1979

Utilization of the silicon-silicon bond in the generation of species unsaturated at silicon

William Dean Wulff
Iowa State University

Recommended Citation

Wulff, William Dean, "Utilization of the silicon-silicon bond in the generation of species unsaturated at silicon " (1979). *Retrospective Theses and Dissertations*. 6677.
https://lib.dr.iastate.edu/rtd/6677

INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand 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 you of complete continuity.
2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. 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 any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University Microfilms International

300 N. ZEEB ROAD, ANN ARBOR, MI 48106
18 BEDFORD ROW, LONDON WC1R 4EJ, ENGLAND

7924275

WULFF, WILLIAM DEAN
UTILIZATION OF THE SILICON-SILICON BOND IN THE GENERATION OF SPECIES UNSATURATED AT SILICON.

IOWA STATE UNIVERSITY, PH.D., 1979

University
Microfilms
International 300 N. ZEEB ROAD, ANN ARBOR, MI 48106

Utilization of the silicon-silicon bond in the generation of species unsaturated at silicon

by

William Dean Wulff

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

1979

TABLE OF CONTENTS

DEDICATION

To Mary

INTRODUCTION

The established chemistry of (p-p) π bonded silicon compounds begins 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 the silicon-silicon and silicon-oxygen double bonds begins shortly after this but is far less developed.

There are no known molecules containing a (p-p) π bonded silicon that are isolable and this appears to be a consequence of reactivity rather than of thermodynamic instability. Chemical information about (p-p) π bonded silicon compounds has been garnered utilizing methods traditional in the study of reactive intermediates.

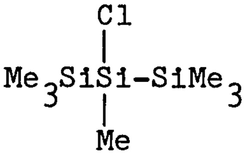
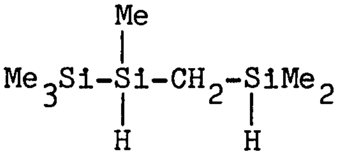
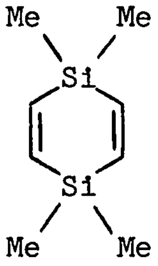
The chemistry of divalent silicon (silylenes) predates that of (p-p) π bonded silicon, yet it was also in 1966 that Atwell and Weyenberg (3) reported a convenient method for the generation of organosilylenes. This report has brought about a dramatic increase in the study of organosilylenes, and has caused silylenes to be viewed not only as systems with the unstable oxidation state of silicon, but as valuable reagents for the synthetic organosilicon chemist.

This thesis will describe new thermal methods for generation of silicon-carbon double bonds <u>via</u> 1,3- and 1,5-migrations of silicon. For the mildest such generator, a silicon-carbon double bond was found to exist in an equilibrium concentration. A serendipitous discovery of a room temperature generator of silicon-oxygen double bonds has permitted an investigation into the chemistry of this scantily characterized species. Some new intramolecular reactions of silylenes are investigated. In addition, the mechanism proposed by Roark and Peddle (4) to account for an intramolecular rearrangement of a silicon-silicon double bond is called into question and evidence presented to support an alternative mechanism.

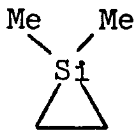
NOMENCLATURE

The nomenclature used in this thesis will, with the exceptions described below, follow the conventions set down by IUPAC. Divalent silicon species will be named as derivatives of the parent silylene ($:SiH_2$). 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.

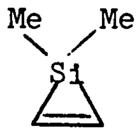
Examples:

Me_2SiClH	dimethylchlorosilane
 $\mathrm{Me_3Si}\overset{\mathrm{Cl}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{-SiMe_3}$	2-chloroheptamethyltrisilane
 $\mathrm{Me_3Si-}\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{Si}}}\mathrm{-CH_2-}\underset{\mathrm{H}}{\mathrm{Si}}\mathrm{Me_2}$	2,2,3,5-tetramethyl-2,3,5-trisilahexane
	1,1,4,4-tetramethyl-1,4-disilacyclohexa-2,5-diene

The saturated and unsaturated three-membered rings containing one silicon atom and two carbon atoms will be named as derivatives of silarane and silarene, respectively.



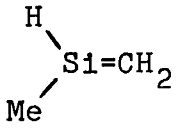
1,1-dimethylsilarane



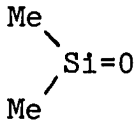
1,1-dimethylsilarene

All compounds containing (p-p) π bonded silicon will be named as derivatives of silene ($H_2Si=CH_2$), disilene ($H_2Si=SiH_2$), and silanone ($H_2Si=O$). Conjugated silenes, disilenes, and silanones will be named as analogs of the corresponding carbon systems.

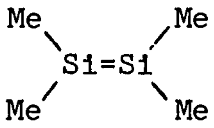
Examples:



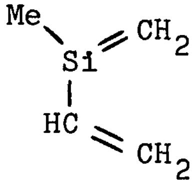
1-methylsilene



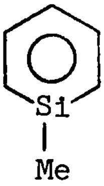
dimethylsilanone



tetramethyldisilene

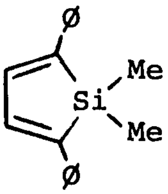


2-methyl-2-silabutadiene



1-methyl-1-silabenzene

Finally, silacyclopentadiene ring systems will be named as derivatives of silole.



1-dimethyl-2,5-diphenylsilole

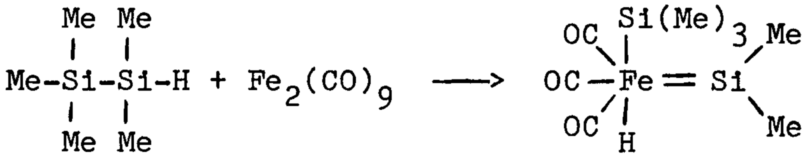
HISTORICAL

The chemical endeavors and results of this thesis are in the area of reactive intermediates in organosilicon chemistry. The particular species that are involved are silylenes, silenes, disilenes, and silanones. The known chemistry of each of these species is reviewed separately. In addition, the various thermal migrations of silicon are reviewed briefly as they are utilized in new approaches to the generation of silene and silanones.

Silylenes

It has been forty years since dichlorosilylene became the first divalent silicon species to be prepared and observed spectroscopically. Even though interest in carbenes began about the same time, development of the chemistry of silylenes lagged behind that of carbenes because of the comparative dearth of methods for silylene generation available to the experimentalist. It was not until twelve years ago that Atwell and Weyenberg gave us the first convenient method for organosilylene generation that precipitated a flurry of activity in this area in the past decade (3).

Silylenes are more stable than their carbon analogs, however, no molecule incorporating a divalent silicon atom has yet been isolated. Sakurai and coworkers (5) have just reported the preparation of 1, the first example of a transition metal silylene complex.



1

The ground state of silylene (SiH_2) has been shown to be a singlet (14 kcal/mole below triplet) by fixed-frequency laser photoelectron spectrometry (6). The bond angle in silylene has been experimentally determined by double-flash ultraviolet spectroscopy to be 92°5' (7). These values are in good agreement with other experimental and theoretical results (8).

The material covered in this review of silylenes will largely concentrate on developments in the last decade. The chemistry of silylenes prior to this time will only be briefly mentioned as it has been covered in several reviews (8-12). Prior to the report of Atwell and Weyenberg, the methods for generation of silylenes were both harsh and limited in the variety of silylenes that could be produced.

Dihalosilylenes can be produced by reduction of tetrahalosilanes with elemental silicon at temperatures in excess of 800°C (10). Also, dichlorosilylene can be prepared from the thermal decomposition of trichlorosilane or organodichlorosilanes (11).

$$\mathrm{SiX_4}\,_{(g)} + \mathrm{Si^o}\,_{(s)} \underset{>800°C}{\rightleftharpoons} 2\ \mathrm{:SiX_2}\,_{(g)}$$

$$2\ \mathrm{HSiCl_3} \xrightarrow{650-670°C} \mathrm{SiCl_4} + \mathrm{H_2} + \mathrm{:SiCl_2}$$

$$\mathrm{R(H)SiCl_2} \xrightarrow{640-690°C} \mathrm{RH} + \mathrm{:SiCl_2}$$

A very limited method for generation of organosilylenes is the gas phase reduction of dimethyldichlorosilane (10). This method is not generally amenable to the study of the chemistry of dimethylsilylene.

$$\mathrm{Me_2SiCl_2} + 2\ \mathrm{K(Na)} \xrightarrow{260-280°C} 2\ \mathrm{KCl} + \mathrm{:SiMe_2}$$

Skell and Owen have found that silicon vapor co-condensed with various silylhydrides gives up to 30% yields of trisilanes (13). These were suggested to arise from initial insertion of a silicon atom into a silicon-hydrogen bond to give a silylsilylene which subsequently insert into another molecule of silane.

$$\mathrm{Si^o} + \mathrm{HSiMe_3} \longrightarrow \mathrm{H{-}\ddot{S}i{-}SiMe_3}$$

$$\mathrm{H{-}\ddot{S}i{-}SiMe_3} + \mathrm{HSiMe_3} \longrightarrow \mathrm{Me_3SiSiH_2SiMe_3}$$

Gasper and coworkers have found that recoiling silicon atoms, produced in a nuclear reaction from $^{31}\mathrm{PH_3}$ (14), react with silane to give mainly disilane products (15). They have suggested that the disilane and silane products arise from silylene intermediates formed by primary abstraction or insertion-dissociation processes (16). However, they have recently reported that the products of the reaction of 1,3-butadiene with recoiling silicon atoms in the presence of silane differ from the products of thermally generated SiH_2 with butadiene, raising the possibility that silylene intermediates are not important in recoiling silicon atom reactions (17-19).

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

half-life
2.6 hours

$$^{31}Si^{\circ} \xrightarrow{SiH_4} {}^{31}SiH_4 + H_3{}^{31}SiSiH_3 + H_3Si{}^{31}SiH_2SiH_3$$

13% 48% 7%

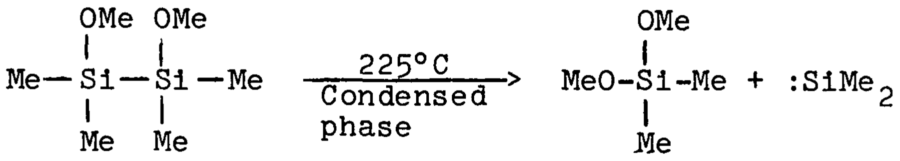
In the last twelve years a variety of mild methods of silylene generation have appeared and these can be classified as either thermal extrusion processes or photochemical extrusion processes.

Silylenes from thermal extrusion

Thermal decomposition of hexahalodisilanes was first reported by Friedel and Ladenburg (20).

$$Si_2I_6 \xrightarrow{\Delta} SiI_4 + (SiI_2)_n$$

Atwell and Weyenberg found that alkoxydisilanes undergo a similar decomposition under much milder conditions and made possible the generation of organosilylenes at relatively mild temperatures (3).



$$\mathrm{Me{-}Si(OMe)(Me){-}Si(OMe)(Me){-}Me} \xrightarrow[\text{Condensed phase}]{225°\mathrm{C}} \mathrm{MeO{-}Si(OMe)(Me){-}Me} + \mathrm{:SiMe_2}$$

Since that time, the generation of silylenes <u>via</u> thermally induced alpha eliminations has become very important synthetically. A partial listing of the silylenes for which this method of generation has come into common synthetic usage is found in Table 1.

Table 1. Silylenes from disilanes

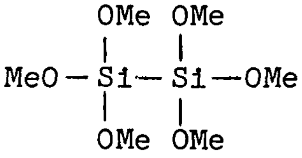
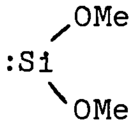
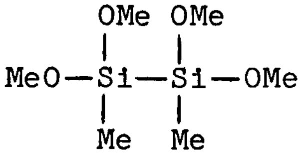
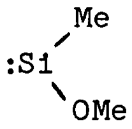
Disilane Generator	Temperature (°C) liquid phase (gas phase)	Silylene(s)	Reference
 $\mathrm{MeO{-}Si(OMe)_2{-}Si(OMe)_2{-}OMe}$	200		21
 $\mathrm{MeO{-}Si(OMe)(Me){-}Si(OMe)(Me){-}OMe}$	185(400)		21-24

Table 1. Continued

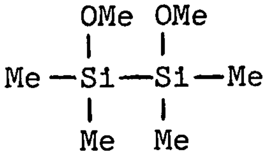
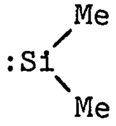
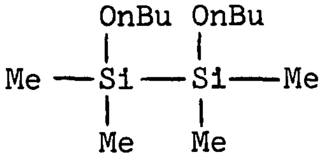
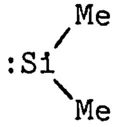
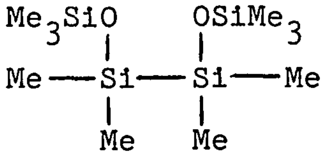
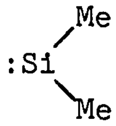
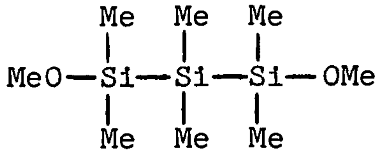
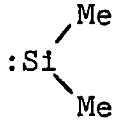
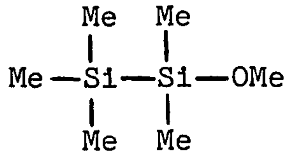
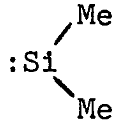
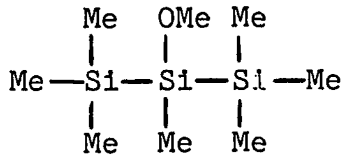
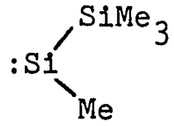
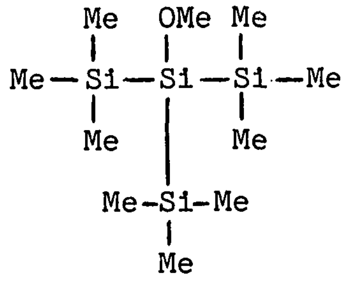
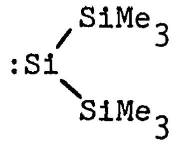
Disilane Generator	Temperature (°C) liquid phase (gas phase)	Silylene(s)	Reference
 $\mathrm{Me_2(MeO)Si{-}Si(OMe)Me_2}$	225	 $:\mathrm{SiMe_2}$	3,21,25-30
 $\mathrm{Me_2(OnBu)Si{-}Si(OnBu)Me_2}$	225	 $:\mathrm{SiMe_2}$	31
 $\mathrm{Me_2(Me_3SiO)Si{-}Si(OSiMe_3)Me_2}$	>225	 $:\mathrm{SiMe_2}$	31
 $\mathrm{MeO{-}SiMe_2{-}SiMe_2{-}SiMe_2{-}OMe}$	275	 $:\mathrm{SiMe_2}$	21
 $\mathrm{Me_3Si{-}SiMe_2{-}OMe}$	>275	 $:\mathrm{SiMe_2}$	31
 $\mathrm{Me_3Si{-}Si(OMe)Me{-}SiMe_3}$	350	 $:\mathrm{Si(SiMe_3)Me}$	32
 $\mathrm{Me_3Si{-}Si(OMe)(SiMe_3){-}SiMe_3}$	250	 $:\mathrm{Si(SiMe_3)_2}$	32

Table 1. Continued

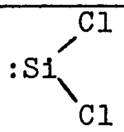
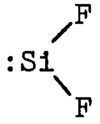
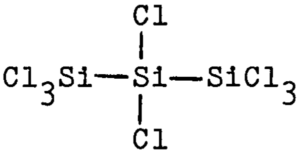
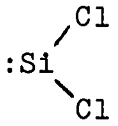
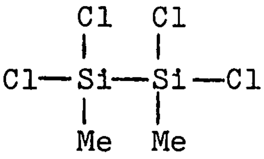
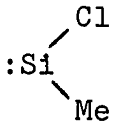
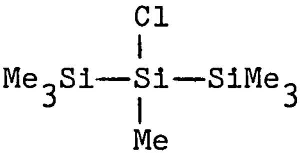
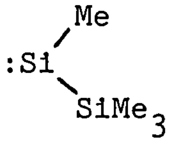
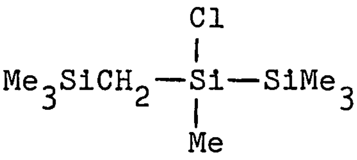
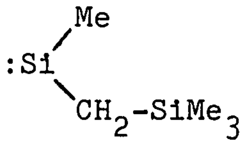
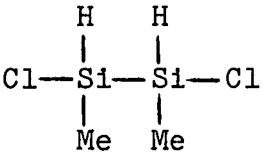
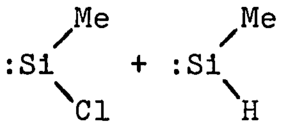
Disilane Generator	Temperature (°C) liquid phase (gas phase)	Silylene(s)	Reference
$Cl_3Si{-}SiCl_3$	(600)		33-40
$F_3Si{-}SiF_3$	(700)		41,42
 $Cl_3Si{-}Si(Cl)_2{-}SiCl_3$	(500)		34
 $Cl{-}Si(Cl)(Me){-}Si(Cl)(Me){-}Cl$	(580)		43
 $Me_3Si{-}Si(Cl)(Me){-}SiMe_3$	(630)		44
 $Me_3SiCH_2{-}Si(Cl)(Me){-}SiMe_3$	(600)		44
 $Cl{-}Si(H)(Me){-}Si(H)(Me){-}Cl$	(395)	 4.4/1.0	42

Table 1. Continued

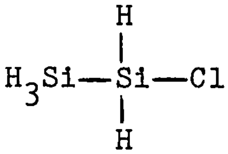
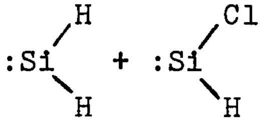
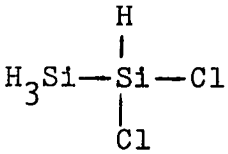
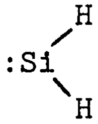
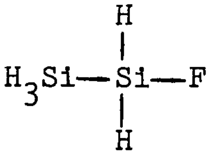
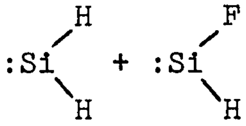
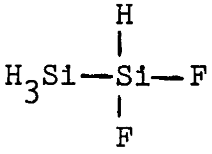
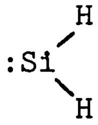
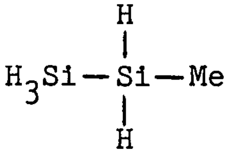
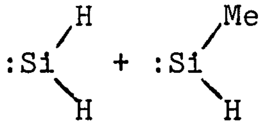
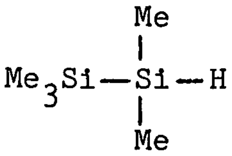
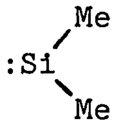
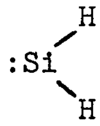
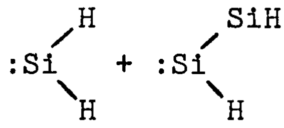
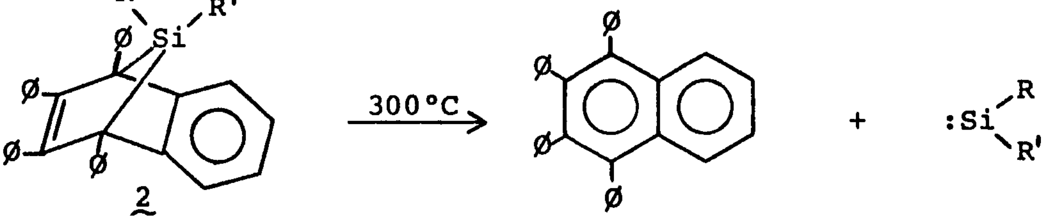
Disilane Generator	Temperature (°C) liquid phase (gas phase)	Silylene(s)	Reference
 $\mathrm{H_3Si{-}\overset{H}{\underset{H}{Si}}{-}Cl}$	(390)	 0.8/1.0	42
 $\mathrm{H_3Si{-}\overset{H}{\underset{Cl}{Si}}{-}Cl}$	(370)		42
 $\mathrm{H_3Si{-}\overset{H}{\underset{H}{Si}}{-}F}$	(390)	 6.0/1.0	42
 $\mathrm{H_3Si{-}\overset{H}{\underset{F}{Si}}{-}F}$	(400)		42
 $\mathrm{H_3Si{-}\overset{H}{\underset{H}{Si}}{-}Me}$	(330)	 1.0/0.86	45
 $\mathrm{Me_3Si{-}\overset{Me}{\underset{Me}{Si}}{-}H}$	(300)		46

Table 1. Continued

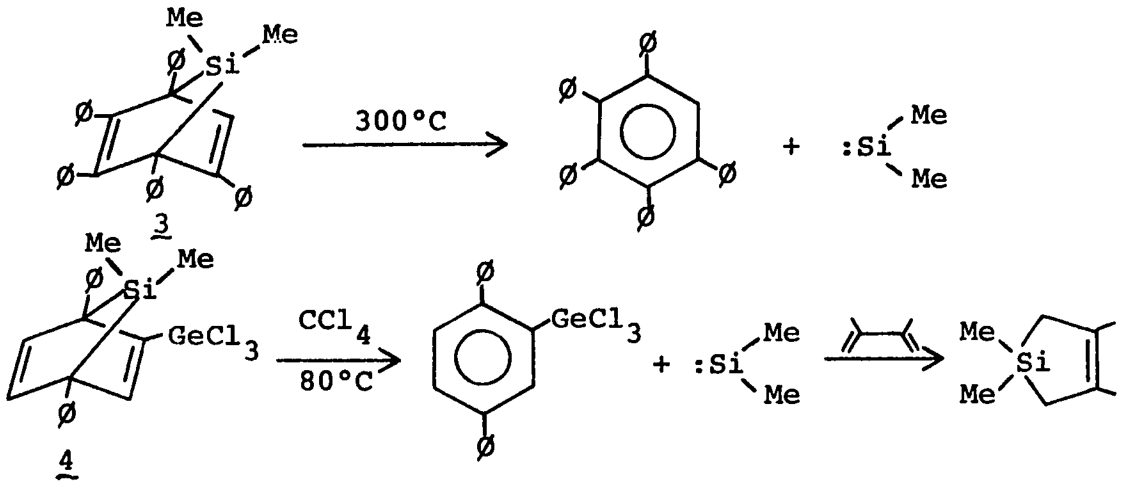
Disilane Generator	Temperature (°C) liquid phase (gas phase)	Silylene(s)	Reference
$H_3Si-SiH_3$	(435)	 $:SiH_2$	19,47
$H_3Si-SiH_2-SiH_3$	(330)	 $:SiH_2 + :SiH(SiH_3)$ 1.0/3.6	45,48

Silylenes can also be generated <u>via</u> thermal extrusion from 7-silanorbornadienes. Compounds 2 and 3 were demonstrated to be silylene generators by Gilman and coworkers in 1964 (49,50). Despite the thermal requirements and the synthetic limitations, these generators are still used today (32). The 7-silanorbornadiene 4 has been reported to generate dimethylsilylene at 80°C, but surprisingly has not been utilized as a silylene generator (51).



2

a) R=R'=Me; b) R=R'=Me; c) R=Me, R'=Ø



3

4

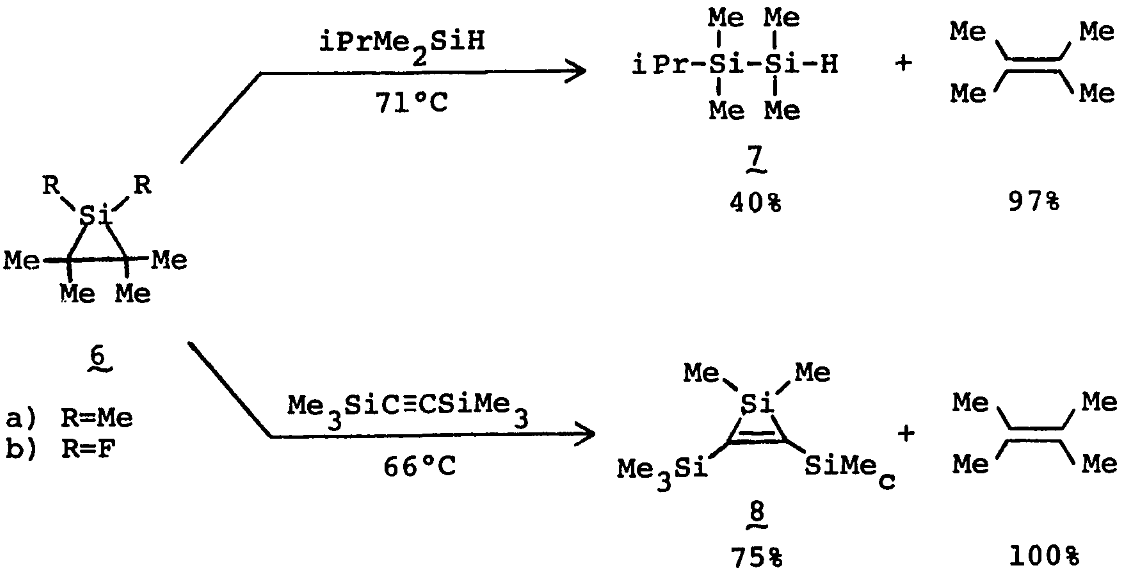
It has long been thought that trimethylsilyl-aluminum compounds decomposed thermally to give dimethylsilylene (52). They have never been utilized as silylene generators, perhaps because these compounds often decompose at the temperatures necessary for their preparation. Very recently, base stabilized tris-(trimethylsilyl) aluminum 5 has been prepared for the first time and was found to slowly decompose at 50°C to give polysilanes and methylaluminum compounds (53). Perhaps this compound will have utility as a mild silylene generator.

$$\mathrm{AlMe_2(SiMe_3)} \xrightarrow{80°\mathrm{C}} \mathrm{AlMe_3} + \mathrm{:SiMe_2}$$

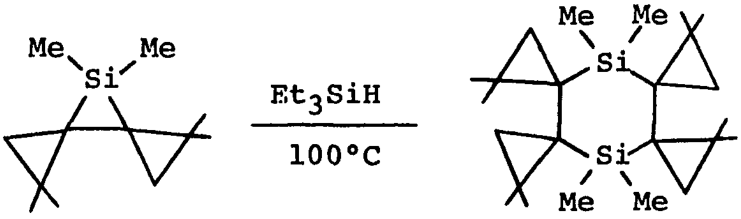
$$\mathrm{THF\!:\ Al(SiMe_3)_3}$$

5

The mildest thermal method of dimethylsilylene generation available to the experimentalist today is the extrusion from hexamethylsilarane 6a (54-57). 6a was prepared for the first time only three years ago by Seyferth and Annarelli (58) and was quickly established to be a mild silylene generator as indicated by the formation of 7, the insertion product of dimethylsilylene and isopropyldimethylsilane (54). Seyferth and coworkers found that they could transfer dimethylsilylene to bis-(trimethylsilyl)acetylene and obtain the silarene 8, a consequence of the fact that silarenes do not thermally extrude silylene (55).



Some of the limitations of silaranes as silylene precursors are beginning to be uncovered. The 1,1-difluorosilarane **6b** does not thermally extrude difluorosilylene (59). Other ring substituted silaranes such as **9** also do not extrude silylenes, but instead appear to dimerize (54). The strained silicon-carbon bond in silaranes is a problem in that it can compete with added reagents for dimethylsilylene with resultant formation of 1,2-disilacyclobutanes, or it can react directly with added reagents such as styrene so that observation of desired reactions of silylenes is thwarted (60).



9

Silylenes from photochemical extrusion

Photochemically induced extrusion of dimethylsilylene from cyclic polysilanes was discovered by Ishikawa and Kumada only seven years ago (61). They found that dodecamethylcyclohexasilane will undergo photo-induced, stepwise, extrusion of dimethylsilylene at ambient temperatures to give octamethylcyclotetrasilane. The generality of this reaction was quickly demonstrated by a number of workers for a variety of linear and cyclic polysilanes. The reaction is currently one of the most valuable methods for silylene generation. Table 2 gives a listing of the polysilanes that have been used to date as silylene precursors.

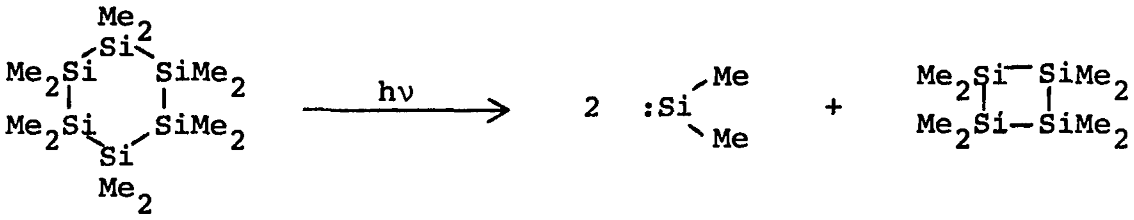


Table 2. Silylenes *via* photo-extrusion from polysilanes

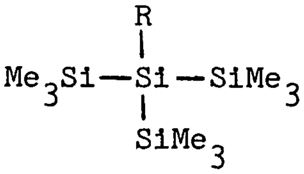
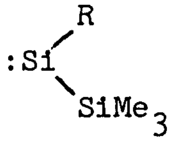
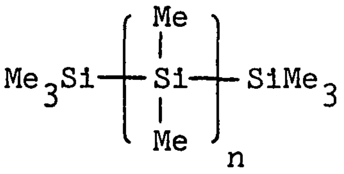
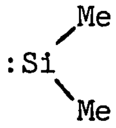
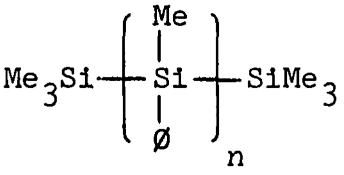
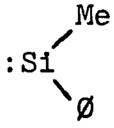
Polysilane	Silylene	References
 $Me_3Si-Si(R)(SiMe_3)-SiMe_3$ R = Me, Ø		62-64
 $Me_3Si-[SiMe_2]_n-SiMe_3$ n = 1-6		65-67
 $Me_3Si-[SiMeØ]_n-SiMe_3$ n = 1,2		67-73

Table 2. (Continued)

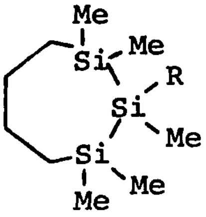
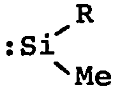
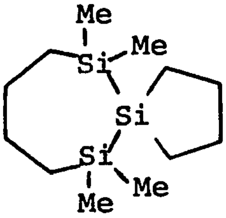
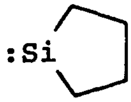
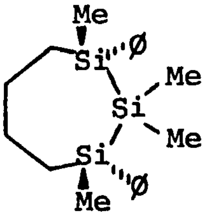
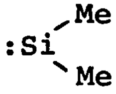
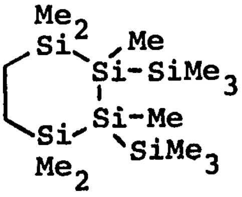
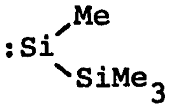
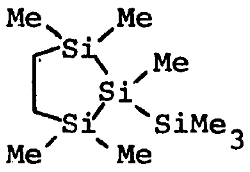
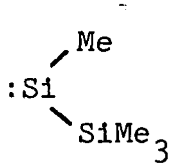
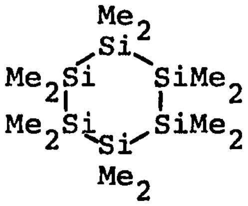
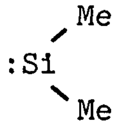
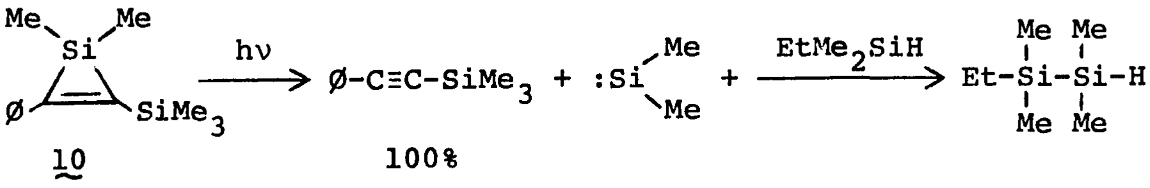
Polysilane	Silylene	References
 R=Me, iPr		74
		74
		75
		76

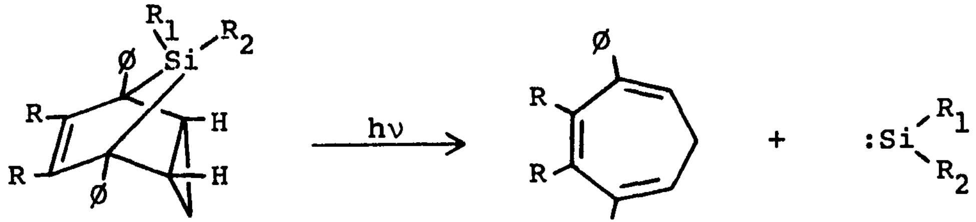
Table 2. (Continued)

Polysilane	Silylene	References
		76
		61,73,76-80

There are a few other molecules that are known to photochemically extrude silylenes. Sakurai and coworkers have found that the silarene 10 upon irradiation generates dimethylsilylene with concomitant formation of phenyltrimethylsilylacetylene (81). This will probably not become a useful precursor of silylenes as Seyferth and coworkers have found that similar silarenes photochemically suffer two-atom insertion reactions with ketones, olefins, and dienes to give five-membered ring products (60).



Another class of photochemical generators that have not received much attention are the 8-silatricyclo[3.2.1.0^{2,4}]oct-6-enes 11 recently reported by Sakurai and coworkers (82). The yields of silylenes, as measured by their products of trapping with germylhydrides, silylhydrides, and butadienes, are relatively low.



11

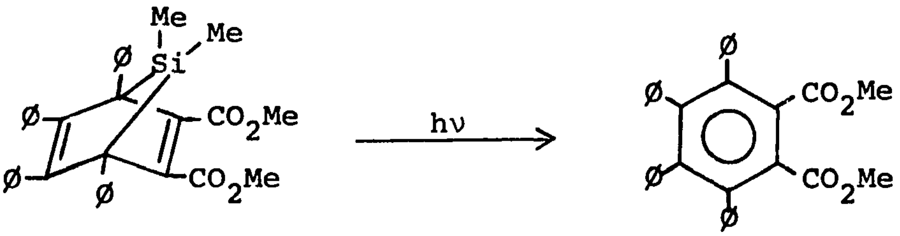
R=H or Ø

R$_1$=R$_2$=Me

R$_1$=R$_2$=Ø

R$_1$=Me, R$_2$=Ø

Photochemical extrusion of dimethylsilylene was apparently observed by Balasubramanian and George when they found that photolysis of the 7-silanorbornadiene 12 gave an 88% yield of tetraphenylphathalate (83). No attempt was made to establish that dimethylsilylene was generated.

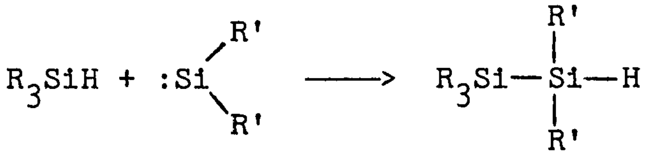


12

88%

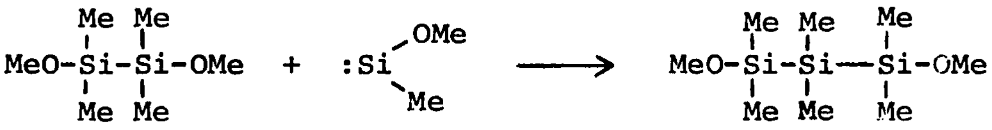
Insertion reactions of silylenes

Silylenes are known to insert into a variety of sigma bonds. Insertion into a silicon-hydrogen bond is the most frequently employed and thoroughly examined insertion reaction. Experimentally, a silylhydride is often the reagent of choice for the trapping of a silylene particularly when the intermediacy of a silylene is at issue. Mechanistically, this insertion reaction has been found to be reversible and to occur in a concerted fashion as discussed in a recent review on this reaction (8).

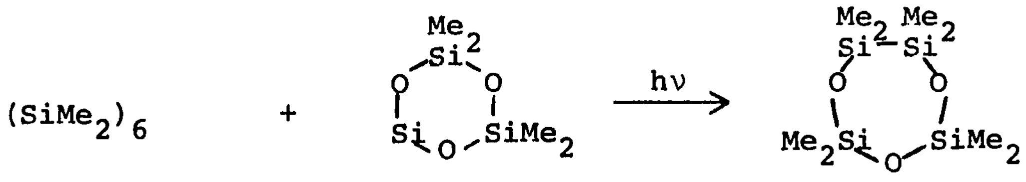


$$R_3SiH + :SiR'_2 \longrightarrow R_3Si{-}SiR'_2{-}H$$

Silylene insertion into a silicon-oxygen single bond was observed by Atwell and Weyenberg who found that methylmethoxysilylene will insert into sym-tetramethyldimethoxysilane (10). Dimethoxysilylene will also insert into a silicon-oxygen bond (27); however, it was found to be less reactive than methylmethoxysilylene in that it would not insert into trimethylsilane (8), or react with diphenylacetylene (21).

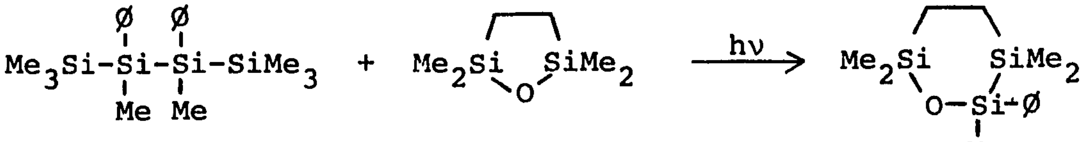


The first report of a silylene insertion into a silicon-oxygen bond of hexamethylcyclotrisiloxane 13 has recently appeared by Soysa and coworkers (78). Okinoshima and Weber have found that 14 is a far better trap than 13 since phenylmethylsilylene is trapped by 14 but not by 13 (73).



13

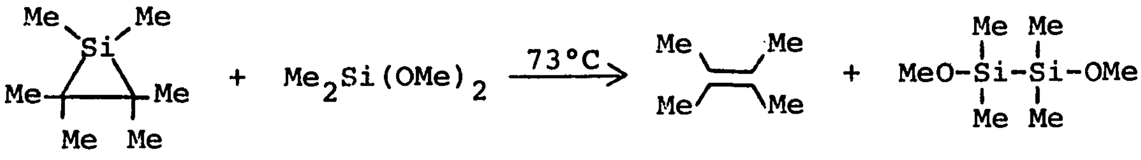
52%



14

40%

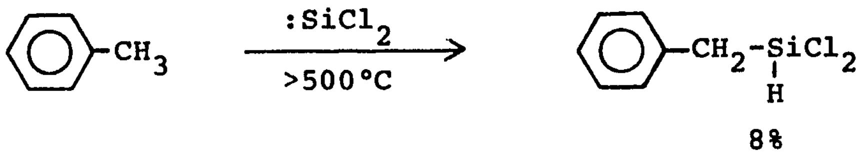
Although it is known that dimethylsilylene is not trapped by dimethyldimethoxysilane above 200°C (10), Seyferth and Annarelli have shown that this will occur under the conditions necessary to thermally decompose hexamethylsilarane 6a (54). This reaction was also observed to occur when dimethylsilylene is generated photochemically (80).

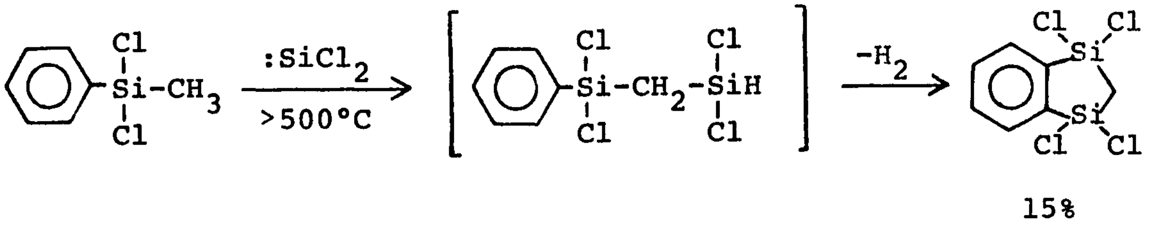


6a

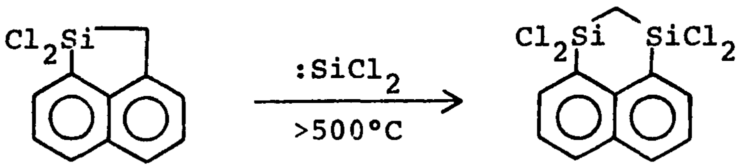
Other insertion reactions of silylene have been discussed in a recent review (11). Among these are insertion into E-X (E = B,P,C,Si and X = F,Cl), and insertion into E-H (E = Si,Ge,O,N,S, or halogen).

Unlike carbenes, silylenes do not readily insert into carbon-hydrogen bonds and this has been suggested to be in keeping with the decreased reactivity of silylenes compared to carbenes (84). The only examples of carbon-hydrogen insertion come from Chernyshev and coworkers (36, 37). They generated dichlorosilylene at temperatures above 500°C and found products from insertion into methyl hydrogens of methyl substituted aryl compounds and methylchlorosilanes. These reactions generally occurred in low yields and often led to secondary reactions of the initial insertion adducts.

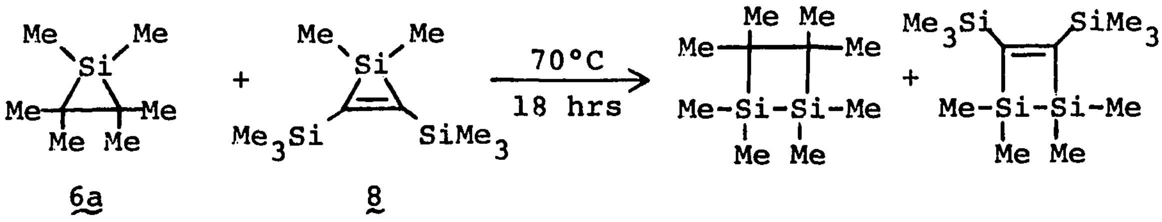




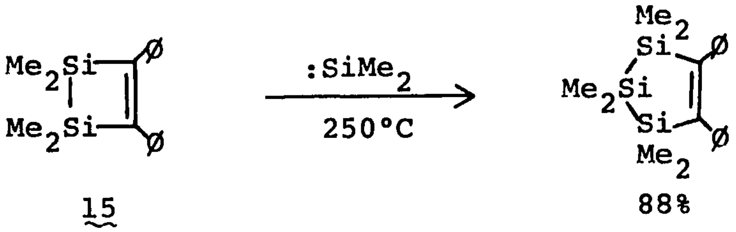
Chernyshev and coworkers also claim to have the first reported example of silylene insertion into a carbon-carbon bond (36).



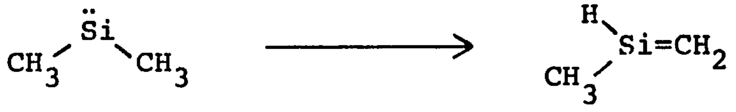
The first example of silylene insertion into a silicon-carbon bond was discovered by Seyferth and Vick (57). They found that thermal decomposition of 6a in the presence of the silarene 8, resulted in dimethylsilylene insertion into the strained silicon-carbon bonds of both of the three-membered rings.



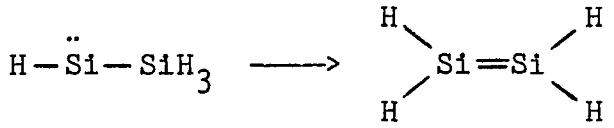
Insertion of a silylene into a silicon-silicon bond had previously only been suggested (15), but Sakurai has now found that dimethylsilylene reacts with the disilacyclobutene 15 to give a one-to-one adduct that most reasonably results from silicon-silicon bond insertion (85).



Unlike carbenes, silylenes have not been shown to undergo intramolecular insertion in alpha hydrogens. It has been suggested only twice in the fourteen years since dimethylsilylene was first generated by Skell and Goldstein (84), that alpha insertion into a methyl hydrogen may occur to give 1-methylsilene (25,30).



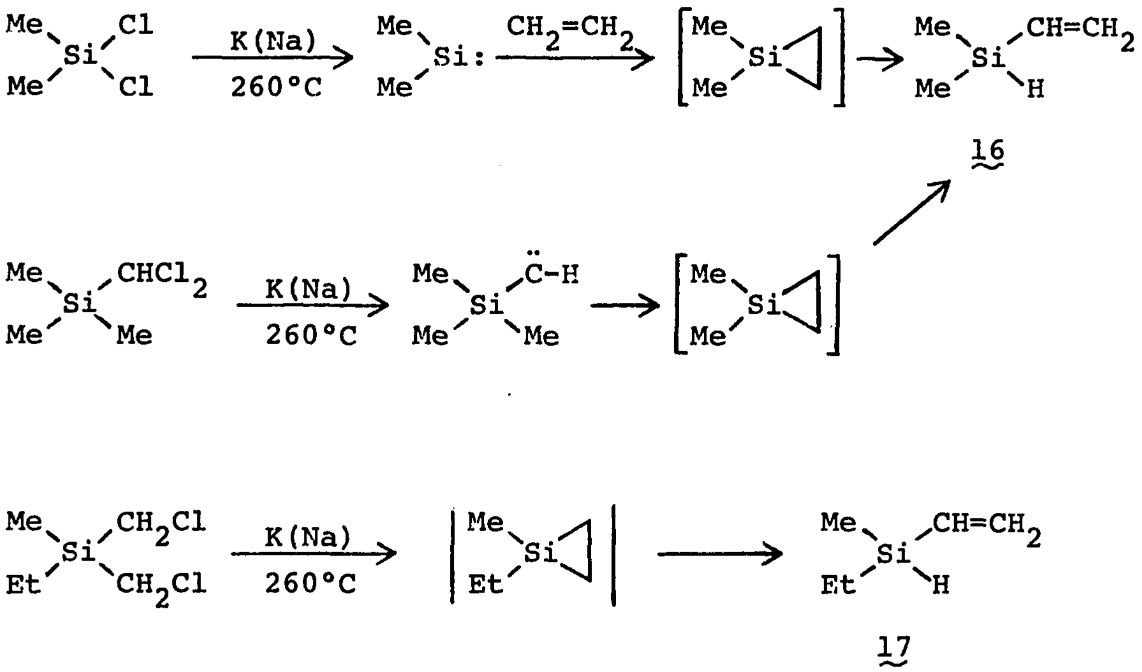
Jenkins and coworkers have suggested that insertion into a hydrogen on an alpha silicon may occur in silylsilylene to give disilene (48). If this proves to be correct, it will be the first example of such an insertion and only the third method for the generation of a disilene.



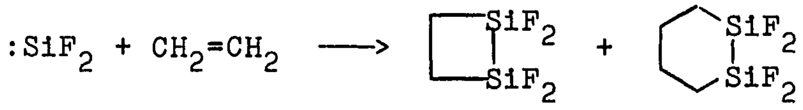
Silylene addition to olefins

It is now known that silaranes are fairly thermally sensitive compounds. The half-life of hexamethylsilarane is five hours at 63°C (58). Thus, preparation of isolable silaranes via silylene addition to olefins could not be possible until mild methods of silylene generation had been developed. This was first achieved by Ishikawa and Kumada in 1974 (67). Prior to this time, however, many groups attempted to study this reaction at the high temperatures required for silylene generation (10). Skell and Goldstein were able to deduce the intermediacy of 1,1-dimethylsilarane in the gas phase reaction of dimethyldichlorosilane, ethylene, and alkali metal vapor (84) (Scheme 1). The observed product of the reaction was dimethylvinylsilane 16 which was argued to result from thermal rearrangement of the silarane. Strength was added to this argument by the fact that similar reductions of trimethylchloromethylsilane and bis-(chloromethyl)ethylmethyl silane gave the corresponding vinylsilanes 16 and 17.

Scheme 1

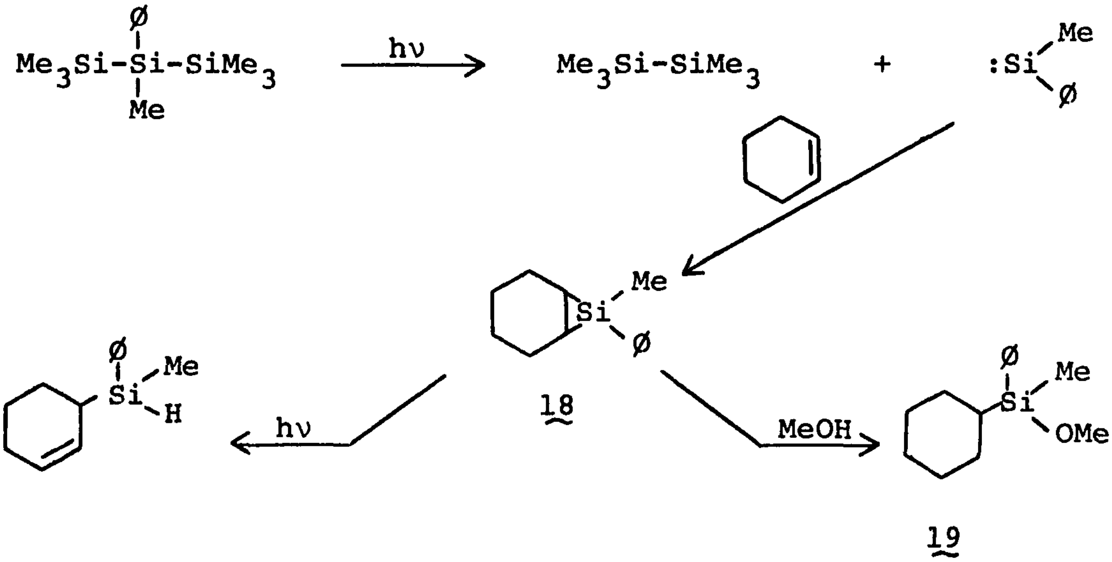


Difluorosilylene exhibits anomalous behavior in its reaction with ethylene. Both of the products from this reaction contain two adjacent silicon atoms and have been suggested to be the result of initial difluorosilylene dimerization (86). This reaction has been recently reinterpreted in terms of a 1,1-difluorosilarane intermediate (59), and in terms of a diradical mechanism (87). The chemistry of difluorosilylene will be further discussed in the Historical section on disilenes.

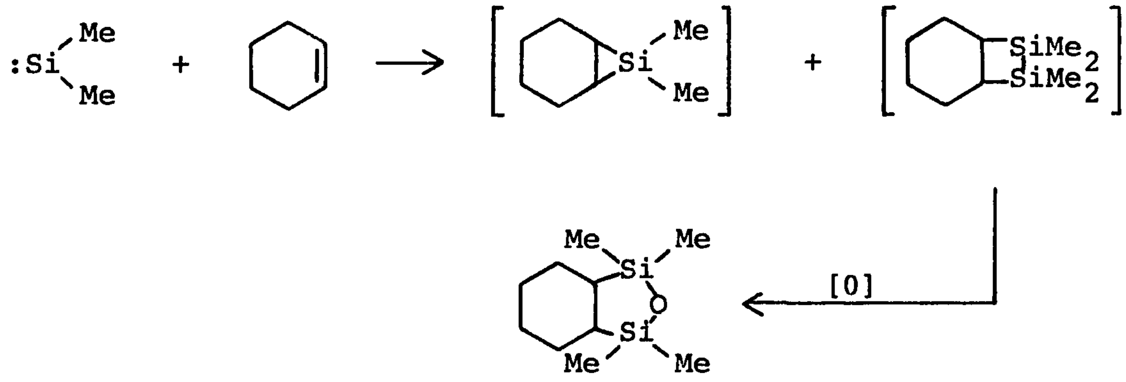


The next report of any substance on this subject appeared by Ishikawa and Kumada (67). They found that photochemically-generated phenylmethylsilylene adds to cyclohexene to give the silanorcarane 18 (Scheme 2). Compound 18 was stable in solution and reacted with methanol in the expected manner to give the methoxysilane 19. If 18 was subjected to higher energy irradiation, it rearranged to the silane 20. However, no spectroscopic evidence for 18 was reported.

Scheme 2

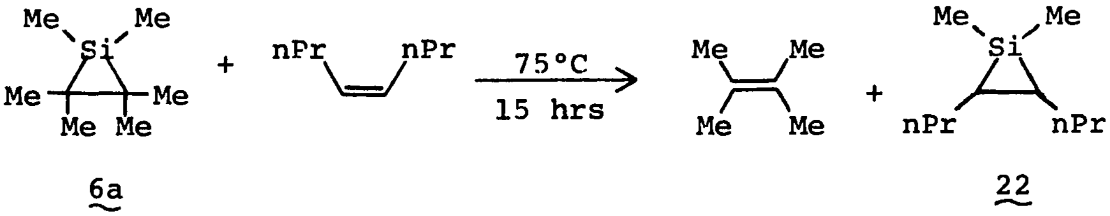


A similar result was observed for photochemically-generated dimethylsilylene (67). The minor product 21 can be accounted for by the recently established insertion of silylenes into the silicon-carbon bond of silaranes and by the fact that 1,2-disilacyclobutanes are known to air oxidize to give 1-oxa-2,5-disilacyclopentanes (57). Ishikawa and coworkers have studied the reaction of photochemically generated silylenes with a wide variety of olefins (68,71).



