1982

Thermal rearrangements of reactive intermediates in organosilicon chemistry

Stephanie Ann Burns
Iowa State University

Recommended Citation

Burns, Stephanie Ann, "Thermal rearrangements of reactive intermediates in organosilicon chemistry " (1982). *Retrospective Theses and Dissertations*. 7494.
https://lib.dr.iastate.edu/rtd/7494

INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

University
Microfilms
International

300 N. Zeeb Road
Ann Arbor, MI 48106

8224212

Burns, Stephanie Ann

THERMAL REARRANGEMENTS OF REACTIVE INTERMEDIATES IN ORGANOSILICON CHEMISTRY

Iowa State University PH.D. 1982

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

Thermal rearrangements of reactive intermediates in organosilicon chemistry

by

Stephanie Ann Burns

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

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1982

TABLE OF CONTENTS

DEDICATION

To Gary

INTRODUCTION

The established chemistry of (p-p) π bonded silicon compounds began in 1966 with the report of a silicon-carbon double bond by Nametkin and coworkers (1) and shortly thereafter by Gusel'nikov and Flowers (2). The chemistry of divalent silicon (silylenes) predates that of (p-p) π bonded silicon with the report by Skell and Goldstein of the first organosilylene (3). It was with the pioneering work of Gilman and coworkers (4, 5) and Atwell and Weyenberg (6) that a dramatic increase in the study of silylenes was brought about.

Our present knowledge and understanding of free radical chemistry is derived almost entirely from the reactions of alkyl and aryl radicals. However, increasing progress is being made in studying the reactions of radicals based upon silicon. It is now possible to draw some generalizations of physical properties, stereochemistry, structure and reactivity, and the scope of the synthetic utility of Group IVB radicals. Silicon radicals have many features in common with carbon radicals; there are however, some striking differences.

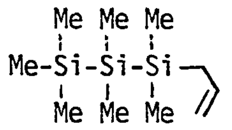
This dissertation will describe the attempted generation of a (p-p) π bonded silicon via a 1,5-migration of silicon from carbon to oxygen. In addition, the gas phase generation of silicon radicals from allyl, benzyl and polysilanes will be presented. Depending upon the nature of the radical, intramolecular rearrangements and cyclizations, and disproportionations occur. Evidence is presented for initial silicon-allyl bond homolysis in the thermal decomposition of trimethylallylsilane and a new mechanism for the formation of trimethylvinylsilane is put forth. An unprecedented silene to silylene rearrangement via a 1,2-migration of silicon was discovered. This rearrangement was observed in silenes generated from radical disproportionation or from retro Diels-Alder reactions. Evidence for a sequential silylene to silene to silylene rearrangement was obtained. Finally, a new reaction of silylenes and acetylene was discovered. This reaction involves an unprecedented rearrangement of a 1-silacyclopropene to a vinylsilylene by the migration of a trimethylsilyl group or hydrogen from silicon.

NOMENCLATURE

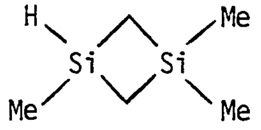
The nomenclature used in this dissertation will, with the exceptions described below, follow the conventions set down by IUPAC. Simple organosilicon compounds will be named as derivatives of silane (SiH_4), while more complicated linear and cyclic systems will be named as sila-analogs of the corresponding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

Examples:

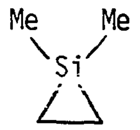
$MeSiCl_2H$ Methyldichlorosilane



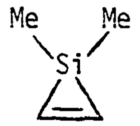
1-Allylheptamethyltrisilane



1,1,3-Trimethyl-1,3-disilacyclobutane



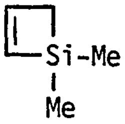
1,1-Dimethyl-1-silacyclopropane



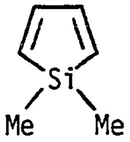
1,1-Dimethyl-1-silacycloprop-2-ene

The unsaturated four-membered rings containing one silicon atom will be named as derivatives of siletene. Silacyclopentadiene ring systems will be named as derivatives of siloles

Examples:



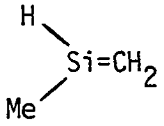
1,1-Dimethylsiletene



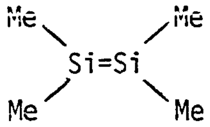
1,1-Dimethylsilole

All compounds containing (p-p) π-bonded silicon will be named as derivatives of silene ($H_2Si{=}CH_2$) and disilene ($H_2Si{=}SiH_2$). Divalent silicon species will be named as derivatives of silylene ($:SiH_2$). Silicon centered radicals will be named as derivatives of the silane, followed by the word radical

Examples:

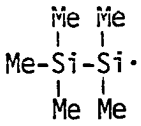


1-Methylsilene



Tetramethyldisilene

$Me_3Si\cdot$ Trimethylsilyl radical



$Me{-}SiMe_2{-}SiMe_2\cdot$

Pentamethyldisilanyl radical

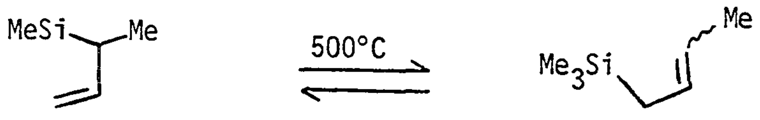
HISTORICAL

Thermal 1,3- and 1,5-Rearrangements of Silicon

An attempt to generate a silicon carbon double bond via a thermal 1,5-rearrangement of silicon, from silicon to oxygen, will be presented in this thesis. A brief summary of the literature pertaining to 1,3- and 1,5-rearrangements of silicon will be discussed. Only those systems involving a migration of silicon along an atomic framework containing carbon, oxygen and silicon will be included. A more thorough review of these and other molecular rearrangements has recently been published by Brook and Bassindale (7).

1,3-Rearrangements of silicon

The most thoroughly studied thermal 1,3-rearrangements have been those occurring in allylsilanes and beta-ketosilanes. Kwart and Slutsky observed gas phase unimolecular 1,3-migrations in allylic silanes (8, 9). For example, the thermolysis of α-methylallyltrimethylsilane 1 in a gas phase flow system led to an equilibrium mixture of 1 and the γ-isomer 2



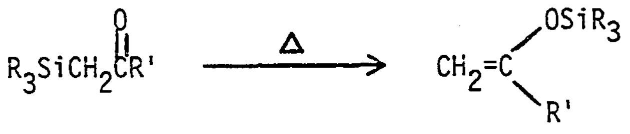
1 2

A concerted, symmetrical transition state is suggested by the following experimental results: 1) the complete absence of beta substituent rate effects; 2) the lack of influence on the activation parameters when substituents were varied on both the allylic framework and the migrating silicon center; 3) and the unimolecular kinetics of the rearrangement.

Very few sigmatropic rearrangements occur in cyclopropenes. However, the relatively rapid rearrangement of a trimethylsilyl group in cyclopropenes has been described by Coleman and coworkers (10). Pyrolysis of 3 in benzene at 117-148°C in sealed ampules results in a clean equilibration between 3 and a new cyclopropene 4. The rearrangement shows unimolecular kinetics and no solvent effects upon the rate, in accordance with a sigmatropic rearrangement. The activation energies for the 1,3-silicon migration were found to be 31.2 kcal/mol (3 → 4) and 32.8 kcal/mol (4 → 3). The activation energy falls in between that for the 1,3-trimethylsilyl shifts in allylsilanes (Ea ≈ 48 kcal/mol) and the 1,5-trimethylsilyl shift in 5-trimethylsilylcyclopentadiene (Ea = 13.0 kcal/mol).

3 4

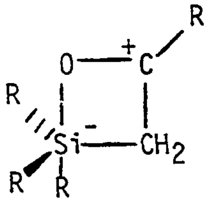
Brook and coworkers have reported that a number of beta ketosilanes can be thermally isomerized at 100-180°C to the corresponding siloxyalkenes (11, 12).



$$R_3SiCH_2\overset{O}{\overset{\|}{C}}R' \xrightarrow{\Delta} CH_2{=}C\begin{matrix}\nearrow OSiR_3\\ \searrow R'\end{matrix}$$

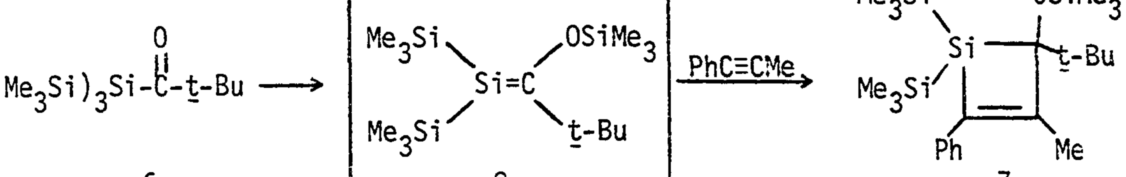
R or R'=Me,Ph

Based on the sensitivity of the activation parameters to substitution, solvent effects and heavy isotope effects, Kwart and Barnette have postulated that the rearrangement involves the four-center, zwitterionic transition state 5 (13). In this system, the high energy of the Si-O bond being created enables the silicon to undergo octet expansion to form the penta-coordinate silicon.



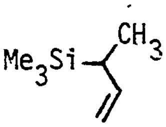
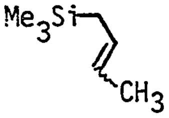
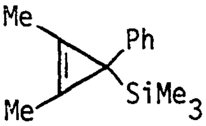
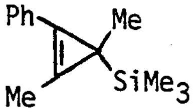
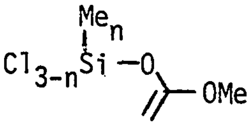
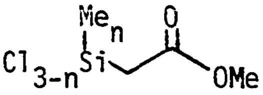
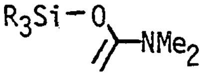
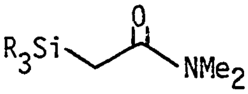
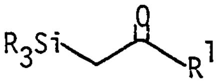
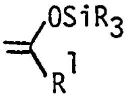
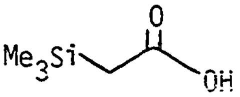
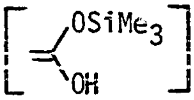
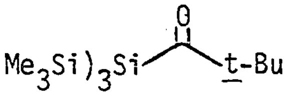
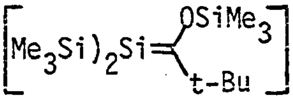
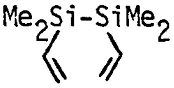
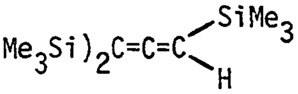
5

Thermal 1,3 migrations from silicon to generate silicon-carbon double bonds have recently been discovered. In 1979, Brook and coworkers extended their work on β-ketosilanes to acylpolysilanes (14). The thermolysis of various acylpolysilanes leads to mixtures of compounds, however, in the presence of traps the reactions are very clean. For example, thermolysis of 6 at 160-170°C in 1-phenylpropyne gives 7, the expected trapping product of silene 8, in 72% yield.

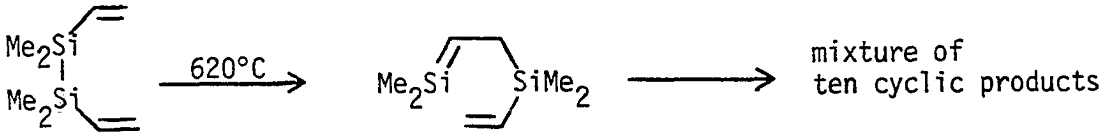


6 8 7

Table 1. 1,3-Thermal migrations of silicon

Reactant	Product	Tempera-ture(C°)	Ea (kcal/mol)	ΔS‡ (e.u.)	Refer-ence
		500	47.7	-6.2	8,9
		117- 148	31		10
		70- 90			16,17
		20			17
		100- 180	23-31	-15 to -3	11,12,13
		above m.p.			7
		160			14
		620			15
$Me_3Si)_3C-C\equiv CH$	 $Me_3Si)_2C{=}C{=}C\begin{smallmatrix}SiMe_3\\ H\end{smallmatrix}$	550			13

Barton and Wulff probed the thermally induced 1,3-silicon migration from silicon to carbon (15). In the thermolysis of 1,2-divinyl-1,1,2,2-tetramethyldisilane **9**, a complex mixture of products is obtained. However, all of the cyclic products were rationalized by invoking an initial 1,3-silicon rearrangement to form silene **10**. For a more complete discussion of the products arising from **9**, see the Historical section on silene rearrangements.



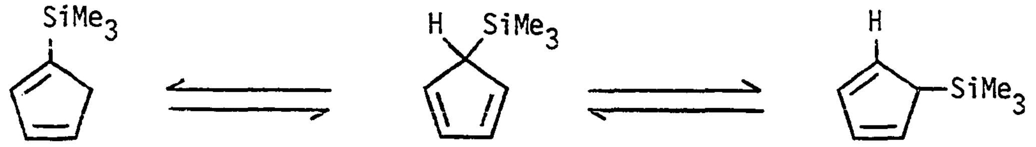
9 **10**

Due to the ultimate complexity of the reaction, it is unlikely that the thermal 1,3-migration of silicon from silicon to carbon will be synthetically useful.

The thermal 1,3-migrations of silicon are tabulated in Table 1 along with available activation parameters.

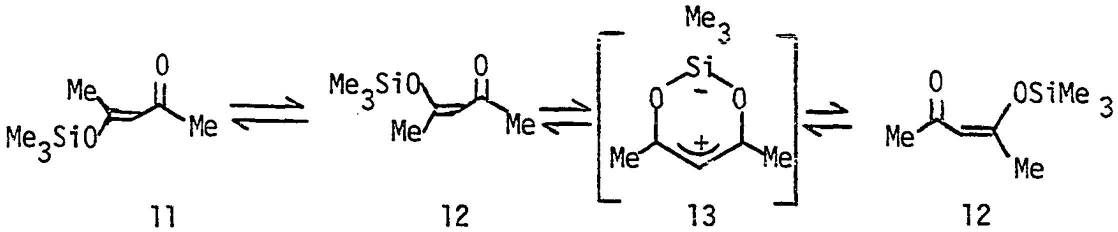
1,5-Rearrangements of silicon

The best known examples of 1,5-migrations of silicon are in silyl-substituted cyclopentadienes. A good review on the fluxional behavior of group IV cyclopentadienes and indenes is that by Larrabee in 1974 (18). Ashe has conclusively shown that silacyclopentadienes are σ-bonded and that both the silyl group and hydrogen migrate (19).



The rate of silicon migration was found to be 10^6 times greater than that of hydrogen at 80°C. The activation energy for the 1,5-migration of silicon ranges from 13 to 19 kcal/mol depending on the nature of the substituent. This is considerably lower than that of the 1,3-silicon migration in allylsilanes (Ea ≅ 48 kcal/mol) and the 1,5-hydrogen migration in the silylcyclopentadienes (Ea ≅ 26 kcal/mol). In fact, only at -10°C could distinct vinylic protons be observed by NMR.

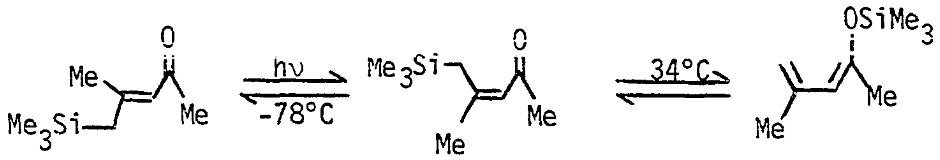
In 1969, it was shown by Howe and Pinnavaia that trialkylsilyl acetylacetonates exist as an equilibrium mixture of cis and trans isomers (20). For example, the ratio of 11 to 12 is 0.66 at room temperature. Moreover, the cis isomer was shown to undergo a rapid intramolecular rearrangement at 39°C which interchanges the allylic and acetyl methyl groups on the acetylacetone moity. The trans isomer 11 shows no rearrangement up to 120°C.



11 12 13 12

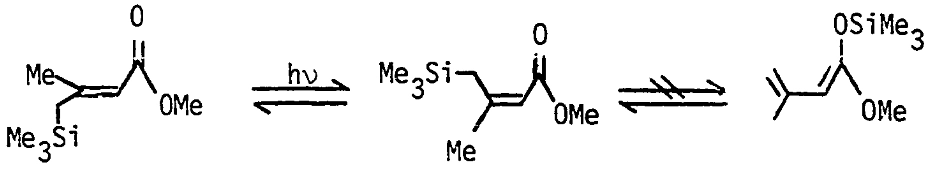
Later, Pinnavaia and coworkers studied the kinetics of the rearrangement for a series of substituted triorganosilicon acetylacetonates using NMR line broadening techniques (21). The activation energy and enthalpy were estimated to be 13.8 kcal/mol and -0.8 eu respectively. More recently, Pinnavaia and McClarin (22), as well as Reich and Murcia (23) have argued that the extreme facility with which the migration occurs is consistent with an internal nucleophilic displacement involving the intermediate 13.

Recently, a thermal 1,5-rearrangement of silicon from carbon to oxygen has been observed by Casey and coworkers (24). When a toluene solution of 14 is photolyzed at -76°C, a photostationary state consisting of 14 and its Z isomer, 15, is reached in one hour (14/15 = 56:44). Upon heating to 34°C, isomer 15 is converted quantitatively to a single isomer of 2-methyl-4-trimethysiloxy)-2, 4-pentadiene 16. The free energy of activation was estimated to be 23 kcal/mol. This constitutes the first example of a 1,5-silicon rearrangement from carbon to oxygen.



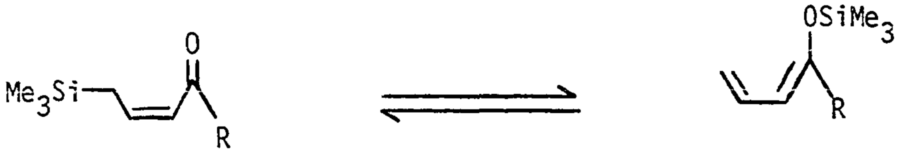
14 15 16

As in the case of the ketone, the corresponding ester can be photoquilibrated. Irradiation of a pentane solution of 17 provides a photostationary state consisting of 63:37 mixture of 17/18. But, in contrast to the ketone system, both 17 and 18 are thermally stable upon prolonged heating at 140°C. Furthermore, when the expected product of a 1,5-silicon migration 19 is heated at 117°C, a 46% yield of 18 is attained.



17 18 19

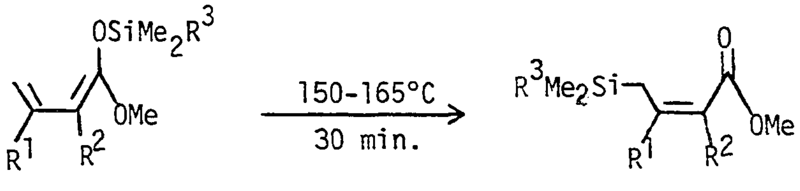
Thus, γ-silyl ketone 15 undergoes a 1,5-silicon rearrangement from carbon to oxygen to give the siloxy diene, while the 1-methoxy-1-siloxy diene 19 forms the γ-silyl ester by the migration of silicon from oxygen to carbon. This contrasting behavior can be explained on thermodynamic grounds. The migration from carbon to oxygen is favored by the greater Si-O bond strength (128 kcal/mol) relative to the Si-C bond strength (~90 kcal/mol). Working in opposition to this, the greater bond strength of C = O (173 kcal/mol) relative to C = C (145 kcal/mol) favors migration of silicon from oxygen to carbon. For the ketone 15 the Si-O bond strength term dominates, whereas for the ester 18 the C = O bond strength term dominates.



A (SiO-SiC) > (C=O-C=C) $R=CH_3$

B (C=O-C=C) > (SiO-SiC) $R=OCH_3$

A series of substituted 1-methoxy-1-(trialkylsiloxy)butadienes 20 has been studied by Anderson and coworkers (25). These authors noted that the 1,5-migration of silicon from oxygen to carbon is more facile when R^1 is an electron releasing group. This suggests an intermediate in which positive charge is being created on the diene moiety. These data are summarized in Table 2.

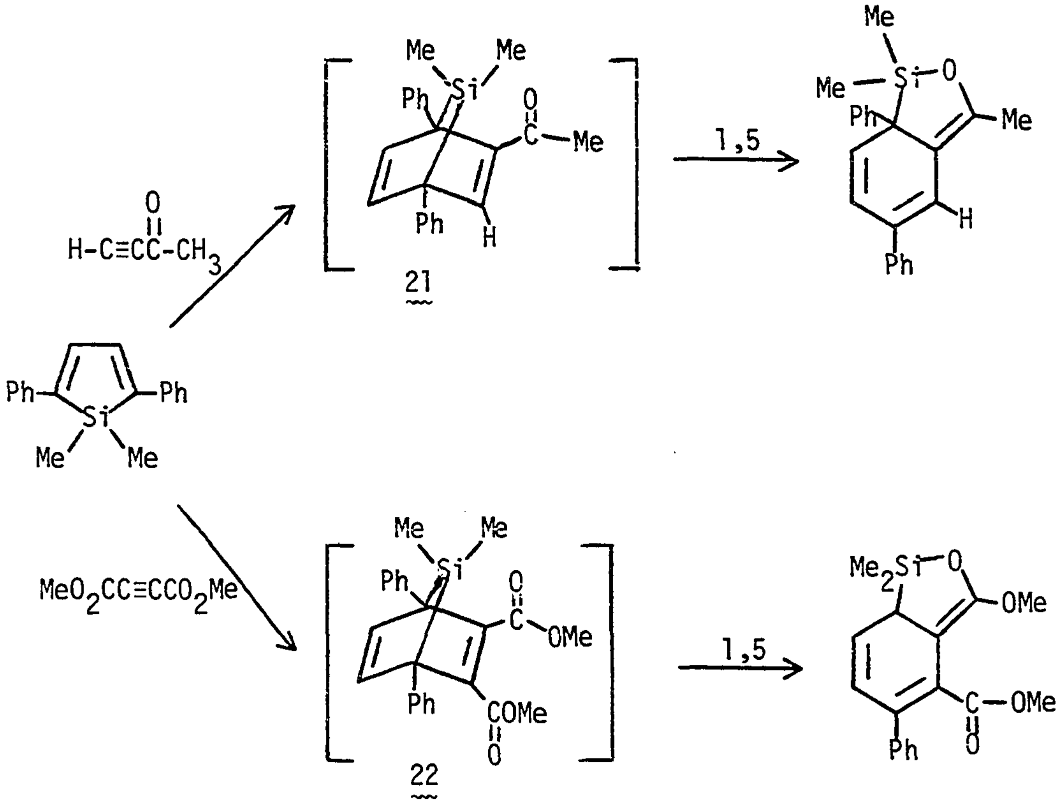


20

Table 2. Thermal 1,5-rearrangement from carbon to oxygen

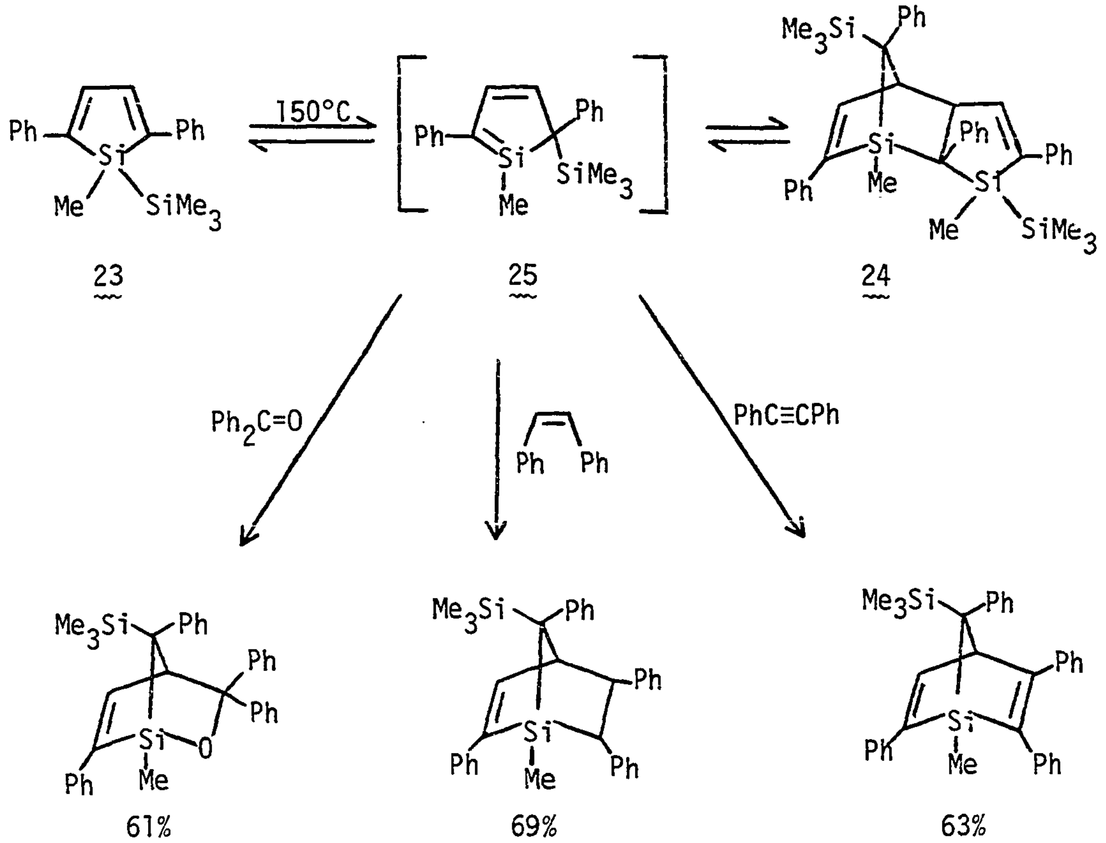
R^1	R^2	R^3	Yield (%)
Me	H	Me	14
Me_3SiO	H	Me	70
Me_3SiO	Me	Me	90
Me_3SiO	MeO	Me	86
Me_3SiO	H	Bu^t	75
H	H	Bu^t	0

Interestingly, in the 2-carboxy-7-silanorbornadienes, 1,5-silicon migrations from carbon to oxygen occur in both the ketone 21 and ester 22 (26). Obviously, the relief of ring strain favors the formation of the fused 5-6 ring system thus, the (SiO - SiC) bond strength term dominates.



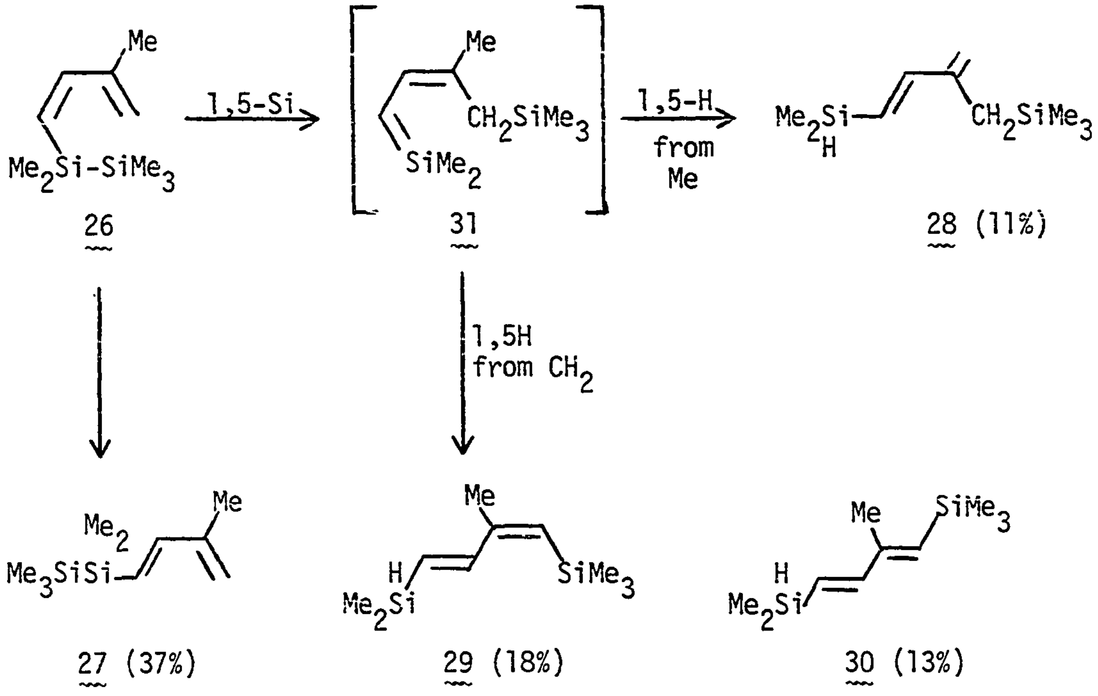
Recently, Barton and coworkers have utilized the facile 1,5-silicon rearrangement to generate a silene intermediate (27). When silole 23 is heated at 150°C in an evacuated sealed tube an equilibrium mixture of 23 and the dimer 24 is obtained. This result was best explained by invoking an initial 1,5-silicon migration to generate the intermediate silene 25, which then with the starting silole in a 4+2 fashion. Conclusive evidence for silene 25 was shown by various trapping experiments, all of which proceed in excellent yields (Scheme 1).

Scheme 1



The generality of the thermal 1,5-migration of silicon to produce a silene was extended to the linear system recently, by Wulff (28). The pyrolysis of the *cis*-disilanylbutadiene 26 at 635°C produces four products. The major product 27 is simply the trans isomer of starting material. The other three products 28 - 30 are easily derived from the intermediate silene 31 via 1,5-hydrogen migrations to the silene as shown in Scheme 2.

Scheme 2

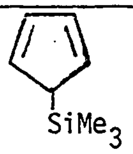
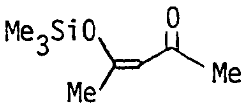
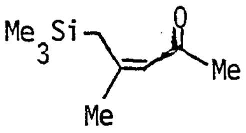
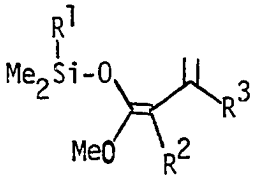
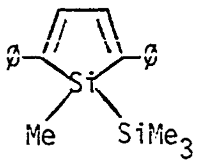
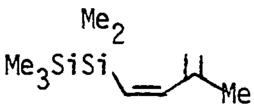


In general, the thermal 1,5-rearrangements of silicon occur at a faster rate and with lower activation energies than the corresponding 1,3-rearrangements. These 1,5-silicon migrations along with available activation parameters are summarized in Table 3.

Intramolecular Rearrangements of Reactive Intermediates

The chemical endeavors and results of this thesis are in the area of rearrangements of reactive intermediates in organosilicon chemistry. The particular species that are involved are silylenes, silenes and silicon radicals. A complete discussion of the chemistries of each of these reactive intermediates will not be presented since thorough, recent

Table 3. 1,5-Thermal rearrangements of silicon

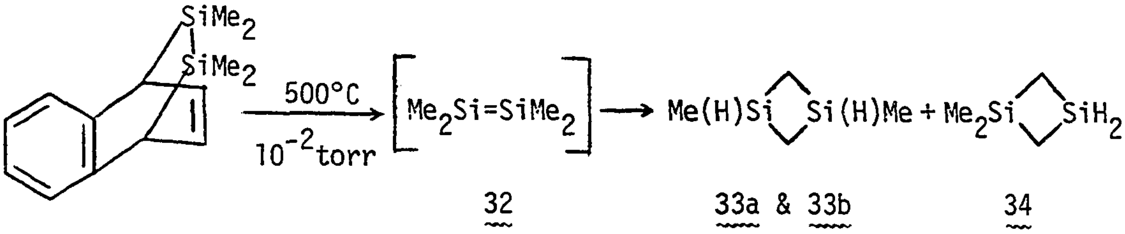
Reactant	Temperature(C°)	Ea (kcal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	Reference
	20	13.0		-9.2	18,19
	>20	13.8		-0.8	20,21
	34		23		24
	117-165		30		24,25
	150				27
	635 (gas)				28

reviews on silylenes (29-33), silenes (34-36) and silicon radicals (37-41) exist. However, a summary of the known intramolecular rearrangements along with pertinent theoretical calculations will be presented.

Silylene Rearrangements

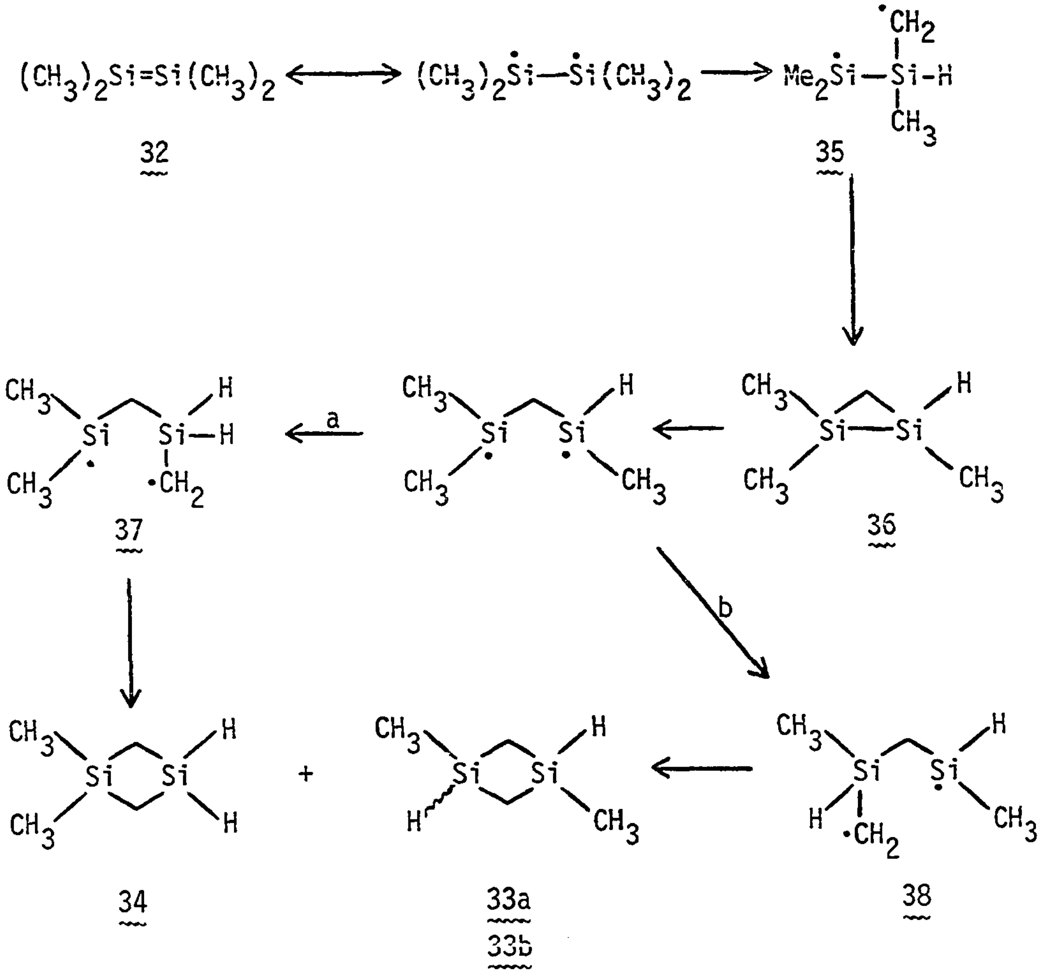
There are very few silylene rearrangements known, though they constitute the most interesting phenomena in the chemistry of silylenes to be discovered in years.

Roark and Peddle found that when tetramethyldisilene 32 is thermally generated in the absence of a trap, three isomeric 1,3-disilacyclobutanes 33a, 33b and 34 are produced in 10% and 30% yields, respectively (42).

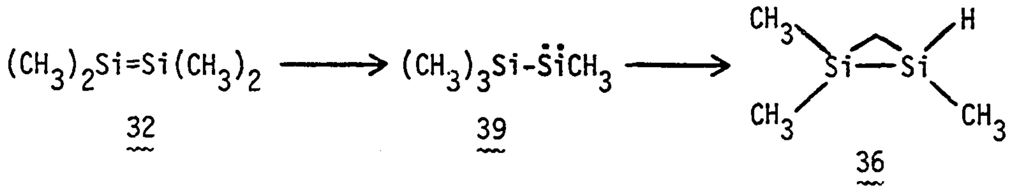


Roark and Peddle proposed the mechanism shown in Scheme 3 to account for the rearranged products. The key feature of the mechanism is the unprecedented (and unlikely) 1,2-migration of a hydrogen from carbon to a silicon radical to generate 35, which then ring closes to the disilacyclopropane 36. Rupture of the silicon-silicon bond in 36 followed by another 1,2-hydrogen migration from carbon to a silicon radical which could occur in two ways: path a generating 37, and path b generating 38. A final ring closure of each of these intermediates accounts for the two observed products.

Scheme 3

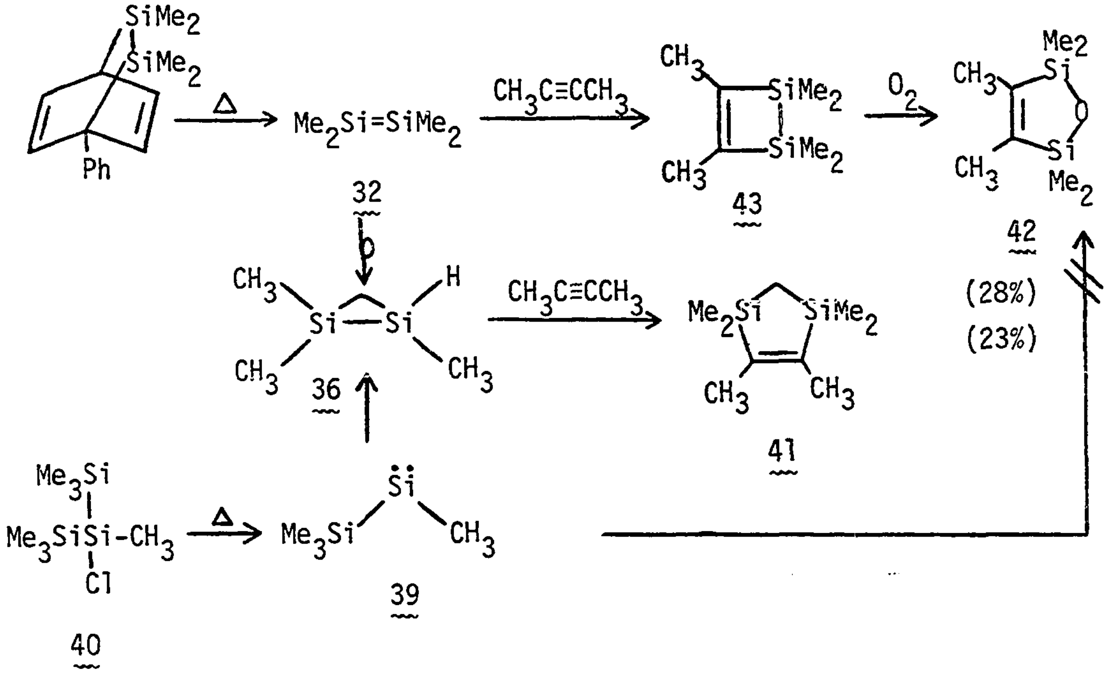


Examination of an alternate mechanism by Wulff and coworkers led to the first proposed intramolecular silylene rearrangements (43). These authors proposed that the intermediate disilacyclopropane 36 could be formed alternatively from the disilene 32 by a methyl migration to form trimethylsilylsilylene 39 and a subsequent C-H insertion.



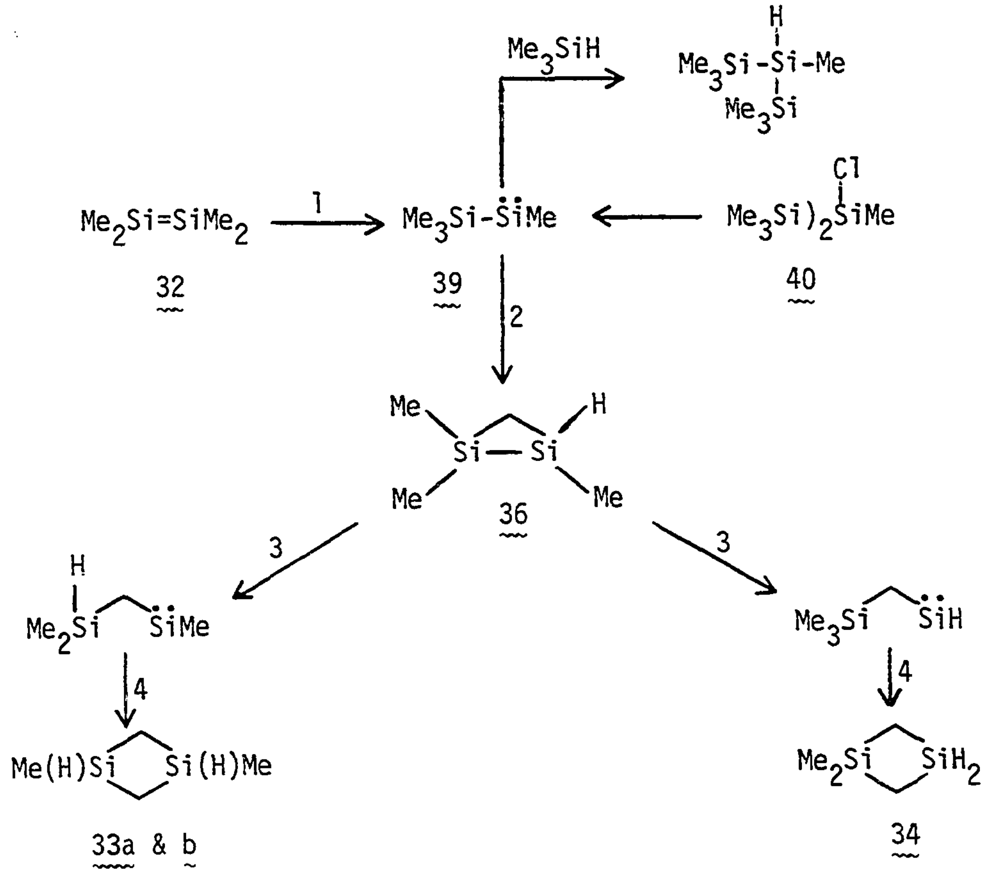
The intermediate silylene 39 was independently generated by an α-elimination of trimethylchlorosilane from 2-chloroheptamethyltrisilane, 40. The vacuum-flow pyrolysis of 40 at 700°C furnished the isomeric 1,3-disilacyclobutanes 33a, 33b and 34 in 15% and 28% yields respectively. The possibility of the reverse reaction, silylene 39 rearranging to disilene 32 and then proceeding on to products, was eliminated by a trapping experiment. Since the disilene 32 is known to react with 2-butyne in the gas phase (44), 40 and 2-butyne were pyrolyzed in a nitrogen flow at 600°C to search for disilene 32. The major product of this reaction was 1,1,3,3-tetramethyl-1,3-disilacyclopent-4-ene 41 (23%), which is also the major product of the gas phase generation of tetramethyldisilene 32 (Scheme 4). However, in the latter system a second product, 42, is also formed by oxygen insertion into the initial 2+2 addition product 43. None of product 42 was formed in the thermolysis of 40 and 2-butene. A summary of the trapping results is presented in Scheme 4.

Scheme 4



The complete mechanism proposed by Wulff and coworkers for the formation of 33a, 33b and 34 from tetramethyldisilene involves a novel sequence of reactions including: (1) the already discussed rearrangement of disilene 32 to 39; (2) alpha-trimethylsilylsilene C-H insertion to form disilacyclopropane 36; (3) competitive α-eliminations generating β-silylenes; (4) further intramolecular C-H insertions to form the 1,3-disilacyclobutanes.

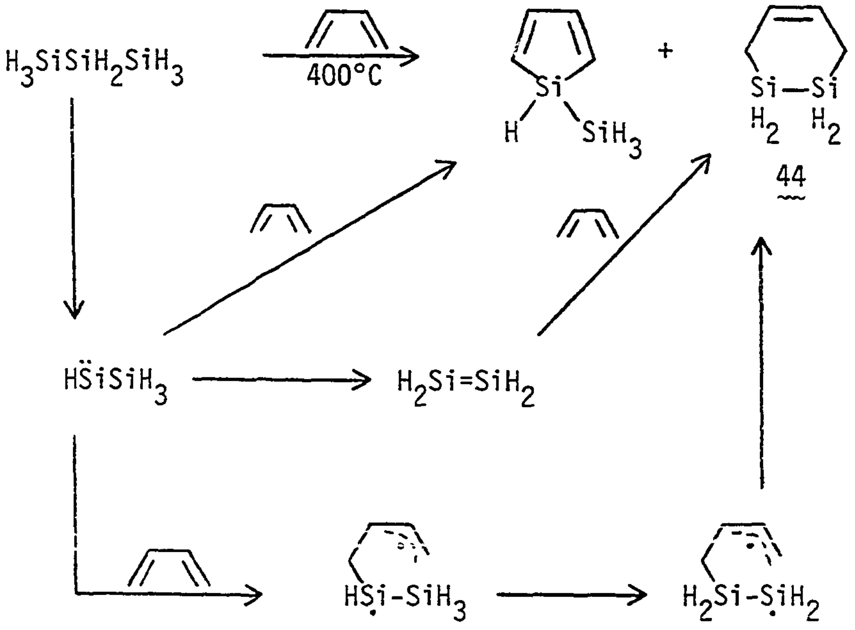
Scheme 5



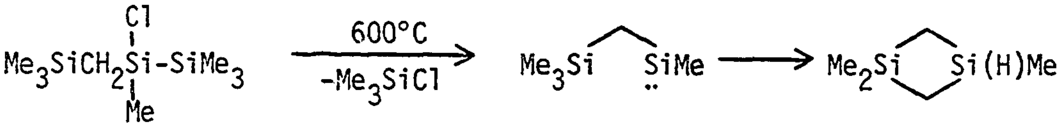
Strong evidence for the disilene to silylene rearrangement was also provided by the trapping of silene 39 with trimethylsilane following the generation of disilene 32. The results of Barton and Wulff are in agreement with ab initio SCF-MO calculations performed by Snyder and Wasserman (45). Singlet silylsilylene is predicted to be 8.6 kcal/mol more stable than planer disilene, which in turn is 2.5 kcal/mol more stable than triplet silylsilylene.

In contrast to this prediction, Jenkins and coworkers suggested that rearrangement of silylsilene to disilene accounts for the formation of 1,2-disilacyclohex-4-ene 44 in the thermolysis of trisilane at 400°C (46). However, as pointed out by the authors, this is not demanded because a radical-type trapping of the silylsylene also explains the formation of 44 (Scheme 6).

Scheme 6



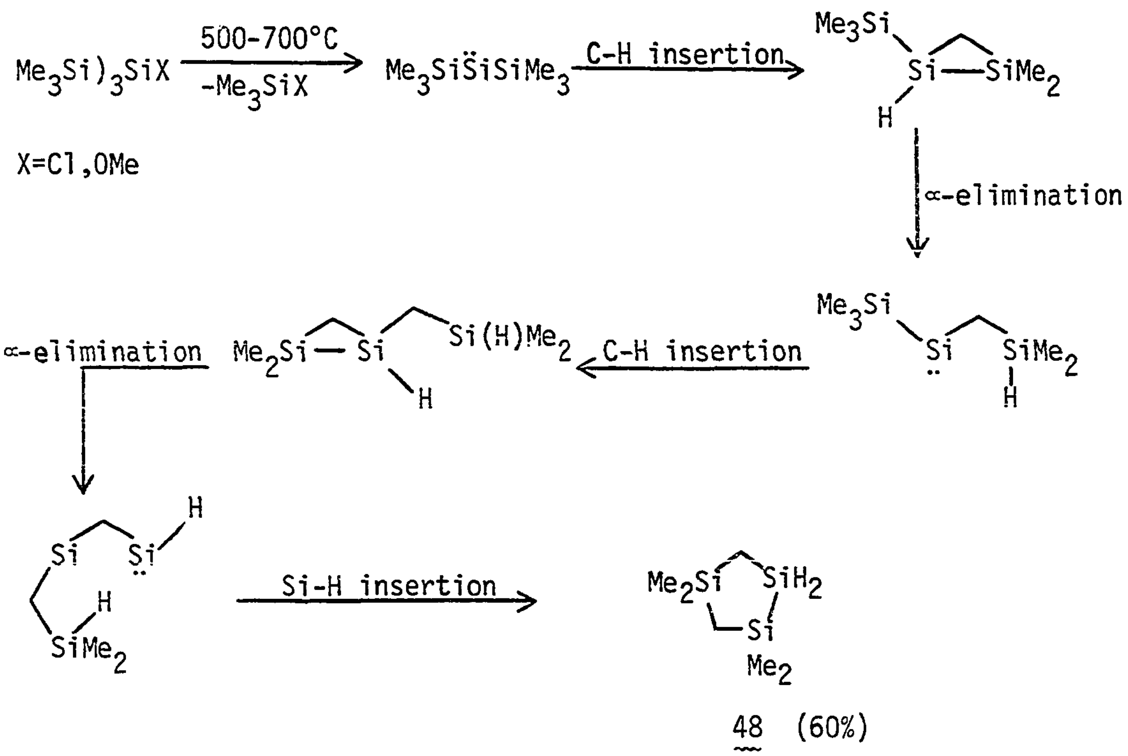
That β-trimethylsilyl silenes undergo C-H insertions was also demonstrated by Wulff and coworkers. The α-elimination of trimethylchlorosilane from 45 to generate (trimethylsilylmethyl) methylsilylene 46 leads to a 39% yield of trimethyl-1,3-disilacyclobutane 47.



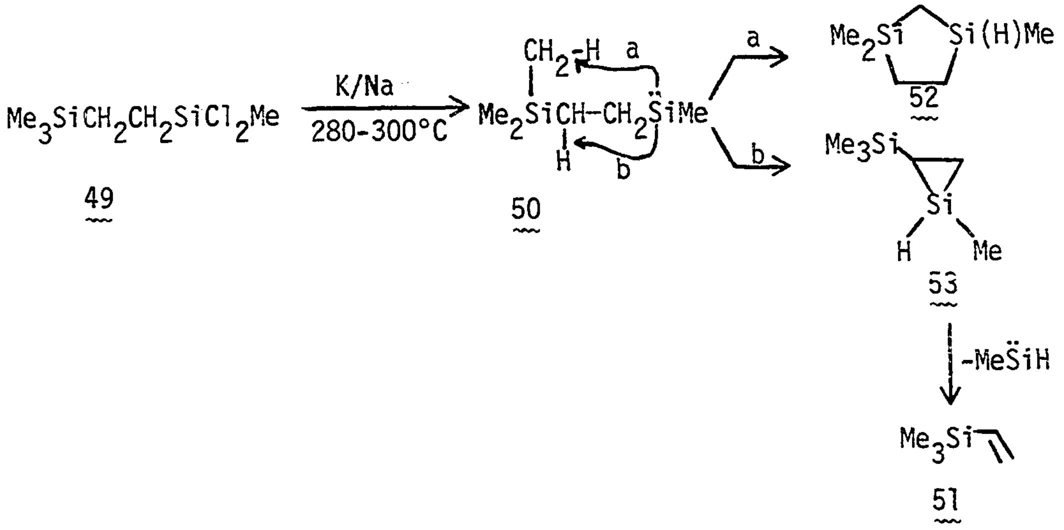
45 46 47

Chen et al. have found further evidence for the C-H insertions of α- and β-trimethylsilyl silylenes (47). When bis(trimethylsilyl)silylene is generated in the gas phase by a conventional α-elimination, the major product is 1,1,4,4-tetramethyl-1,2,4-trisilacyclopentane, 48 in 60% yield. The formation of 48 can be rationalized by a series of intramolecular rearrangements involving C-H insertions to form disilacyclopropanes, α-eliminations that open these highly strained rings to β-silylsilylenes, and a further intramolecular Si-H insertion (Scheme 7).

Scheme 7

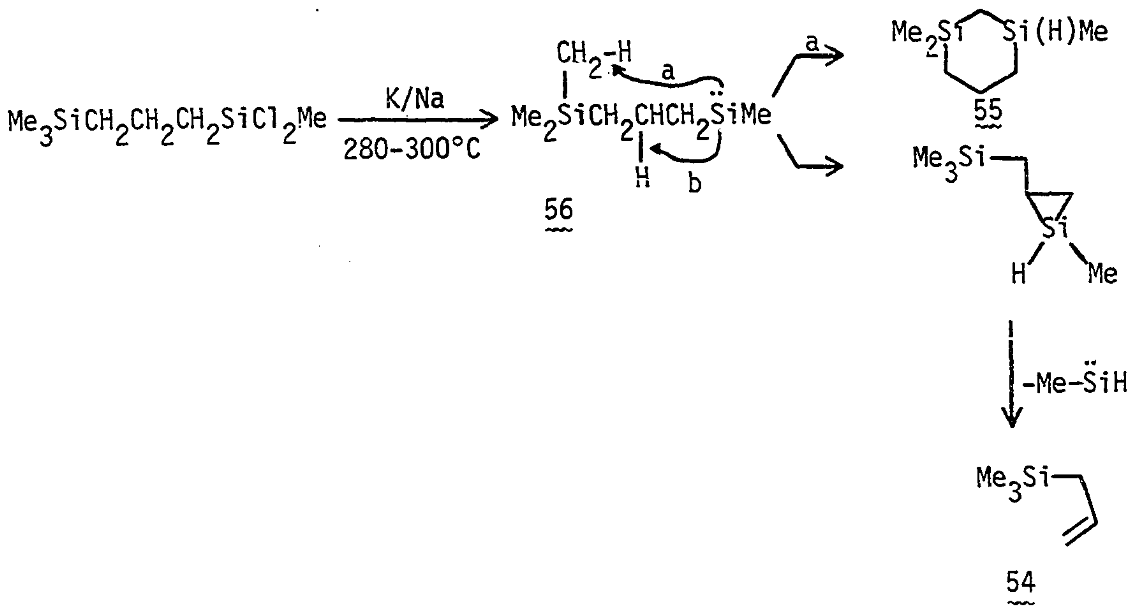


An interesting study on the intramolecular C-H insertions of silylenes has been that of Gusel'nikov and coworkers (48). The influence of methylene bridges between silicon atoms was examined by the dechlorination of (methyldichlorosilyl)(trimethylsilyl) alkanes. The reaction of 49 with K/Na vapor at 280-300°C and a pressure of 0.1-1.0 torr generates the γ-trimethylsilylsilylene 50. The two products isolated in this thermolysis were trimethylvinylsilane, 51, and 1,1,3-trimethyl-1,3-disilacyclopentane, 52, in 52.4% and 6.6% respectively. These products originate from 50 by either a silicon methyl C-H insertion (path a) or by a β-methylene C-H insertion to generate the silacyclopropane 53 followed by methylsilylene extrusion (path b).

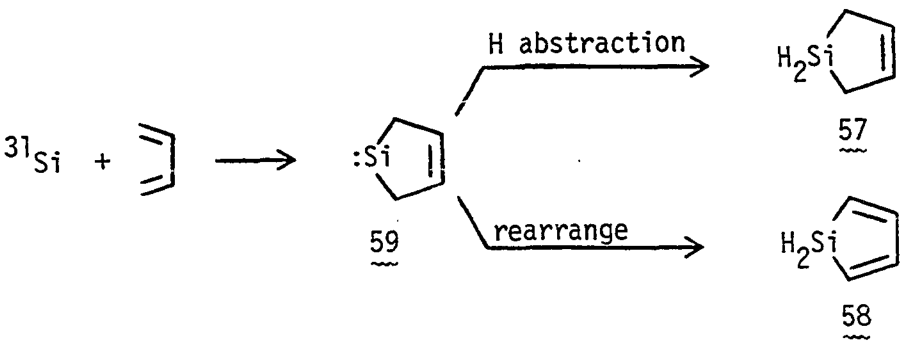


Extending the methylene bridge by one results in the formation of trimethylallylsilane, 54 (45.5%), and 1,1,3-trimethyl-1,3-silacyclohexane, 55 (4.5%). An analogous mechanism was postulated (Scheme 8). It should be noted that in both of these systems no products are formed that indicate α-methylene or (in the case of 56) γ-methylene C-H insertion. Also, β-methylene C-H insertion is favored by a factor of 9:1.

