**

Disilane **234** was added mechanically at a rate of 2.2 ml/hour to a one foot quartz tube filled with quartz chips and enclosed in a tube furnace. The volatiles were swept through the tube into a cold trap cooled to -196°C with a stream of nitrogen at approximately 35 ml/minute. At a temperature of 450°C , **234** was still present in the pyrolysate, however, at 520°C all of **234** was found to have decomposed. Analysis of the pyrolysate obtained at 520°C (which represented a 72% mass mass recovery) revealed the presence of two major products, one dominate minor product, and a plethora (<10) of nondominant minor products. The three former products were isolated by preparative gas chromatography on a 6 ft X 1/4 inch, 30% SE-30/chrom W column at an initial temperature of 80°C followed by manual temperature programing to 200°C. The identities of all three products were established on the basis of their GCMS and NMR spectra. The yields of the two major products were determined by GC, using 1,2-dimethoxytetramethyldisilane as a standard. The yield of the dominant minor product was not directly determined; instead, it was estimated by consideration of its GC peak area relative to those of the major products. The identities, spectral data, and yields of these products are given below.

Trimethylmethoxysilane NMR (CCl_4) δ 0.05 (S, 9H), 3.29 (S, 3H); GCMS, m/e (% rel. int.) 104 (8), 91 (21), 89 (100), 73 (20), 60 (43), 59 (62), 58 (33); both these spectra matched those of authentic sample; 56% yield (based on reacted **234**).

Trimethoxymethylsilane NMR (CCl_4) δ 0.00 (S, 3H), 3.43 (S, 9H);

GCMS, m/e (% rel. int.) 136 (3), 121 (100), 105 (42), 91 (88), 75 (58), 60 (30), 59 (59); 33% yield (based on Me_3SiOMe obtained).

Syn-methyldimethoxydisiloxane NMR (CCl_4) δ 0.06 (S, 6H), 3.49 (S, 12H); GCMS, m/e (% rel. int.) 211 (87) (parent - Me), 195 (44), 194 (32), 181 (100), 165 (38), 151 (77), 149 (26), 135 (37), 121 (20), 105 (43), 91 (16), 90 (16), 75 (30), 73 (12), 59 (20); 10% yield (based on reacted **234**).

In a repeat of the above reaction with a nitrogen flow rate of 57 ml/minute, under otherwise identical conditions, the pyrolysate, which represented a 52% mass recovery, was identical to that reported above with the exception that sym-methyldimethoxydisiloxane was not present. Instead, dimethyldimethoxysilane (10% yield) was found. This product was isolated by preparative gas chromatography on a 10 ft X 1/4 inch, 20% DC-550/chrom W column at 80°C and identified on the basis of the following spectral data. The yield of $Me_2Si(OMe)_2$ was estimated by consideration of its GC peak area relative to that of Me_3SiOMe.

Dimethyldimethoxysilane NMR (CCl_4) δ 0.02 (S, 6H), 3.41 (S, 6H); GCMS, m/e (% rel. int.) 105 (100) (parent - Me), 89 (11), 75 (71), 59 (45); both these spectra matched those of authentic sample; 10% yield based on reacted **234**.

Copyrolysis of **234** and Dimethyldimethoxysilane

A solution of 0.4829 g (2.7 X 10^{-3} mol) of **234** and 1.942 g (1.6 X 10^{-2} mol) dimethydimethoxysilane was pyrolyzed in the same manner as described above. The volatiles were swept through the tube and into a cold trap cooled to -196°C with a nitrogen flow of 45 ml/minute. The pyrolysate, which represented a 69% mass recovery, was found to contain as major products only Me_3SiOMe (50% yield based on reacted 234) and $MeSi(OMe)_3$ (38% yield based on Me_3SiOMe). The identity of these two products were established by NMR and GCMS following isolation by preparative gas chromatograph utilizing similar conditions to those reported above. The yields of these products were determined by GC using 1,2-dimethoxytetramethyldisilane as a standard.

Synthesis of Bis(α-bromoisopropyl)methylbromosilane (239)

The synthesis is a modification of the procedure of Cartledge and Jones for the bromination of dimethylisopropylchlorosilane (311). A 50 ml 3 neck flask was equipped with a reflux condensor, magnetic stirring bar, 25 ml equalizing pressure addition funnel, and a gas inlet situated such that nitrogen could be continually bubbled through the reaction solution. The flask was charged with 7.4 g (0.057 mol) of diisopropylmethylsilane and the equalizing pressure addition funnel was charged with 27.1 g (0.17 mol) of bromine. Nitrogen was then gently bubbled through the solution (nitrogen flow was maintained throughout the course of the reaction) and the contents of the flask were cooled to -23°C. Bromine was then added slowly to the stirred diisopropylmethylsilane. During the addition of approximately the first 25% of bromine, the reaction is very vigorous and care must be taken not to add the bromine at too fast a rate. When approximately the first equivalent of bromine had been added and the visible uptake of bromine had become very slow, the contents of the flask were heated to 65°C. The remainder of the bromine was then added at such a rate as to just maintain a red solution color. When the addition was complete (approximately 18 hours after heating to 65°C), the contents of the flask were transferred to a sublimation apparatus and sublimed at 0.05 Torr and 25°C to afford 17 g (0.047 mol, 82% yield) of bis(α-bromoisopropyl)methylbromosilane as a waxy solid (M.P. 68-70°C): NMR (CCl_4) δ 0.9 (S, 3H), 2.0 (d, diastereotopic methyls, 12H); IR (CCl_4) 2980, 2960, 2930, 2870, 1460, 1446, 1383, 1365, 1255, 1085, and 890 cm^{-1}; mass spectrum, m/e (% rel. int.) 248 (1.9), 246 (4.9), 244 (4.2) (parent - C_3H_5Br), 205 (22), 203 (45), 201 (22), 165 (10), 163 (10), 139 (19), 137 (20), 123 (100), 121 (99), 109 (23), 107 (18), 83 (43), 55 (11).

Reaction of 239 with Trimethylsilyllithium

Trimethylsilyllithium was prepared according to the method of Still (312). Thus, to a stirred solution of 0.73 g (0.0015 mol) of hexamethyldisilane and 3 ml of dry HMPA under an atmosphere of nitrogen and cooled to 0°C was added a solution of methyllithium (0.52 ml, 1.91 M, 1×10^{-3} mol) in Et_2O. Upon the addition of methyllithium, the reaction immediately turned dark red. The resulting solution was then stirred at 0°C for 5 minutes after which a solution of 0.367 g (1×10^{-3} mol) of bis(α-bromoisopropyl)methylbromosilane (239) in 5 ml of dry THF was added rapidly by syringe. Following the addition of 239, the reaction was diluted with 5 ml of dry THF and then stirred at 0°C for 10 minutes. Methyl iodide (0.2 ml, 0.46 g, 3×10^{-3} mol) was then added to quench any unreacted trimethylsilyllithium. The solution was then poured onto 50 ml of pentane and the resulting solution was filtered, washed thrice with H_2O, and dried over $MgSO_4$. After en vacuo removal of the volatiles, analysis of the resulting reaction mixture by gas-chromatography (GC) revealed the presence of greater than 10 products. Due to the number of products, none of which could be cleanly separated by GC, no attempt was made to effect their isolation and characterization.

Reaction of 239 with Vinylmagnesium Bromide

To a stirred solution of 17 g (0.047 mol) of 239 and 100 ml of dry THF was added over two hours a solution of vinylmagnesium bromide (52 ml, 1.1 M, 0.057 mol) in THF. When the addition was complete, the reaction was brought to reflux and maintained at reflux for 12 hours. The resulting reaction mixture was then hydrolyzed with sat. aqueous NH_4Cl and extracted twice with Et_2O. The organic fractions were combined and dried over $MgSO_4$. En vacuo removal of the solvent afforded 14.08 g of a reaction mixture that by GC analysis contained 5 compounds, two of which predominated. GCMS analysis of the mixture revealed that the two major products were isomeric and that neither possessed a mass spectrum consistent with the desired product. Moreover, the major product with the longer GC retention time was found to be identical to the major product obtained from the reaction of 239 with methanol and pyridine (vide infra). These results were taken as evidence that the desired reaction had not taken place and therefore no attempt was made to further characterize the products of this reaction.

Mass spectral data for the two major products of this reaction are: Compound A, the product with the shorter GC retention time, m/e (% rel.

int.) 184 (3.9), 182 (8.5), 180 (4.9), 169 (1.7), 167 (4.1), 165 (2.8), 141 (62), 139 (67), 103 (55), 101 (40), 85 (28), 84 (26), 76 (23), 75 (100), 61 (40), 60 (20); Compound B, the product with the longer GC retention time, m/e (% rel. int.) 184 (9.8), 182 (16), 180 (6.6), 167 (3.2), 166 (4.0), 165 (3.9), 164 (3.8), 141 (100), 139 (96), 123 (26), 121 (26), 102 (15), 101 (46), 75 (51), 61 (28), 60 (19), 45 (51).

Reaction of **239** with Cyclopentadienyllithium

To a stirred solution of 3.5 g (0.053 mol) of freshly cracked cyclopentadiene and 30 ml of dry THF cooled to -78°C and maintained under an atmosphere nitrogen was added a solution of *n*-butyllithium (24 ml, 2.2 M, 0.053 mol) in *n*-hexane. After the addition was complete, the reaction was stirred at -78°C for approximately 30 minutes. A solution of 20 ml of dry THF and 17 g (0.047 mol) of **239** was then added rapidly to the stirred suspension of cyclopentadienyllithium (maintained at -78°C). After the addition was complete, the reaction was allowed to warm to room temperature and was then stirred at room temperature for approximately 12 hours. The reaction mixture was then hydrolyzed with H_2O and extracted twice with Et_2O. The organic fractions were combined and dried over $MgSO_4$. After *en vacuo* removal of the solvent, the resulting dark brown solution was chromatographed on fluorasil to afford one silicon containing fraction (eluted with hexanes) that on the basis of NMR analysis was >80% unreacted **239**. The lack of olefinic absorptions in the NMR clearly indicated that the desired reaction had not occurred.

Reaction of 239 with Methanol and Pyridine

To a stirred solution of 2.35 g (0.0065 mol) of 239 and 25 ml of dry THF was added 0.52 g (0.0066 mol) of pyridine followed by 0.21 g (0.0066 mol) of dry methanol. When the additions were complete, the reaction mixture was stirred at room temperature for 12 hours. The reaction was then diluted with an equal volume of pentane and washed with H_2O until the organic phase no longer contained the smell of pyridine. After *en vacuo* removal of the pentane, analysis of the reaction mixture by GCMS revealed the presence of two major products in a ratio of about 4 to 1. The two compounds, which were isomeric, were found not to be consistent with the desired product and were therefore not isolated and further characterized. The mass spectral data for these two compounds are: compound A, the product with the shorter GC retention time, m/e (% rel. int.) 184 (10), 182 (15), 180 (6), 167 (3.5), 166 (4.9), 165 (4.3), 164 (4.7), 141 (100), 139 (98), 123 (37), 121 (38), 102 (18), 101 (43), 87 (15), 75 (58), 61 (41), 60 (36), 45 (60); compound B, the product with the longer retention time, m/e (% rel. int.) 182 (0.3), 180 (0.3), 167 (3.5), 165 (3.8), 141 (16), 139 (17), 127 (10), 102 (11), 101 (100), 83 (15), 82 (16), 75 (84), 61 (20), 45 (29). Compound A of this reaction was found by GCMS to be identical to compound B obtained for the reaction of vinylmagnesium bromide with 239.