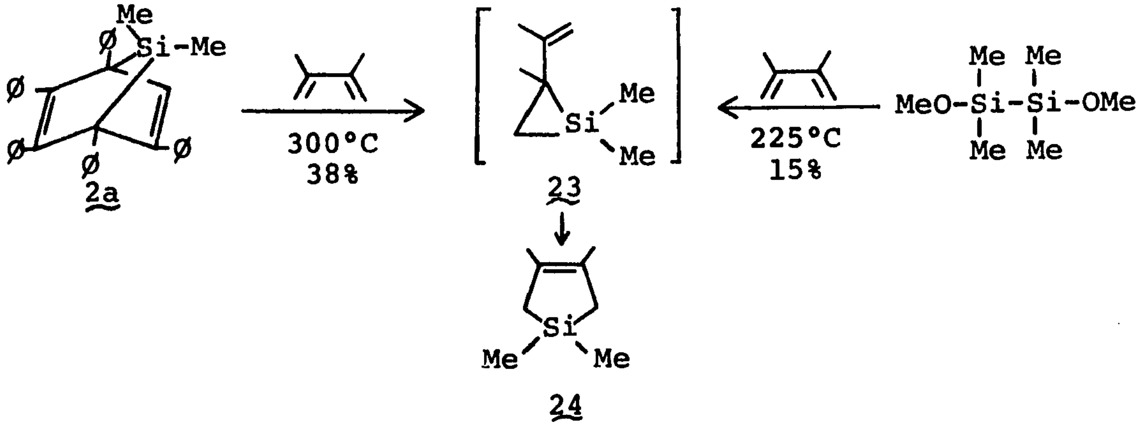
21

Dimethylsilylene transfer from hexamethylsilarane **6a** to olefins has been achieved by Seyferth and Annarelli (56). When **6a** was heated at 75°C for fifteen hours in the presence of excess cis-4-octene, a 69% yield of the silarane **22** was formed as measured by its trapping with methanol. In a similar fashion dimethylsilylene transfer was also successful with cyclooctene, 1-trimethylsilylpropene, and 2,3-dimethyl-2-pentene. Transfer to allyltrimethylsilane and 1-decene was unsuccessful and was attributed to the lesser thermal stability of mono-substituted silaranes. Reaction with styrene resulted in its insertion into the silicon-carbon bond of 6a.

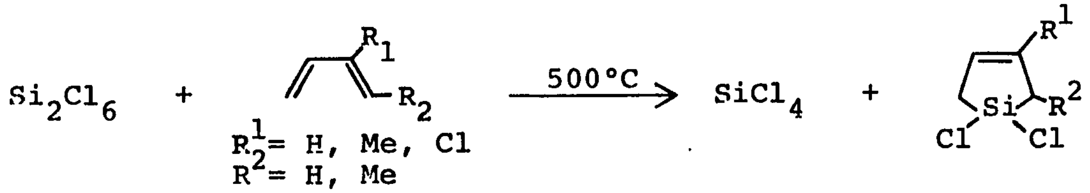


Silylene addition to dienes

The addition of silylenes to dienes was first reported by Atwell and Weyenberg (21). They observed that dimethylsilylene, generated from either tetramethyldimethoxydisilane or from the 7,7-dimethyl-7-silanorbornadiene, 2a, reacted with 2,3-dimethylbutadiene to give the 1,4-addition product 24. They proposed that an initial 1,2-addition occurred to give the vinylsilarane 23, which then rearranged to 24 at these temperatures. Other silylenes such as methylmethoxysilylene (31) and R_2Si: (R = Cl, F, OR, H) were also found to give 1,4-addition products (10,27).

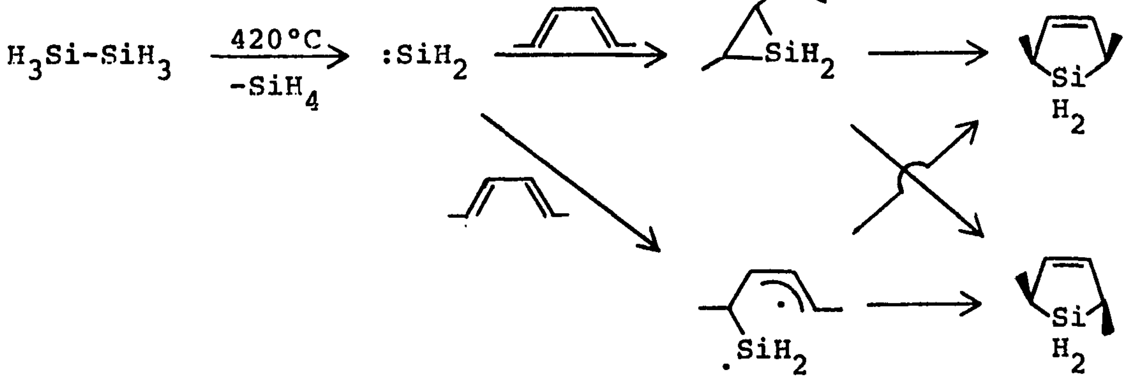


Chernyshev and coworkers found that dichlorosilylene generated from hexachlorodisilane at 500°C also reacts with dienes to give silacyclopentenes (33,39). Quite surprisingly, they found that the yields of the 1,4-addition products were greater than 90% for all dienes used.

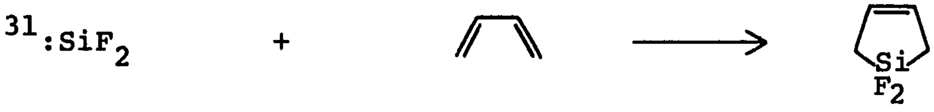


Although most researchers have from the beginning felt that silylene addition to dienes proceeded via an initial 1,2-addition, supportive evidence did not come until 1974 (8,18). Gaspar and Hwang reported that addition of silylene to trans-2-trans-4-hexadiene gave a six-to-one mixture of cis and trans isomers of 2,5-dimethyl-1-silacyclopent-3-enes (Scheme 3). A concerted 1,4-addition would have produced only the cis isomer. The results are consistent with either a diradical or a silarane as an intermediate.

Scheme 3



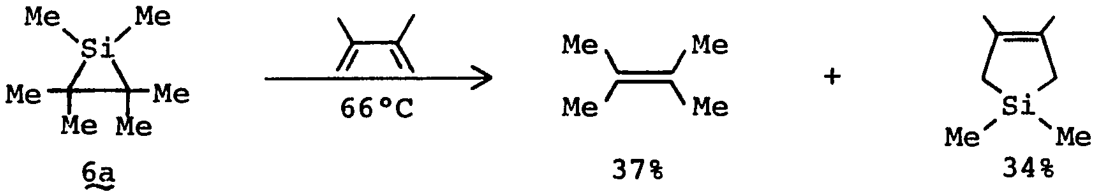
A claim has been made that triplet ^{31}:SiF$_2$ adds in a conserted fashion to butadiene (88). It has been documented, however, that the chemistry of nucleogenic and thermal silylenes does differ. For example, Zeck and coworkers have found that nucleogenic difluorosilylene gives a 1,4-addition product with butadiene (89), whereas Thompson and Margrave have found that thermally-produced difluorosilylene reacts with butadiene to give the 1,2-disilacyclohexene 26 (90). This later reaction will be further discussed in the Historical section on disilenes. Hwang and Gaspar have recently discussed a second example (19). They found that the products from the reaction of butadiene and cyclopentadiene with thermally produced :SiH$_2$ are different from those with ^{31}:SiH$_2$.



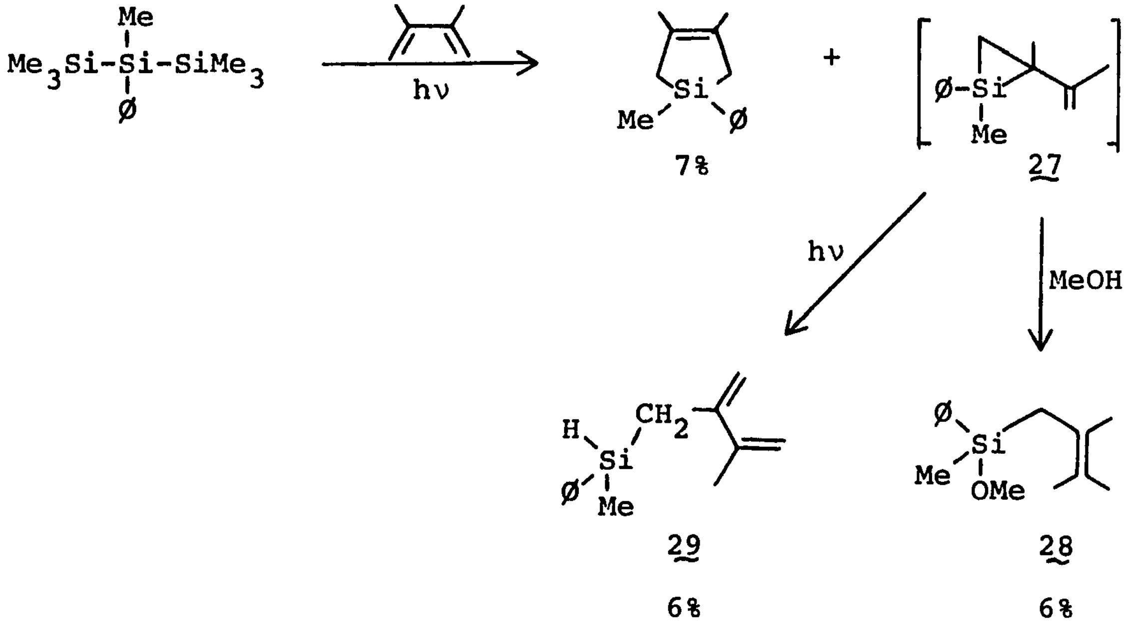
25

26

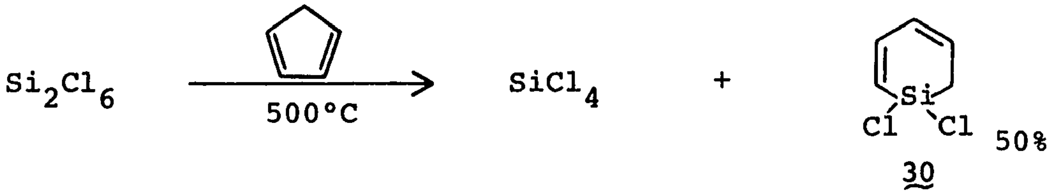
An opportunity to observe the initial 1,2-adduct of a silylene and a diene came when Seyferth and Annarelli found that hexamethylsilarane 6a liberated dimethylsilylene under mild thermal conditions. Unfortunately, they found that when **6a** was heated with 2,3-dimethylbutadiene only the 1,4-addition product was formed (54).



Involvement of a 1,2-addition intermediate was established in the reaction of 2,3-dimethylbutadiene with photochemically generated phenylmethylsilylene in 1975 by Ishikawa, Ohi and Kumada (69). Along with the 1,4-addition product, they found two products, **28** and **29**, that support the intermediacy of the silarane **27**. Compound **28** would result from 1,4-addition of methanol to **27**, and **29** represents a product that would result from a known photoisomerization of silaranes.



In 1972, Chernyshev and coworkers found that dichlorosilylene adds to cyclopentadiene to give 1,1-dichloro-1-silacyclohexa-2,4-diene 30 (33). This apparent carbon-carbon bond insertion reaction has proven to be fairly general for cyclic dienes. Table 3 lists the known reactions of cyclic dienes with silylenes.



Barton and Banasiak (29) have found that dimethylsilylene reacts with cyclopentadiene to give two isomeric silacyclohexadienes 32 and 33 (Scheme 4). This result can be used to argue that silylenes also react with cyclic dienes *via* silarane intermediates. In this case, if the silarane 31 undergoes carbon-carbon bond rupture, the resulting diradical can account for the products 32 and 33 *via* hydrogen abstractions.

Scheme 4

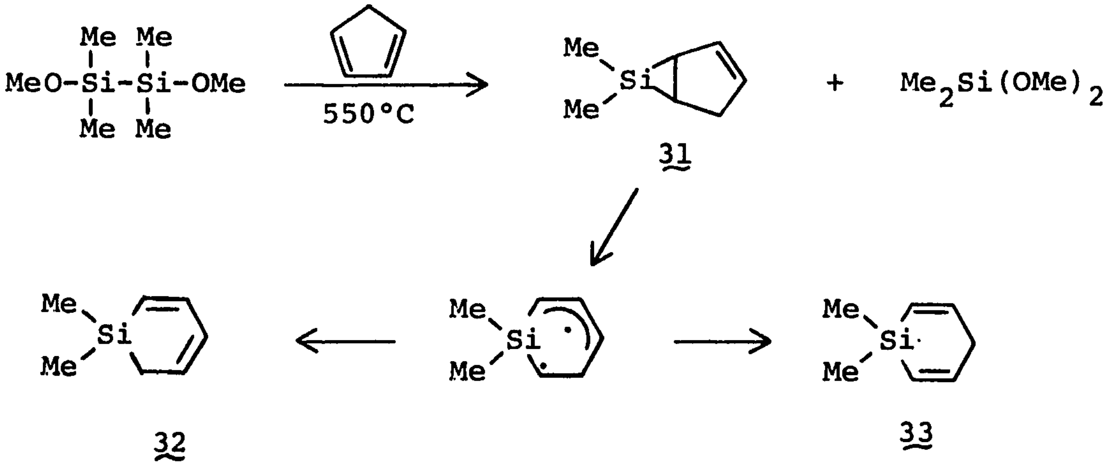


Table 3. Addition of silylenes to cyclic dienes

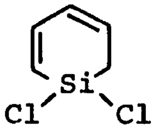
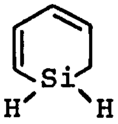
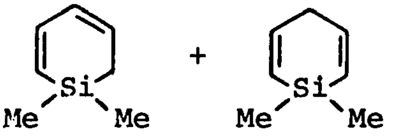
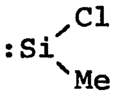
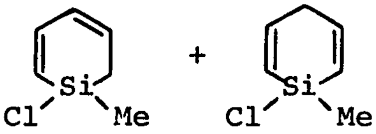
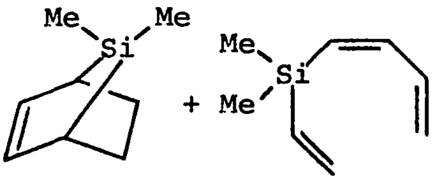
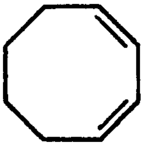
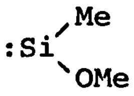
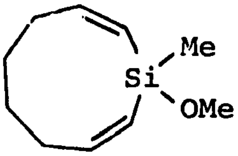
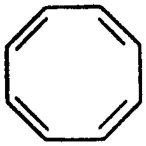
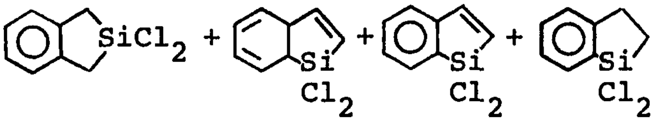
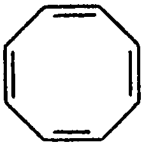
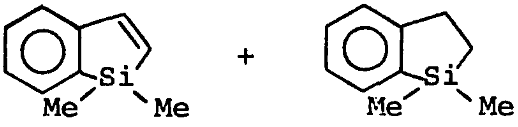
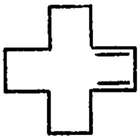
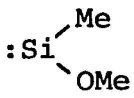
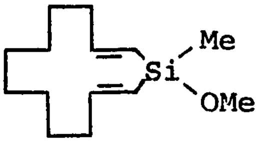
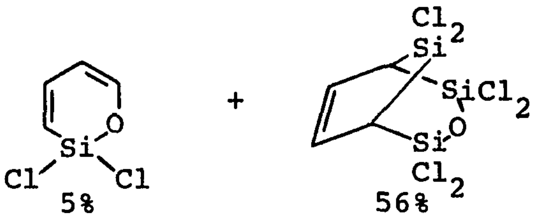
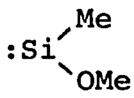
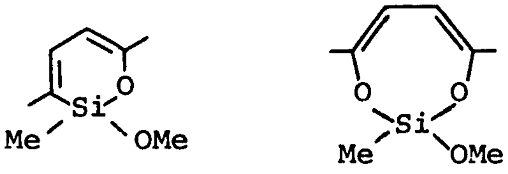
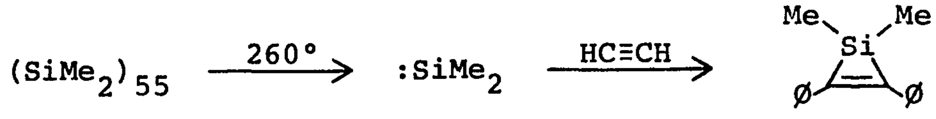
Diene	Silylene	Product	References
	$:SiCl_2$	 50%	33,47
	$:SiH_2$	 10%	47
	$:SiMe_2$	 29% 11%	29,47
	 $:SiClMe$	 39% 5%	43
	$:SiMe_2$	 10% 10%	47
	 $:SiMe(OMe)$		24

Table 3. (Continued)

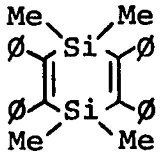
Diene	Silylene	Product	References
	$:SiCl_2$	 7% 8% 17% 13%	35
	$:SiMe_2$	 30% 15%	91
	 $:Si(Me)(OMe)$		24
	$:SiCl_2$	 5% 56%	33
	 $:Si(Me)(OMe)$	 3.3% 1.5%	23

Silylene addition to acetylenes

The reaction of acetylenes with silylenes begins in 1962 with the report by Volpin and coworkers that dimethylsilylene, generated from the thermolysis of a polydimethylsilane, reacts with diphenylacetylene to give the diphenyldimethylsilarene 34 (92). This product was shown by West and Bailey actually to be the 1,4-disilacyclohexa-2,4-diene 35 (93).



34

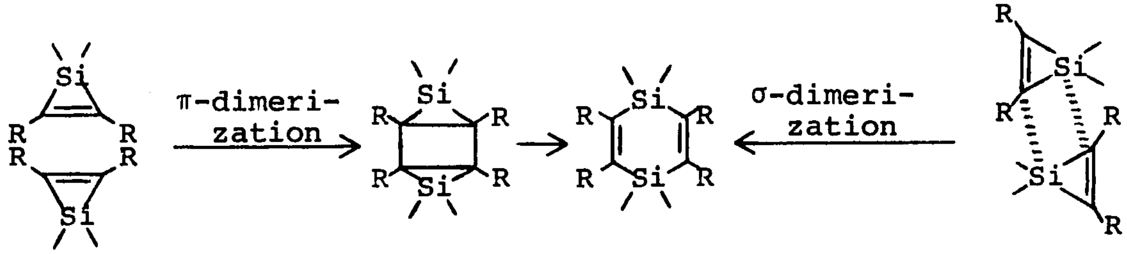


35

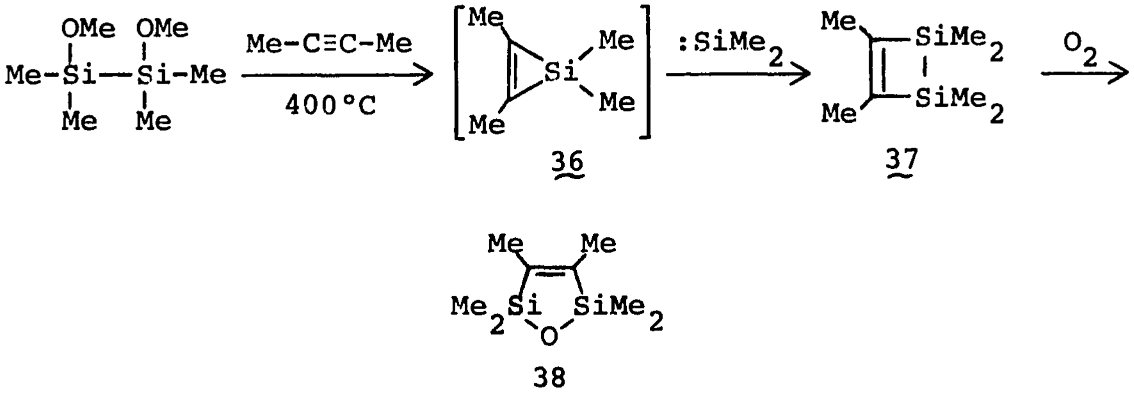
Two years later, Gilman, Cottis and Atwell observed the formation of 35 from the reaction of diphenylacetylene with dimethylsilylene generated from a 7-silanorbornadiene (49). This reaction was soon after demonstrated to be general for a variety of acetylenes and silylenes in both the gas and liquid phases (3,10,21,22,33,34).

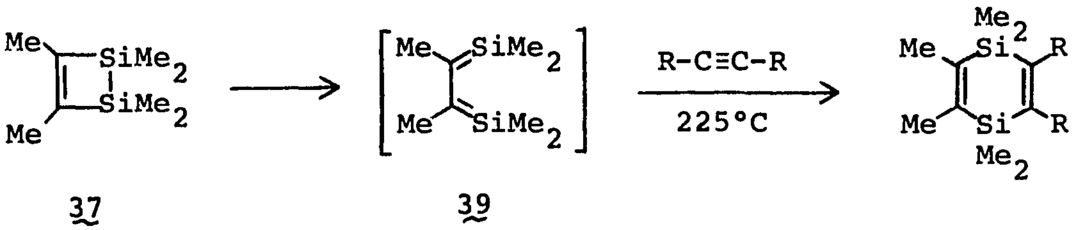
Atwell and Weyenberg initiated an investigation (21) into the mechanism of this reaction that continues today. As a result, the chemistry that has been uncovered has had a profound influence on the development of organosilicon chemistry. In addition, this reaction immediately became accepted as a chemical means for the detection of silylenes.

Beginning with the assumption that a silarene is an intermediate in this reaction, Atwell and Weyenberg carried out an experiment with a mixture of acetylenes, the results of which allowed them to eliminate the possibility of a π-dimerization of the silarene. The results were consistent with a σ-dimerization mechanism, and Atwell and Weyenberg resigned themselves to this conclusion.



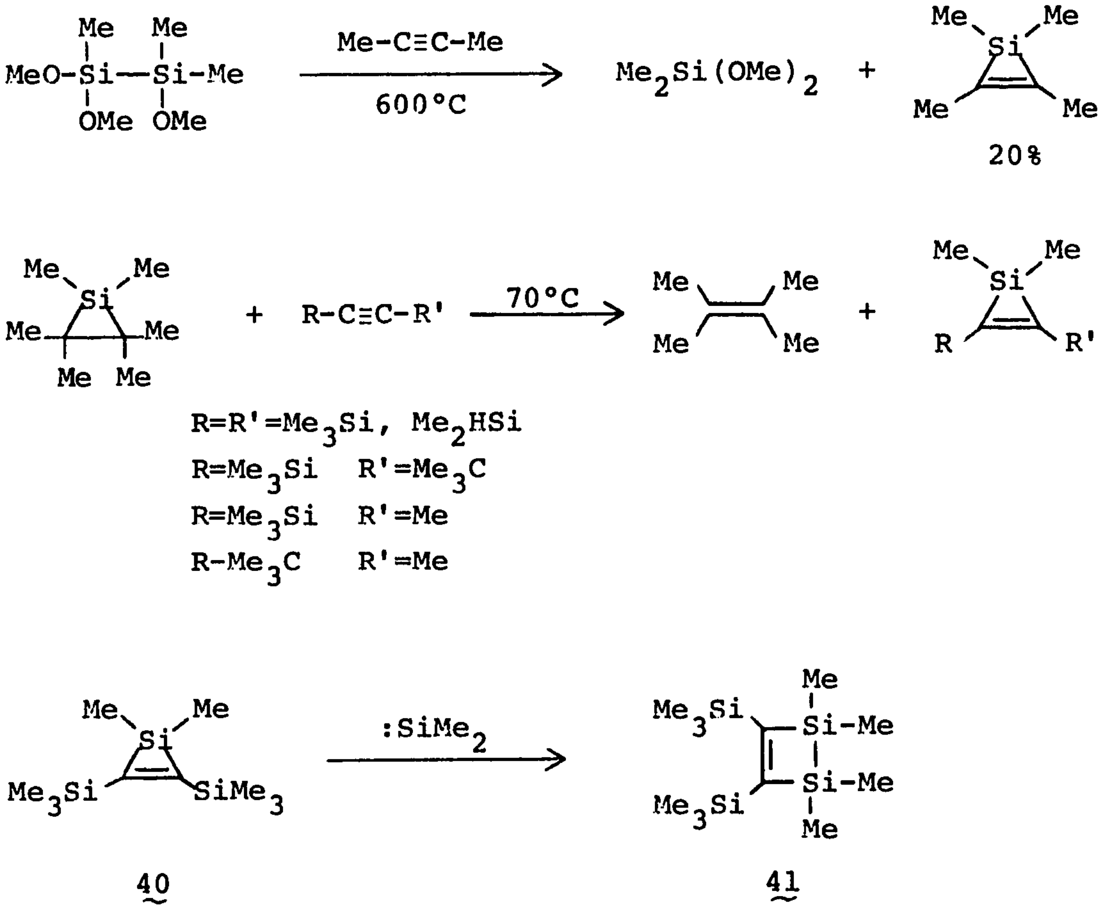
Investigations of alternative mechanisms to σ-dimerization followed the discovery that dimethylsilylene reacts with 2-butyne to give hexamethyl-1,2-disilacyclobutene 37 (28). Atwell and Uhlman proposed that the silarene 36 was formed by initial addition of dimethylsilylene to the acetylene and that 37 can be accounted for by insertion of a second silylene into 36. When exposed to air, 37 was oxidized to hexamethyl-1-oxa-2,5-disilacyclopentene 38. This suggests another mechanism for the silylene-acetylene reaction, the last step of which was examined by Barton and Kilgour (94,95). They found that 37 would react with acetylenes to give 1,4-disilacyclohexadienes. They suggested that this may occur by initial ring opening of 37 to the 1,4-disilabutadiene 39 followed by a 4 + 2 cycloaddition.





Support for the intermediacy of a silarene in these reactions followed from the direct observation of silarenes from silylene-acetylene reactions carried out under a variety of conditions (Scheme 5). Conlin and Gaspar obtained tetramethylsilarene in 20% yield from the co-pyrolysis of 2-butyne and sym-tetramethyldimethoxydisilane at 600°C (26). Seyferth and coworkers found that they could affect dimethylsilylene transfer from hexamethylsilarane to a variety of acetylenes (55,57). Support for the second step of this mechanism came with the observation by Seyferth and Vick that the silarene 40 will suffer insertion of dimethylsilylene to give 41 (57).

Scheme 5



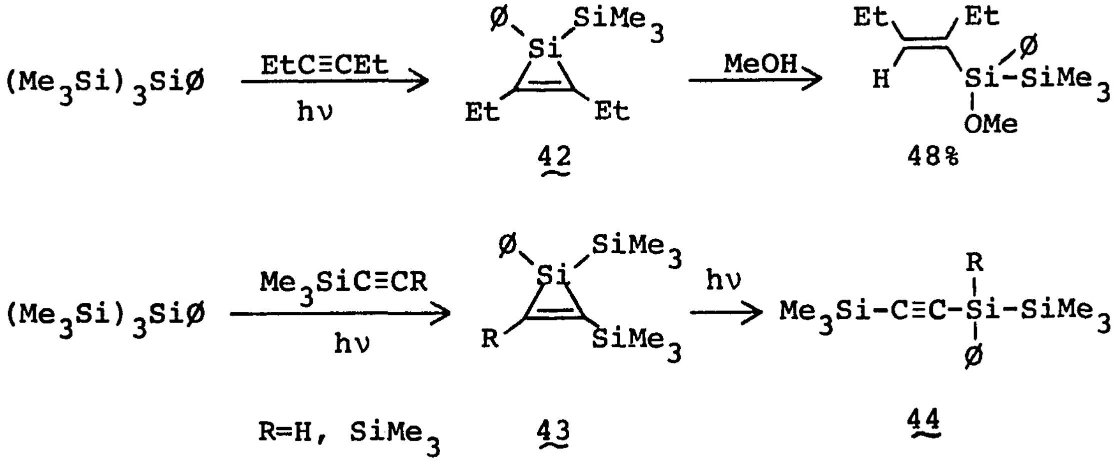
R=R'=Me_3Si, Me_2HSi
R=Me_3Si R'=Me_3C
R=Me_3Si R'=Me
R-Me_3C R'=Me

40

41

Ishikawa, Nakagawa and Kumada found that photochemically generated phenyltrimethylsilylsilylene adds to 3-hexyne to give the silarene 42 as indicated by trapping with methanol

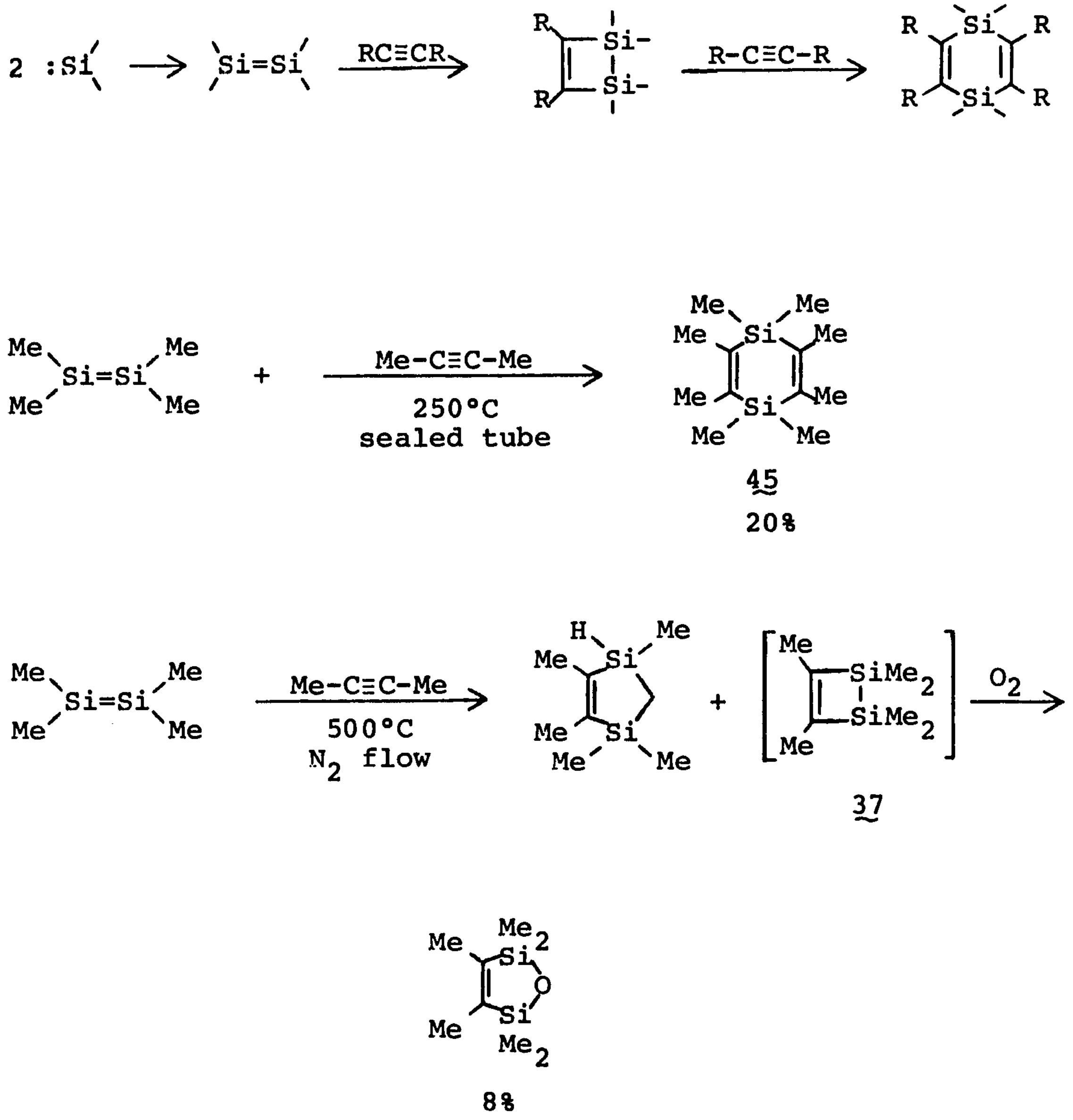
(62). They also found that with a terminal or silyl-substituted acetylene, a second product, 44, was formed that was accounted for by a direct photochemical rearrangement of the silarene 43. This is the reverse of a photo-induced rearrangement of disilanylacetylenes to silarenes that has been observed by Sakurai et al. (96) and Ishikawa et al. (97).



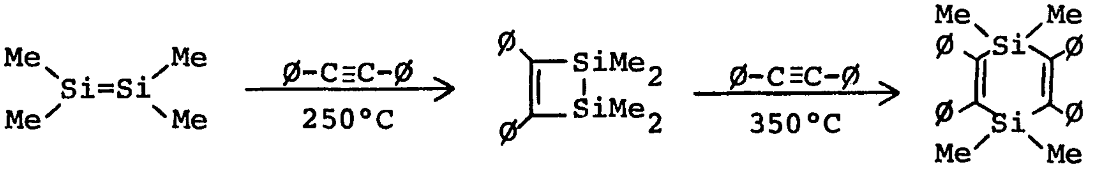
Another possible mechanism involves the dimerization of a silylene to give a disilene, a reaction which now appears to occur in at least some situations (25,32), followed by a 2+2 cycloaddition of the disilene and acetylene to give a 1,2-disilacyclobutene (Scheme 6). Barton and Kilgour have obtained results that are consistent with this mechanism (95). They found that when tetramethyldisilene is generated in the presence of 2-butyne in the liquid phase, the

1,4-disilacyclohexadiene 45 is obtained in 20% yield. In the gas phase, however, this same reaction produced the oxygenated product of 1,2-disilacyclobutene 37 rather than 45.

Scheme 6



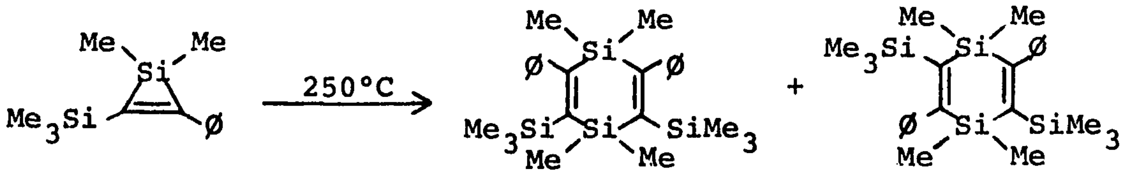
To further confuse the issue, Sakurai and coworkers found that tetramethyldisilene will react with diphenylacetylene in the condensed phase to give a 64% yield of the disilacyclobutene 46, which when isolated, would not react with diphenylacetylene in the condensed phase to give more than a 1% yield of 35 (85).



46 64%

35 1%

Ishikawa and coworkers have reported that if the silarene 47 is heated at 250°C in an inert solvent it will dimerize to give the two disilacyclohexadienes 48 and 49 that one would expect to obtain from a σ-dimerization mechanism (98). Although several mechanisms have been shown to be possible for the formation of 1,4-disilacyclohexadienes from the reaction of silylenes with acetylenes, it is unlikely that any of them can exclusively account for product formation under all of the conditions for which the reaction is known to occur.

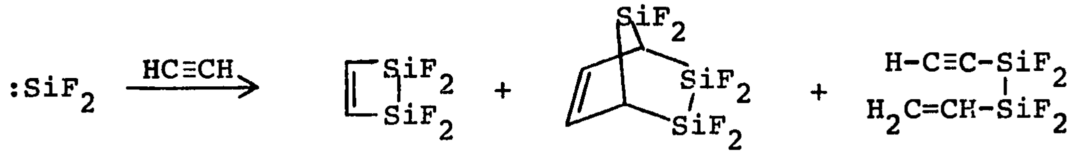


47

48
20%

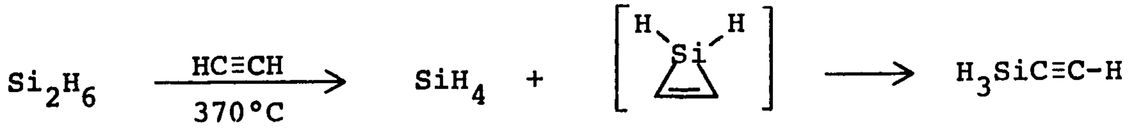
49
60%

The reaction of difluorosilylene with acetylenes differs from that of other silylenes. When thermally produced difluorosilylene is co-condensed with acetylene, the observed products are 50, 51 and 52 (99). As in other reactions, difluorosilylene appears to dimerize before it reacts.



50 51 52

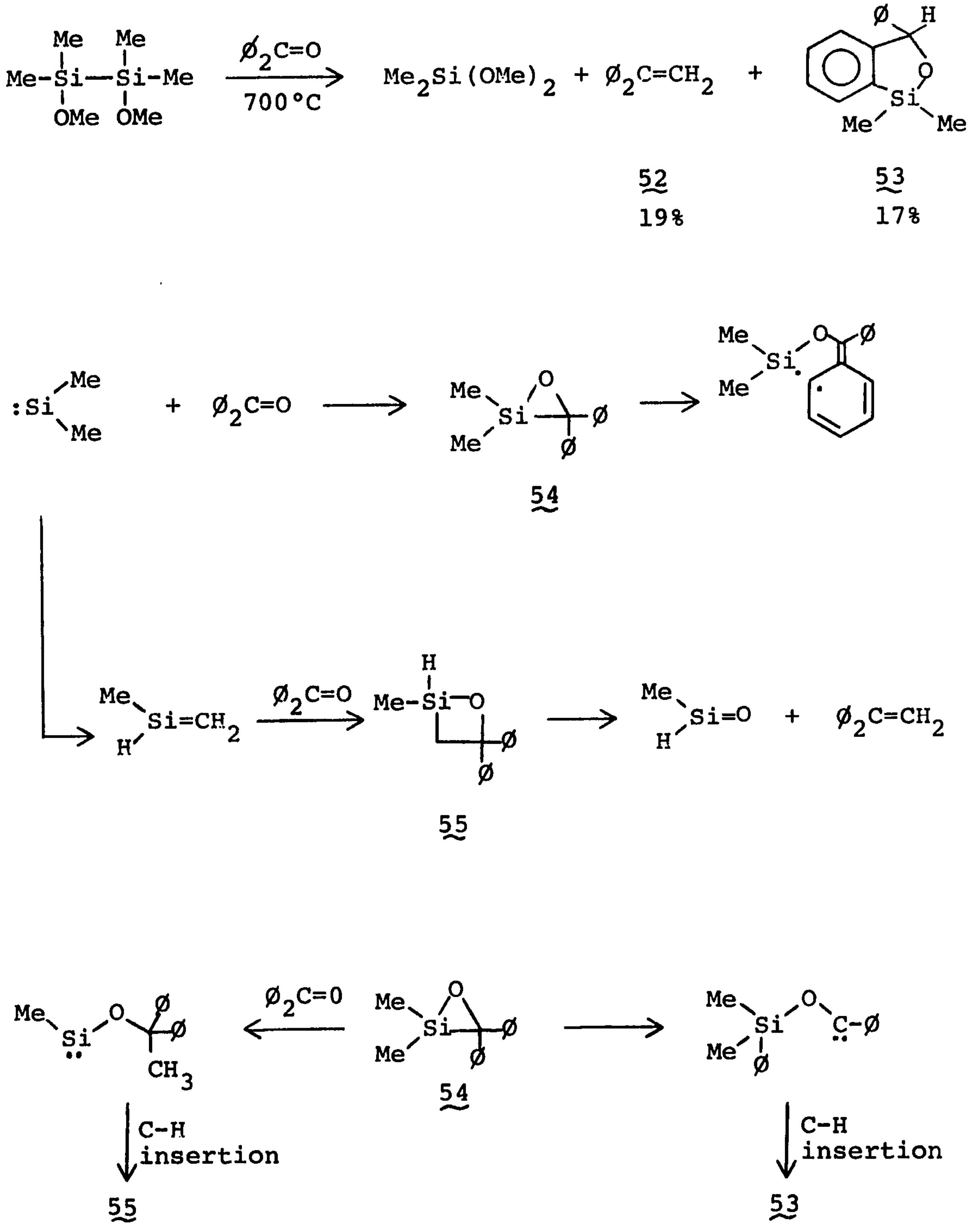
Haas and Ring have reported that silylene reacts with acetylene to give ethynylsilane (100). Although this product could be accounted for by direct insertion into a carbon-hydrogen bond, they argue for a silarene intermediate.



Silylene addition to carbonyls

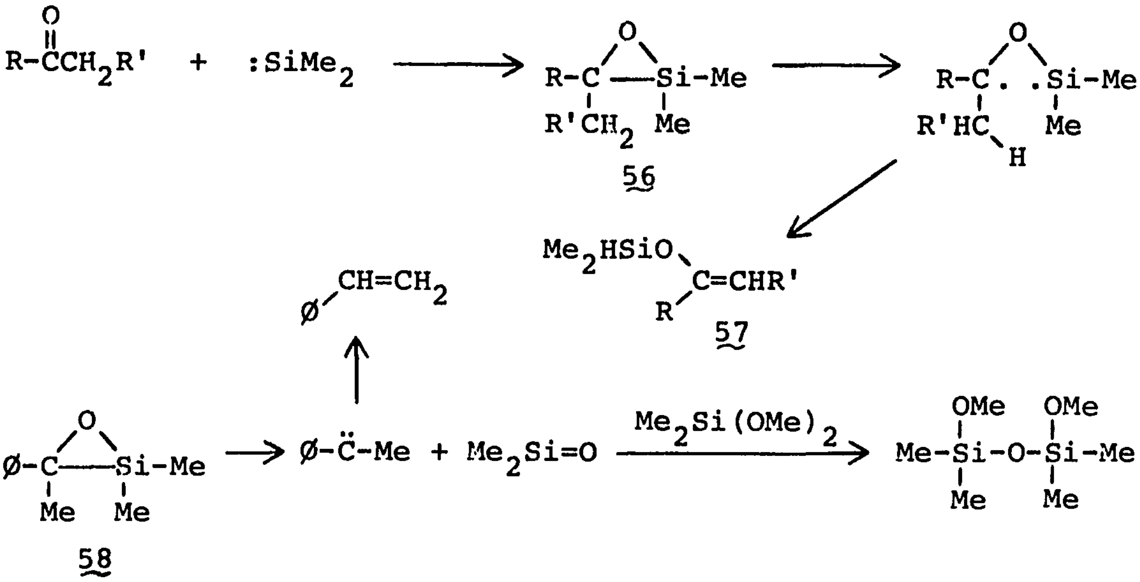
The first report of addition of a silylene to the π-bond of a carbonyl was by Ando and coworkers in 1977 (30). When dimethylsilylene was generated at 700°C in the presence of benzophenone, the resulting products of interest were 52 and 53. The latter was postulated as arising from an intermediate oxasilacyclopropane 54, which rearranged to the observed bicyclic product (Scheme 7). The diphenylethene was suggested to result from an initial alpha-hydrogen insertion in dimethylsilylene to give 1-methylsilene, which is then trapped by benzophenone to give the siloxetane 55. Siloxetanes are commonly believed to thermally rupture to give olefins and silanones (101). Insertions into an alpha hydrogen with silene formation has not been observed before although it has been suggested once before (25). Interestingly, at 500°C no diphenylethene was formed and the yield of 53 increased. An alternative mechanism suggested by some results to be presented in this thesis is that 54 may undergo alpha elimination from either carbon or silicon (Scheme 7). 53 and 55 could then be accounted for by subsequent carbon-hydrogen insertions. This could preclude the necessity of an alpha insertion occurring in dimethylsilylene and account for the absence of 52 at 500°C since the alpha elimination from silicon is expected to be the least favorable.

Scheme 7


Me-Si(Me)(OMe)-Si(Me)(OMe)-Me
Ø2C=O
700°C
Me2Si(OMe)2 + Ø2C=CH2 +
52
19%
53
17%
:SiMe2 + Ø2C=O
54
Me(H)Si=CH2
55
Me(H)Si=O + Ø2C=CH2
C-H insertion
55
C-H insertion
53

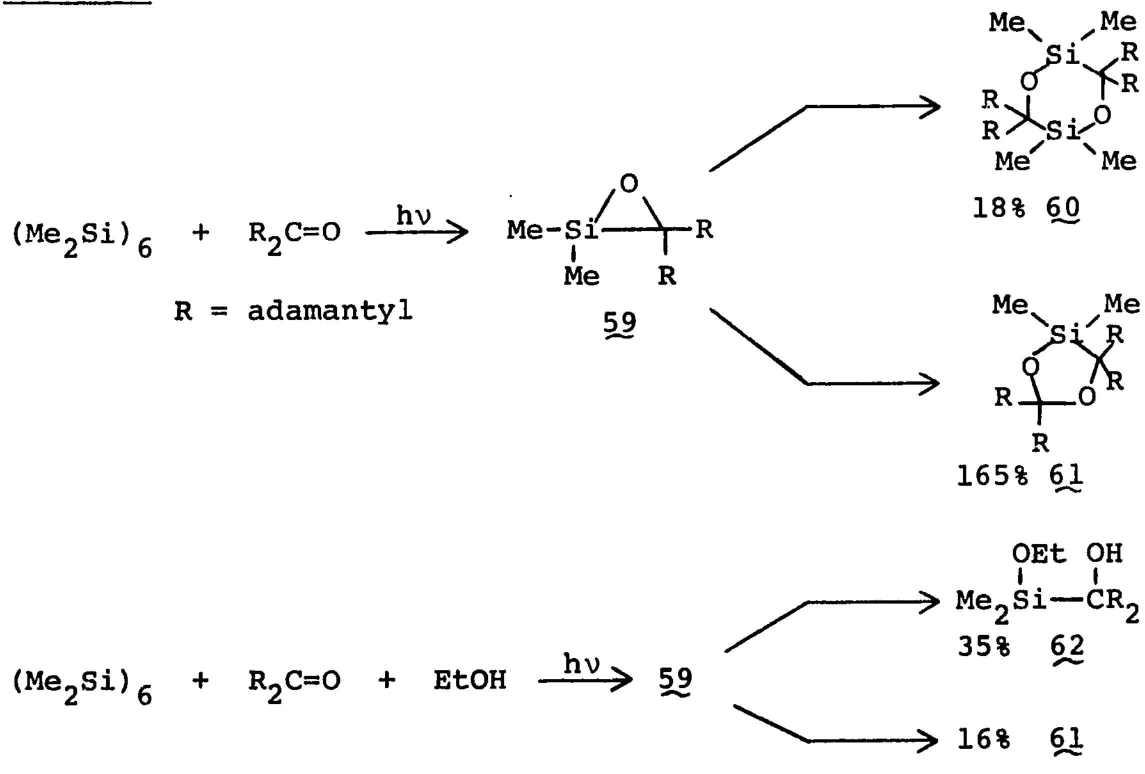
With enolizable ketones, the products obtained 57 correspond to simple silylene insertion into the oxygen-hydrogen bond of the enol of the carbonyl (Scheme 8). Ando and coworkers argued that these products were also derived from an oxasilacyclopropane 56 since they found that dimethylsilylene did not react with ethanol under similar conditions. In the case of acetophenone, the products were styrene and sym-tetramethyldimethoxydisiloxane, the known product of trapping of dimethylsilanone and dimethyldimethoxysilane. Again, these products were attributed to an oxasilacyclopropane intermediate 58.

Scheme 8



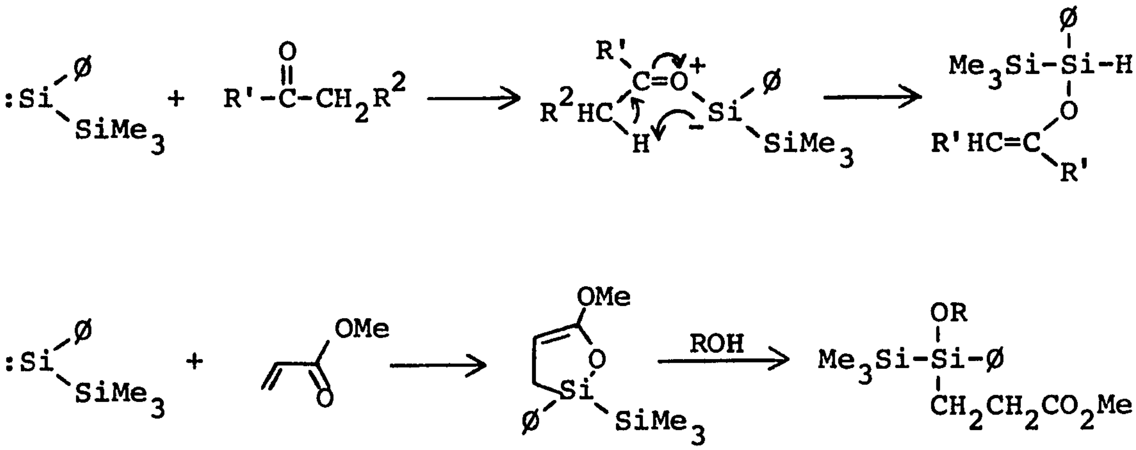
Ando and coworkers followed up this work by a report on the reaction of nonenolizable ketones with photochemically generated silylenes (79). They found that under these mild conditions dimethylsilylene reacted with adamantanone to give two products that could also be accounted for by an intermediate oxasilacyclopropane (Scheme 9). The major product 61 is an adduct of a molecule of the oxasilacyclopropane 59 and a molecule of adamantanone. The minor product 60 is a dimer of 59. Seyferth and Lim have recently presented evidence that an oxasilacyclopropane will dimerize in this manner (102). Strong evidence for the intermediacy of 59 was obtained when the same reaction was carried out in the presence of ethanol and it was found (with appropriate control experiments) that 62 was a primary product of the reaction.

Scheme 9



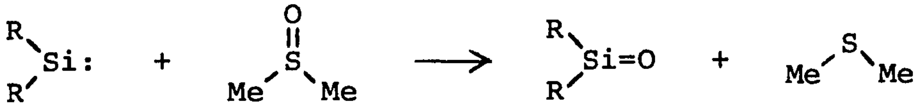
In somewhat of a contrast to these results, Ishikawa and coworkers have reported that photochemically produced phenyltrimethylsilylsilylene reacts with enolizable ketones to give products that also appear to result from silylene insertion into the oxygen-hydrogen bond of the enol form (Scheme 10). They contend that these results can be best explained by a concerted pathway and not by an oxasilacyclopropane intermediate. In the reaction with methylacrylate they believe that an initial 1,4-addition takes place and not a 1,2-addition.

Scheme 10

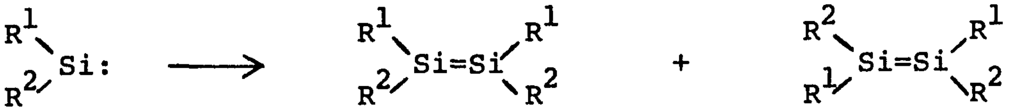


Miscellaneous reactions of silylenes

In a recent series of papers Soysa, Okinoshima and Weber have reported finding that photochemically generated silylenes will deoxygenate dimethylsulfoxide to give dimethylsulfide and a silanone (72,78,103). This reaction will be further discussed in the Historical section on silanones.



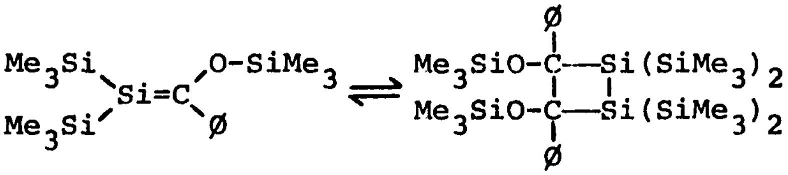
Conlin and Gaspar (25), and more recently Sakurai (32), have claimed that organosilylenes under certain conditions will dimerize to give disilenes. These results, along with the special case of difluorosilylene will be discussed in the Historical section on disilenes.



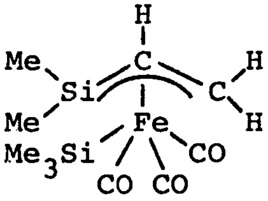
Silenes

The first evidence for a (p-p) π bond between silicon and carbon was published in 1966 by Nametkin and coworkers (1) and shortly thereafter by Gusel'nikov and Flowers (2). Since that time, silenes have been to a very large degree the most actively studied of the (p-p) π bonded silicon species. This is true to the extent that a comprehensive coverage of the chemistry of silenes would be far too long for the purposes of this review. The chemistry of silenes has been the subject of several reviews (101, 104-106).

To date, all attempts to isolate a silene have failed. Recently, however, Brook and coworkers have reported that the sterically hindered silene 63 is in equilibrium with its head to head dimer 64 (107). Shortly thereafter, Sakurai and coworkers reported the preparation of 65, the only known π-complex of a silene and a transition metal (108). Two groups of workers have recently published the infrared spectra of 1,1,2-trimethylsilene in an argon matrix at 8°K (109,110).



63 64



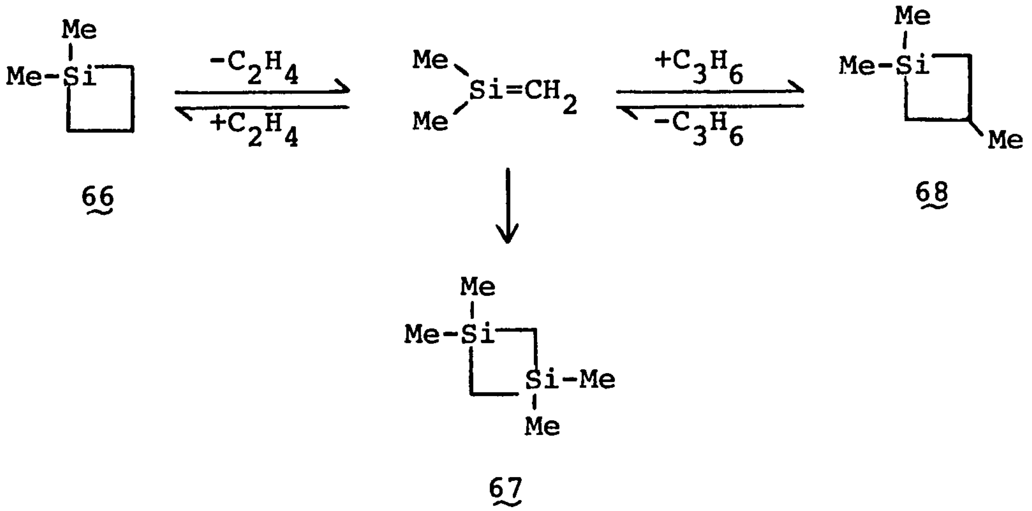
65

Theoretical considerations of the π-bond strength for unsubstituted silene, with one exception, predict values in the range of 22-46 kcal/mole (106). Walsh has used the kinetic data of Flowers and Gusel'nikov to calculate that the π-bond energy of 1,1-dimethylsilene should be in the range of 28-46 kcal/mole (111). *Ab initio* calculations by Ahlrichs and Heinzman give a value of 46 kcal/mole for the π-bond energy of unsubstituted silene (112). The only other *ab initio* study predicts that silene has a ground state triplet! The difference is that Ahlrich and Heinzmann included in their calculation the polar nature of silenes. Considerable polarity in silenes has been both predicted from numerous calculations and deduced from their chemical reactivity.