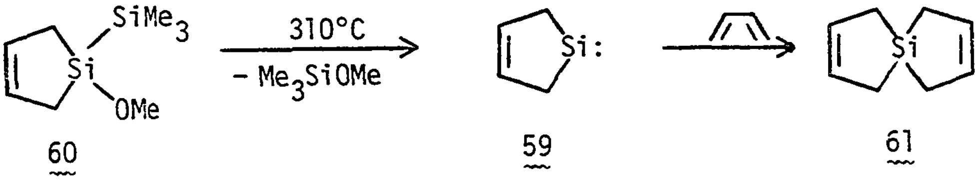
Scheme 8



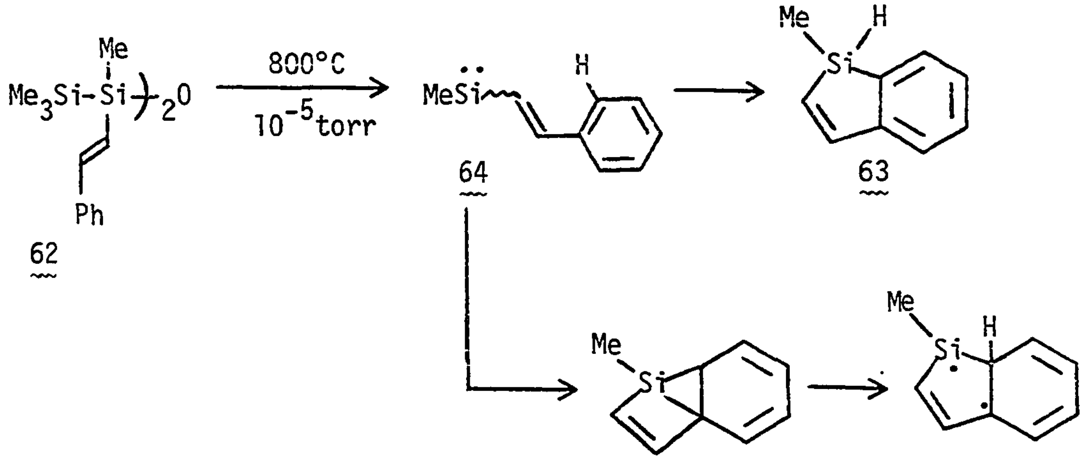
An intramolecular silylene rearrangement has been suggested in the reaction of recoiling silicon-31 atoms with 1,3-butadiene (49,50,51). This reaction produces [^{31}Si]-1-silacylopent-3-ene 57 and [^{31}Si]-1-sila-1,3-cyclopentadiene, 58. The formation of 58 remains controversial. Though never isolated, its identification was verified by the fact that it can be catalytically hydrogenated to 57 (51) and by its predicted chromatographic behavior. One possible mechanism for this reaction involves the addition of silicon-31 atoms to butadiene furnishing the intermediate silylene 59, which rearranges to 58 or hydrogen abstracts yielding 57.



Evidence that silylene 59 is a possible intermediate in this hot atom experiment was presented by Gaspar *et al*. (52). Thermal generation of 59 by an α-elimination of Me_3SiOMe from 60 in the presence of butadiene leads to a 32% yield of the spiro adduct 61, a minor product observed in the recoiling ^{31}Si experiment.

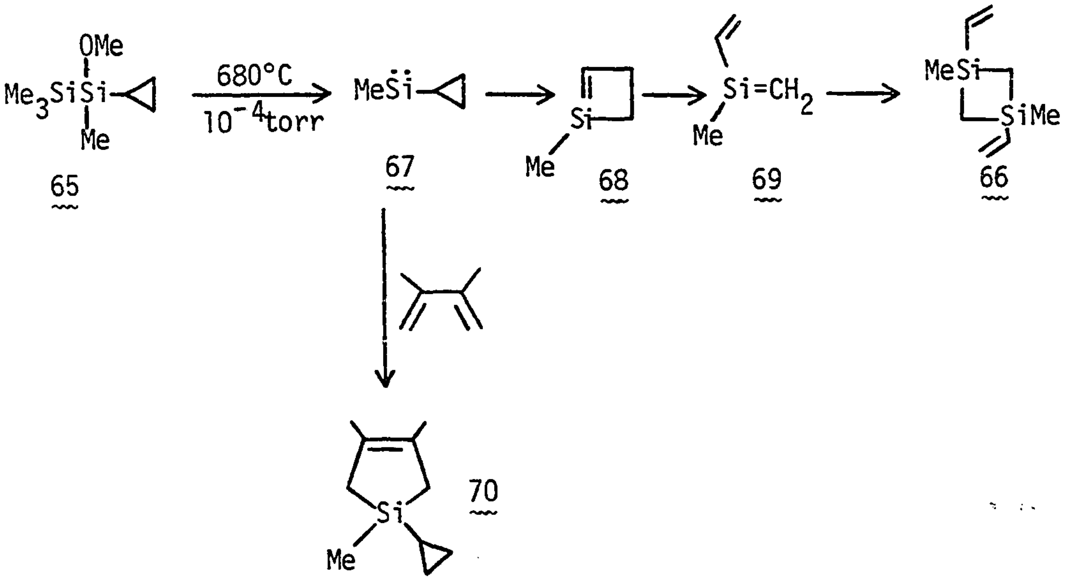


Goure has obtained evidence that styryl silylene rearranges to silaindane (41). Thermolysis of 62 at 800°C and 10^{-5} torr affords as major products, styrene and 1-methyl-1-silaindene 63, in 14% and 20% yield respectively. Styrene is thought to arise from a radical pathway, however it was suggested that silylene 64 is formed via an α-elimination and that 64 undergoes an ortho C-H insertion, generating 63 directly. Although this cannot be distinguished from addition of the silylene to the benzene ring, followed by Si-C bond homolysis and hydrogen abstraction.



Conlin and Gaspar (53) have made the suggestion that the origin of 1,3-dimethyl-1,3-disilacyclobutane from generation of dimethylsilylene above 600°C could in principle arise from rearrangement of this silylene to methylsilene, followed by dimerization. However, as already discussed, dimerization of dimethylsilylene to tetramethyldisilene could also explain the formation of the disilacyclobutane. The first example of a thermally-induced silylene to silene rearrangement is that reported by Barton and coworkers (54). The vacuum pyrolysis of 1-cyclopropyl-1-methoxytetramethyldisilane 65 at 680°C yields trimethylmethoxysilane (99%) and 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane, 66 (42%). The likely mechanism involves α-elimination of trimethylmethoxysilane to form silylene 67, ring expansion of 67 to 1-methyl-1-silacyclobutene 68, ring opening of 68 to vinylsilene 69, and the usual head-to-tail dimerization of 69. Evidence that silylene 67 is indeed involved was obtained by the efficient trapping of 67 with 2,3-dimethylbutadiene yielding 70 in 43% (Scheme 9).

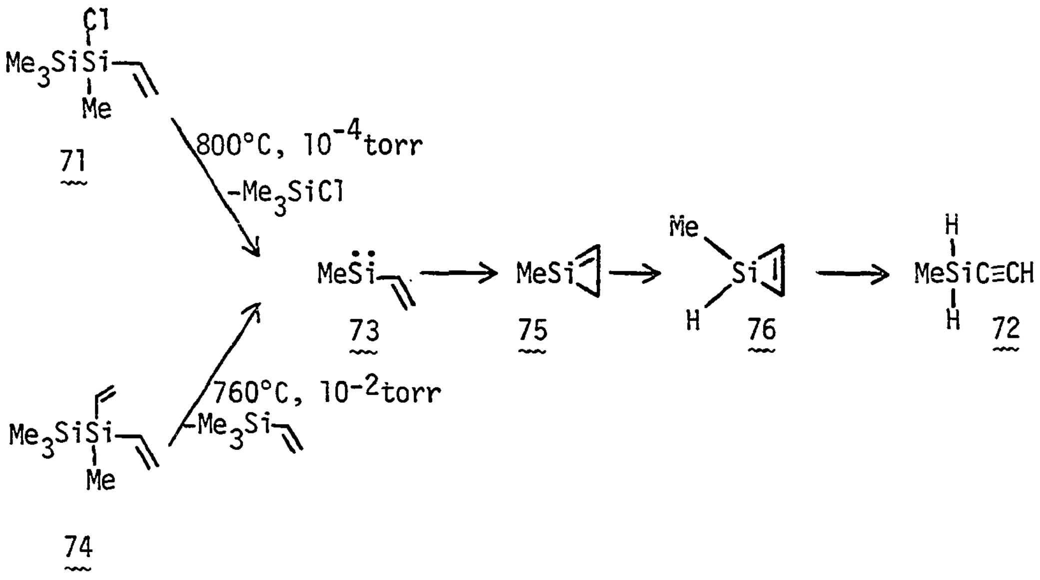
Scheme 9



In the same report, Barton *et al.* presented evidence for a vinylsilylene rearrangement. The thermolysis of 71 affords two products of α-elimination, trimethylchlorosilane (30%) and trimethylvinylsilane (11%), along with ethynylmethylsilane 72 (12%). The reasonable conclusion was made that 72 arises from isomerization of silylene 73. This was substantiated by the fact that in the thermolysis of 1,1-divinyltetramethyldisilane 74 the two major products are trimethylvinylsilane (through an α-elimination) and 72. The isomerization of 73 most likely involves intramolecular π-addition to form 1-sila-1-cyclopropene 75, followed by hydrogen migration to silicon generating 1-methyl-1-silacycloprop-2-ene 76, which undergoes a final hydrogen migration to give 72 (Scheme 10).

The formation of silylacetylenes from the gas phase copyrolysis of silylene precursors and terminal acetylenes has been argued to involve rearrangement of intermediate silacyclopropenes (53, 55).

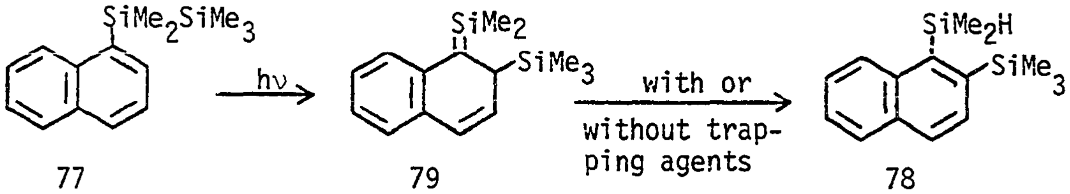
Scheme 10



Silene Rearrangements

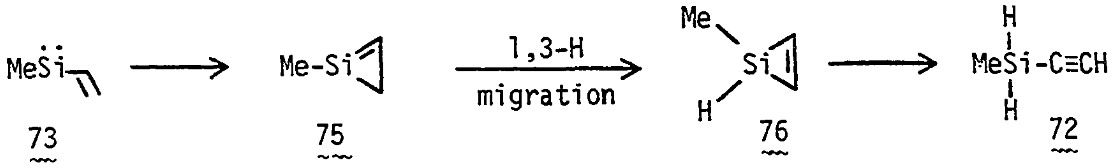
The generation of compounds containing (p-p)π silicon-carbon double bonds in the absence of standard trapping agents (such as alcohols, carbonyls, alkenes, dienes and acetylenes) leads to two types of reactions. The reactive silene can undergo head-to-tail (or less frequently, head-to-head) dimerization or when possible, intramolecular rearrangement. Brook and coworkers have achieved the first isolation of a sterically hindered silene generated by a photochemically induced 1,3-migration of silicon in an acyl polysilane (56).

Classification of the known silene rearrangements results in only a handful of different types of rearrangements, some furnishing stable compounds directly, and others generating additional reactive intermediates. One type of rearrangement is hydrogen migration from carbon to the silene-silicon. For example, the photolysis of arylpentamethyldisilanes has been reported to proceed via a 1,3-migration of silicon to generate silenes (57-60). An alternate pathway for the formation of silenes in these photolyses has been suggested and will be discussed in the Historical section on silicon radical rearrangements. The silene produced from benzenoid aryldisilanes readily adds to many types of substrates such as alcohols, olefins and acetylenes. However, the chemical behavior of 1-disilanylnaphthalene is quite different. The reactive intermediate generated from photolysis of 1-pentamethyldisilanylnaphthalene **77** does not add to these substrates, and an isomer of **77** is always obtained (61). Thus, when a benzene solution of **77** is irradiated in the presence of isobutene a 41% yield of **78** is obtained. Irradiation of **77** in the absence of trapping agent results in a 64% yield of **78**. The production of **78** can be explained by an intramolecular hydrogen migration in the intermediate silene **79**.

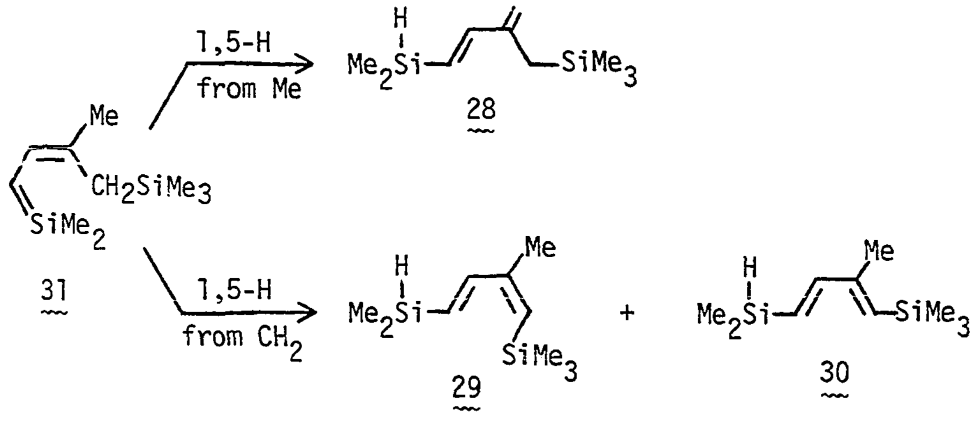


77 **79** **78**

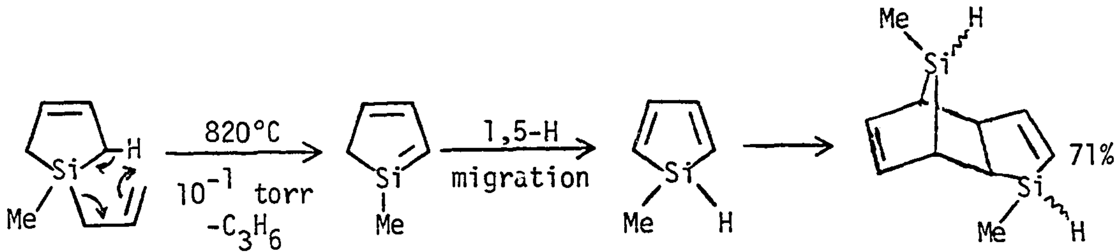
As previously discussed, Barton and coworkers have postulated that the formation of ethynylmethylsilane 72 from the thermal generation of methylvinylsilylene involves a 1,3-migration of hydrogen in the intermediate 1-sila-1-cyclopropene 75 (54).



Hydrogen migrations also occur in the thermally generated 1-silabutadiene 31 (28). A 1,5-hydrogen shift from either the methyl or the methylene group results in the formation of 28 - 30. These migrations occur to the exclusion of ring closure to form siletenes.



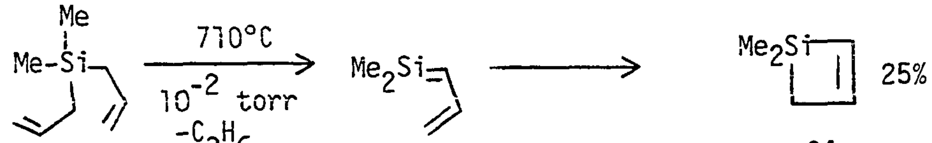
Barton and Burns have used a 1,5-hydrogen migration to a silene to generate the first carbon-unsubstituted silole (62). In the retroene elimination of propene from 1-allyl-1-methyl-1-silacyclopent-3-ene 80, the initially formed 1-sila-1,3-cyclopentadiene rearranges to the silole 81 via a hydrogen migration. The silole 81 is not isolable and in the absence of traps dimerizes in a Diels-Alder manner to 82.



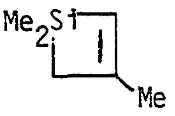
80 81 82

Thus, the authors were able to utilize an intramolecular silene rearrangement to generate a synthetically challenging molecule.

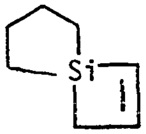
In the absence of a hydrogen atom δ to the silicon, 1-silabutadienes cyclize to siletenes (63). The retroene elimination of propene from diallyldimethylsilane gives rise to 1,1-dimethyl-1-silabutadiene 83, which then ring closes to dimethylsiletene 84. Other siletenes prepared via this type of silene rearrangement are 85 - 87.



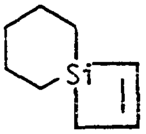
83 84



85

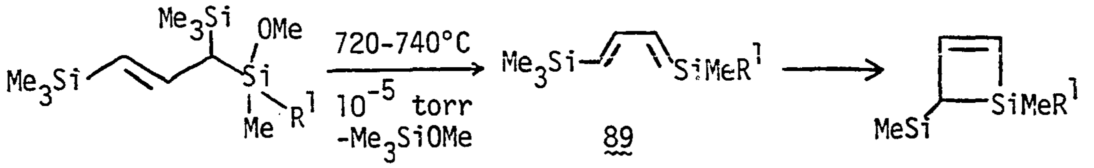


86



87

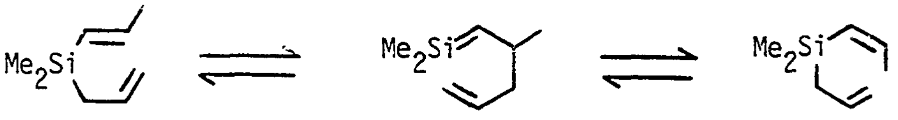
The retroene elimination in diallylsilanes to generate siletenes is not amenable to functionalization at the ring carbon or silicon. Burns and Barton were able to overcome this restriction through the use of an alternate method of generation of 1-silabutadienes (64). A thermally induced β-elimination of trimethylmethoxysilane from 88 gives silene 89 which subsequently ring closes to the functionalized siletene 90 in 60% yield. Similar results were obtained when silicon was functionalized (91 → 92).



R^1=Me, 88
R^1=OMe; 91

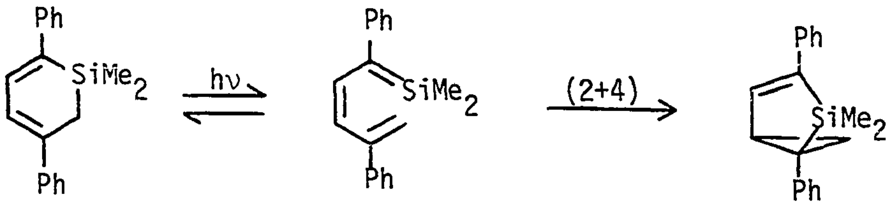
R^1=Me, 90 (60%)
R^1=OMe; 92 (74%)

Slutsky and Kwart attributed the geometric isomerization of cis- and trans-propenylallyldimethylsilane to a [3,3]-sigmatropic rearrangement based on the activation energy and low A factor (65). This rearrangement proceeds through a Si-C double-bonded intermediate which is in equilibrium with 93 and 94.



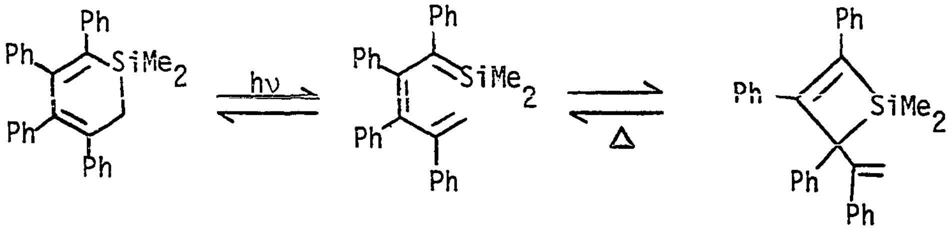
93 94

The photolysis of silacyclohexadienes is thought to involve the intermediacy of silahexatrienes (66). For example, photolysis of 1,1-dimethyl-2,5-diphenyl-1-sila-2,4-cyclohexadiene 95 for 40 hours affords the silabicyclo[3.1.0]hex-3-ene 96, isolated as an oil in 38% yield. The authors postulate an electrocyclic ring opening of 95 to the 1-silahexatriene 97 followed by an intramolecular (2+4) cycloaddition to 96. The intermediacy of silahexatriene 97 was supported by its efficient trapping with methanol in 50% yield



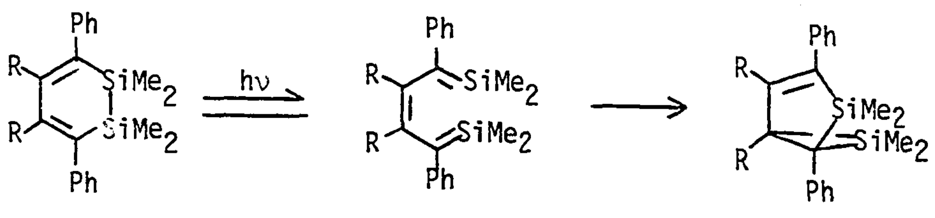
95 97 96

Contrary to the diphenyl system, the tetraphenyl derivative 98 undergoes a photochemically induced ring opening to 99 which then (2+2) cycloadds intramolecularly to 100. Interestingly, by heating a 1:1 mixture of 98 and 100 in benzene at 55°C, 100 returns quantitatively to 98.



98 99 100

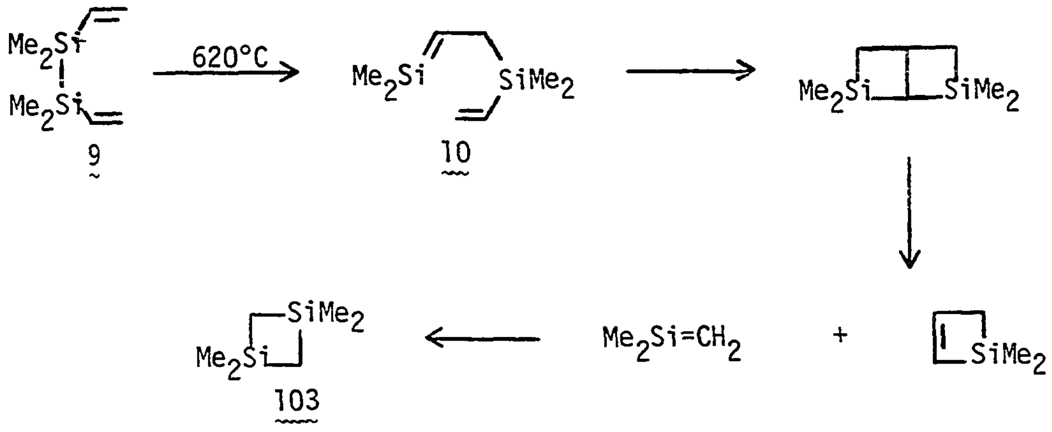
When the similar 1,2-disilacyclohexadienes 101 and 102 were photolyzed both the diphenyl and tetraphenyl compounds reacted to form 2,6-disilabicyclo[3.1.0]hex-3-ene (67). The authors suggest that these products could arise from intramolecular (2+4) cycloaddion of intermediate 1,6-disilahexatrienes in view of the reactions previously discussed.



R=H; 101
R=Ph; 102

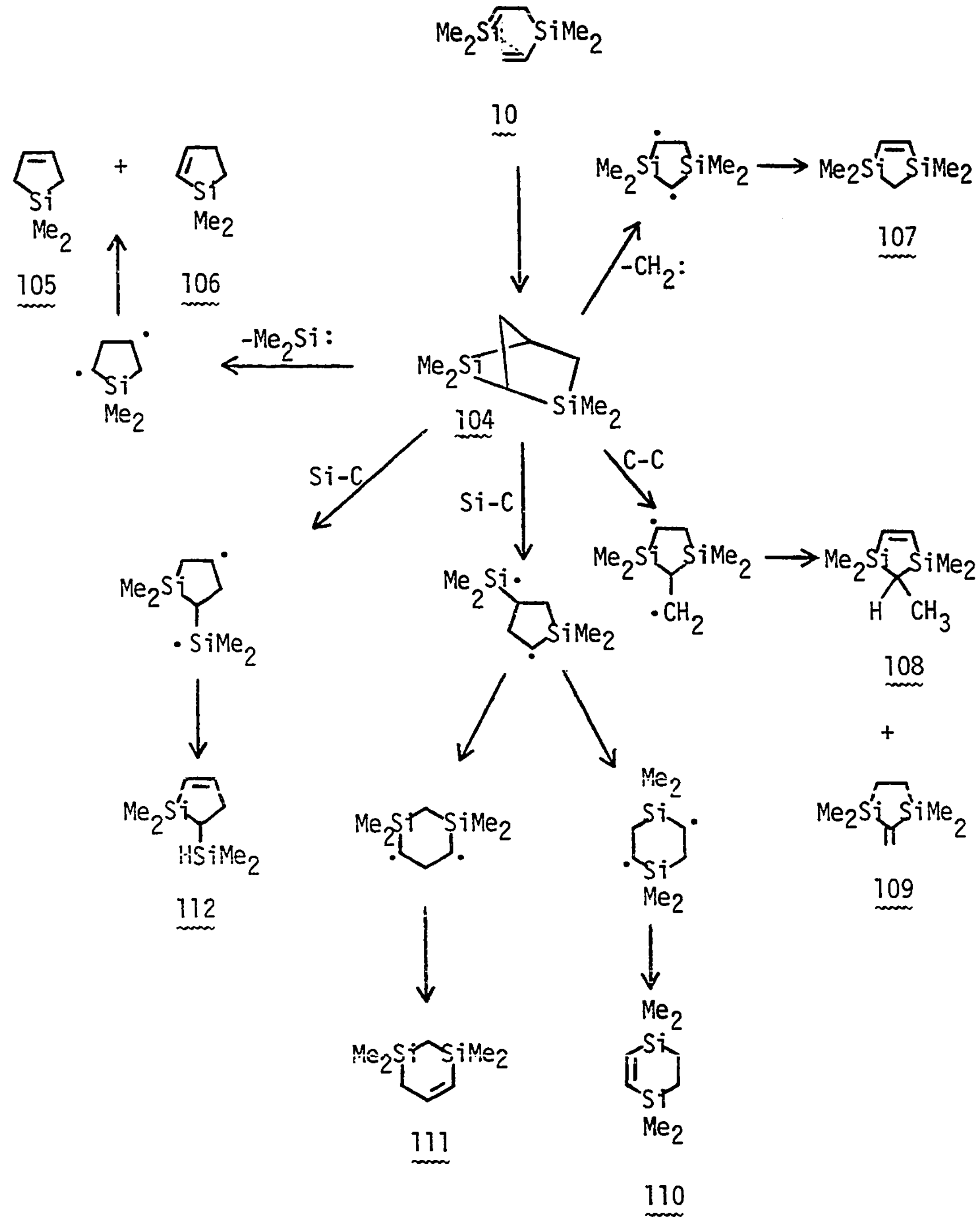
These, along with the photochemistry of other organosilanes, have been summarized in two recent reviews by Ishikawa and Kumada (68, 69).

Barton and Wulff have postulated an intramolecular silene rearrangement to account for the cyclic products produced in the flow pyrolysis of 1,2-divinyltetramethyldisilane 9 at 620°C (15). The major product in this reaction, 103, suggested the initial 1,3-silicon shift generating silene 10. The authors suggest intramolecular (2+2) cyclization of 10 to afford 3,3,6,6-tetramethyldisilabicyclo[2.2.0]hexane, followed by 1,1-dimethylsilene extrusion and dimerization to account for the production of 103.

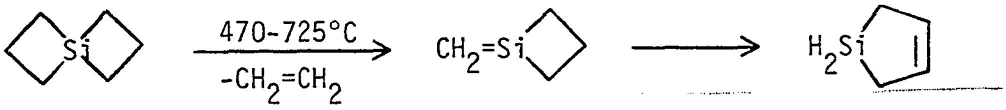


These authors also postulated the closure of **10** could occur in the opposite sense to give **104**, an intermediate which accounts for the remaining cyclic products obtained in the thermolysis of **9**. As summarized in Scheme 11, intermediate **104** produces **105** and **106** from dimethylsilylene extrusion, **107** from methylene extrusion, **108** and **109** from C-C bond homolysis, and **110** - **112** from Si-C bond rupture.

Scheme 11

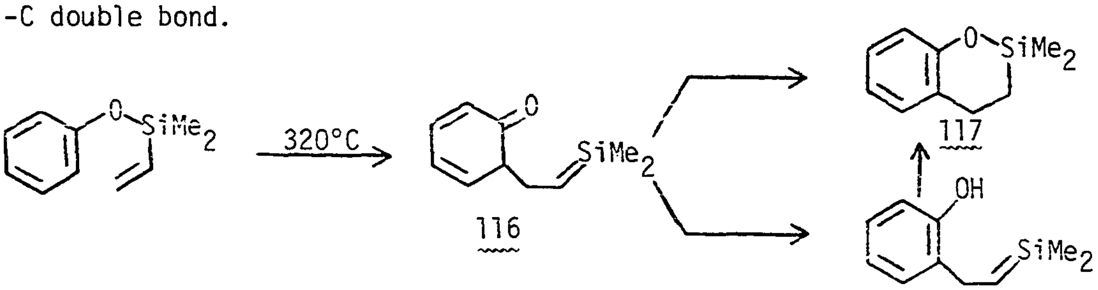

10
104
105
106
107
108
109
110
111
112
-Me$_2$Si:
-CH$_2$:
Si-C
Si-C
C-C
Me$_2$Si
SiMe$_2$
Me$_2$
HSiMe$_2$
H
CH$_3$
CH$_2$

The thermal decomposition of 4-sila spiro[3.3]heptane 113 possibly represents the first report by anyone of an intramolecular silene rearrangement (70). Nametkin et al. report the pyrolysis of 113 at 470 to 725°C under reduced pressures (10^{-2} torr) affords 1-silacyclopent-3-ene 114 as the sole silicon containing product. Although no detailed mechanism was put forth, it was suggested that silene 115 is initially formed and rearranges to 114.



113 115 114

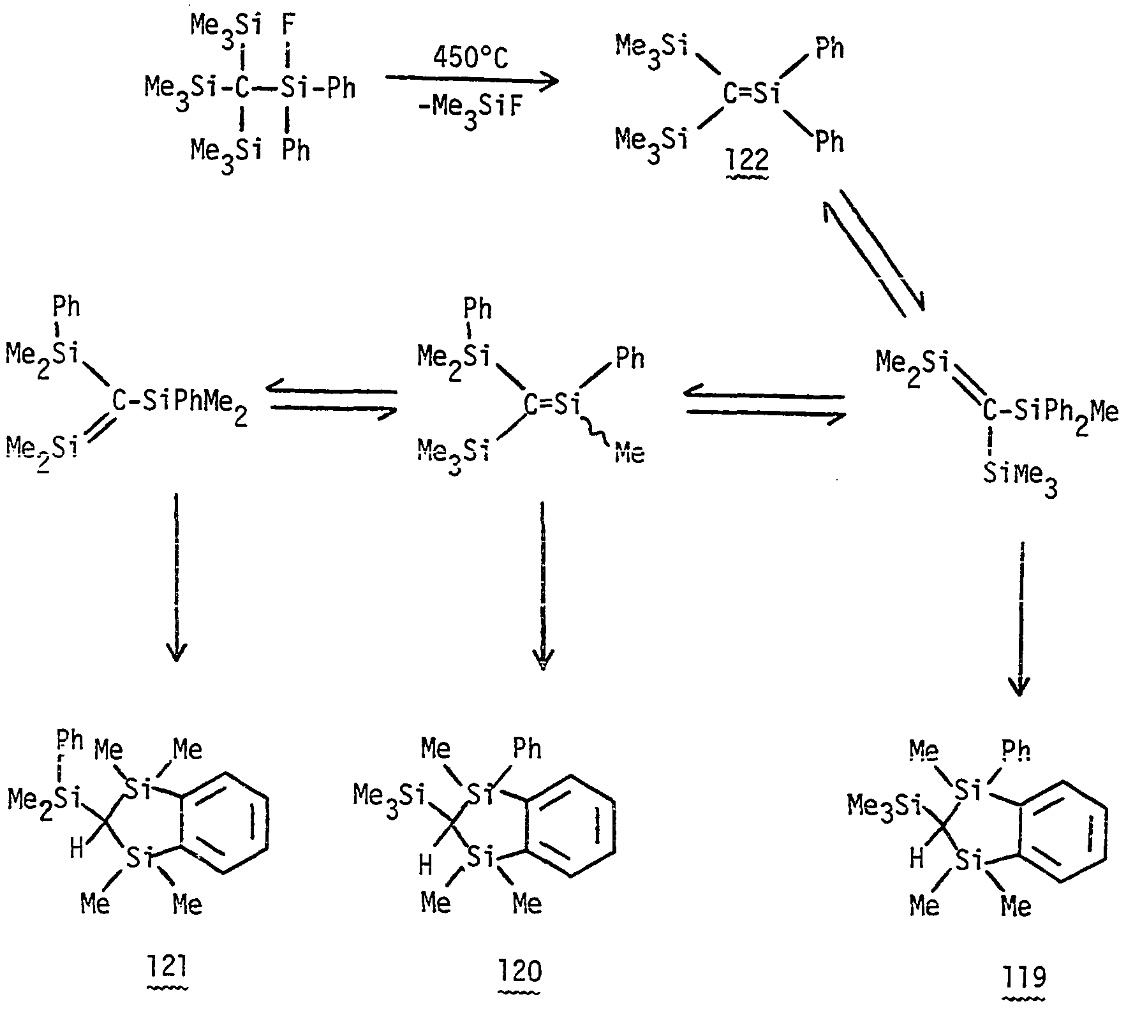
In 1979, Ancelle et al. reported that a Claisen rearrangement occurs when phenoxydiemthylvinylsilane is heated at 320°C in a sealed tube (71). The Claisen product 116 rearranges to 117 either by a direct six-center mechanism (72), or by enolization and subsequent O-H trapping of the Si-C double bond.



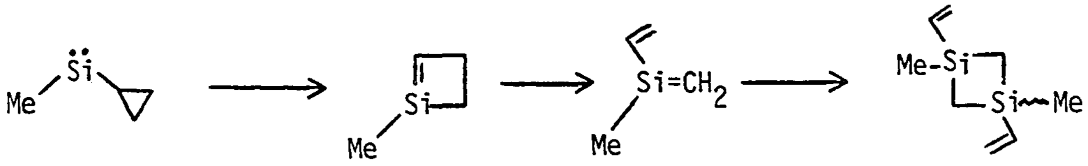
116 117

The compound [tris(trimethylsilyl)methyl](diphenyl)fluorosilane 118 loses trimethyl fluorosilane under reflux or upon passage through a tube at 450°C to give three products 119 - 121 (73). Diasteriomers 119 and 120 were identified by standard techniques including X-ray crystallography, while the structure of compound 121 was based upon its 'H NMR and mass spectrum. All three products are isomers of the sila-olefin 122, formed via a β-elimination of Me_3SiF. It was suggested by Eaborn and coworkers that a rapid equilibrium between four silenes is established and internal cyclizations involving unprecedented additions of aryl C-H bonds across Si-C double bonds (Scheme 12). Consistent with this, is the observation that a mixture of four silicon alkoxides, thought to be isomers of $(Me_3Si)_2CHSiPh_2OMe$, is produced when methanol is passed through the hot tube with 118.

Scheme 12



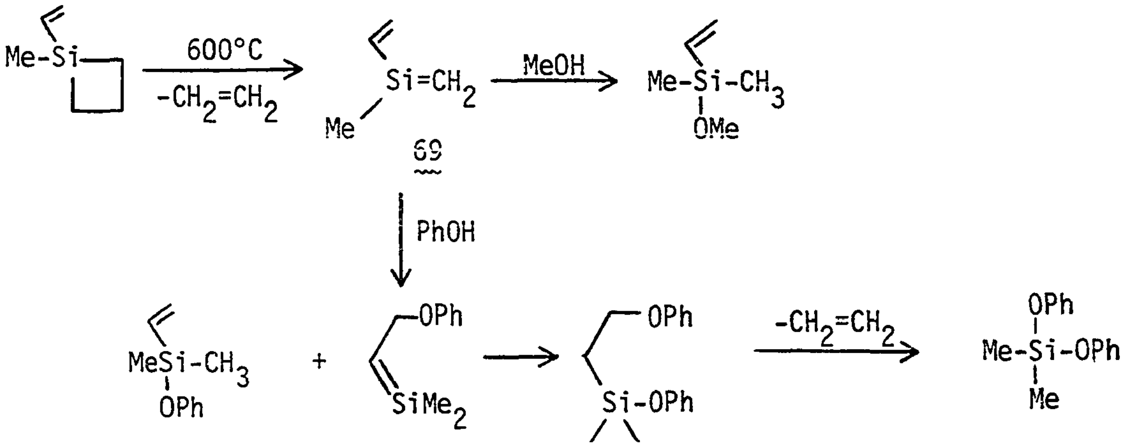
The investigation (54) of the thermal silylene to silene rearrangement of 67 (discussed in the Historical section on silylene rearrangements) also furnished an example of a silene to silene rearrangement (68 → 69).



67 68 69

Bertrand and coworkers have trapped 69, generated from 118 with alcohols (74). These authors consider and discount the reverse silene to silene rearrangement (69 → 68) as an explaination for the phenol trapping product 119. They favor the mechanism outlined in Scheme 13.

Scheme 13



69

119

Silicon Radical Rearrangements

As with silenes and silylenes, a wide variety of reactions of silicon radicals are known and well documented (37-40), but relatively few intramolecular rearrangements of these radicals have been observed.

There are very few good thermal methods for generating silicon radicals. Though hexamethyldisilane decomposes at 600°C to furnish silicon radicals (75), triarylsilyl radicals are not formed in the pyrolyses of hexaaryldisilanes (76). Thermolyses of disilanes that are substituted with either hydrogen, a halogen or an alkoxy group on silicon proceed through silylenes by α-eliminations. Due to this, cleavage of silicon-silicon bonds to generate silicon radicals has not found general utility. The thermolyses of trialkyl silanes results in cleavage of the Si-H bond to generate silicon radicals (77).

The most common methods for production of silicon radicals are hydrogen abstraction by an organic initiator from a hydrosilane (78), mercury photosensitized cleavage of silylhydrides (79), and from decomposition of bis(silyl)mercury compounds (80, 81).

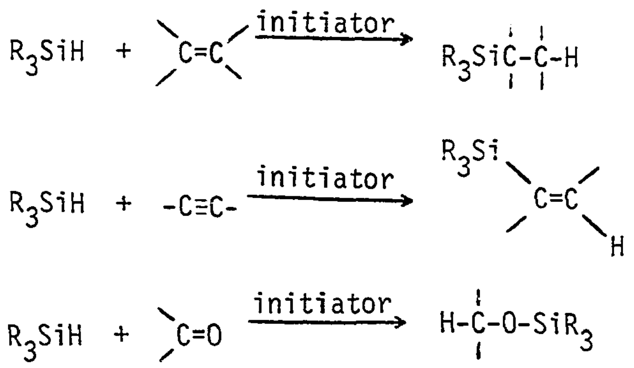
The most common types of reactions that silicon radicals undergo are summarized below.

1. Abstraction of halogen (82, 83).

   $R_3Si\cdot + RX \rightarrow R_3SiX + R\cdot \quad X = Br > C\ell > F$

2. Addition to multiple bonds-free radical hydrosilylation (40).

   $Cl_3SiH > RCl_2SiH > R_2ClSiH >> R_3SiH$

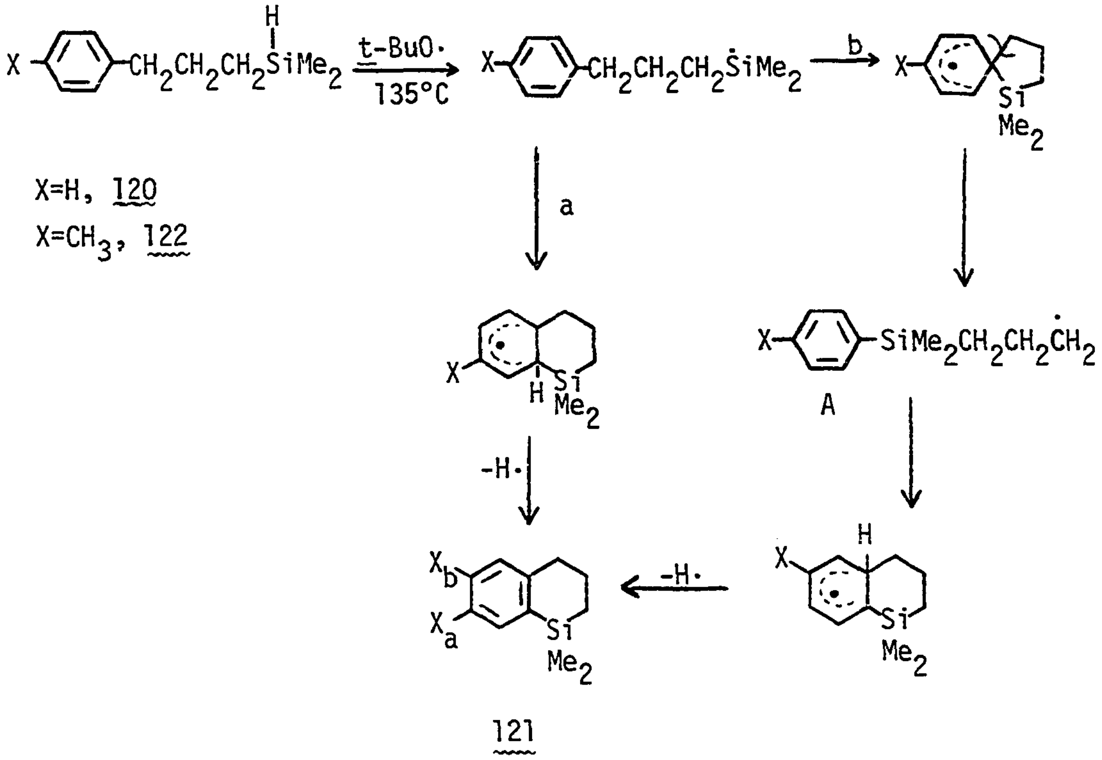


3. Aromatic Substitution (84, 85).

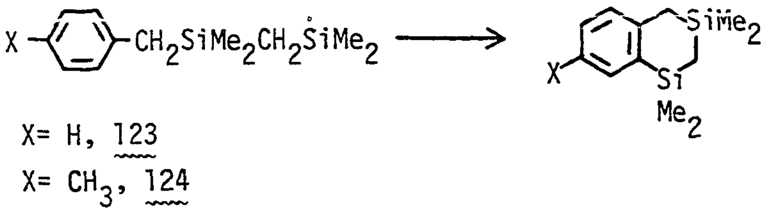
$R_3Si\cdot + ArH \rightarrow R_3SiAr + H\cdot$

Intramolecular cyclization of silicon radicals involving homolytic aromatic substitution was first reported by Sakurai *et al*. in 1969 (86). The di-*tert*-butyl peroxide initiated reaction of (3-phenylpropyl)-dimethylsilane 120 at 135°C (15 hours in a sealed tube) furnishes 1,1-dimethyl-1-silatetralin 121 as the sole silicon containing product. Two mechanisms were considered for this cyclization, a direct homolytic aromatic silylation (Scheme 14, path a) or a phenyl migration from carbon to the silicon radical, followed by carbon radical cyclization (Scheme 14, path b). The mechanistic distinction between these two pathways was easily made by incorporating a methyl group para to the propyl group (122). The exclusive formation of the isomer in which the silicon is meta to the methyl group led to the conclusion that cyclization occurs via the silicon radicals (path a).

Scheme 14



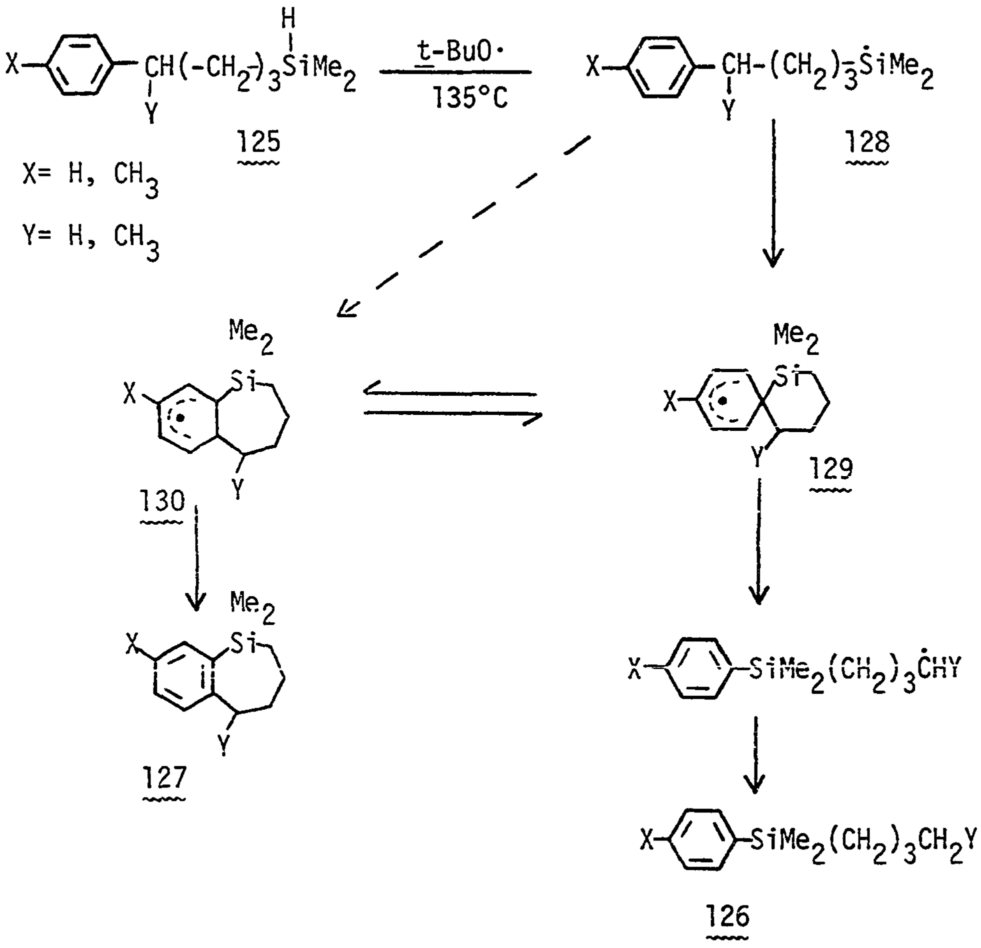
Analogous results were obtained in the 2,4,4-trimethyl-5-aryl-2,4-disilapentane systems 123 and 124. In these systems,no products arising



from hydrogen abstraction of an intermediate carbon radical of the type A (Scheme 14) were observed.

Later,Sakurai and Hosomi found that in 4-arylbutyl)dimethylsilanes aryl migration from carbon to silicon occurs by a free radical mechanism (87). For example, when 4-phenylbutyl)dimethylsilane 125 is heated at 135°C for 15 hours in the presence of di-*tert*-butyl peroxide, both rearranged and cyclized products are formed (126 and 127 respectively). The same results were obtained when (4-p-tolylbutyl)dimethylsilane and (4-phenyl-3-methylbutyl)dimethylsilane were reacted. These results suggest the following mechanism (Scheme 15) for the competition between rearrangement and cyclization. The initially formed silicon radical 128 cyclizes to form the spiro adduct 129, which either ring expands to 130, or suffers C-C bond homolysis and hydrogen abstration. An alternate cyclization of 128 to yield 130 directly is not addressed by the authors.

Scheme 15



Results of the examination of a number of compounds of the general formula $ArCHY(CH_2)nSiMe_2H$ are summarized in Table 4. Only when n = 3 does a competition between cyclization and rearrangement occur. When n = 2 cyclization is the exclusive mode of reaction. The authors reason that this is due to the stability of the ring in the radical of type 130. When this ring-expanded radical contains a six-membered ring (n = 2), only products arising from this pathway are observed. However, when this radical contains a seven-membered ring (n = 3), an alternate pathway comes into play, and both cyclized and rearranged products result. When n = 0,1,4, and 5 neither of these processes occur due to the unfavorable spiro adduct that these would form (three-, four-, seven-, and eight-membered rings).

Table 4. Reaction of x-Ph-$CHY(CH_2)nSiMe_2H$ with di-t-butylperoxide at 135°C

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

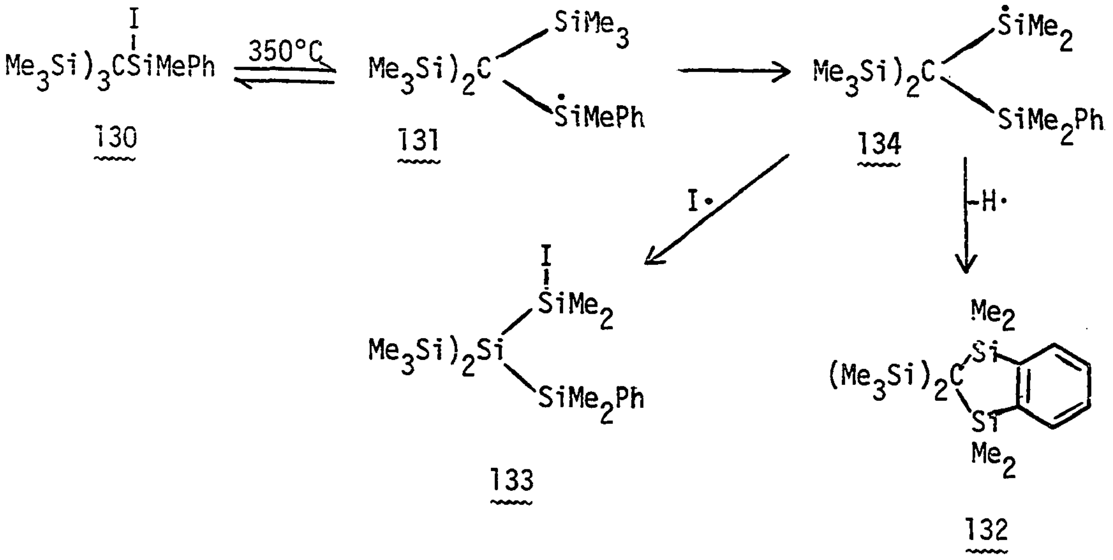
At higher temperatures (370 and 440°C) rearranged products are observed from a variety of arylalkylsilanes (88). These gas phase reactions give products that correspond formally to an aryl migration from carbon to a silicon radical, via the already discussed mechanism of *ipso*-substitution. The data from these reactions are shown in Table 5. The general reaction being the following;

Table 5. Thermal rearrangement of X-Ph-G-$SiMe_2H$

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

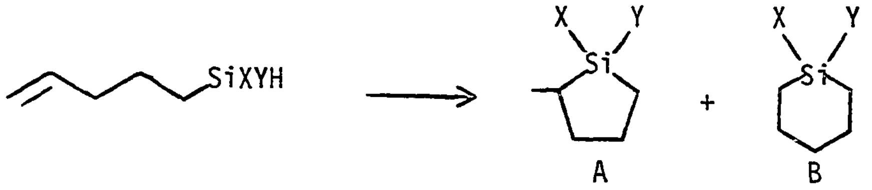
The results follow the free radical initiated results in that when the number of atoms separating the silicon and the aryl group is 2, 5, and 6, the cyclization to the spiro radical does not occur, and thus no rearranged products are observed (or are produced in low yields). However, at these elevated temperatures formation of the three-membered spiro adduct does occur, contrary to the peroxide-initiated reactions (compare Table 4, n = 0 and Table 5, G = CH_2).

Very recently Eaborn and Safa have postulated that the thermolysis of [tris(trimethylsilyl)methyl]diphenylsilyliodide **130** involves a rearrangement of radical **131**, formed by cleavage of the Si-I bond (89). Thermolysis of **130** at ca. 350°C produces **132** as the major product, **133** and an unidentified mixture of at least five species. The mechanism these authors favor involves homolytic dissociation of the original iodide to radical **131**, rearrangement of **131** to **134**, the latter either captures iodine atom to give **133** or, by free radical aromatic substitution, ring closes to **132**.



Intramolecular addition of silicon radicals to carbon-carbon double bonds occurs resulting in cyclization products of the type A or B (40). These results are presented in Table 6. Evidently, as the bulkiness of the substituents on silicon is increased, the more six-membered ring is formed. Also, if a silicon radical is substituted by more electronegative groups, it becomes more nonplanar, thus more reactive, predominantly forming five-membered rings.

Table 6. Intramolecular hydrosilylations of 4-pentenylsilane catalyzed by di-*t*-butylperoxide



		% yield at 135°C		% yield at 30°C	
X	Y	A	B	A	B
Me	Ph	0.65	5.46	1.47	9.48
Ph	Ph	0.74	6.1	3.1	12.6
i-Pr	Cl	3.94	5.47	-	-
Me	Cl	71.6	12.6	4.8	2.9

The first report of an intramolecular silicon radical rearrangement was that of Shiina and Kumada in 1958 (90). This is the only example of a rearrangement that does not involve addition to a π-bond. These authors found that hexamethyldisilane, **135**, readily rearranges at 600°C to give (trimethylsilylmethyl)dimethylsilane 136 and trimethylsilane. No decomposition of 135 occurs at 400°C. A chain mechanism involving

$$\underset{135}{Me_3SiSiMe_3} \xrightarrow{600°C} \underset{136}{Me_3SiCH_2SiMe_2H} + Me_3SiH$$

initial cleavage of the Si-Si bond was proposed. The key feature of this mechanism is the 1,2-trimethylsilyl migration of radical 137.

$$135 \longrightarrow 2\ Me_3Si\cdot$$

$$Me_3Si\cdot + Me_3SiSiMe_3 \longrightarrow \underset{137}{Me_3SiSiMe_2CH_2\cdot} + Me_3SiH$$

$$\underset{137}{Me_3SiSiMe_2CH_2\cdot} \xrightarrow{\bigcirc} Me_3SiCH_2\dot{S}iMe_2$$

$$Me_3SiCH_2\dot{S}iMe_2 + 135 \longrightarrow \underset{136}{Me_3SiCH_2SiMe_2H} + 137$$

The radical 137 can also be generated in the liquid phase at lower temperatures by decomposing organic peroxides in 135 (91); at 80°C rearrangement does not occur, nor does it occur in solution at 129°C (92), indicating that an appreciable activation energy for this rearrangement exists.

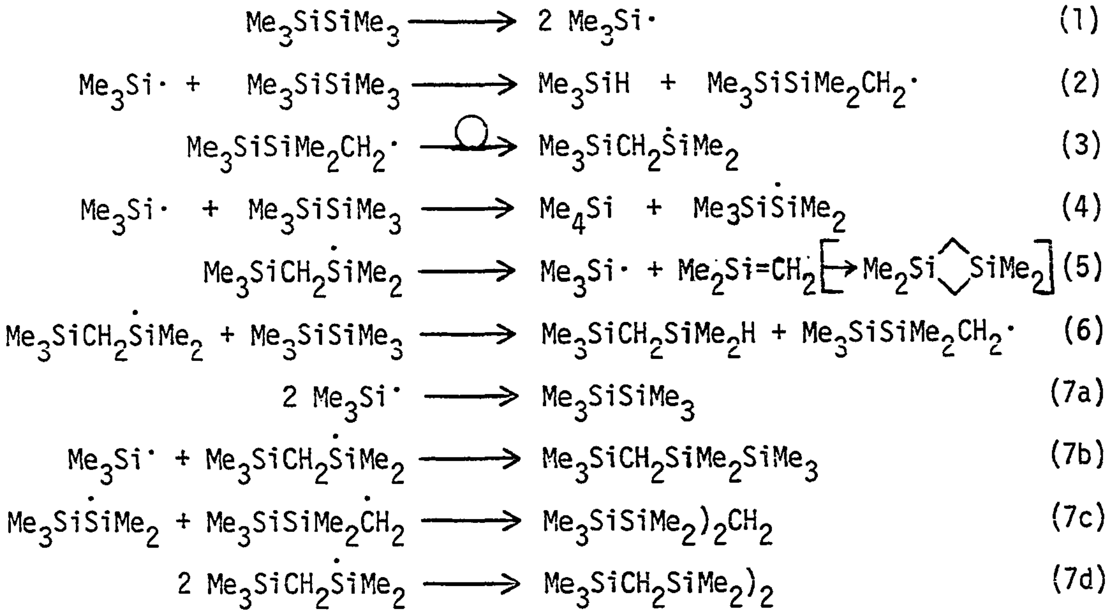
Later, Sakurai and coworkers found that the ratio of trimethylsilane to 136 was 1:4 by GC analysis and concluded that the average chain length is four (91).

In the similar 1,2-diphenyltetramethyldisilane, rearrangement does not occur at 600°C, resulting only in recovered starting material.

$$PhMe_2SiSiMe_2Ph \xrightarrow{600°C} \text{no reaction}$$

The rearrangement of hexamethyldisilane is pressure dependent, occurring at atmospheric pressure in a flow system (90, 92), or at pressure greater than 10 mmHg in a static system (93,94,95). At low pressures, however, other products predominate, the composition and kinetic behavior being strongly dependent upon reaction conditions (95-99). For example, Me_3SiH, Me_4Si, $Me_3SiSi(Me_2)CH_2SiMe_3$, $Me_3SiSiMe_2)_2CH_2$, $Me_3SiCH_2SiMe_2H$ and 1,1,3,3-tetramethyl-1,3-disilacyclbutane have all been observed. In 1975 Davidson and Howard performed a detailed investigation of the thermolysis of hexamethyldisilane in a stirred-flow system (99). The results of their kinetic study provided the mechanism shown in Scheme 16 which accounts for all of these products.