2,3-Dicarbomethoxy-1,4-Diphenyl-7,7-Dimethyl-7-Silanorbornadiene (241)

a) *Attempted preparation in CH_2Cl_2* To a solution of 1.14 g (4.36

mmol) of 242 and 20 ml of methylene chloride was added 0.62 g (4.36 mmol) of dimethyl acetylenedicarboxylate (DMADC) (Aldrich). After approximately five minutes of stirring at room temperature, the solution turned from yellow to red. The solvent was removed *en vacuo* leaving a red oil. The resulting red oil was dissolved in a minimum amount of boiling benzene. Upon cooling, a white solid was collected. Recrystallization from acetone gave white flocculent crystals of dimethyl diphenylphthalate (243) m.p. 184-186°C.: NMR ($CDCl_3$) $\delta = 3.56$ (s, 6H), $\delta = 7.33$ (s, 10H), $\delta = 7.47$ (s, 2H).

b) A solution of 1.91 g (7.29 mmol) of 242 and 30 ml of hexane was degassed by the freeze-thaw method. To this solution was added, by trap-to-trap distillation, 3 ml (24 mmol) of dimethyl acetylenedicarboxylate, which was degassed by the freeze-thaw method prior to addition. The vessel was then sealed and heated slightly to dissolve 242. After cooling to room temperature, the reaction vessel was cooled to about -10°C for 24 hours. After cooling, the presence of a deep red oil and some pale yellow-green crystals were noted. Careful collection of the crystals, under an atmosphere of argon in a glove bag, gave 0.6 g (1.49 mmol, 20%) of 241: m.p. (sealed tube) 80-90°C (d), NMR (CCl_4) δ 0.15 (s, 3H), 0.59 (s, 3H), 3.41 (s, 6H), 6.92 (s, 2H), 7.18 (s, broadened at the base line, 10H); IR (CCl_4) 3060, 3025, 2950, 1721, 1592, 1540, 1494, 1429, 1282, 1239, 1048, 721, and 690 cm^{-1}; mass spectrum (70 ev) (% rel. int.) 389 (13), 345 (19), 315 (22), 105 (47), 98 (31), 97 (25), 89 (67), 83 (90), 75 (32), 71 (23), 70 (29), 69 (44), 59 (29), 57 (48), 55 (100); calculated for $C_{24}H_{24}O_4Si$ m/e 404.14439, measured 404.14614; calculated for $C_{23}H_{21}O_4Si$ (parent - CH_3)

389.12091, measured 389.12101.

c) *In situ* preparation of **241** A solution of 0.52 g (1.98 mmol) of **242** and 10 ml of CCl_4 was deoxygenated by bubbling argon through the solution for about 15 minutes. To this solution was added 0.29 g (2.0 mmol) of freshly distilled DMADC, which was deoxygenated by bubbling argon through it for 15 minutes prior to addition. After stirring at room temperature for about 20 minutes, examination of the reaction mixture by NMR showed only **241** and excess DMADC to be present. This solution was found to be adequate for subsequent reactions of **241**. However, attempts to isolate **241** by *en vacuo* removal of the solvent, or addition of dodecane and *en vacuo* removal of CCl_4, afforded a deep red oil, or a red dodecane solution, from which only dimethyl tetraphenylphthalate **243** could be isolated.

Isomerization of **241** to 7,7-Dimethyl-3,6-Diphenyl-2-Carbomethoxy-9-Methoxybicyclo[4.3.0]nona-2,4,9-Triene (**251**)

a) A CCl_4 solution of **241**, prepared *in situ* as described above, was placed in a NMR tube and degassed by the freeze-thaw method. The tube was then sealed and placed in an oven thermostated at 105-110°C. After thermolysis for about 10 hours, analysis by NMR showed the **241** had completely isomerized to **251** and some minor unidentified decomposition products. Based on relative peak areas, **251** accounted for >80% of the products formed. The identification of **251** was made on the basis of its spectral data: NMR (CCl_4) δ 0.01 (s, 3H), 0.50 (s, 3H), 3.55 (s, 3H), 3.79 (s, 3H) 6.41 (AB quartet, J = 10 Hz, 2H), 7.39 (broad multiplet, 10H);

IR (CCl_4) 3060, 3022, 2942, 1728, 1621, 1595, 1442, 1431, 1256, 1130, 1050, 853, and 695 cm^{-1}. Continued thermolysis of this solution led to the gradual decomposition of 251 and the formation of dimethyl tetraphenylphthalate.

A repeat of this reaction in $DCCl_3$ afforded the following ^{13}C NMR spectrum for 251: (ppm relative to TMS) δ -3.17, -3.39, 51.54, 55.50, a plethora of signals between 125.06 and 130.48, 139.79, 145.10, 159.24, and 169.81. After sitting under vacuum at 0°C for 18 months this solution was found to be unchanged, however, exposure to the air resulted in the rapid decomposition of 251 giving dimethyl tetraphenylphthalate.

ESR Experiments

a) A solution of 0.064 g (0.24 mmol) of 242 and CCl_4 was placed in a NMR tube and degassed by the freeze-thaw method. DMADC, 0.015 g (0.11 mmol), was degassed by evacuation at 28°C and 0.02 torr, and then trap-to-trap distilled into the NMR tube. After sealing the tube, analysis by ESR revealed an unsymmetrical signal that appeared to be a mixture of at least two radicals. No definitive identification of the radicals present could be made.

b) A solution of silanorbornadiene 241, isolated as previously described, and CCl_4 was placed in a septum-sealed NMR tube under an atmosphere of argon. Analysis by ESR showed no radical signal. After 72 hours at 0°C under argon about 10% of 241 was found, by NMR, to have rearranged to 251. However, no ESR signal was observed during this period. Further isomerization (approximately 25%) of 241 to 251 was found after 18 hours at room temperature in the dark. Analysis of this sample by ESR showed no observable radical signal. Oxygen was then bubbled through the tube to observe the effect of O_2 upon the isomerization. After standing under O_2 for 1 hour at room temperature in the dark, 241 was found by NMR to have completely decomposed, giving dimethyl tetraphenylphthalate and unidentifiable silicon containing products. Repetition of this experiment in D_6-benzene also failed to produce an ESR signal.

Photolysis of 241

A CCl_4 solution of 241, prepared in situ in a pyrex NMR tube, was irradiated with a medium pressure Hg lamp at room temperature. After irradiation for 120 minutes, a large amount of precipitate was found. NMR analysis of this suspension revealed a new $Si\text{-}CH_3$ signal at δ 0.79. Based on the relative peak areas of 241 and the new signal at δ 0.79, approximately 50% of 241 had decomposed. The precipitate, following isolation by filtration, was found to be dimethyl 1,4-diphenylphthalate by comparison of its NMR with that of authentic dimethyl 1,4-diphenylphthalate. Based on NMR chemical shifts, the new $Si\text{-}CH_3$ signal at δ 0.79 was identified as dimethyldichlorosilane.

7,7,9-Trimethyl-3,6-Diphenyl-7-Sila-8-Oxabicyclo[4.3.0]nona-2,4,9-Triene (253)

A solution of 0.54 g (2.1 mmol) of silole 242 and 6 ml of CCl_4 was deoxygenated by bubbling argon through the solution for 15 minutes at room temperature. To this solution was added 0.44 g (6.4 mmol) of 3-butynone, with continuous argon bubbling. Argon bubbling was maintained for 15 minutes after the addition of 3-butynone to assure complete deoxygenation. After stirring for 44 hours at room temperature in the dark under an atmosphere of argon, analysis by NMR revealed only the presence of 253, excess 3-butynone, and small amounts of decomposition products. Based on relative peak areas of the Si-CH_3 absorptions, 253 accounted for >85% of the products formed. En vacuo removal of the volatiles afforded a brown-red oil identified as 253: NMR (CCl_4) δ -0.08 (s, 3H), 0.35 (s, 3H), 2.10 (s, 3H), 6.35 (broad d, 2H), 6.48 (broad s, 1H), 7.10 (broad multiplet, 10H); IR (CCl_4) 3065, 3040, 2965, 1660, 1630, 1598, 1495, 1447, 1380, 1255, 1210. 1027, 845, and 690 cm^{-1}; mass spectrum (70 ev) (% rel. int.) 330 (70), 329 (49), 315 (35), 272 (21), 271 (27), 257 (28), 253 (100), 241 (48), 77 (52), 75 (71); calculated for $C_{22}H_{22}OSi$ m/e 330.14400, measured 330.14320. Attempted purification of 253 by column chromatography (neutral alumina, CCl_4 elution) afforded 2',5'-diphenylacetophenone: NMR (CCl_4) δ 1.96 (s, 3H), 7.55 (s, broadened at the base line, 13H); IR (CCl_4) 3060, 3025, 2970, 1689, 1600, 1470, 1445, 1350, 1250, 1215, and 690 cm^{-1}.

1,2-Dicarbomethoxy-3,4,5,6,7-Pentaphenyl-7-Methyl-7-Silanorbornadiene (259c)

A solution of 1.008 g (2.12 mmol) of 1,2,3,4,5-pentaphenylmethylsilole (23) and 15 ml of CCl_4 was placed in a septum-sealed round bottom flask equipped with a magnetic stirring bar. The reaction vessel was then deoxygenated by bubbling argon through the solution for 15 minutes. After the addition of 0.578 g (4.07 mmol) of DMADC, the reaction was stirred at room temperature for 18 hours. The volatiles were then removed en vacuo, and the resulting residue was crystallized from CH_2Cl_2/hexane to afford 0.8069 g (1.31 mmol, 62% yield) of 259c, m.p. (sealed tube) 208-211°C, which was identified on the basis of the following spectra: NMR (CCl_4) δ 0.69 (s, 3H), 3.6 (s, 6H), broad absorption from 6.3 to 7.7 with the major signal centered at 6.81 (25H); IR (CCl_4) 3104, 3070, 3000, 1730, 1600, 1431, 1232, 1060, 860, and 700 cm^{-1}; mass spectrum (70 ev) (% rel. int.) 618 (2), 603 (23), 602 (49), 560 (44), 558 (87), 540 (32), 498 (13), 434 (21), 172 (16), 168 (35), 152 (45), 57 (100), 56 (87), calculated for $C_{41}H_{34}O_4Si$ m/e 618.22265, measured 618.22377.

1,2,3,4,5,7-Hexaphenyl-7-Methyl-7-Silanorbornadiene (259d)

A mixture of 1.0 g (2.1 mmol) of 1,2,3,4,5-pentaphenylmethylsilole and 0.56 g (5.46 mmol) of phenylacetylene, in an evacuated sealed tube, was heated at 140°C for 12 hours. After thermolysis, the tube was opened and the volatiles were removed en vacuo. The resulting residue was then crystallized from CH_2Cl_2/hexane to afford 0.862 g (1.49 mmol) of 259d, m.p. 203-206°C, which was identified on the basis of the following spectra: NMR (CCl_4) δ 0.65 (s, 3H), broad absorption between 6.2 and 7.9 with the major absorption at 6.9 (31H); IR (CCl_4) 3055, 3020, 1600, 1490, 1440, 1425, 1245, 1100, 1070, 1025, 905, 855, and 690 cm^{-1}; mass spectrum (70 ev) (% rel. int.) 578 (32), 485 (11), 458 (24), 105 (15), 86 (40), 84 (65), 57 (61), 56 (58), 49 (100): calculated for $C_{43}H_{34}Si$ m/e 578.24299, measured 578.24136.

1,2,3,4,5-Pentaphenyl-7,7-Dimethyl-7-Silanorbornadiene 259e

A mixture of 0.753 g (1.82 mmol) of 2,3,4,5-tetraphenyldimethylsilole (242) and 0.54 g (5.26 mmol) of phenylacetylene, in an evacuated sealed tube, was heated at 140°C for ten hours. After thermolysis, the tube was opened and the volatiles were removed en vacuo. The resulting residue was crystallized from CH_2Cl_2/hexane to afford 0.577 g (1.12 mmol, 61% yield) of 259e, m.p. 145.5-147.5°C, that was identified on the basis of the following spectra: NMR (CCl_4) δ 0.35 (s, 3H), 0.63 (s, 3H), broad absorption between 6.2 to δ = 7.2 with the major absorption centered at 6.95 (26H); IR (CCl_4) 3070, 3038, 2960, 1600, 1495, 1443, 1245, 1074, 1030, 905, 877, 855, 840, and 690 cm^{-1}; mass spectrum (70 ev) (% rel. int.) 516 (100), 501 (31), 458 (39), 439 (27), 423 (31), 380 (31), 365 (15), 136 (25), 102 (13); calculated for $C_{38}H_{32}Si$ m/e 516.22734, measured 516.22612.

Photolysis of 259c

a) A solution of 259c and CCl_4 was placed in a quartz NMR tube which was sealed with a rubber septum and deoxygenated by bubbling argon through the tube for 15 minutes. The tube, which was placed in a large container of H_2O, was then irradiated with a 450 W Hanovia lamp through a quartz filter. After irradiation for 210 minutes, analysis by NMR revealed that 259c had completely disappeared. New peaks were observed in the NMR at: δ 0.90 (singlet), 3.31 (singlet), 6.7 (broad singlet) and 6.95 (broad singlet). The photolysate was dissolved in hot 50/50 CCl_4/hexane, which after cooling afforded pale yellow-brown crystals (m.p. 251-255°C) identified as dimethyl tetraphenylphthalate **243** on the basis of the following spectra: NMR (CCl_4) δ 3.3 (s, 6H), broad absorption between 6.3 and 7.2 with major absorptions at 6.7 and 7.0 (20 H); IR (CCl_4) 3065, 3040, 2960, 1734, 1605, 1496, 1438, 1345, 1245, 1174, 1068, and 695 cm^{-1}. These spectral data were found to be identical to that of an authentic sample of **243**. Analysis of the photolysate by GCMS revealed the presence of hexachloroethane and phenylmethyldichlorosilane which were identified on the basis of the following spectral data.