The chemistry of silenes will be surveyed by presenting the most useful methods for their generation and a description of the general types of reactions that they undergo. In addition, the known chemistry of conjugated silenes will be comprehensively discussed.

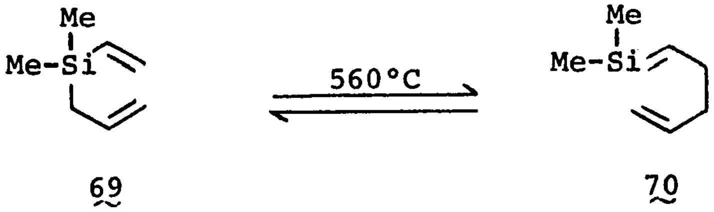
Methods of silene generation

The first silene was generated by the thermal decomposition of silacyclobutanes (1,2) which in the following years have become the most commonly used silene generators (106). Kinetic studies have demonstrated that the decomposition is unimolecular, and it was found that the kinetic parameters were nearly identical to those for the thermal decomposition of 1,1-dimethylcyclobutane to ethene and isobutene (101). The decomposition of silacyclobutanes to silenes and olefins was found to be reversible. Nametkin and coworkers (113,114) found that co-pyrolysis of **66** and excess propene at 560°C gave a 61% yield of **67** and a 1.4% yield of **68**. Similarly, co-pyrolysis of **68** and excess ethylene gave **67** and a 6.8% yield of **66**. These constitute the only known examples of a 2+2 cycloaddition of a silene and an olefin.



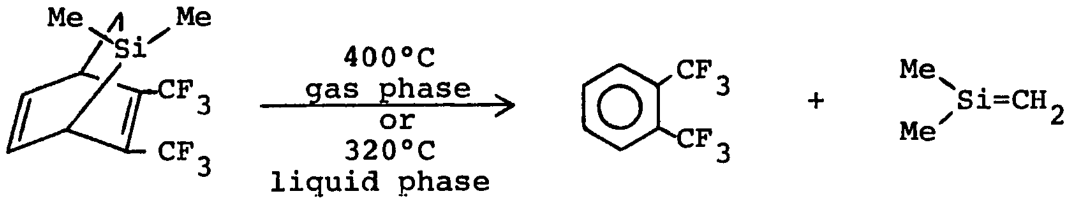
66 68 67

Slutsky and Kwart have found that 69 will undergo a reversible Cope rearrangement at 560°C to give the silene 70 (115). The Cope rearrangement has not become a useful method for silene generation.



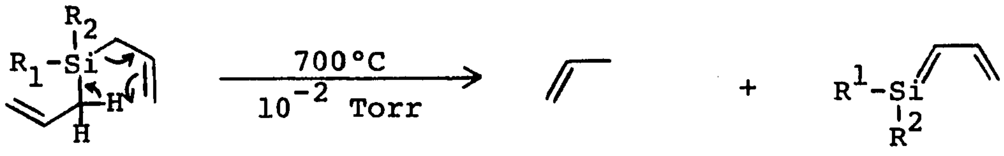
69 70

Barton and Kline have reported that the 7-silabicyclooctadiene 71 will thermally extrude 1,1-dimethylsilene 72 under a variety of conditions (both neat and flow) (116). This has proved to be a valuable method of silene generation as 72 can be trapped in yields as high as 94%.

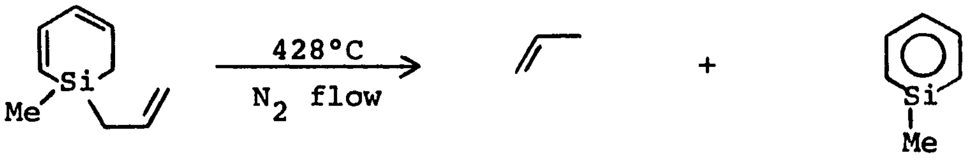


71 72

A very new method of thermal generation of silenes is the retro-ene reaction of diallylsilanes 73 discovered by Block and Revelle (117). Already, utility has been found for this reaction in the thermal generation of 1-methyl-1-silabenzene 74 by Barton and Burns (118).

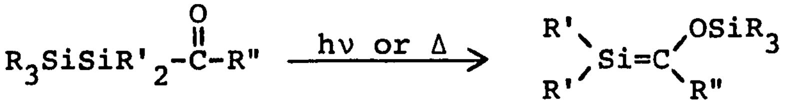


73



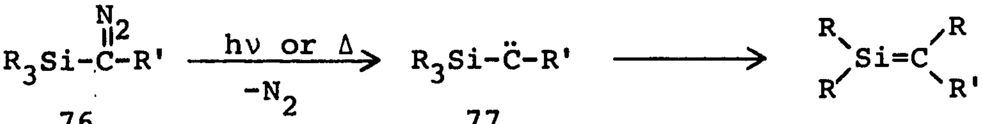
74

Brook and coworkers have found that acylpolysilanes 75 will both thermally (160°C) and photochemically generate silenes *via* a 1,3-migration of silicon from silicon to oxygen (107).



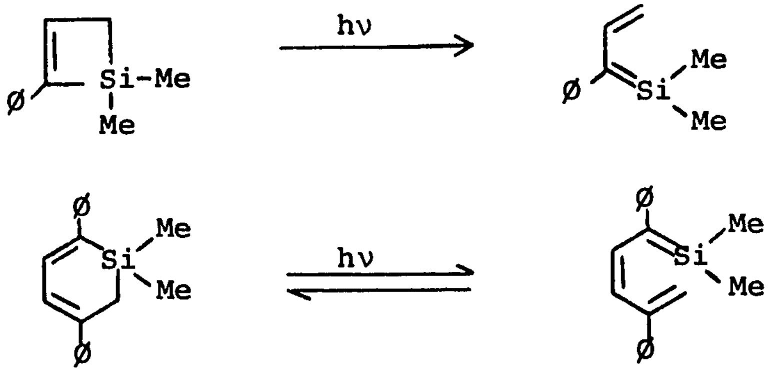
75

Alpha-silyldiazo compounds 76 also will give silenes under either photochemical or thermal (>400°C) conditions (109,119,120). The silenes result from carbon migration in the initially formed alpha silylcarbenes 77. It was found that migration of methyl predominates over both phenyl and benzyl groups (106).

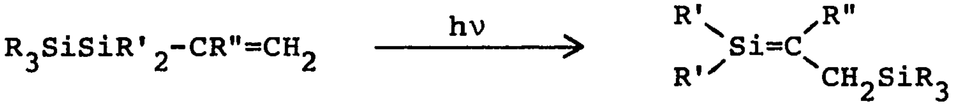


76 77

Silenes have also been generated by the photo-induced ring openings of silacyclobutenes (121) and silacyclohexadienes (122).

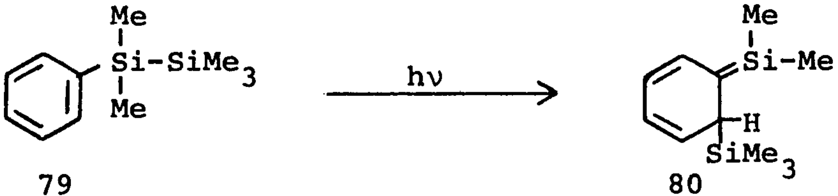


A potentially very useful method for the photochemical generation of silenes is the photo-induced 1,3-migration of silicon in 1-alkenyldisilanes **78** (123,124). In a similar fashion, the photolysis of a ethynyldisilane gave a sila-allene (97).



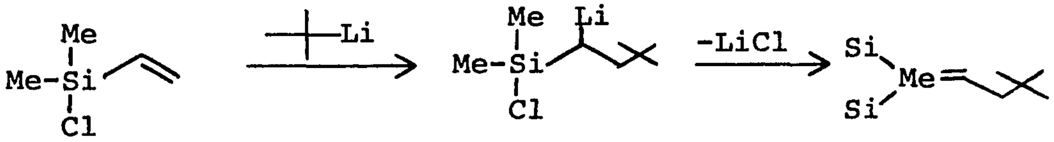
78

Aryldisilanes **79** also undergo 1,3-migration of silicon to give silene intermediates (125). The reaction of a wide variety of reagents with intermediates of the type **80** have recently been summarized (106). In the case of 1-aryl-2-vinyldisilanes, only migration to vinyl occurs (123).

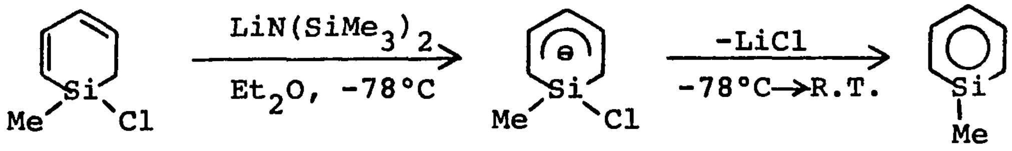


79 **80**

In the last two years a number of groups have reported the generation of silenes <u>via</u> salt elimination. Jones and Lim have found that t-butyllithium will add to vinyldimethylchlorosilane, followed by lithium chloride elimination to give the silene **81** (126). Barton and Banasiak have found that the silacyclohexadiene **82** can be deprotonated at -78°C and subsequent warming to room temperature results in the formation of 74 *via* lithium chloride elimination (43). Wiberg and Preiner have found that lithium alkoxide elimination will occur from 84 to give the silene 85 (127).

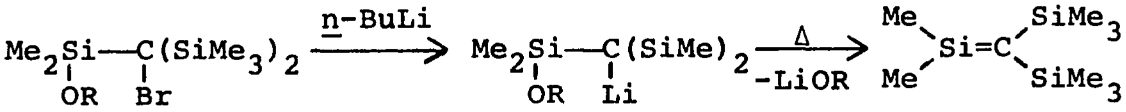


81



82

74



83

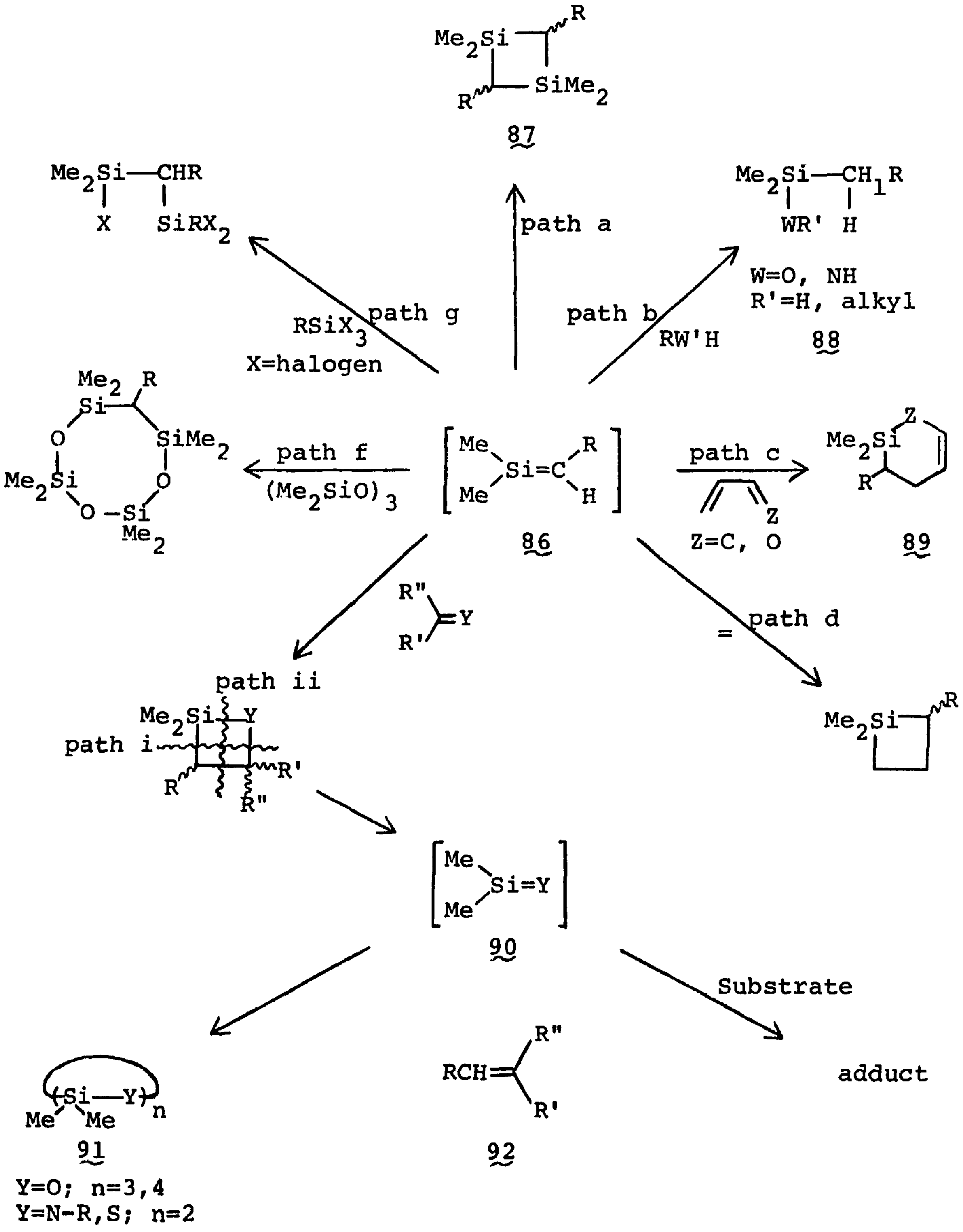
84

85

Reactions of silenes

In the absence of an added trapping reagent, silenes will dimerize in a head-to-tail fashion to give 1,3-disilacyclobutanes (Scheme 11, path a). The exceptions to this occur only when the silene, is highly substituted in which case head-to-head dimerization can occur (107,128). The study of the chemistry of silenes is thus hindered not

Scheme 11

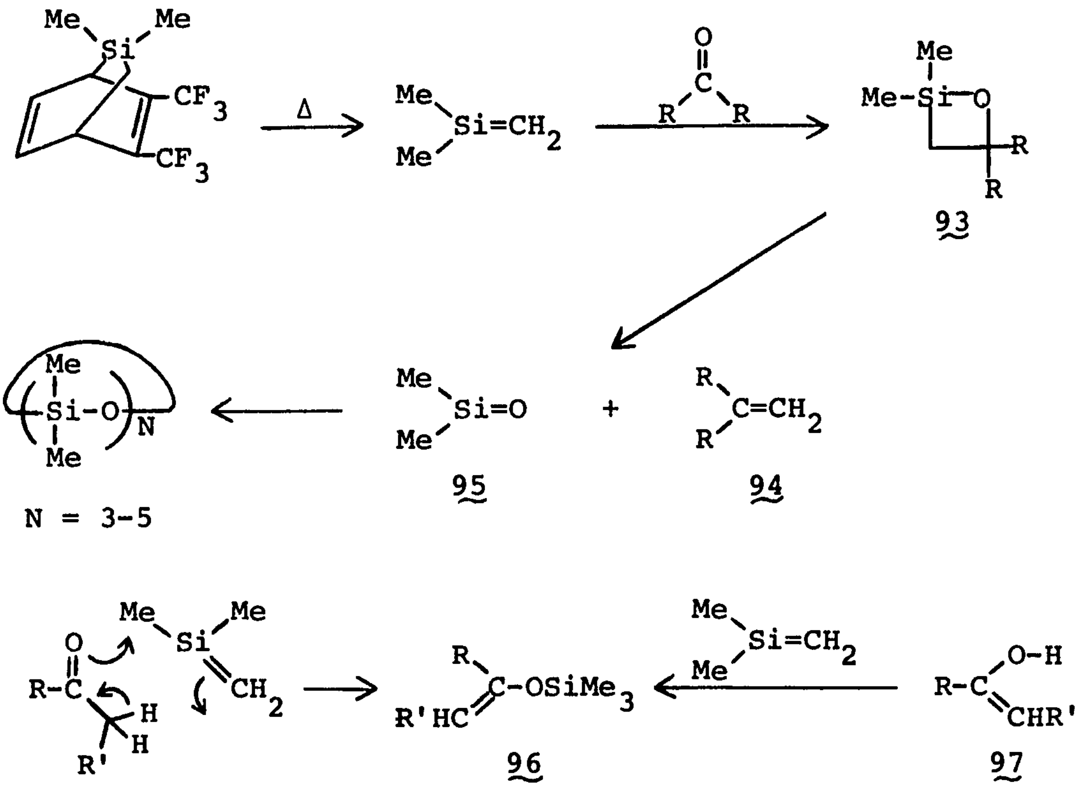

87
path a
88
W=O, NH
R'=H, alkyl
path b
RW'H
path g
RSiX3
X=halogen
path f
(Me2SiO)3
86
path c
Z=C, O
89
path d
path ii
path i
90
Substrate
adduct
91
Y=O; n=3,4
Y=N-R,S; n=2
92

only by the fact that silenes are nonisolable reactive intermediates, but also by the fact that study is limited to those reactions in which the added reagent can compete with silene dimerization. Scheme 11, taken from reference 106, gives a visual summary of most of the known reactions of silenes.

The first reported reactions of silenes are with water and ammonia (path b) to give silanols and silylamines (2). Alcohols and amines will add to silenes in a similar fashion. The direction of addition is consistent with a polar π-bond in which the silicon is positively charged and the carbon negatively charged.

The direction of addition to carbonyl compounds (path c and path e) is also consistent with a polar nature of silenes in which the carbon bears the majority of the electron density. The reaction with carbonyls was discovered in 1972 by Barton, Kline and Garvey when examining the reaction of 1,1-dimethylsilene with various carbonyl compounds (129a,b). The observation of **94** indicated a Wittig-type addition of methylene to the carbonyl (Scheme 12). They proposed a siloxetane intermediate **93**, which was attributed to a 2+2 cycloaddition of the silene and the carbonyl compound. The olefin **94** is then accounted for by decomposition of **93** to **94** and dimethylsilanone **95**, which cyclooligomerizes to the observed silicon containing products of the reaction. Shortly thereafter, the selection of aldehydes and ketones was enlarged (130,131) and in addition found that with aliphatic enolizable carbonyl compounds a second product was formed, 96. They envisioned this product as arising from a concerted ene- reaction, although it can also be accounted for by silene insertion into the oxygen-hydrogen bond of the enol 97. Carbonyl compounds, along with alcohols, have become the most widely used traps for silenes and both are used diagnostically when the intermediacy of a silene is in question.

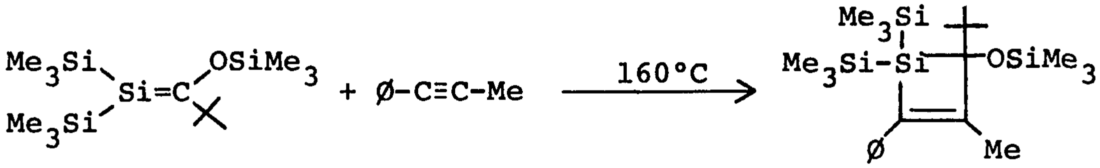
Scheme 12



Very similar results are observed for reactions with imines (132) and for thiocarbonyl compounds (133) (Scheme 11, path 3). Valkovich and Weber (134) have found that silenes will react with acrolein to give the 2+4 cycloaddition product **89** (path c) and also products attributable to an initial 2+2 cycloaddition (path e). Compound **89** could also have resulted from an initial 2+2 cycloaddition to give a siloxetane which subsequently rearranged to the six-membered ring.

Dienes are also a commonly used trap for silenes (path c) and in all cases only the 2+4 cycloadduct is found (106). As mentioned in the section on generation of silenes, there is only one report of the reaction of a silene and an olefin (path d) and the yield of the resulting silacyclobutane was quite poor (113). The only known reaction of a siloxane and a silene is the insertion of silenes into the silicon-oxygen bond of hexamethylcyclotrisiloxane (path f) (135). There is one report of insertion of silenes into silicon-halogen bonds (path g) (136). Moderate yields of insertion products are obtained with tetrahalosilanes, and at best, poor yields are obtained with organohalosilanes due to competition with silene dimerization.

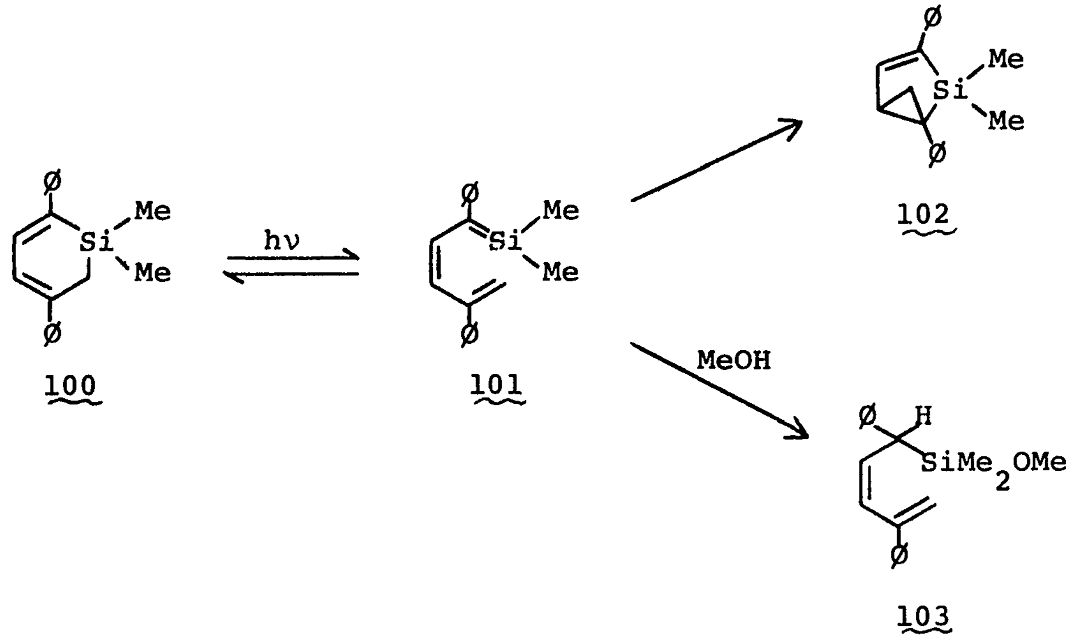
Recently, Brook and coworkers (107) have reported the first 2+2 cycloaddition of a silene and an acetylene. They found that silene **98** will add to methylphenylacetylene to give a 72% yield of the silacyclobutene 99. Wiberg and Preiner have found that silenes will also give 2+2 cycloadducts with azo compounds (127).


98 99

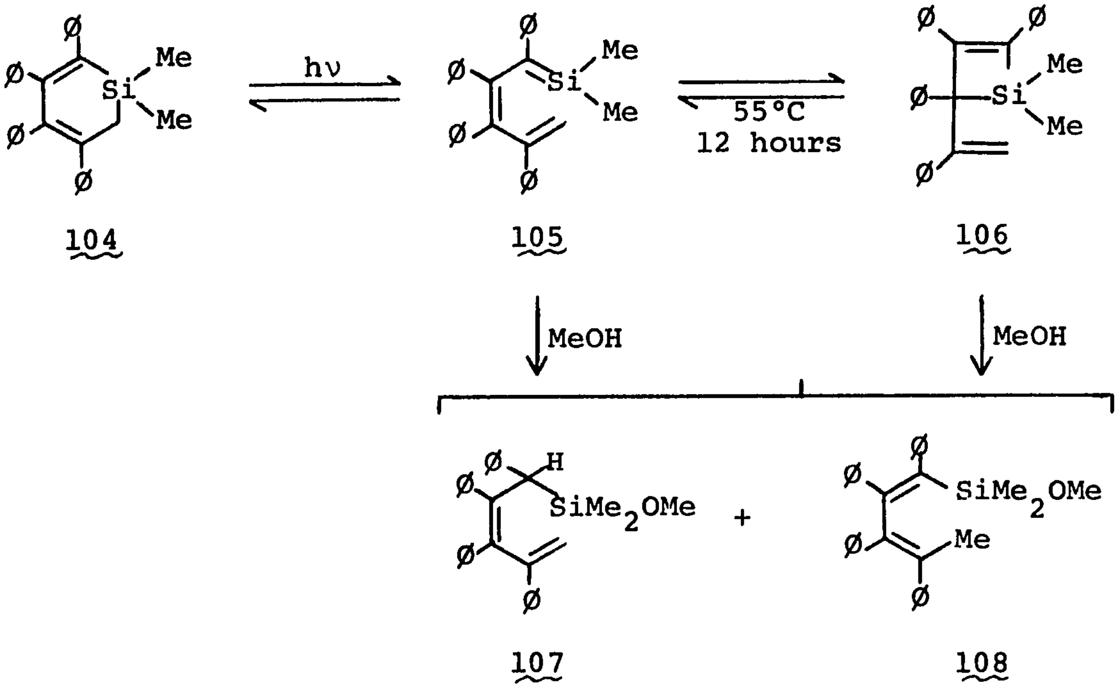
Conjugated silenes

In this section the preparation and reactions of conjugated silenes will be reviewed. This will include silenes that are conjugated with vinyl groups and other silenes, but will not include simple aryl-substituted silenes. Reports concerning conjugated silenes have been sparse and sporadic and often when they do occur, such silenes were of secondary interest.

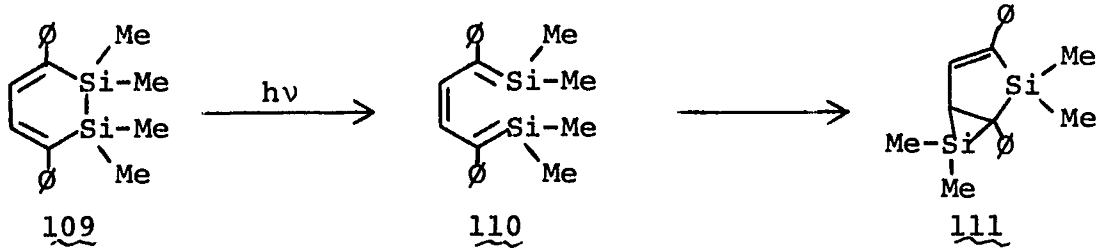
In 1974, Nakadaira, Kanuchi and Sakurai (122) reported that the silacyclohexadiene 100 will undergo reversible photochemical ring opening to give the 1-silahexatriene 101. In the absence of added traps, 101 underwent an intramolecular 2+4 cycloaddition to give 102 in 38% yield. In the presence of methanol, a 50% yield of 103 was obtained indicating that methanol reacts with the 1-silahexatriene functionality *via* 1,2-addition.



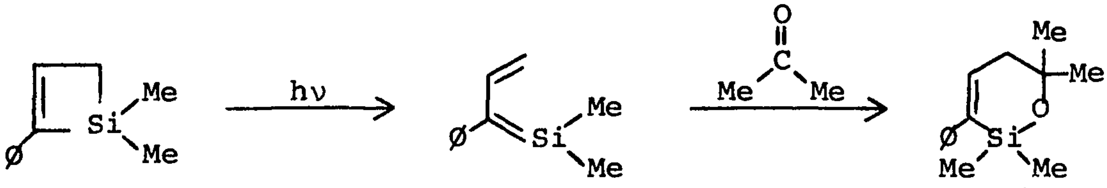
They also found that 104 will undergo reversible photochemical ring opening to give the 1-silahexatriene 105. In the absence of added traps, 105 undergoes a 2+2 ring closure to give 106 the observed product of this photolysis. Treatment of a 1:1 mixture of 104 and 106 with methanol results in the formation of the two methanol adducts 107 and 108 in 14% and 41% yields. These adducts correspond to 1,2-addition and 1,6-addition of methanol to 105. Irradiation of 104 in the presence of methanol produces 107 and 108 in 58% and 17% yields. These results suggest that methanol reacts with 105 to give the 1,2-adduct, and that 108 reacts with methanol to give the 1,6-adduct.



Nakadaira, Kanouchi and Sakurai (137) have proposed that the 1,2-disilacyclohexadiene 109 photochemically ring opens to the 1,6-disilahexatriene 110 to account for the observed product 111.

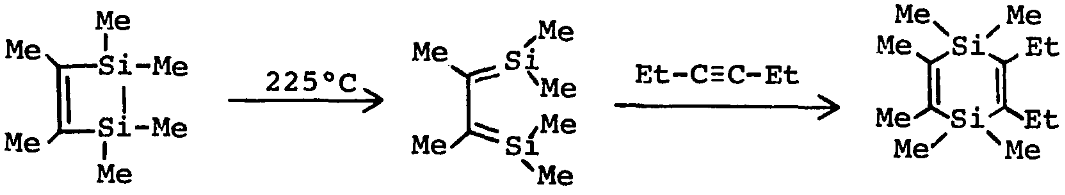


Valkovich and Weber (121) have published evidence that the silacyclobutene 112 will photochemically ring open to give the 1-silabutadiene 113. They found that the photolysis of 112 in the presence of acetone gave an 83% yield of the 2+4 cycloadduct 114. They favored a direct 2+4 cycloaddition over a 2+2 cycloaddition followed by rearrangement because 113 is formed in a cisoid conformation.



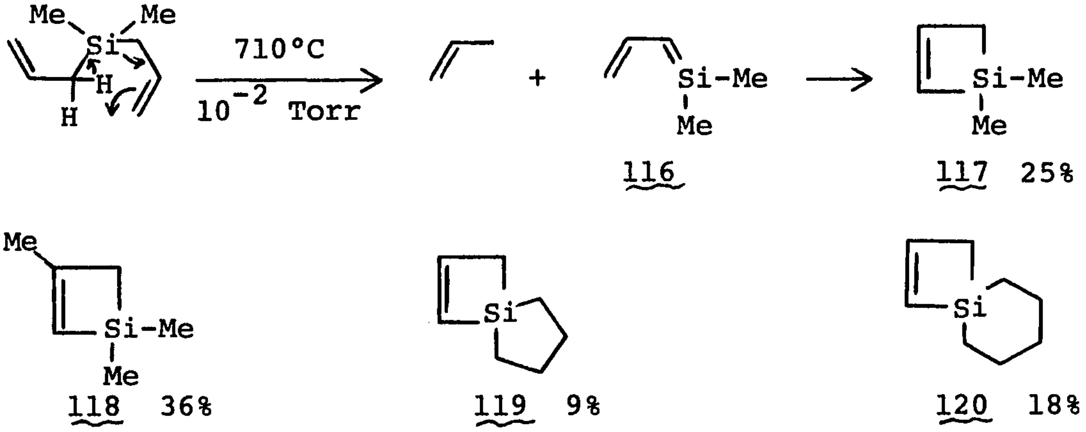
112 113 114

Barton and Kilgour have proposed the possibility of thermal ring opening of 37 to the 1,4-disilabutadiene 39 to account for the formation of 115 when 37 is heated with 3-hexyne (94).



37 39 115

Block and Revelle have proposed 1-silabutadiene intermediates in the pyrolysis of diallylsilanes to account for the formation of the silacyclobutene products (117). This presumably involves the indicated retroene reaction giving rise to propene and the 1-silabutadiene 116 which ring closes to give the silacyclobutene 117 in 25% yield. Other silacyclobutenes that they have prepared in this fashion are 118 - 120.



116

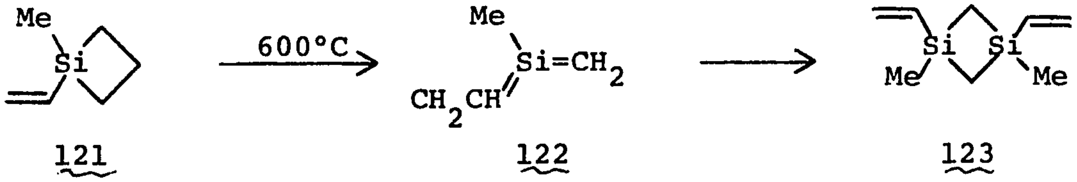
117 25%

118 36%

119 9%

120 18%

The 2-silabutadiene 122 has been generated from the pyrolysis of 1-vinyl-1-methylsilacyclobutane 121 (138). In the absence of an added trap, it dimerizes to the 1,3-disilacyclobutane 123.



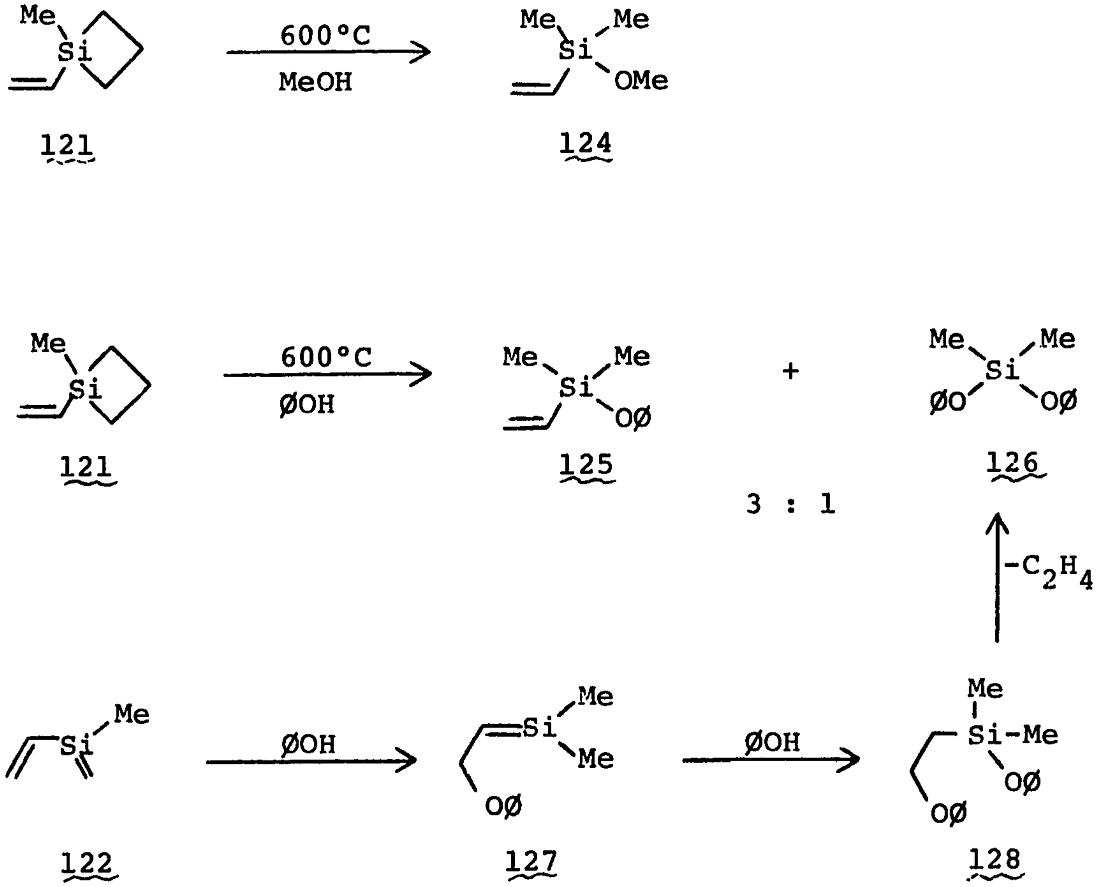
121

122

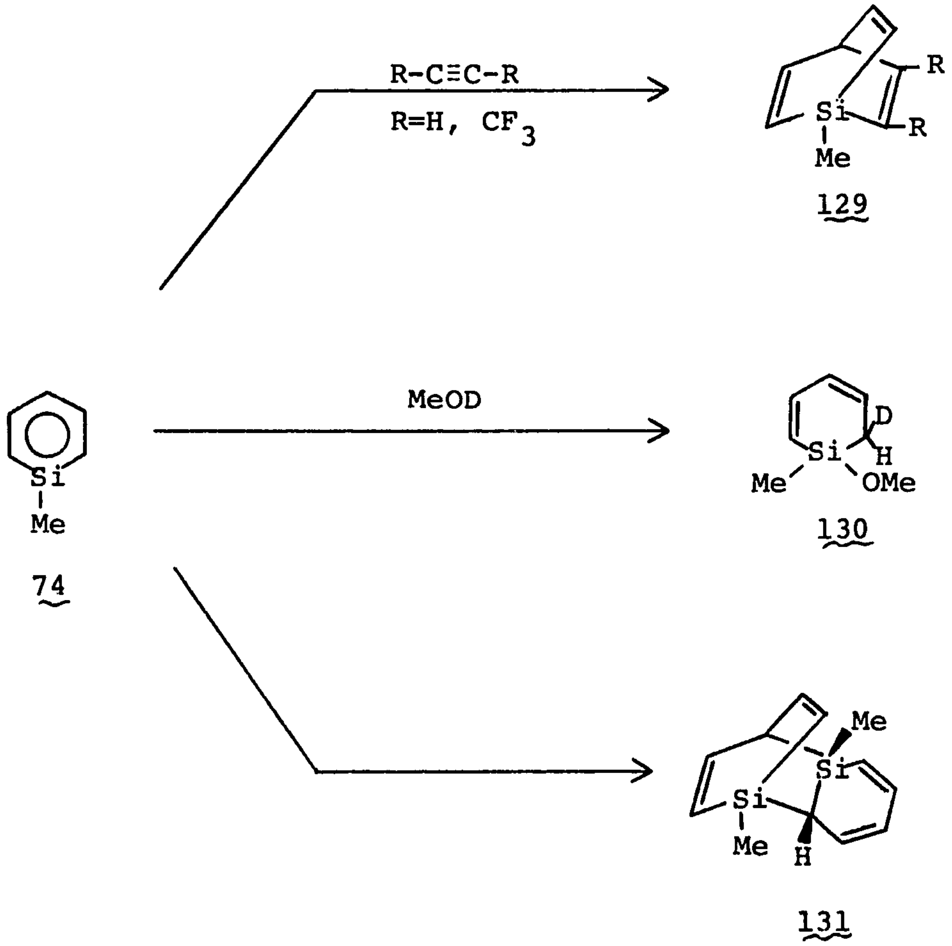
123

Bertrand and coworkers have trapped 122 generated in this fashion with alcohols (139) (Scheme 13). When 121 was co-pyrolyzed with methanol, the product observed was the expected silane 124 that would result from 1,2-addition of methanol to 122. With phenol, two products were obtained. The product corresponding to 1,2-addition was obtained along with dimethyldiphenoxysilane 126. The authors favor a mechanism in which 122 suffers 1,4-addition of phenol to give the silene 127 which reacts with another molecule of phenol to give 128. Compound 126 is then accounted for by β-elimination of silicon and oxygen in 128. This mechanism, as well as several others, cannot unambiguously explain why phenol gives a dialkoxysilane and methanol does not.

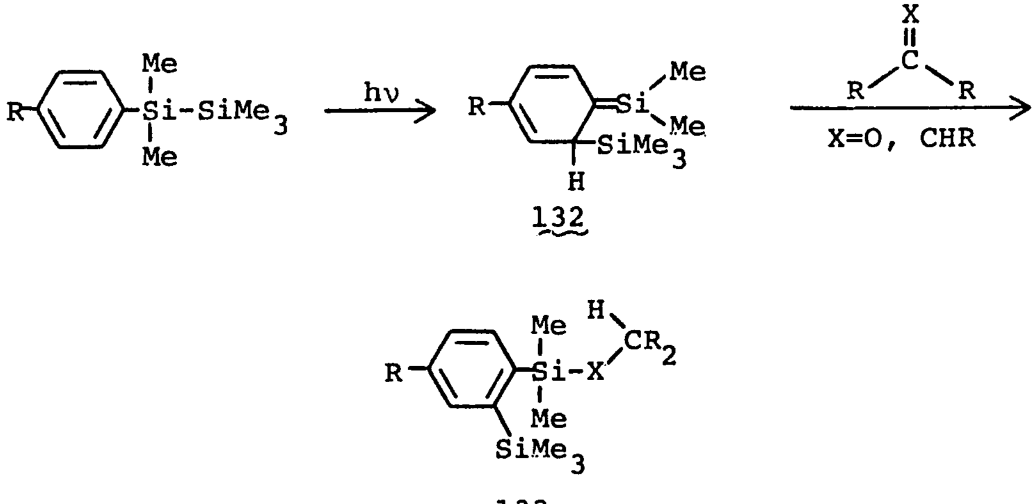
Scheme 13



Barton and coworkers have generated 1-methyl-1-silabenzene 74 by two different methods as mentioned previously in this section (43, 118). They have found that 74 reacts with acetylenes *via* 1,4-addition to give 1-silabicyclooctatrienes 129. Compound 74 reacts with methanol only in a 1,2-fashion to give 130 (140). In the absence of any added trap, 74 reacts with itself to give dimer 131, the result of a 2+4 cycloaddition (140).



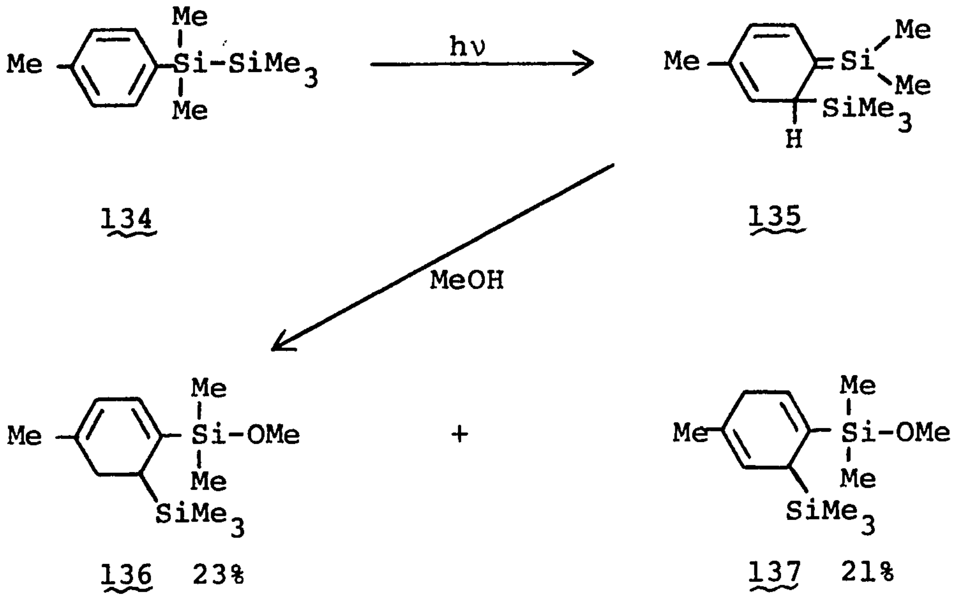
The photolysis of aryldisilanes has been found in most cases to give exocyclic silenes of the type 132 which are formed by a photo-induced 1,3-migration of silicon at the expense of the aromatic ring (106). With the exception of methanol, all reagents (olefins, dienes, acetylenes, and carbonyl compounds) have been found to react with these silenes by an ene reaction to give products of the type 133 in which the aromatic ring is restored.



132

133

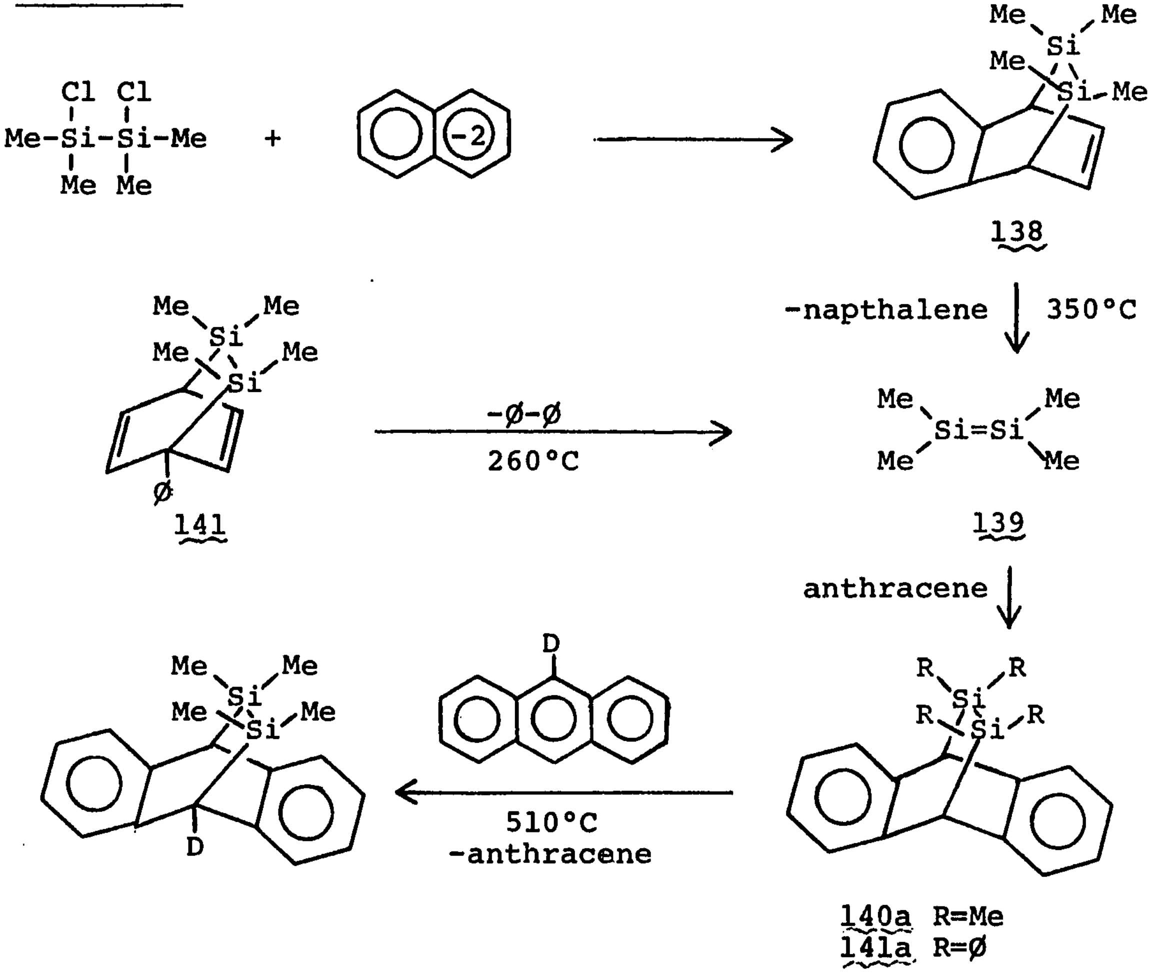
When the photolysis of 132 is carried out in the presence of methanol, the two methanol adducts 136 and 137 are the major products (141). These correspond to 1,6- and 1,4-addition of methanol to 135. No adduct resulting from 1,2-addition of methanol was observed.



Disilenes

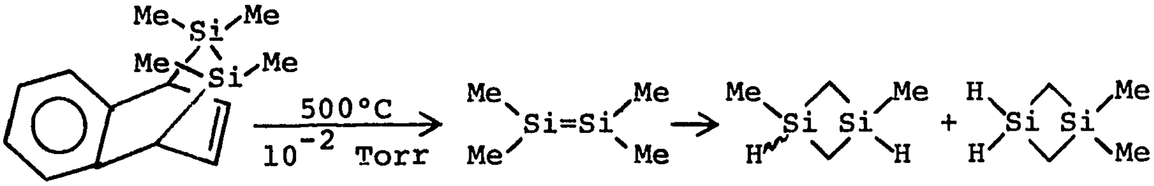
The first disilene was generated by Peddle and coworkers in 1969 (142). They reported that when 138 was heated to 350°C, it undergoes a retro-Diels Alder reaction to give napthalene and tetramethyldisilene 139 (Scheme 14). The disilene was trapped by anthracene to give the 4+2 cycloadduct 140a. Compound 140a was also shown to generate tetramethyldisilene by heating with 9-deuteroanthracene and observing disilene exchange. Compound 141 was shown to be the mildest (260°C) disilene generator again by trapping with anthracene. All three generators, 138, 140a and 141, were prepared by Peddle and coworkers *via* the addition of sym-dichlorotetramethyldisilane to the corresponding aromatic dianion. Smith and Pounds have prepared 140b by the reaction of anthracene, magnesium, magnesium bromide, and diphenyldichlorosilane in good yield (40%), but did not attempt to trap tetraphenyldisilene when 140b was thermally degraded to anthracene (143).

Scheme 14



Thermal decomposition of 7,8-disilabicyclooctadienes is the only method of disilene generation available to the experimentalist. Disilenes have very recently been claimed to result from silylene dimerization under certain conditions. Even if these claims are true, this method will have severely limited utility as will be discussed later in this section. Perhaps as a consequence of the limited methods for their generation, the known chemistry of disilenes is limited to one intramolecular rearrangement and three reactions.

Roark and Peddle found that when tetramethyldisilene 139 was generated in the absence of a trap at reduced pressure, the major volatile products are the two isomeric 1,3-disilacyclobutanes 142 and 143 both of which are isomeric with 139 (144).

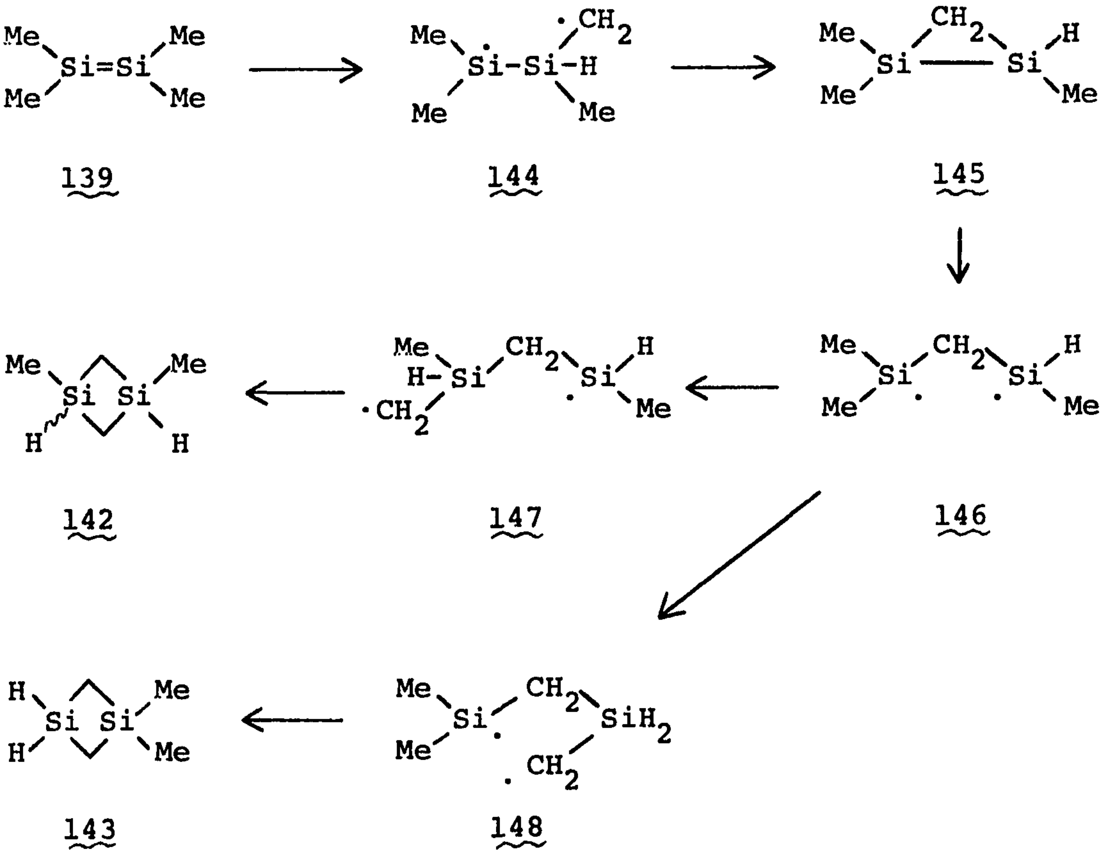


138 139 142 143

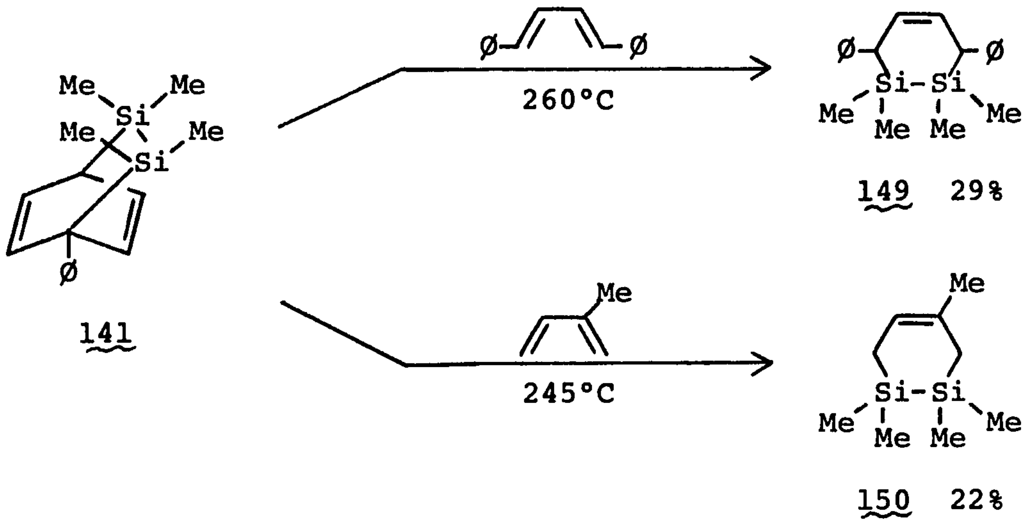
10% 30%

Roark and Peddle proposed the following mechanism to account for the rearranged products (Scheme 15). The first step involves a hydrogen-atom migration from carbon to silicon to give the diradical 144 which then closes to the disilacyclopropane 145. There is, however, no precedent in literature for this type of hydrogen-atom migration. Rupture of the silicon-silicon bond in 145 gives the diradical 146, which was proposed to undergo the same type of hydrogen-atom migration. This can happen in two ways to give the diradicals 147 and 148 which can ring close to account for the two observed products.