Scheme 16



$$Me_3SiSiMe_3 \longrightarrow 2\ Me_3Si\cdot \quad (1)$$

$$Me_3Si\cdot + Me_3SiSiMe_3 \longrightarrow Me_3SiH + Me_3SiSiMe_2CH_2\cdot \quad (2)$$

$$Me_3SiSiMe_2CH_2\cdot \xrightarrow{\Omega} Me_3SiCH_2\dot{S}iMe_2 \quad (3)$$

$$Me_3Si\cdot + Me_3SiSiMe_3 \longrightarrow Me_4Si + Me_3Si\dot{S}iMe_2 \quad (4)$$

$$Me_3SiCH_2\dot{S}iMe_2 \longrightarrow Me_3Si\cdot + Me_2Si{=}CH_2\left[\rightarrow Me_2Si\diamond SiMe_2\right] \quad (5)$$

$$Me_3SiCH_2\dot{S}iMe_2 + Me_3SiSiMe_3 \longrightarrow Me_3SiCH_2SiMe_2H + Me_3SiSiMe_2CH_2\cdot \quad (6)$$

$$2\ Me_3Si^{\cdot} \longrightarrow Me_3SiSiMe_3 \quad (7a)$$

$$Me_3Si^{\cdot} + Me_3SiCH_2\dot{S}iMe_2 \longrightarrow Me_3SiCH_2SiMe_2SiMe_3 \quad (7b)$$

$$Me_3\dot{S}iSiMe_2 + Me_3SiSiMe_2\dot{C}H_2 \longrightarrow Me_3SiSiMe_2)_2CH_2 \quad (7c)$$

$$2\ Me_3SiCH_2\dot{S}iMe_2 \longrightarrow Me_3SiCH_2SiMe_2)_2 \quad (7d)$$

Scheme 16 offers an explanation for the product compositions observed at high and low pressures. At high pressures, reaction (6) is much faster than (5) and the dominant chain sequence is (1), (2), (3), and (6) as has been previously discussed. At low pressures of hexamethyldisilane, reaction (5) can compete with (6) propagating a chain reaction producing the 1,3-disilacyclobutane and increased quantities of trimethylsilane.

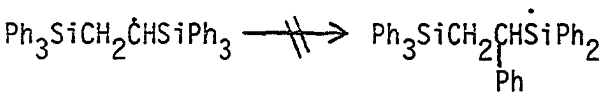
The rearrangement reaction (3) presumably proceeds through a three-centered transition state in which a silicon-silicon bond is being broken while a stronger silicon-carbon bond is being formed. Other rearrangements of silcon containing radicals have not been investigated to the same extent; however, indications are that factors other than simple thermodynamic considerations are important. For example, rearrangements of α-silyl alkyl radicals are not observed, even when thermodynamically favorable. This has been attributed to the (p-d)π stabilization of these radicals. Some examples of "nonrearrangement" are:

$$\mathrm{HMe_2SiCH_2^{\cdot}} \not\longrightarrow \mathrm{Me_3Si^{\cdot}} \qquad (100)$$

$$\mathrm{Me_3SiCH_2^{\cdot}} \not\longrightarrow \mathrm{Me_2(Et)Si^{\cdot}} \qquad (101{,}102)$$

$$\mathrm{PhMe_2SiCH_2^{\cdot}} \not\longrightarrow \mathrm{Me_2(PhCH_2)Si^{\cdot}} \qquad (101{,}102)$$

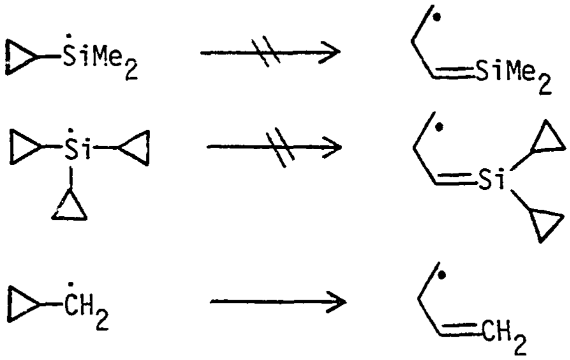
$$\mathrm{Ph_3SiCH_2^{\cdot}} \not\longrightarrow \mathrm{Ph_2(PhCH_2)Si^{\cdot}} \qquad (101)$$



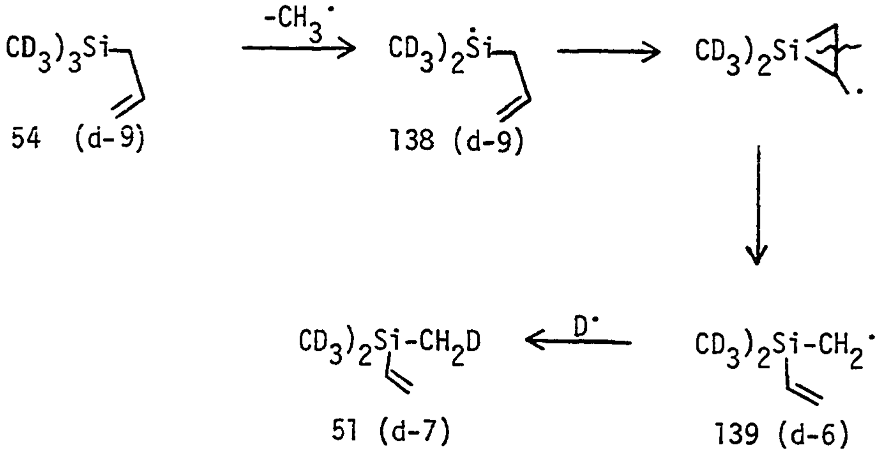
$$\mathrm{Ph_3SiCH_2\dot{C}HSiPh_3} \not\longrightarrow \mathrm{Ph_3SiCH_2}\underset{\mathrm{Ph}}{\overset{\cdot}{\mathrm{C}}}\mathrm{HSiPh_2} \qquad (103)$$

Reactions of the analogous carbon radicals can involve 1,2-rearrangements depending on the conditions used (104, 105), so the silicon and carbon examples apparently stand apart in these cases.

Another interesting "nonrearrangement" is that of cyclopropyldimethylsilyl radical and tricyclopropylsilyl radical generated by the free radical abstraction of hydrogen from the corresponding hydrosilane (40, 106). The analogous cyclopropylcarbinyl radical undergoes facile ring opening to the butenyl radical (107). The relative stability of the silicon-carbon double bond to the carbon-carbon double bond has been used to explain this contrasting behavior. However, it is interesting to note that cleavage of a Si-C bond to generate a silene is thought to occur in pyrolysis of hexamethyldisilane at low pressures [see Scheme 16, reaction (5)].



The mechanism of the thermal conversion of allyltrimethylsilane 54 to trimethylvinylsilane 51 was reported in 1970 by Sakurai and coworkers and was thought to proceed via methylene extrusion (108). Recently, Neider et al. suggested this conversion involves the generation of allyldimethylsilyl radical 138 which rearranges to (dimethylvinylsilyl)-methyl radical 139 (109). These conclusions were based upon a deuterium labeling experiment in which 54, fully deuterated in the methyl groups, produced 51 containing (after correcting for scrambled 54) 2.0 protons in the methyl groups.



Based upon simple bond strengths, cleavage of the silicon-methyl bond in 54 rather than the silicon-allyl bond seems unlikely. Results obtained in this thesis suggest that in allylalkylsilanes, cleavage of the silicon-allyl bond is the primary homolysis process. A complete discussion of these results and their implications will be presented in the Results and Discussion section of this thesis.

Atton and coworkers reported a 1,2-chlorine shift from a carbon to a silicon radical (110). The pyrolysis of (chloromethyl)dimethylsilane at temperatures up to 466°C produces trimethylchlorosilane as the only major product. This reaction was thought to proceed via radical rearrangement 140 → 141.

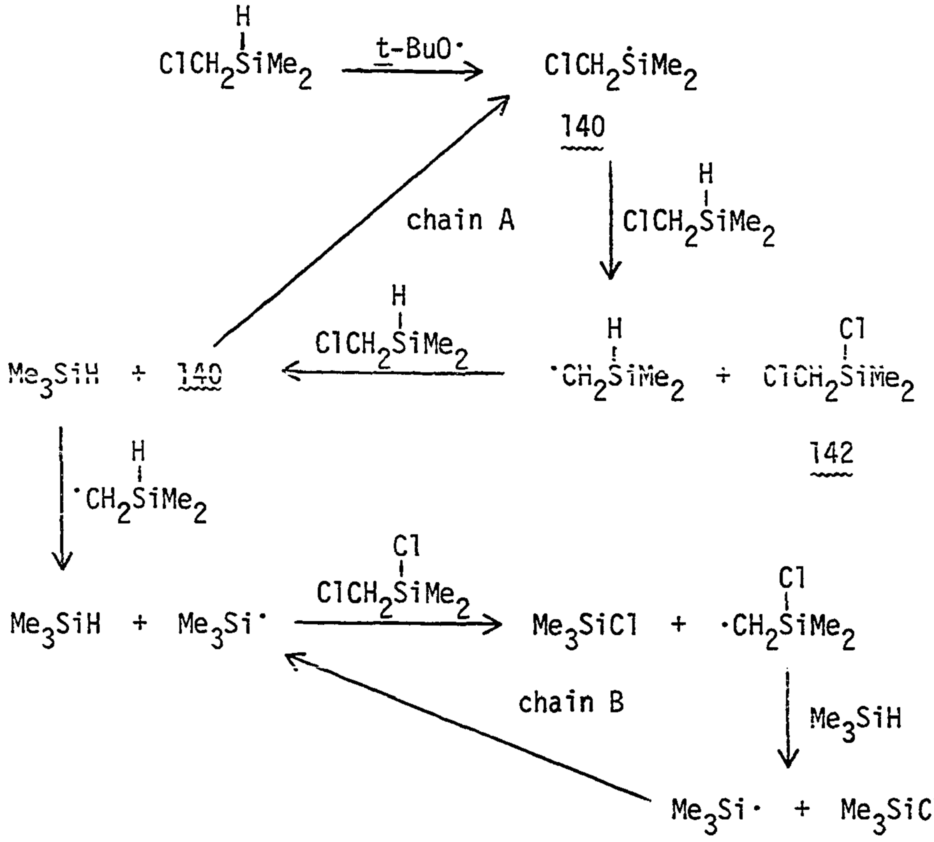
$$CH_3^{\bullet} + ClCH_2SiHMe_2 \longrightarrow CH_4 + ClCH_2\dot{S}iMe_2$$

$$\underset{\underline{140}}{ClCH_2\dot{S}iMe_2} \xrightarrow{\bigcirc} \underset{\underline{141}}{{}^{\bullet}CH_2SiClMe_2}$$

$${}^{\bullet}CH_2SiClMe_2 + ClCH_2SiHMe_2 \longrightarrow Me_3SiCl + ClCH_2\dot{S}iMe_2$$

This was later shown by Jung and Weber to involve the two concurrent chain processes outlined in Scheme 17 (111). At short reaction times (20 minutes) 40% of starting material is gone, forming trimethylsilane and (chloromethyl)dimethylchlorosilane 142 in approximately equal amounts (chain A). Only at longer reaction times does trimethylchlorosilane appear with a concomitant decrease in the amounts of trimethylsilane and 142.

Scheme 17



Although silicon radical disproportionation reactions do not involve rearrangement of the silicon radical, a discussion of the subject is deemed necessary as it is pertinent to the results presented in this thesis.

Until recently, information on the disproportionation of silicon radicals was sparse. Early studies by Nay et al. on the monomethyl-, dimethyl-, and trimethylsilyl radicals generated photochemically ($HgG(^3P_1)$) indicated that disproportionation of these radicals could not be ruled out, but that it occurred to a minor extent (112).

Two separate studies were done in the early 1970s determining the rate of combination of trimethylsilyl radicals (113,114 and 115,116).

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

Watts and Ingold (114) found the rate of combination k_c to be 5.5×10^9 $M^{-1}sec^{-1}$ in solution using kinetic applications of electron paramagnetic resonance spectroscopy (correcting the value of 3.16×10^2 $M^{-1}sec^{-1}$ calculated by Thynne (117)). The gas phase value for this combination rate was determined by Cadman and coworkers (115, 116) using a rotary sector technique. A value of 1.78×10^{11} $M^{-1}sec^{-1}$ was obtained between 44 and 126°C. The difference in these numbers is typical of rate differences observed between gas and solution phase. These authors noted that trimethylsilyl radical disproportionation was not important under their reaction conditions.

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

Strauz et al. also suggest that this reaction is not significant, quoting a value of 0.046 for kd/kc, without experimental details (118).

While early results on the disproportionation of silicon radicals at or near room temperature suggest that this reaction is negligible, it has been advanced under pyrolytic conditions. Davidson and Lambert studied the thermolysis of trimethylsilane between 670 and 758°C (119, 120). The production of di to tetramethyl-1,3-disilacyclobutanes was accounted for by invoking disproportionation reactions, followed by combination of the double-bonded intermediates.

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

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

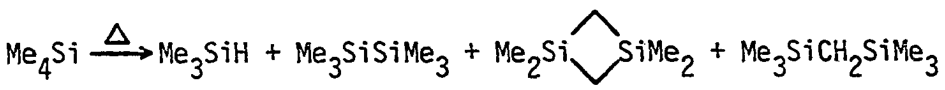
$$\cdot CH_2SiMe_2H + \cdot CH_2SiMe_2H \longrightarrow Me_3SiH + Me_2Si{=}CH_2$$

Results of Paquin et al. (121) and Walsh and Wells (122) suggest that the decomposition of trimethylsilane contains chain processes forming hydrogen and methane. They suggest that the formation of the double-bonded intermediates involves homolytic bond cleavages.

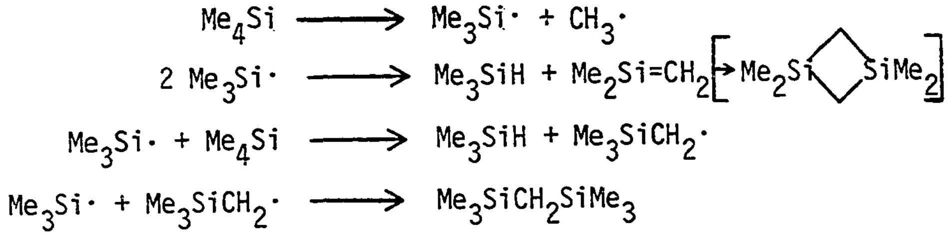
$$Me_2HSiCH_2\cdot \longrightarrow Me_2Si{=}CH_2 + H\cdot$$

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

The pyrolysis of tetramethylsilane was studied by Clifford and coworkers between 537 and 707°C (123). The liquid products in the reaction were trimethylsilane (35%), hexamethyldisilane (15%) 1,1,3,3-tetramethyl-1,3-disilacyclobutane (36-43%) and 2,2,4,4-tetramethyl-2,4-disilapentane (5-11%).



Based upon the kinetic and thermodynamic data, and product composition, these authors propose the following reactions



From the product analysis, a value of kd/kc of 1.2 at 707°C was estimated.

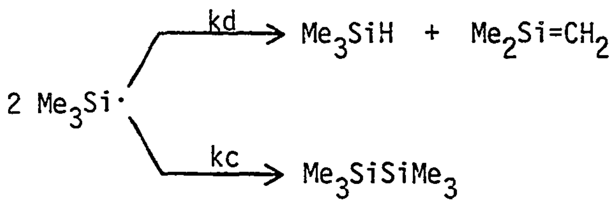
This prompted Baldwin and coworkers (124) to reinvestigate and reinterpret the earlier results of Davidson and Lambert. Computer-aided calculations and experiments on the kinetics of the thermolysis of trimethylsilane and tetramethylsilane enabled mutually consistent mechanisms to be advanced. Though the mechanisms outlined for thermal decomposition of Me_4Si and Me_3SiH involve a large number of steps (12 and 27 respectively), the formation of 1,3-disilaycIobutanes was accounted for by the following dissociation reactions

$$(Me_4Si\ \text{thermolysis})\quad Me_3SiCH_2\cdot \longrightarrow Me_2Si{=}CH_2 + CH_3\cdot$$

$$\left\{\begin{array}{l}Me_3SiH\\ \text{thermolysis}\end{array}\right\}\quad \begin{array}{l}Me_2HSiCH_2\cdot \longrightarrow Me_2Si{=}CH_2 + H\cdot\\ Me_2HSiCH_2\cdot \longrightarrow MeHSi{=}CH_2 + CH_3\cdot\end{array}$$

in accord with the work of Paquin <u>et al</u>. and Walsh and Wells, and not with that of Clifford and coworkers.

Recent insight into the role of disproportionation of trimethylsilyl radicals at room temperature has emerged as a result of studies performed by three separate groups. Tokach and Koob (125, 126) pointed out that disproportionation of trimethylsilyl radicals at or near room temperature could have very well gone unnoticed since dimerization of silenes only occurs at elevated temperatures and the other product, Me_3SiH, is the starting material. Therefore, the photolysis of trimethylsilane was investigated in the presence of methanol. The expected addition product, trimethylmethoxy silane is obtained in good yields, thus allowing for a measure of kd/kc. A value of 0.31 ± 0.08 was obtained at 25°C.

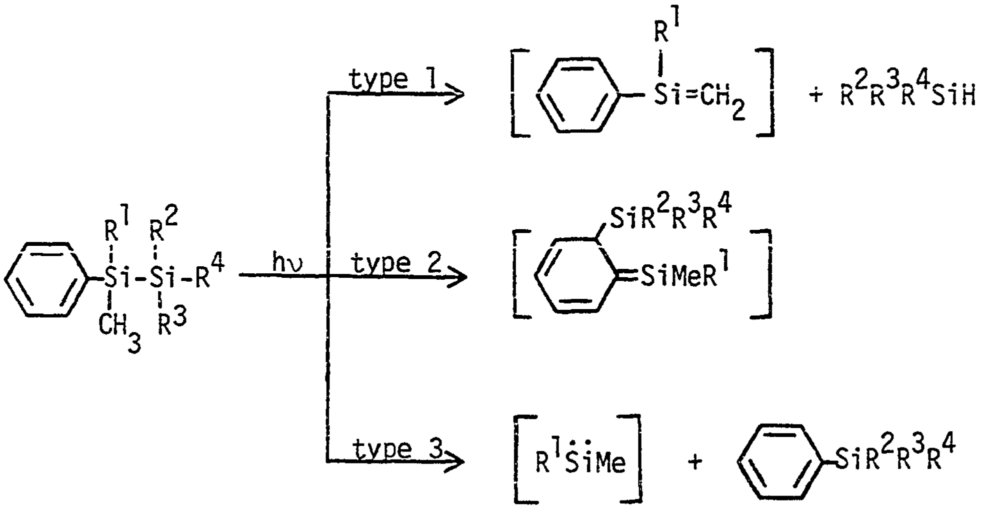


Gaspar and coworkers found that disproportionation of trimethylsilyl radicals is also important in solution. When trimethylsilane is photolyzed in tert-butylperoxide, hexamethyldisilane and tert-butylalcohol are the sole products (127). The initial conclusion was that combination was the exclusive mode of self-reaction for these radicals. However, at longer reaction times a third product, tert-butoxytrimethylsilane, is formed (128). Initially when tert-butylalcohol is in low concentrations, there is no agent present capable of converting the silene into a stable low molecular weight product. With excess tert-butylalcohol present initially,trapping occurs immediately and a value for kd/kc of 0.2 was measured in solution at 25°C. Since the rate of combination of trimethylsilyl radicals is nearly at the diffusion controlled limit (kc = $5.5 \times 10^9\ M^{-1}sec^{-1}$) this disproportionation reaction is remarkably fast.

In the final investigation by Gammie et al. a value of 0.05 ± 0.01 for kd/kc was obtained in the photolysis of bistrimethylsilyl mercury at room temperature (129).

In comparing these values for kd/kc, the differences are substantial, but disproportionation of trimethylsilyl radical is competitive with combination, manifesting the importance of the assistance arising from Si-C double bond formation in the overall energetics of the reaction.

Sakurai and coworkers have shown unequivocally the involvement of free silyl radicals in the photoreaction of aryldisilanes (130). Although this result does not necessarily warrant that all the reaction proceeds by free radicals, it is possible to explain the three types of intermediates observed in these photolyses in the past by an initial

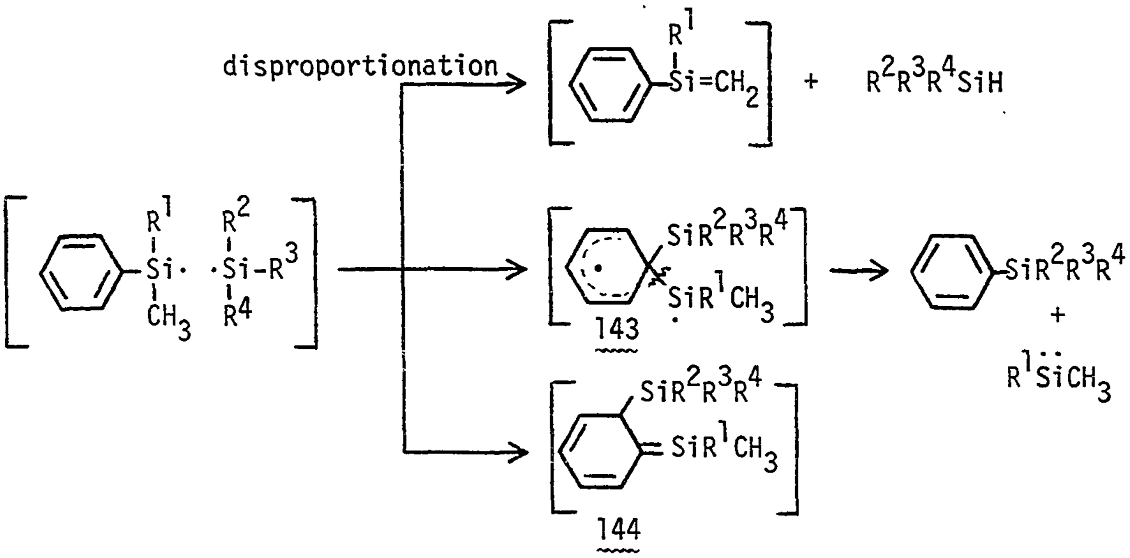


(131)

(57)

(57)

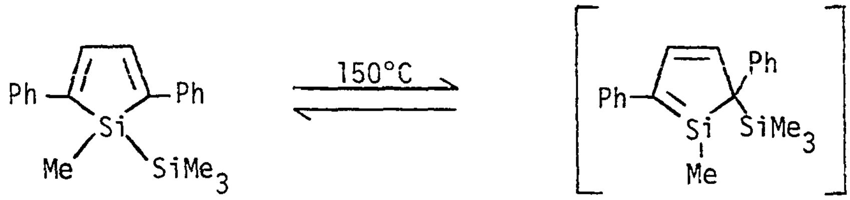
homolytic cleavage of the silicon-silicon bond. The radical pair may undergo disproportionation in the solvent cage to result in type 1 intermediates, and *ipso*-substitution to form **143** which eliminates the silylene resulting in type 2 products. The radical pair can also form **144** by *ipso*-substitution in the ortho position.



RESULTS AND DISCUSSION

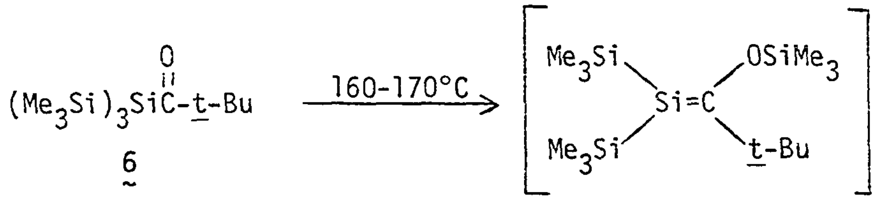
Attempted Generation of a Silene via a 1,5-trimethylsilyl Rearrangement from Silicon to Oxygen

At the outset of this work, thermal 1,5-migrations of the trimethylsilyl group were known to be facile processes (see Historical section on thermal 1,3- and 1,5-rearrangements of silicon). This has recently manifested itself in the generation of (p-p)π bonded silicon via migration from silicon to carbon (27).



23 25

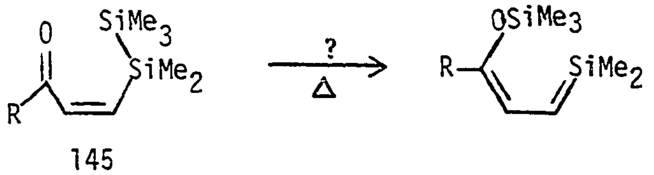
Similarly, thermolysis of acylpolysilane 6 has been shown by Brook and coworkers to produce a silene by the 1,3-rearrangement of silicon from silicon to oxygen (14).



6

The silicon-carbon double bonded intermediates in both of these systems were efficiently trapped in yields greater than 60%.

The union of these rearrangements, the 1,5-migration of silicon from silicon to oxygen, is an unknown process. The desire to generate a silene through this novel unprecedented route, coupled with the hope that the rearrangement may proceed at even milder temperatures, fostered the work presented in this section. It was reasoned that a *cis*-pentamethyldisilanyl enone 145 would be a good candidate for the desired rearrangement. Optimism for this project was

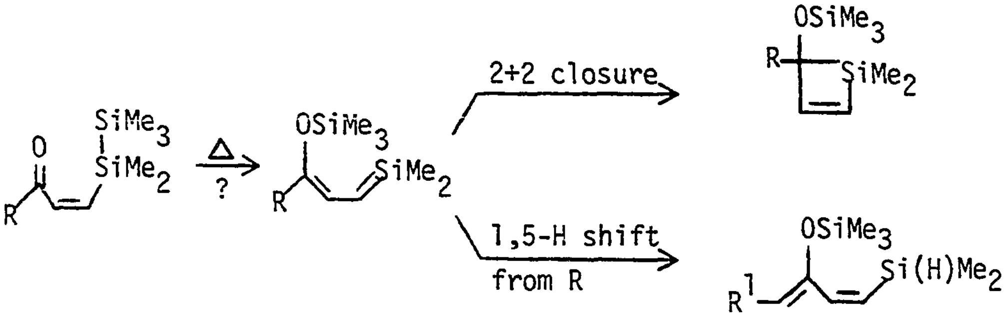


145

two-fold: the literature precedent already cited and the favorable thermodynamics of the rearrangement relative to the silole system, 23 ⇄ 25. In comparison, the migration in both 23 and 145 involves breaking a Si-Si single bond and forming a silicon carbon double bond. The two crucial bonds to consider are the breaking of the C=C and C=O double bonds relative to the formation of the Si-C and Si-O single bonds. Although more energy is required to break the C=O double bond, this would be made up for by the formation of the Si-O bond (132).

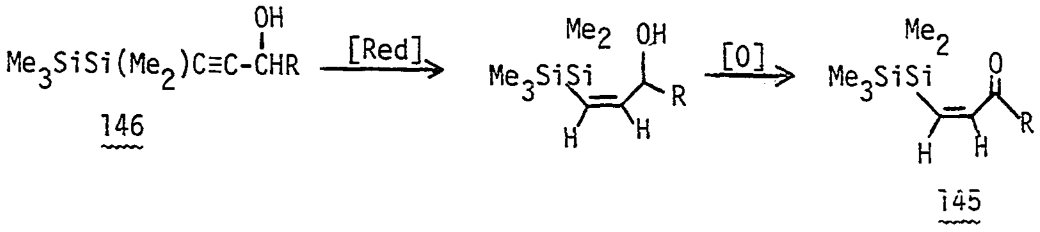
1,5 Si→C; Si-C(-88 kcal/mol) + C=C (64 kcal/mol) = -24 kcal/mol
1,5 Si→O; Si-O(-128 kcal/mol) + C=O (94 kcal/mol) = -34 kcal/mol.

Based upon the known intramolecular rearrangements of silenes (see Historical section on silene rearrangements), the desired 1,5-trimethylsilyl migration could conceivably furnish two products. Ring closure of 1-silabutadienes to generate siletenes is known to occur (63, 64). There are also several examples of 1,5-hydrogen migrations to silicon in



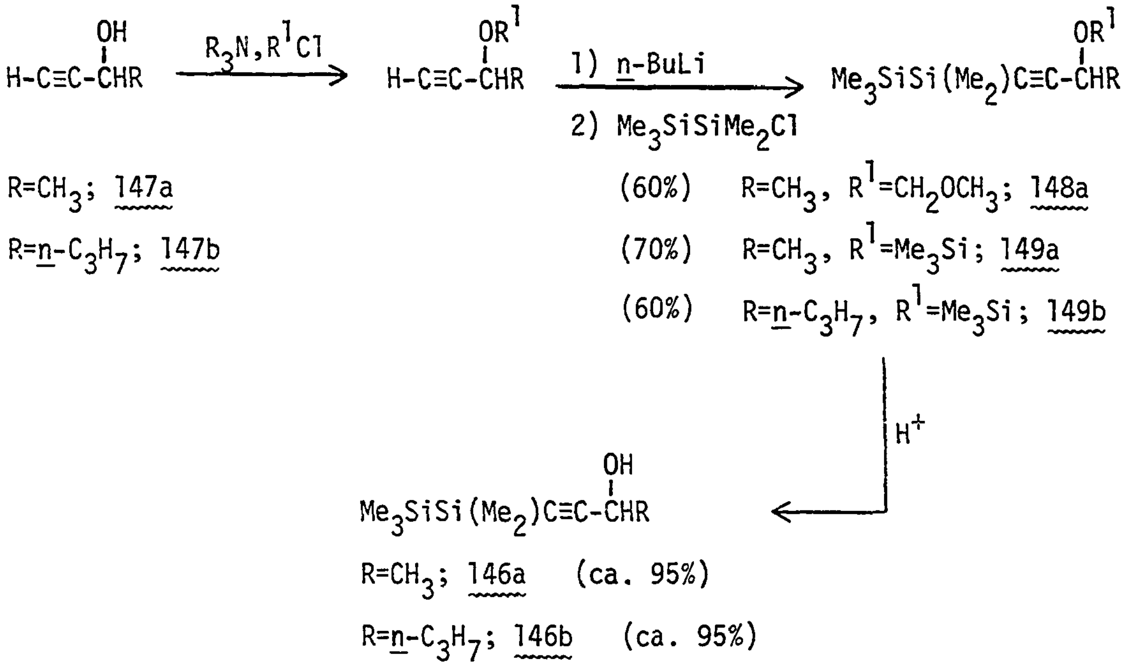
1-silabutadienes (28, 62). Since the 1,5-hydrogen migrations occur to the exclusion of the ring closure, it was felt that products arising from this process were more likely to be observed.

The desired precursor to **145** was the pentamethyldisilanyl ynol **146**, the transformation being envisioned as reduction of the triple bond, followed by oxidation of the alcohol.



The syntheses of **146a** ($R=CH_3$) and **146b** (R=n-propyl) are outlined in Scheme 18. The starting acetylenic alcohols, **147a** and **147b** were chosen because of their availability. Protection of the alcohol with either (chloromethyl)methyl ether or trimethylchlorosilane followed by metallation with n-butyllithium and quenching with pentamethylchlorodisilane proceeded in yields between 60 and 70%. The protecting groups were easily removed with acid.

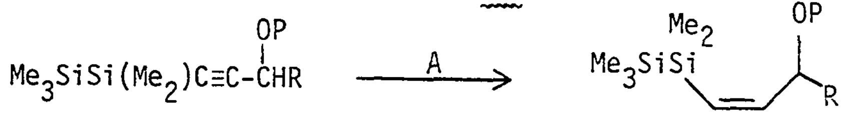
Scheme 18



The reduction of the alcohols 146a and 146b was not as simple as first hoped. A summary of the various reducing agents that failed to give the desired cis-enol 150 appears in Table 7.

Eisch and Foxton have reported that certain group IV alkynes can be selectively reduced to trans- or cis-olefins with diisobutylaluminum

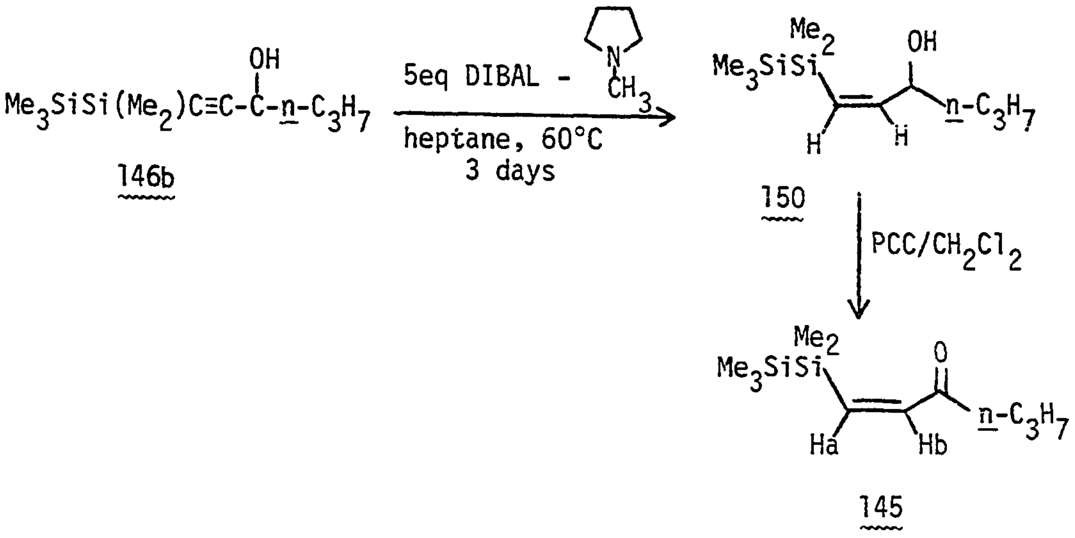
Table 7. Attempted generation of 150



150

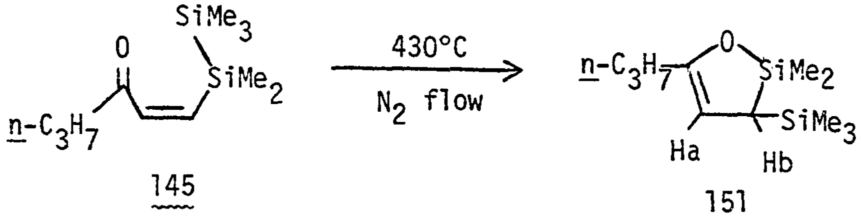
Compound	R	P	A	Reference
146a	CH_3		I $(Sia)_2BH, HOAc, H_2O_2/OH^-$	133
			II $H_2, Pd, BaSO_4$, quinoline	134
			III $H_2, Pd, BaCO_3$, quinoline	
148a	CH_3	CH_2OCH_3	I,II	
			$H_2, Pd, CaCO_3, Pb(OAc)_2$	
			Zn(Cu),MeOH	135
			$BH_3, HOAc, H_2O_2/OH^-$	134
149a	CH_3	Me_3Si	I,II	
146b	n-C_3H_7	H	$(Cy)_2BH, HOAc$	136

hydride and diisobutylaluminum hydride-amine complex respectively (137). This method proved successful for the reduction of 146b. Heating 146b in heptane with a five-fold excess of diisobutylaluminum-N-methylpyrrolidine for 3 days at 60°C affords cis-7,7,8,8-tetramethyl-7,8-disilanona-5-ene-4-ol, 150a in 71% isolated yield. The oxidation of 150a was achieved in 28% yield using pyridiniumchlorochromate (PCC) giving cis-7,7,8,8-tetramethyl-7,8-disilanona-5-ene-4-one, 145.



The NMR of 145 shows olefinic protons at δ7.00 and 6.58 ppm with a coupling constant of 13.0 Hz. This is consistent with the NMR data reported by Eisch and Foxton for *cis*-β-trimethylsilylstyrene (δ7.36(Hα), 5.83(Hβ), Jαβ = 15 Hz). The IR of 145 shows bands at 1692 cm^{-1} (C=O) and 1570 cm^{-1} (C=C).

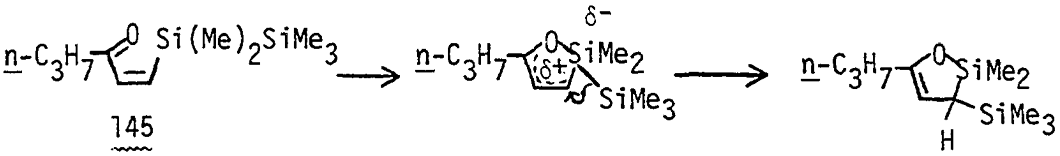
Unfortunately, no evidence for the silene-generating migration was obtained. Thermolysis of 145 at 430°C though a quartz tube packed with quartz chips in a vertical nitrogen-flow system cleanly produced one product with complete decomposition of the starting material. This product was assigned the structure 151 (86%) based upon its 'H NMR, IR, low and high resolution mass spectra. The 'H NMR spectrum shows the



olefinic proton as a doublet (Jab = 3 Hz) at δ4.50 (hν at Hb collapses Ha to a broad singlet). The IR spectrum of 151 is characterized by a moderate band at 1630 cm^{-1} (C=C) and a strong band at 1245 cm^{-1} (C-O). Both the chemical shift of the olefinic proton and the IR absorptions are consistent with those observed in cyclic enol ethers (138).

The facility of this rearrangement is exemplified by the fact that under GC conditions (i.e. injector port 250°C, oven 150°C, SE30 column) 145 furnishes 151 nearly quantitatively.

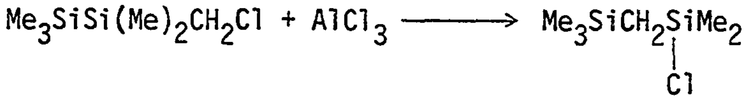
Although coordination of either silicon atom with oxygen is likely, that of the internal silicon accounts for the formation of 151. This zwitterionic complex then decomposes predictably, by a 1,2-migration of the trimethylsilyl group. The desired rearrangement did not occur, however, the cleavage of the silicon-silicon bond and formation of the silicon-oxygen bond was predicted on thermodynamic grounds.



145

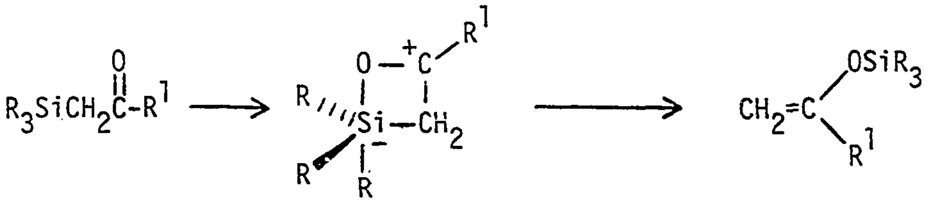
151

The 1,2-migration of silicon to a carbon-bearing partial or full positive charge is well known. For example, (chloromethyl)pentamethyldisilane reacts vigorously with aluminum chloride to give (trimethylsilylmethyl)dimethylchlorosilane through exclusive 1,2-migration of the trimethylsilyl group (139).



$$Me_3SiSi(Me)_2CH_2Cl + AlCl_3 \longrightarrow Me_3SiCH_2\underset{\displaystyle Cl}{\underset{|}{Si}}Me_2$$

The zwitterionic character proposed for this rearrangement is given support by the fact that the 1,3-migration of silicon in beta-ketosilanes is thought to involve the zwitterionic transition state 5 (13).



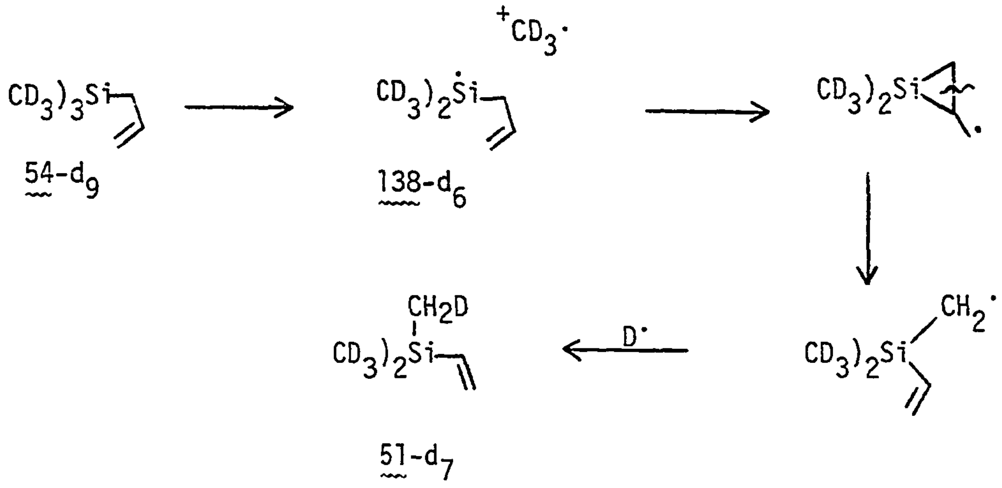
5

Like the thermolysis, the photolysis of enone 145 furnishes the enol ether 151 as the only product; however, the yield is only 11% indicating that polymer formation also occurs.

In summary, it appears that the 1,5-migration of silicon from silicon to oxygen is not a likely process. The presence of the internal silicon provides for an alternate, lower energy route for rearrangement.

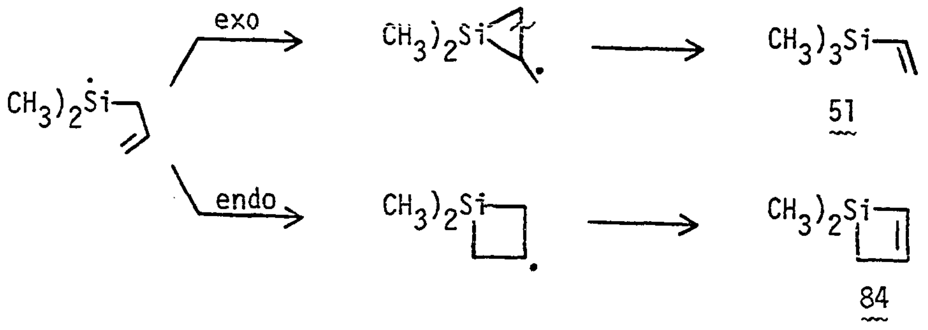
Gas Phase Generation and Reactions of Silicon Radicals

In 1979, Neider *et al.* suggested that the thermal conversion of allyltrimethylsilane 54 to trimethylvinylsilane 51 involves initial cleavage of a silicon methyl bond (109). This suggestion was based upon a deuterium labeling study (no experimental details were given) in which 54, fully deuterated in the methyl position, furnishes 51 with 2.0 protons incorporated in one methyl position. The authors submitted the following mechanism.

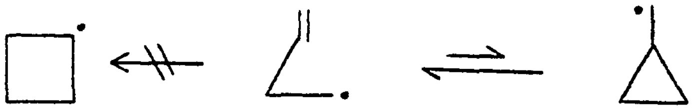


The direct homolysis of a silicon-methyl bond in this system seems unlikely and should not be competitive with silicon-allyl bond cleavage. Assuming that ΔE_{act} for methyl loss versus allyl loss is simply the difference in the ΔH for each process, then methyl loss would be 16 kcal/mole greater than allyl loss (132). Thus, even at the reported 600°C, allyl radicals should be produced more than 3000 times faster than methyl radicals. This suggests that for methyl loss to be competitive, π-participation must be involved to explain the observed deuterium-proton ratio in 51.

An investigation was undertaken to generate allyldimethylsilyl-radical 138 independently to gain information regarding the type of ring



closure this radical follows. Exocyclic ring closure could ultimately furnish trimethylvinylsilane, and endocyclic ring closure could lead to dimethylsiletene 84. The 3-butenyl radical is known to close in an exocyclic manner (140) in line with the guidelines outlined by Baldwin (141) and also Beckwith et al. (142).

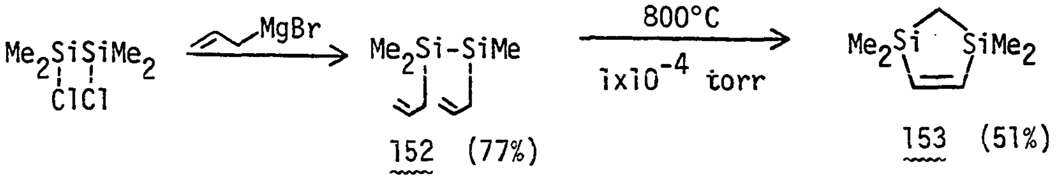


It is not known if silicon radicals parallel their carbon counterparts in ring closures. The only study to date commenting on this is one by Kumada in which 4-pentenylsilyl radicals cyclized to give both exo and endocyclization products, the ratio being dependent upon the stustituent on silicon (40). However, the yields in these cyclizations are quite low (see Historical section on silicon radicals).

Since the silicon-silicon bond is approximately 10 kcal/mol weaker than the silicon-methyl bond (132b), alkylsilyl should be a considerably better leaving group than methyl. In order to maximize the possible rearrangement(s), the symmetrical 1,2-diallyl-1,1,2,2-tetramethyldisilane 152 was chosen. The synthesis of 152 was accomplished in 77% yield from the coupling of 1,2-dichlorotetramethyldisilane and allylmagnesium bromide.

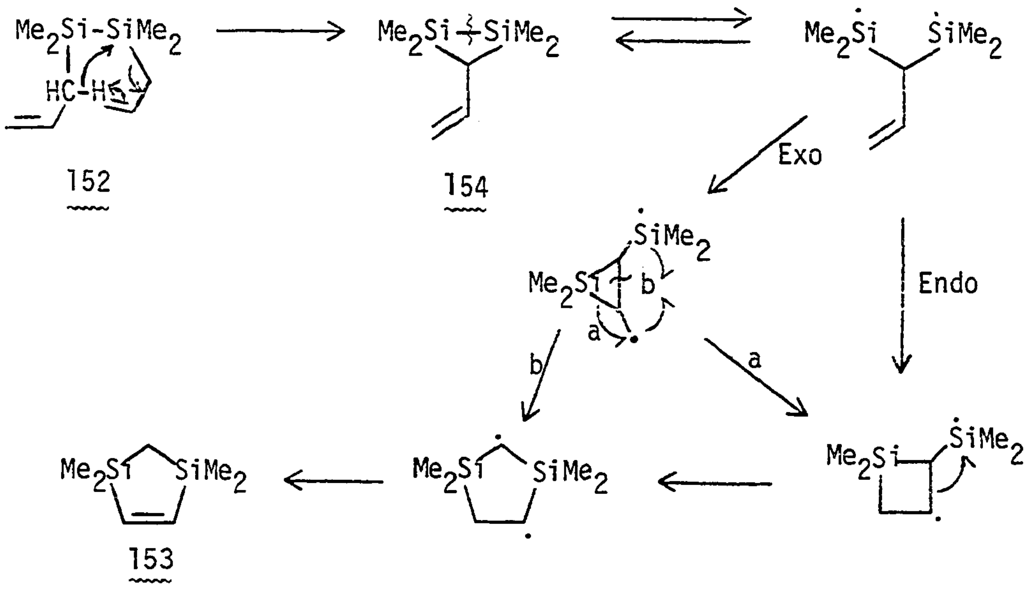
Distillation (25°C, 1 x 10^{-3} torr) of 152 through a quartz tube packed with quartz chips and heated to 800°C afforded a light yellow oil in 74% mass recovery. Analysis of the pyrolysate by gas chromatography on a 12' 15% SE-30 column showed one product other than unreacted 152. This product was isolated by preparative gas chromatography and assigned the structure 1,1,3,3-tetramethyl-1,3-disilacyclopent-4-ene 153 (51%)

based upon its 'H NMR, low and high resolution mass spectra, and IR.



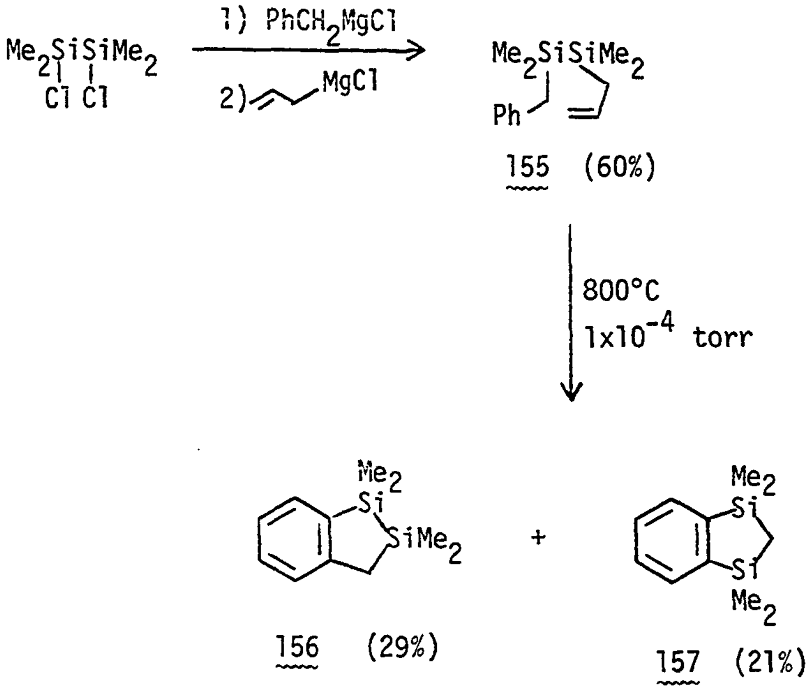
One rationalization for this unexpected product is that 152 undergoes a homoetroene elimination of propene, where one of the silicon atoms is bypassed to achieve the six-electron process (Scheme 19). In analogy certain 1,1-diallylsilanes furnish propene and 1-silabutadienes (63) through a retroene reaction (see Historical section on silene rearrangements). The resulting disilacyclopropane, 154, could then undergo homolysis of the strained Si-Si bond, cyclization (either exo or endo) and ring expansion, furnishing the five-membered ring. Ample precedent for such a ring expansion is found in the gas-phase reaction between silylenes and cycloalkenes (32, 33).

Scheme 19



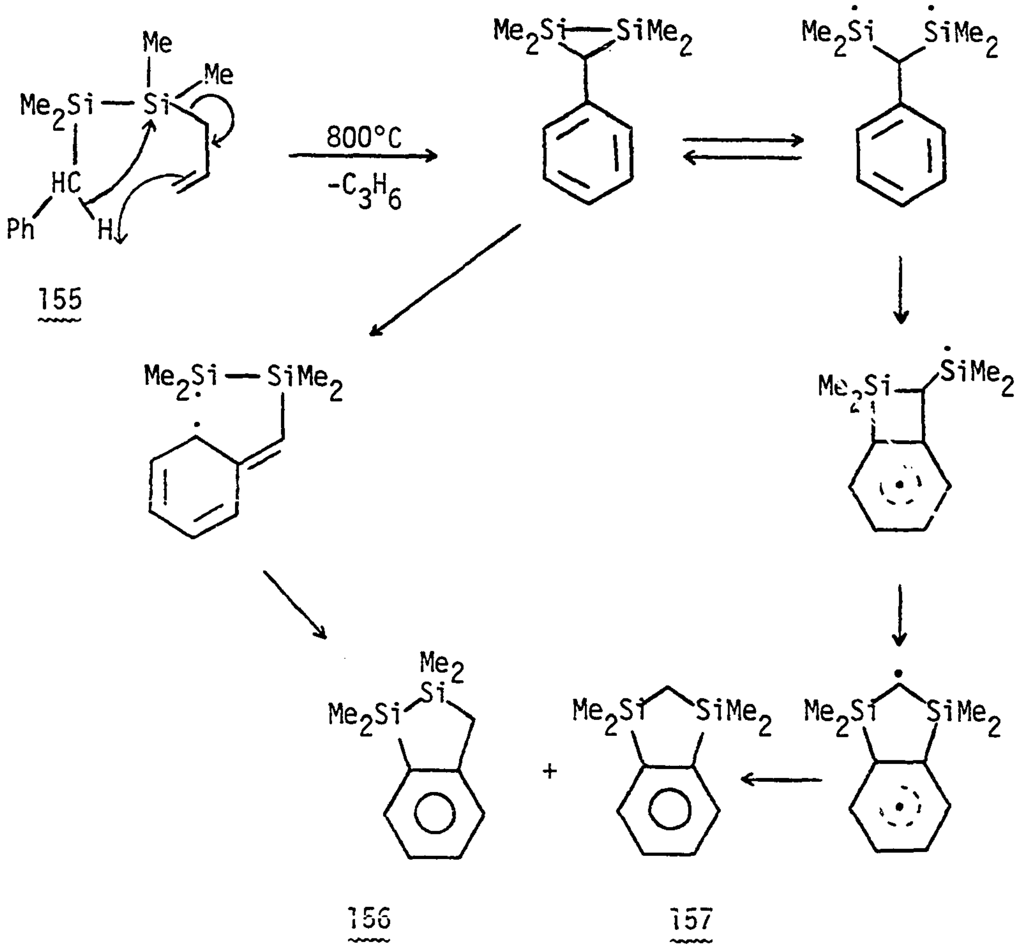
Putting this mechanistic reasoning to a test, one of the allyl groups was replaced with a benzyl group. Since the benzylic methylene should possess similar lability to the allylic methylene, the same general mechanistic pathway was expected. The synthesis of 1-allyl-2-benzyl-1,1,2,2-tetra methyldisilane 155 was accomplished in 60% yield by the sequential addition of benzyl and allylmagnesium chloride to 1,2-dichlorotetramethyldisilane.

Distillation (25°C, 1×10^{-4} torr) of 155 through a quartz tube packed with quartz chips and heated to 800°C afforded a light yellow oil in 78% mass recovery. Analysis of the pyrolysate by gas chromatography revealed the formation of two major products along with unreacted starting material. The two products were isolated by preparative gas chromatography on a 12' 20% SE 30 column. The structural assignment of the 1,1,2,2-tetramethyl-1,2-disilaindane 156 (29% yield) and 1,1,3,3-tetramethyl-1,3-disilaindane 157 (21% yield) was based upon 'H NMR, low and high resolution mass spectral, and IR analyses. In addition, direct comparison was made with the reported spectral data for 156 (143) and 157 (144).



Both of these products can be rationalized as originating from an initial homoretroene elimination of propene as illustrated in Scheme 20.

Scheme 20



However, careful examination of the GC/MS of the product mixture from the thermolysis of 155 revealed that 1,1,3,3-tetramethyl-1,3-disilacyclopent-3-ene, 153 (< 5%), was also a product of this reaction. This observation suggests that an alternative mechanism for the 152→153 transformation be considered; the most obvious one being simple homolysis of either the benzyl- or allyl-silicon bond, accounting for 153, 156 and 157 through radical pathways (see Scheme 21).

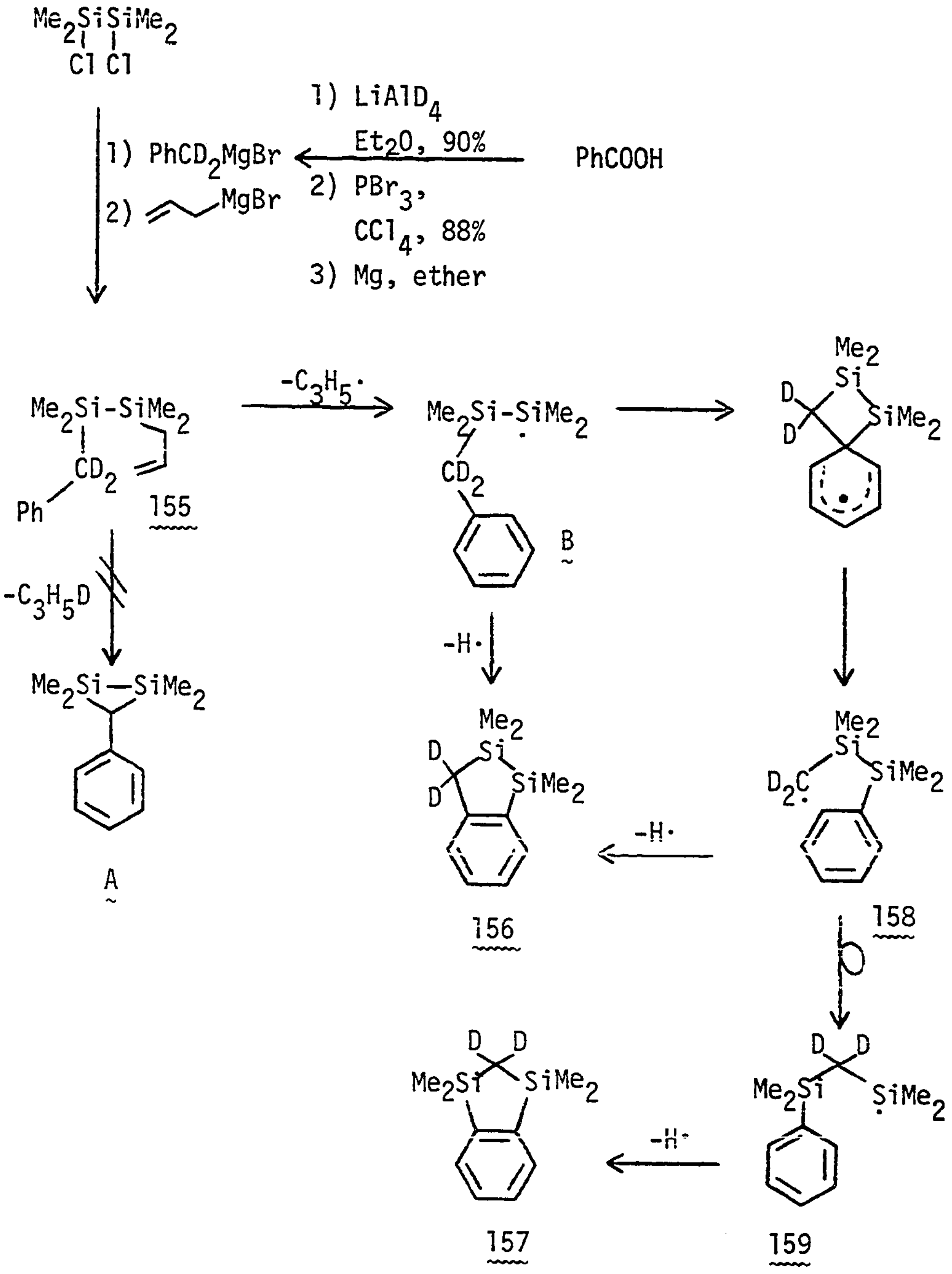
A mechanistic distinction between these two pathways was essential. Examination of the benzyl-allyl system 155 reveals that incorporation of a CD_2 unit in the benzylic position would exclude one of the two mechanisms under consideration.