Hexachloroethane GCMS, m/e (% rel. int.) 203 (25), 201 (41), 199 (25) (parent minus Cl), 168 (13), 166 (28), 164 (21), 121 (29), 119 (96), 117 (100) (CCl_3), 96 (22), 94 (35), 84 (14), 83 (11), 82 (23), 59 (18).

Phenylmethyldichlorosilane GCMS, m/e (% rel. int.) 157 (35), 155 (100) (parent minus Cl), 91 (14), 89 (11), 77 (11), 65 (17), 63 (46), 51 (14).

b) A solution of **259c** and D_6-benzene was placed in a quartz NMR tube which was sealed with a rubber septum and deoxygenated by bubbling argon through the tube for 15 minutes. The photolysis was conducted as described for **259c** in CCl_4. After irradiation for 220 minutes at room temperature, analysis of the photolysate by NMR showed that the $SiCH_3$ singlet of **259c** had completely disappeared. A broad, unidentifiable, hump between δ 0.2 and 1.1 was observed in the NMR plus a new singlet at δ 3.3. Chromatography of the photolysate on neutral alumina with CCl_4 elution afford a white, crystalline product, which was identified as dimethyl tetraphenylphthalate (**243**) on the basis of its NMR and IR spectra.

Photolysis of **259d**

a) The photolysis of **259d** in CCl_4 was conducted in the same manner as for **259c** (*vide supra*). After irradiation for 100 minutes, NMR analysis of the photolysate showed that **259d** had completely disappeared. The $Si\text{-}CH_3$ signal for **259d** had disappeared and was replaced by a new $Si\text{-}CH_3$ signal at δ 0.96. *En vacuo* removal of the volatiles resulted in disappearance of the peak at δ 0.96. The signal at δ 0.96 is consistent with phenylmethyldichlorosilane. The residue was then chromatographed on neutral alumina with CCl_4 elution to afford a white, crystalline, solid, m.p. 248-249°C, which was identified as pentaphenylbenzene on the basis of its melting point and NMR spectra: NMR (CCl_4) δ 6.73 (broad singlet), 7.01 (singlet), 7.25 (singlet). This NMR spectrum was found to be identical to that of authentic pentaphenylbenzene.

b) The photolysis of **259d** in D_6-benzene was conducted in the same manner as for **259c**. After irradiation for 190 minutes at room temperature, the singlet $Si\text{-}CH_3$ absorption of **259d** was found by NMR to have collapsed to a broad hump between δ -0.1 to 1.5. Chromatography of the photolysate on neutral alumina with CCl_4 elution afforded pentaphenylbenzene which was identified on the basis of its melting point (m.p. 247-248°C) and NMR spectrum.

Photolysis of **259e**

a) The procedure for the photolysis of **259e** in CCl_4 was the same as that employed for **259c** with one exception, **259e** was photolyzed at 0°C.

After irradiation for six hours, NMR analysis of the photolysate showed that the Si-CH_3 signals of 259e had completely disappeared, and were replaced by a new signal at δ 0.73. This new signal is consistent with dimethyldichlorosilane. Gas-chromatography-mass-spectrometric (GCMS) analysis of the photolysate revealed the presence of dimethyldichlorosilane; GCMS (% rel. int.) 132 (.5), 130 (4), 128 (5), 117 (15), 115 (65), 113 (100), 95 (4), 95 (4), 93 (4); and trichloromethyldimethylchlorosilane; GCMS (% rel. int.) 195 (0.22), 177 (1.5), 175 (1.4), 135 (8), 133 (8), 115 (16), 113 (23), 95 (34), 93 (100), 65 (20), and 63 (21). After *en vacuo* removal of the volatiles from the photolysate, crystallization of the resulting residue afforded a brown solid, m.p. 234-237°C. This solid was identified as pentaphenylbenzene by comparison of its NMR spectrum with that of authentic pentaphenylbenzene.

b) The procedure for the photolysis of 259e in D_6-benzene was the same as that used for the 259c. Analysis of the reaction by NMR, after irradiation for three hours, showed that the two singlet, Si-CH_3 absorptions of 259e had collapsed to a broad hump between δ -0.1 and 1.3. Chromatography of the photolysate on neutral alumina gave a white, crystalline, solid, m.p. 239-241°C, which was identified as pentaphenylbenzene on the basis of its NMR spectrum.

Thermolysis of 259c

a) A solution of 259c and CCl_4 was placed in a septum-sealed NMR tube, and deoxygenated by bubbling argon through the tube for about 15 minutes. The solution was then heated at 100°C, and the progress of the reaction was monitored by NMR. After heating for three hours, new signals at δ -0.15, 3.42, and 3.96 were observed. These signals continued to grow with continued thermolysis. Thus, after heating for 12 hours, about 5% of 259c was observed to have decomposed, affording the new NMR signals. Further thermolysis did not result in a continued increase in the signals at δ -0.15, 3.42 and 3.96. Instead, after 24.75 hours of heating, the signals at δ -0.15 and 3.96 had decreased in intensity with a concomitant increase in the signal at δ 3.42, and the appearance of a new signal at δ 1.02. After heating at 100°C for 50 hours only the signals at δ 1.02 and 3.42 were observed, in addition to unreacted starting material. Based on the relative peak areas of the Si-CH$_3$ peak of 259c and the new peak at δ = 1.02, about 20% of 259c had decomposed. After heating for 98 hours, about 45% of 259c had decomposed. The signal at δ 1.02 was found not to be due to isomerized 259c when *en vacuo* removal of the volatiles (0.02 torr, 60°C) caused this signal to completely disappear. Thus, NMR analysis of this residue showed only signals due to 259c and the peak at δ 3.42, which based on chemical shifts was attributed to the carbomethoxy methyls of dimethyl tetraphenylphthalate.

b) A solution of 259c and D$_6$-benzene was placed in a septum-sealed NMR tube and deoxygenated by bubbling argon through the solution for about 15 minutes. The solution was then heated at 100°C. NMR analysis, after 24.5 hours, revealed only signals due to 259c. NMR analysis, after 48.5 hours at 100°C, revealed the presence of new signals at δ 0.00, 3.31, and 3.59, which based on relative peaks areas of the Si-CH$_3$ resonance for 259c and the signal at δ 0.00 represented <5% decomposition of 259c. Oxygen was then bubbled through the tube for approximately 5 minutes. In the presence of O_2, thermolysis at 100°C, resulted in a gradual decrease in the intensity of NMR signals of 259c and an increase in the intensity of the signals at δ 0.00, 3.31, and 3.59. NMR analysis, after heating in the presence of O_2 for 29 hours, showed that approximately 50% of 259c had decomposed. After thermolysis for 102 hours in the presence of O_2, only about 10% of 259c remained, on the basis of relative Si-CH_3 peak areas. Based on the NMR and IR spectra, the product of the reaction was tentatively identified as bicycloenol ether 262. NMR (C_6D_6) δ - 0.00, 3.31, 3.59 (all singlets, relative area 1:1:1), broad absorption between δ = 6.70 and δ = 7.90 (relative area not determined); IR (C_6D_6) 3060, 3030, 2950, 1725, 1620, 1595, 1490, 1440, 1430, 1293, 1225, 1200, 1135, 1110, 1057, 1025, 840, and 691 cm^{-1}.

Synthesis of Allyldimethylsilane (263)

A solution of 85 g (0.9 mol) of dimethylchlorosilane and 157.3 g (1.3 mol) of allylbromide was added over a period of three hours to a stirred suspension of 34 g (1.42 mol) of magnesium in dry Et_2O. When the addition was complete, the reaction was stirred at room temperature for 24 hours. Following filtration and distillation of the resulting filtrate, 36 g (0.36 mol, 40% yield) of allyldimethylsilane was obtained, B.P. 52-55°C; NMR (CCl_4) δ 0.02 (d, J = $4H_z$, collapses to a singlet with $h\nu$ at δ 3.91, 6H), 1,56 (d of m, collapses to a broad doublet with J = 8Hz upon $h\nu$ at δ 3.91, 2H), 3.91 (m, 1H, Si-H, collapses to a triplet upon $h\nu$ at δ 0.02), 4.84 (m, 2H), 5.7 (m, 1H); IR (gas-phase) 3080

2965, 2919, 2122, 1633, 1410, 1252, 1155, 1070, 1035, 990, 890, 840, 775, 712, and 650 cm^{-1}; GCMS, m/e (% rel. int.) 100 (21), 85 (42), 72 (33), 59 (100).

Vertical Flow Pyrolysis of 263

The pyrolyses were conducted by adding 263 mechanically at a rate of 2.2 ml/hour to a one foot quartz tube filled with quartz chips and enclosed in a tube furnace. The pyrolysate was swept through the tube with a nitrogen flow rate of 30 ml/minute and was collected in a cold trap cooled to -196°C. At 540°C, the pyrolysate was found by NMR and GC analysis to be mainly unreacted 263. At 610-615°C, the pyrolysate, which typically represented a 62-65% mass recovery, was found by GC to contain 6 major, identifiable products in addition to unreacted 263 (32% yield). These products were isolated by preparative gas chromatography on a 6 ft. X 1/4 inch, 30% SE-30/chrom W column and identified on the basis of the following spectral data. Yields were determined by calibrated GC using cyclooctene as a standard and are based on reacted 263.

Trimethylsilane (266) NMR (CCl_4) δ 0.01 (d, J = 3.5Hz, 9H), 3.79 (unresolved multiplet, 1H); GCMS, m/e (% rel. int.) 73 (68) (parent -H), 59 (100), 5% yield.

Dimethylvinylsilane (267) NMR (CCl_4) δ 0.1 (d, J = 3Hz, 6H), 5.89 (m, 3H, vinyl protons), the Si-H absorption could not be detected; GCMS, m/e (% rel. int.) 86 (10), 71 (29), 59 (32), 57 (100), 4% yield.

Trimethylvinylsilane (268) NMR (CCl_4) δ 0.09 (S, 9H), 5.9 (m, 3H); GCMS, m/e (% rel. int.) 100 (10), 85 (100), 73 (19), 59 (87), 58 (15), 6% yield.

Trimethylallysilane (269) NMR (CCl_4) δ 0.02 (S, 9H), 1.5 (broad doublet, J = 8Hz, 2H), 4.76 (m, 2H), 5.72 (m, 1H); GCMS, m/e (% rel int.) 114 (7), 99 (21), 73 (100), 59 (29), 9% yield.

3,3-Dimethyl-3-Silacyclopentene (270) NMR (CCl_4) δ 0.03 (S, 6H), 0.57 (m, 2H, CH_2 in ring α to Si), 2.38 (m, $2H_c$, allylic), 5.87 (d of t, $1H_A$, vinyl α to Si, J_{AB} = 11 Hz, J_{AC} = 2Hz), 6.76 (d of t, $1H_B$, vinyl β to Si, J_{BC} = 3Hz); GCMS, m/e (% rel. int.) 112 (12), 98 (11), 97 (100), 95 (26), 69 (10).

4,4-Dimethyl-4-Silacyclopentene (271) NMR (CCl_4) δ 0.02 (S, 6H), 1.17 (broad S, 4H), 5.82 (broad S, 2H); GCMS, m/e (% rel. int.) 112 (31), 98 (11), 97 (100), 95 (26), 71 (13), 59 (15), 58 (30), 55 (11).

The combined yields of silacyclopentenes 270 and 271 was 5%. Both isomers were found to be present in approximately an equal amount by GC.

The combined yields of all of the above products plus unreacted 263 accounted for 73% of the total pyrolysate.

Copyrolysis of 263 and Trimethylsilane

Allyldimethylsilane (263) was pyrolyzed under identical conditions to those described above at 610-615°C with the exception that trimethylsilane, at a flow rate of 43 ml/minute, was employed as the carrier gas. Analysis of the pyrolysate (which represented a 21% mass recovery) by

GC and GCMS revealed that it was identical to that obtained when N_2 was used as the carrier gas (vide supra).