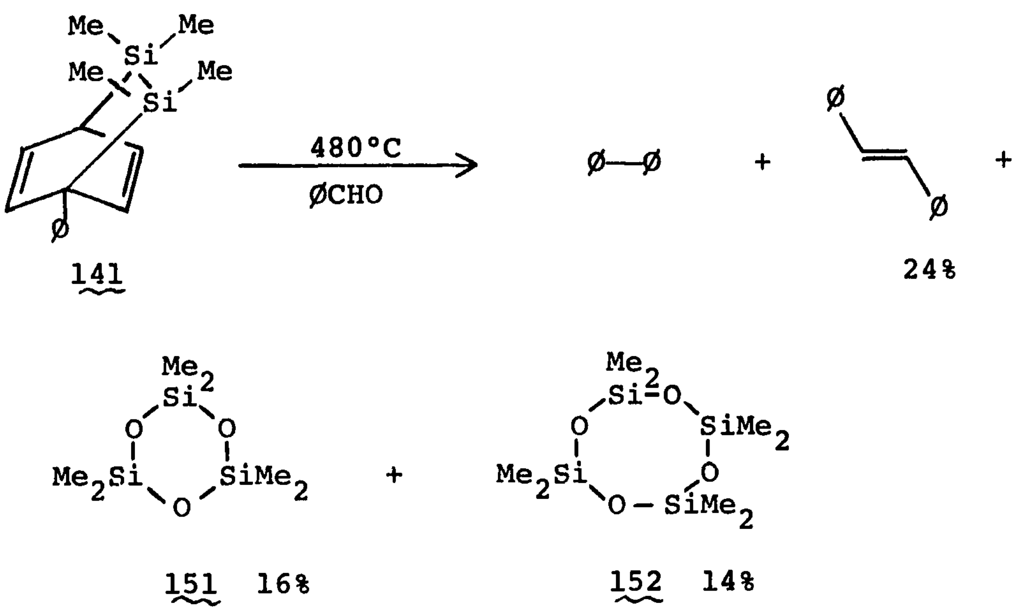
Scheme 15



Disilenes have been trapped by dienes. Roark and Peddle (144) found that when 141 was heated at 260°C with a slight excess of *trans,trans*-1,4-diphenylbutadiene, a 29% yield of the 4+2 cycloadduct 149 was obtained. Barton and Kilgour (95) have reported that the same reaction with isoprene gives a 22% yield of the cycloadduct 150. More recently, Sakurai has found that disilenes will give 4+2 cycloadducts with 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene in 90% yields (32).

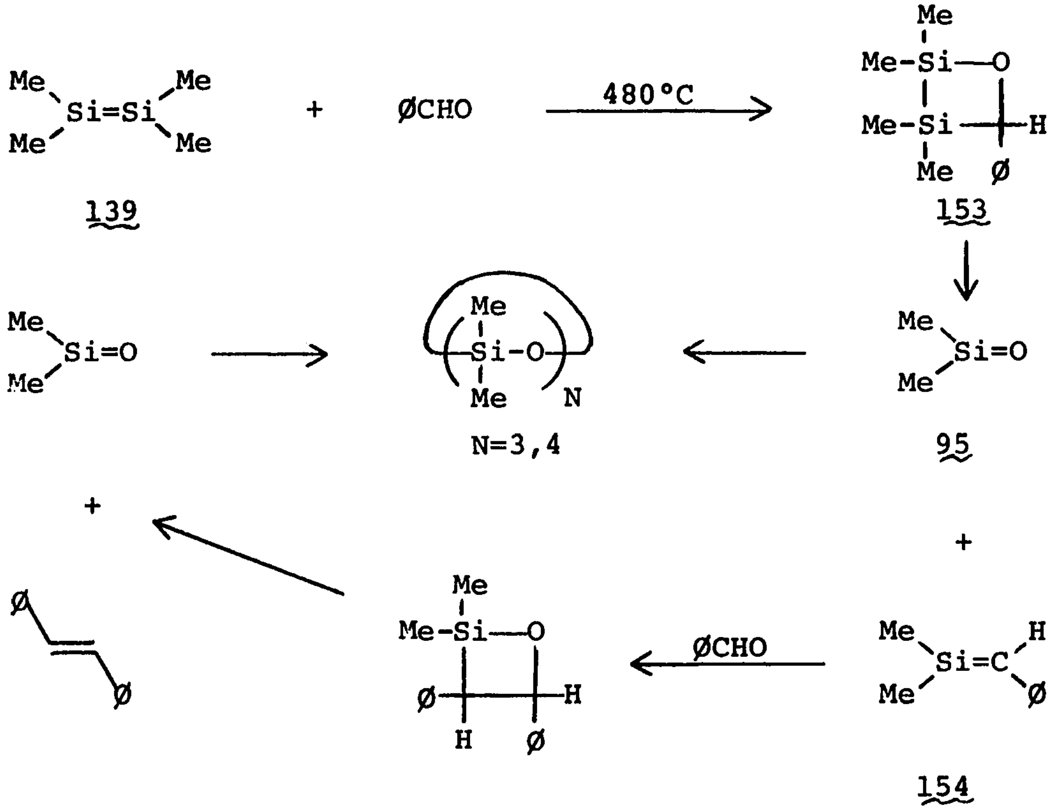


Barton and Kilgour have carried out the only study of the reaction of a disilene and a carbonyl compound (145). They found that the flow pyrolysis of 141 dissolved in a twenty-fold excess of benzaldehyde gave, along with the expected biphenyl, trans-stilbene (24%), and the cyclosiloxanes 151 and 152 in 16% and 14% yields, respectively.



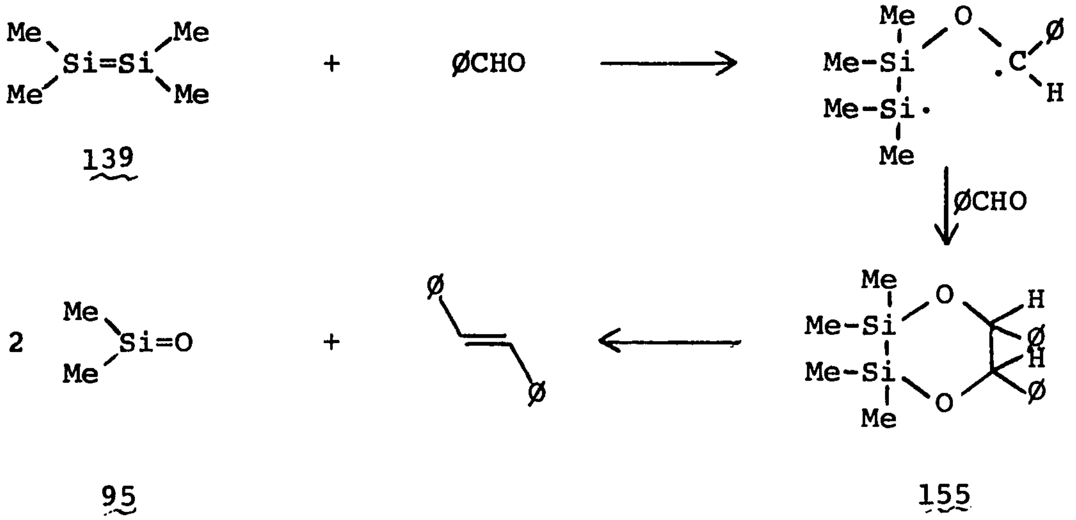
Barton and Kilgour proposed two mechanisms to account for these products. The first is analogous to the mechanism commonly believed to operate in the reaction of silenes and carbonyl compounds (Scheme 16). The initial step involves cycloaddition of tetramethyldisilene and benzaldehyde to give the disilaoxetane 153. This is followed by rupture of the ring to give dimethylsilanone 95 and the silene 154. Based on the known reaction of silenes and benzaldehyde, silene 154 would be expected to react with a second molecule of benzaldehyde to generate *trans*-stilbene and dimethylsilanone which would cyclooligomerize to the observed cyclosiloxanes.

Scheme 16



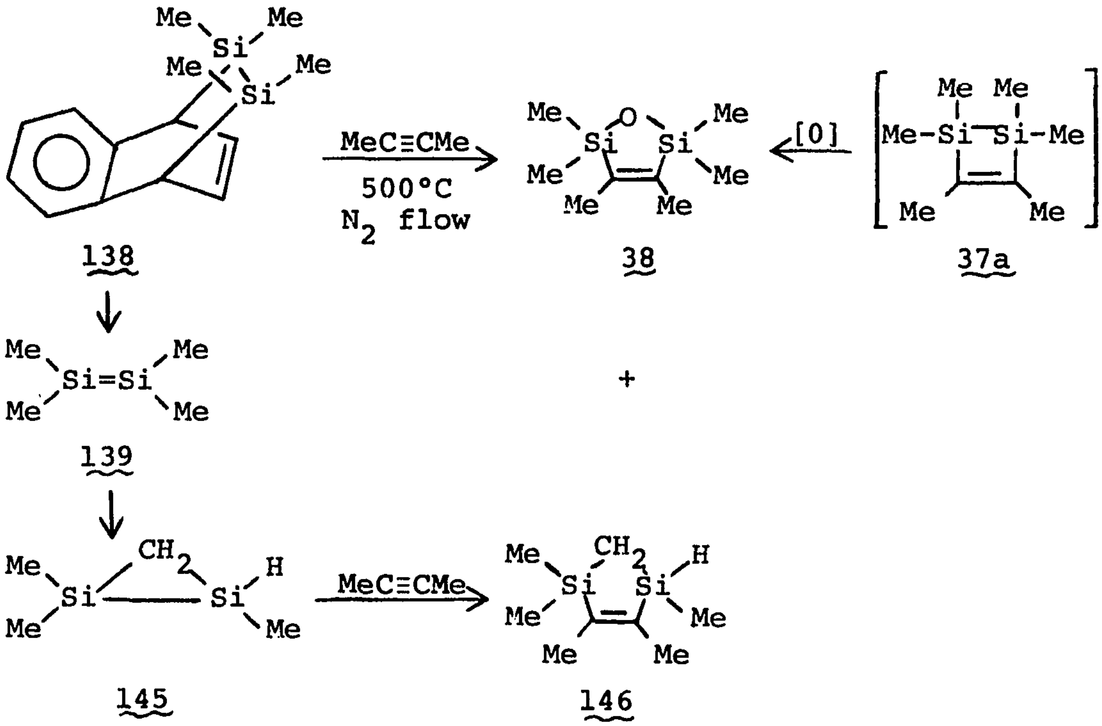
A second mechanism was proposed by Barton and Kilgour, and it involves the addition of two molecules of benzaldehyde to 139 to give the intermediate 155 (Scheme 17). Compound 155 was then proposed to fragment directly to *trans*-stilbene and two molecules of dimethylsilanone. Support for this mechanism followed from the independent synthesis of 155 and subsequent discovery that under these conditions it does give rise to the products of this reaction. Concerning the two mechanisms, the only piece of discriminatory evidence was that the dimer of the silene 154 could not be detected even when only one equivalent of benzaldehyde was used.

Scheme 17

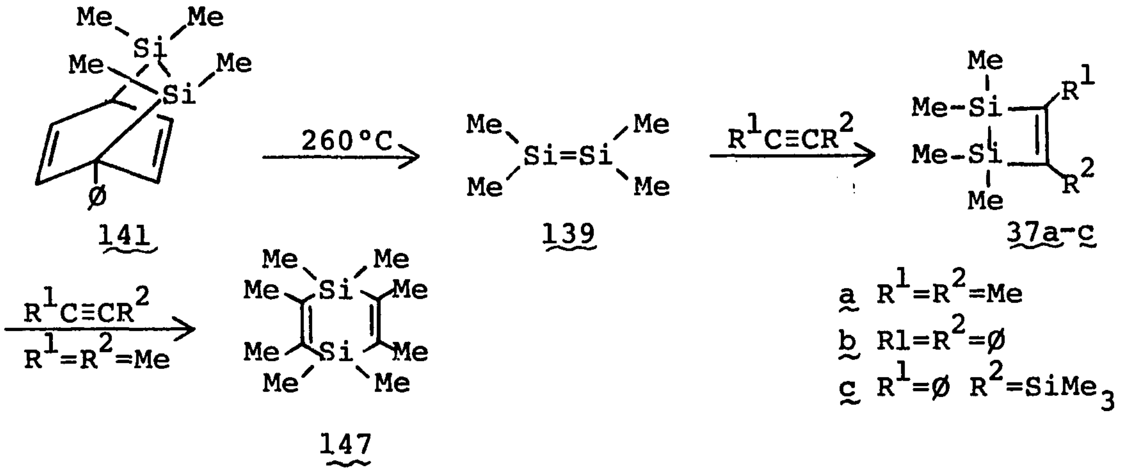


There are two reports concerning the reaction of disilenes with acetylenes. The first, by Barton and Kilgour (95), is the reaction of tetramethyldisilene with 2-butyne. They found that in the gas phase 139 reacts with 2-butyne to give the two five-membered ring products 38 and 146 (Scheme 18). Compound 38 presumably results from an initial cycloaddition of 139 and 2-butyne to give the 1,2-disilacyclobutene 37a, a molecule which has previously been shown to undergo oxidation to 38 upon exposure to air (28). Compound 146 was suggested to result from the addition of 2-butyne to the silicon-silicon bond of 145, the intermediate that was suggested to account for the rearrangement products of untrapped tetramethyldisilene (144) (Scheme 15).

Scheme 18

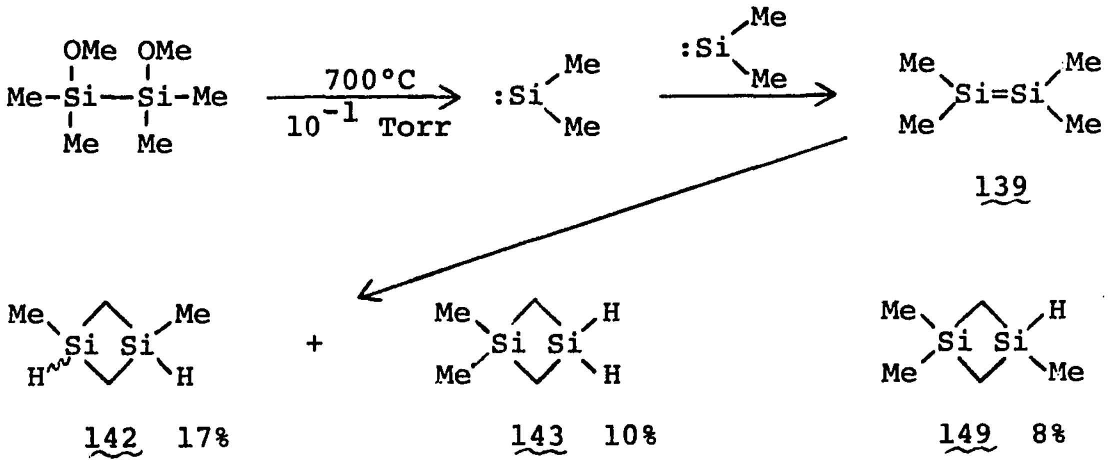


Barton and Kilgour have found that the reaction of tetramethyldisilene and 2-butyne takes a different course in the condensed phase (95). When 141 and 2-butyne are heated at 260°C in a sealed tube, a 20% yield of the 1,4-disilacyclohexadiene 147 is obtained. A likely mechanism for the formation of 147 is the cycloaddition of 2-butyne and 139 to give the intermediate 37a which subsequently reacts with a second molecule of 2-butyne to give 147. The last step was independently verified by Barton and Kilgour when they prepared 37a by the method of Atwell and Uhlman (28) and found that it did react with 2-butyne to give 147 under the same conditions. The first step of the mechanism has been recently verified by Sakurai and coworkers (85). They found that if 139 is generated under the same conditions that it will react with diphenylacetylene and phenyltrimethylsilylacetylene to give 37b and 37c.



Two groups of workers have obtained evidence that disilenes are formed *via* dimerization of silylenes, albeit under disparate conditions. Conlin and Gaspar (25) have found that if dimethylsilylene is generated from the pyrolysis of 148 at 700°C, the two isomeric 1,3-disilacyclobutanes 142 and 143 are obtained (Scheme 18). These are the same two products that Roark and Peddle obtained when tetramethyldisilene was generated in the absence of a trap (144). However, Conlin and Gaspar observed that the relative yields of 142 and 143 were reversed and that a third product 149 was found which Roark and Peddle did not observe. Due to the slightly higher temperature, it was suggested that 149 arose from the cleavage of the 1,4-diradical intermediate 148 (Scheme 15) to give 1,1-dimethylsilene which then adds dimethylsilylene to give 149.

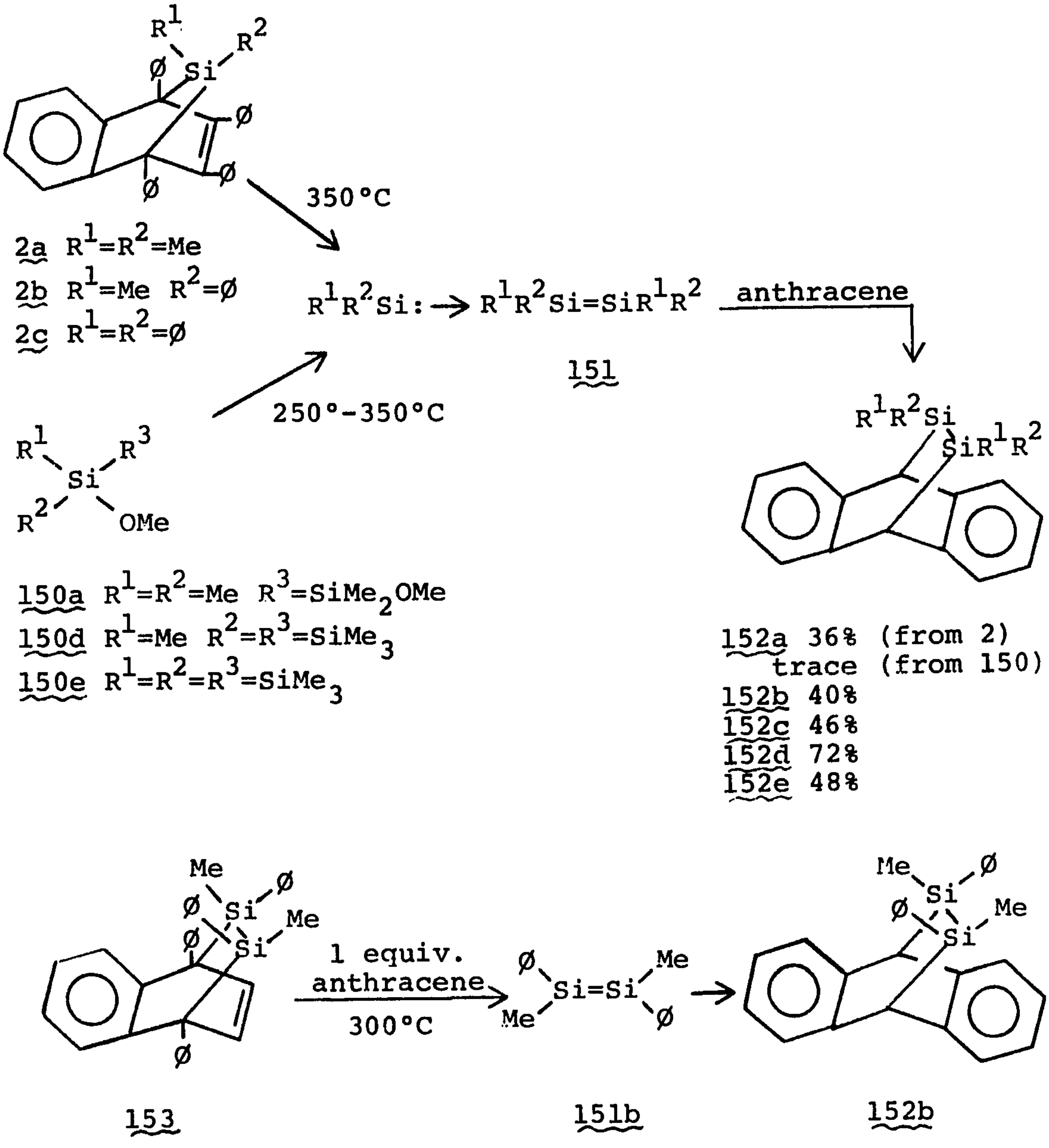
Scheme 19



Sakurai has obtained evidence that various silylenes will dimerize to disilenes in the condensed at 250-350°C (32) (Scheme 20). The silylenes were generated from the thermal decomposition of either 2 or 150 in benzene. When the silylenes were generated in the presence of anthracene, the formation of the adducts 152a-152e was used to argue the intermediacy of disilenes since Roark and Peddle have shown that tetramethyldisilene will cycloadd to anthracene under these conditions (Scheme 14). No evidence was provided to rule out a mechanism involving stepwise addition of two silylenes to anthracene. From the stereochemistry of the adducts 152, it was determined that phenylmethylsilylene dimerized to give a one-to-one mixture of cis and trans disilenes, and methyltrimethylsilylsilylene gave a one-to-three ratio of cis and trans disilenes since Sakurai demonstrated that rotation about the silicon-silicon double bond does not occur under this condition. This was demonstrated by heating the E-isomer of 153 with anthracene and finding that the mixture of adduct 152b was 96% E-isomer and only 4% of the Z-isomer. Similar results were found when starting with the Z-isomer of 153 as 94% retention of stereochemistry was obtained in the adduct 152b.

This high maintenance of stereointegrity for disilenes is not entirely in keeping with the theoretical predictions for the π-bond strength of disilenes. Dewar and coworkers (146) have obtained a value of 20 kcal/mole from MINDO/3 calculations for the π-bond strength of disilene which led them to predict that free rotation would occur at room temperature. Blustin (147) has calculated a value of 33.5 kcal/mole from FSGO calculations and has also predicted that each silicon atom would prefer to be tetrahedral. Curtis (148) has calculated a similar value of 34 kcal/mole from EHMO and CNDO methods.

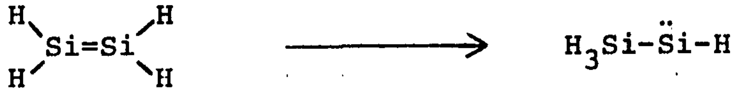
Scheme 20


R^1
R^2
Ø
Si
Ø
Ø
Ø
350°C
2a R^1=R^2=Me
2b R^1=Me R^2=Ø
2c R^1=R^2=Ø
R^{1}R^{2}Si: → R^{1}R^{2}Si=SiR^{1}R^2
151
anthracene
250°-350°C
R^1
R^3
Si
R^2
OMe
150a R^1=R^2=Me R^3=SiMe$_2$OMe
150d R^1=Me R^2=R^3=SiMe$_3$
150e R^1=R^2=R^3=SiMe$_3$
R^{1}R^{2}Si
SiR^{1}R^2
152a 36% (from 2)
trace (from 150)
152b 40%
152c 46%
152d 72%
152e 48%
Me
Ø
Ø
Si
Me
Ø
Si
Ø
153
1 equiv.
anthracene
300°C
Ø
Si=Si
Me
Me
Ø
151b
Me
Ø
Si
Ø
Me
Si
152b

Triplett and Curtis (149), buoyed by these calculations that predict thermodynamic solvency for disilenes, attempted the preparation of tetra-t-butyldisilene with the hope that the bulky substituents would counteract the high chemical reactivity expected for disilenes and permit for the first time their isolation. Unfortunately, **154** was found to be inert to lithium, sodium and magnesium amalgams, to t-butyl lithium-TMEDA complex, and to methyllithium. Polymer formation was observed upon treatment of **154** with molten potassium.

154

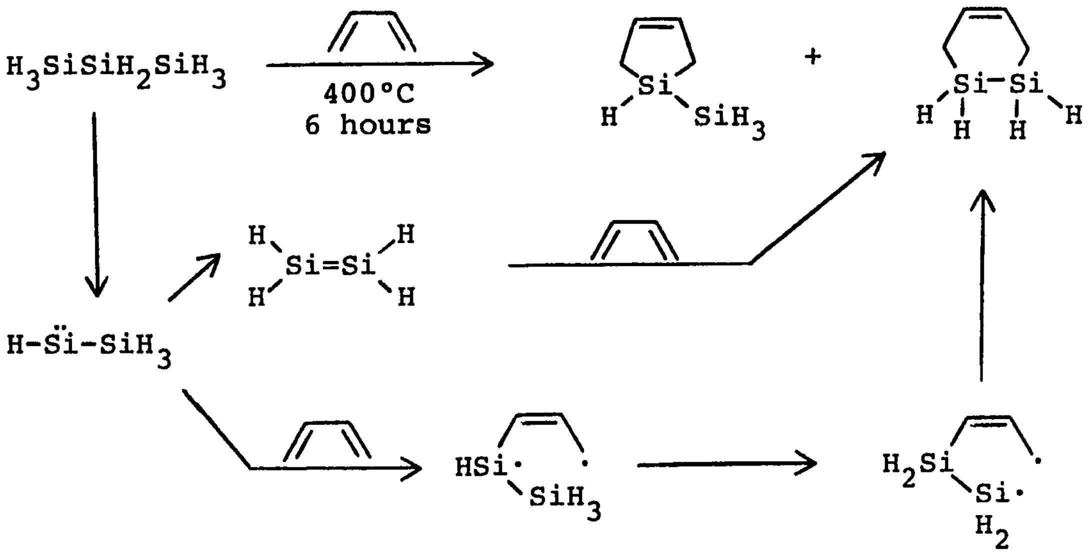
Snyder has carried out *ab initio* calculations on the various isomeric forms of disilene and from the results he has predicted that disilene should prefer to exit as silylsilylene by 9 to 27 kcal/mole depending upon the basis set used (150).



ΔE = -9 to -27 kcal/mole

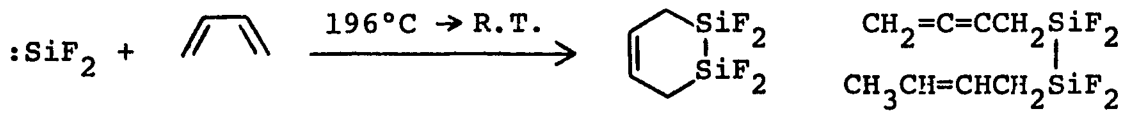
In contrast to this prediction, Jenkins and coworkers (48) have reported experimental evidence that suggests that silylsilylene rearranges to disilene at 400°C in the gas phase (Scheme 21). They observed the formation of the 4+2 adduct of disilene and butadiene when silylsilylene was generated in the presence of butadiene. They did, however, suggest an alternative diradical mechanism.

Scheme 21



The reactions of difluorosilylene with a variety of reagents have been actively studied for more than ten years (99,151). Most of the products of these reactions can be explained by initial dimerization of difluorosilylene to give a species that has been written as either a diradical

$[F_2\dot{S}i-\dot{S}iF_2]$ or a π-bonded disilene $[F_2Si{=}SiF_2]$. For example, when difluorosilylene is co-condensed with butadiene at -196°C and allowed to warm to room temperature, the observed products are **155** and **156** (90). The very low yield of **155** is characteristic for these reactions. Although most of the literature reports are interpreted in terms of a diradical, recently a ludicrous attempt has been made to explain difluorosilylene chemistry in terms of a π-bonded disilene (152). In contrast, an argument has been recently made that many of the reactions of difluorosilylene can be explained without initial dimerization (59).



155 2%

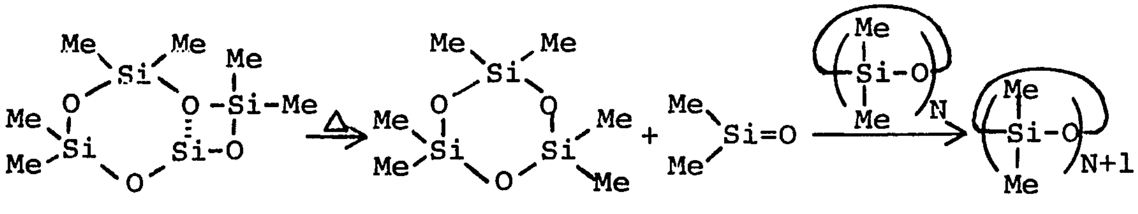
156

Silanones

Although silanones have been proposed as intermediates in various reactions for some time, the only known reactions of silanones, with one exception of insertion into a strained silicon-carbon bond, is insertion into a silicon-oxygen bond of siloxanes, cyclosiloxanes, and alkoxysilanes. Until 1977, the only instances in which the intermediacy of a silanone was envoken were in the thermal redistribution of siloxanes, cyclosiloxanes, and cyclocarbosiloxanes and from the thermal decomposition of various silaoxetanes. In the part year a variety of successful new approaches to silanone generation have been discovered and undoubtedly in the very near future much will be learned about the chemical behavior of silanones. Silanones have been reviewed twice in the past three years (105,153).

In 1952, Adrianov and Sokolov (154) found that the thermolysis of polydimethylsiloxanes (150-200°C) gave a mixture of varying length polysiloxanes related to each other and to starting material by units of Me_2SiO. They proposed the intermediacy of dimethylsilanone to account for these results.

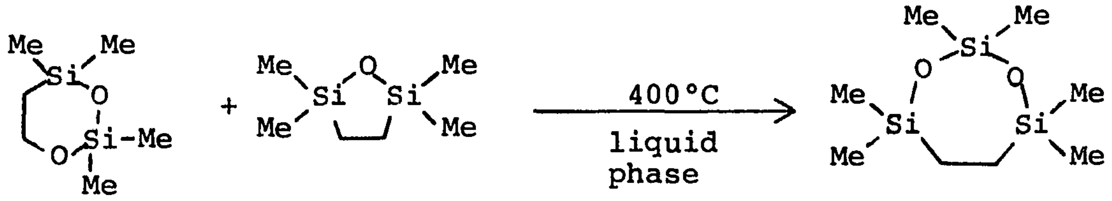
A more extensive understanding of this redistribution reaction was gained from the work of Nametkin and coworkers (155-158). They found that at 500-700°C, a variety of ring-sized cyclosiloxanes and cyclocarbosiloxanes gave new cyclosiloxanes and cyclocarboxilanes that were either larger or smaller than the starting material by units of Me_2SiO or Me_2SiCH_2. In addition, they found that the six-membered cyclotrisiloxane was formed in all cases and that with cyclocarbosiloxanes 1,3-disilacyclobutane was also formed. Kinetic experiments indicated that initial decomposition was first order and as a result Nametkin and coworkers proposed that the degradation occurs *via* a four-centered transition state. For example, 152 was envisioned to unimolecularly extrude dimethylsilanone 95 with concomitant formation of hexamethyl-cyclotrisiloxane 151. Dimethylsilanone then inserts into the silicon-oxygen bond of the various cyclosiloxanes present to give the larger homologs.



152 151 95

Davidson and Thompson (159) did a kinetic study of the pyrolysis of 152 and also found the reaction to be first order. In addition they found that the decomposition of 152 in the presence of ethylene, propene, or butadiene inhibited the formation of $(Me_2SiO)_5$ but not of $(Me_2SiO)_3$. This lends support to the suggested intermediacy of dimethylsilanone 95, although no adducts of 95 with added traps were reported. From their kinetic data, Davidson and Thompson calculated a minimum value of the silicon-oxygen π bond strength of 37.8 kcal/mole. This is the only estimate (experimental or theoretical) of the silanone π bond strength to appear in the literature.

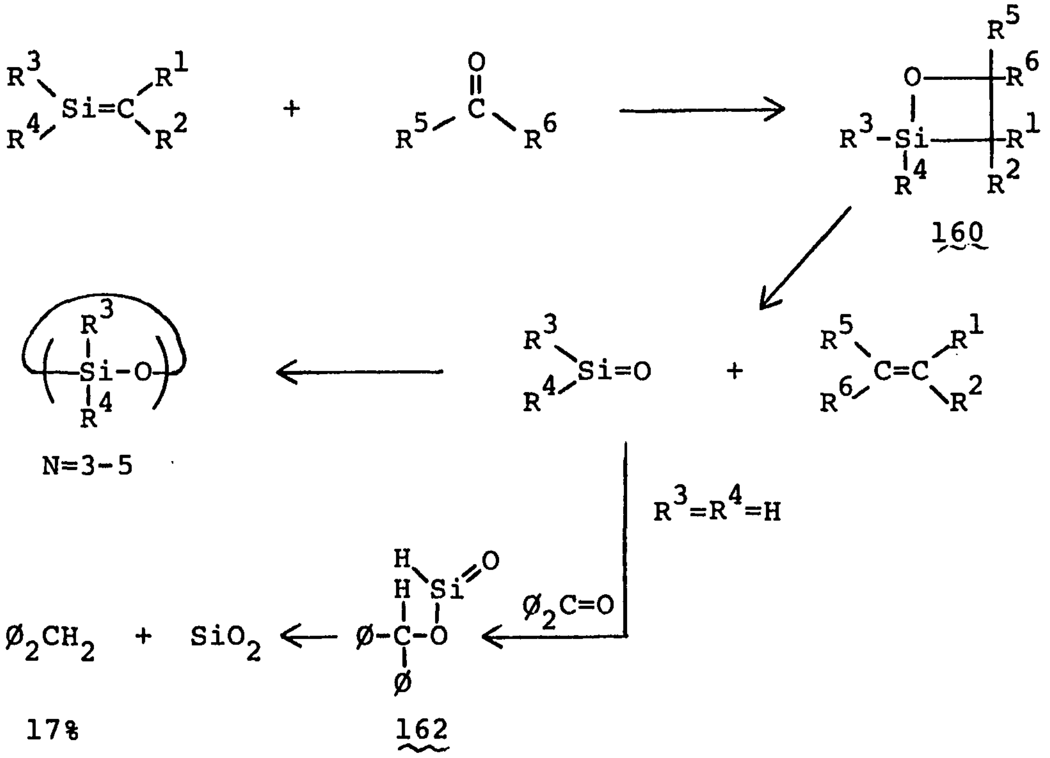
In a similar observation, Barton and Tumey (160) have found that 157 will thermally generate dimethylsilanone at 400°C as indicated by trapping with 158 to give a 74% yield of 159. Compound 158 has previously been shown to be a silanone trap as will be discussed later in this section (72).



157 158 159 74%

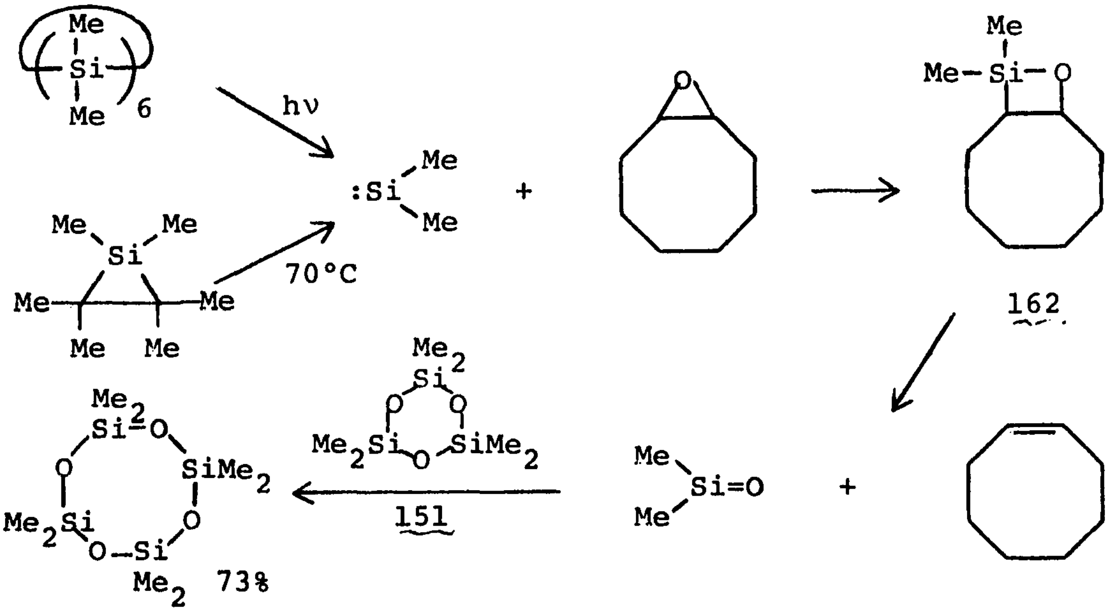
Silanones are also generated in the Wittig-type reaction of silenes and carbonyl compounds (Scheme 22). This reaction, discovered by Barton, Kline and Garvey (129a), involves the 2+2 cycloaddition of a silene and a carbonyl compound to give a siloxetane intermediate 160 which decomposes to a silanone and an olefin. Since its discovery, this reaction has been actively studied by a number of workers for a variety of ketones and silenes. As a result, this reaction is used diagnostically for the detection of silene intermediates (106). This reaction has little or no utility for the study of silanones since they would have to compete for trapping reagents with silenes. There is only one report where the reaction products suggest that a silanone can compete with a silene for a carbonyl trap

Scheme 22

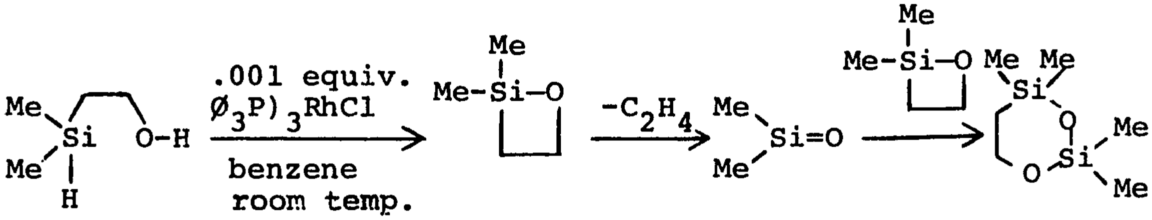


(161). This was with unsubstituted silanone and benzophenone and the observed diphenylmethane was accounted for in terms of the intermediate 161. In all other cases, the silanones generated from this reaction are observed in the form of their cyclic oligomers in generally poor yields. Until recently, this reaction has only been observed with silenes generated at temperature greater than 400°C, so the fact that siloxetanes have not been observed from this reaction is not so surprising. Now, however, there are examples of photochemically generated silenes that give the same products with carbonyl compounds at ambient temperatures indicating that siloxetanes may be quite thermally labile (97,123,124). Carbonyl compounds and double-bonded silicon-nitrogen intermediates also generate silanones in the same manner (132,162). The reaction of tetramethyldisilene with benzaldehyde also results in the formation of dimethylsilanone (145).

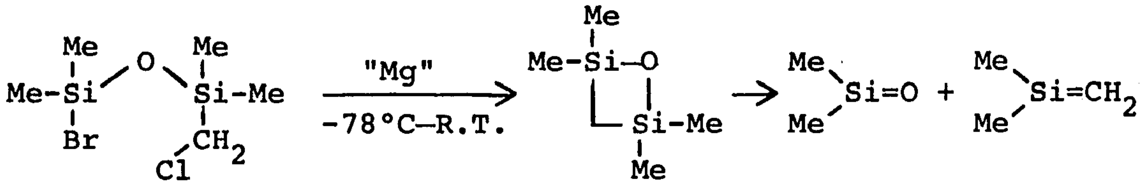
In the past year, considerable evidence has been accumulated to indicate that siloxetanes are indeed thermally unstable at room temperature. Barton and Goure have found that dimethylsilylene generated either photochemically at room temperature or thermally at 70°C will react to give cyclooctene and dimethylsilanone as indicated by trapping with hexamethylcyclotrisiloxane (163). If this reaction does involve the intermediate 162 then it has considerable thermal lability.



Barton and Tumey attempted the preparation of the dimethylsiloxetane 164 via the rhodium catalyzed cyclization of the silylalcohol 163 (160). The product isolated from this reaction, however, was the six-membered ring 157. Again, it appears that the siloxetane 164 thermally decomposes to give dimethylsilanone which this time is trapped by 164 to give 157. This reaction may prove to be a valuable method of silanone generation. Barton and Tumey have obtained evidence that the 2,4-disilaoxetane 166 also is unstable at room temperature. They found that treatment of 165 with activated magnesium gives rise to silenes and silanones as indicated from the various products of trapping.

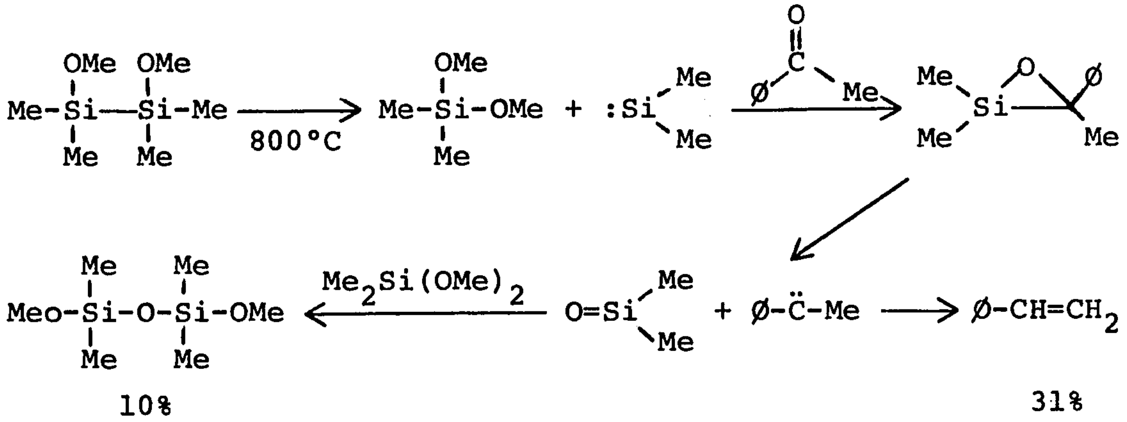


163 164 157 57%



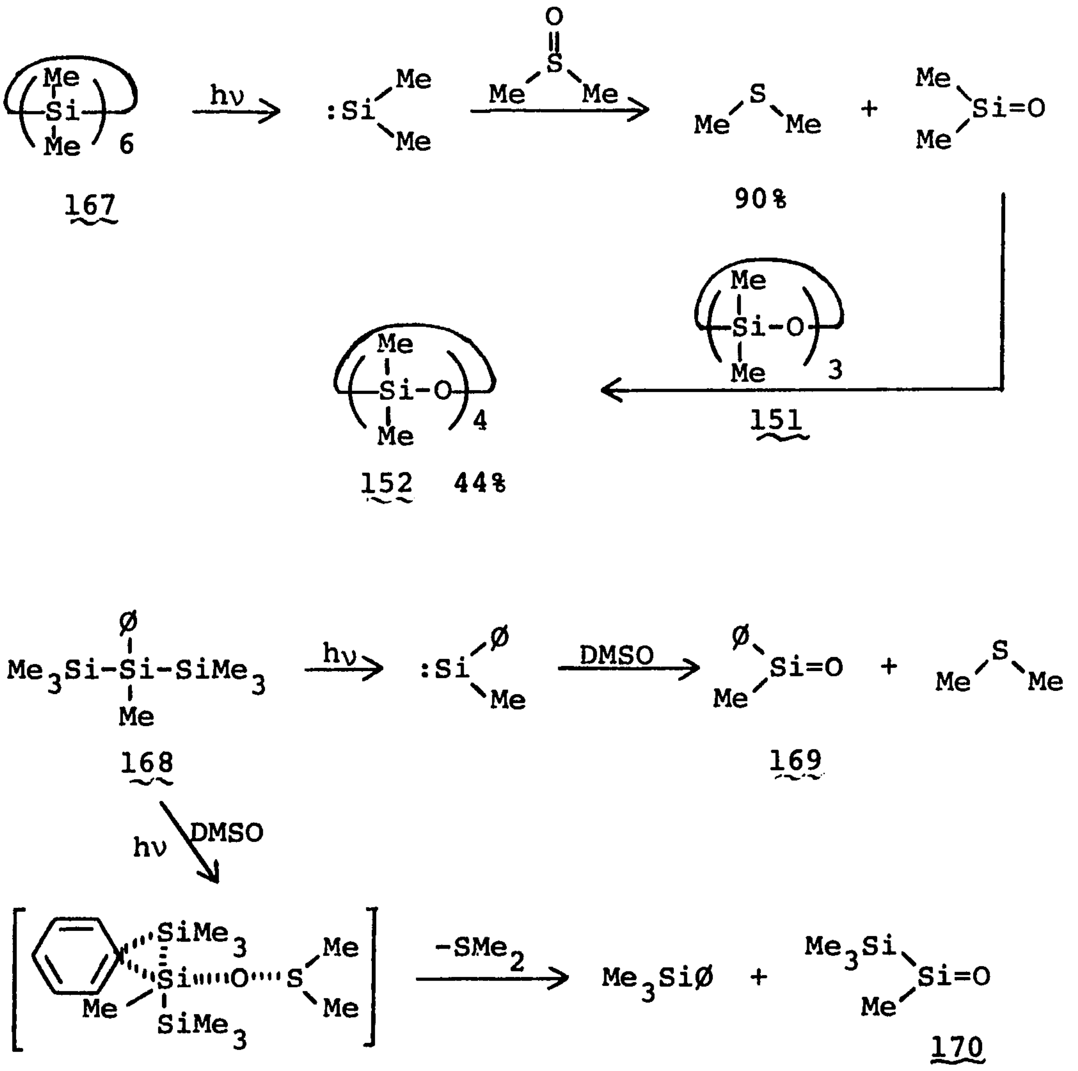
165 166

Ando and coworkers have proposed that dimethylsilylene generated at 800°C deoxygenates acetophenone to account for the formation of styrene and the product of trapping of dimethylsilanone with dimethyldimethoxysilane (30). Silanone formation was not detected, however, for acetophenone or any other ketone at temperatures of 500-700°C.



In the last two years, a series of papers has appeared in which silanones are generated by the reaction of photochemically generated silylene and dimethylsulfoxide (DMSO) (72,78,103). In the first paper dimethylsilylene is generated from the photolysis of 167 in a dioxane solution containing DMSO and the cyclotrisiloxane 151 (78) (Scheme 23). The silylene apparently abstracts oxygen from DMSO to generate dimethylsilanone as indicated by the formation of dimethylsulfide and the silanone trapping product 152. This reaction was found not to be general for all photochemical silylene generators. For example, 168 did give the expected extrusion of phenylmethylsilylene; however, a variety of other products were formed two of which were trimethylphenylsilane and methyltrimethylsilylsilanone 170. These unexpected products were attributed to direct reaction of DMSO and 168. The silanones 169 and 170 were formed in only 13% and 2% yields, respectively, as measured by trapping with 151 and 2,2,5,5-tetramethyl-2-oxa-2,5-disilacyclopentane 158.

Scheme 23



Seyferth and coworkers attempted to carry out the same reaction with DMSO and dimethylsilylene generated from the mild thermolysis of hexamethylsilarane **6** (164) (Figure 1). They found, however, that **6** reacts DMSO at temperatures below those required for silylene extrusion to generate dimethylsilanone as indicated by trapping with dimethyldimethoxysilane. If the reaction is carried out in the absence of a silanone trap, the silanone is trapped by **6** to give **171**. Silarene **8** was also found to react with DMSO and the yields of silanone trapping products were higher. Again in the absence of a silanone trap, the starting material reacted with **95** to give the adduct **172**. The intermediacy of dimethylsilylene in the reaction of **8** and DMSO is unlikely since silarenes do not thermally extrude silylenes. Silaranes and silarenes are known to undergo reactions with a wide variety of functional groups due to the highly reactive and strained silicon-carbon ring bond. Therefore, a likely mechanism for this reaction involves initial attack of DMSO on the silicon atom of **8**. Silanone formation can then be accounted for by either a direct fragmentation or by thermal degradation of silaoxetene **173**. Seyferth and coworkers have found that **6** and **8** will also react with pyridine N-oxide and trimethylamine N-oxide to generate dimethylsilanone.

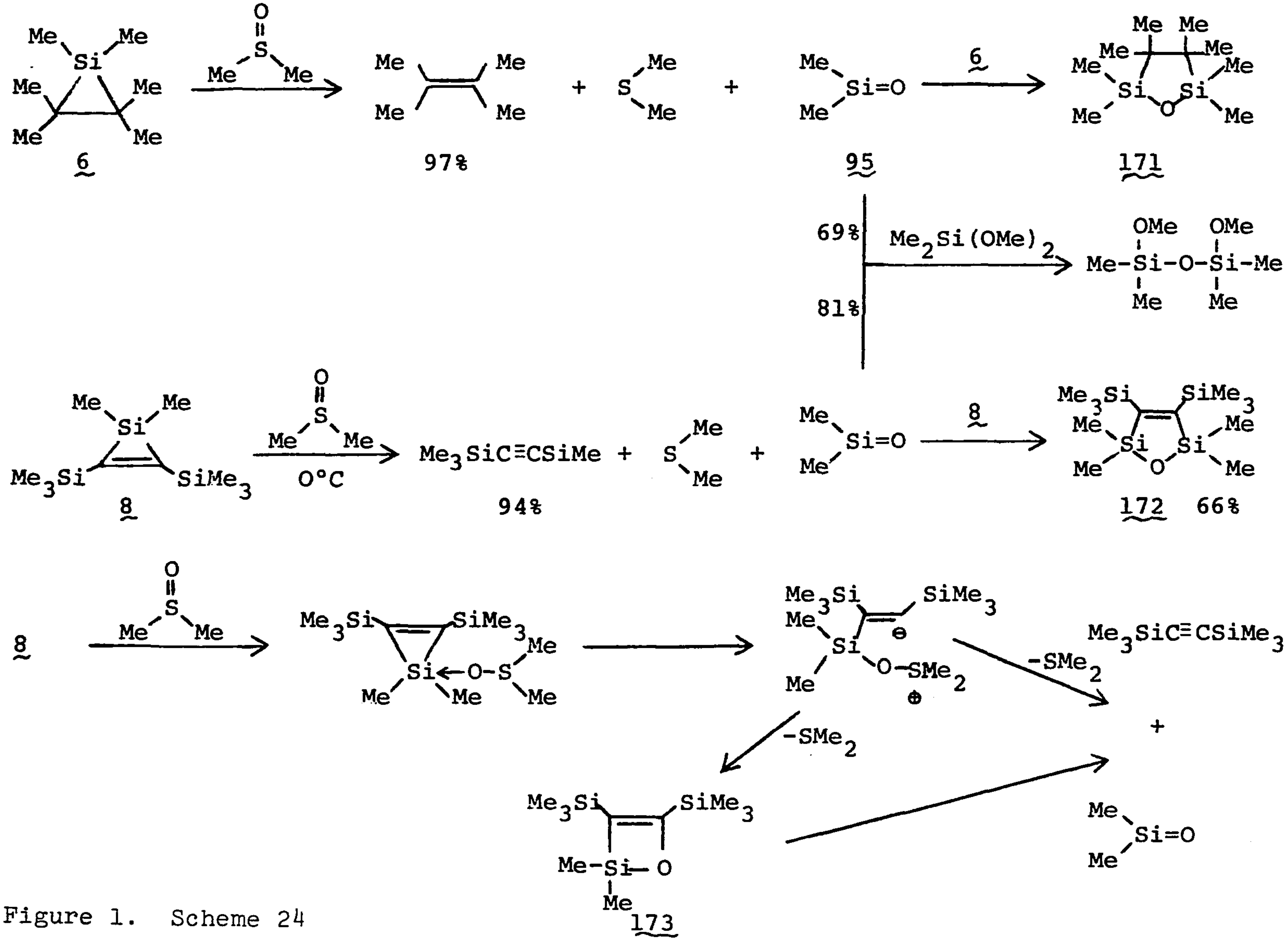
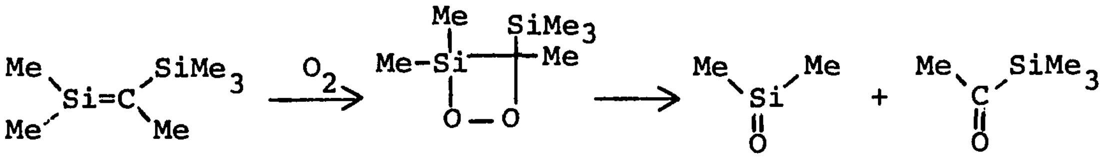


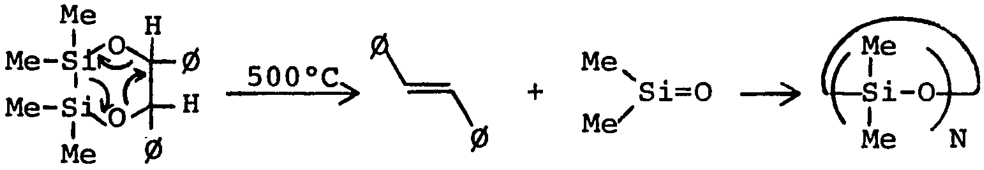
Figure 1. Scheme 24

Barton and Hoekman have recently found that the silene 174 will react with oxygen to give small amounts of the ketone 176 and of the cyclic oligomers of dimethylsilanone (128). The formation of 95 and 176 suggests the intermediacy of the siladioxetane 175. The low yields of the cyclic oligomers of 95 and 176 are misleading since the major products of this reaction result from the reaction of the silene 174 with 95 and 176.