The synthesis of 155 (d-2) was accomplished by the sequential addition of $PhCD_2MgBr$ (three steps from benzoic acid) and allyl magnesium bromide. The deuterium incorporation in 155 was calculated using the method of Bieman (145); values of 0.0%-d_0, 2.8%-d_1, and 97.2%-d_2 were obtained.

In a homoretroene elimination, one deuterium would be removed by extrusion of propene in the initial step, while in the totally free-radical process it is possible to maintain the ingegrity of the CD_2 unit (compare intermediates A and B, Scheme 21).

Pyrolysis of 155-d_2, as described for 155, furnished the disilaindanes 156 and 157 with no significant loss of deuterium (4.88% 156-d_1 and 7.04% 157-d_1) based on mass spectral and 'H-NMR analysis. Certainly, there is no evidence demanding a concerted loss of propene. The free-radical mechanism presented in Scheme 21 easily accounts for the formation of both these products. Initial cleavage of the silicon-allyl bond forms intermediate B which can directly furnish 156 by ortho-ring closure. Alternatively, B can close in an ipso-fashion. Subsequent carbon-carbon bond homolysis generates 158 which can cyclize to 156 or undergo a 1,2-silicon migration to radical 159 and then cyclize to 157. Two features of this radical mechanism have literature precedent. Intramolecular cyclizations of silicon radicals involving

Scheme 21



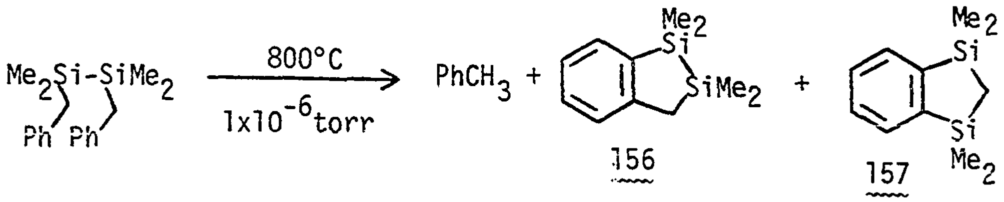
$Me_2SiSiMe_2$ Cl Cl
1) $LiAlD_4$
Et_2O, 90%
2) PBr_3,
CCl_4, 88%
3) Mg, ether
PhCOOH
1) $PhCD_2MgBr$
2) MgBr
$Me_2Si-SiMe_2$
CD_2
Ph
155
$-C_3H_5\cdot$
B
$-C_3H_5D$
A
-H·
156
158
157
159
D
$SiMe_2$
D_2C

homolytic aromatic substitution are well-documented and are presented in the Historical section of this thesis on silicon radicals. In addition, a radical rearrangement analogus to 158→159 has been observed. Rearrangement of 137 occurs under similar conditions (90, 91).

$$Me_3SiSiMe_2CH_2\cdot \xrightarrow{\Delta} Me_3SiCH_2\dot{S}iMe_2$$

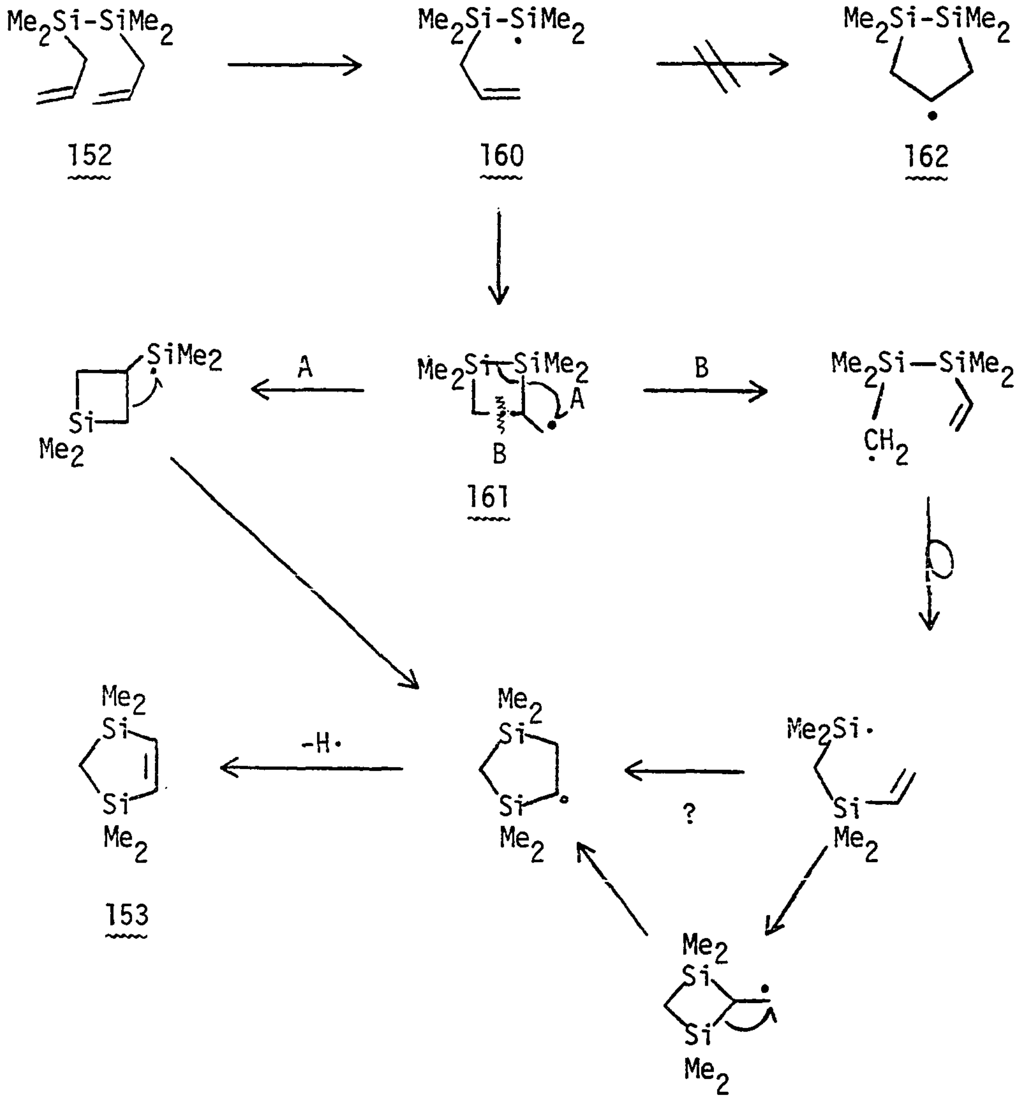
137

Further conformation of the all-radical pathway was obtained from the pyrolysis of 1,2-dibenzyltetramethyldisilane. Cleavage of the benzyl-silicon bond would generate the identical radical as in the thermolysis of 155 (intermediate B, Scheme 21); thus, the disilaindanes 156 and 157 were the predicted products. Thermolysis of 1,2-dibenzyltetramethyldisilane indeed produced toluene, 156 and 157 as the major products.

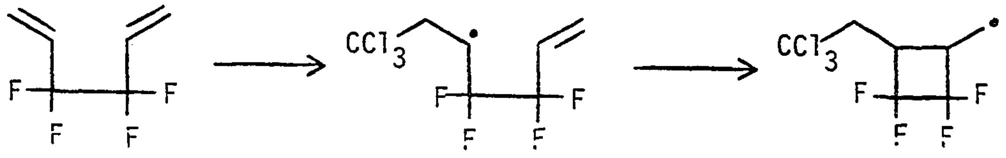


Since these results point to the all-radical process in the benzylated systems, there is no reason to suspect a homoretroene mechanism in the thermochemistry of 1,2-diallyltetramethyldisilane 152. The ramifications to the discovery that these systems under initial allyl cleavage to form silicon radicals are important. First, this stands in contrast to the results presented by Neider *et al.* (109) of the thermolysis of allyltrimethylsilane. Second, it appears that the initially formed disilanylradical 160 (from 152, Scheme 22) cyclizes in an endo fashion to afford 161, as no products with the ring system 162 are formed. This would fit the general rules for carbon radical cyclizations. The radical 161 can ultimately form 153 by two different bond cleavages. Silicon-silicon bond homolysis followed by combination with the carbon

Scheme 22



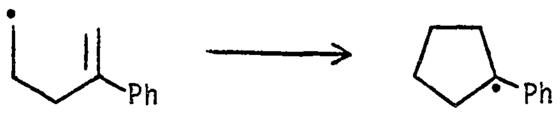
radical (path A) generates an exocyclic silicon radical. Ring expansion of this radical and loss of hydrogen provides 153. Alternatively, radical 161 could undergo homolysis of the carbon-carbon bond, furnishing a disilanyl carbon radical (path B), which after a 1,2-migration of silicon and ring closure could also lead to 153. Interestingly, regardless of the pathway leading to the formation of 153 from 160, the process involved is unprecedented in carbon radical chemistry, or at best, extremely rare. For example, although 1,4-ring closure of the 4-pentenyl radical to give cyclobutylcarbinyl radical meets the stereoelectronic requirements for intramolecular addition, it is disfavored on thermodynamic grounds. It is not surprising that acyclic precursors do not furnish cyclobutane compounds. However, one exception to this is the formation of a cyclobutane derivative by radical addition of carbontetrachloride to the diolefin 163 (146).



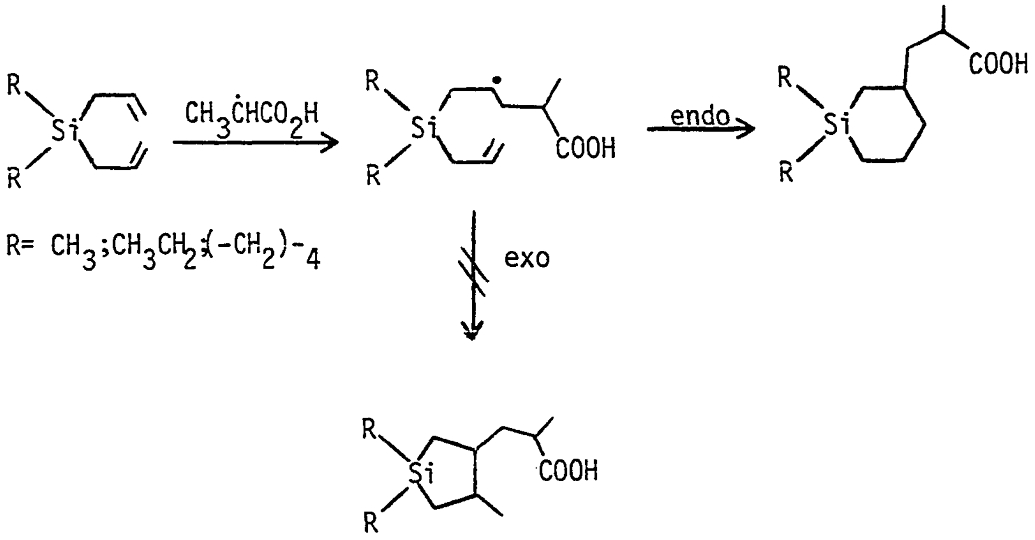
163

The formation of cyclopentyl from 4-pentenyl radical, although thermodynamically favorable, is inconsistent with the rules for ring closure and has not been observed. However some 1,5 ring closures of substituted 4-pentenyl radicals have been reported (147)

e.g.

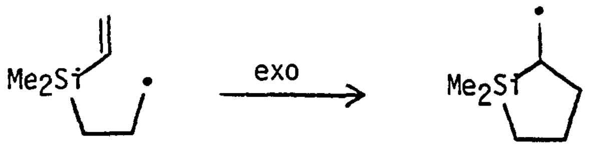


Not only is it difficult to predict the mode of silicon radical ring closures, but there is evidence that the presence of silicon can alter the behavior of carbon radicals. In 1963, Ogibin *et al.* claimed that the addition of the free radical generated from propionic acid and *tert*-butylperoxide produces silacyclohexanes by endo-cyclization of the initially formed radical (148). This work should be viewed cautiously since the mode of ring closure was based solely upon IR spectrometry.

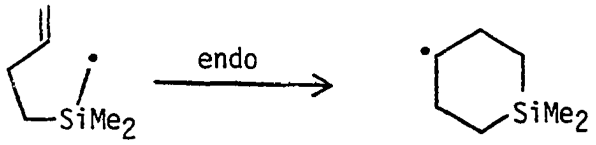


R= $CH_3;CH_3CH_2;(-CH_2)-_4$

A more definitive study has recently been performed by Wilt (149). The mode of ring closure of sila-5-hexen-1-yl radicals was found to be dependent upon the position of the silicon. Cyclization of **164** is quite comparable to the all-carbon system, both in rate and product composition (exocyclization favored). However, closure of radical **165** is exceptional both in reduced rate and reversed regioselectivity. These are the first 5-hexenyl-type radicals bearing neither substituents on the vinyl group



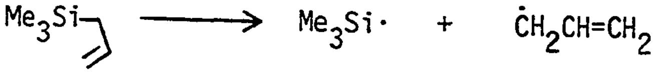
164



165

nor known radical stabilizing groups at the radical center which show such decreased exocyclization.

The results of the thermolysis of both 1,2-diallyl and 1-allyl-2-benzyltetramethyldisilane indicate that in allylsilanes the silicon-allyl bond is initially cleaved. Support for this suggestion has recently been given by Davidson and Wood (150). The kinetics of the pyrolysis of allyltrimethylsilane 54 were studied using a low pressure technique, in which ca. 0.2 mm Hg of 54 was pyrolyzed in a static system and analyzed *in situ* by mass spectrometry. Between 580 and 730°C the main products are almost equimolar amounts of trimethylsilane and propene, accounting for 90% of the decomposed 54. Trimethylvinylsilane is a minor product. The reaction is first order with an activation energy of 73 kcal/mol (thus D[Si-allyl] = 73 kcal/mol). These findings are consistent with the primary process being the following

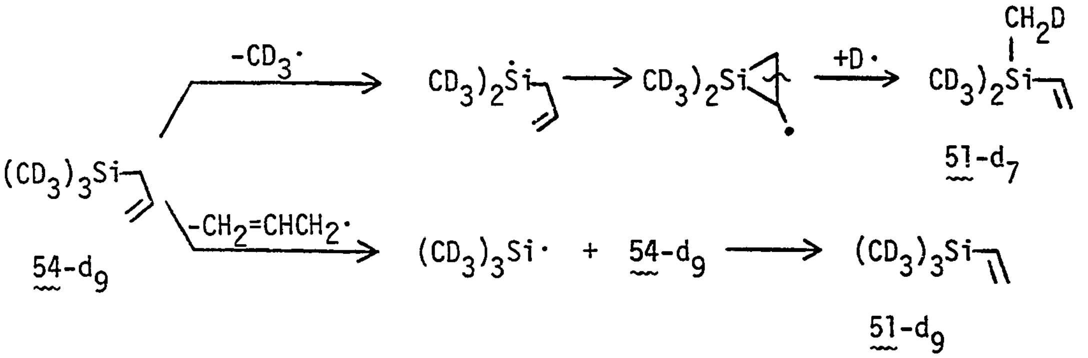


54

Davidson and Wood also found that the product composition in the pyrolysis of 154 depends strongly upon pressure. Thus, increasing the initial pressure of 154 increases the relative yield of trimethylvinylsilane, until by 300 mm Hg it is the major product. The rearrangement of allyltrimethylsilane to vinyltrimethylsilane does not involve a sequence of unimolecular reactions, as previously suggested by Sakurai and Hosomi (108) and Neider *et al*. (109). The formation of trimethylvinylsilane most likely involves a bimolecular addition of trimethylsilyl radical to 54.

The results presented in this thesis along with those presented by Davidson and Wood are in direct disagreement with the labeling study done by Neider and coworkers (109). A resolution of this discrepancy was sought. Labeling either the silicon-methyl position or the allylic-methylene would allow the distinction between silicon-methyl and silicon-allyl bond homolysis to be made. A label placed in the allylic position is complicated by the 1,3-migration of silicon in allylsilanes (see Historical section on 1,3- and 1,5-rearrangements of silicon). The conclusion was made that the most synthetically and economically feasible system was that used by Neider and coworkers, in which deuterium is placed in the methyl positions. The strong belief that the silicon-methyl bond would not cleave preferentially to the silicon-allyl bond prompted a reinvestigation of the work reported by Neider *et al*.

The allyl(nonadeuterotrimethyl)silane-system allows the distinction between these two conflicting mechanisms to be made. If the conversion of 54 to 51 involves silicon-methyl bond homolysis, followed by ring closure and C-C cleavage, the trimethylvinylsilane should contain seven deuteriums (or possibly six, if the last step is proton abstraction). According to Neider and coworkers, 51-d_7 is the observed product. Alternatively, if silicon-allyl bond homolysis is operative then, the bimolecular addition of $(CD_3)_3Si\cdot$ to 54-d_9 and subsequent decomposition would furnish 51-d_9. A discussion of the mechanistic possibilities of this addition-decomposition will be presented later.



Two separate syntheses and thermolyses were performed, converting 54-d_9 to trimethylvinylsilane. An initial thermolysis of 54-d_0 was performed for comparison; it was determined that a temperature of 630°C and a 30 mL/min nitrogen flow were the optimum conditions to perform the flow pyrolysis. These are similar to those employed by Neider _et al._ (600°C, N_2 flow 30 mL/min).

Nonadeuterotrimethylchlorosilane, purchased from Merck and Co., Inc. (99% isotopic purity), was coupled with excess allylmagnesium bromide in ether to furnish deuterated allyltrimethylsilane in 57.6% yield (run 1) and 58.0% yield (run 2). The percent deuterium incorporation in the allyltrimethylsilane 54 was calculated using the method of Biemann (145). The actual ion intensity, corrected intensity and mole percent of deuterated **54** for run 1 and 2 are listed in Table 8. The mass, M, corresponds to the mass of unlabeled **54**. The corrected intensity is the actual intensity minus the contributions of lower mass ions. For example, the intensity of the M + 9 ion 12,992 (run 1) is reduced to 12,984.9 because of the M + 2 from the ion at M + 7. Under the mass spectral conditions employed, no ions are observed due to M - 1, M - 2 M - 3 etc., in the unlabeled allyltrimethylsilane. The calculated values for the mole percent of **54**-d_9 are 98.4% and 96.2% for run 1 and 2, respectively.

Table 8. Percent deuterium incorporation in **54** before pyrolysis

	Mass (M = 114, mass of **54**-d_0)	Actual intensity	Corrected intensity	Mole % of deuterated **54**
Run 1[a]	M+7	208	208	1.6
	M+8	0	0	
	M+9	12,992	12,984.9	98.4
	M+10	1,362	0	
	M+11	435		
Run 2[b]	M+6	77	77	0.8
	M+7	0	0	
	M+8	302	299.1	3.0
	M+9	9,504	9,469.8	96.2
	M+10	1058	0	
	M+11	366		

[a] 25 eV scan. For **54**-d_0; M = 1.00, M+1 = 0.1086, M+2 = 0.03395.

[b] 16 eV scan. For **54**-d_0; M = 1.00, M+1 = 0.1143, m+2 = 0.03790.

Pyrolysis of 54-d_9 through a quartz tube packed with quartz chips heated at 630°C (N_2 flow, 30 mL/min) furnished a clear, colorless liquid in 66% (run 1) and 89% (run 2) mass recovery.

Analysis of the recovered starting material by low eV mass spec revealed that in both runs, 1 and 2, protons were incorporated in the methyl groups. The mole percent of deuterated 54 recovered from each pyrolysis was calculated as described for starting 54, and is listed in Table 9. Taking into account the isotopic purity of the unpyrolyzed 54, there was a 90.9% and 84.7% retention of the d-9 label in run 1 and 2, respectively.

Table 9. Percent deuterium incorporation in 54 after pyrolysis

	Mass (M = 114, mass of 54-d_0)	Actual intensity	Corrected intensity	Mole % of deuterated 54
Run 1[a]	M+6	248	248	1.4
	M+7	342	313.7	1.7
	M+8	1,240	1,194.8	6.6
	M+9	16,224	16,075.6	89.5
	M+10	2,020	137.8	0.8
	M+11	685	0	
	M+12	65	0	
Run 2[a]	M+5	22	22	0.2
	M+6	125	122.5	1.4
	M+7	282	267.2	3.0
	M+8	918	882.8	9.7
	M+9	7,488	7,377.0	81.5
	M+10	1,120	243.6	2.7
	M+11	398	90.6	1.0
	M+12	69	49.4	0.5

[a] 16 eV scan. For 54-d_0; M = 1.00, M+1 = 0.1143, M+2 = 0.0379.

Low eV mass spectra analysis of the trimethylvinylsilane furnished the array of deuterated 51 listed in Table 10. Calculations were performed using the ion intensities of 14 eV and 16 eV and an average taken. Trimethylvinlysilane containing 3 deuteriums (run 2) and 4 deuteriums (run 1) up to and including 12 deuteriums was produced. However, in both runs the major product is 51-d_9 as predicted. The average value for 51-d_9 is certainly a minimum due to the fact that the starting material, 54-d_9, incorporated protons. Using the isotopic purity of recovered 54 (from Table 9), a range of 50.6-56.5% (run 1) and 44.2-54.2% (run 2) can be calculated for the mole percent 51-d_9.

Clearly the results presented by Neider *et al*. are in error. Their claim is that 51-d_7 (M+7) is the only observed isotope. The mole percent of the M+7 isotope is not the largest value and, in fact, represents, at a maximum, only 6% of the observed 51!

A private communication (151) disclosed that the conclusions of Neider *et al*. were based solely upon ^{1}H NMR integration of the deuterated trimethylvinylsilane, isolated by preparative gas chromatography. Criticism of this method is two-fold. First, the ^{1}H NMR integration represents simply the ratio of vinyl protons to silicon-methyl protons. These silicon-methyl protons can be the result of mono-, di-, tri- etc... proton incorporation into the methyl group, and to assume exclusive di-incorporation is a serious error. Second, isolation of small amounts of 51 by preparative gas chromatography using a siloxane-based packing material can introduce impurities having ^{1}H NMR absorptions near those of the silicon-methyl in 51. This problem was encountered in the first

Table 10. Percent deuterium incorporation in 51

	Mass (M = 100, mass of 51-d_0)	Actual intensity		Corrected intensity		Mole % of deuterated 51		Average
		14 eV[a]	16 eV[b]	14 eV	16 eV	14 eV	16 eV	
Run 1	M+4	8	2	8	2.0	0.1	.5	0.3
	M+5	23	10	22.2	8.9	0.4	1.3	0.9
	M+6	67	45	64.5	44.0	1.8	3.7	2.7
	M+7	138	115	130.7	110.3	4.5	7.5	6.0
	M+8	270	314	254.5	301.5	12.2	14.6	13.4
	M+9	899	1,330	868.7	1,266.6	51.3	49.8	50.6
	M+10	414	692	318.4	556.0	22.5	18.2	20.3
	M+11	135	283	67.9	178.7	7.2	3.9	5.6
	M+12	29	112	9.1	0	0	0.5	0.2
Run 2	M+3	-	13		13	0	0.5	0.3
	M+4	10	39	10	37.7	1.2	1.6	1.4
	M+5	24	83	23.0	78.8	2.7	3.2	3.0
	M+6	47	174	44.2	164.8	5.1	6.8	5.9
	M+7	80	234	74.7	214.8	8.6	8.8	8.7
	M+8	127	356	117.8	328.5	13.7	13.5	13.6
	M+9	409	1,072	394.4	1,031.4	45.9	42.5	44.2
	M+10	192	534	148.5	420.1	17.3	17.3	17.3
	M+11	75	206	44.1	124.3	5.1	5.1	5.1
	M+12	13	44	2.6	15.3	0.3	0.6	0.5

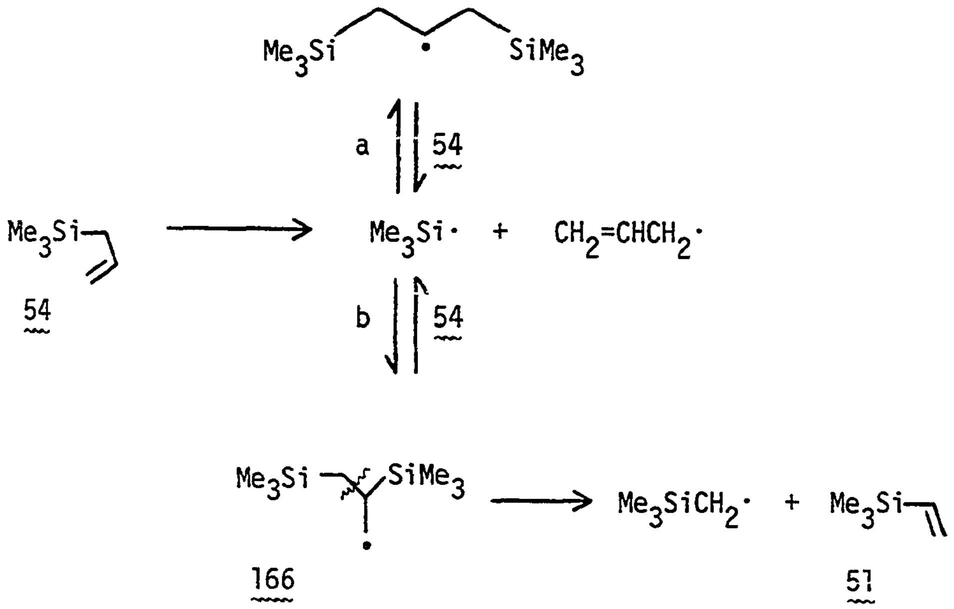
[a] For 51-d_0 M = 1.00, M+1 = 0.09785, M+2 = 0.04158.

[b] For 51-d_0 M = 1.00, M+1 = 0.09790, M+2 = 0.03934.

run. Isolation of deuterated 51 by preparative gas chromatography using a new 16' 20% SE-30 column furnished a mixture, the 'H NMR of which contained peaks corresponding to partially protonated 51 (a silicon-methyl multiplet centered at δ0.04 ppm) and a singlet (δ0.40 ppm) in a ratio of 1:2.

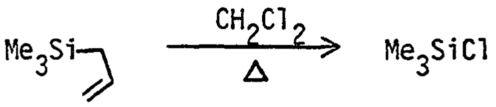
Run 2 furnished a pure sample of deuterated 51. Isolation was accomplished by preparative gas chromatography using a 20' 20% SE-30 column that was aged for three weeks at temperatures greater than 150°C, with continuous helium flow. A 300 MHz 'H NMR was taken which very clearly showed the vinylic ABC pattern and a silicon methyl multiplet centered at δ0.04 ppm. The ratio of vinyl protons to silicon methyl protons was approximately 4.3 to 1. This is also in disagreement with the ratio reported by Neider and coworkers of 1.1 to 1.

The work on the pyrolysis of allyldisilanes presented in this thesis and the kinetic study performed by Davidson and Wood clearly indicate that the first step in the thermal decomposition of allyltrimethylsilane is silicon-allyl bond homolysis. This, coupled with the results of the labeling study, in which 50% of the recovered trimethylvinylsilane maintains the d-9 label, suggests the following mechanism for this conversion.



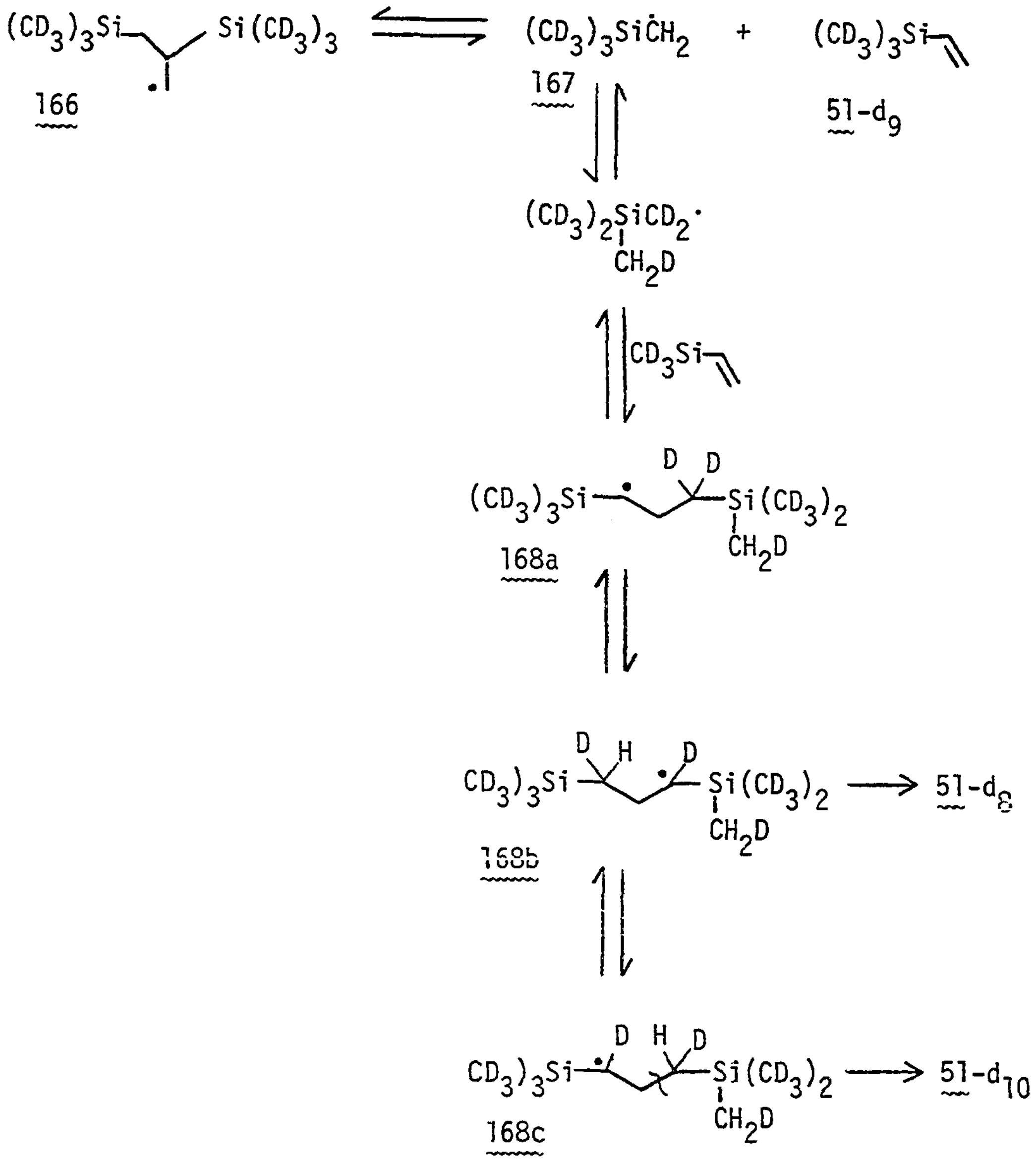
The trimethylsilyl radical formed by homolysis can add to 54 in two ways; addition to the terminal end to produce a symmetrical carbon radical (path a) or, addition to the internal carbon generating radical 166 (path b). Path a is unproductive as β-scission regenerates 54 and trimethylsilyl radical. Radical 166 can undergo a similar cleavage, or a carbon-carbon bond homolysis to give 51 and trimethylsilylmethyl radical (tetramethylsilane is also a product in the thermolysis of 54).

Additional support for this mechanism has appeared recently (152). Conlin and coworkers have reported that copyrolysis of methylene chloride with allyltrimethylsilane produces chlorotrimethylsilane in nearly quantitative yield. It is well-known that



silicon radicals are scavenged by alkyl and aryl halides to produce chlorosilanes (see Historical section on silicon radicals).

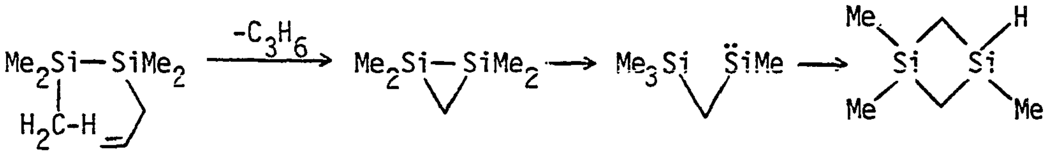
Scheme 23


(CD3)3Si Si(CD3)3
166
(CD3)3SiĊH2 + (CD3)3Si
167
51-d9
(CD3)2SiCD2·
CH2D
CD3Si
(CD3)3Si Si(CD3)2
CH2D
168a
CD3)3Si Si(CD3)2
CH2D
168b
51-d8
CD3)3Si Si(CD3)2
CH2D
168c
51-d10

A final comment on the labeling study pertains to the puzzling formation of significant amounts (20.3% and 17.3% for run 1 and 2 respectively) of trimethylvinyl silane containing ten deuteriums (one more than starting 54) and approximately 5% containing eleven deuteriums. This was also confirmed by ^{2}H NMR, which showed the presence of deuterium in the vinyl group. Although this has no bearing on the conclusion already drawn, possible modes for exchange should be considered. Although purely speculative, one explanation for deuterium exchange is presented in Scheme 23. The initially formed radical could equilibrate and add to 51-d_9 giving radical 168a. Deuterium abstraction by 168a furnishes 168b. Decomposition of 168b accounts for the observed 51-d_8, or further hydrogen abstraction and β-scission leads to 51-d_{10}.

Evidence for the Gas Phase Rearrangement of Silene to Silylene

The pyrolysis of 1-allylpentamethyldisilane 169 was initially undertaken as a test for the necessity of C-H activation in the proposed homoretroene elimination. Thus, it was predicted that 169 would generate 1,1,3-trimethyl-1,3-disilacyclobutane 47. Wulff and coworkers have postulated that disilacyclopropanes decompose via methyl (or, when

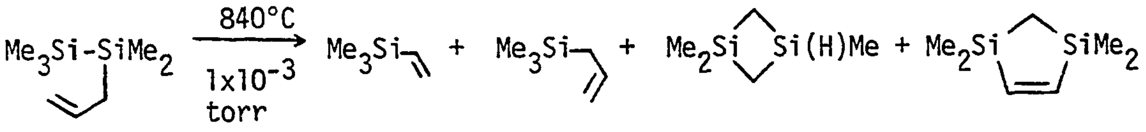


169 46 47

available, hydrogen) migration to silylenes, which C-H insert to form 1,3-disilacyclobutanes (43). They have shown that silylene 46 forms 47 in 39% yield.

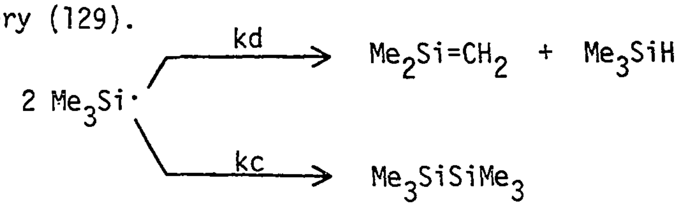
The synthesis of 169 was accomplished in 71.4% yield by the coupling of chloropentamethyldisilane with excess allylmagnesium bromide. Distillation (25°C, 1 x 10^{-3} torr) of 169 through a quartz tube packed with quartz chips heated to 840°C afforded a light yellow oil in 62.3% mass recovery. Analysis of the pyrolysate by preparative gas chromatography (12' 15% SE 30) revealed four major products along with unreacted 166. The products, 47, 51, 54, and 153 were identified by 'H NMR, IR, low resolution mass spectrometry and comparison of GC retension times to those of authentic samples.

Since the homoretroene elimination of propene was now discounted, an alternative mechanism for the formation of 47 had to be considered. Based upon the results presented in the previous section, the obvious

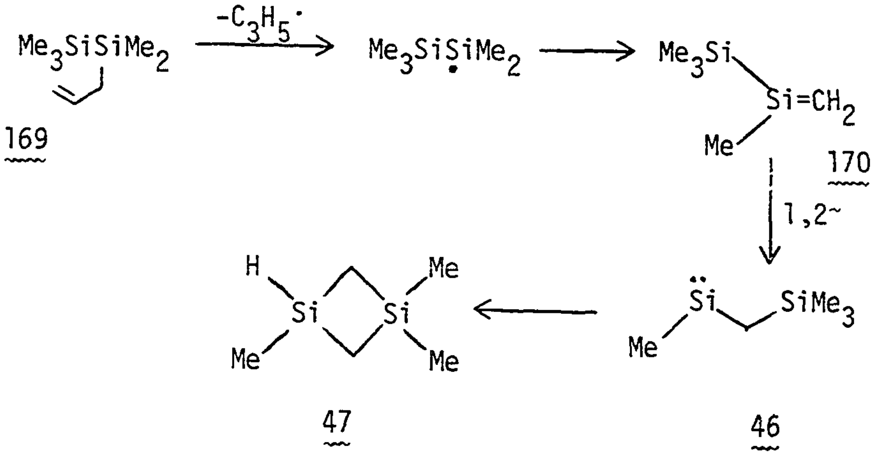


51 (1.6%) 54 (4.5%) 47 (17.8%) 153 (10.3%)

first step is the homolytic cleavage of the silicon-allyl bond. This system is unique in that there is no group capable of trapping the initially formed pentamethyldisilanyl radical. The disproportionation of silicon radicals to form silenes has been postulated to occur both in solution and in the gas phase (see Historical section on silicon radicals). In fact, two recent reports claim that the disproportionation of trimethylsilyl radical is an important reaction at 25°C, and values of kd/kc of 0.31 (126) and 0.2 (128) were quoted. However, a much lower value (0.05) was obtained from the photolysis of bistrimethylsilyl mercury (129).



In the pyrolysis of 169, disproportionation of the pentamethyldisilanyl radical would generate (trimethylsilyl)methylsilene 170. A very attractive route to 47 involves the 1,2-migration of silicon in 170 generating silylene 46 (a known precursor to 47). At the time this work was done, no silene to silylene rearrangements had been observed or postulated. Although unprecedented, it seemed reasonable that silicon, being an extremely good migrating group, might undergo this rearrangement.



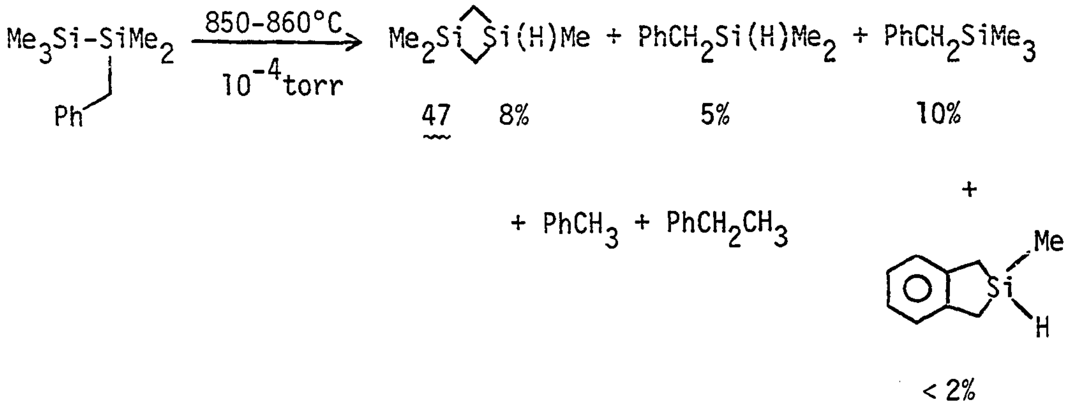
The most recent calculations on the relative energies of silene and methylsilylene are those of Goddard and coworkers (153). At the double-ζ-SCF level of theory singlet methylsilylene is predicted to be 11.6 kcal/mol more stable than singlet silene. The inclusion of d functions on carbon and silicon in the basis set and configuration interaction decrease this energy separation to only 0.4 kcal/mol. These authors also calculated the barrier to the

$$H_2Si{=}CH_2 \qquad \Delta H \sim 0.4 \text{ kcal/mol}$$

$$H\ddot{Si}CH_3 \qquad \text{Eact} \sim 40 \text{ kcal/mol}$$

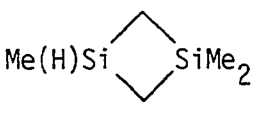
1,2-hydrogen shift converting silene to methylsilylene at ~40 kcal/mol. This activation energy is expected to be lower for 170. For example, the activation energy for the 1,5-migration of silicon in trimethylsilylcyclopentadiene is ~13 kcal/mol lower than that of hydrogen.

To establish the intermediacy of pentamethyldisilanyl radical, 1-benzylpentamethyldisilane was pyrolyzed. The high temperatures required for this reaction (850-860°C, 1 x 10^{-4} torr) produced four silicon containing products along with toluene and benzene. However, the product arising from a benzylic cleavage was indeed the desired 1,3 disilacyclobutane 47.



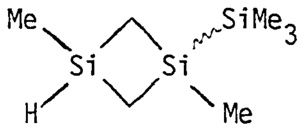
One of the experimental necessities to establish the disproportion of the pentamethyldisilanylradical to silene 170 was to explain the absence of decamethyltetrasilane 171, the expected radical combination product. The pyrolysis of 171 was thus conducted under similar conditions. The distillation of 171 through a quartz tube packed with quartz chips heated to 840°C (10^{-4} torr) furnished a light yellow oil in 82% mass recovery. Isolation of the products by preparative gas chromatography (8' 20% DC 550 column) and identification by 'H NMR and low resolution mass spec confirmed the formation of 47 as the major product (21% yield). The other products were trimethylsilane, pentamethyldisilane, hexamethyl-

$$\underset{171}{Me_3SiSiMe_2SiMe_2SiMe_3} \longrightarrow \underset{5\%}{Me_3SiH} + \underbrace{Me_3SiSiMe_2H + Me_3SiSiMe_3}_{10\%} +$$



47 (21%)

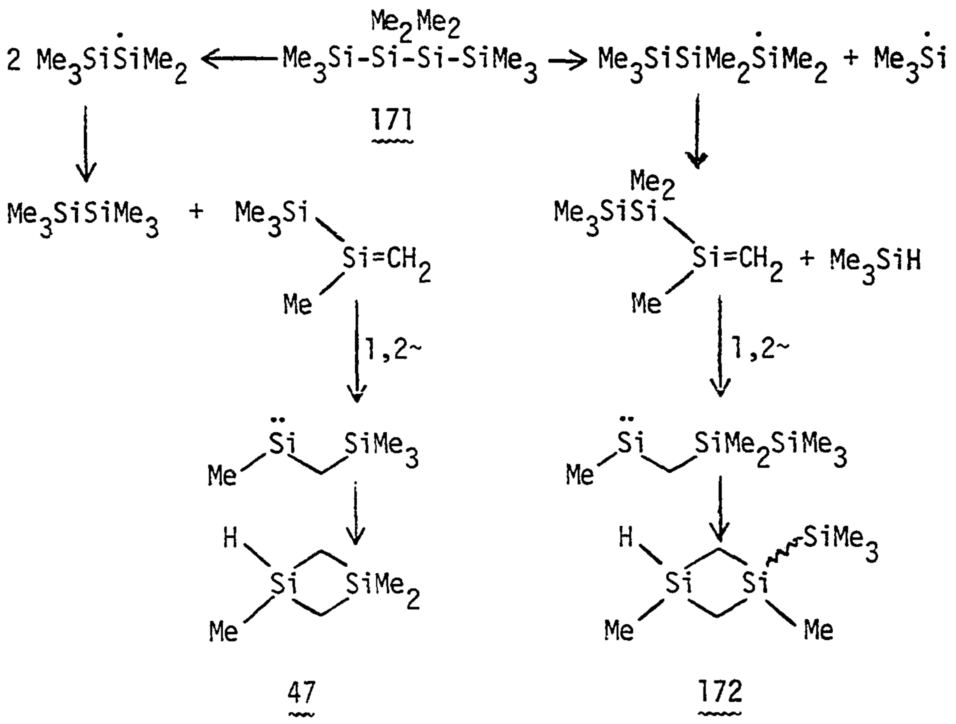
+



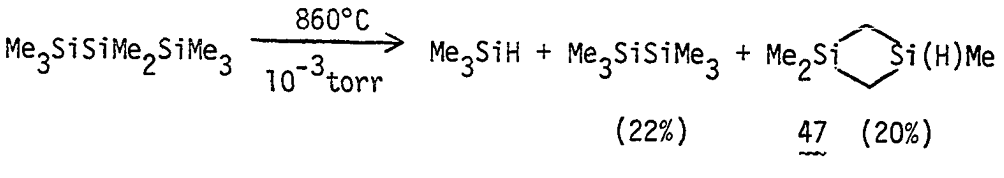
172 (5%)

disilane and a mixture of cis- and trans-trimethylsilyl-1,3-disilacyclobutanes, 172. The formation of 47 is easily explained by Si_2-Si_3 bond homolysis, followed by radical disproportionation to generate silene 170 and pentamethyldisilane (Scheme 24). Alternatively, homolysis of the Si_1-Si_2 bond and subsequent cross disproportionation would generate trimethylsilane and (pentamethyldisilanyl)methylsilene. Analogous 1,2-migration of the pentamethyldisilanyl group and C-H insertion furnishes 172. The formation of hexamethyldisilane undoubtedly arises from combination of trimethylsilylradical (originating from 171 or, under these reaction conditions, from trimethylsilane).

Scheme 24



Cleavage of the silicon-silicon bond proved to be a good source for the generation of silicon radicals. The pyrolysis of octamethyltrisilane (860°C, 10^{-3} torr) cleanly produced 47 (20% yield), trimethylsilane (ca. 5% yield) and hexamethyldisilane (22% yield).



The thermal requirements for cleavage of the silicon-silicon bond are quite high (~800-850°C). Since the silicon-tin bond is ~14 kcal/mol weaker than the silicon-silicon bond, replacement of silicon with tin could potentially furnish silicon radicals at lower temperatures. Having established the products arising from pentamethyldisilanyl radical, 173 was an attractive compound to test this idea. The synthesis of 173 was accomplished in low yield (ca. 20%) by the addition of chloropentamethyldisilane to a THF solution of trimethylstannyl anion at 0°C. Pyrolysis of 173 at 840°C (1×10^{-4} torr) cleanly produced one observable product, hexamethyldisilane in 83% yield, identified on the basis of 'H NMR and low resolution mass spectrometry and comparison of GC retention time with an authentic sample. So clean was this pyrolysis that the 'H NMR of the crude pyrolysate contained one sharp singlet, corresponding to hexamethyldisilane. No tin containing products were obtained although examination of the quartz tube clearly showed polymer deposition.

$$Me_3SnLi + Me_3SiSiMe_2Cl \longrightarrow \underset{173}{Me_3SiSiMe_2SnMe_3} \xrightarrow[1\mathrm{x}10^{-4}\mathrm{torr}]{840°\mathrm{C}} \underset{83\%}{Me_3SiSiMe_3}$$

Hexamethyldisilane probably arises from an alpha-elimination of dimethylstannylene from 173. This alpha-elimination of dimethylstannylene is quite reasonable. Dialkylstannylenes have been generated through the elimination of R_3SnX (X = OAc,Cl,Br,I) at temperatures under 130°C (154, 155). In the absence of trapping agents (usually alkylhalides) polymers of dimethylstannylene are formed (156). Some sterically

$$XR_2SnSnR_2X \xrightarrow{\Delta} R_2SnX_2 + R_2Sn:$$

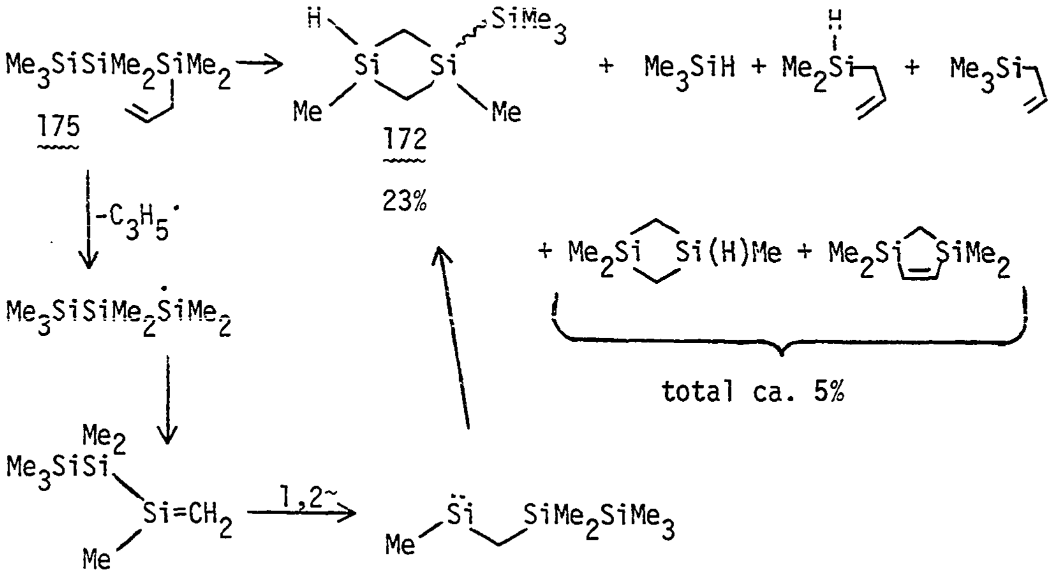
X = OAc, Cl, Br, I
R = n-Bu, Me

hindered stannylenes have been formed and are stable at or near room temperature. For example, 174 has been synthesized and its physical and spectral properties characterized at room temperature (157).

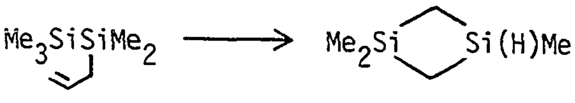
$$(Me_3Si)_2CH\text{-}Sn\text{-}CH(SiMe_3)_2$$

174

In an effort to demonstrate that the mixture of trimethylsilyl-1,3-disilacyclobutane isomers 172 arose from heptamethyltrisilanyl radical, the thermolysis of 1-allylheptamethyltrisilane 175 was studied. Grignard coupling of allylmagnesium bromide and 1-chloroheptamethyltrisilane furnished 175 in 63% yield.



Vacuum pyrolysis (1×10^{-4} torr) at 780°C produced the expected isomeric mixture 172 (23% yield) as the major product, in addition, very small amounts of more volatile products were observed. The total mass recovery was 77%, with recovered starting material and 172 accounting for ca. 70% of the pyrolysate. Thus, it was demonstrated that 172 is produced from the heptamethyltrisilanyl radical. The yield of 172 from the allyl precursor 175 is very close to that of 47 generated from 1-allylpentamethyldisilane 169, indicating the similarity in the two systems, which differ in one Me_2Si unit.

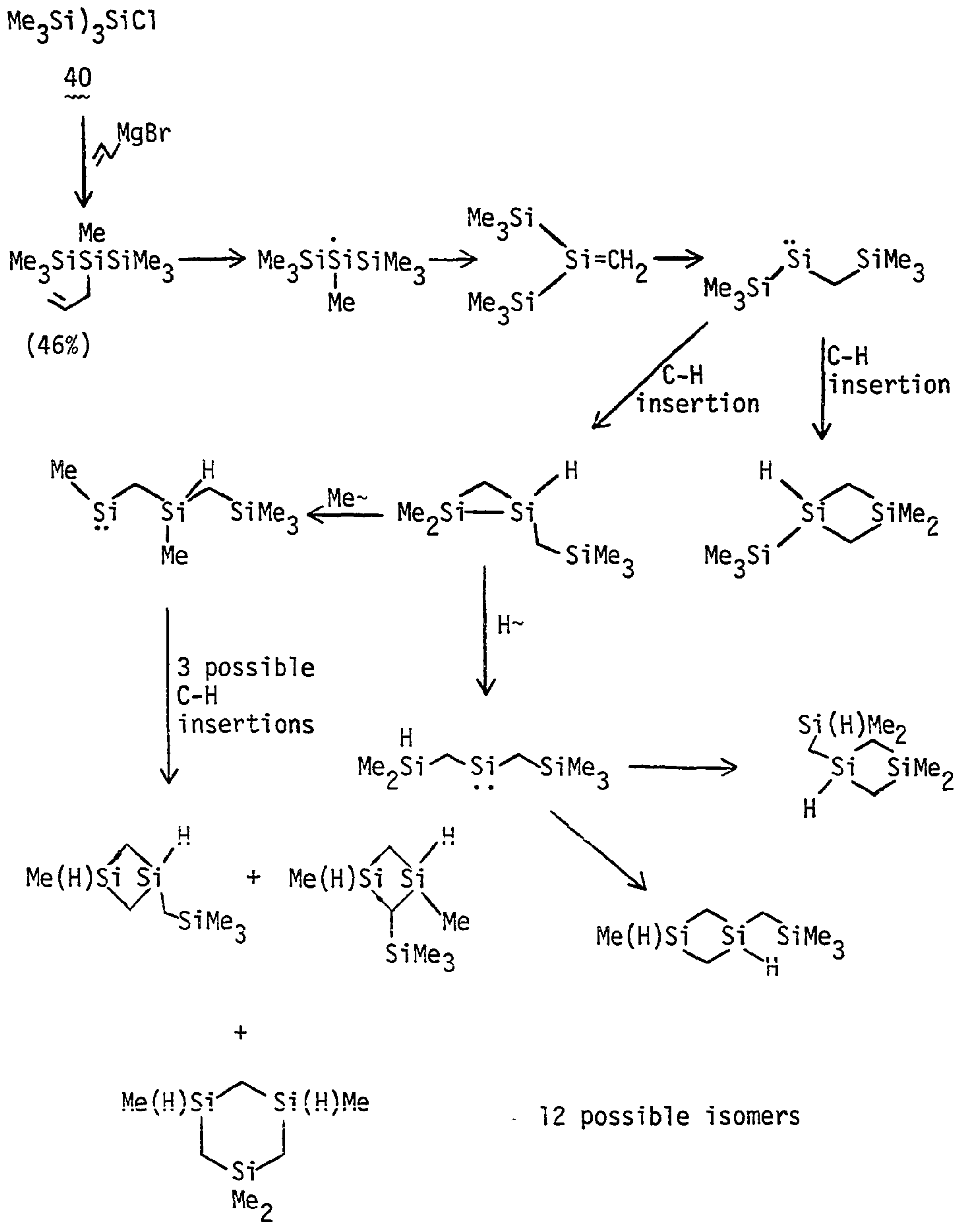


47

18%

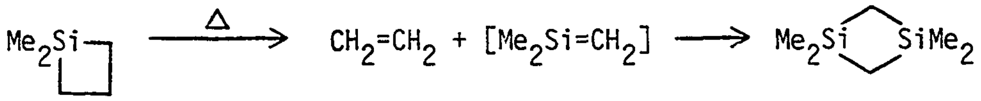
Thus, the sequence of disproportionation, 1,2-migration and C-H insertion to form 1,3-disilacyclobutanes appears to be general for both the disilanyl and 1-trisilanyl radicals. Extension of this to the 2-trisilanyl radical was not as fruitful. Pyrolysis of 2-allylheptamethyltrisilane (prepared in 46% yield from the corresponding chlorosilane 40 and allylmagnesium bromide) at 800°C (1×10^{-3} torr) gave a yellow oil in 77% mass recovery. Analysis of the pyrolysate by GCMS revealed that a mixture of at least two isomers constituted the major product. The molecular weight of these isomers corresponded to starting allylsilane minus propene. Examination of the possible fate of the silylene generated from a 1,2-silicon migration shows that several isomers could, in theory, be generated (Scheme 25) and that separation would be difficult.

Scheme 25

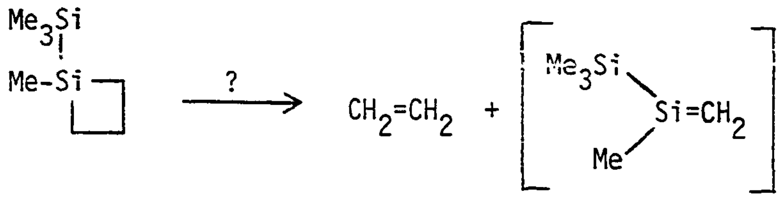

Me3Si)3SiCl
40
MgBr
(46%)
C-H insertion
C-H insertion
Me~
H~
3 possible C-H insertions
12 possible isomers

Although product identification was not made, the formation of the isomers is consistent with disproportionation of the 2-trisilanyl radical, followed by 1,2-rearrangement.