Synthesis of 5-Methyl-5-Sila-1-Hexene (264)

To a stirred suspension of 8.5 g (0.0899 mol) of chlorodimethylsilane, 50 ml of dry Et_2O, and 3 g (0.125 mol) of magnesium was added over 2 hours a solution of 12 g (0.0899 mol) of 4-bromobutene in a equal volume of dry Et_2O containing of a crystal of I_2. When the addition was complete, the reaction was stirred at room temperature for 8 hours, hydrolysed with H_2O, and the ethereal solution obtained by extraction. The ethereal solution was washed once with H_2O, once with sat. aqueous NaCl, and dried over $MgSO_4$. After careful removal of the Et_2O solvent by distillation, 264 was isolated by preparative gas chromatography on a 6 ft. X 1/4 inch, 10% OV-101/chrom W column at 100°C: NMR (CCl_4) δ 0.05 (d, 6H, J = 4Hz, collapses to a singlet with hν at δ 3.79), 0.41 to 0.88 (m, 2H, collapses to a broad and poorly resolved triplet with hν at δ 3.79, collapses to a broad and poorly resolved doublet with hν at δ 2.01, methylene protons σ to Si), 1.80 to 2.29 (m, 2H, allylic methylene β to Si), 3.79 (heptet, 1H, J = 4Hz, Si-H), 4.6 to 5.01 (m, 2H, vinylic methylene protons), 5.34 to 6.04 (m, 1H, collapses to a d of d with J_{AB} = 10Hz and J_{AX} = 17Hz with hν at 2.01, vinylic methine proton); GCMS, m/e (% rel. int.) 114 (0.6), 113 (5), 100 (6), 99 (5), 87 (37), 85 (16), 59 (100).

Vertical Flow Pyrolysis of 264

Butenylsilane (264) (1.3344 g, 0.0117 mol) was added mechanically at the rate of 2.2 ml per hour to a one foot quartz tube filled with quartz chips and enclosed in a tube furnace maintained at 610°C. The volatiles were swept through the tube with a nitrogen flow of 30 ml per minute into a receiver flask cooled to -196°C. The pyrolysate (which represented a 64% mass recovery) was found to contain 8 major products by GC. These products were isolated by preparative gas chromatography on a 10 ft. X 1/4 inch, 20% SE-30/chrom W column at 85°C, and identified as 266 (9.6 yield), 267 (2.2 % yield), 268 (5.0% yield), 263 (6.2% yield), 269 (8.5% yield), unreacted 264 (10% recovery), and 270 and 271 (13% combined yield) on the basis of their GCMS and NMR spectra (*vide supra*). Yields were determined by calibrated GC using cyclooctene as a standard.

Synthesis of 6-Methyl-6-Sila-1-Heptene (265)

A solution of 5 g (0.0336 mol) of 5-bromo-1-pentene, 3.2 g (0.0336) mol) of chlorodimethylsilane, and 15 ml of dry Et_2O was added dropwise over one hour to a stirred suspension of 1 g (0.042 mol) of magnesium chips in 25 ml of dry Et_2O. When the addition was complete, the reaction was stirred at room temperature for 12 hours. The reaction mixture was then poured onto crushed ice and the organic phase was extracted, washed twice with H_2O, dried over $MgSO_4$, and distilled to afford 2.5 g (0.0195 mol, 58% yield) of 265, B.P. 88-94°C: NMR (CCl_4) δ 0.1 (d, 6H, J = 3.9Hz, $SiCH_3$, collapses to a singlet with $h\nu$ at δ 3.9), 0.2 to 0.91

(unsymmetrical m, 4H, methylenes α and β to Si), 1.28 to 1.79 (unsymmetrical m, 2H, allylic methylene), 3.9 (m, 1H, Si-H, collapses to a broad triplet with hν at δ 0.1, J = 2Hz, collapses to an unresolved m with hν at δ 0.6), 4.7 to 5.22 (unsymmetrical m, 2H, vinylic methylene protons), 5.4 to 6.16 (m, 1H, vinylic methine proton); IR (neat) 3080, 2962, 2922, 2860 (w), 2110 (S, Si-H stretch), 1642, 1250, 1055 (b), 909, 885, and 832 cm^{-1}; GCMS, m/e (% rel. int.) 127 (0.1) (parent - H), 113 (5) (parent - CH_3), 100 (6), 87 (37) (parent - allyl), 85 (16), 59 (100).

Vertical Flow Pyrolysis of **265**

Pentenylsilane **265** (1.3307 g, 0.0104 mol) was pyrolyzed under identical conditions employed for the pyrolysis of **264** (*vide supra*). Analysis of the pyrolysate (which represented a 62% mass recovery) by GC revealed the presence of greater than 23 products, of which 8 were major. The major products were isolated by preparative gas chromatography on a 10 ft. X 1/4 inch, 15% SE-30/chrom W column at an initial temperature of 70°C followed by manual temperature programing to 150°C, and identified as **266** (5%), **267** (4.4%), **268** (4%), **269** (4%), **263** (4.3%), **270** and **271** (5.6% combined yield), and unreacted **265** (8.3%) on the basis of their GCMS and NMR spectra (*vide supra*). Yields were determined by calibrated GC using toluene as a standard, and are based on reacted **265**.

Synthesis of Allyldiphenylsilane (**272**)

To a stirred solution of 11.18 g (0.0511 mol) of diphenylchlorosilane and 50 ml of dry Et_2O was added over one hour a solution of allylmagnesium chloride (65 ml, 0.8 M, 0.052 mol) in Et_2O. When the addition was complete, the reaction was stirred at room temperature for approximately 24 hours. The mixture was hydrolyzed with H_2O and the organic phase was collected. The ether solution was washed twice with H_2O, once with saturated, aqueous NaCl, dried over $MgSO_4$, and distilled to afford 5.22 g (0.023 mol, 46% yield) of **272**, B.P. 102-103°C at 0.13 torr; NMR (CCl_4) δ 2.3 (m, 2H, allylic methylene protons), 5.06 (m, 3H, Si-H overlapped by vinylic methylene protons), 6.01 (m, 1H, vinylic methine proton), 7.5 (m, 10H, aromatic protons). The boiling point and NMR data matched those previously reported (313).

Vertical Flow Pyrolysis of **272**

The pyrolyses were conducted by adding **272** mechanically at a rate of 2.1 ml/hour to a one foot quartz tube filled with quartz chips and enclosed in a tube furnace. The volatiles were swept through the tube with a flow of helium at a rate of 45-50 ml/minute into a cold trap cooled to -196°C. At 580°C, the pyrolysate (which represented a 61% mass recovery) was found by GC to contain 8 minor volatile compounds and 8 prominent nonvolatile compounds. The major component of the pyrolysate was found to be unreacted **272** (24% yield) by comparison of its GC retention time and NMR spectrum (following isolation) with those of authentic starting material. The nonvolatile components of this reaction were isolated by preparative gas chromatography on a 6 ft. X 1/4 inch, 30% SE-30/chrom W column at 190°C, and on a 5 ft. X 1/4 inch, XF-1150/

chrom P column at 160°C. The identities of the isolated products were established on the basis of the spectral data presented below. Yields were determined by calibrated GC using benzyldiphenylsilane as a standard, and are based on reacted **272**.

Diphenylsilane (**273**) NMR (CCl_4) δ 4.85 (S, 2H, Si-H), 7.25 (m, 10H, aromatic protons); GCMS, m/e (% rel. int.) 184 (29), 183 (8), 106 (100) (parent - C_6H_6), 105 (68), 79 (12), 78 (12), 53 (28), 51 (11); 17% yield.

Methyldiphenylsilane (**274**) NMR (CCl_4) δ 0.6 (d, 3H, J = 3.6 Hz, Si-CH_3), 4.86 (g, 1H, J = 3.6Hz, Si-H), 7.3 (m, 10H, aromatic protons); GCMS, m/e (% rel. int.) 198 (19), 197 (5), 183 (19), 120 (100), (parent - C_6H_6), 105 (63), 78 (10), 53 (20); 3.4% yield.

Diphenylvinylsilane (**275**) This product could not be separated from **274**, thus **275** was identified solely on the basis of GCMS: m/e (% rel. int.) 210 (16), 209 (4), 183 (20), 182 (46), 132 (100), 131 (41), 130 (24), 107 (15), 106 (19), 105 (81), 79 (15), 53 (33); matched that of an authentic sample prepared by an independent method (*vide infra*). The yield of **275** was not directly determined, but, was estimated to be present in <3% yield.

2,3,4,5,-Dibenzomethylsilole (**276**) NMR (CCl_4) δ 1.57 (d, J = 7 Hz, Si-CH_3, collapses to a singlet with irradiation at δ 4.05), 4.0 (unresolved q, Si-H, collapses to singlet with irradiation at δ 1.57), 7.2 (m, aromatic protons); due to the presence of impurities and the dilute nature of the sample, it could not be integrated; GCMS, m/e (% rel. int.) 196 (38), 181 (100), 166 (27), 165 (31), 119 (11), 117 (11), 105 (11), 103 (10), 91 (16), 89 (11), 77 (18), 51 (12); 10% yield.

Methylvinyldiphenylsilane (277) Due to the low yield of this product plus the presence of small amounts of unreacted 272, 277 was identified solely by GCMS: m/e (% rel. int.) 224 (32), 209 (51), 183 (56), 146 (67), 131 (11), 121 (37), 120 (48), 105 (100), 93 (8), 79 (14), 77 (15), 53 (33), matched that of an authentic sample prepared by an independent method (*vide infra*); yield estimated to be <3%.

1-Methyl-1-Phenyl-1-Silaindane (278) NMR (CCl_4) δ 0.61 (S, 3H, $SiCH_3$), 1.17 (m, 2H, methylene α to Si), 3.15 (m, 2H, benzylic methylene), 7.3 (m, 4H, aromatic protons); GCMS, m/e (% rel. int) 224 (20), 209 (100), (parent - CH_3), 195 (9), 146 (26), 145 (22), 131 (47), 105 (76), 98 (13), 78 (11), 77 (15); 6% yield.

1-Methyl-1-Phenyl-1-Silaindene (279) NMR (CCl_4) δ 0.59 (S, 3H, $SiCH_3$), 6.25 (d, 1H, J = 10.5Hz, methine α to Si), 7.3 (m, 5H, aromatic protons and methine β to Si); GCMS, m/e (% rel. int.) 222 (67), 207 (100), 181 (15), 178 (17), 155 (8), 143 (9), 129 (9), 111 (5), 77 (12); 2% yield.

At a temperature of 620°C, under otherwise identical conditions, pyrolysis of 272 afforded a pyrolysate that was similar to that found at 580°C, with the exception that only trace amounts (<5%) of unreacted 272 remained.

Vacuum Flow Pyrolysis of 272

Silane 272 (1.2138 g, 0.0054 mol) was distilled at room temperature and 1 X 10^{-5} Torr into a horizontal, one foot quartz tube packed with quartz chips and enclosed in a tube furnace thermostated at 800°C. The pyrolysate (0.7117 g, 59% mass recovery) was found by GC to be identical to that obtained upon vertical flow pyrolysis of 272 at 580°C (*vide supra*).

Copyrolysis of 272 and Trimethylsilane

This pyrolysis was conducted by adding 0.6468 g (0.0029 mol) of 272 mechanically at a rate of 2.1 ml/hour to a one foot quartz tube filled with quartz chips and enclosed in a tube furnace thermostated at 610°C. The volatiles were swept through to tube with trimethylsilane at a flow rate of 60 ml/minute into a cold trap cooled to -196°C. The pyrolysate (0.3955 g, 61% mass recovery) was found by GC and GCMS to be essentially identical to that obtained in the absence of trimethylsilane. Silanes 273 (10% yield), 274 (6% yield), 276 (8% yield) and 278 and 279 (8% combined yield) were identified solely by GCMS. Yields were determined by calibrated GC using benzyldiphenylsilane as a standard, and are based on reacted 272. Additionally, triphenylsilane (3% yield) was identified by GCMS: m/e (% rel. int.) 260 (6), 182 (100), 181 (67), 155 (8) 129 (5), 105 (60), 91 (6), 79 (15), 78 (14), 77 (9), 53 (25).

Synthesis of Diphenylvinylsilane (275)

To a stirred solution of 11.18 g (0.051 mol) of diphenylchlorosilane and 50 ml of dry Et_2O was added over a period of one hour a solution of vinylmagnesium bromide (46.5 ml, 1.1 M, 0.051 mol) in THF. When the addition was complete, the reaction was stirred at room temperature for 12 hours. The resulting mixture was hydrolyzed with H_2O, washed twice with H_2O, dried over $MgSO_4$, and the volatiles removed *en vacuo* to afford

8.097 g of a clear, pale yellow oil that by GC and NMR was >90% 275 (7.3 g, 0.035 mol, 68% yield). An analytical sample of 275 was obtained by preparative gas chromatography on a 6 ft. X 1/4 inch, 30% SE-30/chrom W column at 200°C and identified on the basis of the following spectral data: NMR (CCl_4) δ 4.96 (d, 1H, J - 2Hz, Si-H), 5.4 to 6.38 (m, 3H, vinyl protons), 7.2 (m, 10H, aromatic protons); GCMS, m/e (% rel. int.) 210 (15), 209 (4), 183 (15), 182 (25), 181 (26), 132 (100), 131 (34), 130 (19), 105 (63), 79 (11), 78 (12), 53 (25).