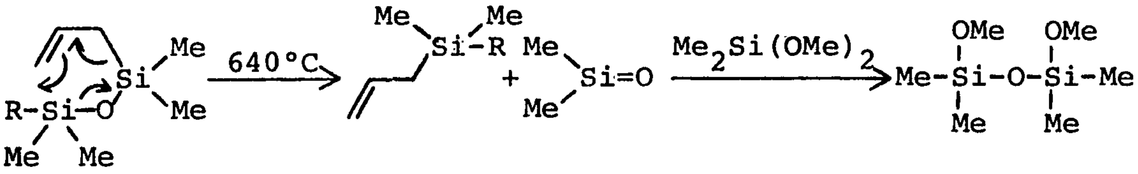


174 175 95 176

Two new methods of silanone generation promise to provide general utility despite the high thermal requirements for both. Barton and Kilgour (145) have found that 155 will fragment to two molecules of dimethylsilanone at 500°C. Barton and Burns (140) have recently discovered that the siloxanes 177a and 177b will generate dimethylsilanone *via* a retroene reaction in a manner analogous to the generation of silenes from the pyrolysis of diallylsilanes (see the Historical section on silenes).



155　73%　95　N=3,4　45%



177a R=$CH_2CH=CH_2$　95　54% (from 177a)

177b R=Me　24% (from 177b)

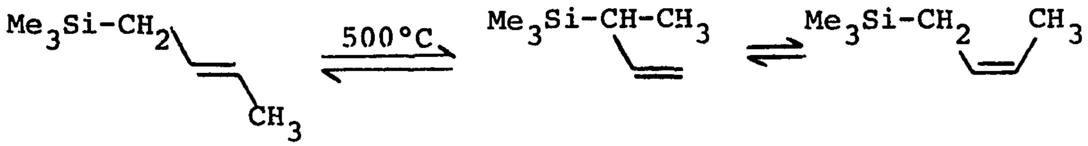
Thermal Migrations of Silicon

Thermal 1,3- and 1,5-migrations of silicon are utilized in the work to be presented in this thesis for the generation of silenes. The literature pertaining to each of these migrations will be briefly summarized.

1,3-Migrations of silicon

The most thoroughly studied 1,3-migrations have been those occurring in allylsilanes, beta silylketones, and silylamides. Slutsky and Kwart (165) have observed that a trimethylsilyl group will undergo a 1,3-migration from carbon to carbon when an allylsilane is heated to 500°C. They found that the pyrolysis of trimethyl-trans-crotylsilane

178 gave an equilibrium mixture of 179 and 180. Kinetic analysis revealed the reaction to be unimolecular and that the entropy of activation suggests a cyclic concerted transition state. The activation barrier was determined to be 48 kcal/mole. With an allylsilane containing a chiral silicon, the migration was observed to occur with complete inversion at silicon.

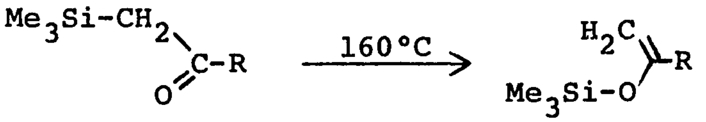


178 34%

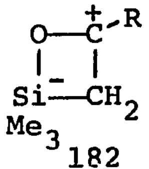
179 5%

180 61%

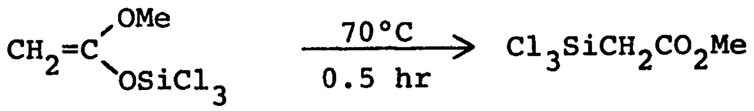
In heteroallylic silanes if the terminal atom has an unshared pair of electrons or supports a large amount of electron density, the 1,3-migration will occur at a much lower temperature than the all carbon system. Brook has observed that this migration occurs with the trimethylsilylcarbonyl compounds 181 at 160°C (166). A mechanistic investigation by Brook revealed the reaction to be first order with a highly ordered transition state suggesting a cyclic concerted process. With optically active silanes, the migration was found to occur with complete retention. Brook initially proposed the trigonal bipyramidal intermediate 182. Later, Brook and coworkers found that the concerted transition state 183 was more compatible with the rho value obtained from a Hammet study of substituted silylacetophenones (167). Recently, Kwart and Barnette found that the results of a kinetic study involving a ^{29}Si label best support the polar intermediate 182 (168). The reverse of this migration has been observed for polyhalogenated silanes such as 184 (169).



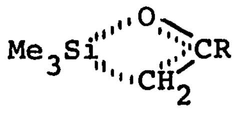
181



182

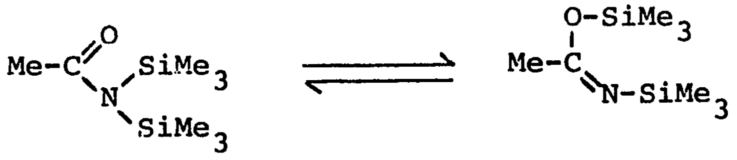


184



183

If the terminal atom and the atom attached to silicon in heteroallylic silanes both have unshared pairs of electrons, then the 1,3-migration of silicon is often reversible at or near room temperature. Itoh and coworkers have found the interconversion of 185 and 186 to be unimolecular and reversible at 36°C (170).



185 186

Table 4 presents key references to the known 1,3-migrations of silicon in allylic and propynylic silanes of the type **187** and **188**.

$$Me_3Si{-}X{-}Y{=}Z \xrightarrow{\Delta} X{=}Y{-}Z{-}SiMe_3$$

187

$$Me_3Si{-}X{-}Y{\equiv}Z \xrightarrow{\Delta} X{=}Y{=}Z{-}SiMe_3$$

188

Table 4. 1,3-Thermal migrations of silicon

Silane	Temperature (°C)	Reference
$R_3Si{-}X{-}Y{=}Z$		
C C C	500	165
C C O	100-180	166-168
O C C	70	169
N C O	35-80	170-172
N S O	25	173
N N N	50	174
N C S	25	171
N P O		175
S P O	35	176
N C N	100	177
N S N	35	178
C P C	150	179
C Se O	30	180
S C O		181
Si C O	160	107

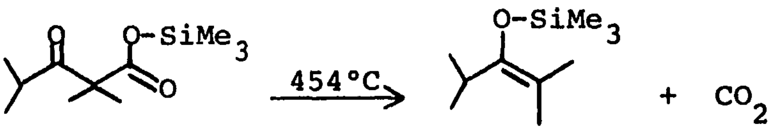
Table 4. (Continued)

Silane	Temperature (°C)	Reference
$R_3Si-X-Y{\equiv}Z$		
C C C	555	165
N C N		182
S C C	120	183
C C N	150	184
N C C	160	185

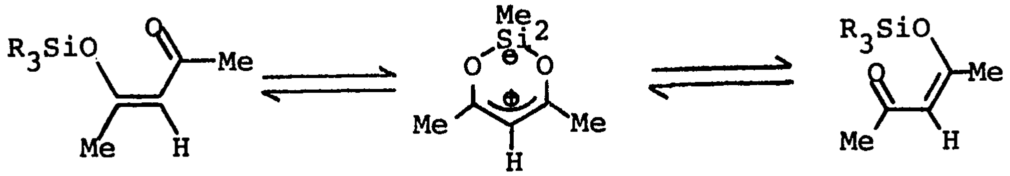
1,5-Migrations of silicon

There are very few thermal 1,5-migrations of silicon known in the literature, especially for linear systems. True 1,5-migration of silicon involving a pentadienylsilyl functionality, with one possible exception, is limited to cyclic systems.

Coates and coworkers have found that a 1,5-migration can occur with participation of a sigma bond in molecules such as 189 (186). These migrations are irreversible since carbon dioxide is lost.



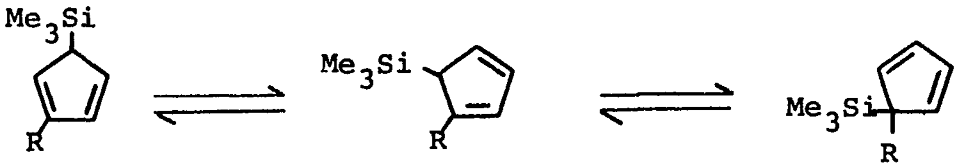
Pinnavaia and coworkers have found that trimethylsilylacetylacetonate 190 undergoes a facile 1,5-migration of silicon from oxygen to oxygen as indicated by equivalent methyl groups in the NMR at 39°C (187). At -54°C, distinct methyl absorptions occur in the NMR. Estimation of the Arrhenius activation energy from line shape analysis gives a value of 13.4 kcal/mole. The trans isomer of the enol 190 did not show broadening of the methyl lines up to 120°C. For compounds of the type 190 in which the silicon atom is chiral, complete retention at the silicon was observed for the migration (188). More recently, Pinnavaia and McClarin (189) as well as Reich and Murcia (190), have argued that the extreme facility with which this migration occurs is consistent with an internal nucleophilic displacement involving the intermediate 191.



190 191

The best known examples of 1,5-migrations of silicon are from silyl-substituted cyclopentadienes, a review of which has appeared in the literature (191). Trimethylsilylcyclopentadiene 192 (R=H) exhibits a temperature dependent NMR spectrum which can be accounted for by

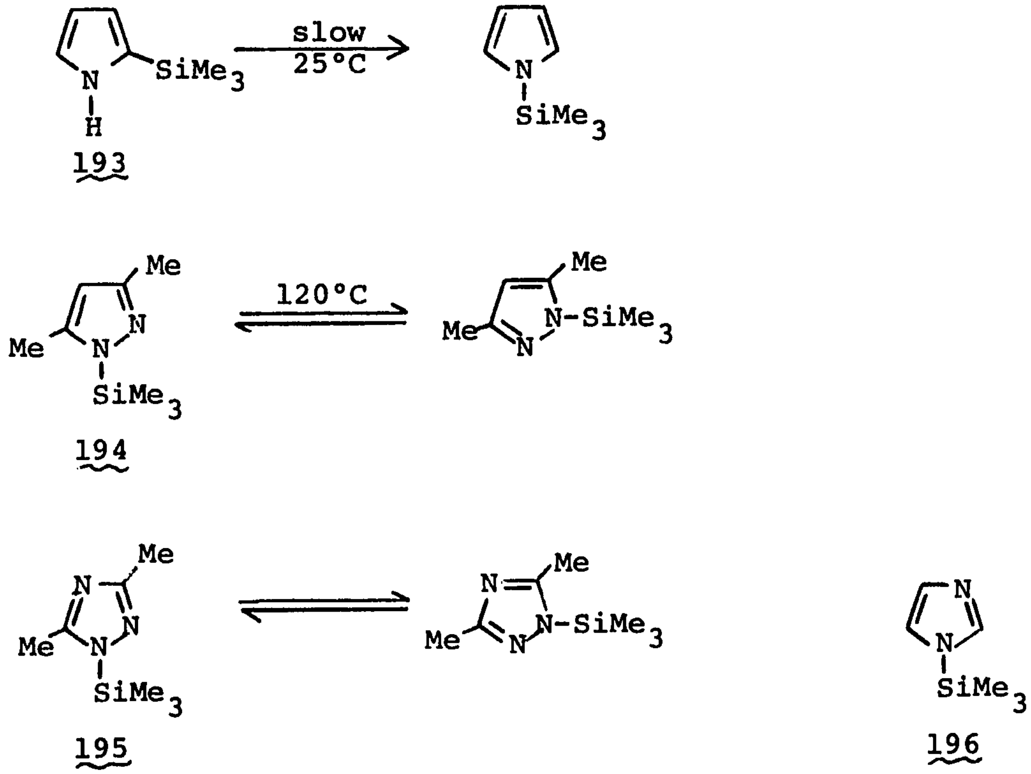
1,5-migrations of either hydrogen or silicon. Ashe was able to show that 1,5-migrations of silicon were responsible (192). Hydrogen migrations do occur but at a rate 10^6 times slower than the trimethylsilyl group. The activation energy for the 1,5-migration of silicon was found to be 13-19 kcal/mole depending on the nature of the substituents. Silicon was found to undergo a similar 1,5-migration in silyl-substituted indenes with an activation energy of 22.5 kcal/mole. Of the group IV elements, only tin would undergo 1,5-migrations in cycloheptatriene and cycloheptadiene.



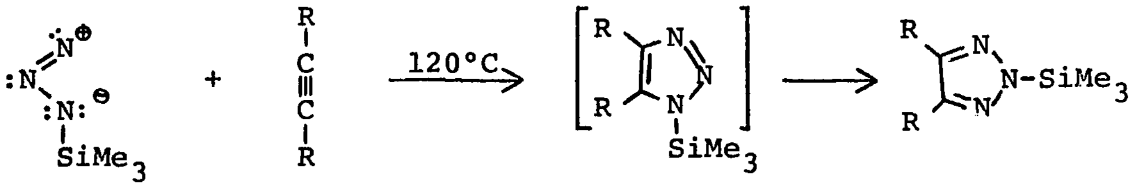
192

There have been numerous reports of 1,5-migrations of silicon in pyroles, imidazoles, diazoles, and triazoles (Scheme 25). Pommier and Lucas have observed slow isomerization of 2-trimethylsilylpyrole 193 to the N-silyl derivative (193). This presumably occurs *via* an initial 1,5-migration of hydrogen. O'Brien and Hrung have observed the coalescence of the two methyl groups of 194 in the NMR at 120°C (194). This was rationalized as resulting from a 1,5-migration of silicon occurring with a measured energy of activation of 28 kcal/mole. Torocheshnikov and coworkers have observed similar behavior for 195 (195). They obtained an activation energy of 27 kcal/mole for a 1,5-migration of silicon in 195. They also obtained a corresponding value of 23 kcal/mole for 194. In addition, they observed proton equivalence in the NMR for 196 even at -80°C. This was assumed to result from intermolecular exchange of trimethylsilyl groups in accordance with the known intermolecular exchange of protons in imidazole.

<u>Scheme 25</u>



Birkofer and Wegner have reported that the products 198 from the reaction of acetylenes with trimethylsilylazide correspond to those expected from a 1,5-trimethylsilyl migration occurring in the initially formed triazoles 197 (196).

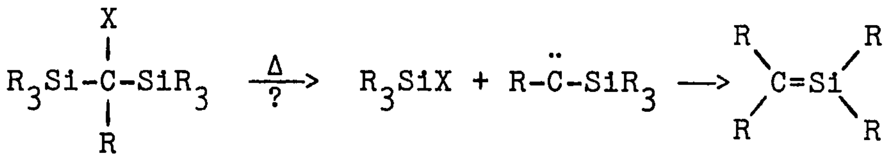


197

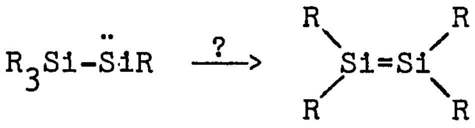
198

RESULTS AND DISCUSSION

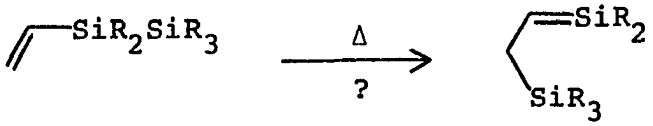
At the time that this work was begun four goals were set forth, all of which involved the generation and chemical characterization of (p-p) π bonded intermediates of silicon. The first was to find out if bis(silyl)methane derivatives will undergo alpha elimination of silicon from carbon to give rise to alpha silylcarbenes. If this were to occur, they would in effect be silene generators since alpha silyl carbenes are known to isomerize the silenes. If this occurred at a low enough temperature, it could fill the need for a mild method of thermal silene generation.



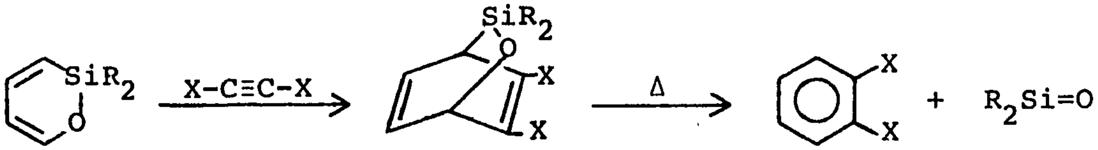
The second goal arises from the question of whether silylsilylene will undergo analogous isomerization to disilenes. This could be of particular importance in light of the limited number of known methods for disilene generation.



Another is to determine whether or not a thermal 1,3-migration of silicon will occur in vinyldisilanes with concomitant silene formation. This is a natural question that arises from a consideration of the large number of thermal 1,3-migrations known for silicon in allylic and hetero-allylic silanes.



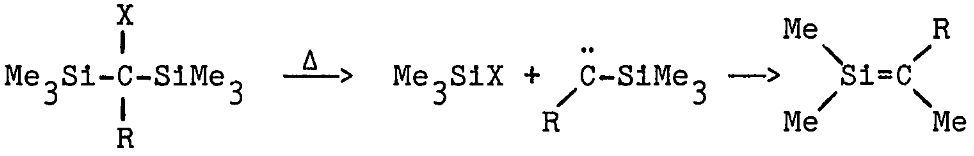
The fourth goal is the development of a method of generation for, and a chemical investigation of silanones, the least understood (p-p) π bonded species. The approach envisioned for the realization of this goal involves the preparation of the then unknown silapyran ring system.



Some of these goals were realized and others were not. In one case, an unexpected result led to the discovery of a thermal 1,5-migration of silicon that proved to be general in other systems and proved to be of synthetic value. The pursuit of another goal led to the discovery of new reactions of silylenes and to an explanation of a curious intramolecular rearrangement of disilenes. After rational approaches had failed, the last goal was serendipitously realized.

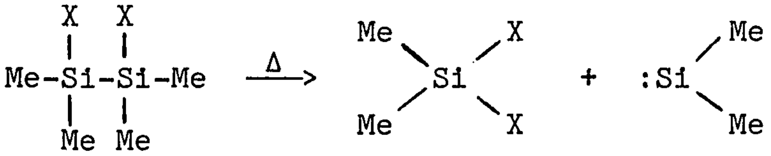
Attempted Generation of Silenes *via* Alpha Elimination of Silicon from Carbon

At the outset of this work all of the known methods for the thermal generation of silenes required temperatures in excess of 320°C. The need for a mild thermal silene generator thus fostered this work to be presented in this section. The approach taken involves the symmetrical bis(trimethylsilyl)methane derivative **199**. Based on the literature, one might expect that with the appropriate substituent X that alpha elimination of silicon and X would occur under relatively mild conditions to give the alpha silyl carbene **200**. Alpha silyl carbenes are known to undergo a facile and efficient migration of an alkyl or aryl group to give silene **201** (128).

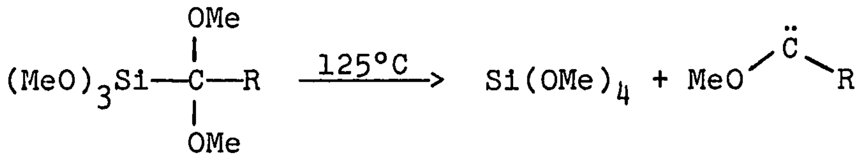


199 **200** **201**

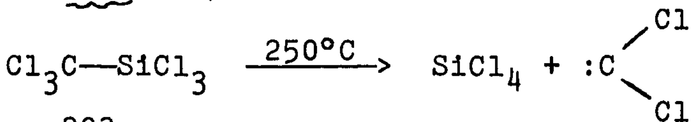
The only questionable step is the initial alpha elimination of silicon from carbon that gives rise to the carbene 200. Alpha elimination of silicon from silicon has been quite extensively studied and, in fact, is the most commonly used method for the thermal generation of silylenes. See the Historical section for a discussion of the generality of this reaction.



Alpha eliminations of silicon from carbon are also known but have not been nearly so extensively studied. For example, Atwell and coworkers (197) have found that 202a will undergo alpha elimination of silicon and oxygen at 125°C to give methoxycarbene. Very similar results were observed for 202b by Brook and Dillon (198). Bevan, Haszeldine, and Young have found that for 203 alpha elimination of silicon and chlorine occurs at 250°C (199).

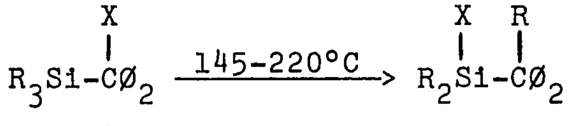


202a R=H
202b R=Ø



203

Not all alpha substituted silanes will thermally degrade via alpha elimination from carbon. Bassindale, Brook, Jones and Lennon have found that silanes of the type 204 undergo a dyatropic thermal isomerization to 205 in which an alkyl or aryl group on silicon is exchanged with the electronegative substituent on carbon (200). Bevan and coworkers have found that 206 will undergo exchange of fluorine and chlorine at 100°C (201).

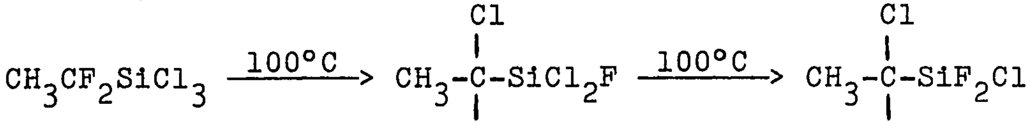


$$R_3Si\text{-}\overset{X}{\overset{|}{C}}\emptyset_2 \xrightarrow{145\text{-}220°C} R_2\overset{X}{\overset{|}{Si}}\text{-}\overset{R}{\overset{|}{C}}\emptyset_2$$

204 205

X = F, Cl, Br, OAc

R = Me, Ø

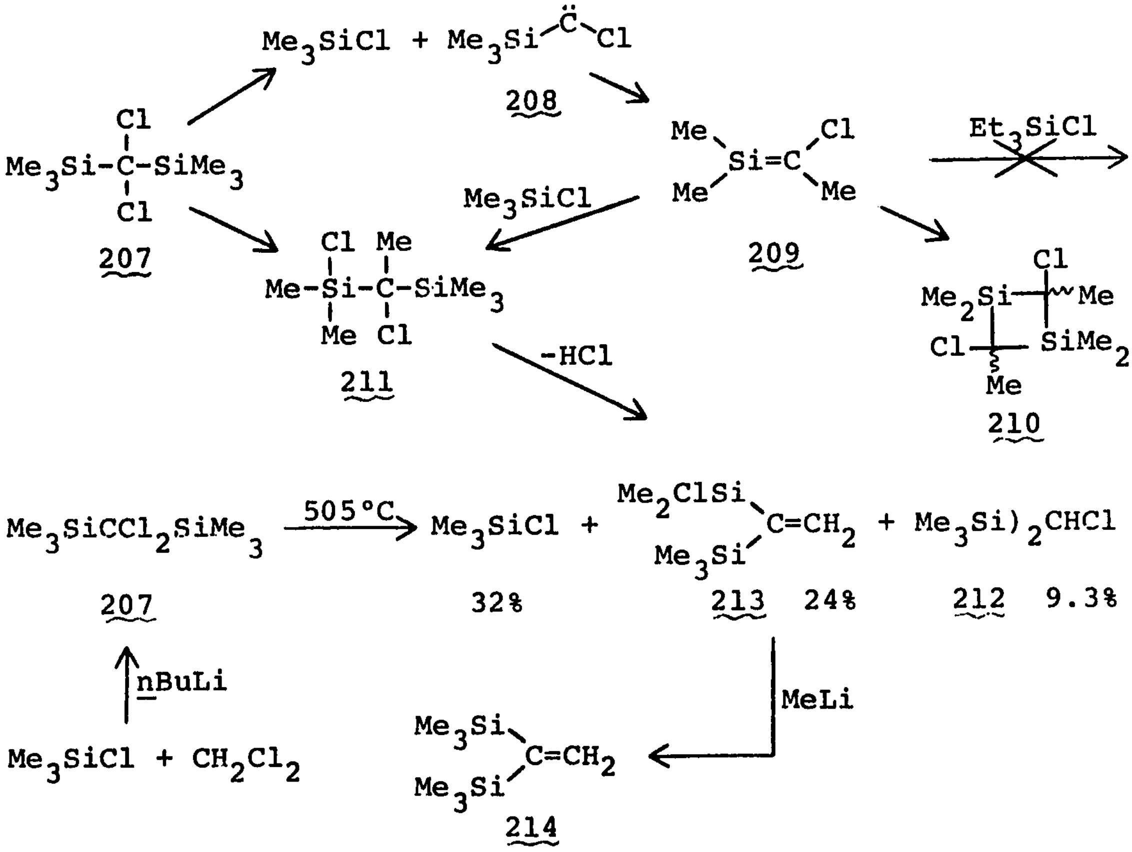


$$CH_3CF_2SiCl_3 \xrightarrow{100°C} CH_3\text{-}\underset{F}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}\text{-}SiCl_2F \xrightarrow{100°C} CH_3\text{-}\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}\text{-}SiF_2Cl$$

206

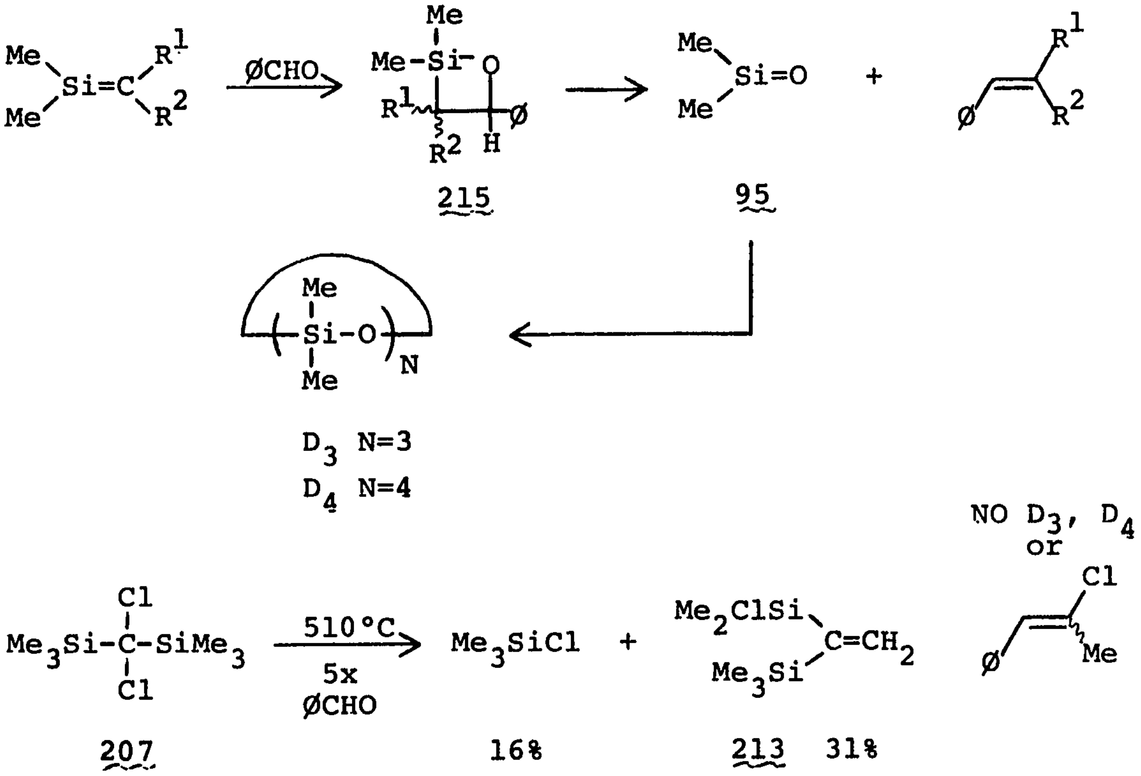
The thermal chemistry of bis-(silyl)methyl compounds has not been previously studied and thus there is no way to know whether alpha elimination or isomerization will occur other than performing the pyrolysis. The compound initially chosen for this study was bis-(trimethylsilyl)dichloromethane 207 which was prepared by the method of Bamford and Pant (202) (Scheme 26). If alpha elimination occurs, then the resultant carbene 208 would be expected to isomerize to the silene 209, which in the absence of any trapping reagent in accordance with the known chemical behavior of silenes would be expected to dimerize to the 1,3-disilacyclobutane 210. If simple thermal isomerization were to occur, one of the possible products is 211 which is related to 207 by the interchange of one chlorine and one methyl. When 207 was pyrolyzed by dropping it through a vertical quartz tube packed with quartz chips and heated to 505°C, the major volatile products were trimethylchlorosilane, 212 and 213, in 32%, 9% and 24% yields, respectively. Trimethylchlorosilane and 212 were identified by comparison of their spectra with those of authentic materials. The structure of 213 was determined from its spectra and by treatment with methyllithium and subsequent comparison of the spectra of the product 214 with those in the literature (203). None of disilacyclobutane 210 was observed. The most likely explanation for the formation of 213 is loss of HCl from the thermally isomerized intermediate 211. Similar isomerizations occur with Lewis acid catalysts; however, the same results were obtained when the pyrolysis tube was pretreated with concentrated ammonium hydroxide. It is still possible that the silene 209 is an intermediate in this reaction because if it were to insert into the silicon-chlorine bond of trimethylchlorosilane, the resultant product would be the isomerized intermediate 211. It has been demonstrated that silenes will insert into silicon-chlorine bonds, although it is in general a poor reaction and for trimethylchlorosilane dimerization largely predominates over insertion (136). Evidence against the insertion of 209 into trimethylchlorosilane was obtained in the co-pyrolysis of 207 with a 9.5-fold excess of triethylchlorosilane. The same products were observed in the same relative yields as in the pyrolysis of 207 alone and no new products were observed by GCMS in which a triethylsilyl group had been incorporated.

Scheme 26



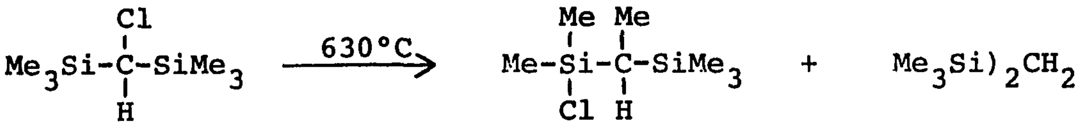
More damaging evidence against the intermediacy of 209 was obtained from the co-pyrolysis of 207 with a five-fold excess of benzaldehyde (Scheme 27). The reaction of silenes with carbonyl compounds is one of the most well-documented reactions of silenes and as a result has been used diagnostically when the intermediacy of a silene is at issue.

Scheme 27



(See Historical section on silenes.) The reaction is a Wittig-type reaction in which olefins and silanones are produced presumably via the intermediate siloxetane 215. The silanones undergo cyclooligomerization to cyclic trimers and tetramers (referred to as D_3 and D_4) which constitute the observed silicon-containing products of this reaction. The products from the co-pyrolysis of 207 and benzaldehyde are trimethylchlorosilane and 213. No D_3, D_4, or 2-chloro-2-methylstyrene were observed in this reaction as determined by GCMS. Thus, no evidence for the intermediacy of 209 could be found for the pyrolysis of 207, and it appears that the major product 213 results from isomerization and HCl elimination.

The loss of HCl from an isomerized intermediate cannot happen in the pyrolysis of 212. Compound 212 was prepared from 207 by reduction with tri-n-butyltin hydride in 72% yield. Compound 212 was pyrolyzed by dropping it into a stream of nitrogen that was being swept through a vertical quartz tube heated to 630°C. (No reaction occurred at 505°C.) The exceptionally clean pyrolysate consisted of the isomerized compound 216 and bis-(trimethylsilyl)methane 217 in 40% and 7% yields, respectively. This result eliminates the possibility of attributing the isomerization of 207 to the presence of HCl.

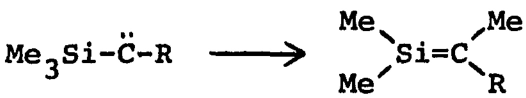


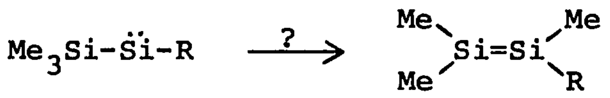
$$Me_3Si-\underset{H}{\overset{Cl}{C}}-SiMe_3 \xrightarrow{630°C} Me-\underset{Cl}{\overset{Me}{Si}}-\underset{H}{\overset{Me}{C}}-SiMe_3 + Me_3Si)_2CH_2$$

212 216 40% 217 7%

Synthesis of 1-Trimethylsilyl-1-methyl-2,5-diphenylsilole 218 and Some Reactions of Trimethylsilyllithium

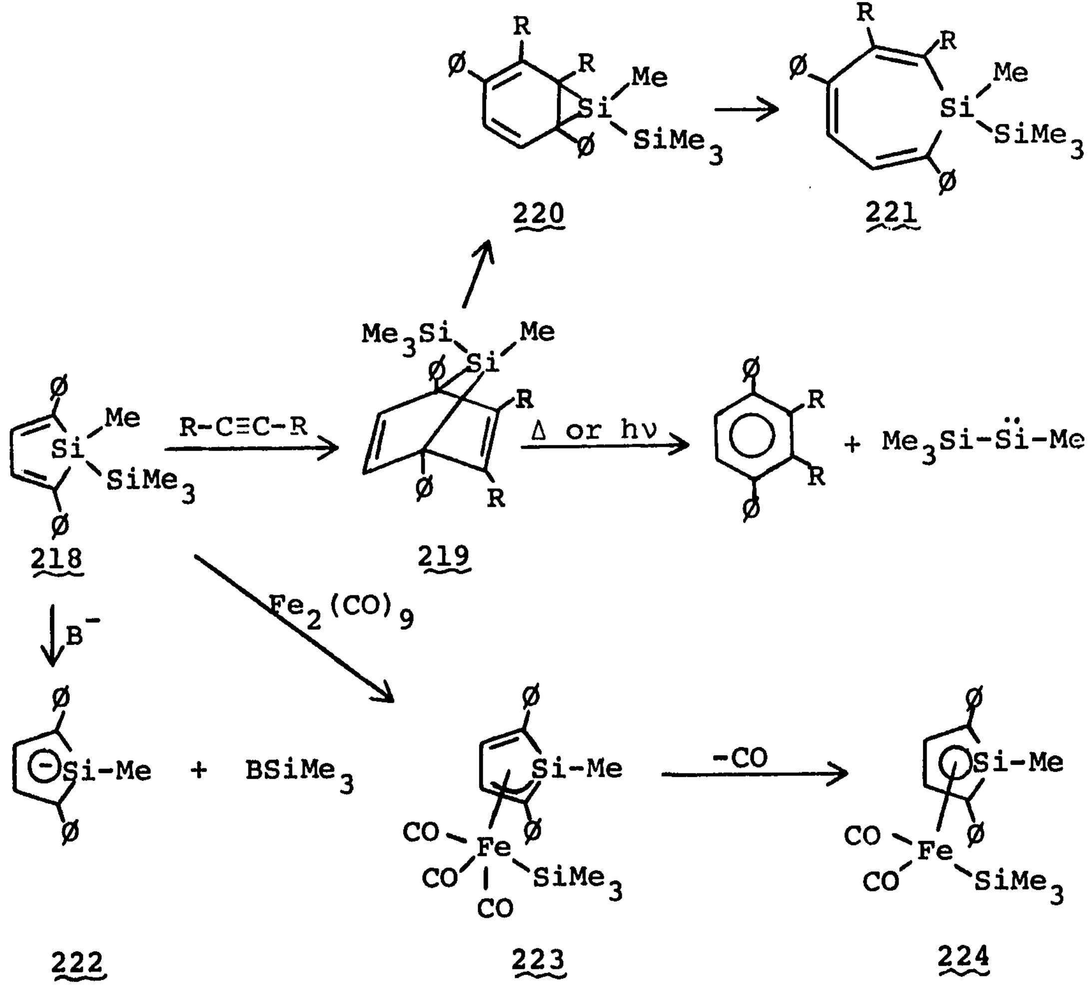
As discussed in the Historical section of this thesis, alkyl or aryl migration from silicon to carbon readily occurs in alpha silylcarbenes to give silenes. The analogous rearrangement of alpha silylsilylenes to disilenes is not known and would be a valuable reaction since at the outset of this work there existed only one method for the generation of disilenes. Silylsilylenes have been generated before; however, in each case a trap had been present so the question concerning the rearrangement to disilenes is still open (62-64,76).





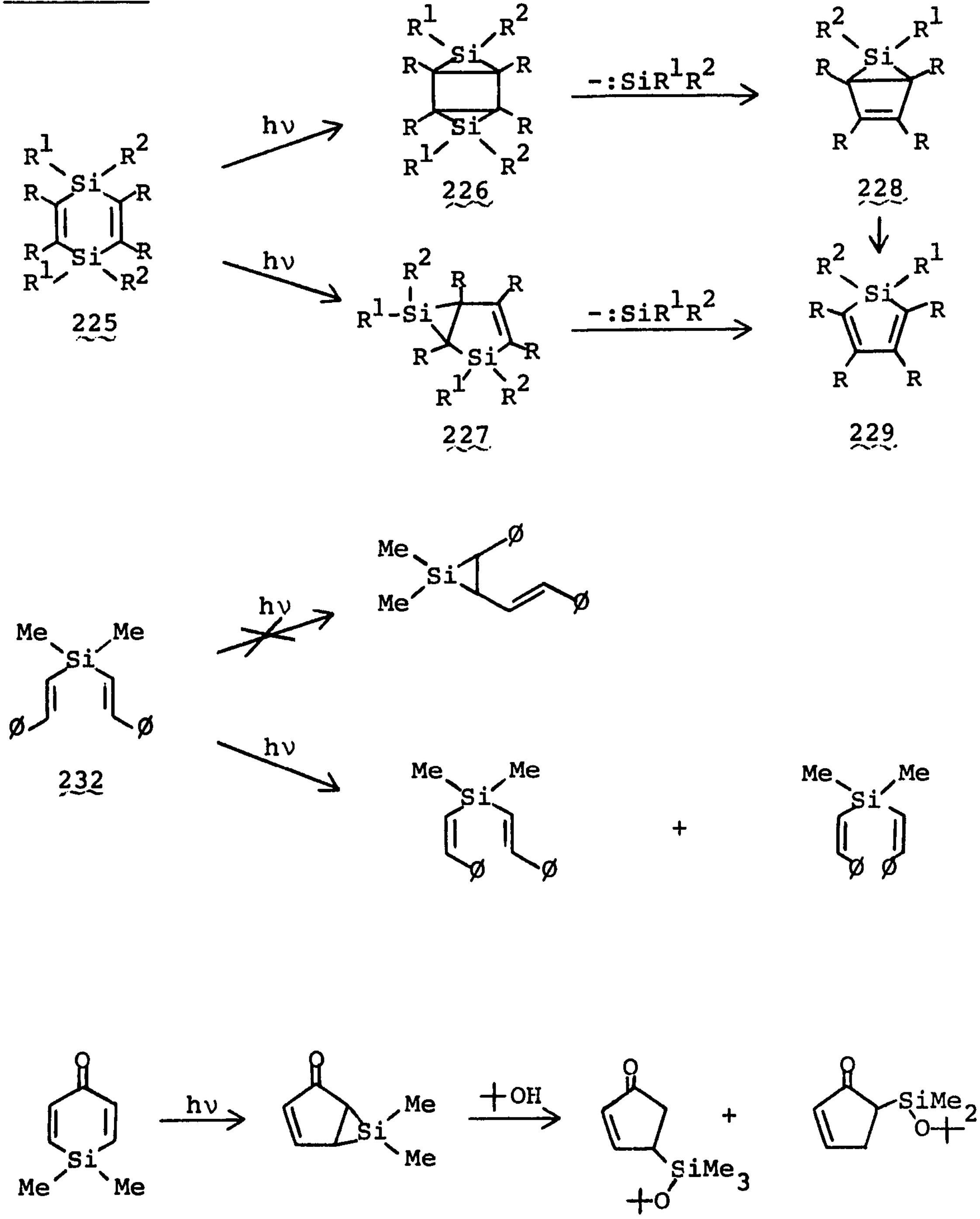
Of the various methods of silylene generation available, the thermolysis of 7-silanorbornadiene 219 was chosen for the generation of methyltrimethylsilylene (Scheme 28). With the appropriate substitutents (R), one would expect 219 to be a thermal and possibly a photochemical generator of trimethylsilylsilylene (see Historical section on silylenes). 7-Silanorbornadienes are most commonly prepared by cycloaddition of acetylenes to silacyclopentadienes (siloles). The synthesis of 219 would require the preparation of 1-trimethylsilyl-1-methyl-2,5-diphenylsilole 218. An added incentive for the utilization of 219 is that it is possible that conditions could be found under which 219 might undergo a 1,3-migration followed by ring opening to give 221. There are no silacycloheptatrienes known in which the silicon is functionalized (204). These compounds are of interest because the existence in solution of a cationic silicon has yet to be convincingly demonstrated. Another reason for the choice of silylene generator 219 is that its immediate precursor 218 may allow entry into the unknown and potentially aromatic anion 222 via base cleavage of disilanes, and into the unknown η^5-silole transition metal complexes such as 224. The generation of silyl anions by the base cleavage of disilanes has become a useful reaction, however, it does have some severe limitations (205-211). Sakurai and coworkers (108) have found that nonacarbonyl diiron will react with vinyldisilanes to give π-silaallyl complexes and by analogy it could be expected that 218 would accordingly form the π-silaallyl complex 223, which if it lost carbon monoxide would give the η^5-silole complex 224.

Scheme 28



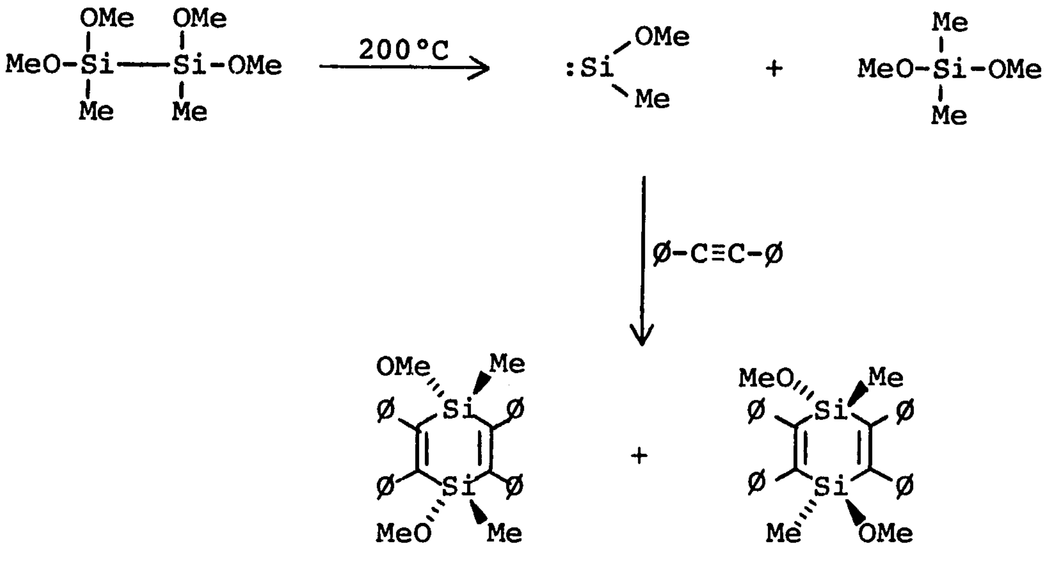
In this section, two unsuccessful approaches and one successful approach to the synthesis of **218** will be described. The general method for the preparation of 2,5-diphenylsiloles is deemed undesirable for the preparation of **218** due to the sensitivity of the silicon-silicon bond to the requisite reagents (212). Thus, the examination of two new approaches to the synthesis of silole ring systems was undertaken (Scheme 29). The first approach involves a photo-induced extrusion of a silylene from 1,4-disilacyclohexadienes of the type **225**. If **225** photochemically undergoes a di-π-methane rearrangement to **227** or a 2+2 cycloaddition to **226**, then in either case a silarane is formed from which extrusion of a silylene is not an unreasonable expectation in view of the known propensity of silaranes to extrude silylenes under very mild conditions (54). This approach to the synthesis of siloles was pursued despite the fact that Krochmal and coworkers (213) have found that photolysis of the divinylsilane **232** resulted not in a di-π-methane rearrangement but rather in cis-trans isomerization; and in light of the fact that Koch and coworkers have found that the products from the photolysis of 1,1-dimethyl-1-silacyclohexa-2,5-dienone in *t*-butyl alcohol are those that would be expected from the trapping of an intermediate that would result from a di-π-methane rearrangement (214).

Scheme 29



The 1,4-disilacyclohexadienes 233a and 233b were prepared as described by Atwell and Weyenberg (21) (Scheme 30). These compounds were selected for this investigation because the methoxyl group will allow the introduction of various functionality. Atwell and Weyenberg reported obtaining a 3:1 mixture of isomers but these were not separated nor were they assigned stereochemistry. Compounds 233a and 233b were separated by HPLC on a 4' Porasil A column with benzene solvent. The ratio of 233a to 233b was found to be 1:3 as determined by a stereochemical assignment made on the basis of the correlation of the change in the chemical shifts of the methoxyl groups in the NMR with added Euroshift F as explained in the Experimental section of this thesis. In benzene and cyclohexane, 233b was inert to photolysis through a Pyrex filter up to a period of 5 days. In a quartz vessel containing an ether solution of 233b, no change was observed after 20 hours of irradiation with 2537 Å light. However, when pure 233b was dissolved in CCl_4, a 1:1 mixture of 233a and 233b was observed by NMR after irradiation for 5 hours through a Pyrex filter. Likewise, a CCl_4 solution of 233a was found to isomerize to 233b. After prolonged irradiation, decomposition occurs to give a large number of products as indicated by NMR and HPLC. These products were not identified.

Scheme 30

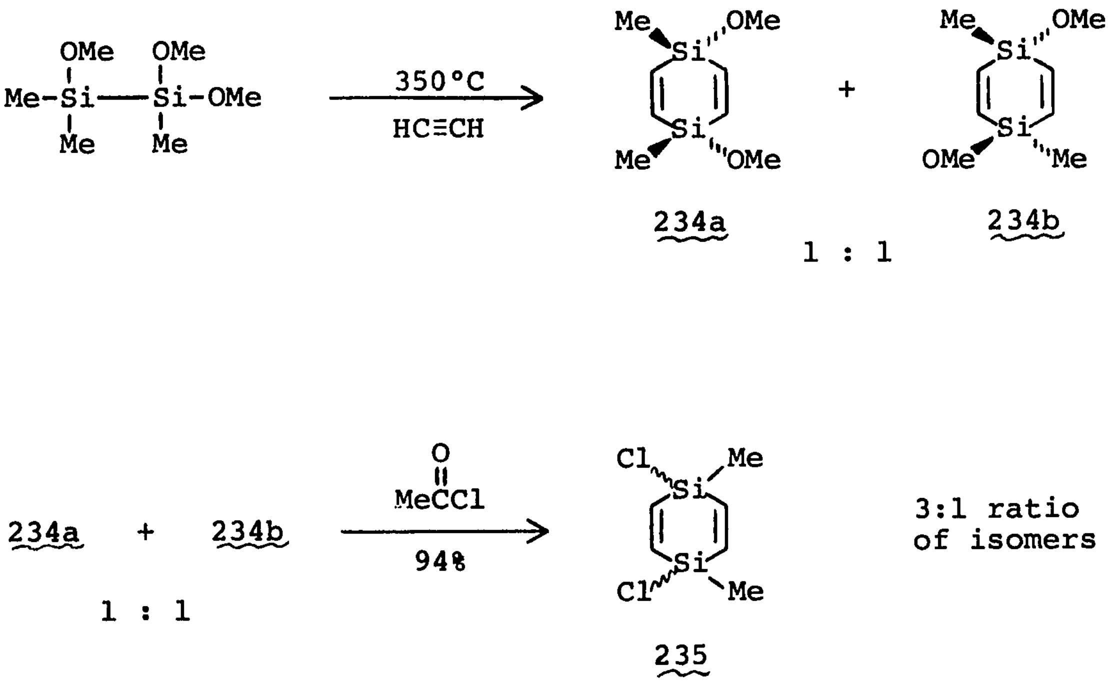


233a 1 : 3 233b

In order to remove any influence the phenyl groups may have on the photolysis, the analogous, 1,4-disilacyclohexadienes 234a and 234b, were prepared by the procedure of Janzen and coworkers (22) (Scheme 31). They reported the formation of only a single isomer from this reaction. However, in each of 4 runs a 1:1 mixture of 234a and 234b was obtained. They were separated by HPLC on a 4' Porasil A column and subsequently each was spectrally characterized. Stereochemical assignment was made by comparison of the relative shifts in the NMR with those for compounds 233a and 233b. Photolysis of 234a in degassed CCl_4 through a

Pyrex filter for 11 hours in a Rayonet reactor resulted in the formation of a 1:1 mixture of 234a and 234b. This result was not observed for compound 235.

Scheme 31



Treatment of a 1:1 mixture of 234a and 234b with acetyl chloride resulted in a 94% yield of a 3:1 mixture of isomers of 235. When a mixture of these isomers of 235 in CCl_4

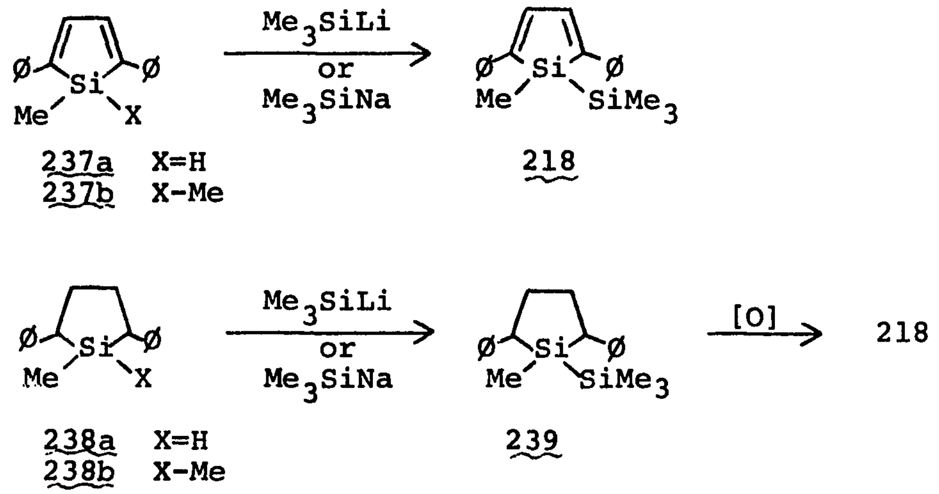
solution was irradiated for 24 hours, no change in the isomer ratio was observed by NMR. Either 235 is photo-stable or the photo-equilibrium ratio of isomers is 3:1. No evidence for silole formation could be obtained in the photolysis of either 233, 234, or 235. These photolysis reactions were not pursued further and the observation of the photo-induced isomerizations of 1,4-disilacyclohexadienes peculiar to CCl_4 solvent was left unexplained.

An alternative to the most common method for the preparation of siloles is to modify the functionality on silicon after the ring forming reaction. A route to the silole 218 that embodies this approach is the coupling reaction of trimethylsilyllithium 240 or trimethylsilylsodium 241 with either the saturated or the unsaturated rings 237 and 238 in each of which the silicon is functionalized with a good leaving group (Scheme 32). The uncertainty of this approach is that 240 and 241, as well as all trialkylsilyl anions have just recently become readily accessible and their reactions with functionalized silanes have yet to be investigated. Sakurai and coworkers have shown that 241 can be generated in HMPA or DMI *via* the cleavage of hexamethyldisilane with sodium methoxide (206, 207,209). Coupling reactions with 241 are limited by competition with an electron transfer process. Still has recently demonstrated that 240 can be generated in HMPA by the cleavage of hexamethyldisilane with methyllithium (208).

Since chlorine is the most widely used leaving group for displacement reactions on silicon, the coupling reaction of trimethylsilyllithium and chlorosilanes was investigated. In an attempt to prepare 245, 2.5 equivalents of 240 was added to a solution of silicon tetrachloride and the observe products were 242, 243 and 244. None of the desired coupling product 245 was observed. It is interesting to note that 242 and 243 were also the major products observed in the attempted coupling reaction of 240 and dibromodifluoromethane.