Having obtained evidence for thermal rearrangement of a silene to a silylene in these systems, it was desirable to generate (trimethylsilyl)-methylsilene 170 by an alternate route. One of the most common methods for silene generation is the thermolysis of monosilacyclobutanes (36). For example, the pyrolysis of 1,1-dimethylsilacyclobutane generates 1,1-dimethylsilene has been firmly established by direct detection (mass spectrometry and matrix isolation) and kinetic and chemical trapping studies. In the absence of trapping agents, silene dimers are formed.



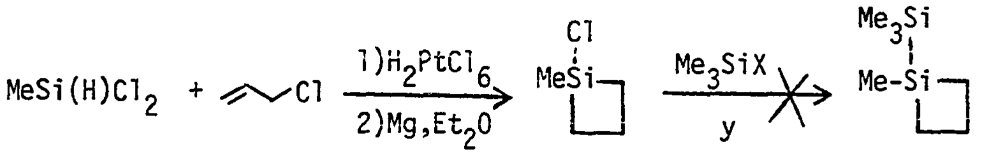
Therefore, 1-trimethylsilyl-1-methyl-1-silacyclobutane 176 would be the obvious precursor to 172.



176 172

Several attempts to synthesize 176 by coupling of trimethylsilyl anion with 1-chloro-1-methyl-1-silacyclobutane 177 (in two steps from methyldichlonesilane and allyl chloride) failed. The reaction mixtures in all cases were complex with products corresponding to ring opening of 177 present. These attempts are summarized in Table 11.

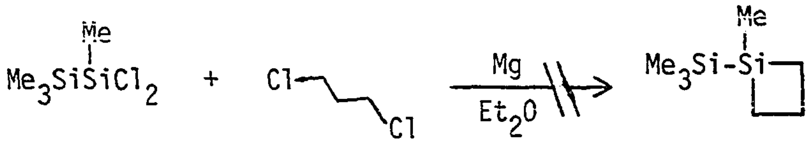
Table 11. Attempted generation of 176 from 177 and trimethylsilyl anion



177 176

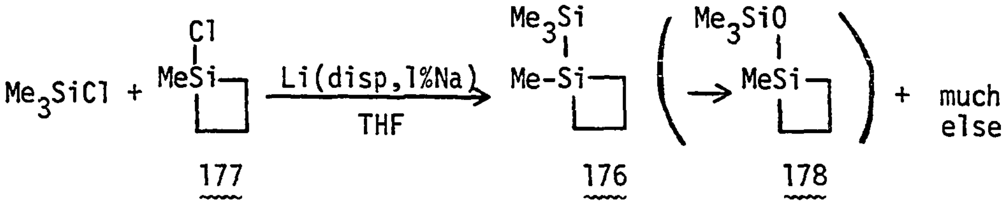
X	Y	Reference
Me_3Si	KH/HMPA	158
Me_3Si	MeLi	159
Cl	Li(metal)	
Cl	Li(disp,noNa)	

An *in situ* coupling of 1,1-dichlorotetramethyldisilane and 1,3-dichloropropane also failed, furnishing only siloxane after workup (and presumably cyclopropane).



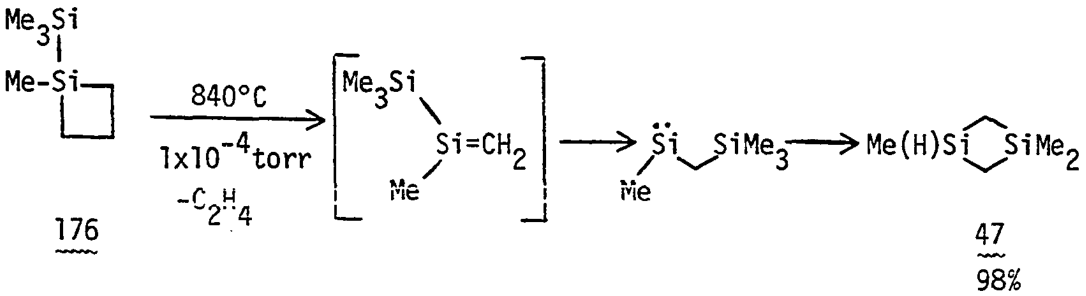
176

The successful synthesis of 176 was attained via coupling of trimethylchlorosilane and 177 with lithium dispersion containing 1% sodium. Isolation of 176 was hampered by its facile oxidation to 178. Separation of 176 and 178 could only be accomplished by preparative gas chromatography, and had to be done immediately prior to thermolysis. The yield of 176 after GC isolation was only 13%; a large amount of ring-opened products was formed.

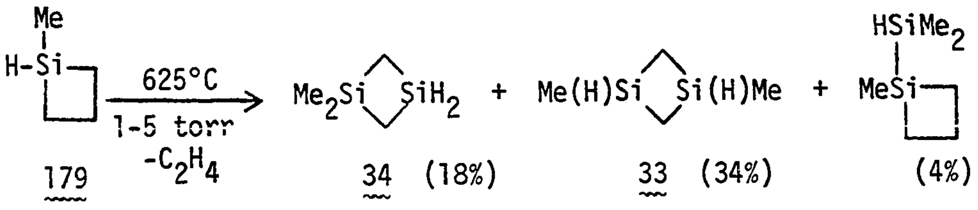


Identification of 176 was based on 'H NMR, low and high resolution mass spectrometry.

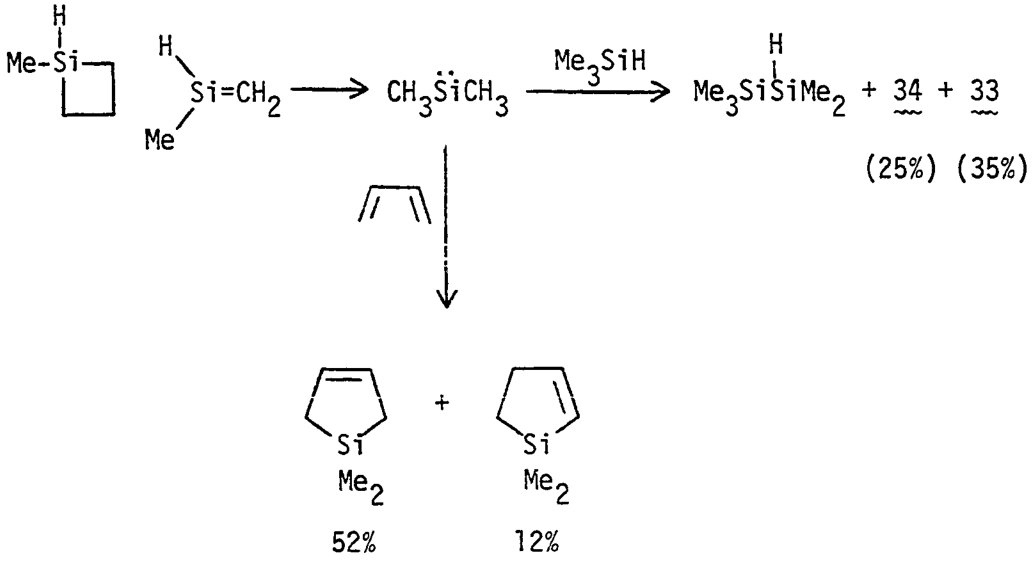
The pyrolysis of 176 was conducted under similar conditions (840°C, 1 x 10^{-4} torr) to those used in the generation of pentamethyldisilanyl-radical. This pyrolysis cleanly produced 47 in 98% yield, giving support to the proposed silene to silylene rearrangement.



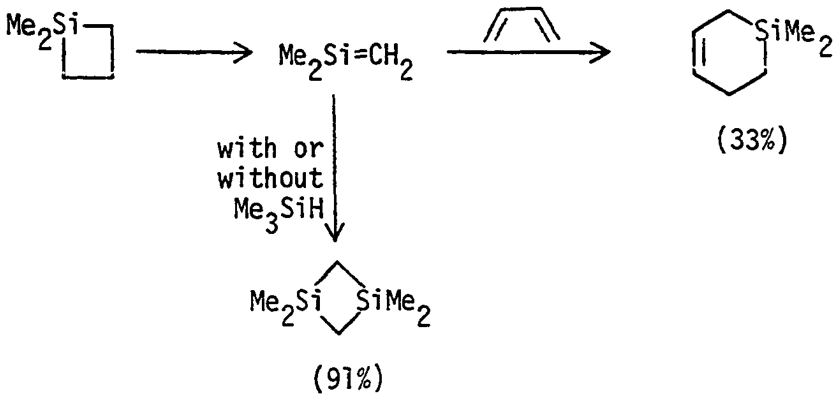
Very recently, Conlin and Wood have claimed evidence for the isomerization of 1-methylsilene (generated from 1-methyl-1-silacyclobutane 179) to dimethylsilylene (160). The low pressure pyrolysis (1-5 torr) of 179 at 625°C in a flow system produces chiefly ethylene, 1,1-dimethyl-1,3-disilacyclobutane 33 (34%), and a small amount of 1-methyl-1-(dimethylsilyl)silacyclobutane (4%).



Both disilacyclobutane products have been reported to be the major products resulting from the gas phase dimerization of dimethylsilylene (53). For a complete discussion of the mechanism of the tetramethyldisilene rearrangement, see the Historical section on silylene rearrangements. Further evidence for the intermediacy of dimethylsilylene was provided by two trapping experiments in which both butadiene and trimethylsilane trapped this intermediate.

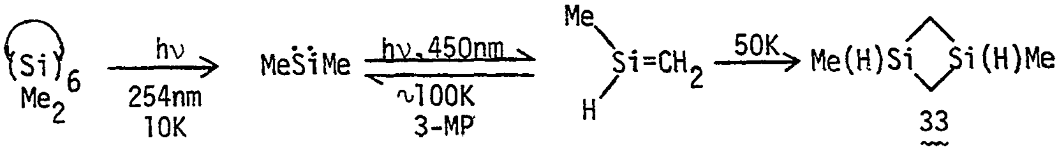


Under identical conditions, 1,1-dimethylsilene is trapped by butadiene to give 1,1-dimethyl-1-silacyclohex-3-ene (33%) and trimethylsilane has no effect on the reaction.



The suggestion was made that the parent silene ($H_2Si=CH_2$) may be even more prone to rearrangement because of a decrease in the π-bond energy.

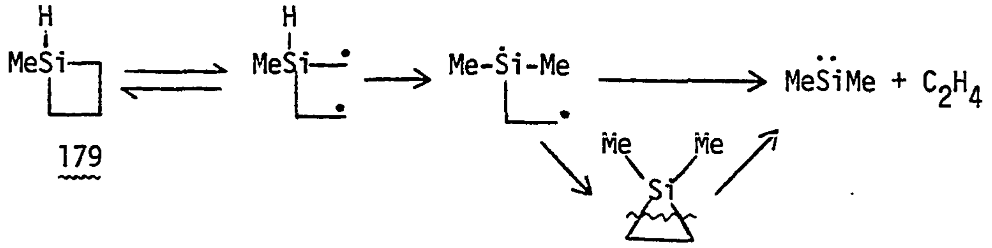
In an accompanying communication, Drahnak and coworkers claim that the isomerization of 1-methylsilene to dimethylsilylene occurs at 100 K! (161). The photolysis of dodecamethylcyclohexasilane in an argon matrix at 10 K produces dimethylsilylene, as a bright yellow species. Bleaching of the matrix with visible light reportedly causes a photoconversion of dimethylsilylene to 1-methylsilene. Thus, annealing of argon, matrices after photoisomerization, containing only 1-methylsilene at 50 K produces 33 from dimerization. However, annealing of hydrocarbon matrices (3-methylpentane) at higher temperatures leads to rapid reversion to dimethylsilylene. Attempts to trap 1-methylsilene (methanol, 2,3-dimethyl-1,3-butadiene and bis(trimethylsilyl)acetylene) results in the



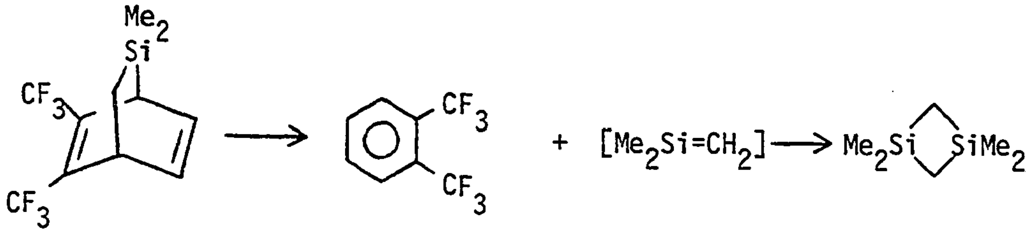
same products obtained for the trapping of dimethylsilylene under similar conditions. The authors concluded that the thermal reversion at 100 K is faster than trapping, but at 50 K the reversion is slowed and self-trapping occurs to form 33.

These results are in direct conflict with the theoretical prediction that the barrier to the isomerization of silene to methylsilylene is approximately 40 kcal/mol (153). In order for this isomerization to occur at 100 K, the barrier would have to be in the order of 5 kcal/mol or less. In light of this discrepancy between theory and experiment, Yoshioka and Schaefer reexamined the barrier at a higher level of theory (162). The inclusion of polarization functions to the DZSCF + CI resulted in a barrier of 43.0 kcal/mol, addition of the Davidson correction lowered the value to 40.6 kcal/mol. It appears that alternate interpretations of the experiments of Drahnak and coworkers and possibly Conlin and Wood should be sought.

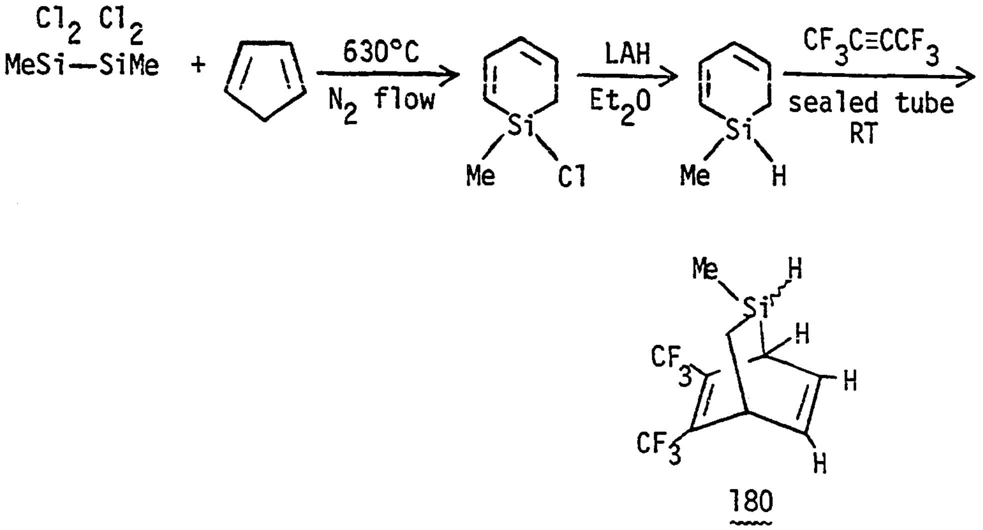
In an effort to clarify these dissenting reports, an examination of a possible alternative mechanism for the decomposition of 1-methyl-1-silacyclobutane was made. There is considerable evidence in the literature that silacyclobutanes undergo thermal decomposition largely through initial C-C, rather than Si-C bond homolysis (163, 164). Therefore, it is entirely possible that hydrogen migration from silicon occurs at the diradical stage, and that final Si-C bond homolysis is the actual process leading to silaethylene.



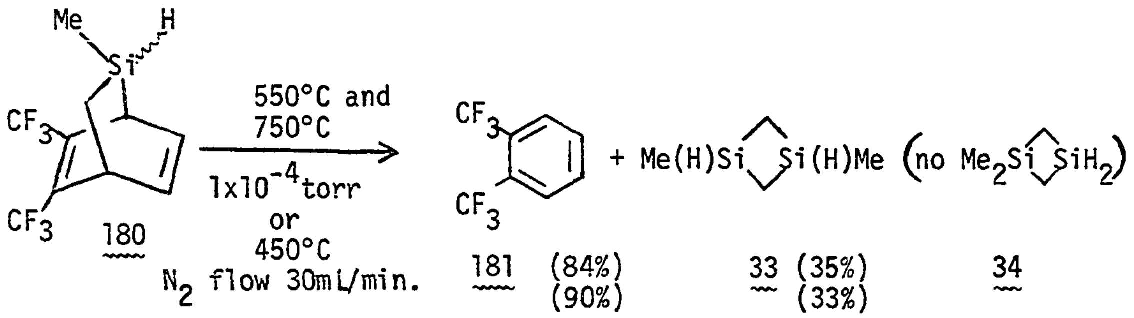
In an effort to probe this mechanistic dichotomy, the generation of 1-methylsilene from a precursor other than a silacyclobutane was sought. The thermal decomposition of silabicyclo[2.2.2]octadienes has been reported to proceed via a retrograde Diels-Alder extrusion of the bridging silene (165).



The synthesis of the corresponding 7-methyl-7-sila-2,3-bis-(trifluoromethyl)bicyclo[2.2.2]octadiene 180 was accomplished in 50% yield by reducing 1-methyl-1-chloro-1-silacyclohexa-2,4-diene (166, 167) with lithiumaluminum hydride, followed by a Diels-Alder reaction with excess hexafluoro-2-butyne in a sealed tube at room temperature for 24 hours. Identification of 180 was based upon high resolution mass spectrometry and ^{1}H NMR [δ0.16(d, 3H, J = 3 HzSiMe, collapses to s with hν at ca. 3.80), 0.40-1.04 (m, 2H, $SiCH_2$ sharpens with hν at ca. 3.80), 3.60-3.92 (m, 2H, $\underline{H}SiC\underline{H}$ sharpens with hν at ca. 6.0), 3.98-4.35 (m, 1H, $CH_2C\underline{H}$ sharpens with hν at ca. 6.0), 5.74-6.38 (m, 2H CH=CH)].



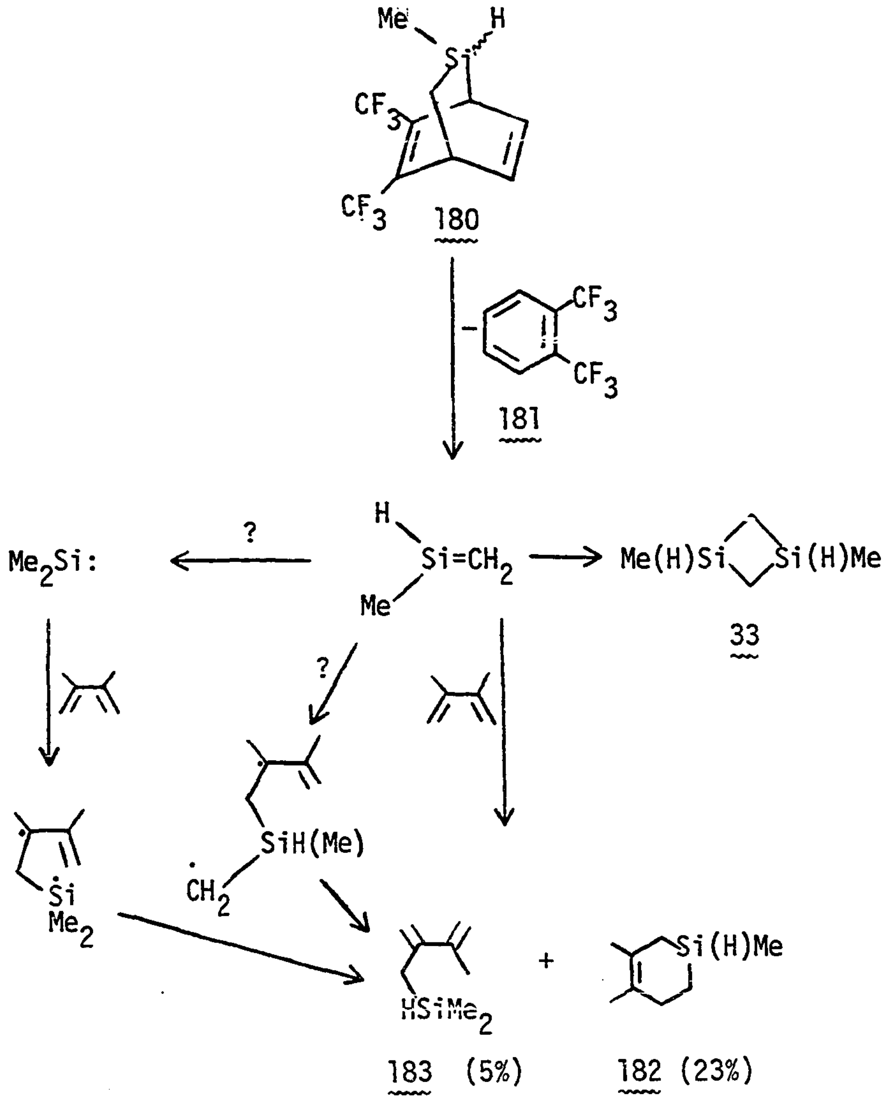
The vacuum pyrolysis of 180 was conducted at 750°C (1 x 10^{-4} torr) through a quartz tube packed with quartz chips. A clear yellow liquid was recovered in 86% mass recovery. Analysis of this liquid showed that 1,2-bis(trifluoromethyl)benzene 181 (84%) and 34 (35%) were the only two products formed, accounting for 98% of the recovered pyrolysate. The ^{1}H NMR of the crude pyrolysate showed that 33 was the only 1,3-disilacyclobutane formed, absorptions that could be attributed to 34 were absent. The products were isolated by preparative gas chromatography (10' 10% OV101 column) and analyzed by direct comparison of their low resolution mass and ^{1}H NMR spectra with authentic samples.



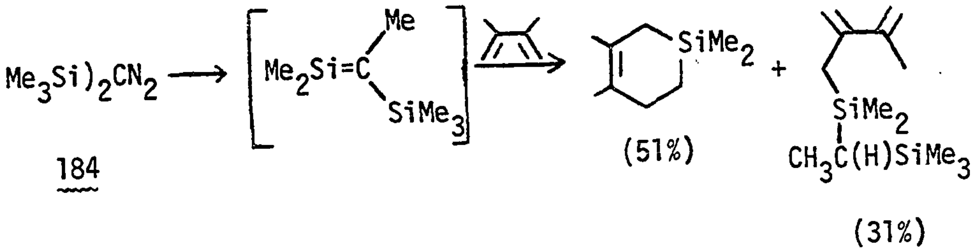
The temperature chosen for this initial pyrolysis was done in order to simulate the conditions used for the decomposition of 1-methyl-1-silacyclobutane. Silabicyclooctadienes decompose at lower temperatures than silacyclobutanes and indeed, 180 is no exception. The same products are produced at 550°C (1 x 10^{-4} torr) and at 450°C (N_2 flow system). The yields in the flow pyrolysis were comparable (90% for hexafluororthoxylene and 33% for 33) to those obtained in the vacuum system, accounting for 93% of the recovered mass.

The formation of 33 in the absence of 34 suggests that 33 is the result of simple dimerization of 1-methylsilene generated from the retrograde Diels-Alder, and that no rearrangement of this silene occurs. This supports the radical-type mechanism suggested for the decomposition of 1-methyl-1-silacyclobutane to dimethylsilylene.

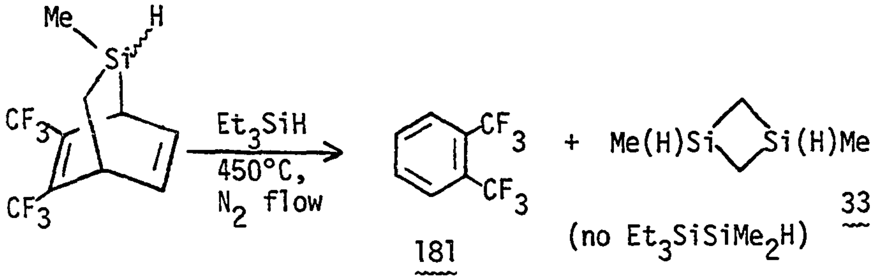
The successful trapping of 1-methylsilene was accomplished. Copyrolysis of 180 with a five-fold excess of 2,3-dimethyl-1-3 butadiene (88% mass recovery) produced 181 (74%), 1,3,4-trimethyl-1-silacyclohex-3-ene 182 (23%), the expected silene-trapping product and 183 (5%). No 1,1,3,4-tetramethyl-1-silacyclopent-3-ene was formed in this pyrolysis. The linear adduct 183 could, in theory, arise from dimethylsilylene by addition to the diene in a stepwise, radical fashion. This is not demanded since this type of linear adduct has previously been observed from the reactions of silenes with 2,3-dimethyl-1,3-butadiene (168).



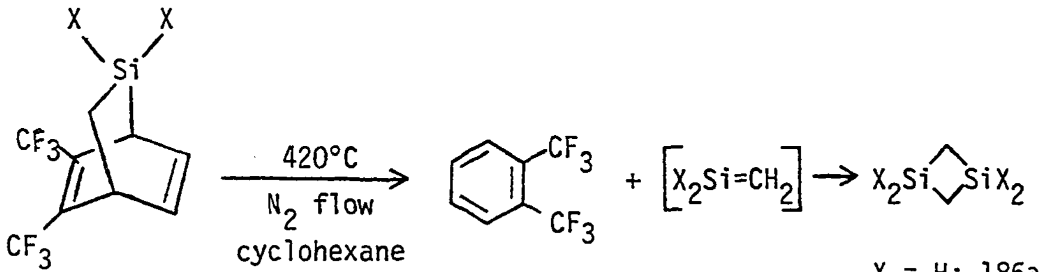
For example, the flow copyrolysis of 184, a known silene generator, and 2,3-dimethyl-1,3-butadiene produces both cyclic and linear trapping products.



To unambiguously demonstrate that dimethylsilylene is not present in the pyrolysis of 180, a copyrolysis was performed with a five fold excess of triethylsilane (450°C, N_2 flow 30 mL/min). Analysis of the pyrolysate by GCMS revealed that 33 was present along with 181, however no 1,1,1-triethyl-2,2-dimethyldisilane was observed.



The pyrolysis of 1-silacyclobutane in the absence of trapping agents gives a complicated reaction mixture in addition to ethylene, hydrogen, and propene (36). Auner and Grobe report that a 560°C silacyclobutane furnishes ethylene (99%) and $(H_2SiCH_2)_n$ polymer (169). They also indicate that silene should be stable in the condensed phase at 77 K (170). To date, complete analysis of the product mixture and elucidation of the mechanism involved in this decomposition have not been reported. Interestingly, Golino et al. reported that the parent silene could be trapped with cyclotrisiloxane (D_3) in 18% yield (171). Very recently, the first successful generation of silene by retrograde Diels-Alder was reported by Maier and coworkers (172). Its detection was made by IR, UV (172) and PE (173) spectroscopy following matrix isolation in argon at 10 K. These authors (172) found that upon thawing the matrix at 35 K, 1,3-disilacyclobutane is formed. Similar to the results reported in this thesis from the generation of 1-methylsilene, 185a or 185b thermally decompose (420°C, N_2 flow, cyclohexane) smoothly to 1,2-bis(trifluoromethyl)benzene and 186a or 186b. Thus, the suggestion (160, 161) that silene may isomerize to methylsilylene seems unlikely.

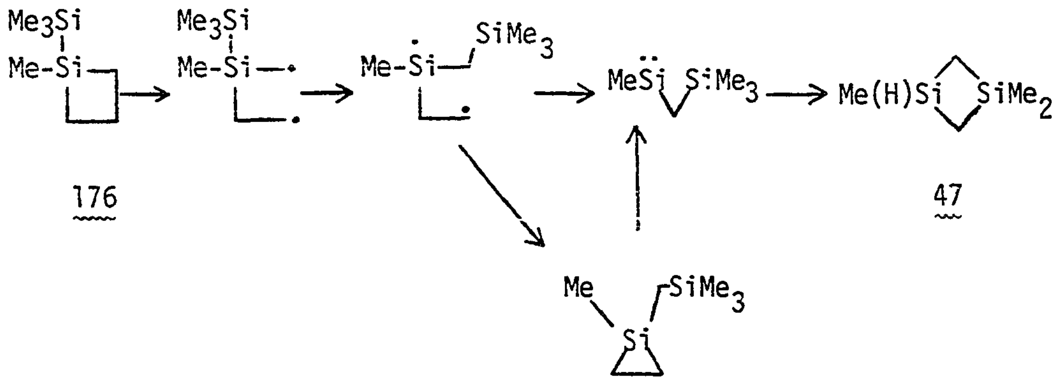


X = H; 185a
X = D; 185b

181

X = H; 186a
X = D; 186b

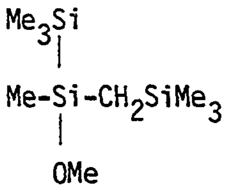
Unfortunately, these results are also applicable to the thermolysis of 1-trimethylsilyl-1-methyl-1-silacyclobutane 176 and thus, do not allow conclusive comments to be made on the proposed 1,2-silicon migration in a silene to form a silylene. The following diradical mechanism is a likely pathway to 47 from 176. Thus, alternate methods for unambiguous generation of 1-trimethylsilyl-1-methylsilene were sought.



176

47

Three possible modes for the generation of this silene were placed under consideration. One was a α-elimination of trimethylmethoxysilane (174) from 187. This was ruled out because it would be impossible to

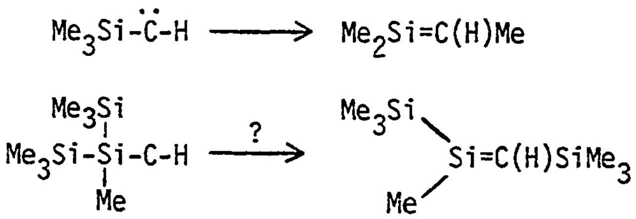


$\mathrm{Me_3Si{-}Si(Me)(OMe){-}CH_2SiMe_3}$

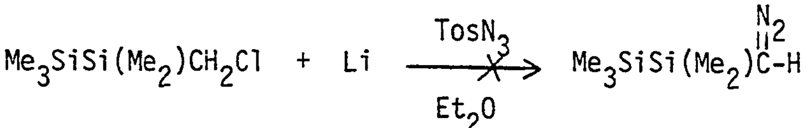
187

distinguish α-elimination followed by 1,2-silicon migration and C-H insertion from β-elimination and C-H insertion, since the same product would be formed in either route.

Another possible precursor to the desired silene is an α-silylcarbene. The 1,2-migration of a methyl group in α-silylcarbenes is a thermodynamically favorable process, and occurs readily, furnishing silenes (168). A trimethylsilyl group should migrate preferentially to a methyl group, necessitating a 2-trisilanylcarbene as the precursor to a 1-silyl-substituted silene.



To test this silicon migration, several attempts were made to synthesize 188 from pentamethyl(chloromethyl)disilane (synthesized by the method of Kumada et al. (139) and tosylazide (175). These reactions were run with both lithium dispersion and lithium wire. At

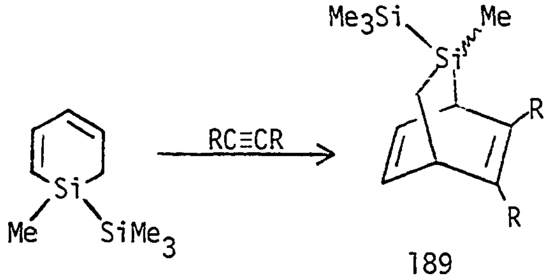


$$\mathrm{Me_3SiSi(Me_2)CH_2Cl} + \mathrm{Li} \not\xrightarrow[\mathrm{Et_2O}]{\mathrm{TosN_3}} \mathrm{Me_3SiSi(Me_2)}\overset{\mathrm{N_2}}{\overset{\|}{\mathrm{C}}}\mathrm{-H}$$

188

low temperatures no anion formation was observed, and at higher temperatures (>0°C) the consumption of starting halide was noted, however analysis of the reaction mixture by ^{1}H NMR showed the absence of an absorption corresponding to the proton on the diazo-carbon and the presence of several silicon-methyl protons. Replacement of the chloride with iodide (176) was equally unsuccessful.

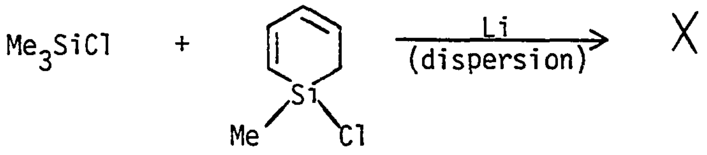
The difficulties encountered with the synthesis of the α-disilanylcarbene prompted the abandonment of this approach with efforts being directed towards the synthesis of a 1-trimethylsilyl-1-methyl-1-silabicyclo[2.2.2]octadiene 189. The synthesis of 189 was envisioned as a Diels-Alder reaction of an acetylene and 1-trimethylsilyl-1-methyl-1-silacyclohexa-2,3-diene 190.



190

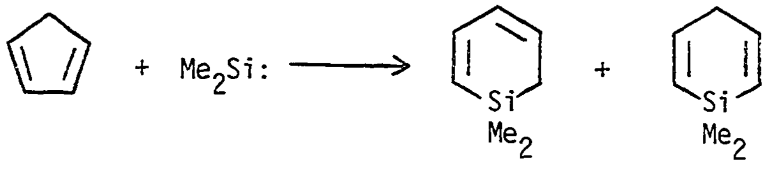
189

The synthesis of the desired precursor, 190, was not initially obvious. The coupling of chlorosilanes with silyl anions has met with little success (28), with one of the few exceptions being the synthesis of 1-trimethylsilyl-1-methyl-1-silacyclobutane in a mere 13% yield. Therefore, it is not surprising that attempted coupling of trimethylchlorosilane with 191 failed.



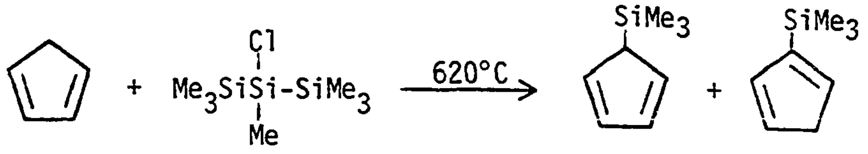
191

The addition of silylenes to cyclopentadiene is an established reaction (166). For example, 192 and 193 are produced from the copyrolysis of cyclopentadiene and dimethylsilylene (167).

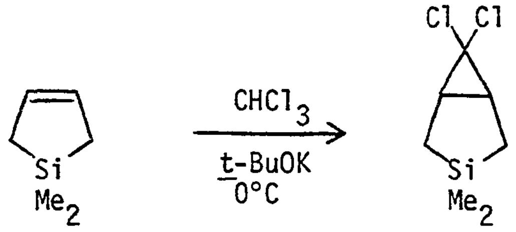


192 (29%) 193 (11%)

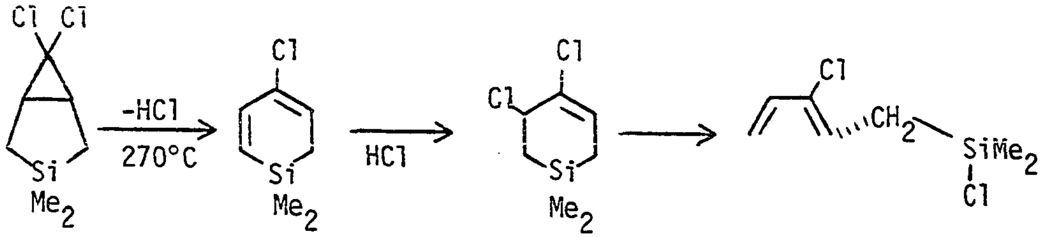
This method proved unsuccessful for gaining entry into the trimethyl-silyl-substituted analogue 190. Pyrolysis of 2-chlorohepamethyltrisilane, a known precursor to trimethylsilylmethyl silylene (43), and excess cyclopentadiene at 620°C (N_2 flow 30 mL/min), gave cleanly the two isomers of trimethylsilylcyclopentadiene. Identification was made by low resolution mass spectrometry and comparison of the ^1H NMR of the isomeric mixture with that of an authentic mixture, following isolation by preparative GC (8' 20% SE 30 column).



In 1978, Bertrand and coworkers reported that the addition of dichlorocarbene to silacyclopentenes occurs smoothly (177). For example, 1,1-dimethyl-1-silacyclopent-3-ene can be converted to 194 in 43% yield.

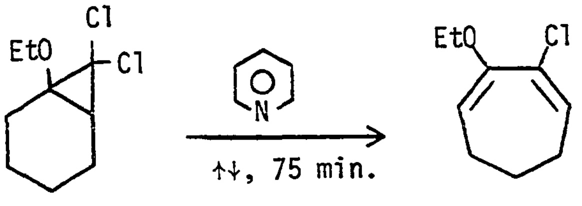

194

Additionally, when 194 was thermalized (270°C, GC injector port) ring opening with loss of HCl occurred giving the conjugated silacyclohexadiene 195 (35%), and 196 (65%) by addition of HCl to 195 and a β-elimination. Extension of this methodology to the synthesis of the desired trimethylsilyl-substituted system left uncertainties in both steps. First, it was unclear how well the silicon-silicon bond would tolerate the conditions of the carbene addition. Second, the ratio of 195 and 196 is dependent upon ring substituents, and it was conceivable that the


194 195 (35%) 196 (65%)

presence of the trimethylsilyl group could favor the ring opened product.

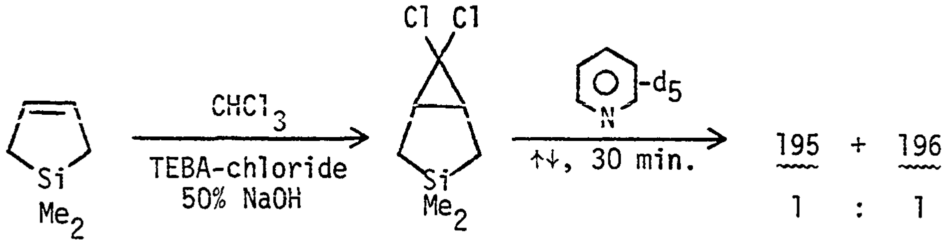
Parham *et al*. effected cyclopropane ring opening of 197 by heating it in pyridine for 75 minutes (178). It was reasoned that the presence of pyridine and the mild temperature of this elimination would minimize the amount of 196 relative to 195.



197

(83%)

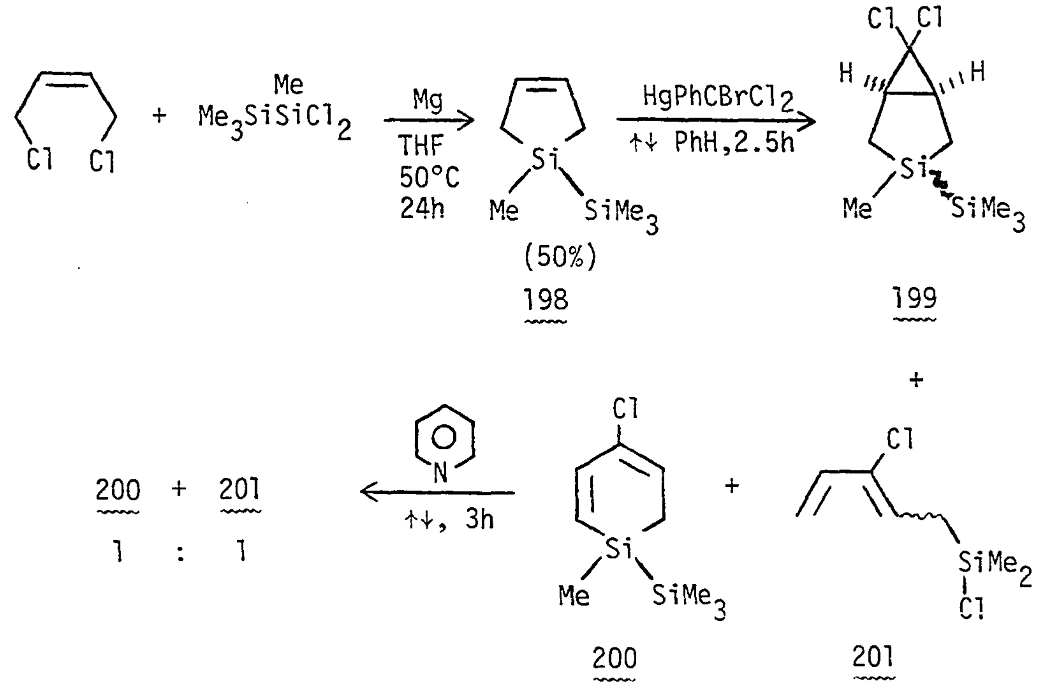
Putting this reasoning to a test 194 was prepared using the method of Makosza and Wawrzyniewiez (179). Heating 194 in pyridine resulted in the clean conversion to 195 and 196. Analysis by ^{1}H NMR clearly showed two methylene doublets, one corresponding to 195 (δ1.43, J = 6Hz) and



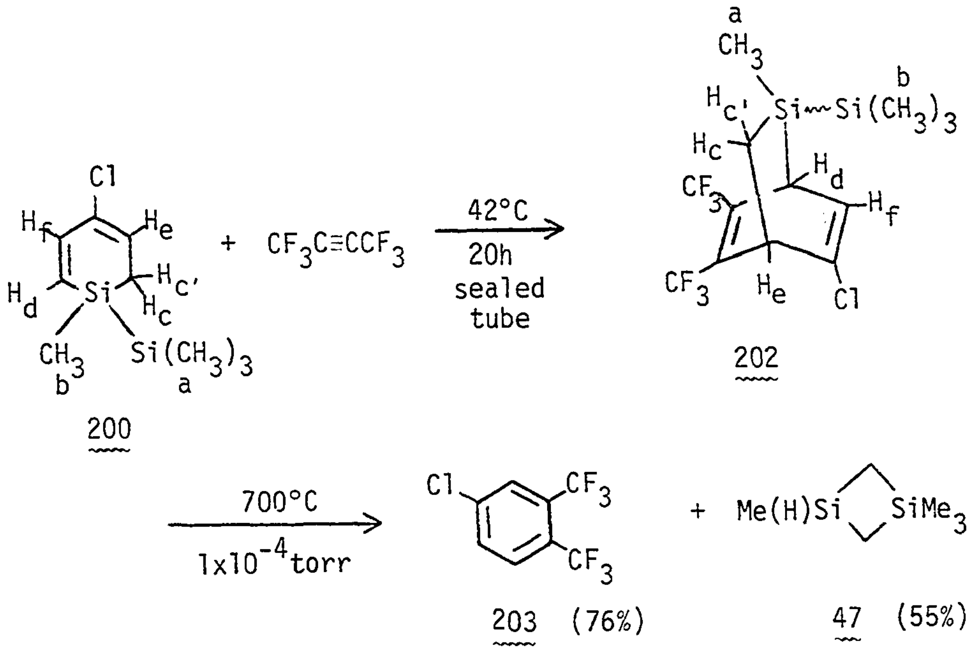
194

another for 196 (δ1.80, J = 10 Hz) in a ratio of 1:1. The amount of 195 formed was increased under the basic conditions employed.

The synthesis of 1-trimethylsilyl-1-methyl-1-silacyclopent-3-ene 198 was accomplished in 50% yield by the coaddition of *cis*-1,4-dichloro-2-butene and 1,1-dichlorotetramethyldisilane to a 50°C solution of magnesium powder in THF. The phase transfer conditions failed to transfer dichlorocarbene to 198, resulting in recovered 198. However, the use of Seyferth's Reagent proved successful (180). Heating 197 in benzene with phenyl(dichlorobromomethyl)mercury for 2.5 h furnished a mixture of three products, the carbene adduct 199, as well as the two thermal products of 199, 200 and 201 in a 5:1:1 ratio. Heating the crude



reaction mixture in pyridine for 3 h followed by converting 201 to the corresponding siloxane and distillation resulted in a 25-30% yield of 200 from 198 [δ(CCl_4) 0.09 (s, 9 Ha), 0.15 (s, 3Hb), 1.58 (d, 2Hcc', Jce = 6 Hz, collapses to S with hν at ca. 5.95), 5.90 (d, 1 Hd, Jdf = 14 Hz), 5.95 (t of d, 1 He, Jef = 1 Hz, collapses to d with hν at ca. 1.58), 6.46 (d of d, 1 Hf), Jde = 0 Hz]. A Diels-Alder reaction of 200 and hexafluoro-2-butyne produced 202 as a mixture of syn and anti isomers



200

202

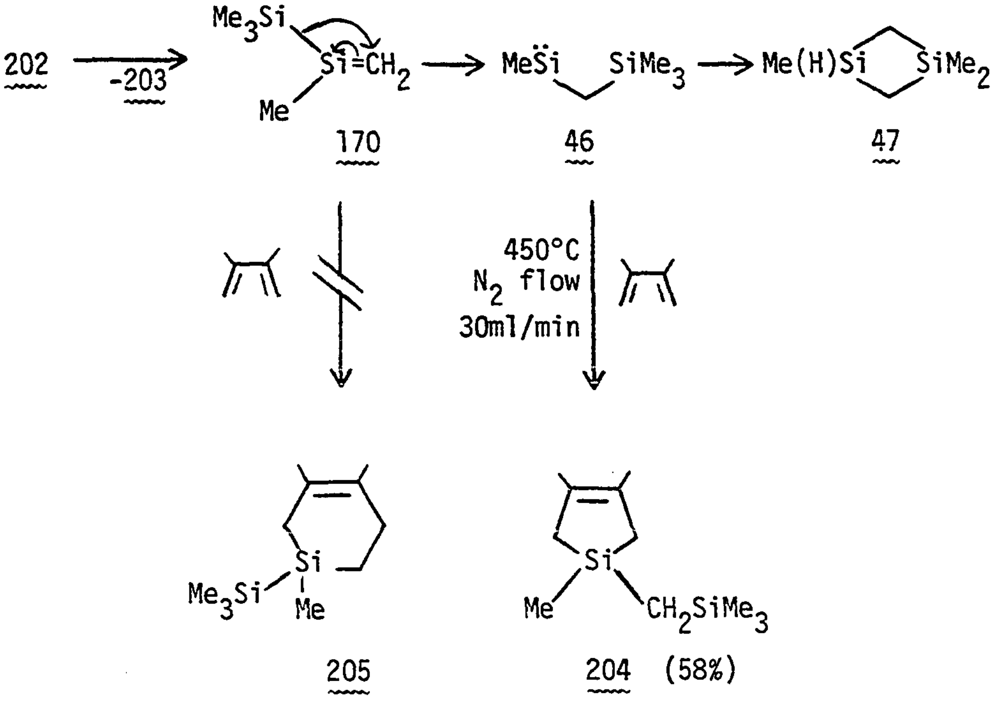
203 (76%)

47 (55%)

in 89% yield [$\delta(CCl_4)$ 0.10 (broad s, 3 Ha), 0.12 (s, 9 Hb), 0.42-1.26 (m, 2HcHc'), 3.65 (d, 1 Hd, Jdf = 7 Hz, collapses to s with hν at ca. 5.92), 4.10 (m, 1 He), 5.92 (d of d, 1 Hf, Jfe = 2 Hz)].

Distillation of 202 (25°C, 1 x 10^{-4} torr) through a quartz tube packed with quartz chips furnished a light yellow oil in 82% mass recovery. This pyrolysis was extremely clean, giving only two products, 203 (76%) and the desired 1,3-disilacyclobutane 47 (55%). As usual, 203 and 47 were isolated and their spectral properties compared to authentic samples.

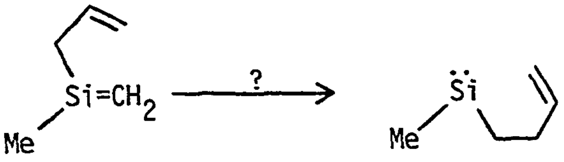
The clean production of 47 from 202 is very strong evidence for the proposed silene to silylene rearrangement (170→46).



The copyrolysis of 202 with a five-fold excess 2,3-dimethyl-1,3-butadiene (450°C, N_2 flow) gave the silylene adduct 204 (58%) as the sole trapping product. Thus, the rearrangement 170 to 46 is faster than silene trapping, as no 205 is formed. Decreasing the temperature to 390°C had no effect upon the product composition.

In conclusion, strong evidence for an unprecedented silene to silylene rearrangement via a 1,2-migration of silicon has been presented. This rearrangement has been observed in silyl and disilanylsilene generated by radical disproportionation reactions and in silylsilene generated by a retro Diels-Alder reaction of the silabicycloocta[2.2.2]-diene 202.

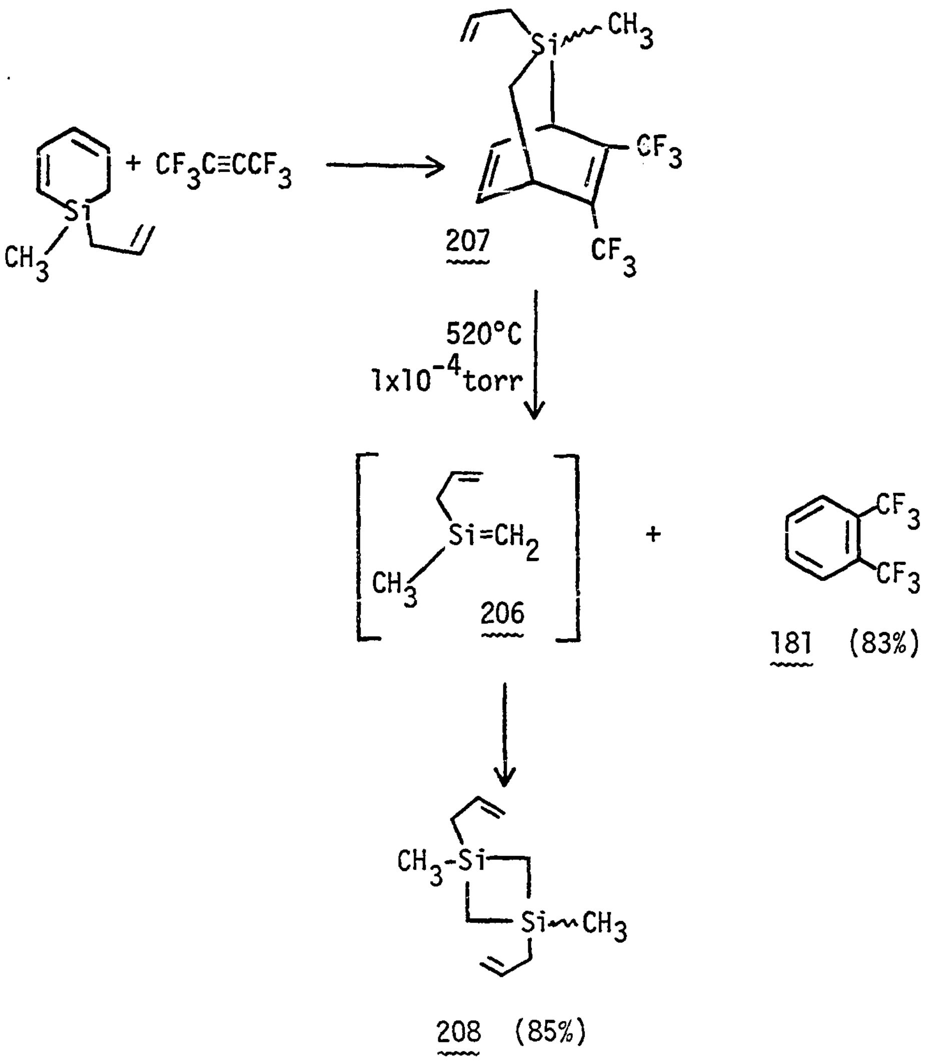
Two efforts were made to observe further silene to silylene rearrangements. One very promising system was the allylmethyl silene 206. This silene seemed an excellent candidate, since the rearrangement would involve a favorable six-electron process.



206

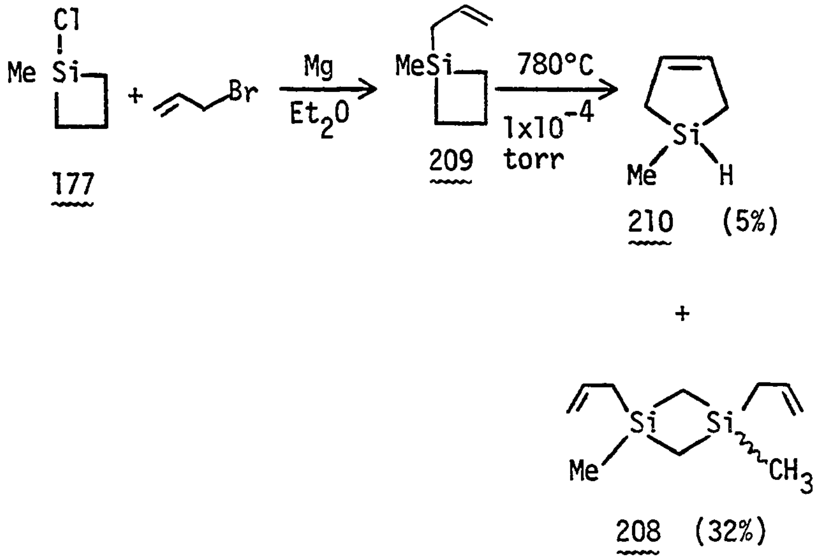
Two methods were used to generate silene 206, the thermal decomposition of the silabicyclo[2.2.2]octadiene 207 was the first method chosen. Synthesis of 207 (as mixture of *syn* and *anti* isomers) was accomplished by the Diels-Alder reaction of 1-allyl-1-methyl-1-silacyclohexa-2,4-diene (181) and hexafluoro-2-butyne in a sealed tube (25°C for 24 h) [δ(CCl_4) δ 0.08 (s, 3H SiMe), 0.48 (d, 2H, J = 4 Hz, collapses to singlet with hν at 4.15), 1.50 (d, 2H, J = 8 Hz $C\underline{H}_2CH{=}CH_2$), 3.66 (d, 1H, J = 6 Hz, collapses to broad s with hν at 6.10), 4.15 (m, 1H, collapses to broad triplet with hν at 6.10, collapses to a d with J = 6 Hz with hν at 0.48), 4.63-6.53 (5H, vinyl m)].

The pyrolysis of 207 (520°C, 1 x 10^{-4} torr) resulted in the formation of 181 (83%) and the silene dimer 208 (85%). Thus, although 206 seemed an excellent candidate for rearrangement to a silylene, it appears that this does not happen, as 206 simply dimerizes in the normal head-to-tail fashion.

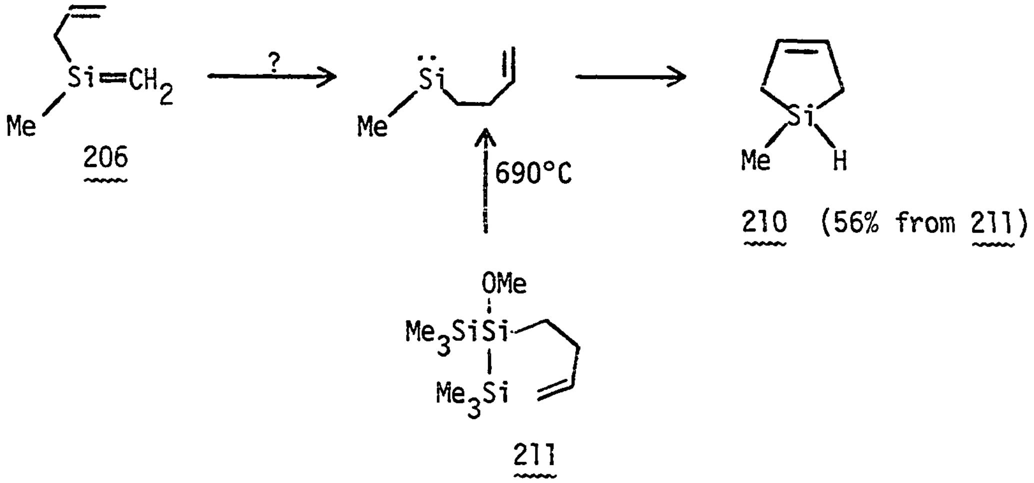


For comparison, the thermal decomposition of 1-allyl-1-methyl-1-silacyclobutane 209 was studied. The synthesis of 209 was accomplished by the addition of a solution containing 177 and allylbromide to magnesium in ether.