Synthesis of Methyldiphenylvinylsilane (277)

To a stirred solution of 16.92 g (0.072 mol) of methyldiphenylchlorosilane and 100 ml of dry THF was added over a period of one hour a solution of vinylmagnesium bromide (70 ml, 1.1M, 0.077 mol) in THF. When the addition was complete, the reaction was brought to reflux and maintained at reflux for about 24 hours. After cooling to room temperature, the mixture was hydrolyzed with dilute HCl and extracted thrice with pentanes. The organic fractions were combined, dried over $MgSO_4$, and concentrated *en vacuo*. The resulting residue was chromatographed on silica gel and then distilled to afford 6.9 g (0.031 mol, 43% yield) of 277, B.P. 84-85°C at 0.1 Torr: NMR (CCl_4) δ 0.58 (5, 3H, $Si-CH_3$), 5.43 - 6.8 (m, 3H, vinyl protons), 7.32 (m, 10H, aromatic protons); GCMS, m/e (% rel. int.) 224 (29), 209 (53), 197 (29), 195 (14), 183 (42), 181 (20), 165 (12), 146 (74), 131 (15), 121 (38), 120 (55), 105 (100), 99 (11), 98 (15), 93 (14), 91 (11), 79 (17), 78 (10), 77 (11), 55 (12), 53 (46).

Vertical Flow Pyrolysis of **277**

The pyrolysis was conducted as described for the vertical flow pyrolysis of **272** (*vide supra*). At 600°C, 0.9481 g (0.0042 mol) of **277** afforded a pyrolysate (0.3862 g, 41% mass recovery) which was found by GC and GCMS to contain mainly unreacted **277** plus small amounts of **274**, **278**, and **279**, in addition to 5 unidentified volatile products. At 650°C, the relative GC peak areas of **274**, unreacted **277**, and **278** and **279** (which appeared together) were approximately equivalent. The identities of these compounds were established by NMR and GCMS (*vide supra*) following isolation by preparative gas chromatography employing the conditions described previously. Yields were determined by calibrated GC using benzyldiphenylsilane as a standard and are based on reacted **277**: unreacted **277**, 0.73%; **274**, 1.1%; combined yields of **278** and **279**, 1%. With the exception of 10 minor (based on relative GC peak areas), unidentified products, and an unidentified impurity in the isolated sample of **278** and **279**, no other products were observed.

Synthesis of Allylbenzyldimethylsilane (**280**)

To a stirred suspension of 8 g (0.33 mol) of magnesium chips in a solution of 21.28 g (0.165 mol) of dimethyldichlorosilane and 120 ml of dry THF was added over a period of 3 hours a solution of 21.38 g (0.165 mol) of benzyl chloride and a crystal of I_2. When the addition was complete, the reaction was stirred at room temperature for 8 hours. Allylbromide (20 g, 0.165 mol) was then added to the resulting mixture.

After stirring at 25°C for 12 hours, the resulting mixture was hydrolyzed with dilute HCl and extracted twice with hexanes. The organic fractions were combined, dried over Na_2SO_4, and fractionated to afford 11.5 g (0.061 mol, 37% yield) of **280**, B.P. 60-61°C at ca. 0.5 Torr: NMR (CCl_4) δ 0.42 (5, 6H, $SiCH_3$), 1.81 (broad d, 2H, J = 8Hz, allylic methylene), 2.4 (5, 2H, benzylic methylene), 4.9-5.2 (unsymmetrical d of m, 2H, vinyl methylene protons), 5.51-6.25 (m, 1H, vinyl methine proton), 7.31 (broad m, 5H, aromatic protons); IR (neat) 3060, 3020, 2950, 2882, 1620, 1590, 1484, 1445, 1395, 1240, 1200, and 1145 cm^{-1}; mass spectrum, m/e (% rel. int.) 190 (6), 151 (16), 149 (100), 121 (43), 99 (28), 59 (19), exact mass calculated for $C_{12}H_{18}Si$, m/e 190.11778, measured 190.11839, exact mass calculated for $C_9H_{13}Si$ (parent - allyl), m/e 149.07865, measured 149.07819.

Vertical Flow Pyrolysis of **280**

The pyrolysis of **280** was conducted by the mechanical addition of **280** at a rate of 2.1 ml/hour to a one foot, vertical quartz tube filled with quartz chips and enclosed in a tube furnace. The volatiles were swept through the tube with a N_2 flow of 53-58 ml/minute into a cold trap cooled to -196°C. At 620°C, the pyrolysate (which represented a 73% mass recovery) was found by GC to be approximately 75% unreacted **280**. At 680-700°C, the pyrolysate (63% mass recovery) contained greater than 18 products in addition to unreacted **280** (9%). The major products were isolated by preparative gas chromatography on a 10 ft. X 1/4 inch, 20% SE-30/chrom W column at an initial temperature of 140°C followed by manual temperature programing to 250°C. The identities of these products were established on the basis of the following spectral data, and their yields (relative to reacted 280) were determined by calibrated GC using xylene as a standard.

Toluene (281) NMR (CCl_4) δ 2.4 (5, 3H), 7.19 (5, 5H), matched that of an sample; GCMS, m/e (% rel. int.) 92 (60), 91 (100), 65 (16), 51 (11), matched with that of authentic sample; 6% yield.

Trimethylphenylsilane (282) NMR (CCl_4) δ 0.4 (5, 9H), 7.35 (m, 5H); GCMS, m/e (% rel. int.) 150 (11), 135 (100), 105 (8), 53 (8), matched with that of an authentic sample; 7.4% yield.

Benzylvinyldimethylsilane (283) NMR (CCl_4) δ 0.5 (5, 6H), 2.2 (5, 2H), 6.2 (m, 3H), 7.25 (m, 5H); GCMS, m/e (% rel. int.) 176 (6), 161 (4), 85 (100); yield estimated to be <0.5%.

Benzyldimethyldisiloxane (284) NMR (CCl_4) δ 0.27 (5, 12H), 2.3 (5, 4H), 7.3 (broad m, 10H); GCMS, m/e (% rel. int.) 312 (0.3) (parent), 223 (100) parent - Me_3SiO), 207 (26), 179 (17), 131 (15), 121 (17), 91 (31), 73 (49), 65 (13), 59 (20), exact mass calculated for $C_{18}H_{24}OSi_2$, m/e 312.13658, measured 312.13602; 23.2% yield.

In addition to these products, and styrene (<1% yield), which was isolated and identified by comparison of its NMR with that of authentic sample, a variety of other products, all formed in <1% yield, with the exception of 53 and 286 for which the combine yield was determined to be 8%, were tentatively identified by GCMS as described below.

Dimethylvinylsilane (267) GCMS, m/e (% rel. int.) 86 (9), 85 (5), 71 (34), 58 (100).

Trimethylsilane (266) GCMS, m/e (% rel. int.) 74 (3), 73 (46), 59 (100), 58 (25), 56 (25), 55 (15).

Trimethylvinylsilane (268) GCMS, m/e (% rel. int.) 100 (5), 85 (85), 74 (12), 73 (14), 67 (10), 66 (24), 65 (15), 59 (100).

Dimethylallylsilane (263) GCMS, m/e (% rel. int.) 100 (7), 99 (2), 85 (20), 72 (12), 59 (100).

Trimethylallylsilane (269) GCMS, m/e (% rel. int.) 114 (4), 99 (13), 73 (100), 59 (21).

Benzyldimethylsilane (285) GCMS, m/e (% rel. int.) 150 (17), 135 (22), 91 (10), 59 (100).

1,1-Dimethyl-1-Silaindene (53) GCMS, m/e (% rel. int.) 160 (30), 145 (100), 143 (13), 119 (8), 105 (10), 77 (6), 73 (9), 53 (17), matched that of an authentic sample prepared by the addition of dimethylsilylene to COT (*vide supra*).

2,2-Dimethyl-2-Silaindane (286) GCMS, m/e (% rel. int.) 162 (57), 147 (100), 145 (57), 105 (18), 53 (17). Although this spectrum is consistent with 1,1-dimethyl-1-silaindane, the finding that a NMR of 286, as a mixture of 286, 53, and 283, contained only singlets in the benzylic region was felt to be more consistent with the isomer assigned. Moreover, 286 was isolated in pure form from the vacuum pyrolysis of 280 and found to have a similar GCMS to that reported here (*vide infra*).

Vacuum Flow Pyrolysis of 280

This pyrolysis was conducted by distilling 280 at room temperature and 1.4 X 10^{-4} Torr into a one foot, horizontal quartz tube filled with quartz chips and enclosed in a tube furnace thermostated at 860°C. The pyrolysate (which represented a 70% mass recovery) was condensed in a cold trap cooled to -196°C. The pyrolysate was found by GC and GCMS to contain greater than 15 products in addition to unreacted 280 (27% yield). The major products were isolated by preparative gas chromatography on a 10 ft. X 1/4 inch, 10% DC-550/chrom W column at an initial temperature of 110°C followed by manual temperature programing to 250°C. The yields of the products were determined by calibrated GC and are based on reacted 280.

Toluene (281), ethylbenzene (288), and styrene (287) were identified by comparison of their GCMS and NMR spectra with those of authentic samples, and were present in 9, 4, and 11% yields, respectively. Silylindene 53 (4% yield) and disiloxane 284 (9% yield) were identified by comparison of their GCMS and NMR spectra to those reported previously (*vide supra*).

2-Methyl-2-Silaindane (289) NMR (CCl_4) δ 0.3 (d, 3H, J = 3Hz, collapses to a singlet with hν at δ 4.35), 2.12 (d of AB quartet, 4H, J_{AB}=16Hz, J_{BX}=J_{AX}=3Hz, collapses to an AB quartet with hν at δ 4.35, benzylic methylene protons), 4.35 (m, 1H, Si-H, collapses to an unresolved quartet with hν at δ 2.12, collapses to a poorly resolved quintet with hν at δ 0.3), 7.0 (m, 4H, aromatic protons); IR (CCl_4) 3080, 3030, 2975, 2900, 2145, (Si-H stretch), 1579 (W), 1530 (W), 1484, 1460, 1399, 1255, 1214, 1132, 942, 898, and 869 cm^{-1}; GCMS, m/e (% rel. int.) 148 (100), 147 (36), 146 (46), 145 (27), 133 (77), 132 (15), 131 (51), 119 (10), 105 (52), 77 (21), 53 (47); 12% yield.

2,2-Dimethyl-2-Silaindane (286) NMR (CCl_4) δ 0.25 (5, 6H, $SiCH_3$), 2.03 (5, 4H, benzylic methylenes), 6.95 (broad m, 4H, aromatic protons); 162 (61), 148 (16), 147 (100), 146 (14), 145 (56), 119 (24), 105 (15), 59 (57); 2% yield.

In addition to these major products, the presence of trace amounts (<2% yield) of 269, 285, and 283 was also found by GCMS.

Synthesis of Benzyldimethylsilane (285)

A solution of 26.2 g (0.202 mol) of benzylchloride, 12.75 g (0.135 mol) of dimethylchlorosilane, and an equal volume of dry Et_2O was added over 2 hours to a stirred suspension of 6 g (0.25 mol) of magnesium in 25 ml of dry Et_2O. When the addition was complete, the reaction was stirred at room temperature for 24 hours. The mixture was poured onto crushed ice, the organic phase was extracted, washed twice with H_2O, dried over $MgSO_4$, and distilled to afford 11.9 g (0.079 mol, 59% yield) of 285, B.P. 85-88°C: NMR (CCl_4) δ 0.02 (d, 6H, J = 3.8Hz, collapses to a singlet with hν at δ 3.98), 2.05 (d, 2H, J = 3.4Hz, benzylic protons, collapses to a singlet with hν at δ 3.98), 3.98 (m, 1H, Si-H, collapses to a triplet with J = 3.4Hz with hν at δ 0.02, collapses to an unresolved multiplet with hν at δ 2.05), 6.95 (broad m, 5H, aromatic protons); GCMS, m/e (% rel. int.) 150 (18), 149 (4), 135 (19), 91 (9), 59 (100).

Vacuum Flow Pyrolysis of 285

The pyrolysis was conducted by distilling 285 at room temperature and 3 X 10^{-4} Torr into a one foot quartz tube filled with quartz chips and enclosed in a tube furnace. The volatiles were condensed into a cold trap cooled to -196°C. At a temperature of 800°C, the pyrolysate (which represented 71% mass recovery) was found by GC to contain only unreacted 285. Similar results were found at 860°C, with the exception that an 85% mass recovery was obtained.