The formation of trisilanes and tetrasilanes from the treatment of disilanes with base has not been observed before. However, Sakurai and Okada have observed a reversible redistribution reaction between different disilanes in the presence of a catalytic amount of sodium methoxide (215) (Scheme 33). They found that treatment of an equilmolar amount of 246 and 247 with a catalytic amount of sodium methoxide resulted in a statistical 1:2:1 mixture of 246, 248 and 247. These results can be explained by nucleophilic attack of a silyl anion on a disilane to give the pentacoordinate intermediate 249 which eliminates a different silyl anion to give a new disilane. In an analogous way the formation of 242 and 243 could be accounted

Scheme 32



$$Me_3SiSiMe_3 \xrightarrow[\text{HMPA}]{\text{MeLi}} Me_4Si + \underset{\underset{\sim}{240}}{Me_3SiLi}$$

$$Me_3SiSiMe \xrightarrow[\text{HMPA or DMI}]{\text{NaOMe}} Me_3SiOMe + \underset{\underset{\sim}{241}}{Me_3SiNa}$$

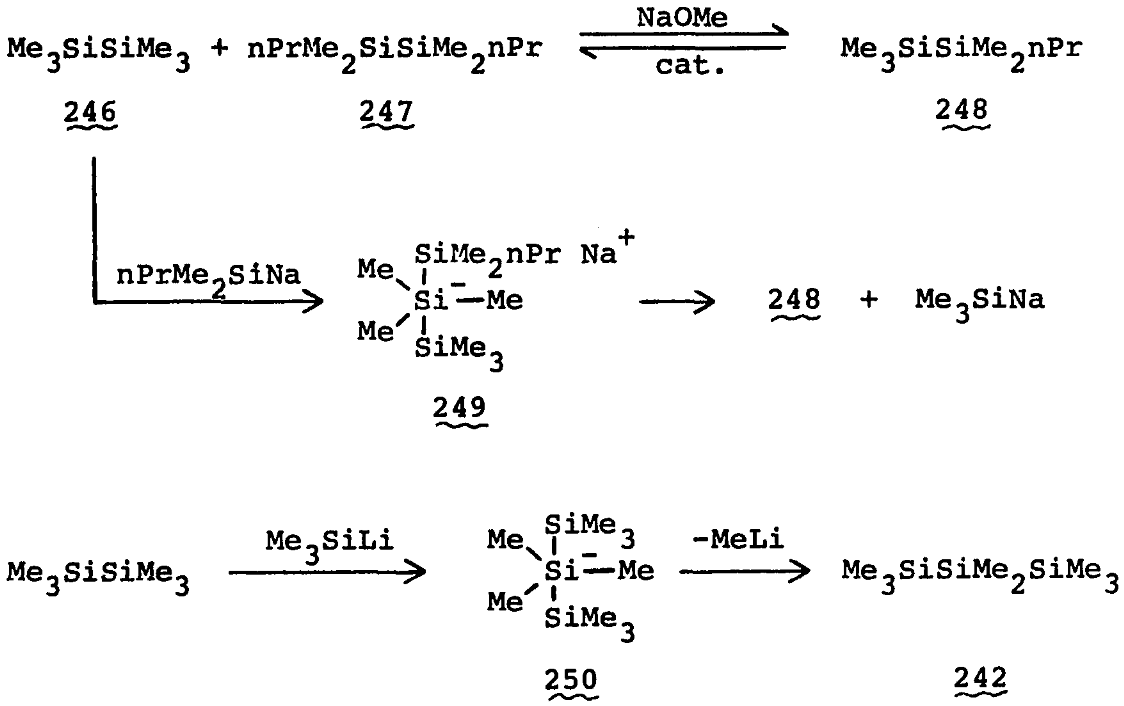
$$\underset{\text{1 equiv.}}{SiCl_4} + \underset{\text{2.5 equiv.}}{Me_3SiLi} \longrightarrow \underset{\underset{\sim}{242}}{Me_3SiSiMe_2SiMe_3} + \underset{\underset{\sim}{243}}{Me_3SiSiMe_2SiMe_2SiMe_3}$$

$$+ \underset{\underset{\sim}{244}}{Me_2N)_3SiCl} \quad \underline{\text{NO}} \quad \underset{\underset{\sim}{245}}{Me_3Si)_2SiCl_2}$$

$$\underset{\text{1 equiv.}}{CF_2Br_2} + \underset{\text{1 equiv.}}{Me_3SiLi} \longrightarrow \underset{\sim}{242} + \underset{\sim}{243}$$

for by the intermediate 250 if elimination of methyllithium rather than trimethylsilyllithium occurs.

Scheme 33



Reactions of 240 with other functionalized silanes were also investigated. Table 5 lists the various silanes that were used and the corresponding yields of disilane products. Coupling reactions were successful with trialkylsilyl hydrides, bromides and perchlorates and unsuccessful with trialkylsilyl chlorides and with vinylsilanes regardless of the other substituents on silicon.

$$R_3SiX + Me_3SiLi \xrightarrow{HMPA} R_3SiSiMe_3$$

Table 5. Reactions with trimethylsilyllithium

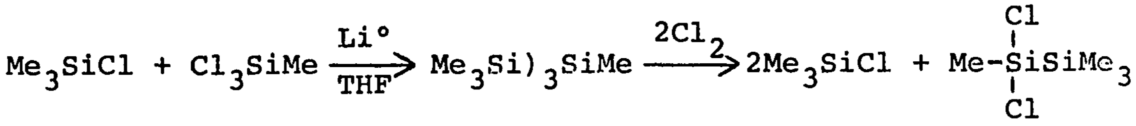
R_3SiX	% Yield of $R_3SiSiMe_3$
$SiCl_4$	0
Et_3SiCl	0
Et_3SiH	41
$(i\cdot prop)_2SiMeH$	32
Et_3SiBr	39
Et_3SiClO_4	55
$CH_2=CH-SiMe_2H$	0
$CH_2=CH-SiMe_2OEt$	0
$CH_2=CH-SiMe_2Br$	0

Despite the discouraging results from the reaction of trimethylsilyllithium 240 with various functionalized silanes, coupling reactions were attempted with the silyl hydrides 237a and 238a. Compound 238a was prepared following the procedure used by Weyenberg and coworkers for the preparation of **238b** (216). Analysis of the residue from the reaction of **238a** and **240** reveals that trimethylsilyl groups were not incorporated. The NMR is most consistent with abstraction of the benzylic protons by **240** and subsequent incorporation of methyl groups upon quenching the reaction with excess methyl iodide.

Compound **237a** was prepared following the procedure used by Atwell and coworkers for the preparation of **237b** (212). NMR analysis of the unpurified material obtained from the reaction of **237a** and **240** reveals that some starting material remains and the appearance of a cluster of absorption at $\delta = 0.20$ to -0.20. However, the absorptions at the positions expected for **218** are absent. Later, after **218** had been successfully prepared, it was confirmed by NMR that **218** was not formed in this reaction.

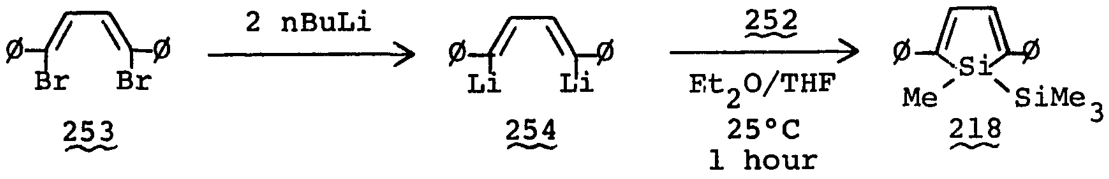
Synthesis of **218** was achieved utilizing a route developed by Atwell and coworkers (212) for the direct synthesis of siloles from dichlorosilanes and the dilithiobutadiene **254**. A preparation for 1,1-dichlorotetramethyldisilane **252** was not found in the literature but rather in the thesis of Harrell (217). The treatment of tris(trimethylsilyl)methyl silane **251** with 2 equivalents of chlorine results in sequential cleavage of the silicon-silicon bonds to give trimethylchlorosilane and **252**.

Compound 251 was prepared by the coupling reaction of trimethylchlorosilane and methyltrichlorosilane as described by Smith (218). Treatment of 252 with the dilithiobutadiene 254 resulted in the formation of the yellow, fluorescent silole 218 in 50% yield.



$$\mathrm{Me_3SiCl + Cl_3SiMe \xrightarrow[THF]{Li^{\circ}} Me_3Si)_3SiMe \xrightarrow{2Cl_2} 2Me_3SiCl + Me{-}\overset{Cl}{\underset{Cl}{Si}}SiMe_3}$$

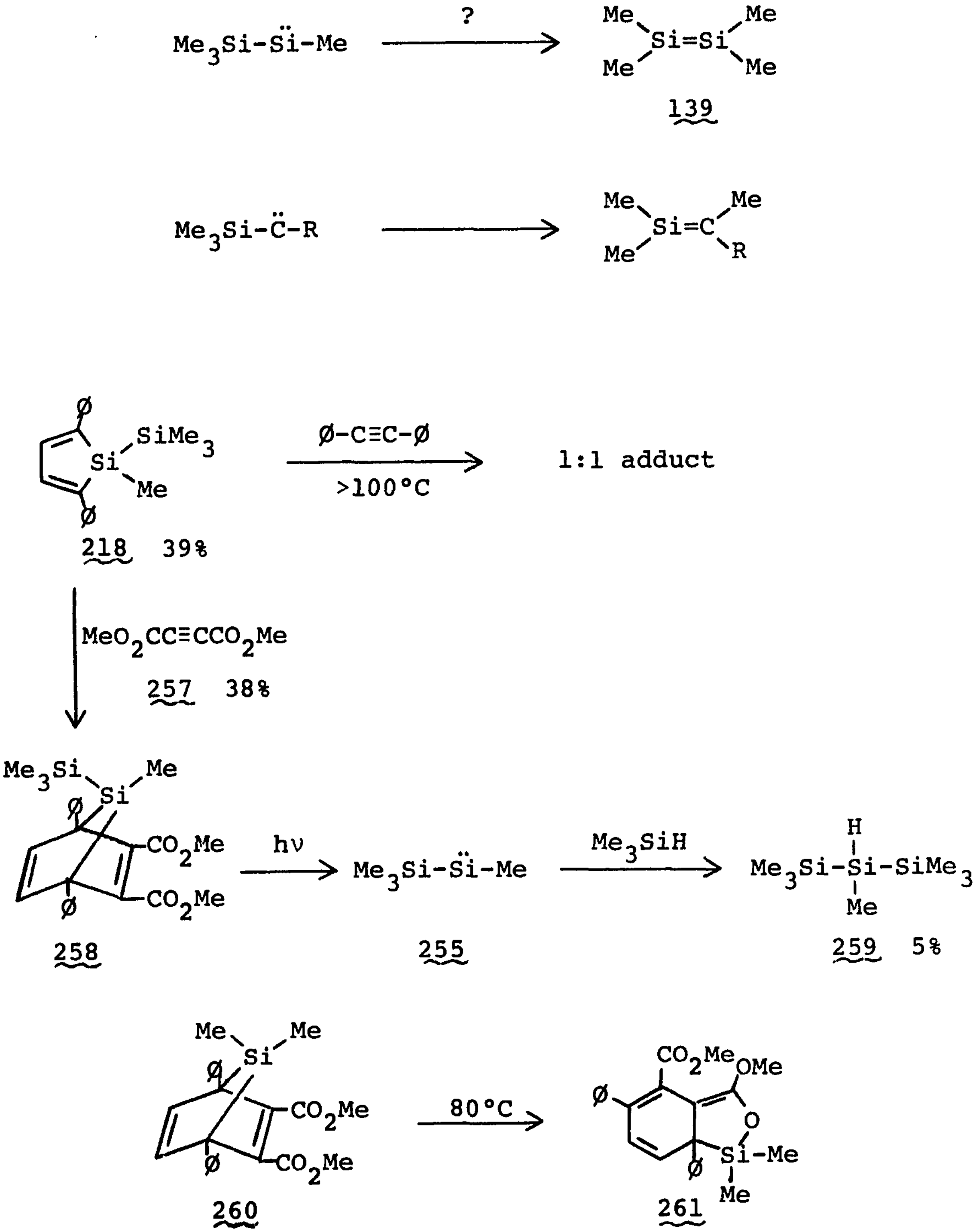
251 252



The Generation and Gas Phase Reactions of Trimethylsilylmethylsilene 255

The study of trimethylsilylmethylsilylene 255 was undertaken to see if it would rearrange to tetramethyldisilene 139 in a similar way that alpha silylcarbenes are known to rearrange to silenes (see Historical section on silenes) (Scheme 34). In the previous section of this thesis the preparation of the silole 218 was described. A 4+2 cycloaddition reaction with an acetylene will render 218 a precursor to 7-trimethylsilyl-7-silanorbornadienes which are expected to be thermal and possibly photochemical generators of 255 in a manner analogous to that known for other silylenes from 7-silanorbornadienes (219).

Scheme 34

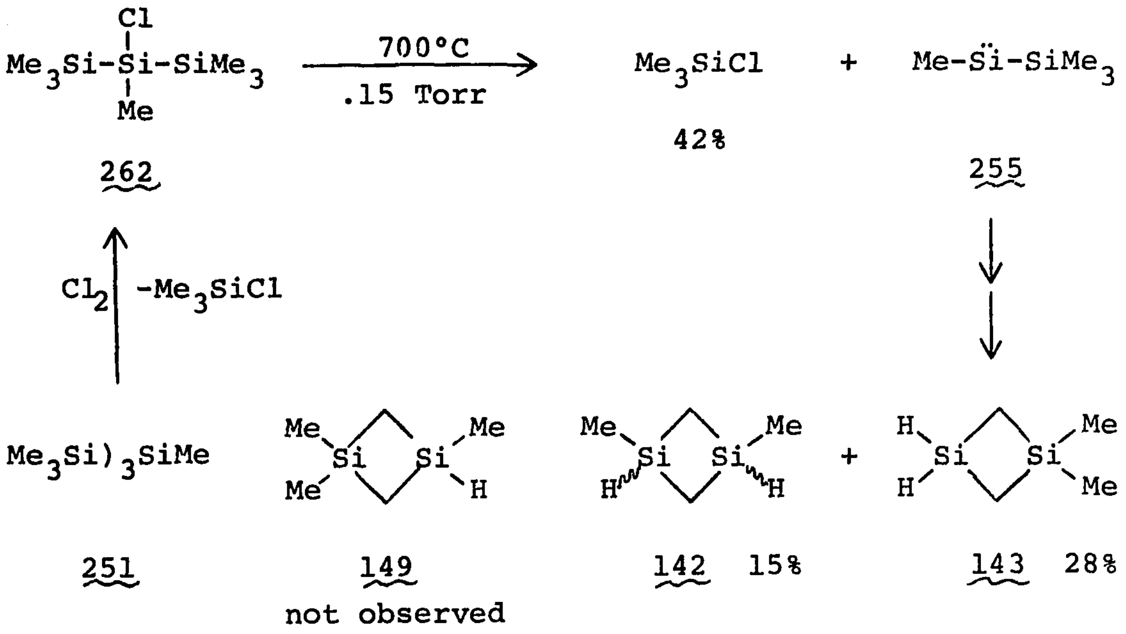

Me3Si-S̈i-Me
?
Me
Me
Si=Si
Me
Me
139
Me3Si-C̈-R
Me
Me
Si=C
Me
R
Ø
Si
SiMe3
Me
Ø
218 39%
Ø-C≡C-Ø
>100°C
1:1 adduct
MeO2CC≡CCO2Me
257 38%
Me3Si
Me
Si
Ø
CO2Me
CO2Me
Ø
258
hν
Me3Si-S̈i-Me
255
Me3SiH
H
Me3Si-Si-SiMe3
Me
259 5%
Me
Me
Si
Ø
CO2Me
CO2Me
Ø
260
80°C
CO2Me
OMe
Ø
O
Si-Me
Ø
Me
261

The only acetylene that gave a cycloadduct with 218 was dimethylacetylene dicarboxylate. The adduct 258 precipitated as a single isomer from a cold hexane solution of 218 and 257 in 39% yield. Diphenylacetylene would react with 218 above 100°C to give a 1:1 adduct; however, it is clear from its NMR spectrum that this is not the symmetrical 4+2 cycloadduct. The nature of this adduct will be discussed in Part 5 of the Results and Discussion.

Concurrent with the successful synthesis of 258, it is found that the very similar 7-silanorbornadiene 260 thermally isomerizes to 261 and does not extrude dimethylsilylene (163). In light of these results, compound 258 was photolyzed and found to generate 255. Irradiation of a benzene solution of 258 and excess trimethylsilane resulted in the generation of 255 as evidenced by its product of trapping 259 with trimethylsilane; however, the yield of 259 was a disappointing 5%. All of this data suggest that a different method for the generation of 255 is needed.

2-Chloroheptamethyltrisilane 262 proved to be a convenient generator of trimethylsilylmethylsilylene 255 in the gas phase at temperatures greater than 500°C. Compound 262 was prepared from 251 as described by Harrell (217) (Scheme 35). When 262 was evaporated (.15 torr) through a horizontal quartz tube heated to 700°C and packed with quartz chips, four volatile products were obtained

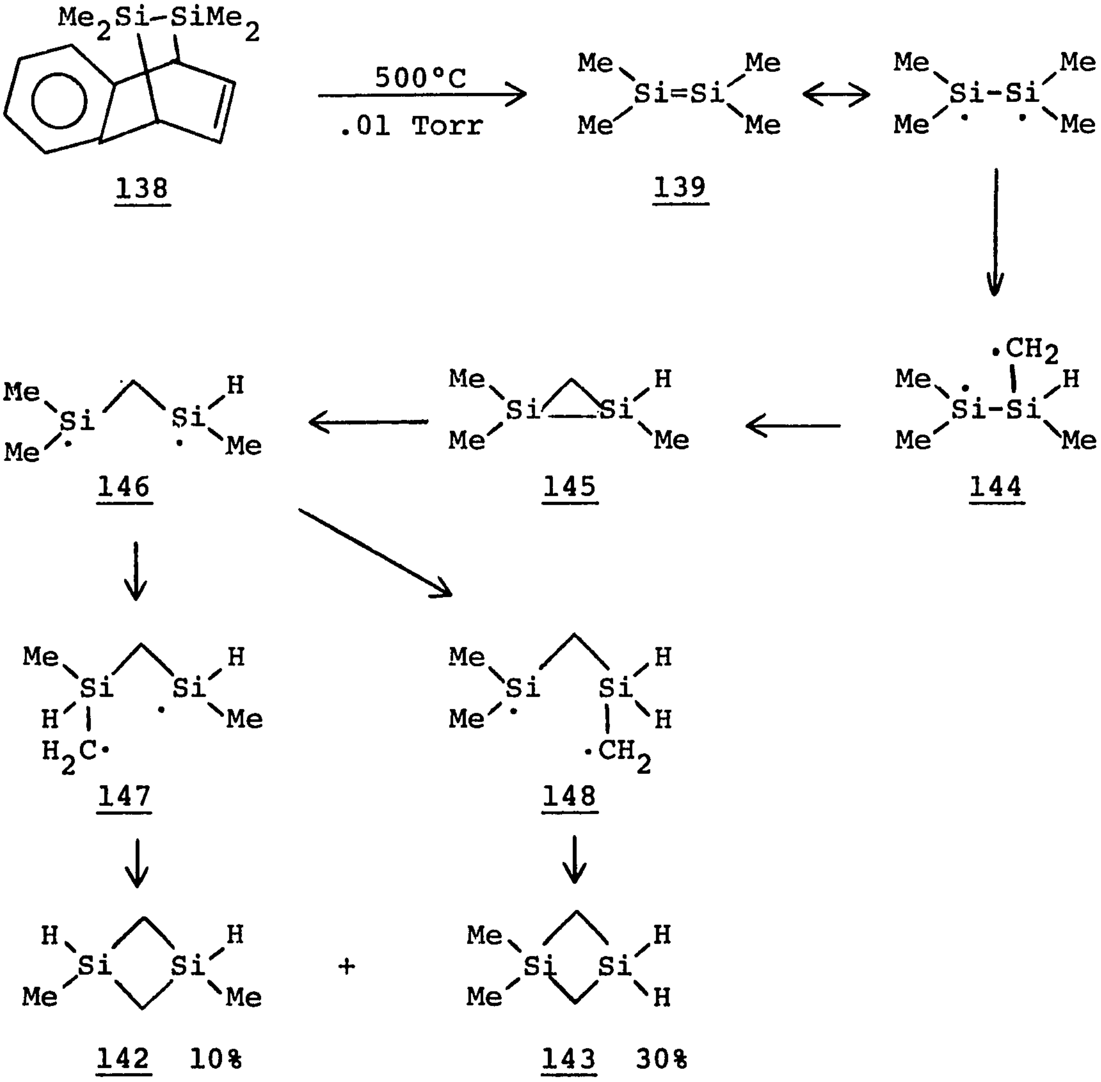
Scheme 35



along with a 42% yield of trimethylchlorosilane and a small amount of trimethylsilane, two disilacyclobutanes were obtained 142 and 143, both of which are isomeric with and presumably derived from trimethylsilylmethylsilylene 255. Compounds 142 and 143 were isolated by preparative G.C. on a 12' x 1/4" 20% DC-550 on Chromsorb P column and identified by comparison of their spectra with those reported in the literature (25). The observation of 142 and 143 from the pyrolysis of 262 is particularly interesting since these are the same two products, obtained in the same relative yields, that were reported by Roark and Peddle (144) to result from the generation of tetramethyldisilene at 500°C (0.01 torr) in the absence of a trapping reagent (Scheme 36). Conlin and Gaspar (25) have reported that in addition to 142 and 143, 149 is also formed when 139 is generated *via* dimerization of dimethylsilylene at 600°C and 0.1 torr. However, 149 was not a product of the pyrolysis of 262 as indicated by the G.C. retention time of an authentic sample of 149.

Roark and Peddle (144) have proposed the mechanism shown in Scheme 36 to account for the formation of 142 and 143. They have shown that 138 does generate tetramethyldisilene 139 by carrying out the co-pyrolysis of 138 with anthracene and *trans*,*trans*-1,4-diphenylbutadiene and obtaining the expected 4+2 cycloaddition products of 139. Their proposed mechanism for the rearrangement of 139 to 142 and 143 involves an initial hydrogen atom migration from carbon to silicon to give the diradical 144. A migration of this type can be argued to be unlikely since hydrogen atom migrations of this type are unknown for silicon-centered radicals (220). Closure of this diradical gives the key intermediate to their mechanism, the disilacyclopropane 145. This is an unknown ring system although evidence for its transient existence in solution has been reported (221). Homolytic rupture of the silicon-silicon bond in 145 gives the diradical 146. This diradical can undergo the same hydrogen atom migration that was envoked for the first step. This can occur in two ways to give the diradicals 147 and 148, together which can account for the two observed dimethyldisilacyclobutanes 142 and 143 upon ring closure. Regardless of the mechanism by which 139 rearranges to 142 and 143, it appears that trimethylsilylmethylsilylene 255, as generated from 262 (Scheme 35), rearranges to tetramethyldisilene 139.

Scheme 36

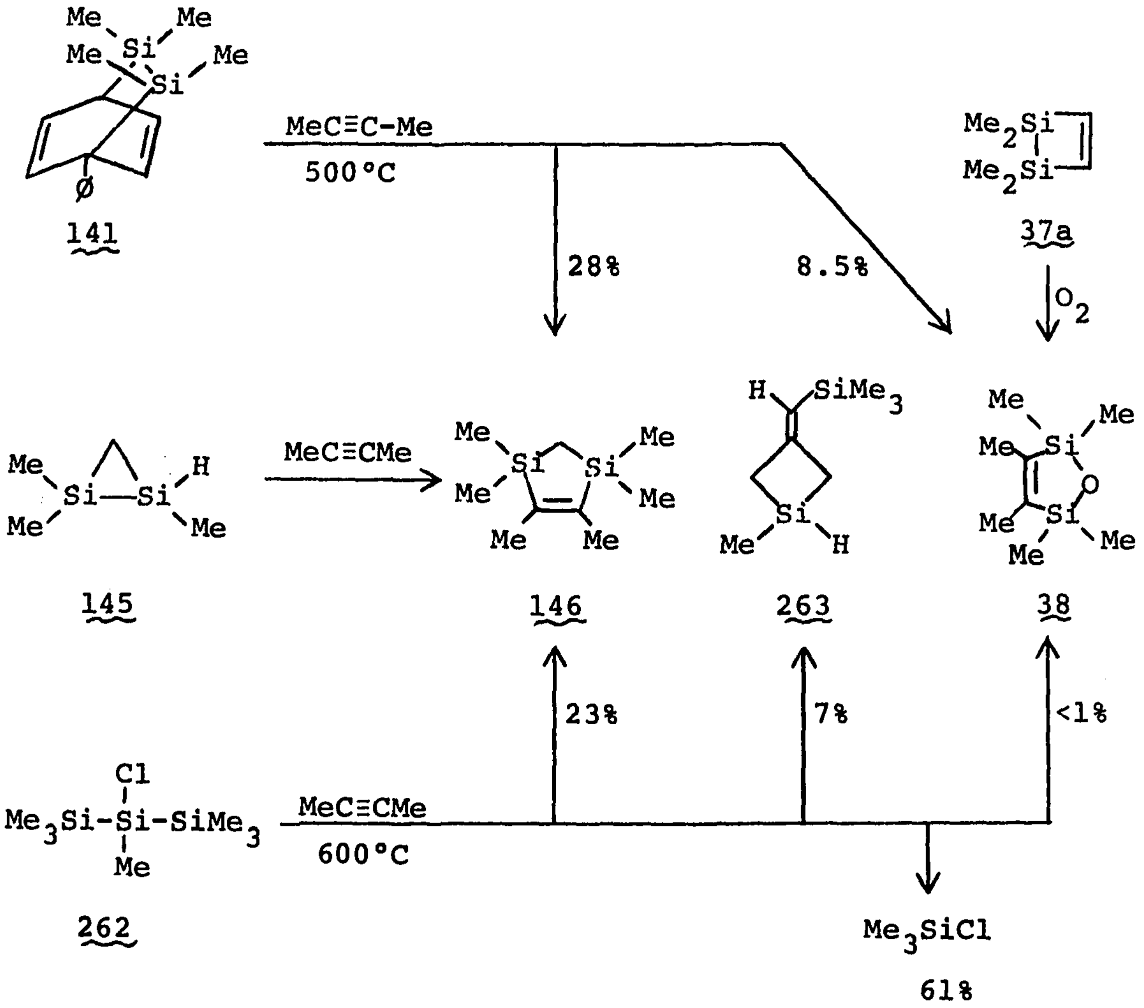


To gain further confirmation that trimethylsilylmethylsilylene 255 does rearrange to tetramethyldisilene 139, the known reactions of 139 with various reactants are compared with the corresponding reactions of 255 generated from 262. Besides the intramolecular rearrangement observed by Roark and Peddle (144), the only known reactions of disilenes are with acetylenes, dienes, and benzaldehyde. Barton and Kilgour (95) have published that the gas-phase reaction of tetramethyldisilene (from 141) and 2-butyne at 500°C gives rise to a 28% yield of 146 and an 8.5% yield of 38 (Scheme 37). They suggested that 146 results from the addition of 2-butyne to the disilacyclopropane 145, an intermediate proposed by Roark and Peddle to account for the intramolecular rearrangement of tetramethyldisilene (Scheme 36). They also suggested that 38 arises from an initial 2+2 cycloaddition of 2-butyne and 139 to give 37a, a molecule which is known to rapidly air oxidize to 38 (28).

The co-pyrolysis of 262 and a 10-fold excess of 2-butyne was carried out by dropping the mixture into a vertical quartz tube that was packed with quartz chips and heated to 600°C. Trimethylchlorosilane and 146 were obtained in 61% and 23% yields, respectively. In addition, a 7% yield of a compound was obtained that is tentatively assigned the structure 263. Compound 263 could also have been formed in the co-pyrolysis of 141 and 2-butyne as it could only be separated from 146 by preparative G.C. with patience.

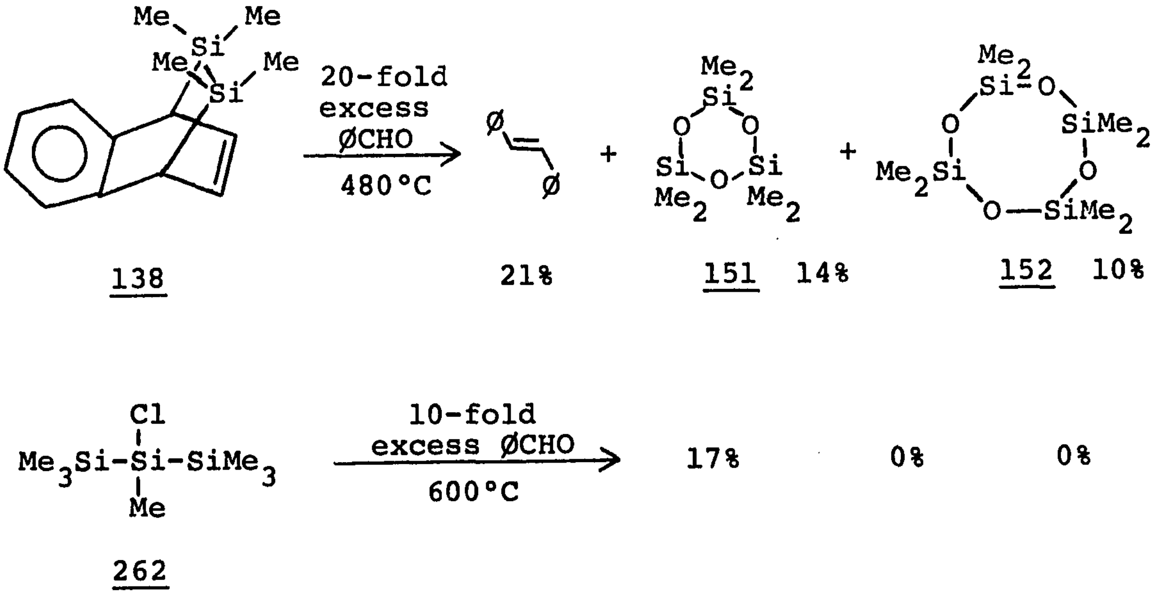
Compound 38 was detected by GCMS, however, the yield is less than 1%. These results are also consistent with initial rearrangement of trimethylsilylmethylsilylene to tetramethyldisilene, but the difference in the yield of 38 from each was disconcerting and prompted a similar comparison with another known reaction of tetramethyldisilene.

Scheme 37

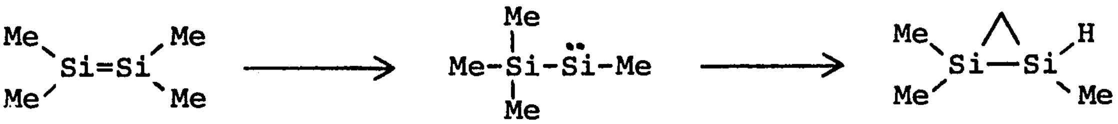


Barton and Kilgour (145) have found that when tetramethyldisilene is generated in the presence of a 20-fold excess of benzaldehyde at 480°C, the products are styrene, hexamethylcyclotrisiloxane 151, and octamethylcyclotetrasiloxane 152 in 21, 14 and 10% yields, respectively (Scheme 38). See the Historical section on disilenes for two possible mechanistic explanations for these products put forth by Barton and Kilgour. When trimethylsilylmethylsilylene is generated from the pyrolysis of 262 at 600°C in the presence of a 10-fold excess of benzaldehyde, a 17% yield of styrene is observed, however, absolutely no 151 or 152 is formed as determined by GCMS and by comparison of the retention times of the products of the pyrolysis with those of 151 and 152 on a 27' x 1/4" 15% SE-30 on Chromsorb W column and on a 12' x 1/4" 20% DC-550 on Chromsorb P column.

Scheme 38



The results of the co-pyrolysis of 262 with 2-butyne and benzaldehyde question whether or not trimethylsilylmethylsilylene 255 does in fact rearrange to tetramethyldisilene 139. A mechanistic alternative that can explain these results is that 139 rearranges to 255 which undergoes an intramolecular carbon-hydrogen insertion to give the disilacyclopropane 145, the key intermediate envoked by Roark and Peddle to account for the rearrangement of 139 to 142 and 143 (Figure 2). That a disilene should prefer to thermodynamically exist as a silylsilylene has recently been predicted from *ab initio* calculations by Snyder for disilene (150). That 139 does isomerize to 255 is demonstrated by the following experiments.



139 255 145

In order to demonstrate that 139 does rearrange to 255, a chemical trap is needed that will trap out 255 from a reaction in which 139 is known to be generated, and at the same time will not intercept 139 before it has a chance to rearrange. Such a trap proved to be a silylhydride. When compound 138 was co-pyrolyzed with trimethylsilane at 630°C, a 17% yield of the trisilane 259 was obtained (Scheme 39).

This is the expected product from the trapping of 255 with Me_3SiH, and thus is evidence for the fact that 139 does indeed rearrange to 255. The co-pyrolysis of 138 with Me_3SiH, however, produced a total of five isomeric compounds, 259 and 264-267, that correspond to adducts of Me_3SiH and 255. The co-pyrolysis of 262 with Me_3SiH at 630°C gave, along with trimethylchlorosilane, the same five isomeric products in almost the same yields. All five compounds were isolated by preparative G.C. on a 12' x 1/4" 20% SE-30 on Chromsorb W column at 67°C where the retention times ranged from 2 1/2 to 3 1/2 hours. Compound 259 was identified by comparison of its IR, NMR and mass spectra with those of an authentic sample. Compounds 265 and 267 were assigned the indicated structures on the basis of their NMR, IR and mass spectra. The spectra for compounds 264 and 266 were difficult to analyze due to either an insufficient amount of sample, possible contamination, or to the complexity of the splitting patterns in the NMR. Compound 264 is tentatively identified as 2,2,5,5-tetramethyl-2,3,5-trisilahexane for the reasons described in the Experimental section.

The formation of 265 in the pyrolysis of 262 and 138 was fortunate since it has served as a basis for an investigation into the immediate fate of the

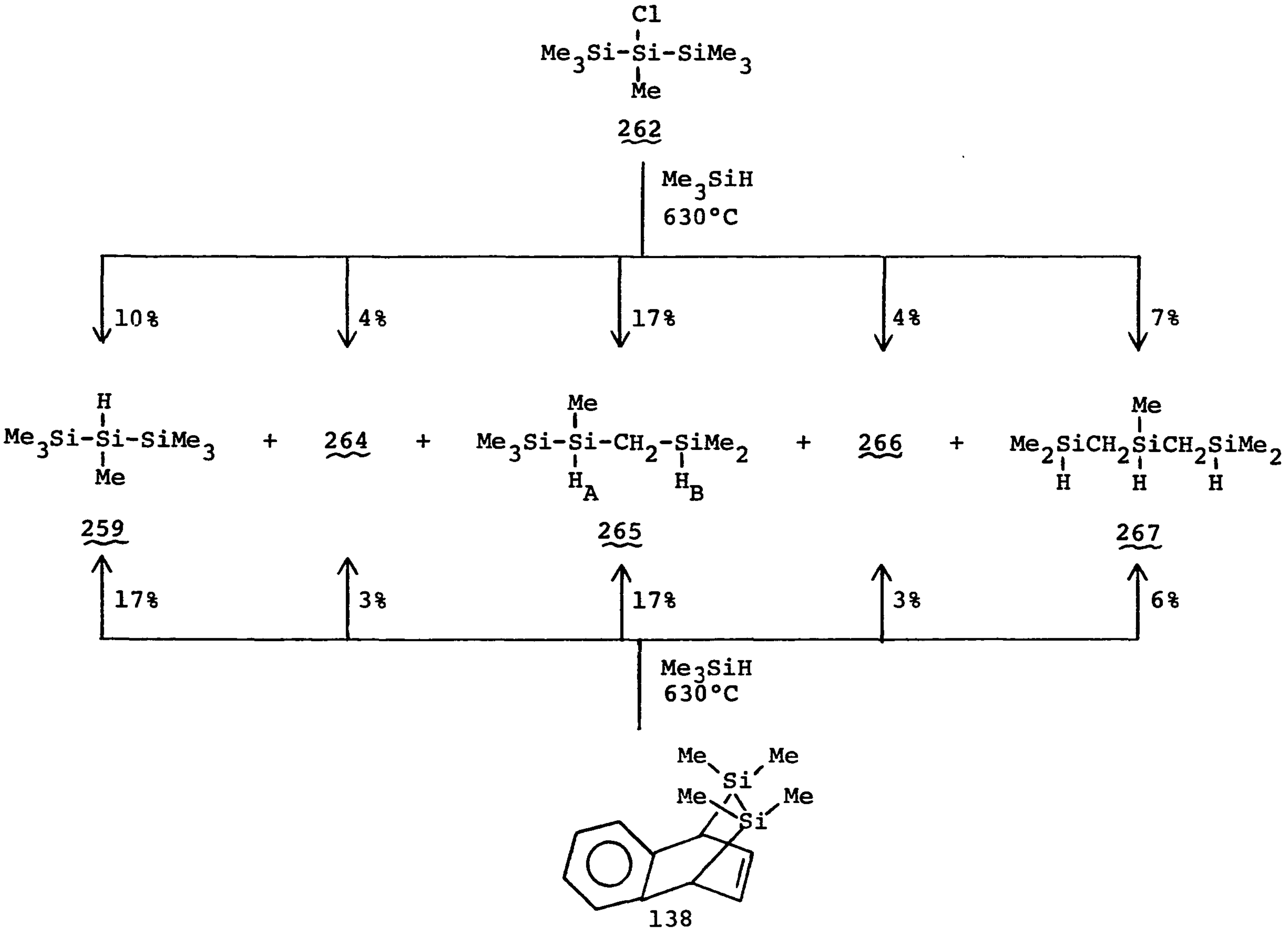
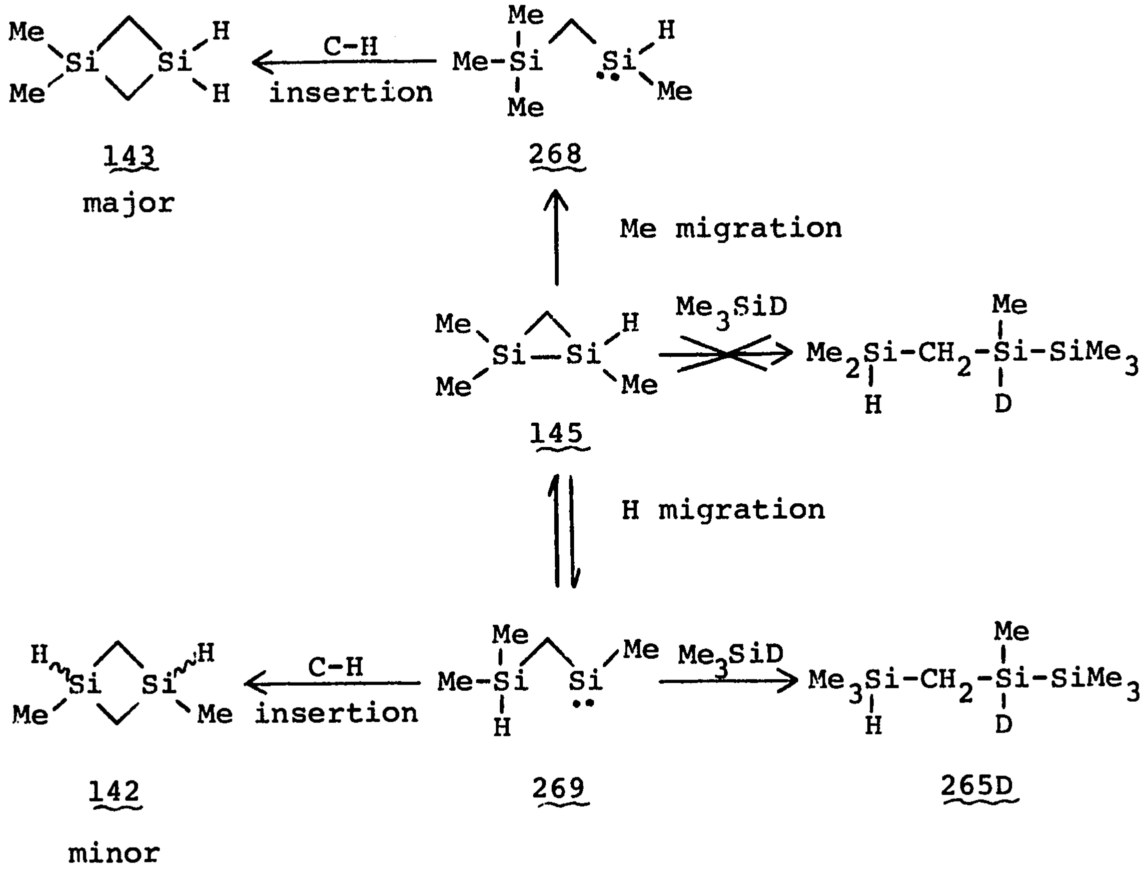


Figure 2. Scheme 39

disilacyclopropane intermediate **145** (Scheme 40). Roark and Peddle (144) proposed that **145** rearranges to **142** and **143** *via* diradical intermediates (Scheme 36). However, since **145** is a disilane it would be reasonable to expect that an alpha elimination of either a methyl or hydrogen might occur, which if followed by carbon-hydrogen insertions could account for **142** and **143**. Although alpha elimination of hydrogen is preferred over methyl, it can be argued that the reason that **143** is the major product is that for silylene **269** insertion into a silicon-hydrogen bond to give **145** should be greatly preferred to the carbon-hydrogen insertion that would result in the formation of **142**.

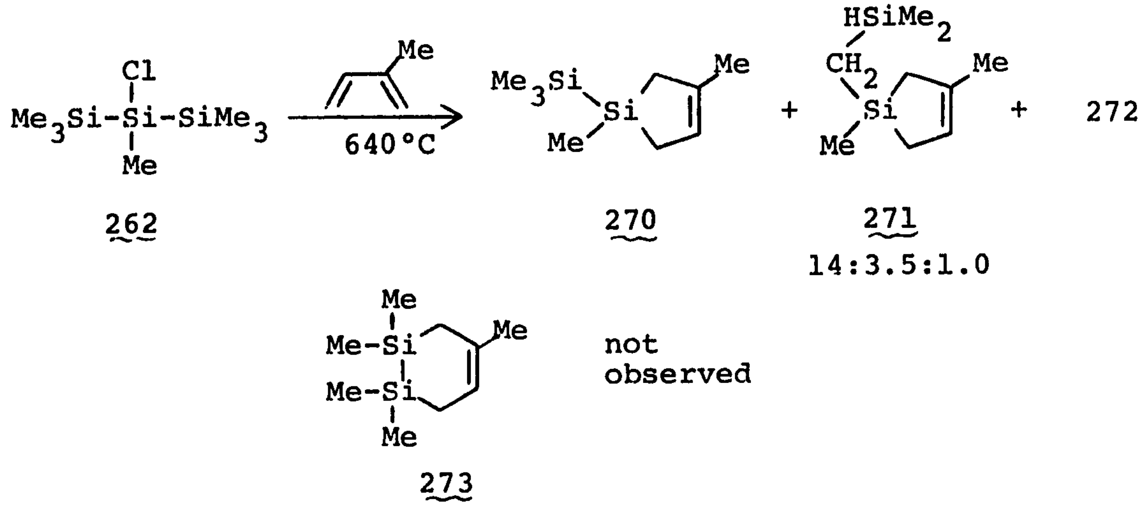
Compound **265** can be accounted for by either trapping of the silylene **269** with Me_3SiH, or by addition of the silicon-hydrogen bond of Me_3SiH to the silicon-silicon bond of **145**. That compound **265** comes from silylene **269** was determined by carrying out the co-pyrolysis of **262** and Me_3SiD and finding that the deuterium is incorporated only at the position H_A. Compound **265D** afforded an NMR spectrum where the silyl hydride sextet of H_A ($\delta = 4.01$, 1:5:10:10:5:1, both J's = $\sim$4.5 Hz) observed for **265** was absent, but the symmetrical nonet for SiH_B remained at $\delta = 4.27$. As required, the silylhydride absorption in the NMR of **259D** was absent. The mechanistic origin of **267** is unclear. It could result from insertion of the silylene **269** into a carbon-hydrogen bond of Me_3SiH; however, in the pyrolysis with Me_3SiD the spectra of 267D indicate random incorporation of two deuteriums among the silicon hydrogens.

Scheme 40



Evidence for the intermediacy of silylene 269 was also obtained from the co-pyrolysis of 262 with a 10-fold excess of isoprene at 640°C (Scheme 41). Three isomeric compounds were obtained that correspond to adducts of isoprene and trimethylsilylmethylsilylene 255. These three compounds, 270-272 were isolated by preparative G.C. on a 10' x 1/4" 20% DC-500 on Chromsorb P column at 120°C. Structural assignments were made for 270 and 271 on the basis of their NMR and mass spectra. They correspond to 1,4-addition of silylenes 255 and 269 to isoprene. A structural assignment was not made for 272; however, its NMR spectra is dissimilar to that published for the tetramethyldisilene adduct of isoprene 273 (95). Thus, no evidence could be obtained in this experiment for crossover from 255 to 139.

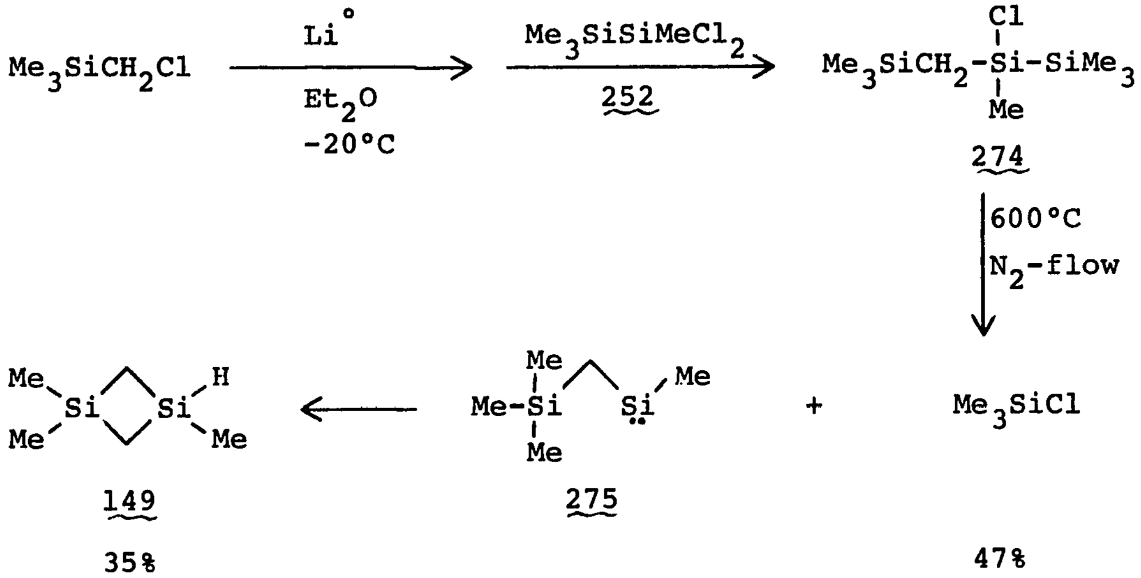
Scheme 41



The alternative mechanism for the rearrangement of the disilacyclopropane **145** to the disilacyclobutanes **142** and **143** that is presented in Scheme 40 requires that an intramolecular silylene insertion into a carbon-hydrogen bond occurs for the silylenes **268** and **269**. Support for these reactions cannot be garnered from the literature. The only reports of silylene insertion into carbon-hydrogen bonds comes from the work of Chernyshev and coworkers; however, the yields for such insertions are quite poor (see Historical section on silylenes).

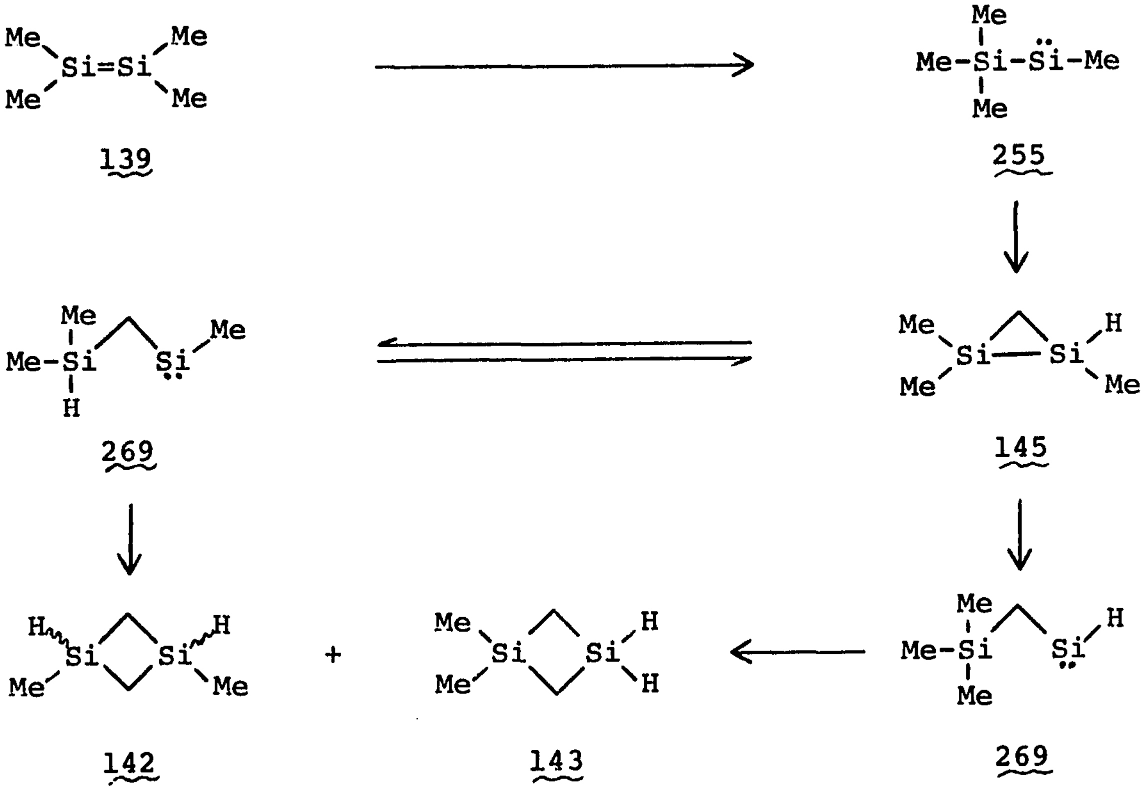
Experiments have been recently performed at Iowa State University by Barton and Goure (222) which demonstrate that, in fact, intramolecular insertions of silylenes into carbon-hydrogen bonds occur quite readily (Scheme 42). They prepared **274** by addition of trimethylsilylmethyl lithium to **252** with the intention that its pyrolysis should result in the formation of trimethylchlorosilane and the silylene **275** *via* an alpha elimination. Pyrolysis of **274** at 600°C resulted in a 39% yield of the trimethyldisilacyclobutane **149**, indicating that insertion into a carbon-hydrogen bond does occur for silylene **275** and thus certainly could occur for silylenes **268** and **269**. The experimental details for the preparation and pyrolysis of **274** are presented in the Experimental section of this thesis.

Scheme 42



This study which began as an investigation of trimethylsilylmethylsilylene 255 has resulted in the acquisition of evidence sufficient to propose a mechanism (Scheme 43) for the rearrangement of tetramethyldisilene 139 to the disilacyclobutanes 142 and 143 that is an alternative to the one originally proposed by Roark and Peddle (Scheme 36). Specifically, when tetramethyldisilene is generated at 600°C in the gas phase in the absence of an added trap it will isomerize to trimethylsilylmethylsilylene 255. The silylene 255 will undergo intramolecular carbon-hydrogen insertion to give the disilacyclopropane 145. Alpha elimination of either a methyl or a hydrogen in 145 then gives rise to the two silylenes 268 and 269 which together can account for the observed products from the rearrangement of 139 *via* intramolecular carbon-hydrogen insertions. The only evidence obtained for the originally sought after isomerization of 255 to 139 was the formation of a trace of 38 when 255 was generated in the presence of 2-butyne. It has recently been observed that bis-(trimethylsilyl)silylene undergoes a similar type of rearrangement (223).

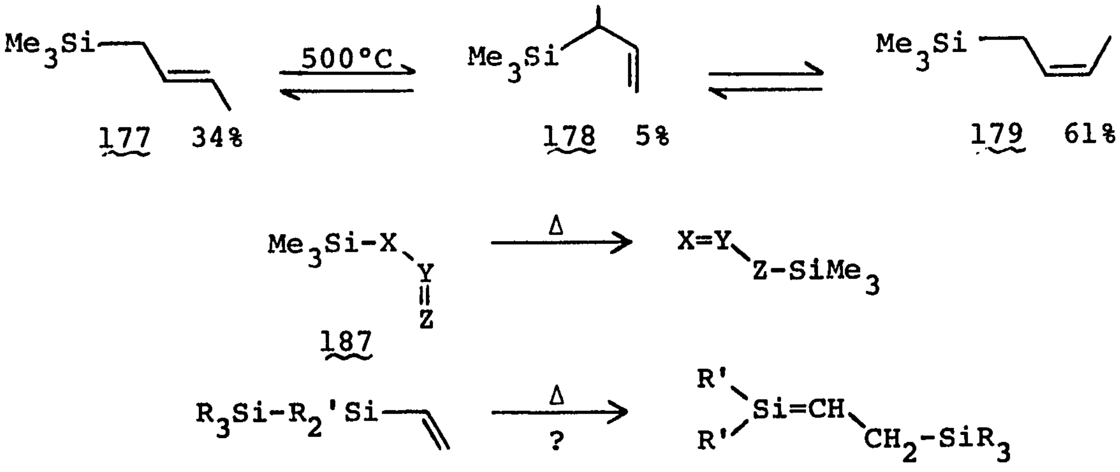
Scheme 43



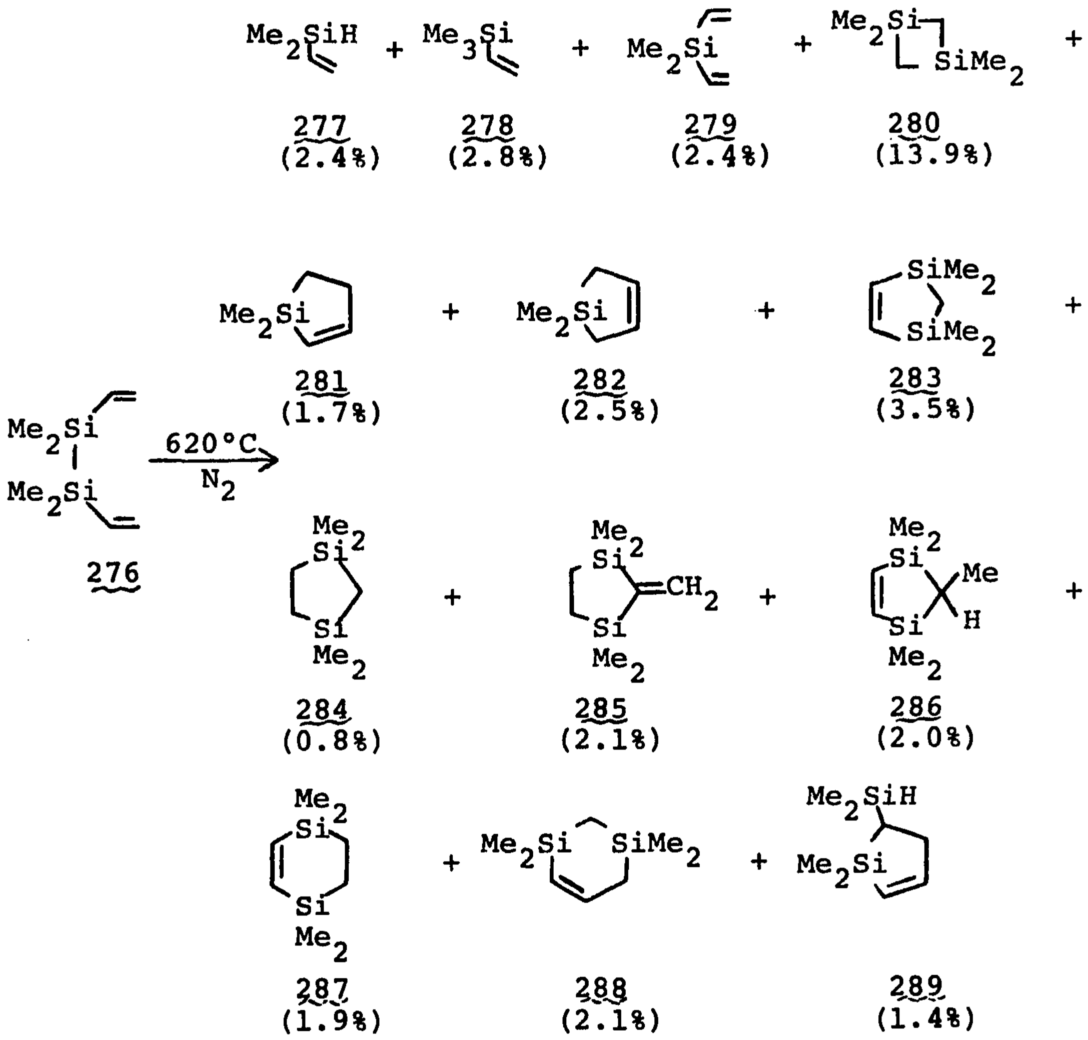
Silene Generation from a Silyl 1,3-Migration

In 1973 Slutsky and Kwart (165) reported that if the allyl silane 177 is heated at 500°C that a 1,3-migration of silicon will occur to give an equilibrium mixture of 177, 178 and 179 (Scheme 44). A large number of examples of 1,3-migrations of silicon are known for heteroallylic silanes where X, Y and Z are a variety of atoms in various combinations (see Historical section for a review of thermal migrations of silicon). In view of these known thermal 1,3-migrations of silicon, an investigation was undertaken to look for the analogous and unknown migration in vinyldisilanes for the reason that such a migration would occur with concomitant formation of a silene. Ishikawa and coworkers have observed that a photo-induced 1,3-migration of silicon in vinyldisilanes does occur to give silenes (123,124).