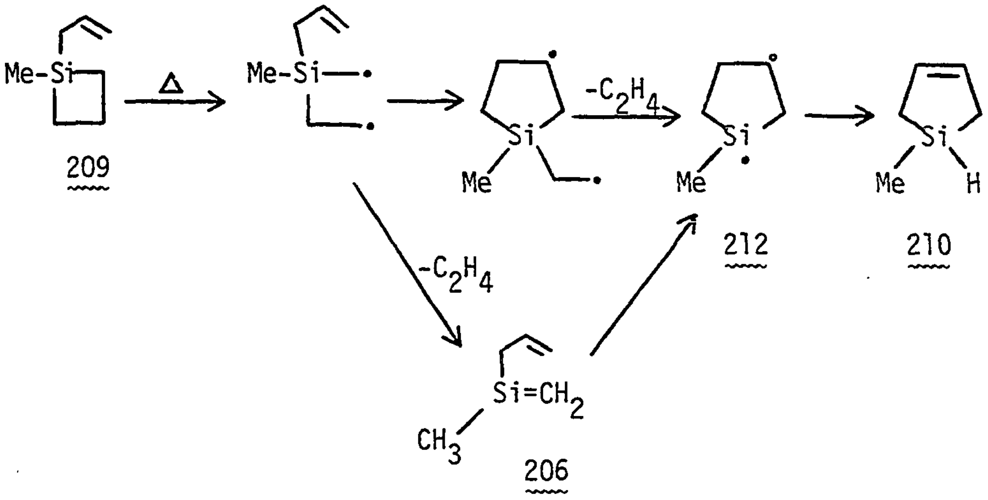
Pyrolysis of 209 at 780°C (1 x 10^{-4} torr) resulted in an 81% mass recovery of a clear oil (75% decomposition of 209). The two products formed in the pyrolysis of 209 were the silene dimer 208 (32%) and 1-methyl-1-silacyclopent-3-ene 210 (5%). As in the case of the bicyclic generator 207, the major product 208 is a result of dimerization of silene 206. However, the formation of 210 could, in theory, arise from a silene



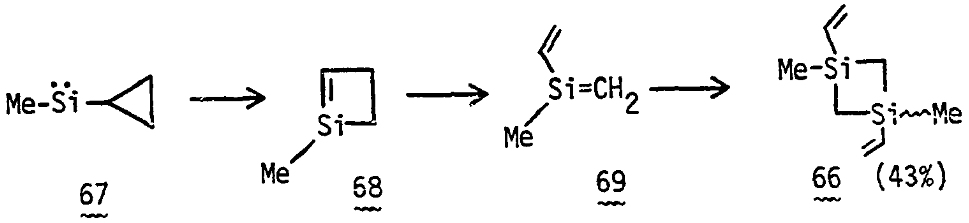
to silylene rearrangement. The intermediate (4-butenyl)methysilylene has recently been generated via an α-elimination of trimethylmethoxysilane from 211 forming 210 in 56% yield (182).



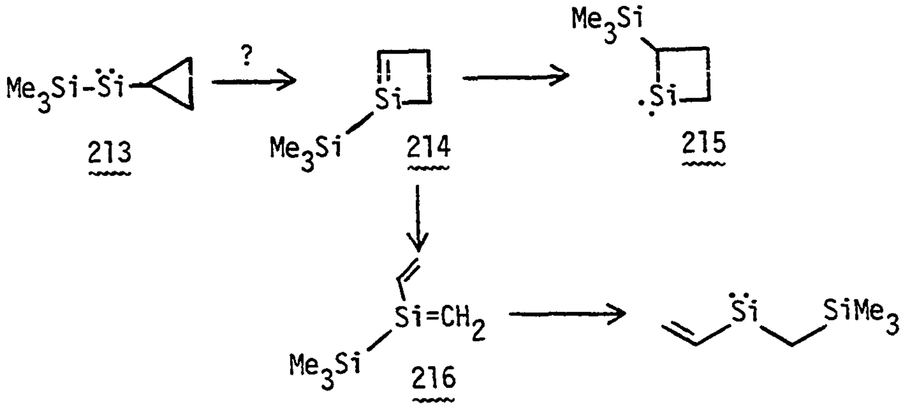
This silene to silylene rearrangement, although attractive, is certainly not demanded. The previous results on the pyrolysis of 1-methyl-1-silacyclobutane suggest decomposition via a rearrangement of an initial diradical formed by carbon-carbon bond homolysis. Thus 210 can be generated by radical addition to the π-bond, loss of ethylene giving diradical 212 and finally, hydrogen abstraction. It is also possible to imagine 212 arising from 206 directly through a di-π-methane sequence.



The second attempt to observe a silene to silylene rearrangement was suggested by work reported by Barton and coworkers (54). They showed that cyclopropylmethylsilylene 67, generated in the gas phase at 680°C (1×10^{-4} torr) undergoes ring expansion to 1-methyl-1-silacyclobut-1-ene 68. Ring opening of 68 to silene 69 and head-to-tail dimerization of 69 gives 66 (43%).

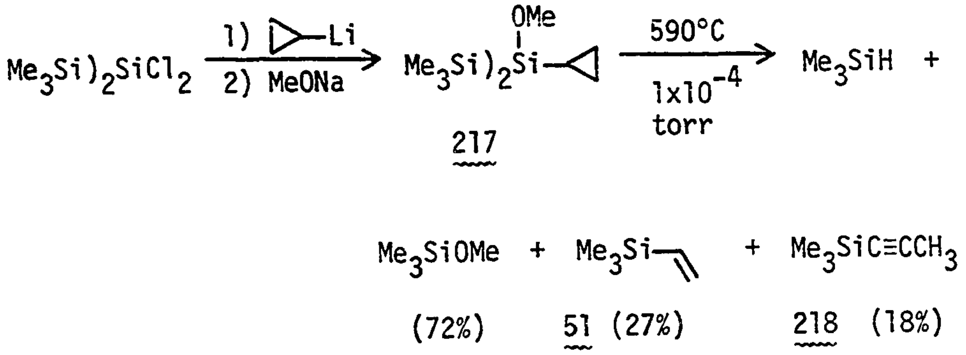


Substitution of the methyl group by a trimethylsilyl group could, in theory, furnish a sequential sequence of rearrangements. The initial silylene could undergo an expansion of the cyclopropane ring, forming



silene 214. As already discussed, silyl substituted silenes undergo 1,2-silicon migration forming silylenes. Thus 214 could rearrange to 215. Alternatively, if ring opening of 214 is faster than silicon migration, the resulting silene 216 is also capable of a 1,2-silicon migration. The desire to incorporate a silene to silylene rearrangement into this sequence led to the study of the thermochemistry of 213.

The desired precurser, 217, was synthesized in 50% overall yield by the slow addition of cyclopropyllithium to bis(trimethylsilyl)dichlorosilane followed by addition of sodium methoxide. Distillation of 217 (25°C, 1 x 10^{-4} torr) through a quartz tube packed with quartz chips and

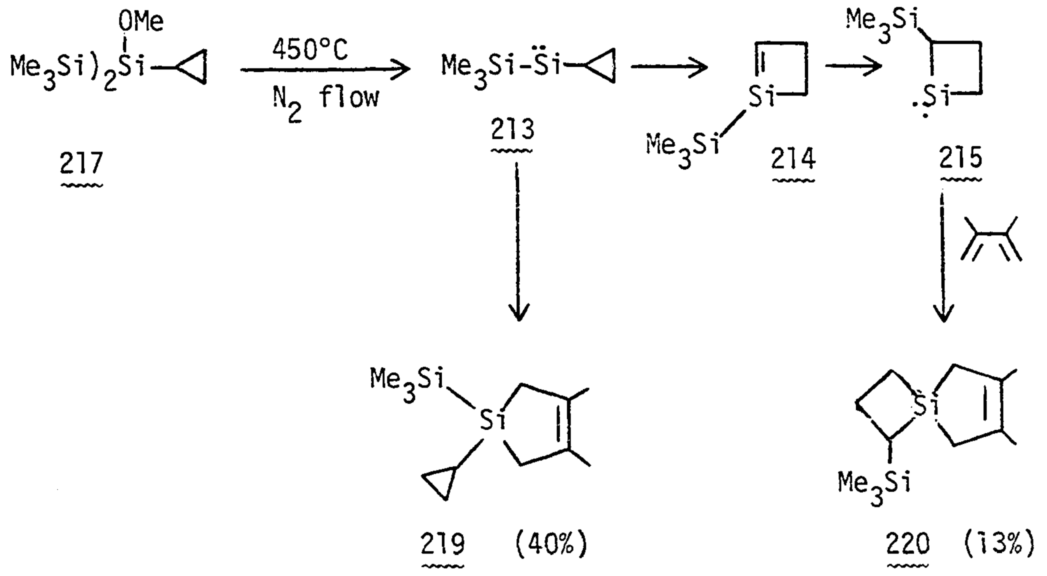


heated at 590°C furnished a light yellow oil in 76% mass recovery. Analysis of this oil by preparative gas chromatography revealed the presence of four products; trimethylsilane, trimethylmethoxysilane (72%), trimethylvinylsilane (27%) and 1-trimethylsilylpropyne, 218 (18%). Other than trimethylmethoxysilane (the expected α-elimination product), none of the products can be easily rationalized based upon the known chemistry of silylenes and silenes.

A trapping experiment was performed to insure the formation of the initial silylene 213 and to determine the supression of products by the trapping of 213. Copyrolysis of 217 with a six-fold excess of 2,3-dimethyl-1,3-butadiene (450°C, N_2 flow) resulted in the formation of two trapping products, along with trimethylmethoxysilane. These products were isolated by preparative gas chromatography (16' 20% SE 30 column) and identified on the basis of there ^1H NMR, ^{13}C NMR, low and high resolution mass spectra. The major product was 219 (40%) [NMR(CCl_4) δ 0.10 (s, 9H SiMe), -0.40-0.72 (m, cyclopropyl H), 1.30 (broad s, 4H,

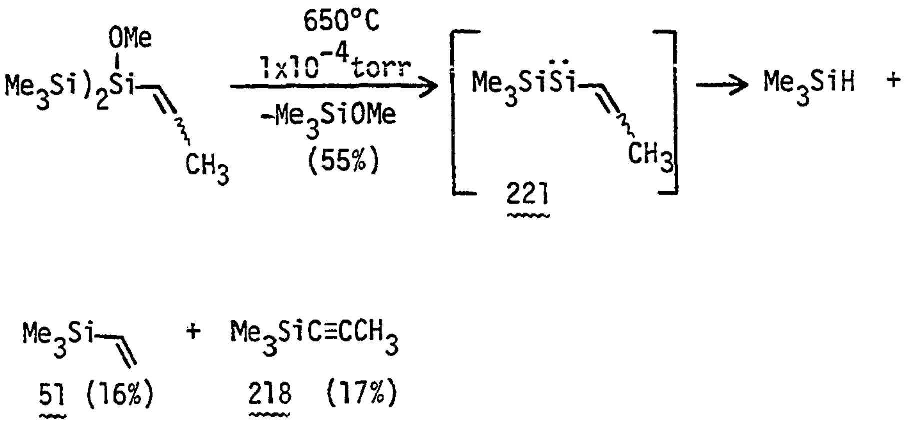
CH_2), 1.65 (broad s, 6H CH_3)]. The ^{13}C spectrum of 219 shows the presence of six different carbons [$^{13}C(C_6D_6)$ δ -7.087, -1.561, 1.905, 19.180, 21.727, 130.887. The three carbons at δ -7.087, -1.561 and 1.905 are consistent with the presence of a trimethylsilylcyclopropylsilane moiety. For example, the ^{13}C spectrum of 217 shows the analogous carbons at δ -5.065, -0.676 and 1.761. The minor product was assigned the structure 220 (13%) [NMR(C_6H_6) δ 0.05 (s, 9H), 0.86 (d of d, 1H, J_{AB} = 10 Hz, $J_{AB'}$ = 7 Hz, collapses to a broad s with hν at 2.12), 1.25 (apparent t, 2H, J = 8 Hz, collapses to broad s with hν at 2.12), 1.58 (broad s, 4H), 1.68 (broad s, 6H), 2.12 (m, 2H) $^{13}C(C_6D_6)$ δ -1.073, 15.334, 16.743, 17.501, 19.072, 19.722, 26.115, 26.873, 130.129, 130.292].

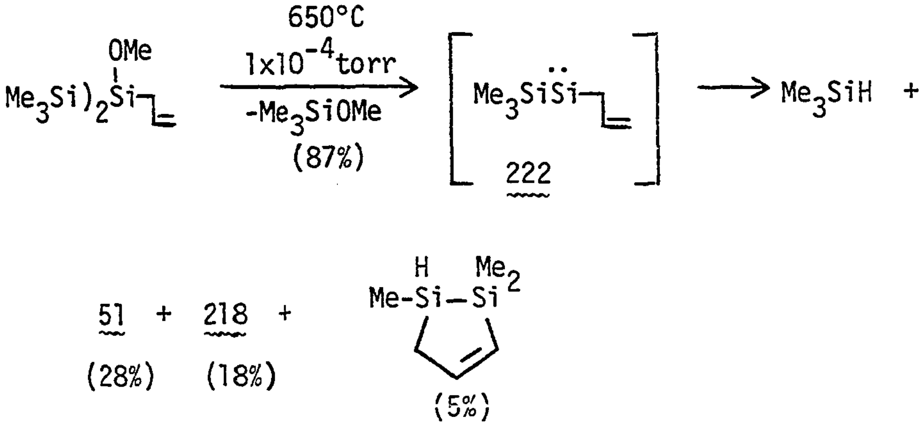
These results are consistent with the initial formation of silylene 213, since the major trapping product is the addition of 213 to 2,3-dimethyl-1,3-butadiene. The formation of 220 suggests the intermediacy of silylene 215. Although this does not demand that 215 originate from 213 via 214, this pathway is the most reasonable. Both the cyclopropyl ring expansion (213→214) and the 1,2-silicon migration now have precedence, and in fact, were predicted to occur.



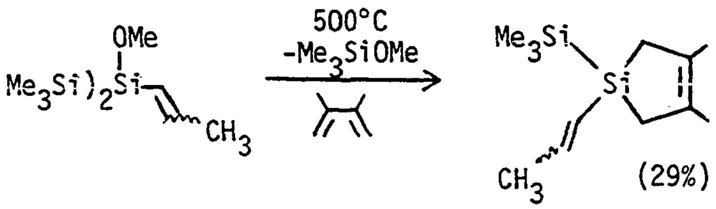
The pathway leading to the products in the untrapped thermolysis of 217 remains a mechanistic puzzle. The formation of trimethylvinylsilane and 1-trimethylsilylpropyne corresponds to the formal loss of $SiCH_2$ and SiH_2 respectively. Upon examination of the two trapped silylenes, 213 and 215, the mechanism clearly involves major sketetal rearrangements.

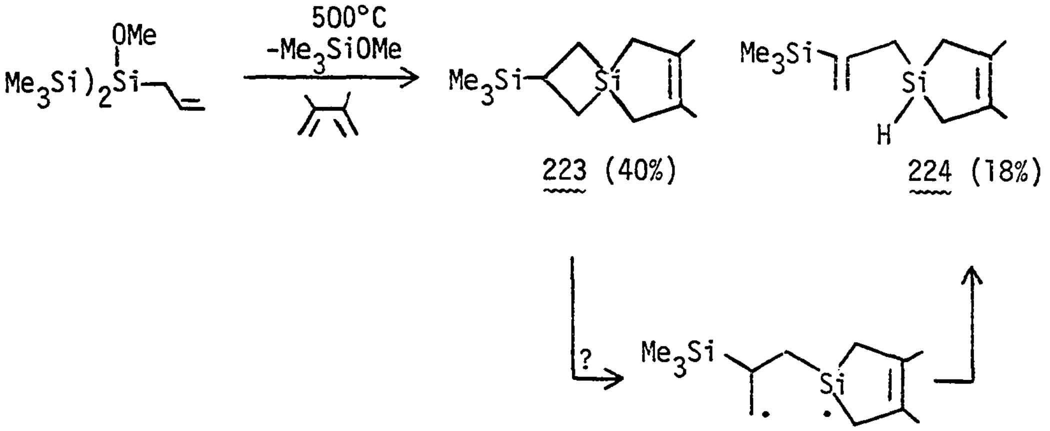
Very recently, G. T. Burns has added more data to this puzzle (182). The thermal generation of two silylenes isomeric to 213, 221 and 222 under similar reaction conditions, afforded nearly the same product mixture, in comparable yields. Copyrolysis of the precurser to silylene 221 with 2,3-dimethyl-1,3-butadiene simply resulted in trapping of the initial silylene, 221, in 29% yield. However, the same trapping experiment performed on the precursor to trimethylsilylallylsilylene, 222, furnished some interesting results. The two major trapping products





formed were 223 (40%) and 224 (18%). It is conceivable that 224 is a thermal product of 223, and with the available data, there is no way to exclude this possibility. It is however, unlikely since it requires the homolysis of a silicon-carbon bond of a silacyclobutane. As already discussed, the favored cleavage in these systems is that of the carbon-carbon bond.

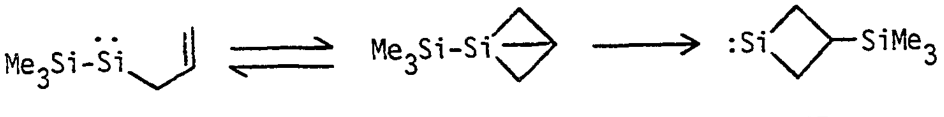




223 (40%)

224 (18%)

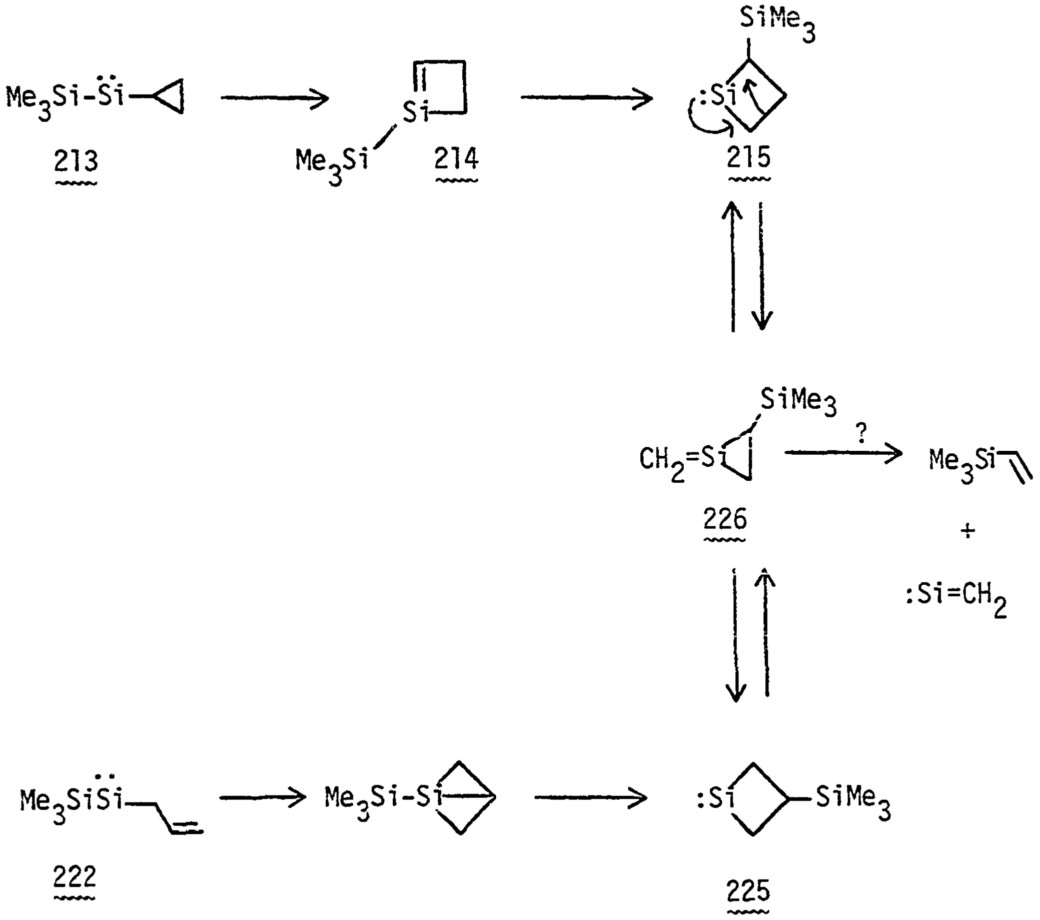
The formation of 223 suggests the intermediacy of 3-trimethylsilyl-1-silacyclobutylidine 225. Intramolecular π-addition of silylene 222 to generate 1-trimethylsilyl-1-silabicyclo[1.1.0]butane followed by 1,2-trimethylsilyl migration accounts for the generation of 225. Very often the central bond in bicyclobutanes reacts in a fashion analogous to a carbon-carbon double bond (183). Thus, this 1,2-trimethylsilyl migration parallels that of (trimethylsilyl)methylsilene.



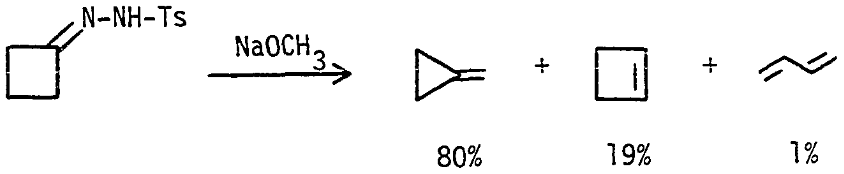
222

225

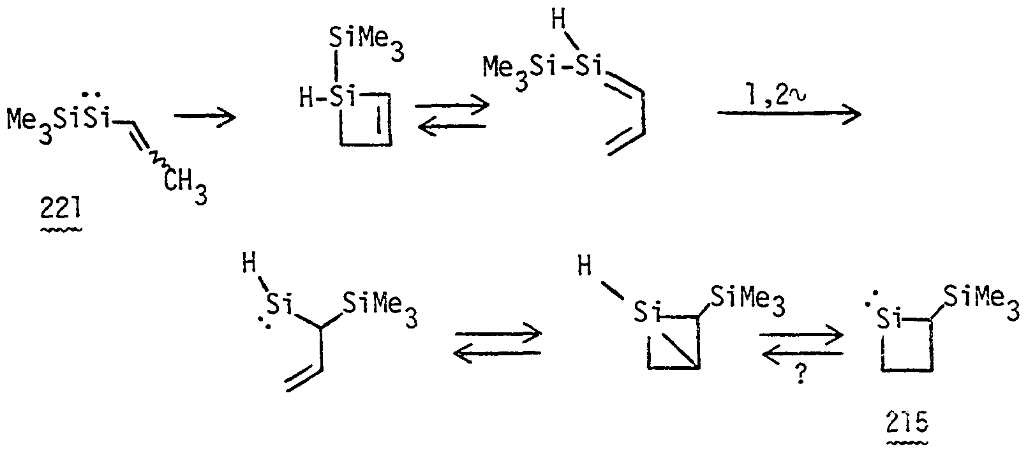
The striking similarities in the product mixtures from the thermal generation of silylenes 213, 221 and 222 seem to great to attribute to coincidence. One attractive solution is that these three silylenes are interconverting via a common intermediate. One possibility is that silylenes 215 and 225 are in equilibrium with silene 226, which could in theory, decompose to trimethylvinyl silane and silylidene. Silylidene has been calculated to be the most stable structure of the $SiCH_2$ energy surface, rather than silacetylene (184). The analogous carbon rearrangement is well-known. The tosylhydrazone of

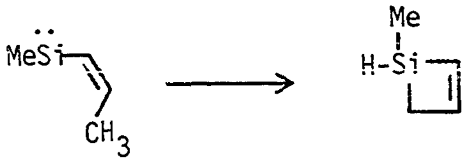


cyclobutanone affords methylenecyclopropane as the major product when pyrolyzed in the presence of excess sodium methoxide (185).

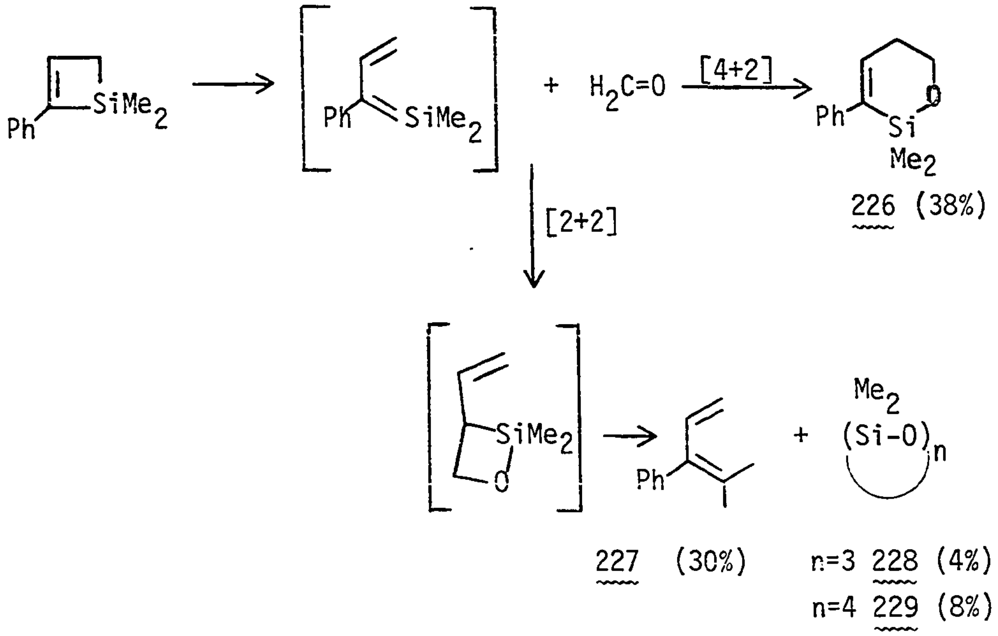


The (trimethylsilyl)1-propenylsilylene 221 can also be woven into this energy surface by the following sequence of rearrangements. The first step in this sequence, the C-H insertion to form 1-trimethylsilylsiletene, is suggested by the fact that (methyl)1-propenylsilylene affords 1-methylsiletene under similar conditions (182). Recently, Tzeng





and coworkers have presented evidence for the thermal ring opening of 1,1-dimethyl-2-phenylsiletene to 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene (186). This intermediate was trapped with formaldehyde furnishing a mixture of products (226→229). These are the expected products from competing [2+2] and [4+2] cycloaddition reactions.



226 (38%)

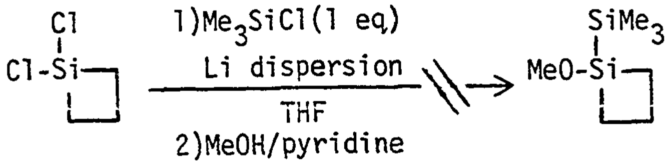
227 (30%)

n=3 228 (4%)

n=4 229 (8%)

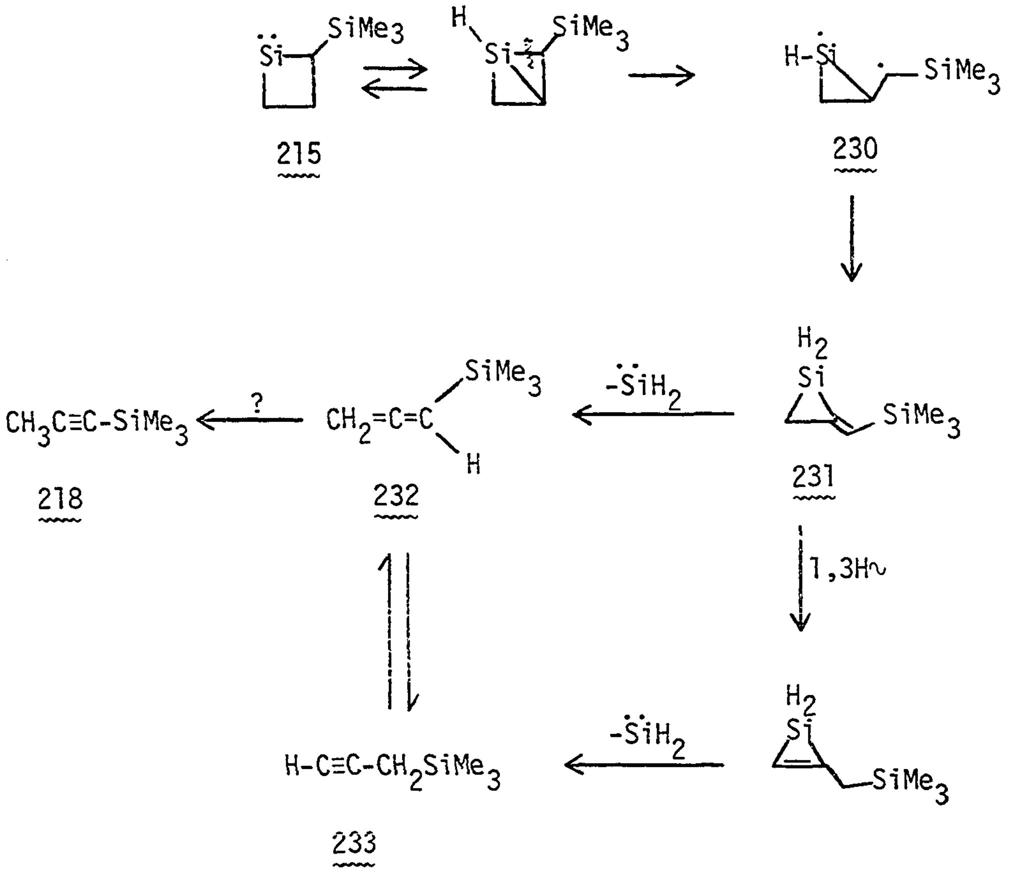
Thus, every step in the sequence 221→215, except the last, has precedence. At this point however, these mechanistic interpretations are simply suggestions in an attempt to explain the data.

One obvious experiment is to independently generate 1-silacyclobutylidene and determine its thermal behavior. Unfortunately, attempts to synthesize the appropriate precursor, 1-trimethylsilyl-1-methoxy-1-silacyclobutane failed. The attempted coupling of trimethylchlorosilane, followed by addition of methanol and pyridine resulted in a complex product mixture with very little formation (GCMS observation only) of the desired product. The major course of the reaction appears to be ring opening.



The formation of 1-trimethylsilylpropyne 218 from the three isomeric silylenes is intriguing. Initially, it was thought that silylene 215 conceivably underwent C-H insertion followed by Si-C bond homolysis

Scheme 26

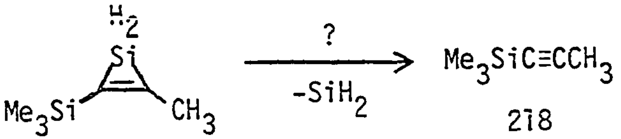


forming diradical 230 (Scheme 26). This diradical could hydrogen abstract forming 231, and by extrusion of silylene generate trimethylsilylallene 232. Alternatively, 231 could rearrange by a formal 1,3-hydrogen migration and then extrude silylene forming 233. Slutsky and Kwart (9) have shown that 232 and 233 interconvert via reversible 1,3-trimethylsilyl migrations at 550°C, with an activation energy of 49.9 kcal/mol (see Historical section on 1,3- and 1,5-migrations of silicon). However, an irreversible 1,3-hydrogen migration from 232 could produce 218 at higher temperatures.

This mechanism was easily tested by subjecting 233 to the pyrolysis conditions. The synthesis of 233 was accomplished in 70% according to the method of Masson and coworkers (187). Distillation of 233 (0°C, 1 x 10^{-4} torr) through a quartz tube packed with quartz chips and heated at 700°C afforded a clear liquid in 78% mass recovery. Examination of the pyrolysate by NMR clearly showed that 233 did not isomerize to 218.

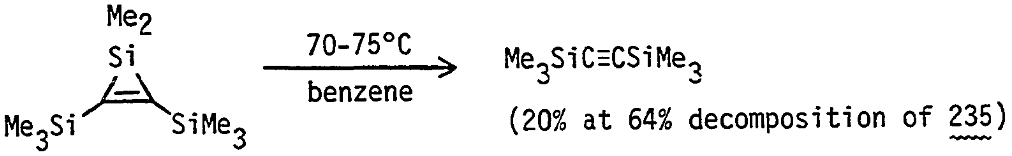
$$\underset{233}{\mathrm{Me_3SiCH_2C{\equiv}CH}} \;\cancel{\xrightarrow[1\mathrm{x}10^{-4}\mathrm{torr}]{700^\circ\mathrm{C}}}\; \underset{218}{\mathrm{Me_3SiC{\equiv}CCH_3}}$$

Thus, the origin of 218 remains unanswered. One possible precurser to 218 is 2-trimethylsilyl-3-methyl-1-silacyclopropene 234, through



234

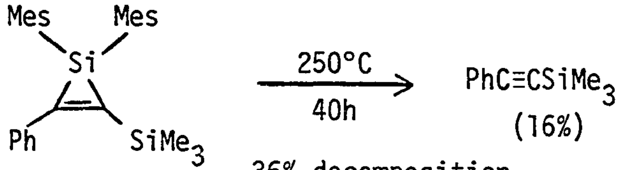
extrusion of silylene. However, the thermal mode of decomposition of 1-silacycloprop-2-enes appears to be very dependent upon both the substituents on silicon and carbon. For example, Seyferth and coworkers note that 235 has a half-life in benzene at 70-75°C of about 60 hours (188). During the course of this decomposition,bis(trimethylsilyl)-acetylene is formed. Although no trapping experiments were performed, this is suggestive of extrusion of dimethylsilylene.



235

(20% at 64% decomposition of 235)

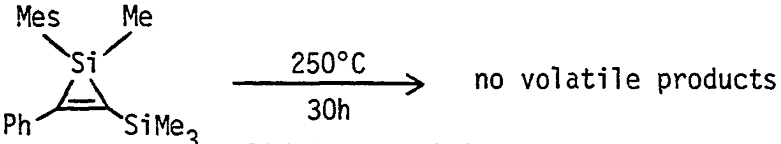
Similarly, 236 appears to extrude dimesitylsilylene when heated at 250°C for forty hours (189). However, replacing one mesityl group with a



(16%)

236

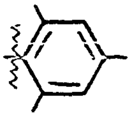
36% decomposition



237

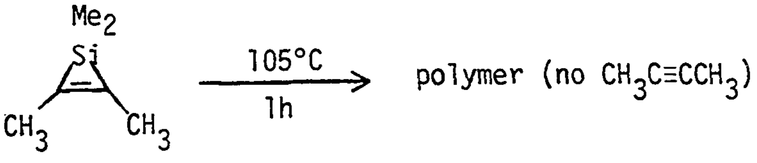
50% decomposition

Mes =



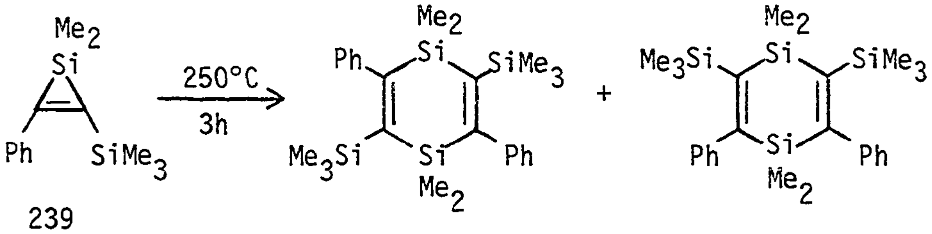
methyl group alters the chemistry. Heating 237 for thirty hours results in a 50% decomposition of 237 and the production of no volatile products.

The tetramethylsilacyclopropene 238 behaves similarly (190). When a solution containing 20% of 238 was heated at 75°C for three hours, no diminution of the characteristic NMR signals for 238 was observed. When the temperature was raised to 105°C the silacyclopropene was destroyed within an hour. The NMR spectrum indicated only polymeric product and no observable 2-butyne.



238

Ishikawa and coworkers (191) report that heating 239 at 250°C in an inert solvent affords 240 (60%) and 241 (20%). This is the only example of 1,3-disilacyclohexa-2,5-diene formation from 1-silacycloprop-2-enes.

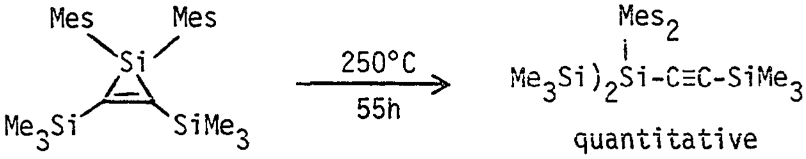


239

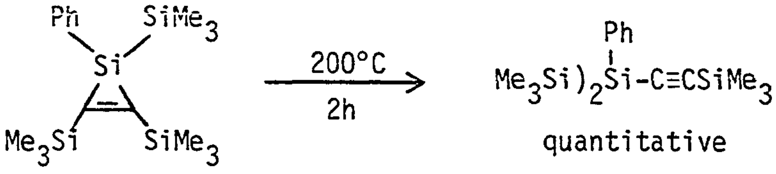
240 (60%)

241 (20%)

Finally, there are two reports that certain silacyclopropenes undergo thermal rearrangements to silylacetylenes (189, 192). Both 242 and 243 experience a 1,2-trimethylsilyl migration from carbon to silicon producing the corresponding acetylene quantitatively.



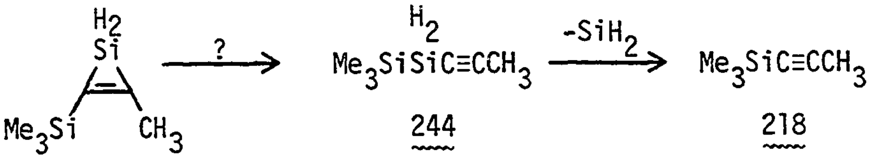
242



243

There appears to be no apparent pattern to the mode of these thermal decompositions, thus limiting ones predictive powers. For example, replacing the phenyl group with a trimethysilyl group, compare 236 and 242, alters the reaction course from silylene extrusion to rearrangement.

If this type of thermal rearrangement were to occur in 234, this could also be a viable route to 218, by extrusion of silylene from 244. A similar reaction has been observed by Sakurai (193) in the thermolysis

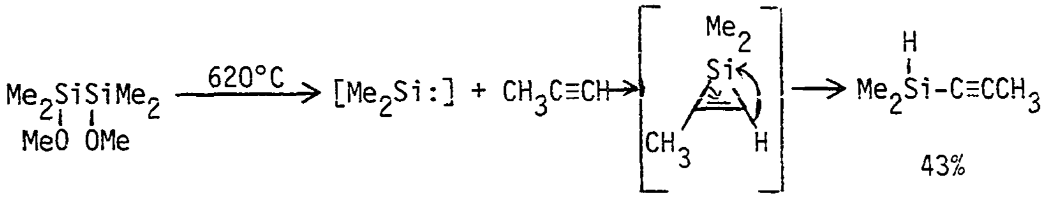


234 244 218

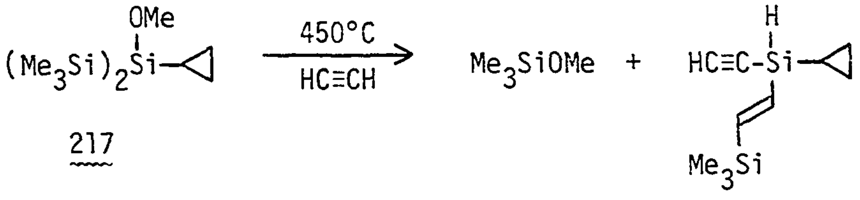
of (pentamethyldisilanyl)trimethylsilylacetylene, furnishing bis-(trimethylsilyl)acetylene.

Although 234 is a reasonable precurser to 218, a viable mechanism for the formation of 234 cannot be put forth. Perhaps as more information is gained on the thermal behavior of 1-silabicyclobutanes and 1-silabutylidenes the mechanism will become clear.

During the course of this study, a new reaction of silacyclopropenes was discovered. The thermolysis of 217 in the presence of acetylene was initially preformed to gain further evidence for 2-trimethylsilyl-1-silacyclobutylidene 215. Acetylene has been shown to trap silylenes in the gas phase furnishing silylacetylenes in good yields (53, 55). For example, generation of dimethylsilylene in the gas phase at 620°C with a ten-fold excess of propyne affords 1-dimethylsilylpropyne in 43%. This reaction presumably involves π-addition of dimethylsilylene to propyne, forming 1,1,2-trimethyl-1-silacycloprop-2-ene, and subsequent hydrogen migration to silicon.



The flow pyrolysis of 217 at 450°C, using acetylene as the carrier gas, produced a light yellow oil in 83% mass recovery. Analysis of the pyrolysate by preparative gas chromatography revealed the presence of one product other than trimethylmethoxysilane. Surprisingly, the trapping



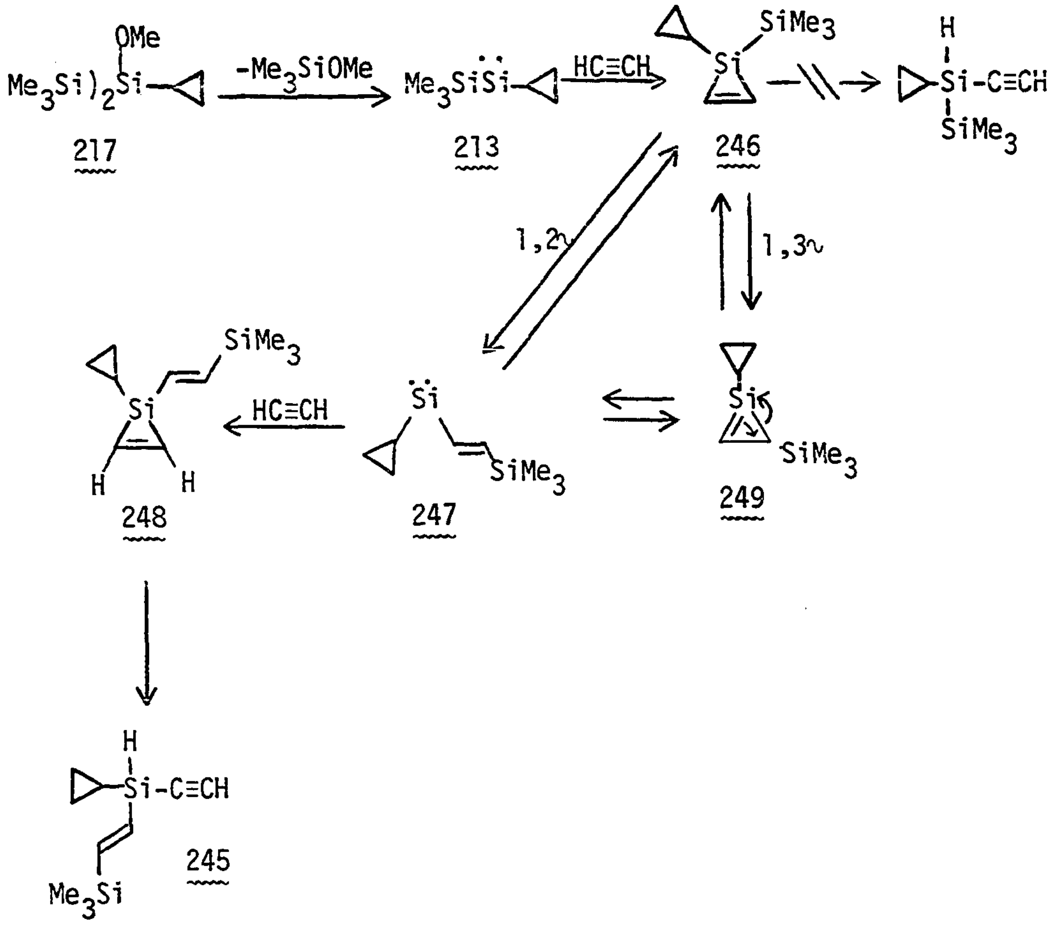
217

245 (52%)

product formed in this reaction, 245 (52%) corresponds to the addition of two moles of acetylene to the initially generated silylene.

An explanation for the formation of 245 is outlined in Scheme 27. Initially silylene 213 adds to acetylene in the expected fashion to give silacyclopropene 246, which does not suffer a 1,2-hydrogen migration. Instead, 246 isomerizes to a new silylene, 247, which then adds to yet another mole of acetylene giving 248. A final hydrogen migration in 248 generates 245. The rearrangement of 246 to 247 can be envisioned in two ways. A 1,2-trimethylsilyl migration generates 247 directly. Alternatively, a 1,3-trimethylsilyl migration to generate 249 followed by ring

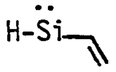
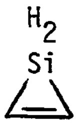
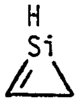
Scheme 27



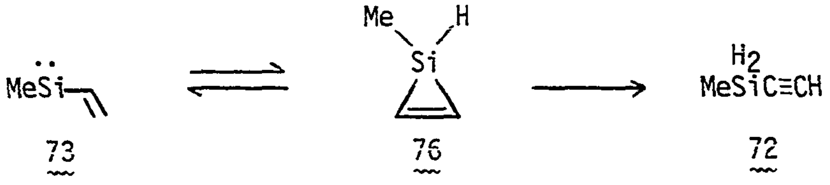
opening is also a possible pathway. Neither of these has been postulated before in silicon chemistry.

Gordon and Koob have recently performed an ab initio study of C_2SiH_4 isomers (194). The parent 1-silacycloprop-1-ene lies >50 kcal/mol higher in energy than either 1-silacycloprop-2-ene or vinylsilylene, the latter two having approximately the same energy. Thus, direct isomerization of 246 to 247 may be the operative mode of rearrangement.

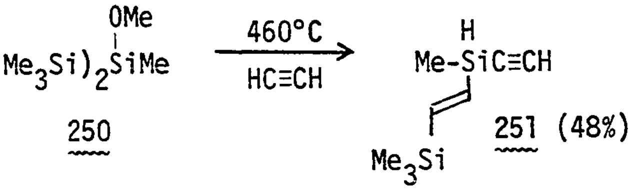
Table 11. Relative Isomer Energies (kcal/mol)

Isomer	6-31G*//3-21G
$HC \equiv CSiH_3$	0.0
	13.36
	14.79
	65.22

Interestingly, the reverse rearrangement has been observed by Barton and coworkers (54). It is postulated that methylvinylsilylene rearranges to 1-methyl-1-silacycloprop-2-ene and ultimately forms 72. This apparent discrepancy is resolved by invoking a reversible nature to the isomerization of 73 to 76. Since 73 was generated in the absence of trapping



agents, this equilibrium is bled off by the irreversible formation of 72. The mechanism outlined in Scheme 27 does not require the presence of the cyclopropyl group for the postulated rearrangements. Indeed, the copyrolysis of 250 with acetylene (460°C) produces the analogous product, 251, in 48%.

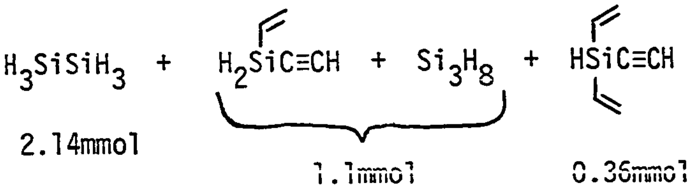


250

251 (48%)

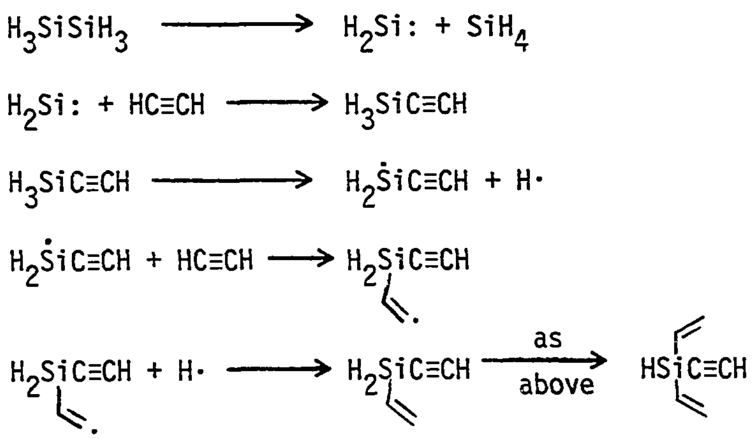
Haas and Ring (55) reported the pyrolysis of disilane with acetylene in 1975. In this reaction three products arising from the addition of silylene (from α-elimination of silane) to acetylene were observed, and are shown below.

$$\underset{7.3\text{mmol}}{H_3SiSiH_3} + \underset{10.9\text{mmol}}{HC{\equiv}CH} \xrightarrow[4h]{370°C} \underset{2.45\text{mmol}}{SiH_4} + \underset{6.8\text{mmol}}{HC{\equiv}CH} + \underset{0.87\text{mmol}}{H_3SiC{\equiv}CH} +$$

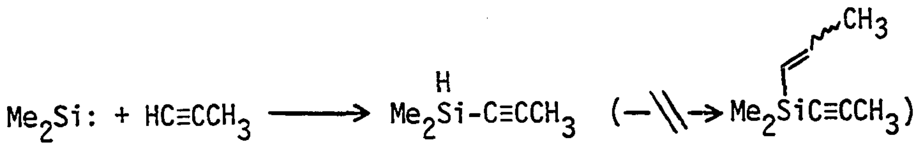


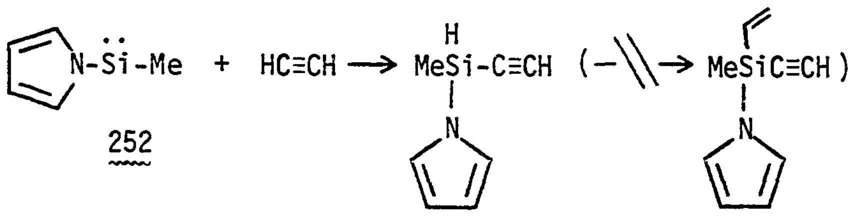
The formation of ethynylvinylsilane and ethynyldivinylsilane was accounted for by the series of radical reaction shown in Scheme 28. These authors suggest that the initially formed ethynyl silane suffers homolytic cleavage of the silicon-hydrogen bond, followed by addition to acetylene and hydrogen abstraction to give ethynylvinylsilane. The sequence is then repeated forming ethynyldivinylsilane.

Scheme 28

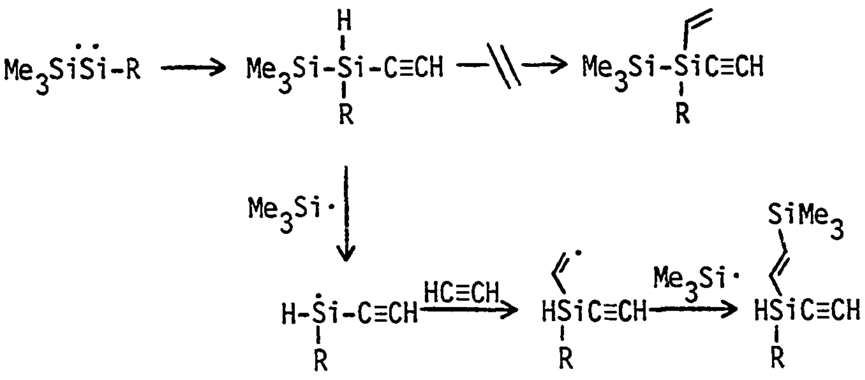


If this radical pathway were operative, one would expect to observe the formation of ethynyltrivinylsilane from further reaction of ethynyldivinylsilane. Also, the formation of ethynylvinyl derivatives does not occur when the initial silylene is substituted with groups other than hydrogen or silicon (as in the two examples presented in this thesis). For example, Conlin and Gaspar (53) make no comment on the formation of 1-(dimethyl)vinylsilylpropyne when dimethylsilylene is generated in the presence of propyne. Similarly silylene 252 (generated at 500°C) reacts with acetylene to furnish only the monoaddition product (182).





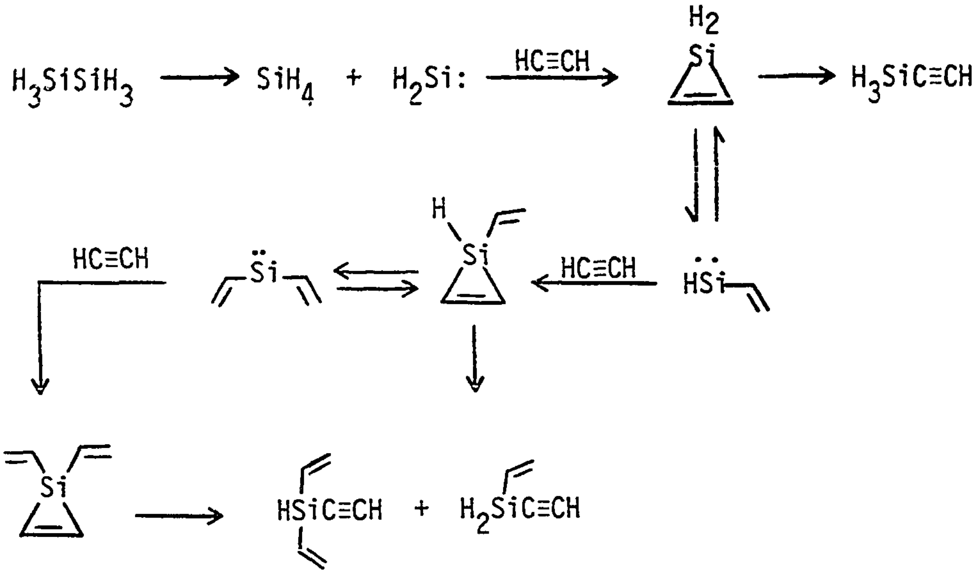
This radical mechanism certainly does not explain the products observed when silyl substituted silylenes are thermalized with acetylene. The products arising from homolytic cleavage of the silicon-hydrogen bond



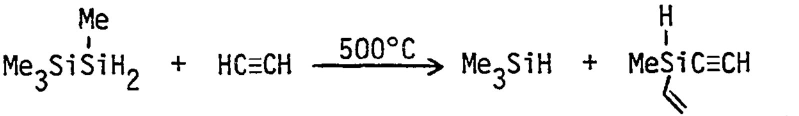
unreasonable

are not observed, and to propose silicon-silicon bond cleavage under the conditions employed is unreasonable.

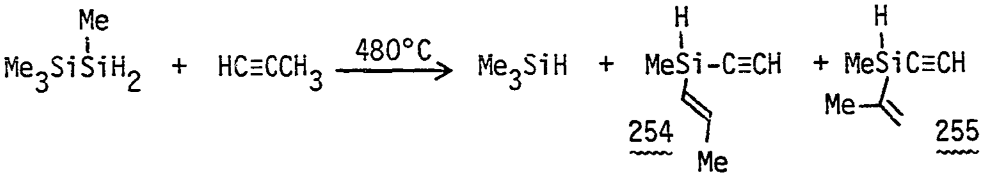
A mechanism paralleling that proposed for the silyl substituted silylene explains the results of Haas and Ring. Silylene addition to acetylene to give 1-silacycloprop-2-ene can produce ethynylsilane or can rearrange to vinylsilylene. This sequence can then be repeated giving both ethynylvinyl and ethynyldivinylsilane. The formation of the mono and divinyl derivatives is therefore a consequence of the presence of one and two hydrogens in the initial silylene. This provides an explanation for the production of simple ethynylsilanes from the addition of acetylene to dialkylsilylenes.



Barton and Burns (182) have shown that methylsilylene adds to acetylene and propyne in a fashion expected based upon the proposed mechanism producing 253-255.



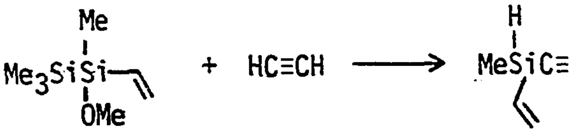
253 (26%)



254 255

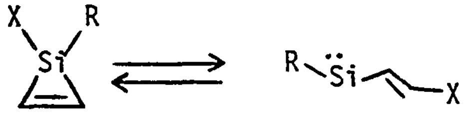
73%

Methylvinylsilylene is the intermediate silylene leading to 253. When independently generated with acetylene, this silylene indeed produces 253 as the major product.



253

Thus, the thermal rearrangement of 1-silacycloprop-2-enes to vinylsilylenes appears to occur when the silicon is substituted with another silicon or hydrogen.



$X = H, SiMe_3$

CONCLUSION

An attempt was made to generate a (p-p) π bonded silicon via a 1,5-trimethylsilyl migration from silicon to oxygen. It was found that the migration does not occur. Thermolysis and photolysis of cis-7,7,8,8-tetramethyl-7,8-disilanon-5-en-4-one affords a cyclic silylenol ether by coordination of the internal silicon with oxygen followed by 1,2-migration of the trimethylsilyl group.

It was shown that 1,2-diallyl, 1,2-dibenzyl and 1-allyl-2-benzyldisilanes thermally decompose to silicon centered radicals. These radicals react by exo addition to the π bond followed by rearrangement or by ipso substitution to form cyclic products. A deuterium labeling study showed that a homoretroene reaction was not operative, and that silicon-allyl or silicon-benzyl bond homolysis was the first step in these thermal decompositions. This suggested that the mechanism for the thermal conversion of allyltrimethylsilane to trimethylvinylsilane follows a similar pathway, bringing into question the mechanism proposed by Neider et al. (109). Support for this was obtained when allyltrimethylsilane, fully deuterated in the methyl position furnished 50% d-9 and 20% d-10 trimethylvinylsilane. A mechanism consistent with this was put forth.

The thermal decomposition of allyl, benzyl and polysilanes was found to generate silicon radicals. The silicon radicals undergo a sequence of: disproportionation to form silylsilenes; rearrangement via 1,2-silicon migration to silylenes; and final C-H insertion to 1,3-disilacyclobutanes. This is the first example of a silene to silylene rearrangement. Conclusive evidence for this rearrangement was obtained when (trimethylsilyl)methylsilene was independently generated from a retro Diels-Alder reaction. The mechanism (160) for the thermal isomerization of methylsilene to dimethylsilylene was brought into question when the same silene generated from a retro Diels-Alder reaction did not isomerize.

In addition, evidence for a sequential silylene to silene to silylene was obtained. Specifically, (trimethylsilyl)cyclopropylsilylene ring expands to 1-trimethylsilyl-1-silacyclobut-1-ene and then undergoes a 1,2-trimethylsilyl migration to afford 2-trimethylsilyl-1-silacyclobutylidene. Both silylenes were trapped with 2,3-dimethyl-1,3-butadiene.