Synthesis of 1-Benzyl-1-Methyl-1-Silacyclobutane (292)

A solution of 2.0 g (0.0167 mol) of 1-chloro-1-methyl-1-silacyclobutane, 3.0 g (0.023 mol) benzylchloride, and 25 ml of dry Et_2O was added over 1 hour to a stirred suspension of 1 g (0.042 mol) of magnesium in 15 ml of dry Et_2O. When the addition was complete, the reaction was stirred at room temperature for 24 hours. The reaction was then poured onto crushed ice and hydrolysed with 10% HCl. The organic phase was extracted, washed twice with H_2O, dried over $MgSO_4$, and the solvent removed *en vacuo* to afford 2.8 g of a clear, colorless liquid that by NMR and GC analysis was greater that 90% 292. On this basis, the amount of 292 obtained was estimated to be 2.5 g (0.0142 mol, 85% yield). Analytical samples of 292, for spectral analysis and pyrolysis, were obtained by preparative gas chromatography on a 10 ft. X 1/4 inch, 15% SE-30/chrom W column at 170°C.

1-Benzyl-1-Methyl-1-Silacyclobutane (292) NMR (CCl_4) δ 0.23 (S, 3H), 0.76 to 1.18 (unsymmetrical triplet, 4H, methylenes σ to Si), 1.67 to 2.24 (m, 2H, methylene β to Si), 2.29 (S, 2H, benzylic methylene), 7.05 (broad m, 5H, aromatic protons); IR (neat) 3085, 3065, 3030, 2970, 2925, 1605, 1495, 1453, 1410, 1395, 1250, 1208, 1153, 1120, 1053, 1029, 923, 904, 870, 799, 780, 755, and 695 cm^{-1}; GCMS, m/e (% rel. int.) 176 (30), 161 (4), 148 (100), 147 (27), 146 (32), 135 (22), 134 (17), 133 (64), 131 (15), 119 (16), 107 (11), 105 (23), 91 (26), 85 (69), 65 (22), 53 (16).

Vacuum Flow Pyrolysis of 292

Silacyclobutane 292 was distilled at room temperature and 7.4 X 10^{-4} Torr into a one foot, horizontal, quartz tube filled with quartz chips and enclosed in a tube furnace thermostated at 820°C. Analysis of the pyrolysate by G.C. revealed the presence of >12 compounds, six of which were present in sufficient quantities to allow for their isolation by preparative gas chromatography on a 10 ft. X 1/4 inch, 15% SE-30/chrom W column at an initial temperature of 150°C followed by manual temperature programing to 250°C.

The identities of 281, 287, and 289 were determined on the basis of their GCMS and NMR spectra (vide supra). 1,2-diphenylethane (293) was identified on the basis of the following spectral data: NMR (CCl_4) δ 3.1 (5, 4H), 7.3 (5, 10H); GCMS, m/e (% rel. int.) 182 (15), 91 (100), 65 (14).

In addition to these products, 1,1-dimethyl-2,3,5,6-dibenzo-1-silacyclohepta-2,5-diene (294) and a mixture of isomeric 1,3-dibenzyl-1,3-dimethyl-1,3-disilacyclobutanes (295), were identified on the basis of the following spectral data. Due to the inability to separate 294 from 295, these assignments are tentative.

1,1-Dimethyl-2,3,5,6-Dibenzo-1-Silacyclohepta-2,5-Diene (294) NMR (CCl_4) δ 0.5 (5, 6H), 2.55 (5, 2H), 5.0 (5, 2H), 7.2 to 7.6 (broad m); GCMS, m/e (% rel. int.) 238 (3), 223 (6), 165 (62), 135 (44), 91 (100), 65 (19).

1,3-Dibenzyl-1,3-Dimethyl-1,3-Disilacyclobutane (as a mixture of isomers, 295) GCMS, m/e (% rel. int.) 296 (2), 281 (2), 205 (100) (parent - C_7H_8), 177 (26), 145 (33), 121 (14), 105 (11), 91 (16), 59 (32).

No attempt was made to determine the absolute yields of the products isolated from this pyrolysis. However, on the basis of the relative GC peak areas and NMR spectra of the crude pyrolysate, 287 and 289 were the major products of the reaction.

Thermolysis of 263 in the presence of a Radical Initiator and Either Ortho-Dichlorobenzene or Cyclooctene

For the reactions employing cyclooctene, 0.5 ml (approximately 0.5 g, 0.005 mol) of 263, 3 ml of cyclooctene, and approximately 0.01 g of either AIBN or benzoyl peroxide were placed in a sealing tube and degassed by the freeze-thaw method. For the reaction utilizing AIBN, thermolysis was conducted at 90-100°C for 3 hours, while that utilizing benzoyl peroxide was heated at 90-100°C for 17 hours. Analysis of the reactions by GC revealed, in both cases, the presence of unreacted 263 and solvent as the only observable products.

For the reactions utilizing ortho-dichlorobenzene, 0.5 ml of 263, 10 ml of ortho-dichlorobenzene, and approximately 0.01 g of either AIBN or benzoyl peroxide were placed in a sealing tube and degassed by the freeze-thaw method. For both of these reactions, thermolyses were conducted at 90-100°C, with that employing AIBN being conducted for 3 hours, and that employing benzoyl peroxide being conducted for 12 hours. Analysis of the reactions by GC revealed, in both cases, the presence of unreacted 263 and solvent as the only observable products.

Synthesis of 2,2,6-Trimethyl-2,6-Disilahept-3-Ene (298)

To a stirred solution of 11.4 g (0.1 mol) of trimethylallylsilane, 11.6 g (0.1 mol) of dry TMEDA, and 100 ml of dry Et_2O was added a solution of n-butyllithium (40 ml, 2.5 M, 0.1 mol) in Et_2O. The reaction was then stirred for 5 hours at room temperature. Chlorodimethylsilane (9.5 g, 0.1 mol) was added rapidly to the resulting solution, followed by stirring at room temperature for 24 hours. The reaction was poured onto crushed ice/H_2O and the organic phase was extracted, washed twice with H_2O, once with sat. aqueous NaCl, dried over Na_2SO_4, and distilled to afford 12 g (0.0689 mol, 70% yield) of 298. B.P. 73-78°C at 31 Torr: NMR (CCl_4) δ 0.03 (5, 9H, $SiMe_3$), 0.04 (d, 6H, J_{DC} = 3.8Hz), 1.66 (d of d, 2H, J_{DC} = 3.8Hz J_{BC} = 7.8Hz, allylic methylene), 3.89 (m, 1H, J = 3.8Hz, Si-H), 5.39 (d, 1H, J_{AB} = 16Hz), 5.93 (d of t, 1H, J_{AB} = 16Hz, J_{BC} = 7.8Hz); IR (neat) 2960, 2900 (W), 2120, 1608, 1400, 1249, 1145, 983, 885, 870, 833, and 695 (B) cm^{-1}; GCMS, m/e (% rel. int.) 172 (2), 157 (6), 129 (8), 98 (64), 83 (23), 73 (100), 59 (34); GCMS, m/e (% rel. int.) 172 (1.6), 157 (6), 144 (1.4), 141 (1.1), 129 (8.2), 98 (64), 83 (23), 73 (100), 59 (34).

Thermolysis of 298 and *t*-Butylbenzoyl Peroxide (300)

a) A thick walled sealing tube, equipped with a constriction for sealing, was charged with 0.8183 g (4.76 X 10^{-3} mol) of 298 and 0.1631 g (8.41 X 10^{-4} mol, 0.25 molar equivalents) of 300. After degassing thrice by the freeze-thaw method, the tube was sealed, and then heated at 140°C for 2.5 hours. Analysis of the reaction mixture by GC and GCMS revealed the presence of unreacted 298 as the only major species present. The identity of 298 was established by comparison of its GC retention time and GCMS spectra with those of an authentic sample.

b) A thick walled sealing tube, equipped with a constriction for sealing, was charged with 0.1244 g (7.23 X 10^{-4} mol) of 298, 2.55 X 10^{-2} g (1.31 X 10^{-4} mol, 0.18 molar equivalents) of 300, and 3 ml of dry benzene. After degassing thrice by the freeze-thaw method, the tube was sealed, and then heated at 110-120°C for 12 hours. Analysis of the resulting solution by GC revealed the presence of unreacted 298 (52% recovery) and solvent as the only detectable species. The identity of 298 was established by comparison of its GC retention time and NMR spectra with those of an authentic sample. The % recovery of 298 was determined by calibrated GC using *t*-butylbenzene as an internal standard.

c) A thick walled sealing tube, equipped with a constriction for sealing, was charged with 0.1300 g (7.56 X 10^{-4} mol) of 298, 2.55 X 10^{-2} g (1.31 X 10^{-4} mol, 0.17 molar equivalents) of 300, and 2 ml of bromocyclohexane. After degassing thrice by the freeze-thaw method, the tube was sealed, and then heated at 120-125°C for 16.75 hours. Analysis of the resulting thermolysate by GC revealed the presence of unreacted 298 and bromocyclohexane as the only detectable species.

Thermolysis of 298 and Di-*t*-Butyl Peroxide (305)

a) A thick walled sealing tube, equipped with a constriction for sealing, was charged with 0.3451 g (2.01 X 10^{-3} mol) of 298, 0.1561 g (1.07 X 10^{-3} mol, 0.53 molar equivalents) of 305, and 3 ml of dry cyclohexane. Both 305 and cyclohexane were passed through a column of alumina prior to use. After degassing thrice by the freeze-thaw method, the tube was sealed, and then heated at 135-140°C for 17 hr. Analysis of the reaction mixture by GC revealed the presence of two compounds in addition to the solvent, cyclohexane. The compound with the shorter GC retention time was identified, after isolation by preparative GC on a 10 ft. X 1/4 inch, 20% SE-30/chrom W column at a temperature of 120°C, as *t*-butyl alcohol by comparison of its GC retention time and NMR spectra with those of an authentic sample. The compound with the longer GC retention time was identified as unreacted 298 by comparison of its GC retention time with that of an authentic sample.

b) A solution of 0.2115 g (1.23 X 10^{-3} mol, 0.049 mol/lt) of 298, 0.916 g (6.27 X 10^{-4} mol, 0.026 mol/lt, 0.51 molar equivalents) of 305, and sufficient cyclohexane such that the total volume of the solution was 25 ml was placed in a thick walled sealing tube equipped with a constriction for sealing. After degassing thrice by the freeze-thaw method, the tube was sealed, and then heated at 140°C for 24 hours. Analysis of the thermolysate by GC revealed that 298 had been completely consumed. However, with the exception of solvent no other compounds were observable by GC. The cyclohexane solvent was removed *en vacuo* affording on oily residue, which by NMR was found to be *t*-butyl alcohol and an unidentifiable silicon containing species on the basis a strong, broad, singlet at δ = 0.00. In a repeat of this reaction, 100 ml of a cyclohexane solution of 1.1968 g (6.958 X 10^{-3} mol, 0.0696 mol/lt) of **298** and 0.5117 g (3.50 X 10^{-3} mol, 0.035 mol/lt, 0.50 molar equivalents) of **305** was degassed as before and heated at 130°C for 14 hours. After thermolysis, the solvent was removed *en vacuo* and the resulting residue was chromatographed (silica-gel, hexane elution) to afford 0.8444 g (70.6% mass recovery) of compound A. Further elution with ethyl acetate afforded 0.0985 g (8.2% mass recovery) of compound B. Both compound A and compound B gave single spots by thin-layer-chromatography, and were therefore assumed to be pure compounds.

Compound A NMR (CCl_4) δ 0.05 (broad S, relative area of 3H), 0.3 to 2.0 (broad, unresolvable m, relative area of 1H), 3.8 to 4.2 (broad unresolvable m), 5.3 to 5.9 (broad, unresolvable m); IR (neat) 2958, 2925, 2910, 2860, 2110, 1585, 1445, 1407, 1245, 1025, and 825 cm^{-1}.

Compound B NMR (CCl_4) δ 0.07 (broad d), 0.1 (broad 5), relative area of signals at δ 0.07 and 0.1 is 2.4H, 0.31 to 2.5 (broad, unresolvable m, relative area of 1H); IR (neat) 2940, 2850, 2102, 1695, (weak), 1585, 1443, 1401, 1245, 1070, and 1010 cm^{-1}.