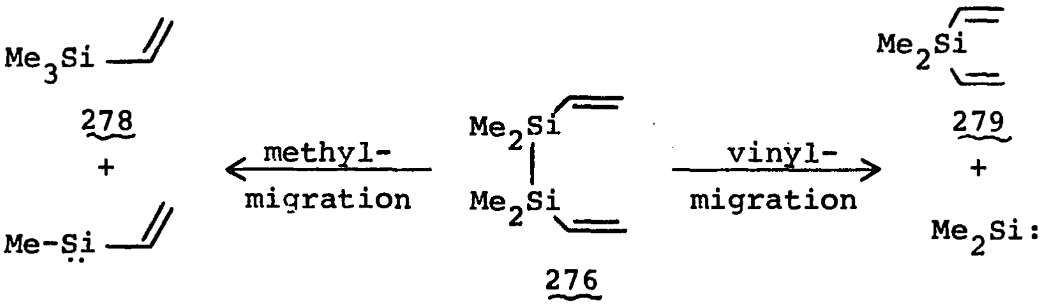
Scheme 44



In order to maximize the possibility of the desired rearrangement, the symmetrical system 1,2-divinyl-1,1,2,2-tetramethyldisilane 276 was chosen. Pyrolysis of 276 was carried out in a vertical nitrogen-flow system at 620°. The reaction produced a complex array of products from which the 13 major compounds 277-289 were isolated by preparative gas chromatography and identified through GCMS, NMR, IR and, when possible, spectral comparison with authentic samples.

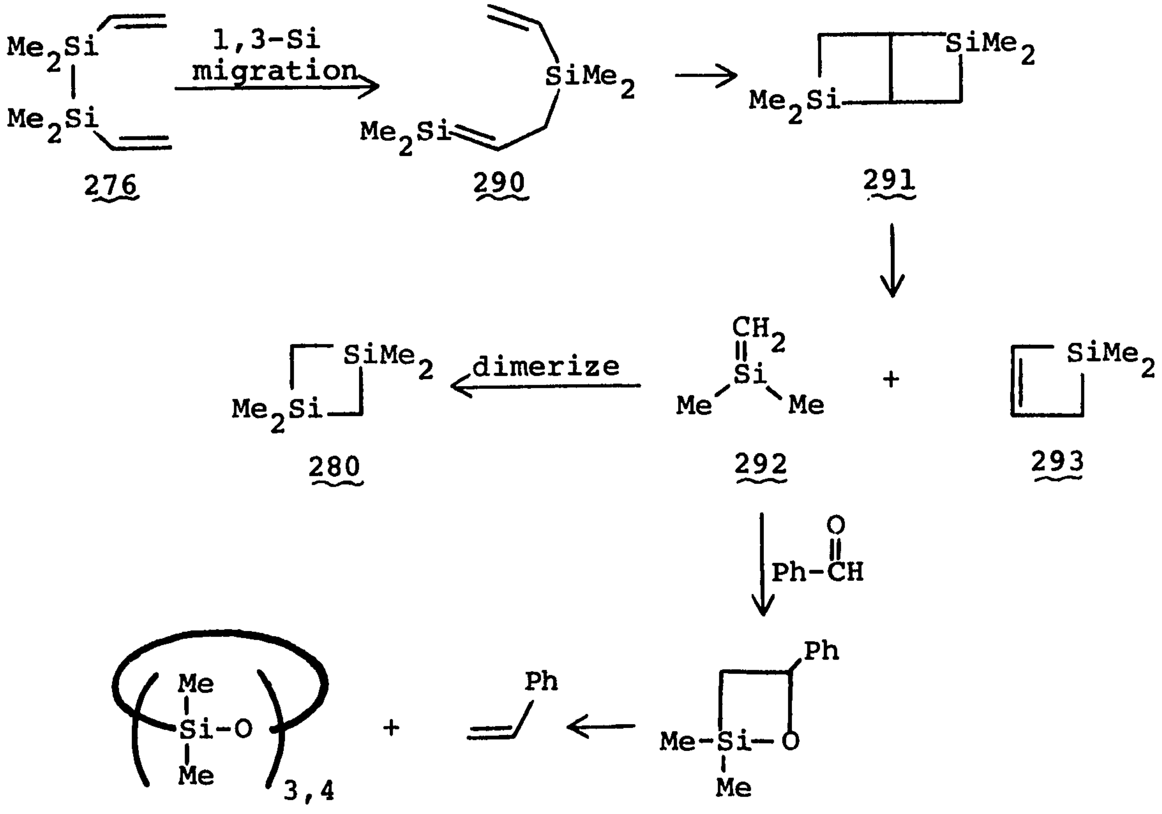


Product 277 likely arises from homolytic cleavage of the Si-Si bond of 276 followed by intermolecular hydrogen abstraction by the dimethylvinylsilyl radical. Products 278 and 279 are also not entirely unexpected as they presumably arise from α-eliminations on silicon to produce methylvinylsilylene and dimethylsilylene.



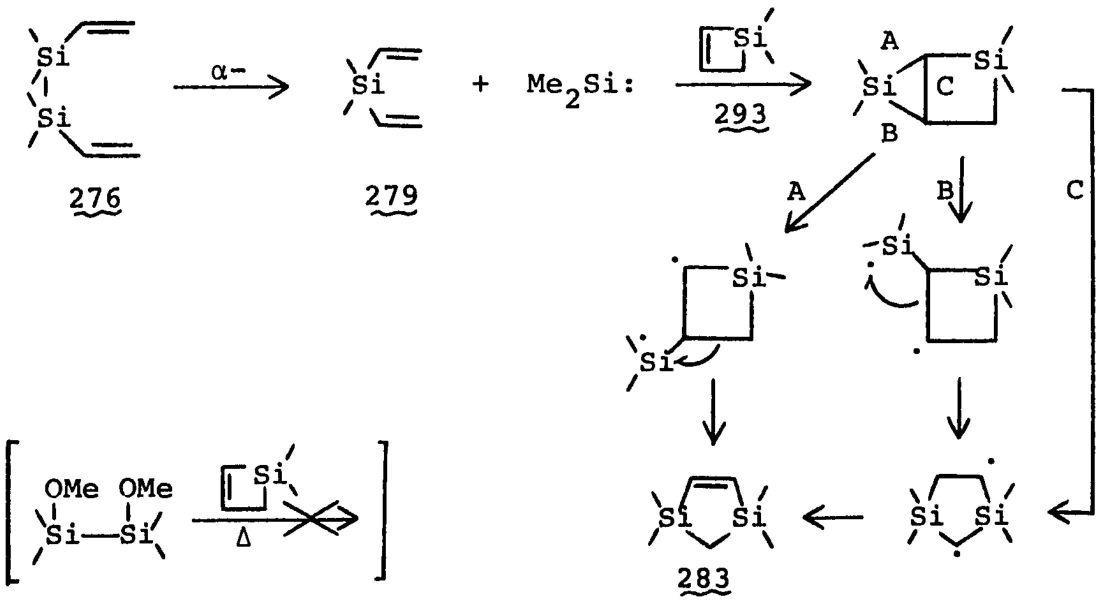
Product 280, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, is usually the major product when 1,1-dimethylsilene 292 is produced under these conditions in the absence of added silene trapping agents (see Historical section on silenes). Its formation is generally accepted as evidence for silene intermediacy in such reactions. Examination of the reaction options of silene 290, the product of a 1,3-silyl shift in 276, suggests a possible source of silene 292. It is well-established that silenes will cycloadd to olefins to form silacyclobutanes although this bimolecular reaction has only been observed as a very minor pathway (113,114). However, intramolecular cyclization of 290 might be expected to be more efficient in the production of 3,3,6,6-tetramethyl-3,6-disilabicyclo[2.2.0]hexane 291. Far more extensively established is the fact that silacyclobutanes undergo thermal cleavage in the gas phase to afford silenes and olefins (224). Thus, 291 should serve as a generator of silene 292, the source of the major product 280 through head-to-tail dimerization.

Silenes are efficiently trapped by aldehydes and ketones (101). This reaction is believed to proceed through an intermediate silaoxetane which suffers thermal cleavage to olefin and silanone ($R_2Si{=}O$), the latter product undergoing cyclic



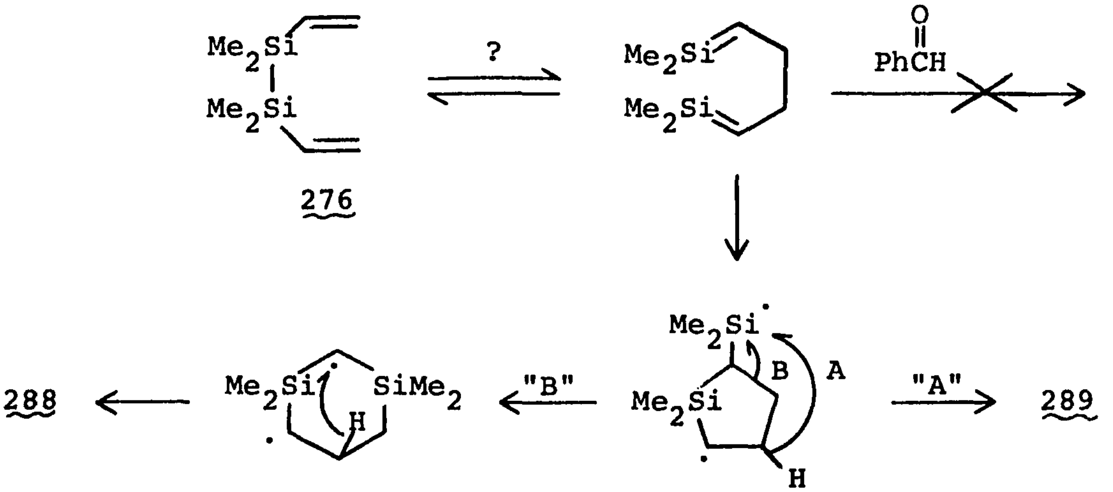
oligomerization. Thus, to probe for the intermediacy of 292 the flow pyrolysis of 276 with a 6-fold excess of benzaldehyde was carried out. Analysis of the resulting product mixture revealed a dramatic decrease in 280 and the appearance of styrene (20.2%), hexamethylcyclotrisiloxane (3.6%), and octamethylcyclotetrasiloxane (4.3%) - the expected products from reaction of benzaldehyde and 292.

A possible origin of 283 is from insertion of dimethylsilylene, produced from the α-elimination of 276 to 279, into silete 283, which was prepared by the method of Block and Revelle (117). Silylene ring expansions of this type are well-precedented for both three- and five-membered rings (see Historical section on silylenes). The ring expansion can take place *via* rupture of any of three bonds in the intermediate silacyclopropane.

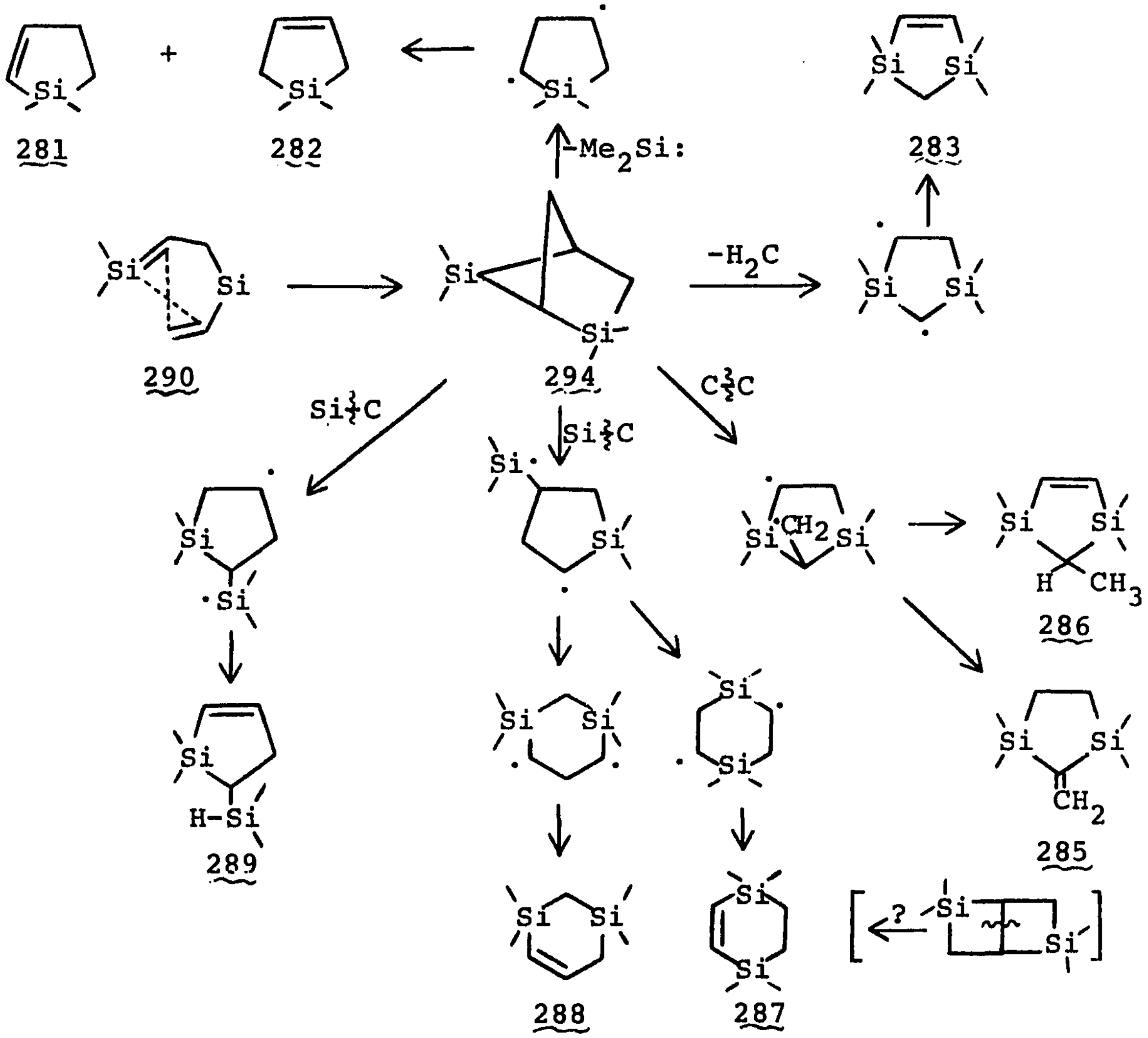


As attractive as this mechanism for the formation of 283 might be, it was found that the co-pyrolysis of the dimethylsilylene generator, 1,2-dimethoxytetramethyldisilane, and silete 293 (3:1) at 615° in a nitrogen flow system produced no 1,3-disilacyclopentene 283. Thus, a more likely route involves an initial 1,3-silyl migration followed by a 2+2 intramolecular cycloaddition to produce disilabicyclo[2.1.1]-hexane 294, methylene extrusion and transannular hydrogen abstraction (vide infra).

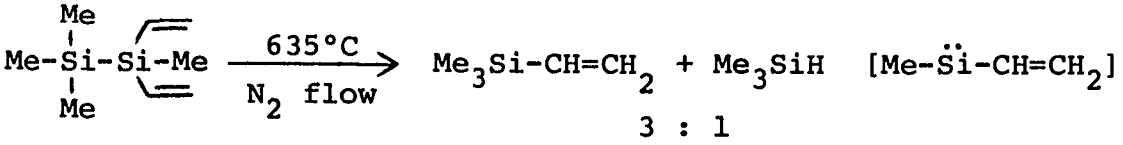
These experiments do not allow for comment on whether or not a reversible Cope rearrangement of 276 is occurring. If indeed this is happening, benzaldehyde is unable to efficiently bleed off the Cope product. However, products 288 and 289 are easily rationalized as originating from an initial Cope rearrangement followed by radical closure and either hydrogen migration (Path A), or ring migration (Path B).



It is not necessary to invoke a Cope rearrangement as the most economical mechanistic rationalization for all of the products of this reaction simply involves 1,3-silyl migration in 276 to form silene 290. Closure to 291 ultimately affords the major product 280, while closure to 294 will produce 281 and 282 from dimethylsilylene extrusion, 283 from methylene extrusion, 285 and 286 from C-C homolysis, and 287, 288 and 289 from Si-C bond rupture.



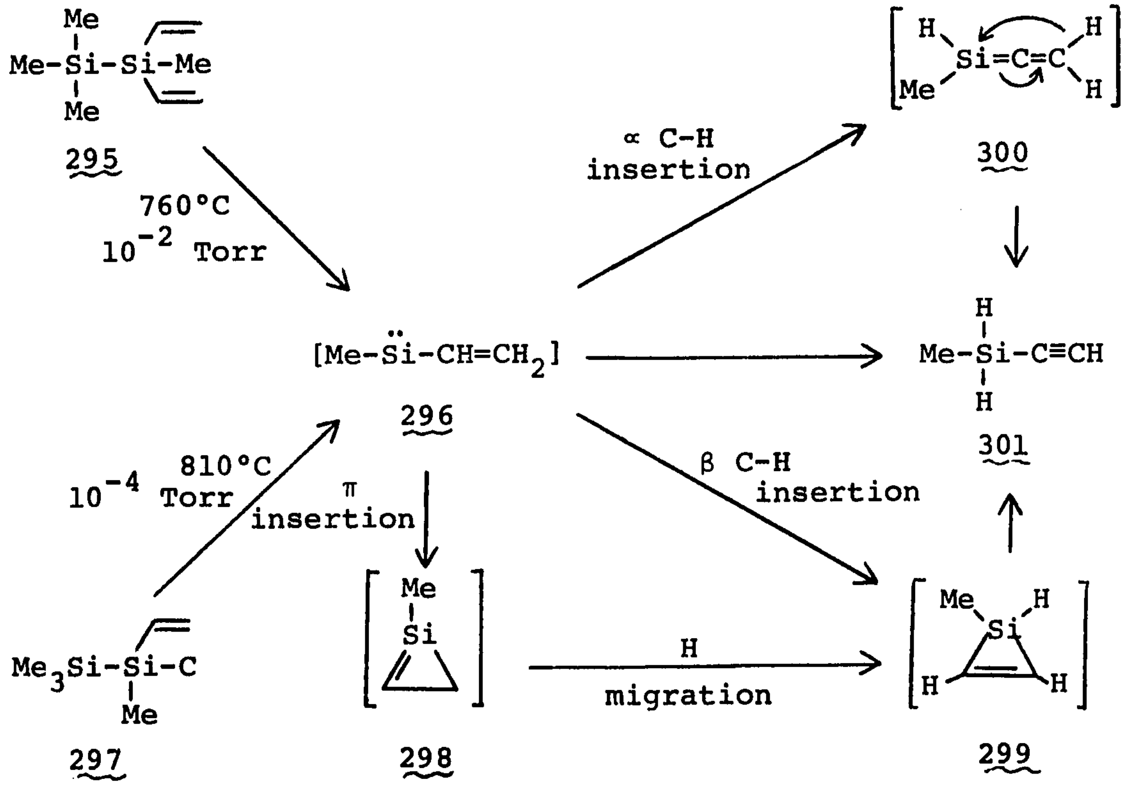
Although it appears that an initial thermal 1,3-migration occurs for 1,2-divinyltetramethyl disilane 276, the events subsequent to 1,3-migration appear to be quite complex. In an attempt to establish generality for the thermal 1,3-migration of silicon in vinyldisilanes, 1,1-divinyltetramethyldisilane 295 was prepared and pyrolyzed. However, when 295 was pyrolyzed by dropping into a vertical quartz tube at 635°C and through which a nitrogen stream was swept, the overwhelmingly predominant products are trimethylsilane and trimethylvinylsilane 278 in a 1:3 ratio. It is thus clear that alpha elimination and not 1,3-migration is the predominant process occurring in the thermolysis of 295. These results led to the conclusion that thermal 1,3-migration of silicon in vinyldisilanes will not be a useful reaction for silene generation.



295 278 ?

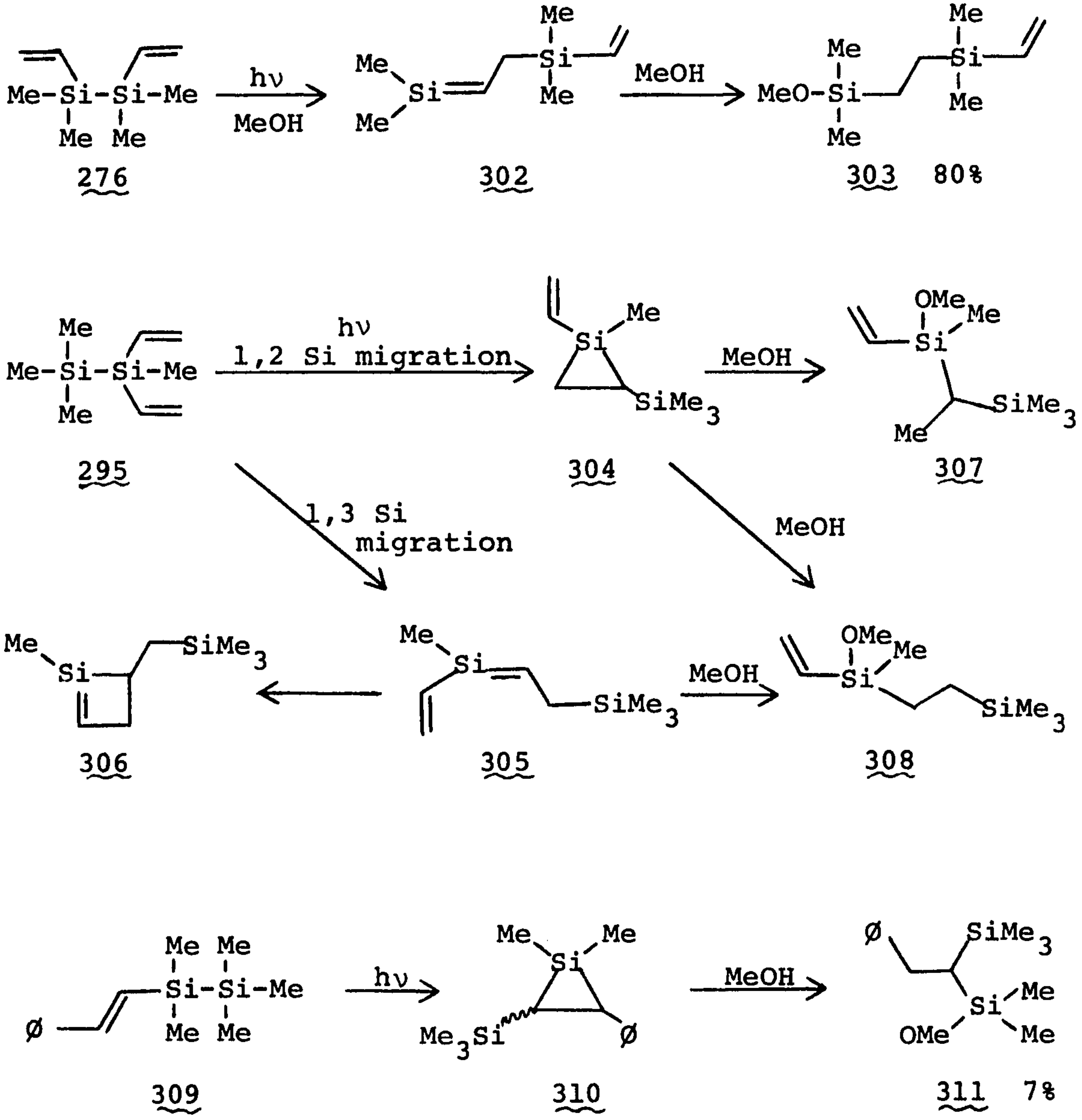
The results from the pyrolysis of 295 also raise a question and that is what happens to the vinylmethylsilylene that should have been generated from the alpha elimination that gave rise to 278. It has very recently been demonstrated by Barton and Goure (163) that vinylmethylsilylene 296, generated by alpha elimination of Me_3SiCl from 297, will isomerize to ethynylmethylsilane 301 (Scheme 45). The mechanistic origin of 301 has not yet been determined. Most likely 301 results from a 1,3-hydrogen migration in 300 or from a 1,2-hydrogen migration in 299. When 295 was pyrolyzed at 760°C and at reduced pressure to maximize intramolecular reactions, the two major products obtained were trimethylsilane and trimethylvinylsilane in a 1:3 ratio. However, the NMR spectrum of the pyrolysate indicates the presence of a trace of 301 based on the NMR of a sample of 301 that was independently synthesized.

Scheme 45



Ishikawa and coworkers (123) have reported that a photo-induced 1,3-migration of silicon will occur in 276 to give the silene 302 which was trapped by methanol in 80% yield to give 303 (Scheme 46). Irradiation of 295 would give the silene 305, which would be of interest because of the possible ring closure to give silene 306. When 295 was photolyzed in the presence of methanol, two products, 307 and 308, were formed in a 2:5 ratio in near quantitative yield as indicated by NMR. Spectral analysis of 307 and 308 eliminated the methanol adduct of 306 as a possibility and instead resulted in the structural assignments indicated. Compound 307 was unexpected and is consistent with the trapping of the silarane 304 with methanol. This corresponds to a 1,2-migration of silicon in 295. Of all the vinyldisilanes studied by Ishikawa and coworkers, only 309 was found to undergo 1,2-migration of silicon and even then as a minor pathway. Compound 308 could result from trapping of either the 1,2-shifted intermediate 304 or the 1,3-shifted intermediate 305.

Scheme 46


276
hν
MeOH
302
MeOH
303 80%
295
hν
1,2 Si migration
304
MeOH
307
1,3 Si migration
MeOH
306
305
MeOH
308
309
hν
310
MeOH
311 7%

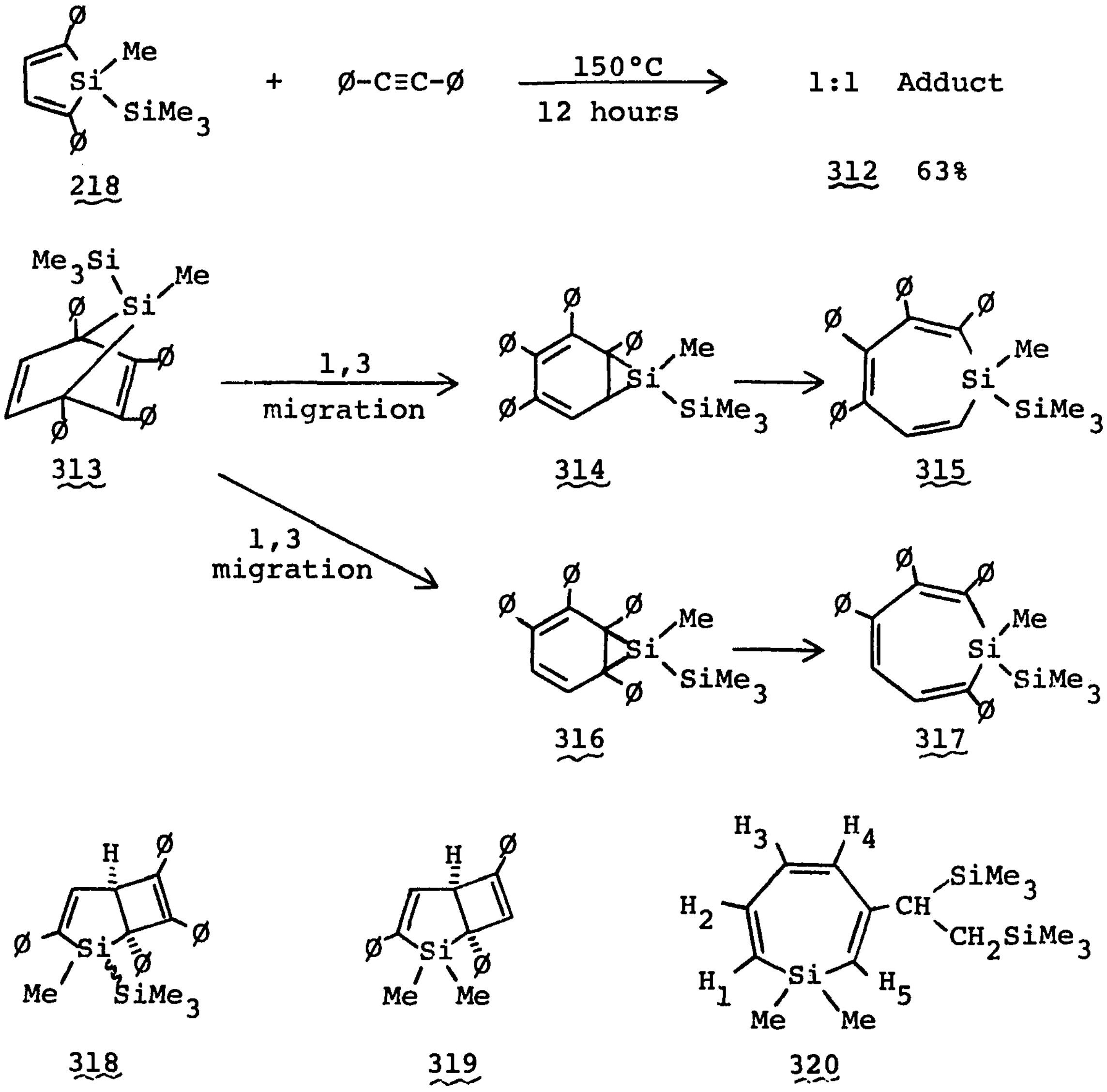
The Structure of the Adduct of 1-Methyl-1-trimethylsilyl-2,5-diphenylsilole 218 and Diphenylacetylene and Some Thermal 1,5-Migrations of Silicon

As mentioned in Part 3 of the Results and Discussion, silole 218 will react with diphenylacetylene at 150°C in 12 hours to give a 1:1 adduct 312 in near quantitative yield as indicated by NMR (Scheme 47). A 63% yield of 312 was obtained after purification by silica gel chromatography and was observed to have the following NMR spectrum: $\delta = -0.07$ (s, 9H), $\delta = 1.01$ (s, 3H), $\delta = 4.67$ (d, 1H, J = 5.6 Hz), $\delta = 6.6 - 7.5$ (m, 20H), $\delta = 7.87$ (d, 1H, J = 5.6 Hz). The NMR spectrum is clearly not consistent with the symmetrical 4+2 cycloadduct 313. Among the structures initially considered for the adduct 312 are the silacycloheptatrienes 315 and 317, as well as the 2+2 cycloadduct 318. Compounds 315 and 317 were considered because of the possibility that the symmetrical adduct 313 could undergo a 1,3-migration of silicon to give the silanorcaradienes 314 and 316 which could open to 315 and 317. Recent evidence has been obtained by Barton and Goure that indicates that migration of silicon can occur in 7-silanorbornadienes (163). However, the coupling constant of 5.6 Hz for the vinyl hydrogens of 312 is not consistent with the expected J values for either 315 or 317. The known compound 320 has coupling constants of

$J_{1,2}$ = 15.1 Hz and $J_{2,3}$ = 2.6 Hz and these values agree closely with those of other known silacycloheptatrienes (225). Structure 318 is inconsistent in that there is a substantial peak in the mass spectrum of 312 due to loss of diphenylacetylene; however, in the mass spectrum of the known compound 319 loss of phenylacetylene is not observed (226). More overriding is the fact that neither of the structures 315, 317 nor 318 are consistent with a silicon-methyl absorption at δ = 1.01. A silicon-methyl absorption this far downfield is extremely rare and is normally only observed for polyhalogenated silanes. Construction of molecular models of 315, 317 and 318 reveals no clear cut reason why the single silicon-methyl should be deshielded to such an extent. The absorption at δ = 1.01 is more consistent with a methyl on carbon than with a methyl on silicon.

A structure can be drawn with the methyl on carbon; however, is requires envoking an unprecedented 1,5-migration of methyl followed by trapping of the resultant intermediate 321 with diphenylacetylene to give 322 (Scheme 48). Despite the unlikelihood of this methyl migration, this hypothesis was tested by heating 237b for 7 days at 150°C with diphenylacetylene. The NMR spectrum of the crude reaction mixture was consistent with a 4:1:8 mixture of 237b, 325 and 326. Product 325 is that expected from the reaction of

Scheme 47

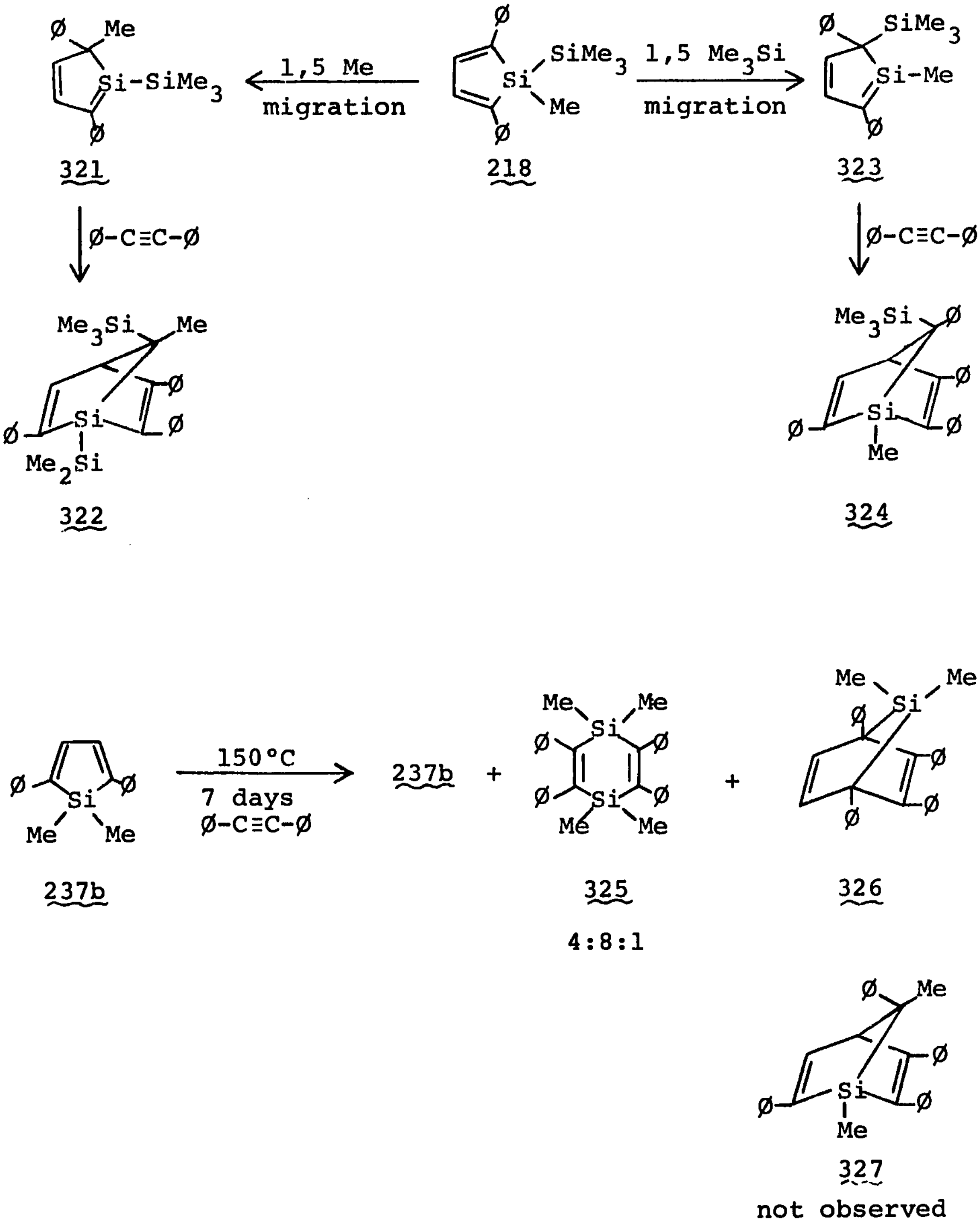

218
Ø–C≡C–Ø
150°C
12 hours
1:1 Adduct
312 63%
313
1,3
migration
314
315
1,3
migration
316
317
318
319
320

dimethylsilylene (extrusion from 326) and diphenylacetylene (see Historical section on silylenes). The NMR spectrum was not consistent with the presence of 327 (methyl on carbon). The unknown compound 326 was isolated as a white solid by extraction with chloroform and crystallization from acetone and identified from its NMR, IR and mass spectra. It is interesting to note that Maruca has reported that 237b and diphenylacetylene react at 60°C to give a yellow 1:1 adduct for which he suggested the structure 326 (227). Shortly thereafter, Clardy and Barton determined by X-ray diffraction that this yellow adduct was not 326 but rather a molecular complex that dissocated upon dissolution (228).

A 1,5-migration of a trimethylsilyl group followed by trapping of the intermediate 323 with diphenylacetylene would result in the formation of the adduce 324. A silicon-methyl absorption of $\delta = 1.01$ for 324 is suspicious even with consideration of the fact that it may be in the deshielding region of the two phenyl groups that flank it on either side. The 1-silanorbornadiene 324 is the most consistent with the spectra of the 1:1 adduct 312; however, at issue is whether an unprecedented 1,5-migration of a trimethylsilyl group from silicon will occur at >100°C with concomitant formation of the silene 323.

A single crystal X-ray determination of the 1:1 adduct 312 was performed by E. V. Arnold and J. Clardy at Cornell

Scheme 48


321
1,5 Me migration
218
1,5 Me3Si migration
323
Ø-C≡C-Ø
322
Ø-C≡C-Ø
324
237b
150°C
7 days
Ø-C≡C-Ø
237b +
325
+
326
4:8:1
327
not observed

University (229). Crystals of 312 belong to the orthorhombic crystal class with $a = 9.509(2)$, $b = 17.394(3)$ and $c = 17.545(3)$ Å. Systematic extinctions indicated the chiral space group $P2_12_12_1$ and density measurements indicated one molecule of $C_{34}H_{34}Si_2$ per asymmetric unit. All unique diffraction maxima within a MoK_α sphere of 0.93 Å were collected and 2074 (96%) were judged observed ($F_o \geq 3\sigma(F_o)$). Solution and refinement were uneventful and the current crystallographic residual is 0.036 for the observed data. Figure 3 is a computer generated drawing of the final X-ray model. These results unambiguously demonstrate that a 1,5-migration of silicon has taken place and that the 1:1 adduct 312 is indeed 324. The bond distances and bond angles for 324 are listed in Table 6 and Table 7, respectively. The distance from the bridgehead silicon to methyl is rather short, 1.855(4), for a carbon-silicon bond, and this may be related to the atypical chemical shift. The NMR spectrum of 324 is consistent with only one isomer and the X-ray data show that this isomer results from approach of diphenylacetylene to the face opposite that of the trimethylsilyl group. The only other synthesis of the 1-silanorbornadiene ring system suffers from excessive length and poor yields (106). When 324 was photolyzed in benzene, two small absorptions (singlets) in the NMR at $\delta = -0.02$ and $\delta = 0.97$ appeared after 45 minutes

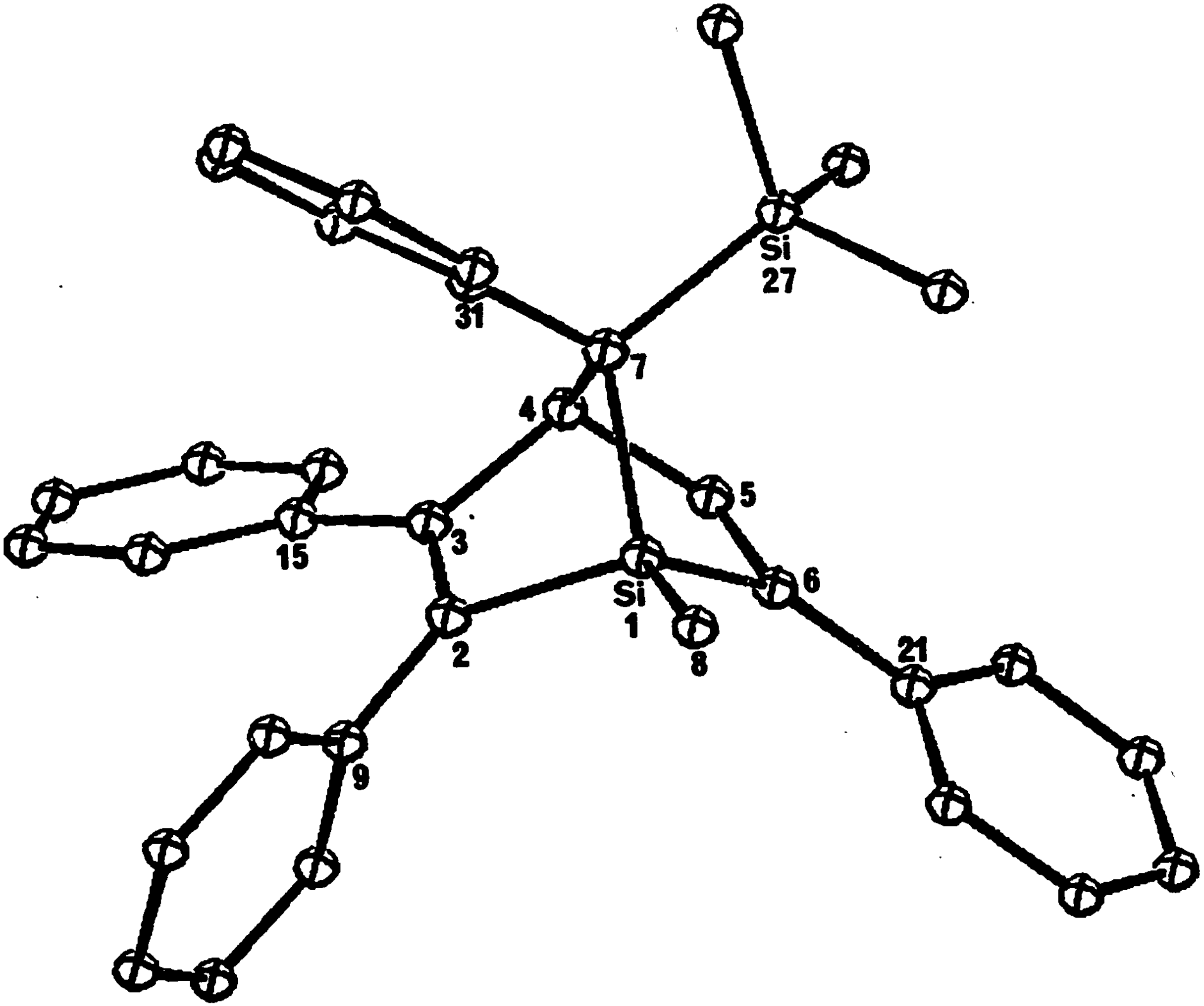


Figure 3. A computer generated drawing of 1-silanorbornadiene 324. Hydrogens are omitted for clarity

Table 6. Bond distances of 324. The standard deviation of the least significant figure of each distance is given in parentheses

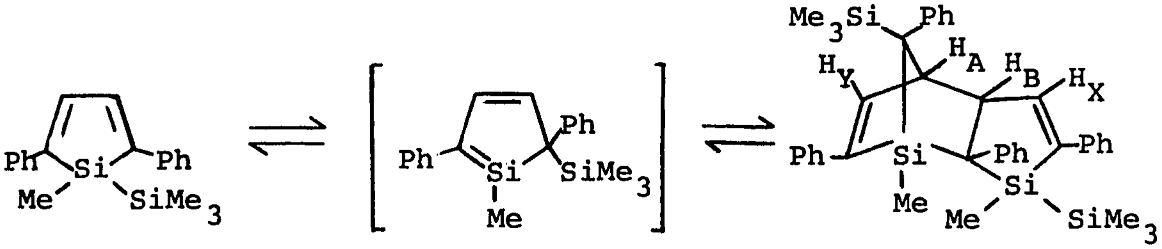
SI 1 - C 2	1.887(3)	C 15 - C 20	1.410(5)
SI 1 - C 6	1.888(3)	C 16 - C 17	1.398(6)
SI 1 - C 7	1.899(3)	C 17 - C 18	1.376(8)
SI 1 - C 8	1.855(4)	C 18 - C 19	1.363(6)
C 2 - C 3	1.338(4)	C 19 - C 20	1.384(5)
C 2 - C 9	1.476(4)	C 21 - C 22	1.376(6)
C 3 - C 4	1.554(4)	C 21 - C 26	1.395(6)
C 3 - C 15	1.478(4)	C 22 - C 23	1.396(6)
C 4 - C 5	1.532(4)	C 23 - C 24	1.359(8)
C 4 - C 7	1.587(3)	C 24 - C 25	1.348(8)
C 5 - C 6	1.326(4)	C 25 - C 26	1.377(7)
C 6 - C 21	1.478(5)	SI27 - C 28	1.860(4)
C 7 - SI27	1.922(2)	SI27 - C 29	1.872(4)
C 7 - C 31	1.512(2)	SI27 - C 30	1.872(3)
C 9 - C 10	1.390(5)	C 31 - C 32	1.404(4)
C 9 - C 14	1.386(5)	C 31 - C 36	1.391(4)
C 10 - C 11	1.400(5)	C 32 - C 33	1.372(5)
C 11 - C 12	1.364(5)	C 33 - C 34	1.386(5)
C 12 - C 13	1.363(5)	C 34 - C 35	1.380(5)
C 13 - C 14	1.398(4)	C 35 - C 36	1.375(5)
C 15 - C 16	1.382(5)		

Table 7. Bond angles of 324. The standard deviation of the least significant figure of each angle is given in parentheses

C 2	- SI 1	- C 6	100.9(1)
C 2	- SI 1	- C 7	91.3(1)
C 2	- SI 1	- C 8	117.9(2)
C 6	- SI 1	- C 7	92.4(1)
C 6	- SI 1	- C 8	121.8(2)
C 7	- SI 1	- C 8	125.6(1)
SI 1	- C 2	- C 3	103.8(2)
SI 1	- C 2	- C 9	129.0(2)
C 3	- C 2	- C 9	127.1(3)
C 2	- C 3	- C 4	112.8(2)
C 2	- C 3	- C 15	128.3(3)
C 4	- C 3	- C 15	118.9(2)
C 3	- C 4	- C 5	108.5(2)
C 3	- C 4	- C 7	105.5(2)
C 5	- C 4	- C 7	105.2(2)
C 4	- C 5	- C 6	116.2(3)
SI 1	- C 6	- C 5	101.4(3)
SI 1	- C 6	- C 21	132.4(2)
C 5	- C 6	- C 21	126.2(3)
SI 1	- C 7	- C 4	87.6(1)
SI 1	- C 7	- SI27	118.6(1)
SI 1	- C 7	- C 31	112.8(2)
C 4	- C 7	- SI27	111.7(2)
C 4	- C 7	- C 31	114.5(1)
SI27	- C 7	- C 31	110.1(2)
C 2	- C 9	- C 10	119.9(3)
C 2	- C 9	- C 14	121.9(3)
C 10	- C 9	- C 14	118.1(3)
C 9	- C 10	- C 11	120.8(3)
C 10	- C 11	- C 12	120.1(3)
C 11	- C 12	- C 13	119.8(3)
C 12	- C 13	- C 14	121.0(3)
C 9	- C 14	- C 13	120.1(3)
C 3	- C 15	- C 16	122.9(3)
C 3	- C 15	- C 20	119.7(3)
C 16	- C 15	- C 20	117.4(3)
C 15	- C 16	- C 17	120.0(4)
C 16	- C 17	- C 18	122.0(4)
C 17	- C 18	- C 19	118.3(4)
C 18	- C 19	- C 20	121.1(4)
C 15	- C 20	- C 19	121.1(3)
C 6	- C 21	- C 22	121.6(3)
C 6	- C 21	- C 26	121.2(3)
C 22	- C 21	- C 26	117.2(3)
C 21	- C 22	- C 23	121.4(4)
C 22	- C 23	- C 24	119.8(5)
C 23	- C 24	- C 25	119.6(4)
C 24	- C 25	- C 26	121.6(5)
C 21	- C 26	- C 25	120.4(4)
C 7	- SI27	- C 28	110.3(1)
C 7	- SI27	- C 29	110.4(1)
C 7	- SI27	- C 30	112.2(1)
C 28	- SI27	- C 29	108.3(2)
C 28	- SI27	- C 30	105.6(2)
C 29	- SI27	- C 30	109.9(2)
C 7	- C 31	- C 32	120.1(2)
C 7	- C 31	- C 36	123.4(2)
C 32	- C 31	- C 36	116.4(2)
C 31	- C 32	- C 33	122.1(3)
C 32	- C 33	- C 34	120.2(3)
C 33	- C 34	- C 35	118.5(3)
C 34	- C 35	- C 36	121.2(3)
C 31	- C 36	- C 35	121.5(3)

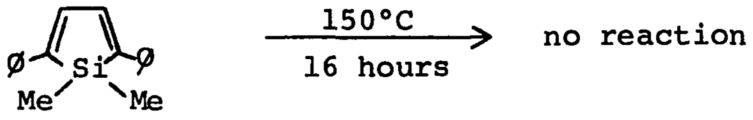
which did not increase with time indicating a possible photo-equilibrium with some other compounds. The photolysis of 324 was not pursued further.

Heating silole 218 in an evacuated, sealed tube at 150° for 9 hours produced a clean mixture of 218 and a white, crystalline product 328 in a 1.1:1.0 ratio, respectively. Product 328 (mp 186.5-188°) was assigned the dimer structure shown on the basis of its spectra: NMR (CCl_4) δ -0.78 (s, 9H, $SiMe_3$), -0.24 (s, 9H, $SiMe_3$), 0.03 (s, SiMe, 3H), 1.18 (s, 3H, SiMe!), 4.02 (t, overlapped d of d, H_B, $J_{AB}=J_{BX}=$ 5 Hz), 4.35 (d of d, H_A, J_{AY}=2.5 Hz, hν at 6.59 collapses to d), 5.90-7.35 (m, 22H, ArH + H_X + H_Y). When 218 is heated for 33 hours at 109°C, the ratio of 218 to 328 is 1.0:1.8.



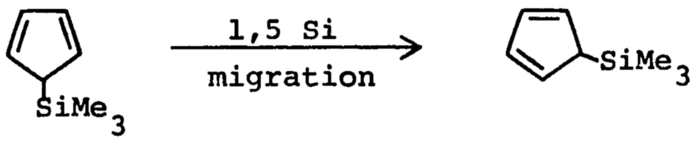
218 323 328

The obvious explanation for the origin of 328 is that silole 218 is undergoing a 1,5-migration of silicon to generate the rearranged silole 323 which, in turn, reacts in a Diels-Alder fashion with starting material 218. Even more important is the observation that heating either 218 or 328 at 150° for any length of time >20 hours produces essentially the same ratio of 218:328. These results quite clearly demonstrate that 218 and 328 are in equilibrium. The steady state concentration of 323 must be quite small since equilibrium of 218 was followed by NMR at 160°C and no absorptions except those for 218 and 328 were observed. That the initial reaction is not simply a Diels-Alder reaction between two molecules of 218, followed by rearrangement, was shown by heating the silole 237b under the same conditions for 16 hours with no change. The diphenylacetylene adduct 324 was found not to be in equilibrium with silole 218 by heating 324 with excess ditolylacetylene for 4 hours at 150°C and observing no acetylene exchange.

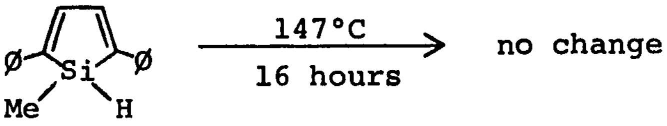


237b

This thermal 1,5-migration of silicon from silicon to carbon has not been previously observed, and in fact very few 1,5-migrations of silicon of any type are known (see Historical section on thermal migrations of silicon). In linear systems the only known 1,5-migrations of silicon are from oxygen to oxygen in silylacetylacetonates. In cyclic systems, 1,5-migrations are known for cyclopentadienylsilanes and for compounds in which silicon is bonded to various nitrogen analogs of cyclopentadiene such as pyroles, imidazoles, and triazoles. Ashe was able to show that the temperature dependence of the NMR spectrum of trimethylsilylcyclopentadiene 192 was due to 1,5-migration of silicon (192). He found that the hydrogen also migrates but at a rate 10^6 times slower than silicon. The same relative migratory aptitude was observed for siloles since it was observed that 237a could be heated at 147°C for 16 hours with no change, and in particular with no formation of a dimer analogous to 328.