Finally, a new reaction of silylenes and acetylenes was discovered. The initial 1-silacycloprop-2-ene, from addition of silicon-substituted silylenes to acetylene, rearranges to a vinylsilylene which then adds to another mole of acetylene. For example, (trimethylsilyl)methylsilylene reacts with acetylene to afford trans-β-(trimethylsilylvinyl)methylethynylsilane in 48% yield.

EXPERIMENTAL

Instrumentation

Routine proton NMR spectra were recorded either on a Varian model A-60, EM-360 or a Hitachi R-20B spectrometer. A Varian HA-100 spectrometer was used to record all 100 MHz spectra and a JEOL FX-90 spectrometer was used to record all 90 MHz spectra. Decoupling experiments were performed either on the Varian EM-360 or the JEOL FX-90 spectrometer. All chemical shifts were reported as parts-per-million (δ scale) using either tetramethylsilane, benzene, chloroform or acetone as internal standards.

^{13}C NMR spectra were recorded on a JEOL FX-90 spectrometer. ^{2}H NMR spectra were recorded on a Bruker WM 300 MHz spectrometer.

Infrared (IR) spectra were recorded on either a Beckman IR-4250 or a Beckman Acculab-2 infrared spectrometer. All bands are recorded in reciprocal centimeters (cm^{-1}).

Exact mass measurements were obtained on a MS-902 mass spectrometer. Gas chromatograph mass spectra (GCMS) were obtained on a Finnegan Model 4023 mass spectrometer. Unless otherwise stated, all mass spectral measurements were made at 70 eV.

All melting points (mp) were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Gas chromatographic (GC) data were obtained on a Varian-Aerograph Series 920 or 1700 gas chromatograph. Column size and packing will be reported as used.

Procedures and Results

Synthesis of 1-chloropentamethyldisilane

The method of Sakurai and coworkers (195) was used to prepare 1-chloropentamethyldisilane.

Synthesis of 1,2-dichloro-1,1,2,2-tetramethyldisilane

The synthesis of 1,2-dichloro-1,1,2,2-tetramethyldisilane was accomplished according to the method of Sakurai and coworkers (195).

Synthesis of 148a

To a stirring solution of 5.012 g (0.0716 mol) of 147a in 200 mL of CH_2Cl_2 at 0°C were added 10.16 g (0.0788 mol) of diisopropylethylamine and 8.59 g (0.107 mol) of (chloromethyl)methylether. After warming to room temperature, stirring was continued for 24 hours. The organic solution was washed with water and dried with magnesium sulfate. After removal of solvent, distillation at 45-50°C at 40 mm Hg afforded 4.18 g (51%) of methoxymethyl protected 1-butyne-3-ol: NMR (CCl_4) δ 1.46 (d, 3H, J = 6 Hz), 2.40 (d, 1H, J = 2 Hz), 3.40 (s, 3H) 4.45 (d of q, 1H) 4.53 (d, 1H, J = 7 Hz overlaps with left side of d of q), 4.90 (d, 1H, J = 7 Hz), calculated for p-1, $C_6H_9O_2$ m/e 113.06025, measured 113.06031.

To a stirring solution of 4.18 g (0.0367 mol) of the protected alcohol, synthesized as above, in 50 mL of dry THF at -78°C (under a nitrogen atmosphere) were added 15.0 mL (0.0375 mol) of a 2.5 M *n*-butyllithium/hexane solution. After stirring for 30 minutes at -78°C, 6.7 g (0.0403 mol) of chloropentamethyldisilane were added. After warming to room temperature for several hours, the organic solution was poured into hexane, washed with water and dried with magnesium sulfate. After removal of the solvent, distillation of the residue at 40-43°C at 0.1 torr afforded 5.42 g (60%) of 148a: NMR (CCl_4) δ 0.10 (s, 9H), 0.18 (s, 6H), 1.37 (d, 3H, J = 7 Hz) 4.33 (q, 1H, J = 7 Hz), 4.44 (d, 1H, J = 7 Hz overlaps with left side of q) 4.76 (d, 1H, J = 7 Hz); IR (neat) 2980, 2965, 2890, 2160, 1730, 1680, 1440, 1395, 1365, 1325, 1240, 1210 cm^{-1}; mass spectrum m/e (% rel. int.) 229 (.1) 214 (.6), 155 (18), 110 (39), 109 (15), 88 (100), 83 (14), 73 (64), calculated for p-CH_3, $C_{10}H_{21}O_2Si_2$ m/e 229.08961, measured 229.08980.

Hydrolysis of 148a to 146a

To a stirring solution of 10% HCl in methanol was added 0.8 g (0.003 mol) of 148a. After stirring 5 minutes at room temperature, the solution was heated at 60°C for 24 hours. The organic solution was washed with water and dried with magnesium sulfate. After removal of solvent, the residue was eluted through silica gel with a 75:25 hexane: ether solution to give 0.58 g (89%) of 146a: NMR (CCl_4) δ 0.08 (s, 9H), 0.13 (s, 6H), 1.35 (d, 3H, J = 7 Hz), 1.70 (broad s, 1 O$\underline{H}$), 4.36 (q, 1H, J = 7 Hz); IR (Neat) 3320, 2970, 2905, 2890, 2185, 1470, 1405, 1245, 1122, 1065, 1015, 930, 835, 800; mass spectrum m/e (% rel. int.) 185 (.4), 157 (18), 147 (53), 111 (10), 110 (41), 109 (24), 73 (100), calculated for p-CH_3, $C_8H_{17}OSi_2$ 185.08180, measured 185.08132.

Synthesis of 149a

To a stirring solution of 4.47 g (0.0638 mol) of 147a in 30 mL DMF at 0°C were added 10.86 g (0.1597 mol of imidazole and 8.32 g (0.0767 mol) of trimethylchlorosilane. After warming to room temperature, stirring was continued for several hours. The organic solution was poured into hexane, washed with water and dried over magnesium sulfate. Following removal of solvent, the residue was eluted through a silica gel column with a 90:10 hexane:ethylacetate solution affording 6.56 g (60%) of the silyl ether of 147a: NMR (CCl_4) δ 0.15 (s, 9H), 1.36 (d, 3H, J = 7 Hz), 2.24 (d, 1H, J = 2 Hz), 4.45 (d of q, 1H).

To a stirring solution of 6.56 g (0.462 mol) of the above ether in 60 mL of dry THF at -78°C (under a nitrogen atmosphere) were added 21.4 mL (0.0513 mol) of a 2.4 M *n*-butyllithium/hexane solution. After stirring for 30 minutes at -78°C, 7.69 g (0.0462 mol) of chloropentamethyldisilane were added. The solution was warmed to room temperature and stirred for several hours. After pouring into hexane, the organic solution was washed with water and dried with magnesium sulfate. After solvent removal, the residue was eluted through a silica gel column with a 90:10 hexane:ethylacetate to give 8.84 g (70%) of 149a: NMR (CCl_4) 0.10 (broad s, 18H, SiMe's overlapped), 1.36 (d, 3H, J = 7 Hz), 4.44 (q, 1H, J = 7 Hz).

Synthesis of 149b

To a stirring solution of 50.0 g (0.510 mol) of 147b in 350 mL of DMF at 0°C were added 86.73 g (1.275 mol) of imidazole and 60.8 g (0.561

mol) of trimethylchlorosilane. After warming to room temperature, stirring was continued for 18 hours. The organic solution was poured into ether, washed with water and dried with magnesium sulfate. After solvent removal, the residue was eluted through a silica gel column with a 90:10 hexane:ethylacetate solution to afford 72.6 g (84%) of the trimethylsilyl ether of 147b: NMR (CCl_4) δ 0.13 (s, 9H), 0.86-1.71 (m, 7H, $CH_2CH_2CH_3$), 2.24 (d, 1H, J = 2Hz), 4.21 (d of t, 1H, J = 2 Hz, J' = 6 Hz); mass spectrum (% rel. int.) 169 (.2), 127 (75), 83 (51), 74 (75), 73 (100).

To a stirring solution of 4.35 g (0.0256 mol) of the above ether in 70 mL of dry THF at -78°C (under a nitrogen atmosphere) were added 11.26 mL (0.0281 mol) of a 2.5 M n-butyllithium/hexane solution. After stirring for 30 minutes at -78°C, 4.25 g (0.0256 mol) of chloropentamethyldisilane were added. The solution was warmed to room temperature and stirring continued for several hours. After pouring into hexane, the organic solution was washed with water and dried with magnesium sulfate. The residue was distilled at 68-72°C at 0.1 torr to afford 4.61 g (60%) of 149b: NMR (CCl_4) δ 0.11 (s, 9H), 0.14 (s, 9H), 0.18 (s, 6H), 0.85-1.75 (m, 7H $CH_2CH_2CH_3$), 4.39 (t, 1H, J = 6 Hz); mass spectrum (% rel. int.) 285 (2), 199 (47) 183 (25) 155 (44), 149 (45), 148 (89), 147 (100), 133 (61), 109 (58), 75 (65), 73 (99) 59 (45), calculated for p-CH_3 $C_{13}H_{29}OSi_3$ 285.15263, measured 285.15289.

Hydrolysis of 149b to 146b

To a stirring solution of 10% HCl in THF was added 11.16 g (0.0372 mol) of 149b at room temperature. After stirring for 1 hour the organic solution was poured into hexane, washed with water, and dried with magnesium sulfate. Following solvent removal, the residue was eluted through a silica gel column with 75:25 hexane:ethylacetate to give 8.45 g (100%) of 146b: NMR (CCl_4) δ 0.12 (s, 9H), 0.18 (s, 6H), 0.82-1.76 (m, 8H, $C(OH)CH_2CH_2CH_2CH_3$, with added D_2O 7H), 4.28 (t, J = 6 Hz); IR (neat) 3700-3050 (broad OH), 2960, 2880, 2165, 1240 cm^{-1}; mass spectrum m/e (% rel. int.) 213 (.2) 211 (.6) 157 (23, 155 (9) 147 (73), 109 (53), 75 (88), 73 (100), 59 (18), measured for p-$CH(OH)CH_2CH_2CH_3$ $C_7H_{15}Si_2$ 155.07098, calculated 155.07124.

Attempt to reduce 146a with $(Sia)_2BH$

Diisoamylbroane was prepared as follows. To a stirring solution of 2.10 g (0.030 mol) of 2-methyl-2-butene in 20 mL dry THF at 0°C were added 15 mL (0.015 mol) of a 1 M borane·THF solution. Stirring was continued for 2 hours. The borane solution was transferred via syringe to a stirring solution of 2.00 g (0.010 mol) of 146a in 25 mL dry THF at 0°C. After stirring for 3 hours, 3 mL glacial acetic acid were added, and the reaction heated at 55°C for 5 hours. Then a mixture of 14 mL of 20% NaOH and 1.4 mL of 30% H_2O_2 was slowly added at room temperature. After stirring 2 hours, the organic solution was poured into ehter, washed with water, and dried with magnesium sulfate. Following solvent removal, analysis of the residue by NMR clearly showed the absence of olefinic protons. The GC trace contained 9 peaks.

Attempted hydrogenation of 146a with Pd, $BaSO_4$, and quinoline

A flask, equipped with a side arm for liquid additions, containing ca. .01 g of 5% Pd/$BaSO_4$ and 0.02 g of quinoline in 10 mL dry methanol was attached to a hydrogen source. The system was flushed with hydrogen for several minutes and an atmospheric pressure of hydrogen was maintained. To this stirring mixture was added 0.5441 g (0.00272 mol) of 146a. After stirring for several hours, no uptake of hydrogen was observed. The catalyst was filtered and methanol removed. Examination of the residue showed only unreacted 146a.

Attempted hydrogenation of 146a with Pd, $BaCO_3$ and quinoline

A flask, equipped with a side arm for liquid additions, containing ca. .01 g of 5% Pd/$BaCO_3$ and 0.02 g of quinoline in 10 mL dry methanol was attached to a hydrogen source. The system was flushed with hydrogen for several minutes, and an atmospheric pressure of hydrogen was maintained. To this stirring mixture was added 0.54 g (0.0027 mol) of 146a. An uptake of hydrogen was observed. After the addition of 50 mL (.002 mol), the reaction was stopped. The catalyst was filtered and methanol removed. Examination of the residue by NMR showed that 146a was consumed, however, no olefinic protons were observed. GCMS showed high molecular weight silicon-containing compounds.

Attempt to reduce 148a with $(Sia)_2BH$

Diisoamylborane was prepared as follows. To a stirring solution of 0.196 g (0.0028 mol) of 2-methyl-2-butene in 10 mL of dry THF at 0°C were added 1.4 mL (1 mmol) of a 1 M borane·THF solution. Stirring was continued for 2 hours. The borane solution was transferred via syringe to a stirring solution of .345 g (0.0014 mol) of 148a in 5 mL of dry THF at 0°C. After stirring for 3 hours, 0.3 mL of glacial acetic acid was added, and the reaction heated at 55°C for 5 hours. A mixture of 1.4 mL of 20% NaOH and 0.4 mL of 30% H_2O_2 was added at room temperature, and stirring continued for several hours. After pouring into ether, the organic solution was washed with water and dried with magnesium sulfate. Following solvent removal, examination of the residue by NMR showed the absence of olefinic protons. The presence of >6 products was shown by GC, the major product (GCMS only) appeared to be the corresponding deprotected alcohol plus oxygen, possibly a disiloxane. This reaction was repeated several times with similar results.

Attempt to hydrogenate 148a with Pd, $BaSO_4$ and quinoline

A mixture of 0.10 g of 5% Pd/$BaSO_4$ and 0.02 g of quinoline in 10 mL of dry methanol was placed in a hydrogenation apparatus and the system was flushed with hydrogen for several minutes. Maintaining an atmospheric pressure of hydrogen, 0.8 g (0.003 mol) of 148a was added. No uptake of hydrogen was observed after 1.5 hours. The catalyst was filtered and methanol removed. Examination of the residue by NMR and IR showed the presence of 146a only.

The above procedure was repeated using hexane as a solvent, resulting in unreacted 146a.

Attempt to hydrogenate 148a with Lindlar's catalyst

This attempted hydrogenation was run as described above using 0.10 g of 5% Pd/$CaCO_3$/$Pd(OAc)_2$ (Lindlar's catalyst) in place of 5% Pd/$BaSO_4$. The results were the same, no consumption of hydrogen was noted. Examination of the residue by NMR and IR showed only starting material.

Attempt to reduce 148a with Zn-Cu/MeOH(135)

To a stirring solution of 0.3332 g (0.001557 mol) of 148a in 10 mL dry methanol at room temperature was added 0.3174 g (.003144 mol) of Zn-Cu couple (196). After refluxing for 20 hours, the Zn-Cu couple was filtered and solvent removed. Examination of the residue by NMR and IR showed the presence of unreacted starting material.

Attempt to reduce 148a with BH_3

To a stirring solution of 0.822 g (3.67 mmol) of 148a in 20 mL of dry THF at 0°C (in a nitrogen atmosphere) were added 3.4 mL (3.4 mmol) of 1 M BH_3·THF solution. After stirring at 0°C for 45 minutes, 1 mL of glacial acetic acid was added and the solution was warmed to room temperature. After stirring for 3 hours the organic solution was poured into hexane, washed with water and dried with magnesium sulfate. Following solvent removal, examination of the residue showed no olefinic protons; the GC showed the presence of 5 products.

Attempt to reduce 149a with H_2, Pd, $BaSO_4$ and quinoline

A hydrogenation apparatus was charged with 0.10 g of 5% Pd/$BaSO_4$ and 0.02 g of quinoline in 10 mL dry methanol. The apparatus was flushed with hydrogen for several minutes and 0.489 g (0.00180 mol) of 149a was introduced. No uptake of hydrogen was observed. Following the removal of catalyst and solvent, only 149a was observed by NMR.

Attempt to reduce 149a with H_2,Pd, $BaCO_3$ and quinoline

This attempted hydrogenation was run as described above using 0.10 g of 5% Pd/$BaCO_3$ in place of Pd/$BaSO_4$. The results were the same, no hydrogen consumption, resulting in recovered 149a.

Attempt to reduce 146b with dicyclohexylborane

The preparation of dicyclohexylborane was as follows. To a stirring solution of 36.63 mL (0.03663 mol) of 1 M BH_3·THF solution at 0°C were added 6.018 g (0.07326 mol) of cyclohexane. The formation of a precipitate was observed and stirring was continued for 2 hours at 0°C.

To the above stirring solution was added 0.855 g (0.0333 mol) of 146b in 5 mL of dry THF. This was stirred 1 hour at 0°C. Following the addition of 1 mL glacial acetic acid, the solution was warmed to room temperature and stirring continued for 2 hours. After pouring into hexane, the organic solution was washed with water and dried with magnesium sulfate. After solvent removal, examination of the residue of NMR showed no olefinic protons.

Reduction of 146b to cis-enol 150a with DIBAL-N-methylpyrrolidine (137)

A two-necked round-bottom flask was equipped with a reflux condenser with a drying tube and a septum inlet. The apparatus was flushed with nitrogen and charged with 120 mL (0.120 mol) of 1 M diisobutylaluminum hydride (DIBAL) in heptane. After cooling to 0°C, 10.2 g (0.120 mol) of N-methylpyrrolidine were added dropwise, keeping the temperature below 5°C. After stirring for 30 minutes, 5.3 g (0.023 mol) of 146b were added. The solution was warmed to 60°C and stirred for 3 days. After cooling to room temperature, the organic solution was poured into a hexane/ice mixture with vigorous stirring for 30 minutes. The salts were filtered through a pad of celite and the filtrate washed with water and dried with magnesium sulfate. After removal of solvent, the residue was eluted through a silica gel column with a 75:25 hexane:ether solution to afford 3.80 g (71%) of 150a: NMR (CCl_4) δ 0.14 (s, 9H), 0.23 (s, 6H), 0.80-1.22 (m, 8H, $C(OH)CH_2CH_2CH_3$), 3.90-4.28 (m, 1H), 5.56 (d, 1H, J = 14 Hz), 6.24 (d of d, J = 14 Hz, J' = 8 Hz, collapses to d, J = 14 Hz with hν at ca. 4.0); IR (neat) 3390 (broad), 2960, 2900, 2880, 1608, 1465, 1400, 1255, 1245, 1115, 1095, 1060, 1010, 830, 790, 720 cm^{-1}; mass spectrum m/e (% rel. int.) 215 (.1), 139 (18), 133 (10), 113 (13), 75 (100), 73 (95), 61 (14), 59 (31), calculated for p-2, $C_{11}H_{24}Si_2O$ 228.13658, measured 228.13715.

Oxidation of cis-enol 150a to cis-enone 145 with PCC

To a stirring solution of 3.0 g (0.014 mol) of pyridiniumchlorochromate (PCC) in 50 ml methylenechloride at 0°C were added 2.99 g (0.013 mol) of 150a. The mixture was stirred for 2 hours while warming to room temperature. The dark brown solid was filtered through a pad of celite and solvent removed. Hexane was added and the newly formed brown precipitate filtered. After removal of solvent, the residue was eluted through silica gel with hexane, affording 0.827 g (28%) of the cis-enone 145: NMR (CCl_4) δ 0.04 (s, 9H), 0.12 (s, 6H), 0.91 (t, 3H, J = 6 Hz), 1.61 (sextet, 2H, J = 6 Hz), 2.44 (t, 2H, J = 6 Hz), 6.44 (d, 1H, J = 14 Hz), 6.80 (d, 1H, J = 14 Hz); IR (neat) 2980, 2950, 1692, 1570, 1420, 1372, 1242, 1130, 1055, 830, 800 cm^{-1}; mass spectrum m/e (% rel. int.) 228 (19), 213 (10), 155 (100), 147 (92), 133 (36), 91 (33), calculated for $C_{11}H_{24}Si_2O$ 228.13658, measured 228.13557.

Pyrolysis of cis-enone 145

Compound 145 was slowly dripped into a vertical quartz tube packed with quartz chips and heated at 430°C. Nitrogen was used as the carrier gas. A flow rate of 30 mL/min was used. The pyrolysate was collected in a trap cooled with liquid nitrogen, and represented an 86% mass recovery. The only product in this pyrolysis was isolated by preparative gas chromatography on a 8' x 1/4" 20% DC550 column at 180°C. This product was identified as 151 (86%) on the basis of its spectra: NMR (CCl_4) δ 0.02 (s, 9H), 0.20 (s, 3H), 0.30 (s, 3H), 0.68-1.11 (m, 4H), 1.48 (center of m, 2H), 2.1 (center of m, 2H), 4.50 (d, 1H, J = 3 Hz); IR (neat 2955, 1630, 1245, 1050, 975, 830 (broad); mass spectrum m/e (% rel. int.) 228 (8), 155 (61), 147 (70), 139 (40), 133 (28), 111 (21), 75 (27), 73 (100) calculated for $C_{11}H_{24}Si_2O$ 228.13658, measured 228.13579.

Photolysis of cis-enone 145

The photolysis was performed using a Hanovia 450L medium pressure lamp. Compound 145 (0.0176 g, 7.72 x 10^{-5} mol) was placed in a quartz NMR tube and dry cycohexane added to 2/3 the total volume. This solution was degassed by bubbling argon through it for 5 minutes. After photolyzing 15 minutes, only one compound was observed by ^1H NMR, that being 151 (11%). All spectral properties were identical to those for 151 produced from the thermolysis of 145.

Synthesis of 1,2-diallyl-1,1,2,2-tetramethyldisilane 152

A three-necked round-bottom flask was equipped with a reflux condenser fitted with a drying tube, a pressure equalized addition funnel with a nitrogen inlet and a mechanical stirrer. The apparatus was flame dried and flushed with nitrogen. The apparatus was charged with 80.0 mL (0.0640 mol) of 0.8 M allylmagnesium bromide in ether (197). To this stirring solution was added 4.74 g (0.0254 mol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane at a rate sufficient to maintain reflux. After stirring for 3 hours the reaction mixture was cooled to -20°C (CCl_4/Dry Ice) and 10% ammonium chloride was added. After warming to room temperature, the two layers were separated and the ether layer washed with water and dried with sodium sulfate. Following removal of solvent, the residue was distilled at 95-100°C/34 torr to afford 3.87 g (76.6%) of 1,2-diallyl-1,1,2,2-tetramethyldisilane: NMR (CCl_4) δ 0.00 (s, 12H), 1.50 (d, 4H, J = 8 Hz), 4.53-6.14 (m, 6H); IR (neat) 3070, 2950, 2890, 1625, 1415, 1390, 1240, 1185, 1140, 1030, 985 cm^{-1}; mass spectrum m/e (% rel. int) 198 (2), 159 (41), 158 (90), 157 (100), 155 (4), 141 (40), 131 (62), 129 (100), 117 (99), 115 (52), 99 (68), 97 (42), 85 (50), 83 (50), 73 (99), 59 (99), 58 (72) calculated for $C_{10}H_{18}Si_2$ 198.126012, measured 198.12593.

Vacuum pyrolysis of 1,2-diallyl-1,1,2,2-tetramethyldisilane 152

A slow distillation of 1.3145 g (6.63 mmol) of 152 was done at 25°C (1×10^{-3} torr) through a quartz tube packed with quartz chips and heated at 800°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 73.6% mass recovery. Analysis of the pyrolysate by GC revealed the presence of one product along with unreacted 152. Isolation of this product was done by preparative gas chromatography (12' 15% SE 30 column). The identification of 1,1,3,3-tetramethyl-1,3-disilacyclopentene 153 (51%) was based on the comparison of its NMR and mass spectra with those published by Fritz and coworkers (198): NMR ($CDCl_3$) δ -0.38 (s, 2H), 0.16 (s, 12H), 7.15 (s, 2H); mass spectrum m/e (% rel. int.) 156 (15), 143 (11), 142 (22), 141 (100), 113 (11), 73 (18), 54 (14).

Synthesis of 1-allyl-2-benzyl-1,1,2,2-tetramethyldisilane 155

A solution of benzylmagnesium chloride was prepared by equipping a two-neck round bottom flask with a condenser, drying tube and septum inlet. The apparatus was flame dried and flushed with nitrogen and charged with 0.84 g (0.037 mol) of magnesium and 50 mL dry ether. To this stirring mixture was added 3.74 g (0.0297 mol) of benzylchloride at a rate sufficient to maintain reflux. After stirring 2 hours, the benzylmagnesium chloride was transferred via double-tipped needle to a stirring solution of 5.00 g (0.0267 mol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane over a period of 1.5 hours. After stirring 5 minutes, 40 mL (0.032 mol) of a 0.8 M solution of allylmagnesium chloride were added. After stirring 1 hour, the solution was cooled to -23°C (CCl_4/Dry Ice) and 10% ammonium chloride was added. The two layers were separated and the organic solution was washed with water and dried with sodium sulfate. After solvent removal, the residue was distilled at 100-105°C (0.1 torr) to afford 3.97 g (60%) of 1-allyl-2-benzyl-1,1,2,2-tetramethyldisilane, 155: NMR (CCl_4) δ 0.01 (s, 6H), 0.05 (s, 6H), 1.55 (d, 2H, J = 8 Hz), 2.15 (s, 2H), 4.58-6.07 (m, 3H), 3.07 (center of aromatic m, 5H); IR (neat) 3060, 3020, 2950, 2890, 1620, 1590, 1485, 1235, 1200, 1145 cm^{-1}; mass spectrum m/e (% rel. int.) 248 (2), 207 (100), 191 (23), 157 (22), 129 (45), 121 (45), 73 (69), 59 (37), calculated for $C_{14}H_{24}Si_2$ 248.14166, measured 248.14170.

Vacuum pyrolysis of 1-allyl-2-benzyl-1,1,2,2-tetramethyldisilane 155

The pyrolysis of 155 was carried out by distilling 0.4156 g (1.678 mmol) of 155 at 25°C (1×10^{-3} torr) through a quartz tube packed with quartz chips and heated at 800°C. The pyrolysate was collected in a trap cooled with liquid nitrogen, and represented a 66% mass recovery. Analysis of the pyrolysate on a 12' 20% SE 30 column showed two major products along with unreacted 155. These were isolated by preparative gas chromatography and identified as 156 and 157. The spectra of both these products are given below. Also produced in this pyrolysis is a small amount (<5%) of 1,1,3,3-tetramethyl-1,3-disilacyclopentene 153 (identified by GCMS).

1,1,2,2-tetramethyl-1,2-disilaindane 156 (29%) yield) The NMR spectrum of 156 matches that reported by Tsui and Zon (199): NMR (CCl_4)

δ 0.22 (s, 6H), 0.30 (s, 6H), 2.27 (s, 2H), 6.97-7.60 (m, 4H); IR (neat) 3050, 2990, 2950, 2890, 1575, 1425, 1240 cm^{-1}; mass spectrum m/e (% rel. int.) 206 (13), 191 (100), 179 (13), 175 (10), 145 (14), 88 (22), 59 (19), calculated for $C_{11}H_{18}Si_2$ 206.094711, measured 206.09436.

1,1,3,3-tetramethyl-1,3-disilaindane **157** (21% yield) The NMR matches that reported by Chernyshev *et al*. (200): NMR (CCl_4) δ -0.05 (s, 2H), 0.30 (s, 12H), 7.10-7.56 (m, 4H); IR (neat) 3045, 2960, 2900, 1400, 1245, 1115, 980, 840, 780; mass spectrum m/e (% rel. int.) 206 (50), 191 (100), 163 (34), 145 (53), 131 (25), 105 (18), 73 (25), 59 (34), calculated for $C_{11}H_{18}Si_2$ 206.094711, measured 206.09436.

Synthesis of benzylbromide-d_2

A three-necked round bottom flask was fitted with a reflux condenser, drying tube, a pressure equalized addition funnel with a nitrogen inlet. The apparatus was flame dried and flushed with nitrogen. The apparatus was charged with 1.50 g (0.0356 mol) of lithiumaluminumdeuteride and 50 mL dry ether. To this stirring mixture was added 5.80 g (0.0475 mol) of benzoic acid in 30 mL of dry ether, at a rate sufficient to maintain reflux. After refluxing for 18 hours, the following sequence of solutions was added with stirring: 1.5 ml of water; 4.5 ml of 15% sodium hydroxide; and 1.5 ml of water. The precipitated salts were filtered and the filtrate washed with 5% sodium bicarbonate and water. Drying with sodium sulfate and removing solvent furnished 4.7146 g of $PhDC_2OH$ (90%): NMR (CCl_4) δ 3.43 (broad s, OH, absent with D_2O added), 7.19 (s, 5H), no benzylic protons were observable by NMR.

A three-necked round-bottom flask was fitted with a condenser and pressure equalized addition funnel. The flask was charged with 4.7146 g (0.04286 mol) of $PhCD_2OH$ in 60 mL of carbon tetrachloride. To this stirring solution was added 7.66 g (0.0214 mol) of phosphorustribromide in 30 mL of carbontetrachloride over a 1 hour period. After stirring for several hours the organic solution was washed with 5% sodium bicarbonate water and dried with sodium sulfate. Following solvent removal, the residue was distilled at 64-66°C (.01 torr) to give 6.5545 g (88%) of $PhCD_2Br$: NMR (CCl_4) δ 7.09 (s), no other protons could be seen; mass spectrum m/e (% rel. int.) 174 (.2), 172 (.2), 93 (95), 74 (61), 59 (100). There was 100% deuterium incorporation in the product.

Synthesis of 155-d_2

Compound 155-d_2 was synthesized according to the procedure described for 155 using $PhCD_2Br$ in place of benzylchloride. The following quantities were used: 2.50 gms (0.0145 mol) of $PhCD_2Br$; 0.5 g (0.02 mol) of magnesium; 2.40 g (0.0129 mol) of 1,2-dichloro-1,2,2-tetramethyldisilane; and 20 mL (0.016 mol) of 0.8 M allylbromide. Compound 155-d_2 was isolated by preparative gas chromatography: NMR: (CCl_4) δ 0.01 (s, 6H), 0.05 (s, 6H), 1.55 (d, 2H, J = 8 Hz), 4.58-6.07 (m, 3H), 7.05 (center of aromatic m, 5H); mass spectrum 250 (1), 209 (60), 193 (13), 157 (15), 129 (33), 122 (30), 121 (18), 73 (100), 59 (58). The percent deuterium incorporation was calculated using the method of Bieman (145) and values of 0% 155-d_0, 2.8% 155-d_1 and 97.2% 155-d_2 were obtained. The p-allyl ion was used these calculations. In the undeuterated compound, the relative intensities were 207 (1.00), 208 (.1987) and 209 (.0827). In the deuterated sample, the intensities were 208 (608), 209 (20,800), 210 (4,408) and 211 (1724).

Vacuum pyrolysis of 155-d_2 (97.2%)

The vacuum pyrolysis of 155-d_2 was conducted as described for 155. Distillation of 155-d_2 (25°C, 1×10^{-3} torr) through a quartz tube packed with quartz chips and heated at 800°C furnished a yellow oil (collected in a liquid nitrogen trap). The GC trace of the pyrolysate was identical to that of the 155 system. Analysis of the two disilaindanes, 156 and 157, by NMR showed no proton incorporation into the ring system. Analysis of the products by GCMS furnished the following values for deuterium incorporation in the products.

3,3,5,5-tetramethyl-3,5-disilacyclopentene 153 This product was formed with almost total loss of the deuterium label, indicating loss of $PhCD_2$ radical. Analysis according to the method of Bieman (145) furnished the following: 153-d_0 (95.5%); 153-d_1 (2.0%) and 153-d_2 (2.5%). The p-CH_3 peak was used for this calculation. In the undeuterated compound the relative intensities were 141 (1.00), 142 (.1649) and 143 (.0731). In the product, the actual intensities were 141 (35136), 142 (6552) and 143 (474).

1,1,2,2-tetramethyl-1,2-disilaindane 156 The percent dueterium incorporation was calculated as above on the parent ion to give the following percent deuterium incorporations: 156-d_0 (0%), 156-d_1 (4.9%) and 156-d_2 (95.1%). In the undeuterated sample the relative intensities were 206 (1.00), 207 (.25) and 208 (.09). In the deuterated sample, the intensities were 207 (4,000), 208 (77952), 209 (17472) and 210 (6840).

1,1,3,3-tetramethyl-1,3-disilaindane 157 The percent deuterium incorporation was calculated and values of 157-d_0 (0%), 157-d_1 (7.0%) and 157-d_2 (93.0%) were obtained. In the undeuterated sample, the relative intensities were 206 (1.00), 207 (.25) and 208 (.09). In the product, the intensities were 207 (1960), 208 (25920), 209 (6088) and 210 (2308).

Synthesis to 1,2-dibenzyl-1,1,2,2-tetramethyldisilane (201)

A two-necked round bottom flask was equipped with a condenser, drying tube, addition funnel and nitrogen inlet. The apparatus was flame dried and flushed with nitrogen. The flask was charged with 2.45 g (0.101 mol) of magnesium turnings and 150 mL of dry ether. Benzylbromide (14.38 g, 0.0841 mol) in 30 mL dry ether was added at a rate sufficient to maintain reflux. This solution was stirred at room temperature for 2 hours, followed by the addition of 7.14 g (0.0382 mol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane in 30 mL of ether. The mixture was refluxed for 2 days, then cooled to -23°C (CCl_4/Dry Ice) and 10% ammonium chloride was added. The two layers were separated and the organic solution washed with water and dried with magnesium sulfate. Solvent removal furnished crystals which were recrystallized from acetone to give 5.70 g of 1,2-dibenzyl-1,1,2,2-tetramethyldisilane (63%), m.p. 40-1°C: NMR (CCl_4) δ -0.03 (s, 12H), 2.04 (s, 4H), 6.75-7.30 (m, 10H); mass spectrum m/e (% rel. int.) 283 (.5), 207 (100), 149 (29), 121 (73), 91 (48), 73 (78), 59 (20).

Pyrolysis of 1,2-dibenzyl-1,1,2,2-tetramethyldisilane

A vacuum pyrolysis of 1,2-dibenzyl-1,1,2,2-tetramethyldisilane was done by distilling it (40°C, 8 x 10^{-6} torr) through a quartz tube packed with quartz chips and heated at 800°C. The pyrolysate was collected in a trap cooled with liquid nitrogen. Analysis of the pyrolysate by GCMS showed that the expected 1,2- and 1,3-disilaindanes **156** and **157** were formed along with starting material. Compounds **156** and **157** were isolated by preparative gas chromatography on a 6' 30% SE 30 column. All spectra properties matched those for these compounds produced from **155**.

Synthesis of Nonadeuterotrimethylallylsilane, **154**-d_9

Nonadeuterotrimethylchlorosilane was purchased from Merck and Co., Inc. in 99% isotopic purity. A two-necked round-bottom flask was equipped with a condenser, drying tube and septum inlet. The apparatus was flame dried and flushed with nitrogen. The flask was charged with 0.83 g (0.034 mol) of magnesium and 40 mL dry ether. A solution of 1.0 g (0.0085 mol) of nonadeuterotrimethylchlorosilane in 5 mL of dry ether was added. To this stirring solution was added 2.06 g (0.0170 mol) of allylbromide in 10 mL of ether. The reaction mixture was stirred at room temperature for 7 hours followed by cooling to -23°C (CCl_4/Dry Ice) and quenching the excess Grignard with 10% ammonium chloride. The two layers were separated and the organic solution washed with water and dried with sodium sulfate. The ether was distilled at 40°C; and the nonadeuterotrimethylallylsilane distilled through a short vigreux column 80°C (b.p. 85-6°C) giving 0.603 g (57.6%). For run 2, the above quantities were doubled, all else remained the same furnishing 1.2158 g (58.0%) of nonadeuterotrimethylallylsilane: NMR (CCl_4) δ 4.56-6.11 (vinyl m, matches that of trimethylallylsilane). The deuterium incorporation was determined by the method of Bieman (145) and values of **54**-d_7 (1.6%), **54**-d_9 (98.4%) and **54**-d_6 (0.8%), **54**-d_8 (3.0%) and **54**-d_9 (96.2%) were obtained in run 1 and run 2 respectively. See Table 8 for the ion intensities used for these calculations.

Pyrolysis of nonadeuterotrimethylallylsilane, **54**-d_9

Run 1 Compound **54**-d_9 was slowly dripped into a vertical quartz tube packed with quartz chips and heated at 630°C using nitrogen as a carrier gas with a flow rate of 30 mL/min. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 60% mass recovery. Analysis of recovered **54** and the trimethylvinylsilane **51** was done by GCMS. See Table 9 and Table 10 for the percent deuterium incorporation and the actual mass spectral intensities. Isolation of **51** was attempted by preparative gas chromatography on a freshly packed 16' 20% SE 30 column: 300 MHz NMR (C_6D_6) δ 0.04-0.01 (m, 1H), 0.40 (s, 1.25H), 5.60-6.51 (m, 3.13H, vinyl ABC pattern). The multiplet at δ 0.04-0.01 represents partial proton incorporation while the singlet at δ 0.40 is an impurity, presumably from column bleed. The methyl protons in trimethylallylsilane absorbs at δ 0.07.

Run 2 The flow pyrolysis in run 2 was conducted as in run 1. The pyrolysate represented an 84.7% mass recovery. The GCMS analyses of both recovered **54** and **51** are presented in Table 9 and Table 10 respectively. Isolation of **51** was accomplished on an aged 20' 20% SE 30 column:

300 MHz ^{1}H NMR (CCl_4) δ 0.04-0.10 (m, 1H), 5.60-6.51 (m, 4.3H, vinyl ABC pattern); 300 MHz ^{2}H NMR (CCl_4) δ 0.0 (s, 15 D) 5.53-5.84 (m, 1 D).

Synthesis of 1-allylpentamethyldisilane 169

A two-necked round-bottom flask was equipped with a condenser, drying tube and septum inlet. The apparatus was flame dried and flushed with nitrogen. The flask was charged with 4.35 g (0.0261 mol) of chloropentamethyldisilane in 40 mL dry ether. To this stirring solution was added 35 mL (0.028 mol) of 0.8 M allylmagnesium bromide. After stirring for 2 hours the reaction mixture was cooled to -23°C (CCl_4/Dry Ice) and 10% ammonium chloride was added. The two layers were separated and the organic solution washed with water and dried with sodium sulfate. After solvent removal, a distillation was done at 80°C (55 torr) to give 3.19 g (71.4%) of 169: NMR (CCl_4) δ 0.00 (s, 6H), 0.03 (s, 9H), 1.50 (d, 2H, J = 8 Hz), 4.55-6.11 (m, 3H); IR (neat) 3080, 2950, 2895, 1625, 14, 1385, 1240, 1145 cm^{-1}; mass spectrum m/e (% rel. int.) 172 (6), 131 (100), 99 (15), 98 (11), 74 (16), 73 (96), 59 (37), calculated for $C_8H_{20}Si_2$ 172.11036, measured 172.11004.

Vacuum pyrolysis of 1-allylpentamethyldisilane 169

Compound 169 was distilled (25°C, 1×10^{-3} torr) through a horizontal quartz tube packed with quartz chips and heated at 830°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 62.3% mass recovery. The products were isolated by preparative gas chromatography on a 12' 15% SE 30 column and were identified as trimethylvinylsilane 51 (1.6%), trimethylallylsilane 54 (4.5%), 1,1,3-trimethyl-1,3-disilacyclobutane 47 (17.8%) and 1,1,3,3-tetramethyl-1,3-disilacyclopentene 153 (10.3%). The identification of these products was upon direct comparison of their ^{1}H NMR and mass spectra with authentic samples (in the case of 51, 54 and 153) and with that reported by Conlin and Gaspar (53) for 47: NMR (CCl_4) δ -0.12 (m, 4H), 0.06 (s, 6H), 0.12 (d, 3H, J = 4 Hz, collapses to a singlet with hν at 4.43), 4.43 (m, 1H, SiH, collapses to a quartet, J = 4 Hz with hν at -0.12).

Synthesis of 1-benzylpentamethyldisilane

A two-necked round bottom flask was equipped with a condenser, drying tube and a septum inlet. The apparatus was flame dried and flushed with nitrogen. The flask was charged with 2.4 g (0.058 mol) of magnesium turnings in 100 mL of dry ether. To this stirring mixture was added 4.4 g (0.035 mol) of benzylchloride. After stirring for 2 hours at room temperature the reaction was cooled to -23°C and 10% ammonium chloride was slowly added. The two layers were separated and the organic solution washed with water and dried with magnesium sulfate. After solvent removal a distillation was done at 85°C/.1 torr to give 5.33 g (80%) of benzylpentamethyldisilane: NMR (CCl_4) δ 0.00 (s, 6H), 0.02 (s, 9H), 2.06 (s, 2H), 6.95 (center of aromatic m, 5H); mass spectrum m/e (% rel. int.) 222 (13), 149 (45), 133 (12), 132 (18), 131 (100), 121 (32), 73 (97), 59 (15) calculated for $C_{12}H_{22}Si_2$ 222.12601, measured 222.12625.

Vacuum pyrolysis of benzylpentamethyldisilane

Benzylpentamethyldisilane was distilled (25°C, 1 x 10^{-4} torr) through a quartz tube packed with quartz chips and heated at 850-860°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 50% mass recovery. The products were isolated by preparative gas chromatography and were identified by matching their ^1H NMR and mass spectra with those of authentic samples. The products were 1,1,3-trimethyl-1,3-disilacyclobutane 47 (8%) (53), dimethylbenzylsilane (5%), trimethylbenzylsilane (10%), 2-methyl-2-silaindane (<2%), toluene and ethylbenzene.

Trimethylbenzylsilane (202) NMR (CCl_4) δ 0.03 (s, 9H), 2.08 (s, 2H), 6.68-7.10 (m, 5H); mass spectrum m/e (% rel. int.) 164 (8), 121 (7), 91 (5), 73 (100), 59 (4).

Dimethylbenzylsilane (101) NMR (CCl_4) δ 0.10 (d, 6H, J = 4 Hz collapses to s with $h\nu$ at 3.84), 2.06 (d, 2H, J = 3 Hz, collapses to s with $h\nu$ a 3.84), 3.84 (m, 1H), 6.79-7.18 (m, 5H); mass spectrum m/e (% rel. int.) 150 (13), 135 (16), 91 (8), 58 (100).

2-Methyl-2-silaindane This compound was isolated as a mixture. The other compound was unidentified. The NMR of 2-methyl-2-silaindane was deciphered: NMR (CCl_4)δ 0.25 (d, 3H, J = 4 Hz, collapses to a s with $h\nu$ at 4.31), 2.00 (d of d, 2H, J = 16 Hz J' = 3 Hz, collapses to d, J = 16 Hz with $h\nu$ at 4.31), 2.11 (d of d, 2H, J = 16 Hz, J' = 3 Hz, collapses to d, J = 16 Hz with $h\nu$ at 4.31), 4.31 (m, 1H), 6.75-7.23 (m, 5H); mass spectra m/e (% rel. int.) 148 (100), 133 (80), 105 (49), 91 (56).

Vacuum pyrolysis of decamethyltetrasilane 171

Compound 171 was synthesized according to the method of Kumada and Ishikawa (203). A vacuum pyrolysis of 1.1571 g (4.416 mmol) of 171 was done by distilling it (0°C, 1 x 10^{-4} torr) through a horizontal quartz tube heated at 840°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 82% mass recovery. The products were isolated by preparative gas chromatography on an 8' 20% DC550 column and were identified as trimethylsilane (5%), pentamethyldisilane, hexamethyldisilane 1,1,3-trimethyl-1,3-disilacyclobutane **47** (21%),and a mixture of *cis*- and *trans*-**172**. The combined yield of pentamethyldisilane and hexamethyldisilane was 10%. The identification of the first three products listed was based upon direct comparison of there ^{1}H NMR and mass spectra with those of authentic samples. The ^{1}H NMR of **47** matched that reported by Conlin and Gaspar (53). The isomeric mixture **172** had the following spectral properties: NMR ($CDCl_3$), δ -0.35 to -0.06 (m, 4H, partially collapses with $h\nu$ at ca. 4.0), 0.07 (s), 0.14 (s), 0.20 (d, J = 2 Hz, collapses to s with $h\nu$ at ca. 4.0), the previous four peaks represent 15H, 3.77 (q, J = 5 Hz), 4.09 (m), these two areas represent 1H; mass spectrum m/e (% rel. int.) 188 (25), 173 (100), 129 (25), 73 (58), 59 (42), calculated for $C_7H_{20}Si_3$ 188.08733, measured 188.08783.

Vacuum pyrolysis of octamethyltrisilane

Octamethyltrisilane was prepared according to the method of Kumada and Ishikawa (203). Octamethyltrisilane was distilled (25°C, 1 x 10^{-3} torr) through a quartz tube packed with quartz chips and heated at 860°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 63% mass recovery. The products were isolated by preparative gas chromatography (8' 20% DC550 column) and were identified as trimethylsilane, hexamethyldisilane (22%) and 1,1,3-trimethyl-1,3-

disilacyclobutane 47 (20%). The ^{1}H NMR and mass spectra for 47 matched those reported by Conlin and Gaspar (53). The first two products were identified by comparison with authentic samples.

Synthesis of (trimethylstannyl)pentamethyldisilane 173

A round-bottom flask was flame dried, flushed with nitrogen and charged with 1.53 g (0.00768 mol) of trimethylchlorostanane, 0.2 g (0.03 mol) of lithium wire (cut into small pieces) and 50 ml of dry THF. After stirring at room temperature for several hours, the dark green solution was cooled to 0°C and 1.28 g (0.00768 mol) of chloropentamethyldisilane were added. After warming to room temperature and stirring 1 hour, the organic solution was washed with water and dried with magnesium sulfate. The residue contained hexamethyldistanane and the desired product which was isolated by preparative gas chromatography on a 6' 30% SE 30 column to give 0.4048 g (18%) of 173: NMR (CCl_4) δ 0.02 (s, 9 Sn Me), 0.05 (s, 9 Si Me), 0.2 (s, 6H); mass spectrum m/e (% rel. int.) p-CH_3 281 (6), 280 (2), 279 (4), 278 (2), 277 (2), 135 (11), 133 (11), 131 (29), 73 (100).

Vacuum pyrolysis of 173

Compound 173 (.4089 g (0.001388 mol) was distilled (25°C, 10^{-4} torr) through a horizontal quartz tube heated at 840°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 40% mass recovery. There was polymer deposited on the quartz tube. Analysis of the pyrolysate by GCMS and ^{1}H NMR showed that only hexamethyldisilane 0.1668 g (82.3%) was present.

Synthesis of 1-allylheptamethyltrisilane 175

A two-necked round-bottom flask was equipped with a condenser, drying tube and pressure equalized addition funnel. The apparatus was flame dried and flushed with nitrogen. The flask was charged with 1.1 g (0.045 mol) of magnesium turnings and 100 mL dry ether. To this stirring mixture was added a mixture of 5.2360 g (0.04326 mol) of allylbromide and 8.8290 g (0.03933 mol) of 1-chloroheptamethyltrisilane (204) in 20 mL of dry ether. The mixture was stirred for several hours at room temperature, then the mixture was cooled to -23°C (CCl_4/Dry Ice) and 10% ammonium chloride was added. The two phases were separated and the organic solution was washed with water and dried with magnesium sulfate. After solvent removal, the residue was distilled at 45°C/.1 torr to give 5.7277 g (63.3%) of 175: NMR (CCl_4) δ 0.17 (broad s, 21H, SiMe), 1.66 (d, 2H, J = 8 Hz), 4.66-5.05 (m, 2H, $CH{=}C\underline{H}_2$), 5.45-6.27 (m, 1H, $C\underline{H}{=}CH_2$); mass spectrum m/e (% rel. int.) 230 (16), 191 (12), 190 (21), 189 (92), 157 (40), 141 (22), 131 (47), 129 (22), 116 (29), 115 (20), 73 (100), 59 (27), 44 (17), calculated for $C_{10}H_{26}Si_3$ 230.13424, measured 230.13456.

Vacuum pyrolysis of 1-allylheptamethyltrisilane 175

Compound 175 was distilled (25°C, 1×10^{-4} torr) through a horizonal quartz tube packed with quartz chips and heated at 740°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 76.8% mass recovery. The GC trace of the crude pyrolysate showed two peaks, one of which was unreacted 175. These compounds were isolated by preparative chromatography (8' 20% DC550 column). The product was identified as 172 by comparing the ^1H NMR and mass spectra with those of 172 produced in the pyrolysis of 171.

Synthesis of 2-allylheptamethyltrisilane

A two-necked round-bottom flask was equipped with a condenser, addition funnel and drying tube. The apparatus was flame dried and flushed with nitrogen. The flask was charged with 5.5 g (0.025 mol) of 2-chloroheptamethyltrisilane (204) in 50 mL of dry ether. To this stirring was added 36 mL (0.03 mol) of 0.8 M allylmagnesium bromide. Following stirring for 4 hours, the reaction mixture was cooled to -23°C (CCl_4/Dry Ice) and 10% ammonium chloride was added. The two layers were separated and the organic solution washed with water and dried with magnesium sulfate. After solvent removal, the residue was distilled at 60°C/0.1 torr to afford 2.57 g (44.7%) of 2-allylheptamethyltrisilane: NMR (CCl_4) δ 0.00 (s, 21H), 1.54 (d, J = 8 Hz), 4.48-6.00 (m, 3H); mass spectrum m/e (% rel. int.) 230 (5), 189 (36), 141 (21), 131 (31), 129 (28), 73 (100), 59 (24) calculated for $C_{10}H_{26}Si_3$ 230.13424, measured 230.13404.

Vacuum pyrolysis of 2-allylheptamethyltrisilane

A vacuum pyrolysis was performed by distilling 2-allylheptamethyltrisilane (25°C, 1×10^{-4} torr) through a quartz tube packed with quartz chips and heated a 800-810°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 56% mass recovery. Analysis of the pyrolysate by GCMS showed that the major product corresponded to the starting material minus 42 (propene). This product was not identified (see Results and Discussion).

Attempted coupling of 1-chloro-1-methyl-1-silacyclobutane 177 with trimethylsilyl anion generated from hexamethyldisilane and KH/HMPA (158)

To a stirring solution of 5.32 g (0.066 mol) of 50% KH in mineral oil and 20 mL of dry HMPA were added 4.8 g (0.0329 mol) of hexamethyldisilane over a period of 2 minutes at room temperature. The solution turned a deep yellow. After stirring 30 minutes an anhydrous filtration was performed. To the filtrate was added 4.0 g (0.033 mol) of 1-chloro-1-methyl-1-silacyclobutane. The yellow color was immediately discharged. The reaction mixture was poured into pentane, washed with water, and dried with magnesium sulfate. Examination of the crude reaction mixture showed that the desired coupling did not occur. The sole volatile product was the disiloxane of 177.

Attempted coupling of 177 with trimethylsilylanion generated from hexamethyldisilane and methyllithium (159)

Trimethylsilyllithium (0.028 mol) was generated from methyllithium and hexamethyldisiloxane in HMPA at 0°C according to the method of Still (159). The HMPA solution of the silyl anion was added to 3.04 g (0.028 mol) of 177 at 0°C. After stirring for 2 hours the reaction mixture was poured into hexane, washed with water and the organic solution was dried with magnesium sulfate. After solvent removal, analysis of the mixture by GCMS showed that none of the desired product had formed.

Attempted coupling of 177 with trimethylchlorosilane using lithium wire

A round-bottom flask was equipped with a condenser, drying tube and mechanical stirrer. The flask was charged with .058 g (.0084 mol) of Li wire in 50 mL of THF, 0.456 g (0.0042 mol) of trimethylchlorosilane and 0.506 g (0.00420 mol) of 177. This was stirred for 3 days at room temperature. The excess Li was filtered and the filtrate poured into hexane and washed with water. The organic solution was dried with sodium sulfate, and the solvent was removed. Examination of the residue by GCMS showed that the desired coupling did not occur. The only product was the disiloxane of 177.

Attempt to synthesize 176 via Grignard coupling

A round-bottomed flask was equipped with a condenser drying tube and septum inlet. The apparatus was flame dried and flushed with nitrogen. The flask was charged with 5.0 g (0.0268 mol) of 1,1-dichloro-1,3,3,3-tetramethyldisilane, 1.95 g (0.0803 mol) of magnesium powder and 200 mL of dry ether. To this stirring solution was added 3.02 g (0.0268 mol) of 1,3-dichloropropane over a 3 hour period. The reaction was stirred for 3 days. The magnesium powder was filtered and the filtrate washed with water and dried with magnesium sulfate. After solvent removal, examination of the residue by GCMS showed the presence of high molecular weight siloxanes, and no 176.

Synthesis of 1-trimethylsilyl-1-methyl-1-silacyclobutane 176

To a stirring solution of 0.90 g (0.0083 mol) of trimethylchlorosilane, 0.4 g (0.017 mol) of 30% Li dispersion (1% Na) in mineral oil and

25 ml of dry THF was added 1.0 g (.0083 mol) of 177. After stirring for 24 hours a trap-to-trap distillation of the volatiles was done at 50 torr. This was done because 176 undergoes air oxidation to 178. Compound 176 was isolated by preparative gas chromatography (8' 20% DC550 column) giving 0.1697 g (12.9%) of this elusive product. An 11% yield was obtained from a GC yield on the crude reaction mixture: NMR (CCl_4) δ 0.12 (s, 9H), 0.32 (s, 3H), 0.75-1.12 (m, 4H), 1.93-2.43 (m, 2H); mass spectrum m/e (% rel. int.) 158 (18), 143 (17), 130 (32), 117 (24), 116 (30), 115 (94), 73 (100), 59 (37), calculated for $C_7H_{18}Si_2$ 158.09471, measured 158.09458.

Vacuum pyrolysis of 176

Compound 176 was distilled through a quartz tube (25°, 1×10^{-4} torr) packed with quartz chips and heated at 840°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 82% mass recovery. Examination of the pyrolysate by ^1H NMR and GCMS clearly showed that 1,1,3-trimethyl-1,3-disilacyclobutane 47 (98-100%) was the only product in this thermolysis. The ^1H NMR and mass spectra of 47 matched those reported by Conlin and Gaspar (53).

LAH reduction of 1-chloro-1-methyl-1-silacyclohexadiene

A round-bottom flask was flushed with nitrogen and charged with 0.365 g (0.00960 mol) of lithium aluminum hydride and 20 mL of anhydrous ether. This was cooled to -23°C (CCl_4/Dry Ice). To this stirring solution was added 5.5182 g (0.03820 mol) of 1-chloro-1-methyl-1-silacyclohexadiene (166, 167). After stirring 3 hours at -23°C a trap-to-trap distillation of the volatiles was done. The distillate contained ether and the desired product. The ether was distilled and fractions were taken. The product was collected at 116-118°C; giving 1.40 g (33%) of 1-methyl-1-silacyclohexadiene: NMR (CCl_4) δ 0.20 (d, J = 4 Hz), collapses to s with hν a 4.16), 1.39-1.76 (m, 2H), 4.16 (q, 1H), 5.52-5.98 (m, 3H), 6.40-6.81 (m, 1H).

Synthesis of 7-methyl-7-sila-2,3-bis(trifluoromethyl)bicyclo[2.2.2]-octadiene, **180**

A thick-walled sealing tube was charged with 1.39 g (0.0126 mol) of 1-methyl-1-silacyclohexadiene. The tube was connected to a vacuum line and was degassed using the freeze-thaw method. Hexafluoro-2-butyne was condensed (-196°C) into the tube to a total volume three times that of the initial volume. The tube was sealed and allowed to stand at room temperature for 24 hours. The tube was opened and the excess hexafluoro-2-butyne allowed to evaporate. The residue was distilled, the fraction boiling at 58°C/0.01 torr was **180** (1.7272 g, 50%): NMR (CCl_4) δ 0.16 (d, 3H, J = 3 Hz, SiMe, collapses to s with hν at 3.80) 0.40-1.04 (m, 2H, $SiCH_2$, partially collapses with hν at 3.80), 3.60-3.92 (m, 2H, HSiCH, partially collapses with hν at 6.0), 3.98-4.35 (m, 1H, $CH_2\underline{CH}$, partially collapses with hν at 6.0), 5.74-6.38 (m, 2H, CH=CH); mass spectrum m/e (% rel. int.) 272 (1) 214 (18), 196 (100), 145 (37), calculated for $C_{10}H_{10}SiF_6$ 272.04561, measured 272.04520.

Vacuum pyrolysis of 180 at 750°C

Compound 180 was distilled (25°C, 1 x 10^{-4} torr) through a quartz tube packed with quartz chips and heated at 750°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 85.5% mass recovery. The two products were isolated by preparative gas chromatography on a 10' 10% OV101 column. The first product was identified as 1,2-bis(trifleuoromethyl)benzene 181 (84%) on the basis of its spectra: NMR (CCl_4) δ 7.86 (m); mass spectrum m/e (% rel. int.) 214 (73), 195 (69), 164 (28), 163 (11), 145 (100), 125 (19), 114 (9), 95 (18), 75 (23), 69 (26), 50 (11). The second product was identified as a mixture of cis- and trans-1,3-dimethyl-1,3-disilacyclobutane 33 (35%). The ^{1}H NMR and mass spectra of 33 matched those reported by Conlin and Gaspar (53): NMR (CCl_4) δ 0.19 (t, 4H, J = 4 Hz collapses to a s with hν at 4.75); 0.40 (d, 6H, J = 4 Hz collapses to s with h at 4.75) 4.75 (m, 1H); mass spectrum m/e (% rel. int.) 116 (77), 115 (21), 101 (100), 99 (22), 85 (11), 73 (46), 69 (18), 59 (46).