Although these two compounds could not be identified on the basis of the spectral data obtained, some conclusions regarding their nature can be made. First, that neither compound could be observed by GC was taken as evidence that the compounds possessed a high molecular weight, and were therefore oligomeric. Secondly, both compounds were found to contain silicon on the basis of their NMR (Si-CH_3 resonance at δ 0.05 for A and 0.07 and 0.1 for B) and IR spectra (Si-H stretch, 2110 cm^{-1} for A and 2102 cm^{-1} for B; Si-CH_3 stretch, 1245 cm^{-1} for both A and B). Thirdly, on the basis of the relative NMR peak areas for the Si-CH_3 and alkyl proton resonance (3:1 for A and 2.4:1 for B) both compounds contained approximately the correct ratio of Si-CH_3 to alkyl protons that would be expected were the compounds oligomers of 298. Thus, oligomerization of 298, by attack of the anticipated silyl radical $Me_3SiCH{=}CHCH_2\dot{S}i(CH_3)_2$ at the double bond of 298, would afford compounds which contain a relative ratio of Si-CH_3 protons to alkyl protons of approximately 3:1. That the relative ratio of Si-CH_3 to alkyl protons for compound B is only 2.4 to 1 may indicate that some solvent radicals are incorporated. Whatever the exact identity of the products of this reaction, the results clearly demonstrate that radicals derived from 298 to not undergo clean intramolecular cyclizations.

c) A solution of 0.1786 g (1.038×10^{-3} mol, 0.042 mol/lt) of 298, approximately 1×10^{-3} g (6.85×10^{-6} mol, 6.6×10^{-3} molar equivalents) of 305, and sufficient dry cyclohexane (passed through a column of alumina prior to use) such that the total volume of the solution was 25 ml was degassed and thermolized at 130°C for 20 hours, following the method described above. Analysis of the resulting reaction mixture by GC revealed that no consumption of 298 had occurred. This result, coupled with the results obtained previously, demonstrates that the reaction of 298 and 305 is not catalytic in 305.

Cothermolysis of **298**, **305**, and CCl_4

a) A solution of 0.1282 g (7.45×10^{-4} mol) of **298**, 0.0042 g (2.88×10^{-5} mol, 0.039 molar equivalents) of **305**, and 0.6 ml of CCl_4 was placed in a jointed NMR tube equipped with a constriction for sealing. After degassing thrice by the freeze-thaw method, the tube was sealed, and then heated at 130°C. After thermolysis for 9 hours, analysis by NMR revealed that no detectable reaction had occurred. Similar results were found after thermolysis for 18 and 24 hours. Thus, after 24 hours, analysis of the reaction by NMR revealed that the solution was identical to that observed prior to heating, with the exception of a small signal at δ 7.24, which on the basis of its chemical shift was assigned to $CHCl_3$. On the basis of the relative NMR peak areas of the signal at δ 7.24 and those due to the allylic methylene of **298** (*vide supra*), and assuming that $CHCl_3$ was formed by Cl abstraction from CCl_4 by the radical expected from **298**, less than 10% of **298** had reacted.

b) A solution of 0.1955 g (1.14×10^{-3} mol) of **298**, 0.0807 g (5.53×10^{-4} mol, 0.49 molar equivalents) of **305**, and 0.7 ml of CCl_4 was placed in a jointed NMR tube equipped with a constriction for sealing, and was degassed and thermalized at 130°C for 12 hours as described previously. Analysis of the reaction mixture by GC revealed the presence of four compounds, in addition to CCl_4. These compounds were isolated by preparative gas-chromatography on a 10 ft X 1/4 inch, 20% SE-30/chrom W column at an initial temperature of 100°C followed by manual temperature programing to 200°C. Unreacted **298**, $CHCl_3$, and *t*-butyl alcohol were identified by comparison of their GC retention times and NMR spectra with those of authentic samples. The identity of 310 was established on the basis of the following NMR spectra. Due to the presence of C_2Cl_6, which had the same GC retention time as 310, a GCMS was not obtainable for 310. The identity of hexachloroethane was established by comparison of its GCMS with that of an authentic sample.

6-Chloro-2,2,6-Trimethyl-2,6-Disilahept-3-Ene (310) NMR (CCl_4) δ 0.09 (5, 9H), 0.42 (5, 6H), 1.92 (d, J_{AX} = 6.5Hz, 2H, allylic CH_2), 5.51 (d, J_{AB} = 18Hz, 1H, vinyl proton α to $SiMe_3$), 6.03 (d of t, J_{AB} = 18Hz, J_{AX} = 6.5Hz, 1H, vinyl proton β to $SiMe_3$).

By consideration of the weighted NMR peak areas of the vinyl protons α to Si for 298 and 310 and the area of the C-H absorbance for $CHCl_3$ the respective yields of 298, 310, and $CHCl_3$ were determined to be 59, 41, and 63%. Due to the inability to separate C_2Cl_6 from 310 by GC or to observe C_2Cl_6 by NMR, its yield could not be determined. The yields of 310 and $CHCl_3$ are based on reacted 298.

Photolysis of 263 in the Presence of Hg

A 40 ml quartz tube equipped with a vacuum stopcock was charged with 0.4 ml (approximately 0.4 g, 0.004 mol) of 263 and a drop of Hg. The tube was then degassed by the freeze-thaw method. Following irradiation for 16 hours at approximately 45°C in a Rayonette photochemical reactor equipped with 2537 Å lamps, the tube was found to contain a small amount of clear, colorless liquid and a layer of colorless crystalline material coating the sides. The liquid, 253, was identified on the basis of its NMR spectrum. The crystalline material was not soluble in either boiling CCl_4 or benzene, and was therefore assumed to be polymeric.

Photolysis of 298 in the Presence of Hg

a) Disilane 298, 0.3321 g (1.93×10^{-3} mol), and a drop of Hg were placed in a quartz tube fitted with a vacuum stopcock. The tube was degassed thrice by the freeze-thaw method, and irradiated for 21 hours at approximately 45°C with a 450 W Hanovia lamp through a quartz filter. Analysis of the photolysate by NMR and GC revealed the presence of unreacted 298 as the only detectable species. The identity of 298 was established by comparison of its GC retention time and NMR spectrum with those of an authentic sample.

b) In a repeat of the above reaction, 0.2793 g (1.62×10^{-3} mol) of 298 and a drop of mercury were photolyzed following the procedure described above. Analysis of the photolysate by GC revealed the presence of two compounds. These compounds were isolated by preparative gas-chromatography on a 6 ft. X 1/4 inch, 10% OV-101/chrom W column at 100°C. The products were identified as 298 by comparison of its NMR spectrum with that of authentic 298, and 2,6,6-trimethyl-2,6-disila-3-heptene (317) on the basis of its NMR spectrum: (CCl_4) δ 0.09 (S, overlaps upfield doublet at $\delta = 0.1$), δ 0.1 (d, upfield signal overlapped by singlet at $\delta = 0.09$), signals at $\delta = 0.09$ and 0.1 account for 15H, 1.65 (d of m, 2H, $J_{AX} = 10Hz$, allylic methylene α to $SiMe_3$, 2H), 3.82 (m, J = 4Hz, 1H), 5.2 (d of d, $J_{AB} = 14Hz$,

J_{Si-H} = 1Hz, 1H, vinylic proton α to $SiMe_2H$), 6.19 (d of t, J_{AB} = 14Hz, J_{AX} = 10Hz, 1H, vinylic proton β to $SiMe_2H$.

The relative ratio of **298** to **317** was determined to be 1:1.15. Under similar reaction conditions, with the exception that photolysis was conducted for 75 hours, the relative ratio of **298** to **317** was found to be 1:1.57. In both cases, the ratio of **298** to **317** was determined by consideration of the relative GC peak areas of **298** and **317**. Additionally, for the later reaction, **298** and **317** were obtained in 88% combined yield.

Synthesis of Allyloxydimethylsilane (**319**)

To a stirred solution of 8.5 g (8.99 X 10^{-2} mol) of dimethylchlorosilane, 7.2 g (9.1 x 10^{-2} mol) of dry pyridine, and 50 ml of dry Skelly-A was added 5.22 g (8.99 X 10^{-2} mol) of allyl alcohol. After stirring at room temperature for 14 hours, the solution, containing large amounts of precipitated pyridinium hydrochloride, was filtered through celite, concentrated _en vacuo_, and distilled to afford 2.85 g (0.025 mol, 27% yield) of **319**, B.P. 58-60°C; NMR (CCl_4) δ 0.2 (d, J = 2Hz, collapses to a singlet with hν at δ = 4.5, 6H), 4.05 (d of t, J_{AX} = 4Hz, J_{AA^1} = 1Hz, allylic methylene, 2H), 4.5 (m, J = 2Hz, collapses to a singlet with hν at δ = 0.2, Si-H, 1H), 4.95 (m, overlapped with upfield multiplet of signal at δ = 5.1), 5.1 (d of m, upfield multiplet overlapped with multiplet at δ = 4.95), signals at δ = 4.95 and 5.1 account for 2H and are assigned to the vinylic methylene protons, 5.7 (m, 1H, vinyl proton β to oxygen); GCMS, m/e (% rel.

int.) 116 (1.6), 115 (14), 101 (57), 99 (56), 85 (15), 75 (100), 71 (22), 61 (46), 59 (97).

Synthesis of 7-Methyl-5-Oxa-6-Silaheptene (320)

To a stirred solution of 13.5 g (1.43 X 10^{-1} mol) of dimethylchlorosilane, 11.3 g (1.43 X 10^{-1} mol) of dry pyridine, and 100 ml of dry Skelly-A was added 10 g (1.43 X 10^{-1} mol) of butene-4-ol over approximately 10 minutes. After stirring for 16 hours at room temperature, the mixture was filtered through celite to remove the precipitated pyridinium hydrochloride, and fractionated to afford 10 g (7.8 X 10^{-2} mol, 55% yield) of 320, B.P. 91-96°C; NMR (CCl_4) δ 0.17 (d, J = 3Hz, collapses to a singlet with $h\nu$ at δ = 4.59, 6H), 2.23 (broad q, J = 7Hz, collapses to a broad d (J = 5.8Hz) with $h\nu$ at δ = 3.61, 2H, allylic methylene), 3.61 (t, J = 7Hz, collapses to a singlet with $h\nu$ at δ = 2.23, 2H, methylene α to oxygen), 4.59 (m, J = 3Hz, collapses to a singlet with $h\nu$ at δ = 0.17, 1H, Si-H), 4.95 (d of m, 2H, vinyl methylene protons), 5.35 to 6.14 (m, 1H, vinyl methine proton).

Photolysis of 319 in the Presence of Hg

A quartz tube, equipped with a vacuum stopcock, was charged with 0.4612 g (3.98 X 10^{-3} mol) of 319 and a drop of Hg. After degassing thrice by the freeze-thaw method, the tube was photolyzed with a 450 W Hanovia lamp through a quartz filter for 21 hours at approximately 45°C. Analysis of the photolysate by NMR revealed the presence of unreacted 319 as the only observable species.

Photolysis of **320** in the Presence of Hg

A 2 lt Hanovia emersion well was charged with 2.297 g (1.77×10^{-2} mol) of **320** and a drop of mercury. The tube was degassed thrice by the freeze-thaw method and irradiated (450 W Hanovia lamp, quartz filter) at approximately 45°C for 15 hours. Analysis of the photolysate by GC revealed that no reaction had occurred, only unreacted **320** was detectable. The photolysate was then reintroduced into the emersion well, degassed thrice by the freeze-thaw method, and irradiated as before for 36 hours, with the exception that the emersion well was heated to 110-120°C to insure that **320** was in the gas phase. When the photolysis was complete, the contents of the emersion well were dissolved in Et_2O to aid their removal. After careful removal of the Et_2O by distillation, 2.5 g of a clear solution was obtained, which by GC contained some residual Et_2O, a small amount of butene-4-ol, and unreacted **320**. The identities of butene-4-ol and unreacted **320** were established, following isolation by preparative gas-chromatography on a 10 ft. X 1/4 inch, 20% DC-550/chrom W column at 110°C, by comparison of their GC retention times and NMR spectra with those of authentic samples. By calibrated GC, using heptane as a standard, 23% recovery of unreacted **320** was found.

The volatiles were then removed *en vacuo* from the photolysate to afford a clear viscous oil, which exhibited the following NMR spectrum: (CCl_4) $\delta = 0.1$ (S, relative area of 8H), 0.75 to 2.05 (broad) hump, relative area of 3H), 3.36 to 4.02 (broad hump, relative area of 1H). After silica-gel chromatography (hexane elution), the residue displayed the following NMR spectrum: (CCl_4) δ = 0.09 (S), 0.75 to 2.36 (broad hump), 3.2 to 4.2 (broad hump). On the basis of the spectral data obtained, this compound(s) could not be identified. However, the finding that this residue would not move through a GC column (10 ft. X 1/4 inch, 20% DC-550/chrom W) at column temperatures as high as 200°C clearly demonstrated that it was of high molecular weight, and therefore, oligomeric.

Synthesis of bis(dimethylallylsilyl)mercury (321)

Following the procedure of Hovland and coworkers (304), a solution of 6.74 g (5 X 10^{-2} mol) of dimethylallylchlorosilane, 228.5 g of 0.8% Na/Hg amalgum (7.95 X 10^{-2} mol of Na), and 20 ml of dry cyclohexane was placed in a thick walled sealing tube equipped with a constriction for sealing. After degassing once by the freeze-thaw method, the tube was sealed, wrapped with aluminum foil, and shaken at room temperature for 10 days. The tube was then transferred to a N_2 flushed dry bag and its contents diluted with 250 ml of dry cyclohexane. The resulting green solution was removed from the Na salts and unreacted amalgum by decantation. After en vacuo removal of the solvent, a viscous, dark-green oil was obtained, which by NMR was approximately 75% 321: (C_6D_6) δ - 0.09 (5, 6H), 1.35 (broadened d, J_{AX} = 8.2Hz, 2H, allylic methylene), 4.50 (d of m, 2H, vinylic methylene), 5.2 to 5.8 (m, 1H, vinylic methine), Hg satellite signals for the singlet at δ - 0.09 were observed with J_{HgH} = 35Hz.

Photolysis of 321

One ml of bis-silylmercurial 321 and 15 ml of dry decalin were placed in a septum sealed quartz tube in an Ar purged glove bag. The resulting solution was deoxygenated by bubbling Ar through the tube for approximately 10 minutes. The tube was then irradiated with a 450 W Hanovia lamp through quartz at approximately 45°C for 24 hours. Analysis of the resulting photolysate by GC revealed the presence of one major compound, in addition to greater than 14 minor products and the solvent. The identity of the major compound was determined to be 1,2-diallyltetramethyldisilane by comparison of its GC retention time with that of an authentic sample. Due to the small quantities of minor products, no attempt was made to effect their isolation and characterization.

Reaction of Diallyldimethylsilane (325) with $CHCl_3$ and Azo-bis-(isobutyryl)nitrile (AIBN)

Following the general procedure of Brace (306), a solution of 1.92 g (1.37 X 10^{-2} mol) of 325, 4.476 g (3.75 X 10^{-2} mol) of spectral grade $CHCl_3$ (Aldrich), and 2.85 X 10^{-2} g (1.74 X 10^{-4} mol) of AIBN was placed in a thick walled sealing tube equipped with a constriction for sealing. The tube was degassed thrice by the freeze-thaw method, sealed, and then heated at 142-143°C for 18 hours. The resulting solution (6.2 g, 97% mass recovery) was found by GC to contain one peak, in addition to $CHCl_3$. The compounds comprising this peak were isolated by preparative gas-chromatography on a 10 ft. X 1/4 inch, 20%

DC-550/chrom W column at 110°C, and by NMR and GCMS were identified as a mixture of isomeric bis(propenyl)dimethylsilanes 325, 328, and 329. By calibrated GC, using t-butylbenzene as a standard, the combined yield of 325, 328, and 329 was found to be 91%, of which 325 was found to account for approximately 58% of the mixture by NMR.

The NMR spectral data for the isolated mixture of 325, 328, and 329 are as follows: (CCl_4) δ 0.09 (5), 0.1 (5), 0.11 (5), the relative area of the signals at δ = 0.09, 0.1, and 0.11 was 6H, 1.55 (d, J = 8Hz, collapses to a singlet with hν at δ = 5.64, relative area of 2.8H), 1.87 (d, J = 4.6Hz, collapses to a singlet with hν at δ = 5.64, relative area of 2H), 4.72 (m, relative area of 1.4H), 4.96 (m, relative area of 1.4H), 5.29 to 6.18 (m, relative area of 2.8H).

Although it was not possible to separate these isomers by preparative gas-chromatography, that 325 was the major isomer was determined by comparison of the NMR spectrum of the mixture with that of authentic 325.

<u>Diallyldimethylsilane (Petrarch)</u> NMR (CCl_4) δ 0.09 (5, 6H), 1.55 (d, J = 8Hz, collapses to a singlet with hν at δ = 5.8, 2H), 4.69 (m, 1H), 4.94 (m, 1H), 5.31 to 6.19 (m, collapses to an AB quartet centered at δ = 5.8, with J_{AB} = 9Hz, with hν at δ = 1.55, 2H).

Analysis of the three $Si\text{-}CH_3$ signals of the isolated mixture by NMR at a 2 ppm sweep width revealed that the relative ratio of signals at δ = 0.11, 0.1, and 0.09 was approximately 1:2:4, respectively. This finding, coupled with the assignment of the signal at δ = 1.87 to the allylic methyls of 328, suggested that the relative ratio of 329 to 328 to 325 was 1:2:4.

While the three isomeric bis(propenyl)dimethylsilanes were not separable by preparative gas-chromatography, the capillary column of the GCMS resolved the three isomers and provided further evidence supporting our structural assignments.

Diallyldimethylsilane (325) GCMS, m/e (% rel. int.) 140 (1.1), 125 (1.2), 99 (100), 97 (12), 83 (7), 73 (12), 71 (30), 59 (96), matched that of authentic sample.

4,4-Dimethyl-4-silahepta-2,5-diene (328) GCMS, m/e (% rel. int.) 140 (3), 125 (63), 99 (16), 85 (71), 83 (13), 73 (20), 59 (100).

4,4-Dimethyl-4-silhepta-2,6-diene (329) GCMS, m/e (% rel. int.) 140 (0.3), 125 (9), 99 (92), 85 (13), 83 (10), 73 (46), 59 (100).

Reaction of 325, CCl_4, and AIBN

Following the procedure of Brace (306), a solution of 15.36 g (1.09×10^{-1} mol) of 325, 25.3 g (1.6×10^{-1} mol) of CCl_4, and 0.18 g (1.09×10^{-3} mol) of AIBN was placed in a N_2 flushed, round bottom flask and refluxed (85-90°C) under a N_2 atmosphere for 24 hours. Analysis of the crude reaction mixture by NMR revealed the presence of approximately 50% unreacted 325. Attempted distillation of the crude mixture, to remove unreacted 325, and CCl_4, initially at a pot temperature of 150°C (760 Torr) and later at a pot temperature of 140°C and 10 torr afforded less than 5 g of volatiles. Apparently, during the attempted distillation the reaction of 325, CCl_4, and

AIBN went to completion. The resulting residue, which accounted for approximately an 85% mass recovery, was found by GC to contain one major product. This product was isolated by preparative gas-chromatography on a 5 ft. X 1/4 inch, 3% OV-225/chrom W column at 150°C and exhibited the following spectral data: ^{1}H NMR, 60 Mhz, (CCl_4) δ 0.2 (5, 6H, $SiMe_2$), 0.88 (unresolved multiplet, 2H), 2.27 (unresolved multiplet, 3H), 2.72 (unresolved multiplet, 2H), 4.91 (d of d, J = 6Hz, J^1 = 3.2Hz, 1H), 5.15 (broad singlet, 1H), 5.39 to 6.16 (m, 1H); ^{1}H NMR, 90 MHz, ($CDCl_3$) δ = 0.46 (S), 1.19 (unresolved multiplet), 2.31 (unresolved multiplet), 2.72 (doublet of AB quartets, J_{AB} = 11.6Hz, J^1 = 4Hz), 4.97 (poorly resolved AB quartet), 5.19 (broad singlet), 5.32 to 6.18 (unresolved multiplet); ^{13}C NMR, 90 MHz, ($CDCl_3$) δ = 2.74, 2.9, 25.22, 32.42, 40.82, 60.21, 118.23, 135.08; the ^{13}C off-resonance decoupled NMR (90 MHz, $CDCl_3$), though poorly resolved even after 170 X 10^3 scans, revealed resonances at δ = 25.22 (t, J = 52.49Hz), 32.42 (d, J = 65.95Hz), 60.21 (t, J = 68.35Hz), 135.08 (d, J = 87.89Hz), the other resonances were not sufficiently resolved to allow for their proton couplings to be determined; IR ($CDCl_3$) 3075, 2960, 2920, 1639, 1436, 1420, 1410, 1254, 1050, 985, 836, 812, and 790 cm^{-1}; mass spectrum (70 ev), m/e (% rel. int.), 251 (0.2), (parent minus C_3H_5), 125 (38), 123 (57), 95 (44), 93 (67), 87 (25), 75 (100), 68 (15), 67 (28), 65 (16), 63 (11), 53 (10), 51 (12), exact mass calculated for $SiC_6H_{11}Cl_4$ (parent minus allyl), m/e 250.93842, measured 250.938.30).

The main product of this reaction could also be isolated by column-chromatography on silica-gell with CCl_4 elution. The finding that the isolated samples obtained by column- and gas-chromatography exhibited identical spectral properties and afforded only one spot by TLC suggested that the isolated product was obtained in a pure form. However, the finding that reaction of this compound with excess MeOH/pyridine (hexane solvent, 24 hours at room temperature) afforded, following aqueous workup, a reaction mixture which by GC analysis contained two products cast doublt on the assumed purity. The two products from the MeOH/pyridine reaction were isolated by preparative gas-chromatography on a 5 ft. X 1/4 inch, 20% FX-1150/chrom-P column at 175°C. The product with the shorter GC retention time (332) exhibited the following spectral data: ^{1}H NMR, 60 MHz, (CCl$_4$) δ = 0.31 (S, 6H), 1.0 (unresolved multiplet, 2H), 2.39 (unresolved multiplet, 3H), 2.85 (unresolved multiplet, 2H), 3.5 (S, 3H, OMe), 5.05 (m, 1H), 5.25 (broad singlet, 1H); 5.47 to 6.4 (unresolved multiplet, 1H); GCMS, m/e (% rel. int.) 127 (8), 125 (33), 123 (27), 111 (18), 109 (45), 95 (6), 93 (18), 89 (100), 81 (6), 79 (12), 68 (57), 67 (48), 59 (83). The compound with the longer GC retention time was found to have identical GCMS and NMR spectra to that of the isolated starting material.

A second attempt was made to gain evidence regarding the identity of the product obtained from the reaction of 325, CCl$_4$, and AIBN. Thus, the product of this reaction was allowed to stir in THF containing a large excess of LAH for 48 hours at room temperature. After filtration through celite, the THF filtrate was subjected to an aqueous workup. Analysis of the reaction mixture by GCMS revealed the presence of unreacted starting material as the only observable compound.

Despite the extensive spectral data obtained for the product isolated from this reaction, its identity could not be unambiguously distinguished between 6,8,8,8-tetrachloro-4,4-dimethyl-4-silaoctene (**330**) and 2,6,6,6-tetrachloro-2-methyl-4-allyl-2-silahexane (**331**). As discussed in the Results and Discussion section, the results obtained from the MeOH/pyridine reaction and LAH also failed to provide data which would allow for an unambiguous structural assignment.

In a repeat of the reaction of **325**, CCl_4, and AIBN, a solution of 7.68 g (5.47×10^{-2} mol) of **325**, 22.4 g (1.87×10^{-1} mol) of CCl_4, and 0.09 g (5.49×10^{-4} mol) of AIBN was refluxed (pot temperature of 85-90°C) for 48 hours under an atmosphere of nitrogen. After *en vacuo* removal of the volatiles, 2.3 g of an oily residue was obtained, which by GC contained two major products and four minor products. The major products were isolated by preparative gas-chromatography on a 5 ft. X 1/4 inch, 3% OV-225/chrom W column at an initial temperature of 130°C followed by manual temperature programming to 160°C. The compound with the shorter GC retention time exhibited the following spectral data: ^1H - NMR, 90 MHz, ($CDCl_3$) δ = -0.01 (S), 0.06 (S), 0.07 to 1.51 (complex, unresolvable multiplets), 1.52 (S), 1.89 (unresolved doublet of multiplets), 2.63 (d, J = 2.2Hz), 2.69 (d, J = 2.4Hz), since the signals were not sufficiently separated from one another the spectrum could not be integrated; ^{13}C-NMR, 90 MHz, ($CDCl_3$) δ = -4.14, -1.65, 13.3, 21.32, 23.64, 35.56, 37.40, 65.41;

IR (CCl_4) 2970, 2921, 2876, 1448, 1410, 1251, 1158, 1061, 1019, 891, and 840 cm^{-1}; mass spectrum (70 ev), m/e (% rel. int.) 147 (8), 136 (3), 127 (31), 121 (16), 119 (31), 99 (42), 95 (43), 93 (100), 79 (20), 77 (14), 72 (18), 67 (12), 65 (11), 63 (14), 61 (23), 59 (46); mass spectrum (21 ev), m/e (% rel. int.) 219 (3), 217 (8), 215 (8), 147 (17), 134 (28), 127 (71), 121 (21), 119 (16), 111 (10), 99 (26), 96 (14), 95 (59), 93 (100), 89 (21), 79 (19), 68 (14). For a discussion regarding the identity of this compound, refer to the Results and Discussion section.

The product with the longer GC retention time was found to exhibit identical spectral properties to the product islated from the reaction of **325**, CCl_4, and AIBN described previously.

The relative ratio of these two products was approximately 2:1.

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