Vacuum pyrolysis of 180 at 550°C

Compound 180 was distilled (25°C, 1 x 10^{-4} torr) through a quartz tube packed with quartz chips and heated at 550°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 75% mass recovery. The two products were isolated by preparative gas chromatography and identified as 181 and 33 as described for the vacuum pyrolysis of 180 at 750°C (previous procedure).

Flow pyrolysis of 180 at 450°C

Compound 180 was slowly dripped through a verticle quartz tube packed with quartz chips and heated at 450°C. Nitrogen was used as a carrier gas at a flow rate of 30 mL/minute. The pyrolyate was collected in a trap cooled with liquid nitrogen and represented an 83.5% mass recovery. The products were isolated by preparative gas chromatography on a 10' 10% OV101 column and identified as 1,2-bis(trifluoromethyl)-benzene 181 (90%) and *cis*- and *trans*-1,3-dimethyl-1,3-disilacyclobutane 33 (33%). The identification of these products was done as described in the vacuum pyrolyses of 180 (previous two procedures).

Copyrolysis of 180 and 2,3-dimethyl-1,3-butadiene

A solution consisting of 0.1239 g (0.4555 mmol) of 180 and 0.19 g (2.3 mmol) of 2,3-dimethyl-1,3-butadiene was slowly dripped into a verticle quartz tube packed with quartz chips and heated at 450°C. A continuous nitrogen flow of 30 mL/min was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. The three products were isolated by preparative gas chromatography and identified as 1,2-bis(trifluoromethyl)orthoxylene 181 (74%), 1,3,4-trimethyl-1-silacyclohex-3-ene 182 (23%) and 183 (5%). Compound 181 was identified by comparison of its ^{1}H NMR and mass spectra with those of an authentic sample. Compounds 182 and 183 were identified on the basis of their ^{1}H NMR, low and high resolution mass spectra which are tabulated below.

Compound 182 NMR (CCl_4) δ 0.05 (d, 3H, J = 4 Hz, collapses to s with hν at 3.80), 0.20-1.00 (m, 2H partially decouples with hν at 3.80

and 2.30), 1.22 (broad s, 2H), 165 (broad s, 6H), 2.30 (t, 2H, 6 Hz, collapses to broad s with hν at 0.40), 3.67-3.90 (m, SiH); mass spectrum m/e (% rel. int.) 140 (49), 125 (57), 123 (11), 112 (26), 111 (43), 99 (15), 98 (59), 97 (100), 85 (32), 84 (18), 83 (43), 91 (13), 73 (16), 71 (31), 67 (21), 59 (84), 58 (42), calculated for $C_8H_{16}Si$ 140.10213, measured 140.10238.

Compound 183 NMR (CCl_4) δ 0.06 (d, 6H, J = 4 Hz, collapses to a s with hν at 3.89), 1.78 (d, 2H, J = 4 Hz) collapses to a s with hν at 3.89), 1.88 (broad s, 3H), 3.89 (m, SiH), 4.68-5.09 (m, 4H); mass spectrum m/e (% rel. int.) 140 (7), 139 (.6), 125 (40), 97 (17), 85 (13), 83 (12), 73 (10), 72 (10), 59 (100), 58 (20), calculated for $C_8H_{16}Si$ 140.10213, measured 140.10241.

Copyrolysis of 180 and triethylsilane

A solution consisting of 0.1040 g (0.3823 mmol) of 180 and 0.30 g (2.6 mmol) of triethylsilane was slowly dripped into a verticle quartz tube packed with quartz chips and heated at 450°C. Nitrogen (30 mL/min) was used to sweep the pyrotysate into a trap cooled with liquid nitrogen. Analysis of the pyrolysate by GCMS showed that only 1,2-bis(trifluoromethyl)benzene 181 and cis- and trans-1,3-dimethyl-1,3-butadiene were present, no 3,3,3-triethyl-1,1-dimethyldisilane was observed.

Attempt to synthesize 188 via a diazo-transfer reaction

The apparatus employed consisted of two three-necked round-bottom flasks connected vertically, with a glass-wool plug and stopcock between them. The upper flask was equipped with a nitrogen inlet, overhead stirrer, a septum inlet, and a surrounding cooling bath. The lower flask was equipped with a septum inlet and magnetic stirrer. The apparatus was flame dried and flushed with nitrogen. A 30% dispersion of lithium (0.7 g, 0.003 mol) was placed in the top flask and washed three times with ether. Ether (50 mL) was finally added and the mixture cooled to -23°C (CCl_4/ Dry Ice). Pentamethyl(chloromethyl)disilane (139) (2.6625 g, 0.01475 mol) was added via syringe. The reaction was stirred at -23°C for 4 hours, then at room temperature for 1 day. At this time the solution was yellow and contained some purple-red salts. This solution was added through the glass-wool plug to a stirring solution of 2.7 g (0.014 mol) of tosyl azide in 20 mL of dry ether at 0°C. This mixture was stirred for 4 hours at 0°C and then 24 hours at room temperature. The precipitated salts were filtered and the filtrate washed with slightly alkaline water and dried with magnesium sulfate. After removal of the ether, examination of the residue by ^1H-NMR showed the presence of tosyl azide, but none of the desired product.

Synthesis of (iodomethyl)pentamethyldisilane

To a stirring solution of 0.066 mol of thioanisole anion [from thioanisole, n-butyllithium and DABCO (175)] in dry THF at 0°C were added 11.0 g (0.066 mol) of chloropentamethyldisilane (192). The mixture was warmed to room temperature and stirred for 1 day. The organic solution was poured into hexane, washed with water and dried with magnesium sulfate. After solvent removal, only one product was present by ^1H-NMR which was identified as (phenylthiomethyl)pentamethyldisilane (16.0 g, 95%): NMR (CCl_4) δ 0.08 (s, 9H), 0.13 (s, 6H), 2.15 (s, 2H), 7.18 (s, 5H).

To a stirring solution of 16.0 g (0.063 mol) of (phenylthiomethyl)-pentamethyldisilane was added 9.4 g (0.065 mol) of sodium chloride, 9.2 g (0.065 mol) of methyliodide and 80 mL of dry DMF. The reaction mixture was heated (oil bath 75°C) for 18 hours. After cooling to room temperature, the solution was poured into hexane, washed with water and dried with magnesium sulfate. After solvent removal, the residue was eluted through a silica gel column with hexane giving 9.44 g (55%) of (iodomethyl)-pentamethyldisilane: NMR (CCl_4) δ 0.12 (s, 9H), 0.15 (s, 6H), 2.10 (s, 2H); mass spectrum m/e (% rel. int.) 257 (.3), 145 (18), 85 (17), 73 (100), 59 (11); calculated for $C_5H_{14}Si_2I$ (p-CH_3) 256.96788, measured 256.96807.

Attempt to synthesize 188 via a diazo-transfer reaction

The apparatus employed consisted of two three-necked round bottom flasks connected vertically, with a glass-wool plug and stopcock between them. The upper flask was equipped with a nitrogen inlet, overhead stirrer, a septum inlet and a surrounding cooling bath. The lower flask was equipped with a septum inlet and magnetic stirrer. The apparatus was flame dried and flushed with nitrogen. A 30% dispersion of lithium (0.67 g, 0.029 mol) was placed in the upper flask and washed three times with ether. Ether (40 mL) was finally added and the mixture cooled to -23°C (CCl_4/Dry Ice) and (iodomethyl)pentamethyldisilane (2.00 g, 0.00735 mol) was added via syringe. After stirring 2 hours at -23°C this solution was added through the glass-wool plug to a stirring solution of 1.44 g

(0.00735 mol) of tosyl azide in ether at 0°C. After stirring for 5 hours at 0°C, the reaction mixture was warmed to room temperature and stirred for 18 hours. The salts were filtered and the filtrate washed with slightly alkaline water and dried with magnesium sulfate. Examination of the residue, following solvent removal, showed the presence of tosyl azide and unreacted (iodomethyl)pentamethyldisilane. Attempts to generate the anion at higher temperatures (>0°C) resulted in coupling to give 1,2-bis(pentamethyldisilanyl)ethane.

Attempt to couple 191 with trimethylchlorosilane

To a stirring solution of 0.04 g (2 mmol) of 30% lithium dispersion in mineral oil in 25 mL of dry THF was added 0.22 g (2.0 mmol) of trimethylchlorosilane. After stirring for 5 minutes, 0.287 g (1.99 mmol) of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene. After stirring 1 hour the lithium was consumed. The reaction mixture was washed with water and dried with magnesium sulfate. Following solvent removal, examination of the residue by ^1H NMR showed that none of the desired product was present (no olefinic protons).

Copyrolysis of cyclopentadiene and 2-chloroheptamethyltrisilane

A solution consisting of a 0.65 g of 2-chloroheptamethyltrisilane (204) and cyclopentadiene (1:4 by volume) was slowly dripped into a vertical quartz tube packed with quartz chips and heated at 620°C. The pryolysate was swept into a trap cooled with Dry Ice and 2-propanol. A trap-to-trap distillation removing the cyclopentadiene was done at 40 torr. Examination of the residue by GCMS showed the presence of unreacted 2-chloroheptamethyltrisilane and trimethylsilylcyclopentadiene (a mixture of both isomers). These isomers were isolated by preparative gas chromatography and their ^{1}H NMR spectra compared with that of an authentic sample.

Synthesis of 194

The method employed for dichlorocarbene addition was that of Makoza (179). To a stirring solution of 0.0470 g (0.420 mmol) of 1,1-dimethyl-1-silacyclopent-3-ene, 0.50 g (0.420 mmol) of alcohol-free chloroform in 0.84 mL of 50% sodium hydroxide was added ca. 0.016 g of (triethyl)-benzylammonium chloride. Stirring was continued for 2 hours. The solution was poured into pentane washed with water and dried with sodium sulfate. Following the removal of solvent, the residue was passed through a silica gel column with hexane to give 194 (.3 g, 36%). The ^{1}H NMR of 194 matched that reported by Bertrand and coworkers (177).

Thermal decomposition of 194 in pyridine

Compound 194 (0.3 g, 0.15 mmol) was placed in an NMR tube and pyridine-d_5 was added to one-half the total volume. The NMR tube was placed in an oil bath and heated at 110°C for 40 minutes. After this period of time 194 could not be observed by ^{1}H NMR. The two products formed were 195 and 196 in a 1:1 ratio. The ^{1}H NMR of the mixture clearly matched those described for 195 and 196 (179). The methylene protons in 195 (δ 1.43, d, J = 6 Hz) and 196 (δ 1.80, d, J = 10 Hz) were used as a basis for the determination of the relative ratio.

Synthesis of 1-trimethylsilyl-1-methyl-1-silacyclopent-3-ene 198

A three-neck round-bottom flask was equipped with a condenser, drying tube and pressure equalized addition funnel. The flask was charged with 1.0 g (0.04 mol) of magnesium powder and 20 mL of dry THF. A solution of 1.7409 g (0.01392 mol) of cis-1,4-dichloro-2-butene, 2.5417 g (0.01360 mol) of 1,1-dichloro-1,2,2,2-tetramethyldisilane (205) in 30 mL of dry THF was added at 50°C. The reaction was stirred at 50°C for 24 hours. After cooling, the organic solution was poured into pentane and the salts and excess magnesium were filtered. The filtrate was washed with water and dried with magnesium sulfate. After solvent removal, the residue was distilled (100°C, 85 torr) to give 1.16 g (50%) of 198: NMR (CCl_4) δ 0.10 (s, 9H), 0.15 (s, 3H), 1.34 (broad s, 4H, sharpens with $h\nu$ a 5.73), 5.73 (broad s, 2H, sharpens with $h\nu$ at 1.34); mass spectrum m/e (% rel. int.) 170 (12), 156 (10), 155 (65), 117 (10), 116 (69), 101 (22), 97 (17), 96 (17), 95 (19), 73 (100), 59 (2) calculated for $C_8H_{18}Si_2$ 170.09471, measured 170.09475.

Synthesis of 199

Phenyl(dichlorobromomethyl)mercury was prepared as described by Seyferth and Lambert (180). A round-bottom flask was charged with 4.8138 g (0.0283 mol) of 198, 12.48 g (0.0283 mol) of phenyl(dichlorobromomethyl)mercury and 100 mL of dry benzene. This solution was refluxed for 2.5 hours. After cooling, hexane was added and the phenylmercuric chloride salts removed. The ^1H NMR of the residue (4.0 g) showed the presence of the desired dichlorocarbene-addition product 199 small amounts of 200 and 201. Compound 199 was identified as a mixture of syn and anti isomers: NMR (CCl_4) δ 0.10 (s), 0.16 (s) total area of these peaks 12H, 1.0 (m, 4H), 2.0 (m, 2H).

Synthesis of 1-methyl-1-trimethylsilyl-4-chloro-1-silacyclohexa-2,4-diene 200

A round-bottom flask was charged with 2.00 g of a mixture of 199, 200 and 201 (prepared as described in the previous procedure) and 25 mL of dry pyridine. After heating at 100°C for 3 hours the solution was cooled and hexane was added. The organic mixture was washed with water (to convert 201 to a disiloxane) and dried with magnesium sulfate. After solvent removal, the residue was distilled at 50°C/.1 torr to give 0.8117 g (26% from 198) of 200: NMR (CCl_4) δ 0.09 (s, 9Ha), 0.15 (s, 3Hb), 1.58 (d, 2Hcc', Jce = 6 Hz, collapses to s with hν at 5.95), 5.90 (d, 1Hd, Jdf = 14 Hz), 5.95 (t of d, 1He, Jef = 1 Hz, collapses to d with hν at 1.58, the left-hand side of this d of d overlaps the left hand side of the d centered at 5.90), 6.46 (d of d, 1Hf), Jde = 0 Hz; mass spectrum m/e (% rel. int.) 218 (.04), 216 (.16), 151 (2), 19 (4), 123 (40), 122 (28), 108 (15), 95 (18), 93 (31), 83 (11), 73 (100), 68 (11), 65 (10), 59 (15), calculated for $C_9H_{17}Si_2Cl$ 216.05574, measured 216.05560.

Synthesis of 202

Compound 200 (0.976 g, 4.5 mmol) was placed in a thick-walled sealing tube. The tube was attached to a vacuum line and degassed using the freeze-thaw method. Hexafluoro-2-butyne was condensed into the tube (-196°C) to three heated at 42°C for 20 hours. After opening the

the hexafluoro-2-butyne was allowed to evaporate to give 1.5226 g (89%) of 202 as a mixture of *syn* and *anti* isomers: NMR (CCl_4) δ 0.10 (broad s, 3Ha), 0.12 (s, 9Hb), 0.42-1.26 (m, 2Hcc'), 3.56 (d, 1Hd, Jdf = 7 Hz, collapses to s with hν at 5.92), 4.10 (m, 1He), 5.92 (d of d, 1Hf, Jfe = 2 Hz), mass spectrum m/e (% rel. int.) no parent ion seen 250 (11), 248 (34), 231 (19), 229 (37), 229 (37), 190 (38), 182 (13), 180 (19), 163 (15), 155 (12), 153 (13), 152 (17), 149 (33), 130 (39), 115 (93), 73 (100), calculated for $C_{10}H_8SiClF_6$ (p-$SiMe_3$) 304.99879, measure 304.99885.

Vacuum pyrolysis of 202

Compound 202 (.2982 g, 0.788 mmol) was distilled (25°C, 1 x 10^{-4} torr) was distilled through a quartz tube packed with quartz chips and heated at 700°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 82% mass recovery. The products were isolated by preparative gas chromatography and identified as 1,2-bis-(trifluoromethyl)-4-chlorobenzene 203 (76%) and 1,1,3-trimethyl-1,3-disilacyclobutane 47 (55%). Compound 47 was identified by comparison of its ^1H NMR and mass spectra with those of an authentic sample and with those reported by Conlin and Gaspar (53). Compound 203 was identified on the basis of the following: NMR (CCl_4) δ 7.63-8.03 (m); mass spectrum m/e (% rel. int.) 248 (100), 231 (19), 229 (62), 99 (17), 75 (45), 74 (32), 69 (45), calculated for $C_8H_3ClF_6$ 247.98276, measured 247.98261.

Copyrolysis of 202 with 2,3-dimethyl-1,3-butadiene

A solution consisting of 0.3243 g (0.857 mmol) of 202 and 0.4355 g (5.30 mmol) of 2,3-dimethyl-1,3-butadiene was slowly dripped into a verticle quartz tube packed with quartz chips and heated at 450°C. The pryolysate was swept into a trap cooled with liquid nitrogen. The products were isolated by preparative gas chromatography on a 6' 20% SE 30 column and were identified as 1,2-bis(trifluoromethyl)-4-chlorobenzene 203 (33%) and 1-trimethylsilylmetnyl-1,3,4-trimethyl-1-silacyclopent-3-ene 204 (58%). Compound 203 was identified by comparison of its ^1H NMR and mass spectra with those for 203 generated from the vacuum pyrolysis of 202 (see previous procedure). Compound 204 was identified on the basis of the following spectral data: NMR (CCl_4) δ -0.18 (s, 2H), 0.01 (s, 9H), 0.10 (s, 3H), 1.25 (broad s, 4H), 1.62 (broad s, 6H); mass spectrum m/e (% rel. int.) 212 (31), 197 (29), 156 (13), 155 (74), 141 (16), 131 (33), 131 (42), 129 (13), 115 (54), 99 (18), 97 (10), 85 (14), 83 (15), 73 (100), 59 (56) calculated for $C_{11}H_{24}Si_2$ 212.14166, measured 212.14154.

Synthesis of 207

A thick walled sealing tube was charged with 1.6257 g (0.0108 mmol) of 1-allyl-1-methyl-1-silacyclohexa-2,4-diene (181) and degassed. Hexafluoro-2-butyne was condensed (-196) into the tube to a total volume three times that of the diene. The tube was sealed and allowed to stand at room temperature for 24 hours. After evaporation of the excess hexafluoro-2-butyne, a light yellow oil remained. Distillation at 53-56°C at 0.1 torr afforded a 60% yield (2.0442 g) of 207: NMR (CCl_4) δ 0.08 (s, 3H, SiMe), 0.48 (d, 2H, J = 4 Hz, collapses to a s with hν at 4.15), 1.50 (d, 2H, J = 8 Hz, $C\underline{H}_2CH{=}CH_2$), 3.66 (d, 1H, J = 6 Hz, collapses to a broad s with hν at 6.10), 4.15 (m, 1H, collapses to a broad triplet with hν at 6.10, collapses to a doublet with hν at 0.48), 4.63-6.53 (5H, vinyl m); mass spectrum m/e (% rel. int.) 295 (1), 195 (100), 170 (15), 157 (11), 145 (18), 97 (31), 83 (34), 70 (19), calculated for $C_{12}H_{11}F_6Si$ (p-Me) 297.05343, measured 297.05476; calculated for $C_{10}H_{18}F_6Si$ (p-propene) 270.02996, measured 270.03902.

Vacuum pyrolysis of 207

The vacuum pyrolysis of 207 was carried out by evaporating (25°C, 1 x 10^{-4} torr) it through a horizontal quartz tube packed with quartz chips and heated at 520°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 93.5% mass recovery. Two products were isolated by preparative gas chromatography on a 10' 10% OV101 column and identified as 1,2-bis(trifluoromethyl)benzene 181 (83%) and the head-to-tail silene dimer 208 (85%). Compound 181 was identified by comparison of its GC retention time and mass spectrum with that of an authentic sample. Compound 208 was identified on the basis of its spectra: NMR (CCl_4) δ 0.00 (s, 4H, $SiCH_2Si$), 0.22 (s, 6H, SiMe), 1.64 (d, 4H. J = 8 Hz), 4.61-5.04 (m, 4H, $CH_2CH{=}C\underline{H}_2$), 5.37-6.03 (m, 2H, $CH_2C\underline{H}{=}CH_2$); mass spectrum m/e (% rel. int.) 196 (1), 181 (3), 168 (4), 156 (15), 155 (93), 129 (13), 128 (14), 127 (100), 115 (18), 113 (32), 99 (18), 97 (10), 85 (16), 83 (11), 73 (19), 71 (15), 69 (15), 59 (49), 55 (12), calculated for $C_{10}H_{20}Si_2$ 196.11036, measured 196.11021.

Synthesis of 1-allyl-1-methyl-1-silacyclobutane 209

A three-necked round-bottom flask was equipped with a reflux condenser, drying tube and pressure equalized addition funnel. The flask was flame dried and flushed with nitrogen. The flask was charged with 0.70 g (0.029 mol) of magnesium and 50 mL of dry ether. A solution of 3.0456 g (0.02528 mol) of 1-chloro-1-methyl-1-silacyclobutane, 3.36 g (0.028 mol) of allylbromide in 20 mL of dry ether was added dropwise. After stirring for 10 hours the organic solution was washed with water and dried with magnesium sulfate. After solvent removal, the residue was distilled (23°/.1 torr) to afford 1.96 g (63.6%) of 209: NMR (CCl_4) δ 0.30 (s, 3H, SiMe), 0.77-2.40 (m, 8H, $C\underline{H}_2CH{=}CH_2$ and $C\underline{H}_2C\underline{H}_2C\underline{H}_2$), 4.72-5.09 (m, 2H, $CH_2CH{=}C\underline{H}_2$), 5.40-6.15 (m, 1H, $C\underline{H}{=}CH_2$); mass spectrum 126 (5), 99 (12), 98 (96), 97 (75), 86 (9), 85 (100), 84 (13), 83 (71), 70 (44), 69 (13), 67 (10), 59 (27), 5 (21), 55 (33), 53 (14), calculated for $C_7H_{12}Si$ 124.07083, measured 124.07078.

Vacuum pyrolysis of 209

A vacuum pyrolysis of 209 (1.5644 g, 0.0126 mol) was conducted by distilling (25°C, 1×10^{-4} torr) it through a horizontal quartz tube heated at 780°C. The pyrolysate was condensed into a trap cooled with liquid nitrogen and represented on 81% mass recovery. The products were isolated by preparative gas chromatography on an 8' 20% DC550 column. The major product was identified as the silene dimer 208 (32%), all spectra matching those described for 208 produced in the vacuum pyrolysis of 207. The minor product was identified as 1-methyl-1-silacyclopent-3-

ene 210 (5%) based on its spectra (which were compared to those of an authentic sample): NMR (CCl_4) δ 0.20 (d, 2H, J = 4 Hz, collapses to a singlet with $h\nu$ at 4.24), 1.40 (m, 4H), 4.24 (m, 1H, SiH), 5.80 (broad s, 2H); mass spectrum m/e (% rel. int.) 98 (65), 97 (100), 83 (77), 81 (23), 70 (54), 67 (11), 57 (11), 55 (55), 54 (14), 53 (27).

Synthesis of 2-cyclopropyl-2-methoxyhexamethyltrisilane 217

A three-neck round-bottom flask was equipped with an overhead stirrer, nitrogen inlet and a septum inlet. The flask was flame dired and flushed with nitrogen. The flask was charged with 0.83 g (0.12 mol) of ether-washed lithium shot and 200 mL of dry ether. This was cooled tO 0°C and 5.0526 g (0.0417 mol) of cyclopropylbromide were slowly added via a syringe. The addition took 2 hours, during which time a slow stream of nitrogen was passed over the solution. After stirring at 0°C for 2 hours this solution was added via a double-tipped needle to a stirring solution of 10.20 g (0.0417 mol) of 2,2-dichlorohexamethyltrisilane (206) at 0°C. This transfer took 2 hours. The mixture was warmed to room temperature and stirred for 6 hours. Sodium methoxide (2.67 g, 0.049 mol) was added and the mixture stirred 1 hour. The salts were removed as well as solvent. The residue was distilled (102° at 12 torr) to afford 5.13 g (50%) of 217: NMR (CCl_4) δ 0.14 (s, 18H), -0.30 to 0.72 (m, 5 cyclopropyl H), 3.35 (s, 3H, $SiOC\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ -5.065, -0.676, 1.761, 53.233; mass spectrum m/e (% rel. int.) 246 (.6), 231 (5), 173 (24), 157 (34), 145 (24), 143 (25), 127 (36), 89 (36), 73 (100), 59 (73), calculated for $C_{10}H_{26}OSi_3$ 246.12916, measured 246.12917.

Vacuum pyrolysis of 2-cyclopropyl-2-methoxyhexamethyldisilane 217

Compound 217 (0.4631 g, 1.88 mmol) was distilled 25°C, 1×10^{-4} torr) through a horizontal quartz tube packed with quartz chips and heated at 590°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 76.3% mass recovery. The products were isolated by preparative gas chromatography on a 16' 20% SE 30 column and were identified as trimethylvinylsilane (29%) trimethylmethoxysilane (82%) isolated as a 1:2.5 mixture) and 1-trimethylsilylpropyne 218 (35%) The NMR yields were also determined and found to be 27%, 72% and 18%, for these three compounds respectively. There was also produced in this pyrolysis an undetermined amount of trimethylsilane. Trimethylvinylsilane and trimethylmethoxysilane were identified by direct comparison of there ^{1}H NMR and mass spectra with those of authentic samples. Compound 218 was identified on the basis of its spectra: NMR (CCl_4) δ 0.12 (s, 9H), 1.83 (s, 3H); mass spectrum m/e (% rel. int.) 112 (18), 97 (100), 83 (5), 71 (4), 69 (20), 67 (12), 55 (11), calculated for $C_6H_{12}Si$ 112.07083, measured 112.07119.

Copyrolysis of 217 and 2,3-dimethyl-1,3-butadiene

A solution consisting of 0.5597 g (0.00275 mol) of 217 and 1.12 g (0.0136 mol) of 2,3-dimethyl-1,3-butadiene was slowly dripped into a verticle quartz tube packed with quartz chips and heated at 450°C. Nitrogen (30 mL/min) was used to sweep the pyrolysate into a trap cooled with liquid nitrogen and represented an 89% mass recovery. Two trapping products were formed along with trimethylmethoxysilane. These products isolated by preparative gas chromatography on a 16' 20% SE 30 column. The major product was identified as 1-cyclopropyl-1-trimethylsilyl-3,4-dimethyl-1-silacyclopent-3-ene 219 (40%) based on its spectra: NMR (CCl_4) δ 0.10 (s, 9H SiMe), -0.40-0.72 (m, cyclopropyl H), 1.30 (broad s, 4H, CH_2), 1.65 (broad s, 6H, CH_3), ^{13}C NMR (C_6D_6) δ -7.087, -1.5161, 1.905, 19.180, 21.727, 130.887; mass spectrum m/e (% rel. int.) 224 (13), 151 (17), 127 (31), 125 (13), 124 (32), 123 (86), 122 (10), 111 (8), 109 (100), 99 (16), 85 (11), 83 (22), 81 (11), 73 (75), 69 (27), 67 (12), 59 (47), 55 (15), calculated for $C_{12}H_{24}Si_2$ 224.14166, measured 224.14181. The second major product was the spiro adduct 220 (13%), identified on the basis of its spectral data: NMR (C_6D_6) δ 0.05 (s, 9H, SiMe), 0.86 (d of d, 1H, J_{AB} = 10 Hz, $J_{AB'}$ = 7 Hz, collapses to a broad s with hν at 2.12), 1.25 (apparent t, 2H, J = 8 Hz, collapses to a broad s with hν at 2.12), 1.58 (broad s, 4H), 1.68 (broad s, 6H, CH_3), 2.12 (m, 2H); ^{13}C NMR (C_6D_6) δ -1.073, 15.334, 16.743, 17.501, 19.072, 19.722, 26.115, 26.873, 130.129, 130.292; mass spectrum m/e (% rel. int.) 224 (38), 196 (12), 182 (15), 181 (35), 155 (8), 154 (13), 141 (15), 137 (17), 136 (34), 127 (27), 124 (100), 123 (24), 110 (24), 109 (44), 99 (29), 85 (20), 83 (26), 73 (85), 71 (14), 69 (20), 59 (74), calculated for $C_{12}H_{24}Si_2$ 224.14116, measured 224.14202.

Attempt to synthesize 1-trimethylsilyl-1-methoxy-1-silacyclobutane

To a stirring solution of 0.3 g (0.013 mol) of lithium dispersion (30% in mineral oil was added a mixture of 2.0 g (0.014 mol) of 1,1-dichloro-1-silacyclobutane and 1.54 g (0.014 mol) of trimethylchlorosilane. After stirring for 2 hours at room temperature, 0.45 g (0.014 mol) of methanol and 1.1 g (0.014 mol) of pyridine were added as a mixture in hexane. After removal of salts and solvent, the residue was examined by GCMS. The presence of >10 products was noted. Some corresponded to ring opening of the silacyclobutane. None of the desired product was formed.

Copyrolysis of 214 and acetylene

Compound 214 was slowly dripped into a horizontal quartz tube packed with quartz chips and heated at 450°C. Acetylene (25 mL/min) was used as a carrier gas, sweeping the pyrolysate into a trap cooled with liquid nitrogen and represented an 83% mass recovery. The acetylene was purified by first bubbling it through concentrated sulfuric acid, and then passing it through a pad of basic alumina. Two products were formed in this pyrolysis, trimethoxysilane and *trans*-(β-trimethylsilylvinyl)(cyclopropyl)ethynylsilane 245 (52%). Compound 245 was isolated by preparative gas chromatography on a 10' 20% SE 30 column and was identified on the basis of its spectral properties: NMR (CS_2) -0.40-0.90 (m, 5H, cyclopropyl), 0.16 (s, 9H , SiMe), 2.26 (d, 1H, J = 1 Hz), collapses to a singlet with h at 4.23), 4.23 (m, 1H, SiH), 6.68 (d of d, 1H, J = 20 Hz, J' = 6 Hz, collapses to a doublet with hν at 4.23), 6.98 (d, 1H, J = 20 Hz); mass spectrum m/e (% rel. int.) 179 (25), 153 (35), 151 (48), 101 (27), 93 (26), 85 (26), 83 (40), 73 (100), 59 (46), calculated for $C_9H_{15}Si_2(p-CH_3)$ 179.07123, measured 179.07119.

Copyrolysis of 2-methoxyheptamethyltrisilane and acetylene

The pyrolysis was conducted by slowly dripping 2-methoxyheptamethyltrisilane (0.8368 g, 0.0338 mol) through a quartz tube packed with quartz chips. Acetylene was used as a carrier gas and was purified by bubbling it through concentrated sulfuric acid and then passing it through a column of basic alumina. A flow rate of 25 mL/min was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. This represented a 100% mass recovery. Two products were produced in this pyrolysis, trimethoxysilane and trans-(β-trimethylsilylvinyl)(methyl)ethynylsilane 251 (48%). Compound 251 was identified on the basis of its spectra: NMR (CS_2) 0.15 (s, 9H), 0.29 (d, 3H, J = 4 Hz, collapses to a singlet with hν at 4.37), 2.29 (d, 1H, J = 1 Hz, collapses to a singlet with hν at 4.37), 4.37 (m, 1H, SiH), 6.51 (d of d, 1H, J = 20 Hz, J' = 6 Hz, collapses to a doublet J = 20 Hz with hν at 4.37), 6.79 (d, 1H, J = 20 Hz); mass spectrum m/e (% rel. int.) 168 (.2), 153 (67), 127 (22), 83 (43), 73 (100), 59 (42), calculated for $C_7H_{13}Si_2$ (p-CH_3) 153.05558, measured 153.05592.

BIBLIOGRAPHY

1. Nametkin, N. S.; Vdovin, V. M.; Gusel'nikov, L. E.; Zavlyalov, V. I. Izv. Akad. Nauk SSSR, Ser. Khim. 1966, 589.

2. Gusel'nikov, L. E.; Flowers, M. C. J. Chem. Soc., Chem. Commun. 1967, 864.

3. Skell, P. S.; Goldstein, E. J. J. Amer. Chem. Soc. 1964, 86, 1442.

4. Gilman, H.; Cottis, S. G.; Atwell, W. H. J. Amer. Chem. Soc. 1964, 86, 1596.

5. Gilman, H.; Cottis, S. G.; Atwell, W. H. J. Amer. Chem. Soc. 1964, 86, 5584.

6. Atwell, W. H.; Weyenberg, D. R. J. Organometal. Chem. 1966, 5, 594.

7. Brook, A. G.; Bassindale, A. R. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. II, Chapter 9.

8. Kwart, H.; Slutsky, J. J. Amer. Chem. Soc. 1972, 94, 2515.

9. Slutsky, J.; Kwart, H. J. Amer. Chem. Soc. 1973, 95, 8678.

10. Coleman, B.; Conrad, N. D.; Baum, M. W.; Jones, M,, Jr. J. Amer. Chem. Soc., 1979, 101, 7743.

11. Brook, A. G.; MacRae, D. M.; Limburg, W. W. J. Amer. Chem. Soc. 1967, 89, 5493.

12. Brook, A. G.; MacRae, D. M., Bassindale, A. R. J. Organometal. Chem. 1975, 86, 185.

13. Kwart, H.; Barnette, W. E. J. Amer. Chem. Soc. 1977, 99, 614.

14. Brook, A. G.; Harris, J. L.; Sheikh, M. E. J. Amer. Chem. Soc. 1979, 101, 83.

15. Barton, T. J.; Wulff, W. D. J. Organometal. Chem. 1979, 168, 23.

16. Lutsenko, I. F.; Baukov, Y. L.; Burlanchenko, G. S.; Khasapov, B. N. J. Organometal. Chem. 1966, 5, 20.

17. Lutsenko, I. F.; Baukov, Y. L.; Kostyuk, A. S.; Savel'eva, N. I.; Krysina, V. K. J. Organometal. Chem. 1969, 17, 241.

18. Larrabee, R. B. J. Organometal. Chem. 1974, 74, 313.

19. Ashe, A. J., III J. Amer. Chem. Soc. 1970, 92, 1233.

20. Howe, J. J.; Pinnavaia, T. J. J. Amer. Chem. Soc. 1969, 91, 5378.

21. Pinnavaia, T. J.; Collins, W. T.; Howe, J. J. J. Amer. Chem. Soc. 1970, 92, 4544.

22. Pinnavaia, T. J.; McClarin, J. A. J. Amer. Chem. Soc. 1974, 96, 3012.

23. Reich, H. J.; Murcia, D. A. J. Amer. Chem. Soc. 1973, 95, 3418.

24. Casey, C. P.; Jones, C. R.; Tukada, H. J. Org. Chem. 1981, 46, 2089.

25. Anderson, G.; Cameron, D. W.; Feutrill, G. I.; Read, R. W. Tetrahedron Lett. 1981, 4347.

26. Barton, T. J.; Goure, W. F.; Witiak, J. L.; Wulff, W. D. J. Organometal. Chem. 1982, 225, 87.

27. Barton, T. J.; Wulff, W. D.; Arnold, E. V.; Clardy, J. J. Amer. Chem. Soc. 1979, 101, 2733.

28. Wulff, W. D. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1979.

29. Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A. Russian Chem. Rev. 1976, 45, 913.

30. Nefedor, O. M.; Kolesnikor, S. P.; Jaffe, A. I. Organometal. Chem. Rev. 1977, 5, 181.

31. Gaspar, P. P.; Herold, B. J. In "Carbene Chemistry," 2nd ed.; Kirmse, W., Ed.; Academic Press: New York, 1971; Chapter 13.

32. Gaspar, P. P. In "Reactive Intermediates"; Jones, M. R.; Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. I, Chapter 7.

33. Gaspar, P. P. In "Reactive Intermediates"; Jones, M. R.; Moss, R. A., Eds.; Wiley-Interscience: New York, 1981; Vol. II, p. 335.

34. Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. Acc. Chem. Res. 1975, 8, 18.

35. Jutzi, P. Angew. Chem., Int. Ed. Engl. 1975, 14, 232.

36. Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* 1979, 79, 529.

37. Friswell, N. J.; Gowenlock, B. G. *Adv. Free Radical Chem.* 1965, 1, 39.

38. Jackson, R. A. *Adv. Free Radical Chem.* 1969, 3, 231.

39. Davidson, I. M. T. *Q. Rev.* 1971, 25, 111.

40. Sakurai, H. In "Free Radicals"; Kochi, J. K., Ed.; John Wiley and Sons: New York, 1973; Vol. II, Chapter 25.

41. Goure, W. F. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1982.

42. Roark, D. N.; Peddle, G. J. D. *J. Amer. Chem. Soc.* 1972, 94, 5837.

43. Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Amer. Chem. Soc.*, 1978, 100, 6236.

44. Barton, T. J.; Kilgour, J. A. *J. Amer. Chem. Soc.* 1976, 98, 7746.

45. Snyder, L. C.; Wasserman, Z. R. *J. Amer. Chem. Soc.* 1979, 101, 5222.

46. Jenkins, R. L.; Kedrowski, R. A.; Elliot, L. E.; Tappen, D. C.; Ring, M. A. *J. Organometal. Chem.* 1975, 86, 347.

47. Chen, Y. S.; Cohen, B. H.; Gaspar, P. P. *J. Organometal. Chem.* 1980, 195, C1.

48. Gusel'nikov, L. E.; Lopatnikova, E.; Polyakov, Y. P.; Nametkin, N. S. *Dokl. Akad. Nauk. SSSR* 1980, 253, 1387.

49. Gaspar, P. P.; Hwang, R.-J.; Eckelman, W. C. *J. Chem. Soc., Chem. Commun.* 1974, 242.

50. Hwang, R.-J.; Gaspar, P. P. *J. Amer. Chem. Soc.* 1978, 100, 6626.

51. Siefert, E. E.; Loh, K.-L.; Ferrieri, R. A.; Tang, Y.-N. *J. Amer. Chem. Soc.* 1980, 102, 2285.

52. Gaspar, P. P.; Chen, Y.-S.; Helfer, A. P. *J. Amer. Chem. Soc.* 1981, 101, 7344.

53. Conlin, R. T.; Gaspar, P. P. *J. Amer. Chem. Soc.* 1976, 98, 868.

54. Barton, T. J.; Burns, G. T.; Goure, W. F.; Wulff, W. D. *J. Amer. Chem. Soc.* 1982, 104, 1149.

55. Haas, C. H.; Ring, M. A. Inorg. Chem. 1975, 14, 2253.

56. Brook, A. G.; Abdesaken, F.; Gutenkunst, B.; Gutenkunst, G.; Kallury, R. K. J. Chem. Soc., Chem. Commun. 1981, 191.

57. Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. J. Amer. Chem. Soc. 1975, 97, 5923.

58. Ishikawa, M.; Fuchikami, T.; Kumada, M. J. Organometal. Chem. 1976, 118, 139.

59. Ishikawa, M.; Fuchikami, T.; Kumada, M. J. Organometal. Chem. 1976, 118, 155.

60. Ishikawa, M.; Fuchikami, T.; Kumada, M. J. Organometal. Chem. 1978, 162, 223.

61. Ishikawa, M.; Oda, M.; Miyoshi, N.; Fábry, L.; Kumada, M.; Yamabe, T.; Akagi, K.; Fukui, K. J. Amer. Chem. Soc. 1979, 101, 4612.

62. Barton, T. J.; Burns, G. T. J. Organometal. Chem. 1979, 179, C17.

63. Block, E.; Revelle, L. K. J. Amer. Chem. Soc. 1978, 100, 5246.

64. Burns, G. T.; Barton, T. J. J. Organometal. Chem. 1981, 216, C5.

65. Slutsky, J.; Kwart, H. J. Org. Chem. 1973, 38, 3658.

66. Nakadaira, Y.; Kanouchi, S.; Sakurai, H. J. Amer. Chem. Soc. 1974, 96, 5621.

67. Nakadaira, Y.; Kanouchi, S.; Sakurai, H. J. Amer. Chem. Soc. 1974, 96, 5623.

68. Ishikawa, M.; Kumada, M. Rev. Silicon, Germanium, Tin, Lead Comp. 1979, 4, 7.

69. Ishikawa, M.; Kumada, M. Adv. Organomet. Chem. 1981, 19, 51.

70. Nametkin, N. S.; Gusel'nikov, L. E.; Orlov, V. Y.; Ushakova, R. L., Kuz'min, O. V.; Vdovin, V. M. Dokl. Akad. Nauk. SSSR 1973, 211, 106.

71. Ancelle, J.; Bertrand, G.; Joanny, M.; Mazerolles, P. Tetrahedron Lett. 1979, 3153.

72. Golino, C. M.; Bush, R. D.; Roark, D. N.; Sommer, L. H. J. Organometal. Chem. 1974, 66, 29.

73. Eaborn, C.; Harper, D. A. R.; Hitchcock, P. B.; Hopper, S. P.; Safa, K. D.; Washburne, S. S.; Walton, D. R. M. J. Organometal. Chem. 1980, 186, 309.

74. Bertrand, G.; Manuel, G.; Mazerolles, P. Tetrahedron Lett. 1978, 2149.

75. Shiina, K.; Kumada, M. J. Org. Chem. 1958, 23, 139.

76. Gilman, H.; Dunn, G. E. J. Amer. Chem. Soc. 1951, 73, 5077.

77. Mares, F.; Chvalovsky, V. J. Organometal. Chem. 1966, 6, 327.

78. Krusic, P. J.; Kochi, J. K. J. Amer. Chem. Soc. 1969, 91, 3938.

79. Nay, M. A.; Woodall, G. N. C.; Strausz, O. P.; Gunning, H. E. J. Amer. Chem. Soc. 1965, 87, 179.

80. Wiberg, E.; Stecher, O.; Kreuzbichler, H. J.; Stande, E. Angew. Chem., Int. Ed. Engl. 1963, 2, 507.

81. Eaborn, C.; Jackson, R. A.; Walsingham, R. W. J. Chem. Soc. Chem., Commun. 1965, 300.

82. Curtice, J.; Gilman, H.; Hammond, G. S. J. Amer. Chem. Soc. 1957, 79, 4754.

83. Haszeldine, R. N.; Young, J. C. J. Chem. Soc. 1960, 4503.

84. Eaborn, C.; Jackson, R. A.; Pearce, R. J. Chem. Soc., Chem. Commun. 1967, 920.

85. Sakurai, H.; Hosomi, A.; Kumada, M. Tetrahedron Lett. 1969, 1755.

86. Sakurai, H.; Hosomi, A.; Kumada, M. Tetrahedron Lett. 1969, 1757.

87. Sakurai, H.; Hosomi, A. J. Amer. Chem. Soc. 1970, 92, 7507.

88. Sakurai, H.; Hosomi, A.; Kumada, M. J. Chem. Soc., Chem. Commun. 1969, 521.

89. Eaborn, C.; Safa, K. D. J. Organometal. Chem. 1981, 206, 169.

90. Shiina, K.; Kumada, M. J. Org. Chem. 1958, 23, 139.

91. Sakurai, H.; Koh, R.; Hosomi, A.; Kumada, M. Bull. Chem. Soc. Japan 1966, 39, 2050.

92. Sakurai, H.; Kishida, T.; Hosomi, A.; Kumada, M. *J. Organometal. Chem.* 1967, 8, 65.

93. Eaborn, C.; Simme, J. M. *J. Chem. Soc., Chem. Commun.* 1968, 1426.

94. Davidson, I. M. T.; Eaborn, C.; Simme, J. M. *J. Chem. Soc., Faraday Trans. I* 1974, 70, 249.

95. Davidson, I. M. T.; Howard, A. B. *J. Chem. Soc., Chem. Commun.* 1973, 323.

96. Connor, J. A.; Hazzeldine, R. N.; Leigh, G. J.; Sedgwick, R. D. *J. Chem. Soc. A* 1967, 768.

97. Band, S. J.; Davidson, I. M. T.; Lambert, C. A.; Stephenson, I. L. *J. Chem. Soc., Chem. Commun.* 1967, 723.

98. Davidson, I. M. T.; Stephenson, I. L. *J. Chem. Soc. A* 1968, 282.

99. Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. I* 1975, 71, 69.

100. Davidson, I. M. T.; Lambert, C. A. *J. Chem. Soc., Chem. Commun.* 1969, 1276.

101. Wilt, J. W.; Kolewe, O.; Kraemer, J. F. *J. Amer. Chem. Soc.* 1969, 91. 2624.

102. Yamamoto, K.; Nakamishi, K.; Kumada, M. *J. Organometal. Chem.* 1967, 7, 197.

103. Eaborn, C.; Niederprün, H. *J. Chem. Soc.* 1963, 797.

104. Weinstock, J.; Lewis, E. S. *J. Amer. Chem. Soc.* 1957, 79, 6243.

105. Wilt, J. W.; Maravetz, L. L.; Zawadzki, J. Z. *J. Org. Chem.* 1966, 31, 3018.

106. Sakurai, H.; Hosomi, A.; Kumada, M. *Bull. Chem. Soc. Japan* 1967, 40, 1551.

107. Breslow, R. "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963; p. 233.

108. Sakurai, H.; Hosomi, A. *J. Chem. Soc., Chem. Commun.* 1970, 767.

109. Neider, S. M.; Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* 1979, 3793.

110. Atton, D.; Bone, S. A.; Davidson, I. M. T. J. Organometal. Chem. 1972, 39, C47.

111. Jung, I. N.; Weber, W. P. J. Org. Chem. 1976, 41, 946.

112. Nay, M. A.; Woodall, G. N. C.; Strausz, O. P.; Gunning, H. E. J. Amer. Chem. Soc. 1965, 87, 179.

113. Frangopol, P. T.; Ingold, K. U. J. Organometal. Chem. 1970, 25, C9.

114. Watts, G. B.; Ingold, K. U. J. Amer. Chem. Soc. 1972, 94, 491.

115. Cadman, P.; Tilsley, G. M.; Trotman-Dickenson, A. F. J. Chem. Soc., Chem. Commun. 1970, 1721.

116. Cadman, P.; Tilsley, G. M.; Trotman-Dickenson, A. F. J. Chem. Soc., Faraday Trans. I 1972, 68, 1849.

117. Thynne, J. C. J. J. Organometal. Chem. 1969, 17, 155.

118. Strausz, O. P.; Gammie, L.; Theodorakoupoulos, G.; Mezey, P. G.; Csizmadia, I. G. J. Amer. Chem. Soc. 1976, 98, 1622.

119. Davidson, I. M. T.; Lambert, C. A. J. Chem. Soc., Chem. Commun. 1969, 1276.

120. Davidson, I. M. T.; Lambert, C. A. J. Chem. Soc. A 1971, 882.

121. Paquin, D. P.; O'connor, R. J.; Ring, M. A. J. Organometal. Chem. 1974, 80, 341.

122. Walsh, R.; Wells, J. M. J. Chem. Soc., Chem. Commun. 1973, 513.

123. Clifford, R. P.; Gowenlock, B. G.; Johnson, C. A. F.; Stevenson, J. J. Organometal. Chem. 1972, 34, 53.

124. Baldwin, A. C.; Davidson, I. M. T.; Reed, M. D. J. Chem. Soc., Faraday Trans. I 1978, 74, 2171.

125. Tokach, S. K.; Koob, R. D. J. Phys. Chem. 1979, 83, 774.

126. Tokach, S. K.; Koob, R. D. J. Amer. Chem. Soc. 1980, 102, 376.

127. Gaspar, P. P.; Haizlip, A. D.; Choo, K. Y. J. Amer. Chem. Soc. 1972, 94, 9032.

128. Cornett, B. J.; Choo, K. Y.; Gaspar, P. P. J. Amer. Chem. Soc. 1980, 102, 377.

129. Gammie, L.; Safarik, I.; Strauz, O. P.; Roberge, R.; Sandorfy, C. *J. Amer. Chem. Soc.* 1980, 102, 378.

130. Sakurai, H.; Nakadaira, Y.; Kira, M.; Sugiyama, H.; Yoshida, K.; Takiguchi, T. *J. Organometal. Chem.* 1980, 184, C36.

131. Boudjouk, P.; Roberts, J. R.; Golino, C. M.; Sommer, L. H. *J. Amer. Chem. Soc.* 1972, 94, 7926.

132. a. Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry"; Plenum Press: New York, 1977; Part I, p. 11.

b. Walsh, R. *Accts. Chem. Res.* 1981, 14, 246.

133. Zweifel, G.; Polston, N. L. *J. Amer. Chem. Soc.* 1970, 92, 4068.

134. Cram, D. J.; Allinger, N. L. *J. Amer. Chem. Soc.* 1956, 78, 2518.

135. Sondengam, B. L.; Charles, G.; Akam, T. M. *Tetrahedron Lett.* 1980, 1069.

136. Zweifel, G.; Ayyangar, N. R.; Brown, H. C. *J. Amer. Chem. Soc.* 1963, 85, 2072.

137. Eisch, J. J.; Foxton, M. W. *J. Organometal. Chem.* 1968, 11, P24.

138. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds," 3rd ed.; John Wiley and Sons, Inc.: New York, 1974; Chapter 3.

139. Kumada, M.; Nakajima, J. I.; Ishikawa, M.; Yamamoto, Y. *J. Org.* Chem. 1958, 23, 292.

140. Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Amer. Chem. Soc.* 1980, 102, 1734.

141. Baldwin, J. E. *J. Amer. Chem. Soc., Chem. Commun.* 1976, 734.

142. Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Amer. Chem. Soc., Chem. Commun.* 1980, 482.

143. Tsui, F. P.; Zon, G. *J. Organometal. Chem.* 1974, 70, C3.

144. Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A.; Zhavoronkova, T. A. *Zh. Obshch. Khim.* 1976, 46, 1278.

145. Biemann, K. "Mass Spectrometry Organic Chemical Applications"; McGraw-Hill Book Company, Inc.: New York, 1962; pp. 223-225.

146. Piccardi, P.; Massardo, P.; Modena, M.; Santoro, E. *J. Chem. Soc., Perkin Trans. I* 1973, 982.

147. Wilt, J. W.; Maravetz, L. L.; Zawadzki, J. F. J. Org. Chem. 1966, 31, 3018.

148. Ogibin, Y. N.; Nikishin, G. I.; Petrov, A. D. Izv. Akad. Nauk. SSSR, Ser. Khim. 1963, 1816.

149. Wilt, J. W. J. Amer. Chem. Soc. 1981, 103, 5251.

150. Davidson, I. M. T.; Wood, I. T. J. Organometal. Chem. 1980, 202, C65.

151. Jones, M., Jr., Princeton University, Princeton, private communication.

152. Conlin, R. T.; Bessellieu, M. P.; Jones, P. R.; Pierce, R. A. Organometallics, 1982, 1, 396.

153. Goddard, J. D.; Yasunori, Y.; Schaefer, H. F., III J. Amer. Chem. Soc. 1980, 102, 7644.

154. Schröer, U.; Neumann, W. P. Angew. Chem., Int. Ed. Engl. 1975, 14, 246.

155. Grugel, C.; Neumann, W. P.; Seifort, P. Tetrahedron Lett. 1977, 2205.

156. Kunô, K.; Kobayashi, K.; Kawanisi, M. J. Organometal. Chem. 1977, 137, 349.

157. Davidson, P. J.; Harris, D. H.; Lappert, M. E. J. Chem. Soc., Dalton Trans. 1976, 2268.

158. Corriu, R. P. J.; Guerin, C. J. Chem. Soc., Chem. Commun. 1980, 168.

159. Still, W. C. J. Org. Chem. 1976, 41, 3063.

160. Conlin, R. T.; Wood, D. L. J. Amer. Chem. Soc. 1981, 103, 1843.

161. Drahnak, T. J.; Michl, J.; West, R. J. Amer. Chem. Soc. 1981, 103, 1845.

162. Yoshioka, Y.; Schaefer, H. F., III J. Amer. Chem. Soc. 1981, 103, 7366.

163. Barton, T. J.; Marquardt, G.; Kilgour, J. A. J. Organometal. Chem. 1975, 85, 317.

164. Golino, C. M.; Bush, R. D.; On, P.; Sommer, L. H. J. Amer. Chem. Soc. 1975, 97, 1957.

165. Barton, T. J.; Kline, E. J. Organometal. Chem. 1972, 42, C21.

166. Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A. Dokl. Akad. Nauk. SSSR 1972, 205, 868.

167. Hwang, R. J.; Conlin, R. T.; Gaspar, P. P. J. Organometal. Chem. 1975, 94, C38.

168. Barton, T. J.; Hoekman, S. K. J. Amer. Chem. Soc. 1980, 102, 1584.

169. Auner, N.; Grobe, J. J. Organometal. Chem. 1980, 188, 151.

170. Auner, N.; Grobe, J. Anorg. Allg. Chem. 1979, 459, 15.

171. Golino, C. M.; Bush, R. D.; Sommer, L. H. J. Amer. Chem. Soc. 1975, 97, 7371.

172. Maier, G.; Mihm, G.; Reisenauer, P. Angew. Chem. Int. Ed. Engl. 1981, 20, 597.

173. Rosmus, P.; Bock, H.; Solouki, B.; Maier, G.; Mihm, G. Angew. Chem., Int. Ed. Engl. 1981, 20, 59.

174. Burns, G. T.; Barton, T. J. Tetrahedron Lett. 1981, 7.

175. Barton, T. J.; Hoekman, S. K. Synth. React. Inorg. Met.-Org. Chem. 1979, 9, 297.

176. Corey, E. J.; Jautelat, M. Tetrahedron Lett. 1968, 5787.

177. Bertrand, G.; Manuel, G.; Mazerolles, P. J. Organometal. Chem. 1978, 144, 303.

178. Parham, W. E.; Soeder, R. W.; Throckmorton, J. R.; Kund, K.; Dodson, R. M. J. Amer. Chem. Soc. 1965, 87, 321.

179. Makosza, M.; Wawrzyniewicz, M. Tetrahedron Lett. 1969, 4639.

180. Seyferth, D.; Lambert, R. J. Organometal. Chem. 1969, 16, 21.

181. Barton, T. J.; Burns, G. T. J. Amer. Chem. Soc. 1978, 100, 5426.

182. Barton, T. J.; Burns, G. T., Iowa State University, unpublished results.

183. Wiberg, K. B. Adv. in Alicy. Chem. 1968, 2, 185.

184. Gordon, M. S.; Pople, J. A. J. Amer. Chem. Soc. 1981, 103, 2945.

185. Friedman, L.; Schechter, H. J. Amer. Chem. Soc. 1960, 82, 1002.

186. Tzeng, D.; Fong, R. H.; Soysa, H. S. D.; Weber, W. P. *J. Organometal. Chem.* 1981, 219, 153.

187. Masson, J.-C.; Quan, M. L.; Cadiot, P. *Bull. de la Soc. Chim. de France* 1967, 777.

188. Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Amer. Chem. Soc.* 1976, 98, 6382.

189. Ishikawa, M.; Nishimura, K.; Sugisawa, H.; Kumada, M. *J. Organometal. Chem.* 1980, 194, 147.

190. Conlin, R. T.; Gaspar, P. P. *J. Amer. Chem. Soc.* 1976, 98, 3715.

191. Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organometal. Chem.* 1977, 142, C45.

192. Ishikawa, M.; Nakagawa, K.-I.; Kumada, M. *J. Organometal. Chem.* 1980, 190, 117.

193. Sakurai, H., Tohoku University, Sendai, private communication.

194. Gordon, M. S.; Koob, R. D. *J. Amer. Chem. Soc.* 1981, 103, 2939.

195. Sakurai, H.; Tominaga, K.; Wanatabe, T.; Kumada, M. *Tetrahedron Lett.* 1966, 5493.

196. LeGoff, E. *J. Org. Chem.* 1964, 29, 2048.

197. "Organic Synthesis," 1st ed.; John Wiley and Sons: New York, 1963; Collective volume IV, p. 749.

198. Fritz, G.; Kummer, D.; Sonntag, Z. *Z. Anorg. Allg. Chem.* 1966, 342, 113.

199. Tsui, F. P.; Zon, G. *J. Organometal. Chem.* 1974, 70, C3.

200. Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A.; Zhavoronkova, T. A. *Zh. Obshch. Khim.* 1976, 46, 1278.

201. Gilman, H.; Shiina, K.; Aoki, D.; Gaj, B. J.; Wittenberg, D.; Brennan, T. *J. Organometal. Chem.* 1968, 13, 323.

202. Bott, R. W.; Eaborn, C.; Rushton, B. M. *J. Organometal. Chem.* 1965, 3, 455.

203. Kumada, M.; Ishikawa, M. *J. Organometal. Chem.* 1963, 1, 153.

204. Kumada, M.; Ishikawa, M.; Maeda, S. J. Organometal. Chem. 1964, 2, 478.

205. Kumada, M.; Kondo, T.; Mimura, K.; Ishikawa, M.; Yamamoto, K.; Ikeda, S.; Kondo, M. J. Organometal. Chem. 1977, 43, 293.

206. Gilman, H.; Harrell, R. L., J. Organometal. Chem. 1966, 5, 199.

ACKNOWLEDGEMENTS

I would like to express thanks to my fellow group members, both past and present. In particular, Gary Burns and Bill Goure for their many helpful discussions and suggestions.

Dr. Barton has a talent and enthusiasm for chemistry that are unmatched. To him I give special thanks for his leadership and friendship.

I would like to thank my family, my father, mother, brothers, sister and my dear grandmother. Each has given me personal support in countless ways. My appreciation also goes to my father-in-law and my mother-in-law for the kindness they have shown me.

Above all, words cannot express the gratitude I feel for the unyielding love, consistent strength, and encouragement that my husband, Gary, has unselfishly given to me.