192

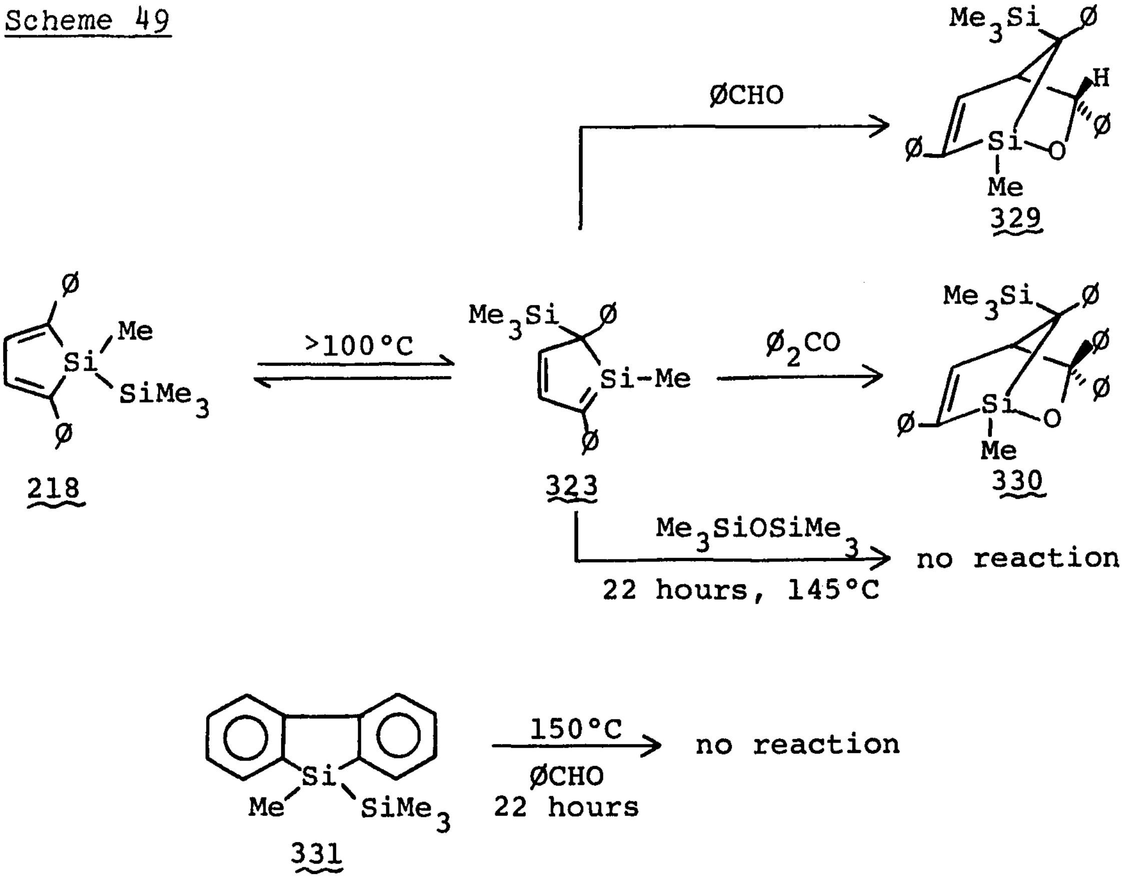


237a

The fact that a solution of silole 218 at temperatures greater than 100°C contains an equilibrium concentration of the silene 323 can be very valuable in the investigation of the chemical behavior of silenes (Scheme 49). Such a solution can effectively be an equivalent to having an isolable silene. Any added reagent will always have a molecule of silene to react with because it will not have to compete with silene dimerization. This should result in higher yields in trapping reactions and allow for study of the reactions of silenes with reagents that cannot normally compete with silene dimerization.

Since the carbonyl group is well known to be an excellent trap for the silicon-carbon double bond (see Historical section on silenes), silole 218 was heated at 150°C for 7-10 hours with equimolar quantities of benzaldehyde and benzophenone and in each case the corresponding adducts 329 and 330 were obtained in quantitative yields as indicated by NMR (Scheme 49). As in the case with the diphenylacetylene adduct 324, the NMR is consistent with the formation of only one isomer of each of the adducts 329 and 330. Both of these adducts proved to be sensitive to silica gel and attempted crystallization of 329 resulted only in oil formation. Adduct 330 was obtained in a 61% yield from a single crystallization from hexane as a white solid (m.p. 188-189.5°C) that was fully characterized by its NMR, IR and mass spectra. While 329 and 330 formally represent a 1,4-addition of the carbonyl group to 323, it is possible that they result from an initial 1,2-addition to the silicon-carbon double bond in 323 followed by rearrangement. A similar mechanistic dilemma exists in the work of Valkovich and Weber (121,134). An initial 1,5-migration of silicon did not occur for the trimethylsilyldibenzosilole 331 as indicated by the lack of reaction when heated with benzaldehyde at 150°C for 22 hours presumably because the 1,5-migration of silicon would occur at the expense of the resonance energy of at least one of the aromatic rings. Hexamethylcyclotrisiloxane is the only compound known to react with a silene *via* insertion into a silicon-oxygen single bond (135). Hexamethyldisiloxane, however, would not react with 218 when heated to 145°C for 22 hours.

Scheme 49



In view of the known behavior of trimethylsilylcyclopentadiene (191), the obvious question can be asked that after the first 1,5-migration of silicon occurs to give the intermediate **323**, does the silicon undergo a second 1,5-migration in the same direction to give the silene **323** (Scheme 50). It is possible that this is occurring, but has remained undetected since all of the trapping reactions described to this point involve 1,4-cycloadditions. A 1,4-addition to silene **332** gives an adduct that contains a silicon-carbon double bond, and, thus, is expected to be less favorable. To detect the presence of **332**, a trap is needed which is known to undergo 1,2-addition to silenes and such a reagent is an alcohol (see Historical section on silenes).

When **218** was heated with a 12-fold excess of methanol in benzene at 146°C for 3 hours, a 1.2:1.0 mixture of **333** and **334** was obtained (Scheme 50). Both adducts resisted repeated attempts at crystallization; however, separation was affected by HPLC (C-18 μ-Bondapak, 85% $MeOH/H_2O$). The structures of **333** and **334** were assigned on the basis of their NMR, IR and mass spectra, and on the spectra of the deuteroanalogs obtained from the reaction of MeOD and **218**.

These adducts quite clearly do not result from the trapping of **332**, but rather from 1,2- and 1,4-addition to **323**. It is still possible that a second 1,5-migration does occur, and that in this case methanol intercepts **323** before this can happen. The most striking observation is that the NMR spectra are consistent with the formation of only one diastereomer of 333 and 334. This corresponds to addition of methanol to only one face of 323. The high stereoselectivity of all of the trapping reactions of 323 is not expected from the differences in the steric bulk of trimethylsilyl group and the phenyl group. In addition, the ratio of 333:334 changes to 2.4:1.0 when a 125-fold excess of methanol is used. Table 8 lists the ratios of 333:334 obtained at various methanol concentrations. The reaction with methanol was followed by NMR and it was observed that 333 and 334 grow simultaneously. A 1.2:1.0 mixture of 333 and 334 was heated with methanol under conditions where a 2.4:1.0 ratio is obtained, and no interconversion of 333 and 334 was observed.

Scheme 50

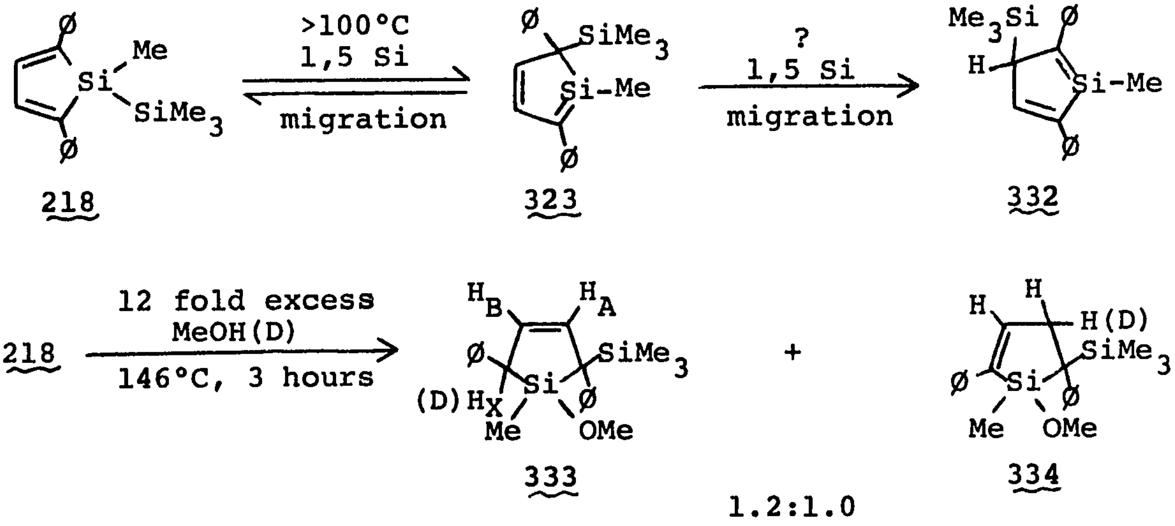


Table 8. Reactions of methanol with 2 ml of a benzene solution containing 0.281 mmoles of 218 at 145°C

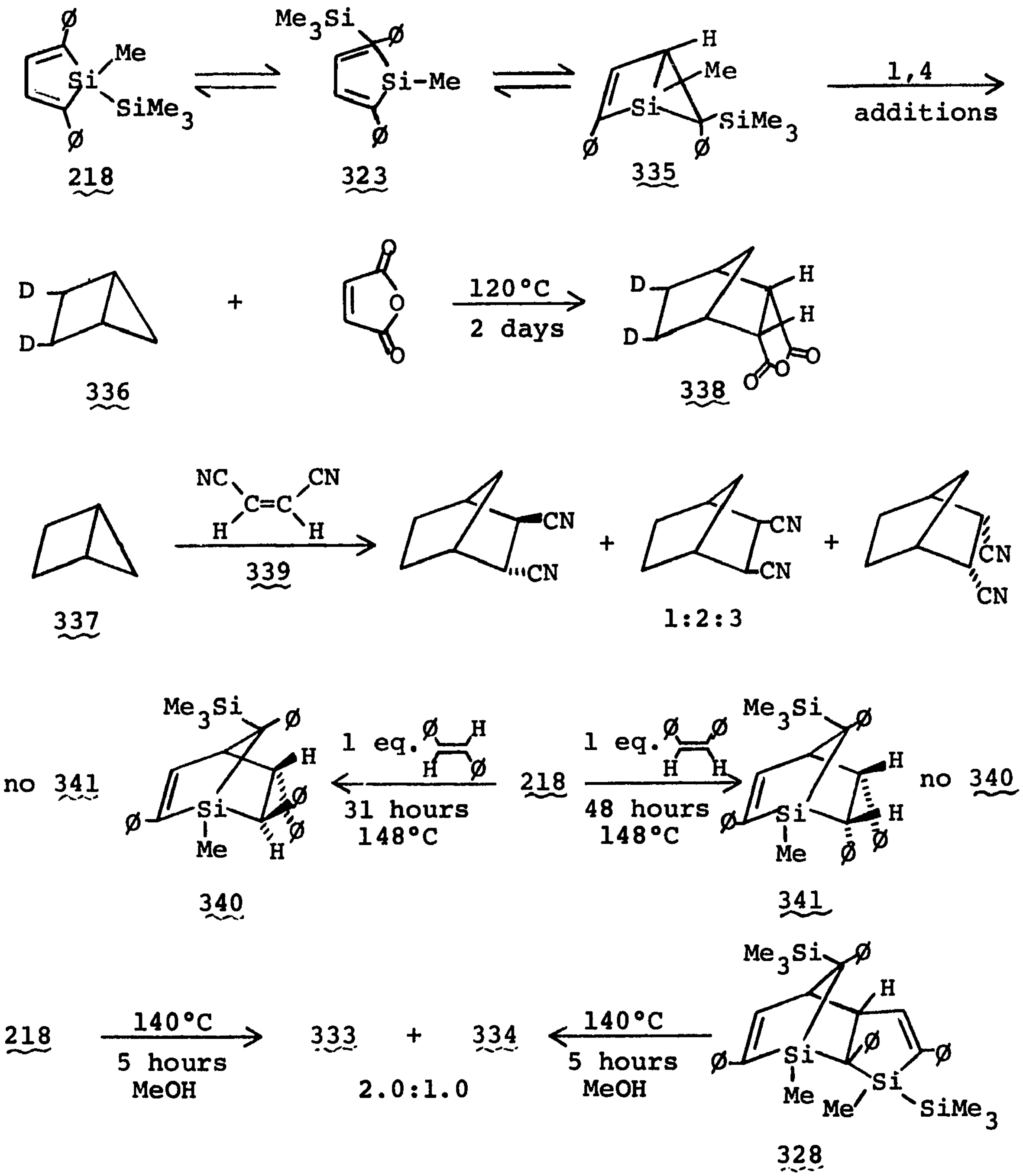
Equivalents of MeOH	Mole Ratio 333:334
1	2.6
5	1.3
8	1.25
12	1.2
25	1.5
125	2.4

These results can be explained by the presence of a second intermediate (Scheme 51). The 1-silabicyclopentene 335 is an attractive possibility because it can explain the high stereoselectivity of the 1,4-additions if upon ring closure 323 folds in only one way and if the trapping reagents approach and react with 335 from only one side.

High stereoselectivity was observed by Gassman for addition of olefins and acetylenes to the bridging bond in bicyclopentanes (230). Maleic anhydride was found to approach and react with bicyclopentane from only one side, and surprisingly this was found to be from the endo side as determined by the reaction with the labeled compound **336**. In addition, Gassman found that the reaction is nonconcerted and involves a diradical intermediate as evidenced by the lack of stereochemical retention in the reaction of *cis*-dicyanoethylene with **337**. To investigate the possibility of a nonconcerted mechanism for the additions to either **323** or **335**, silole **218** was heated for 2 days at 148°C with one equivalent of *cis*-stilbene. The NMR spectrum of the reaction mixture indicated a near quantitative formation of only one isomer of the adduct **341**. This adduct was isolated (69%) by chromatography on silica gel to give a white solid (m.p. 117.5-119°C) that was assigned the structure **341** on the basis of its spectra. The NMR spectrum, (CCl_4) $\delta = -0.11$ (s, 9H), $\delta = 0.85$ (s, 3H), $\delta = 3.01$ (d, H_A, $J_{AB} = 11$ Hz, collapses to singlet upon hν at 7.5), $\delta = 4.17$ (m, H_B and H_C, simultaneous irradiation at 3.01 and 7.50 produces an AB quartet, $J_{BC} = 3.5$ Hz), $\delta = 6.39$-7.57 (m, 21H, ArH + d at 7.5, H_X, $J_{CX} = 5$ Hz, collapses to a singlet upon hν at 4.25) is consistent with retention of stereochemistry since the coupling constant ($J = 11$ Hz) for the olefin derived hydrogens is close to that expected for an exo-*cis*-relationship (231). Similar results were obtained for the analogous reaction with *trans*-stilbene. The beta silyl hydrogen of adduct **340** (d, J = 7 Hz) is shifted 0.40 ppm with respect to the same hydrogen of adduct **341**. Within the limits of detection by NMR, it was found that no *trans*-adduct **340** was formed in the reaction with *cis*-stilbene and that no *cis*-adduct **341** was formed in the reaction with *trans*-stilbene. Since the stereochemistry was retained, no comment can be made concerning the concertedness of the addition. The time required for reaction with *cis*-stilbene reflects the fact that the reaction of a silene and an olefin is poorly precedented and requires very high concentrations of olefins to be competitive with silene dimerization (see Historical section on silenes).

A second intermediate can also explain the dependence on methanol concentration if two opposing factors are operative. These are that reaction of **335** is of higher order in methanol than is the reaction with **323** and that due to increasing methanol concentration, a smaller fraction of **323** closes to **335**. Confirmation of this was sought (assuming that **328** undergoes a retrograde Diels-Alder reaction to give **335** and **218**) by heating **218** and **328** in pure methanol under similar conditions. The assumption must be incorrect since both gave **333** and **334** in the same relative amounts.

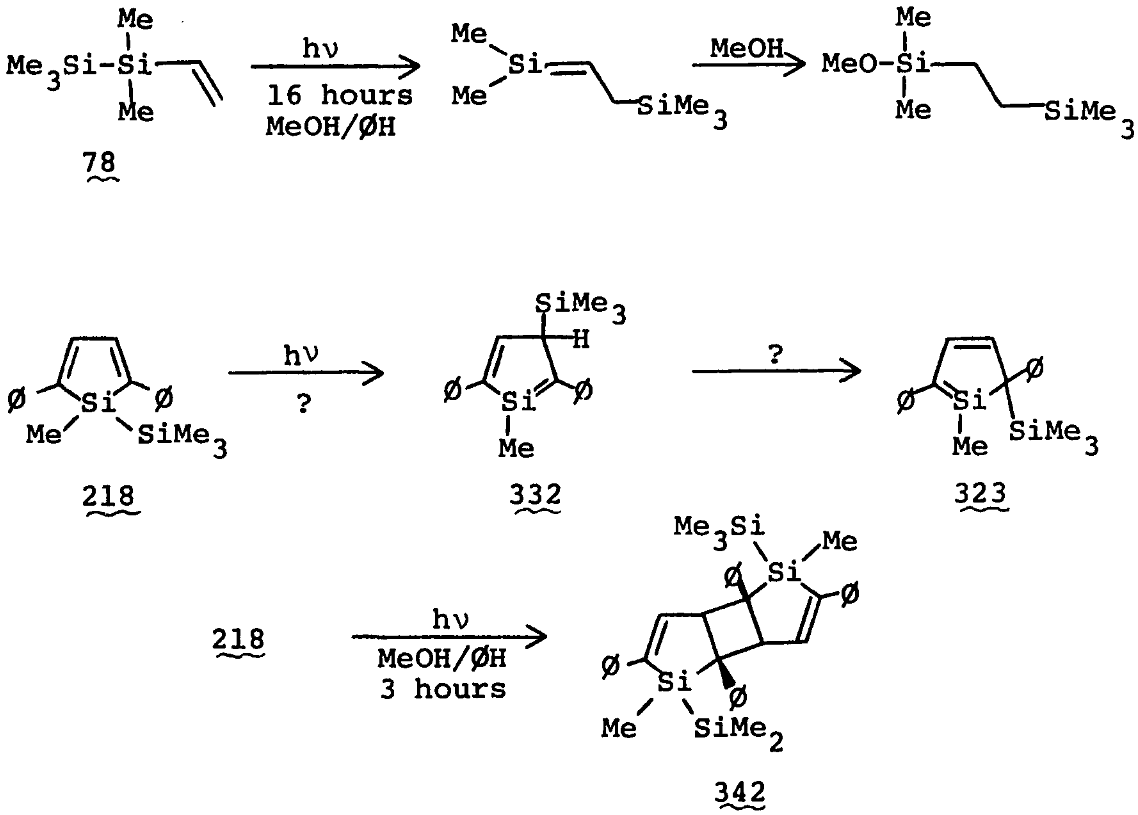
Scheme 51


Ø
Me
Si
SiMe$_3$
Ø
218
Me$_3$Si
Ø
Si-Me
Ø
323
H
Me
Si
SiMe$_3$
Ø
Ø
335
1,4
additions
D
D
336
+
O
O
O
120°C
2 days
D
D
H
H
O
O
O
338
NC
CN
C=C
H
H
339
337
CN
CN
+
CN
CN
+
CN
CN
1:2:3
no 341
Me$_3$Si
Ø
H
Ø
Ø
Ø
Si
Me
H
340
1 eq.
Ø
H
H
Ø
31 hours
148°C
218
1 eq.
Ø
Ø
H
H
48 hours
148°C
Me$_3$Si
Ø
H
H
Ø
Si
Me
Ø
Ø
341
no 340
218
140°C
5 hours
MeOH
333
+
334
2.0:1.0
140°C
5 hours
MeOH
Me$_3$Si
Ø
H
Ø
Ø
Si
Me
Si
Me
SiMe$_3$
Ø
328

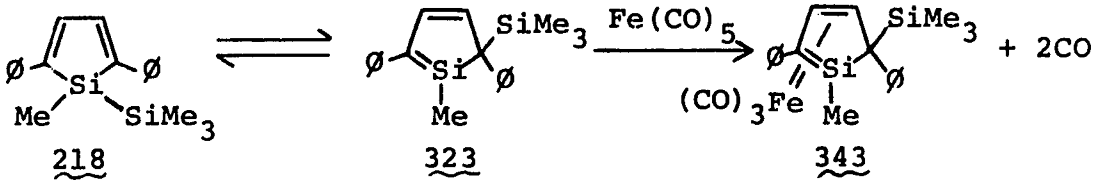
In looking for the continued migration of silicon around the ring in **218**, it was found that trapping with methanol gave adducts that corresponded to trapping of the initial 1,5-shifted intermediate **323**. If the intermediate from the second 1,5-shift, **332**, could be generated directly, then at least the reverse of the second 1,5-migration could be demonstrated if the silene **323** could be trapped (Scheme 52). According to the work of Ishikawa and coworkers (123), **332** should be generated directly from the photolysis of **218**. They found that irradiation of the vinyl disilane **78** over a period of 16 hours resulted in a 1,3-migration of silicon as indicated by trapping of the resultant silene with methanol. However, the only product (major) identified from the photolysis of **218** in methanol and benzene was **342**, the 2+2 dimer of **218**. This is not an entirely unexpected result since Barton and Nelson have found that 1,1-dimethyl-2,5-diphenylsilole will rapidly photodimerize to the analogous 2+2 cyclodimer (232). In very dilute solutions of **218** and methanol in benzene and cyclohexane, only polymeric material was obtained upon photolysis.

It would be of interest to trap the silene **323** with iron pentacarbonyl since there exists only one report in

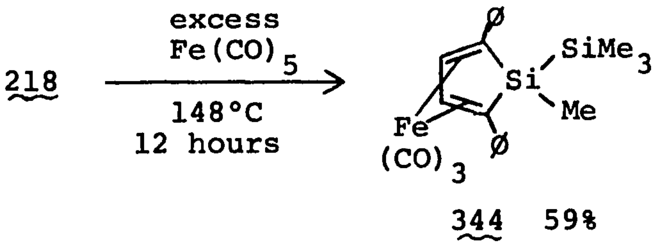
Scheme 52



the literature of a transition metal complex of a silene (108). When 218 was heated with excess Fe(CO)$_5$ at 148°C for 12 hours, the siladiene complex 343 was not obtained. Instead an adduct was obtained that was isolated (69%) by chromatography on silica gel as a red solid (m.p. 128.5-129.5°C) and, on the basis of its spectra, assigned to the structure of the iron tricarbonyl diene complex of the unrearranged silole 218. Stereochemical assignment was made on the basis of assignments made for similar complexes by Sakurai (233).



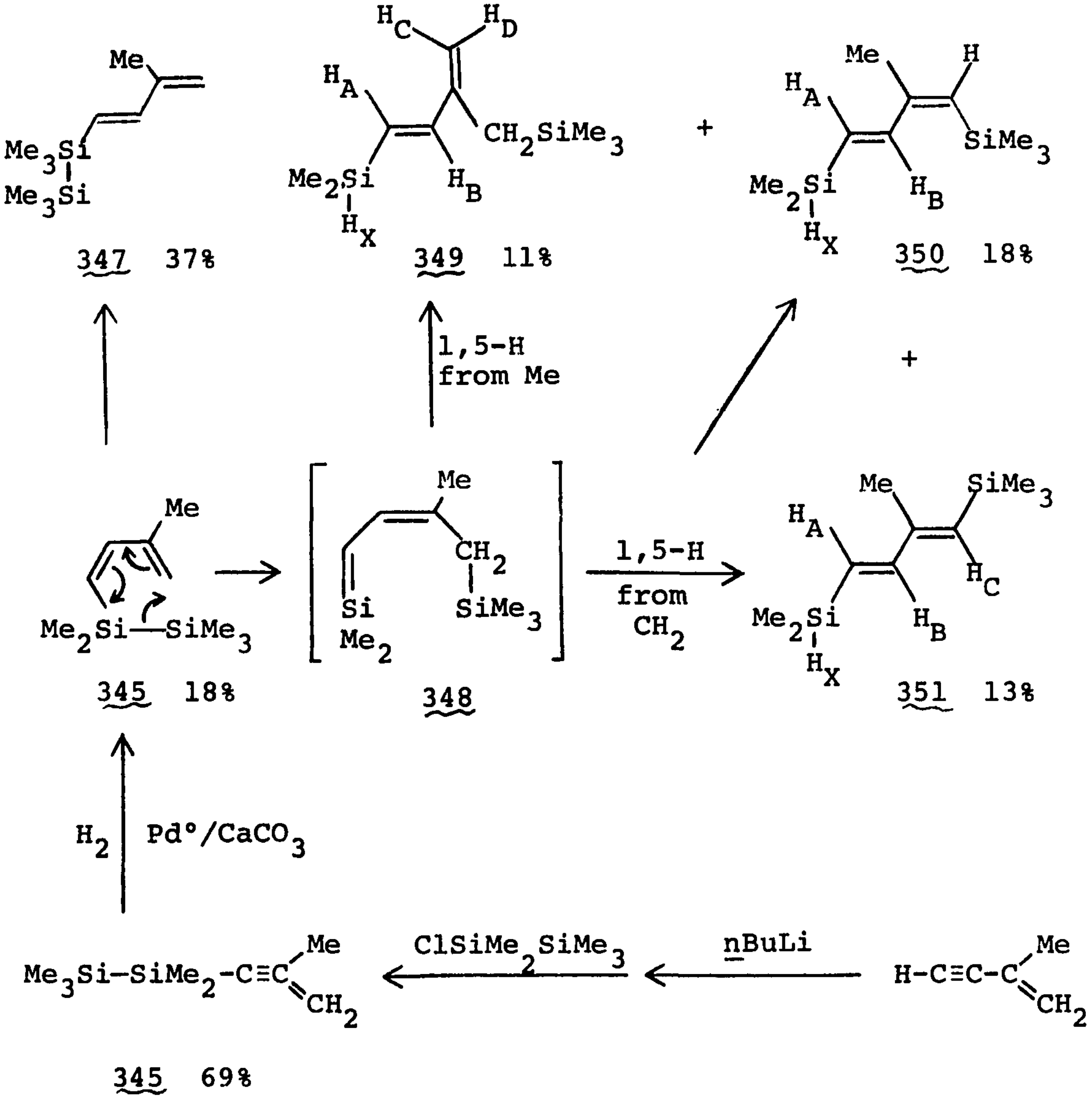
218 323 343



344 59%

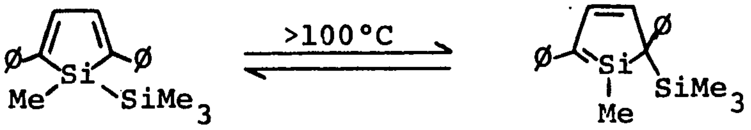
In order to determine generality of the silene-producing, 1,5-trimethylsilyl migration, a linear system, cis-1-pentamethyldisilanyl-3-methyl-1,3-butadiene 346, was prepared (Scheme 53). Reduction of the eneyne 345 with Lindlar's catalyst gave a mixture of isomers from which 346 (18% GC yield) was isolated by preparative GC on a 12' x 1/4" 20% DC-550 on Chromsorb P column at 124°C. Pyrolysis of 346 was conducted in a vacuum flow system (0.07 torr) at 635°C. Only four products were obtained, and all were isolated by preparative GC and assigned the indicated structures on the basis of their NMR, IR, and mass spectra. The major product **347** was identified as the trans isomer of the starting material. The other three products are derived from the silene **348** which results from a 1,5-migration of silicon in **346**. 1-Silabutadienes have been reported as intermediates before and all have been observed to close to silacyclobutenes (see Historical section on silenes). In none of the literature examples, however, have there been hydrogens in a position to undergo 1,5-migration to the silene silicon. In this case 1,5-hydrogen migration occurs to the exclusion of ring closure. The minor product **349** (11% GC yield) results from 1,5-hydrogen migration from the methyl group. Compounds **350** and **351** result from 1,5-hydrogen migration from the methylene group. Thus, the generality of the thermal 1,5-migration of silicon from silicon to carbon has been extended to a linear system.

Scheme 53

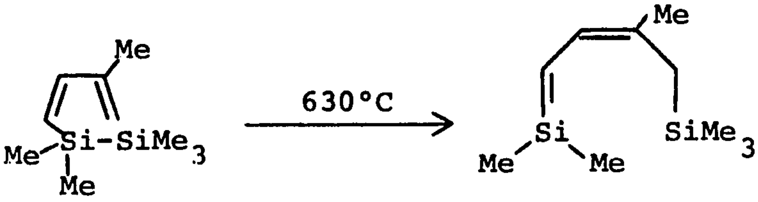

347 37%
349 11%
350 18%
351 13%
345 18%
348
345 69%
1,5-H from Me
1,5-H from CH$_2$
H$_2$ Pd°/CaCO$_3$
ClSiMe$_2$SiMe$_3$
nBuLi
Me$_3$Si–SiMe$_2$–C≡C(Me)=CH$_2$
H–C≡C–C(Me)=CH$_2$
Me$_2$Si–SiMe$_3$
CH$_2$SiMe$_3$
H$_A$
H$_B$
H$_C$
H$_D$
H$_X$
+

Serendipitous Synthesis of a Sila-α-Pyran -- Convenient, Penultimate Precursor to Dimethylsilanone

In the previous section it was established that 1-disilanyl-1,3-butadienes undergo thermal rearrangement *via* 1,5-silyl migrations to produce 1-sila-1,3-butadienes. It was found that the silole **218** undergoes reversible rearrangement to **323** at temperatures above 100°C. It was also observed that the linear disilanylbutadiene **346** rearranges to **348** at 630°C.



218 **323**

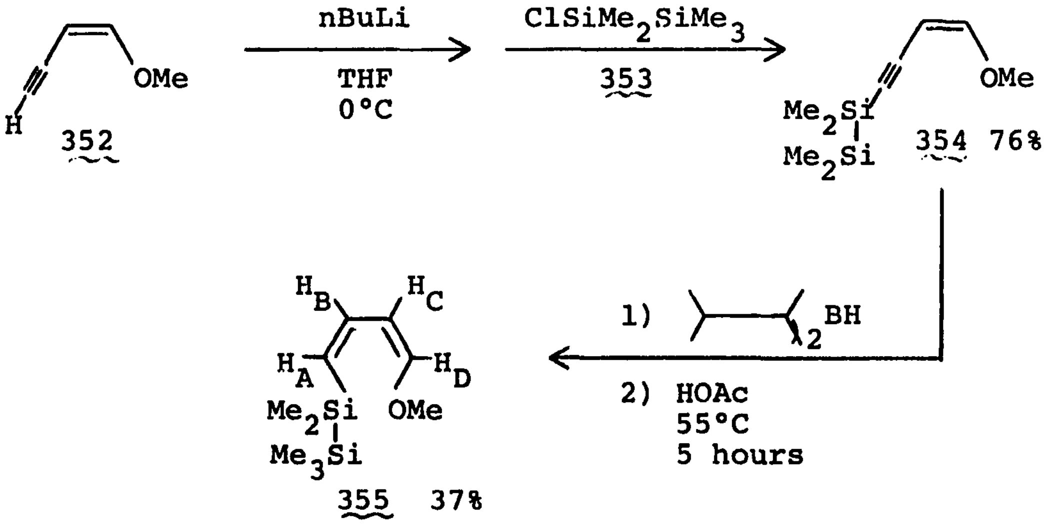


346 **348**

An attempt was made to use this rearrangement in the synthesis of silole **358** (Scheme 54), which at that time would have been the first example of a silole with all the ring-carbons unsubstituted. However, recently Barton and Burns have generated 1-methylsilole and have found it to dimerize

(140). To this end, cis-1-pentamethyldisilanyl-4-methoxy-1-yne-3-ene 354 was prepared from n-butyllithium-induced coupling of pentamethylchlorodisilane 353 and cis-methoxybut-1-yne-3-ene 352 in 75% yield (Scheme 53). Attempted cis-reduction of the triple bond with hydrogen and Lindlar's catalyst afforded only mixtures of randomly reduced 354. However, hydroboration with disiamylborane (234) followed by acidic cleavage of the vinyl borane in acetic acid proved the cis,cis-1-pentamethyl-4-methoxy-1,3-butadiene 355 in 37% yield: NMR (CCl_4) $\delta = 0.03$ (s, 9H), $\delta = 0.15$ (s, 6H), $\delta = 3.63$ (s, 3H), $\delta = 5.05$ (H_C, d of d of d, $J_{BC} = 12$ Hz, $J_{CD} = 6.5$ Hz, $J_{AC} = 1.0$ Hz), $\delta = 5.32$ (H_A, d of t, $J_{AB} = 14$ Hz, $J_{AD} = 1.0$ Hz), $\delta = 5.84$ (H_D, d of t, $J_{BD} = 0.5$ Hz), $\delta = 7.01$ (H_B, d of d of d).

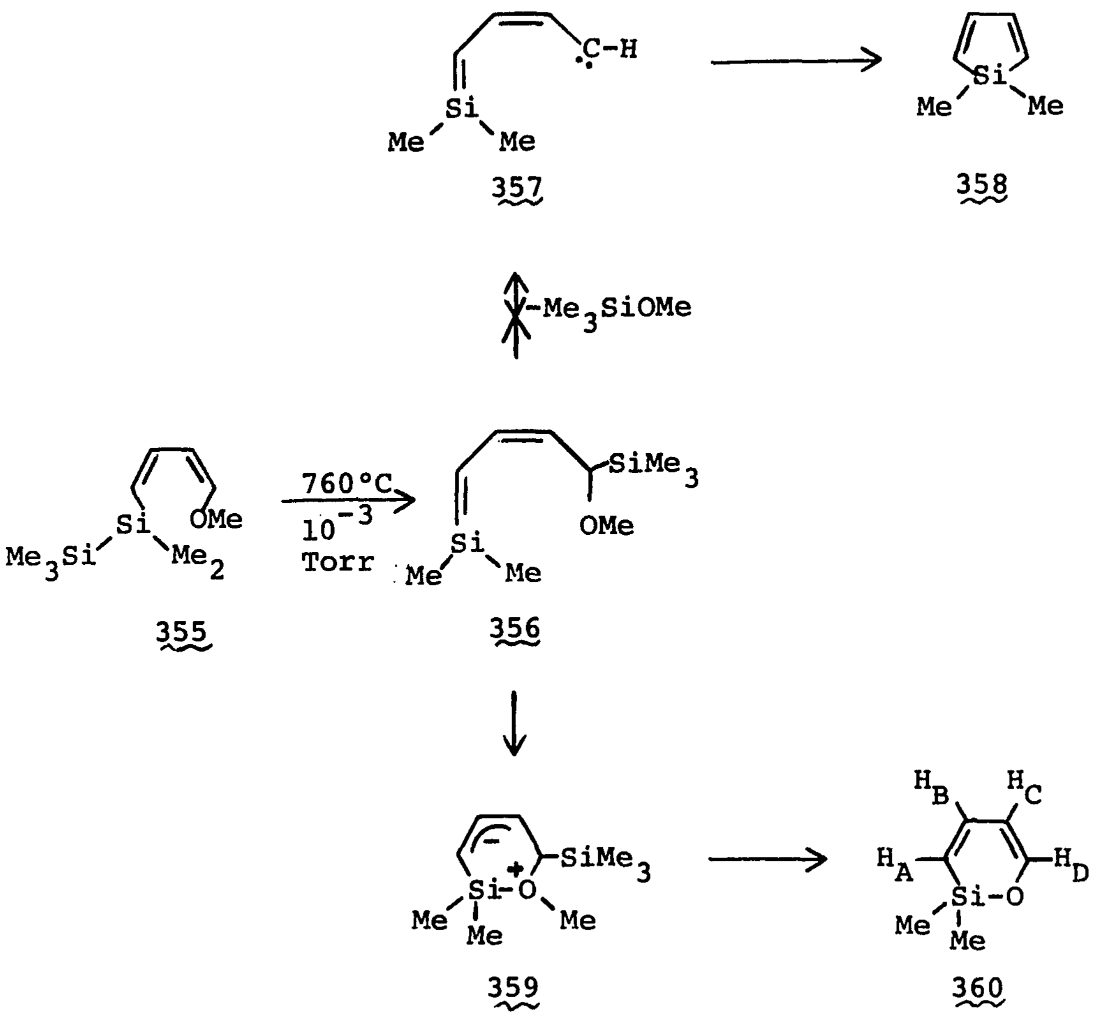
Scheme 53



If the 1,5-migration of a trimethylsilyl group occurs as expected based on the work presented in this thesis, this should result in the generation of the silene 356 (Scheme 54). There are examples in the literature of alpha eliminations of oxygen and silicon from carbon that result in carbene formation (197,198) (see the first part of the Results and Discussion section of this thesis). If such an alpha elimination occurs for 356, then the resultant carbene 357 would be expected to close to 1,1-dimethylsilole 358. However, flow pyrolysis of 355 (760°C, 10^{-3} torr) afforded in 52% yield a product which resulted from the loss of the elements of tetramethylsilane (30%) from 355. This product was identified as 2,2-dimethyl-1-oxo-2-silacyclohexa-3,5-diene 360 (an oxasilin): NMR (CCl_4) $\delta = 0.29$ (s, 6H), $\delta = 5.07$ (H_C, t of d, $J_{CD} = J_{CB} = 6$ Hz, $J_{AC} = 1.0$ Hz), $\delta = 5.54$ (H_A, d of t, $J_{AB} = 14$ Hz, $J_{AD} \sim J_{AC}$), $\delta = 6.54$ (H_D, overlapped with H_B), $\delta = 6.71$ (H_B, d of d of d, $J_{BD} \sim 1$ Hz).

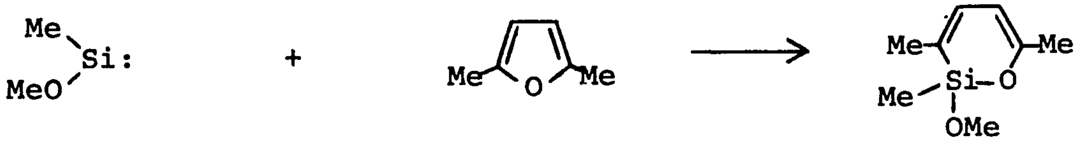
The formation of 360 is easily rationalized when it is recognized that the methoxyl oxygen of 356 is in close proximity to an undoubtedly polar silicon-carbon double bond. Silicon-oxygen bond formation to produce zwitterion 359 would render the methoxy methyl labile with regard to involvement in the β-elimination of tetramethylsilane.

Scheme 54

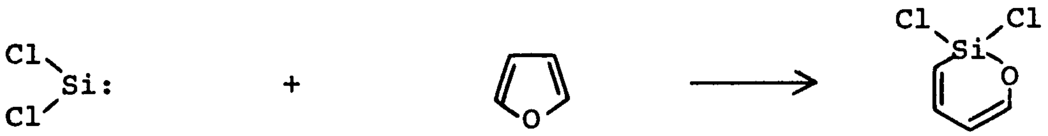


Oxasilin 360 is the third example of this ring system to be reported. Childs and Weber obtained 2-methoxy-2,3,6-trimethyl-1-oxo-2-silacyclohexa-3,5-diene 361 in 3.3% yield from the reaction of methoxymethylsilylene and 2,5-dimethylfuran (23) (Scheme 55). Unfortunately, an insufficient amount of 361 was accumulated to attempt any chemical investigations due to the fact that isolation of 361 was accomplished by preparative GC on two different columns. This work of Childs and Weber could not be reproduced by this author in four attempts. Chernyshev and coworkers have reported that dichlorosilylene will add to furan to give, among other products, the dichlorooxasilin 362 in 5% yield (33). However, 362 could not be isolated and was identified only by GC mass spectroscopy. Recently, in an incredibly terse communication the synthesis of the iron tricarbonyl complex 363 was reported by Bykovets, Labartkava, Krasnova and Chernyshev; however, no references were cited (235).

Scheme 55

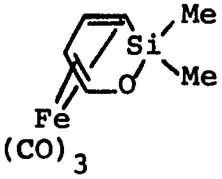


361 3.3%



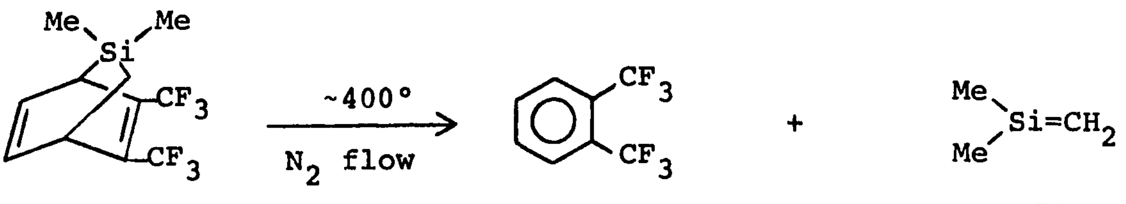
362 5%

not isolated
identified by GCMS



363

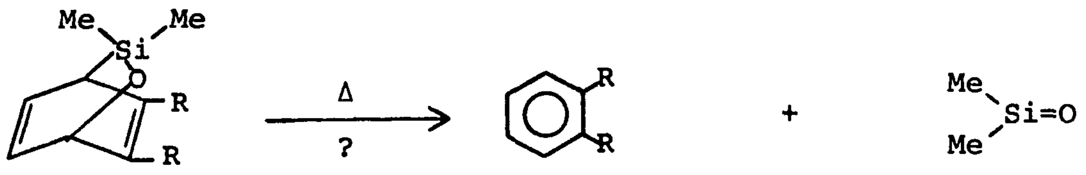
The 1,2-oxasilin ring system is one which has been long sought after by silicon chemists as it can be viewed as a potential penultimate precursor to silanones. It has been established that the 7-silabicyclo[2.2.2]octadiene ring system 71 extrudes the silene bridge at high temperatures (*ca.* 400°C) in the gas phase (116). It might thus be expected that the analogous adduct of an oxasilin and an acetylene could undergo aromatization *via* thermal extrusion of silanones. The chemistry of silanones is virtually unexplored (see Historical section of this thesis). With the exception of insertion into the strained silicon-carbon bond of silaranes, the known chemistry of silanones is limited to reactions involving insertion into a silicon-oxygen single bond. The reason for this dearth in silanone chemistry is probably due to the fact that there are no mild, thermal methods for the generation of silanones, in which both the generator and the reaction by-products are inert to the silicon-oxygen double bond.



71

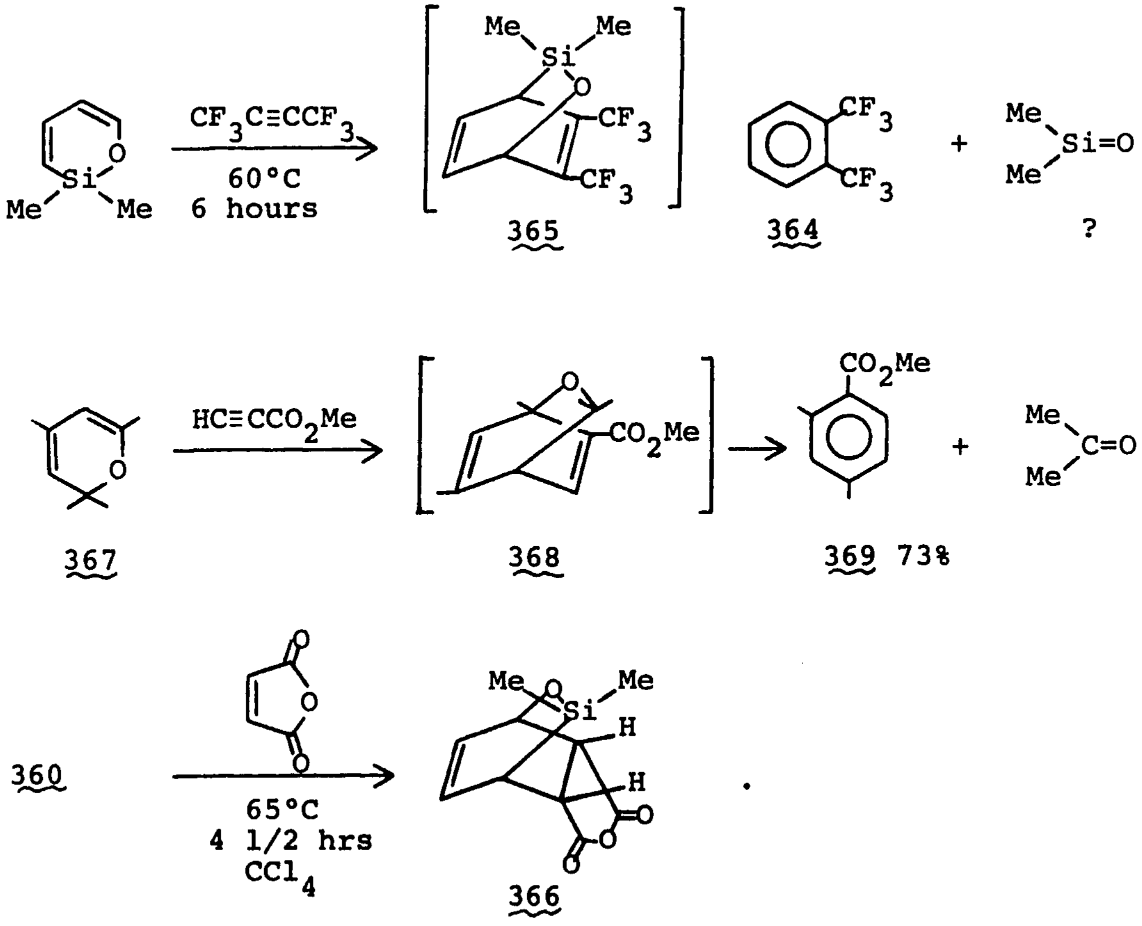
364

72



Given the thermal stability of **71**, it was quite surprising to find that, while perfluoro-2-butyne reacts completely with **360** at room temperature in *ca*, one day (6 hours at 60°C), 1,2-bis(trifluoromethyl)benzene is formed at the same rate (as observed by NMR) (Scheme 56). No absorptions were observed in the NMR that could be attributable to the adduct **365**. Thus, it appears that the initial adduct **365** quickly decomposes even at room temperature through extrusion

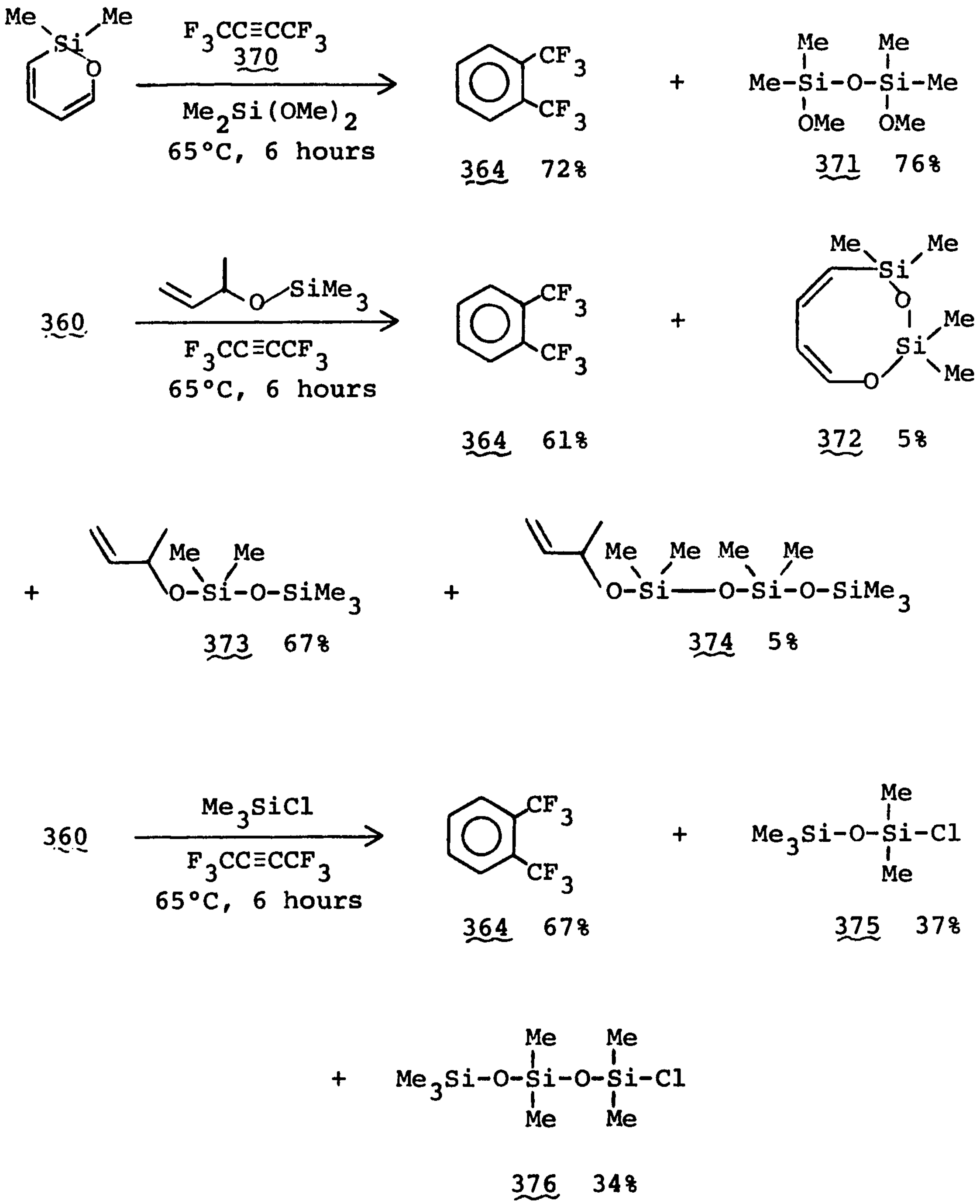
Scheme 56



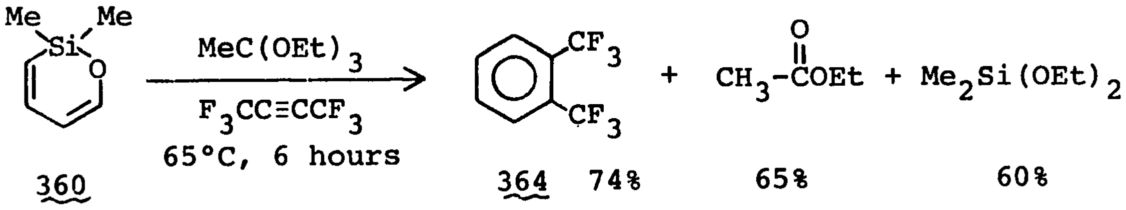
of the silanone bridge. If the cyclic trimer or tetramer of dimethylsilanone is formed, it would only be in small amounts. Salomon and coworkers found that when the pyran 367 was refluxed with methyl propiolate for 100 hours that methyl-2,4-dimethylbenzoate was obtained in a 73% yield (236) indicating similar instability of 368, the carbon analog of 365. The adduct of 360 and maleic anhydride is stable at 65°C. Although 366 was not isolated, it was formed in near quantitative yield as indicated by NMR.

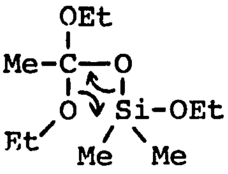
That the adduct 365 does indeed extrude dimethylsilanone was demonstrated by carrying out the reaction of 360 and perfluoro-2-butyne 370 in the presence of excess dimethyldimethoxysilane (a known trap for silanones (30,164)), and obtaining, along with a 72% yield of 364, a 76% yield of 371, the expected trapping product of dimethylsilanone (Scheme 57). When dimethylsilanone is similarly generated in the presence of a large excess of 3-butenyloxy trimethylsilyl ether, three products are obtained that resulted from silanone insertion into a silicon-oxygen single bond. Compounds 372, 373, and 374 account for 82% of the dimethylsilanone generated (based on the amount of 364 formed). The first example of silanone insertion into a silicon-chlorine bond was obtained when dimethylsilanone was generated in the presence of a large excess of trimethylchlorosilane yielding both the mono and bis adducts 375 and 376 that together account for 71% of the silanone generated.

Scheme 57

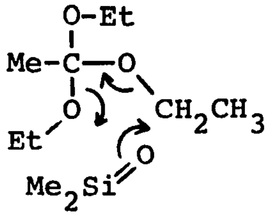

Me
Me
Si
O
F3CC≡CCF3
370
Me2Si(OMe)2
65°C, 6 hours
CF3
CF3
364 72%
+
Me Me
Me-Si-O-Si-Me
OMe OMe
371 76%
360
SiMe3
O
F3CC≡CCF3
65°C, 6 hours
CF3
CF3
364 61%
+
Me Me Si O Me Si Me O
372 5%
+
Me Me
O-Si-O-SiMe3
373 67%
+
Me Me Me Me
O-Si—O-Si-O-SiMe3
374 5%
360
Me3SiCl
F3CC≡CCF3
65°C, 6 hours
CF3
CF3
364 67%
+
Me
Me3Si-O-Si-Cl
Me
375 37%
+
Me Me
Me3Si-O-Si-O-Si-Cl
Me Me
376 34%

Insertion of a silanone into a carbon-oxygen bond has not been observed before. When dimethylsilanone was generated in the presence of excess triethyl orthoacetate, ethyl acetate (65%) and dimethyldiethoxysilane (61%) were obtained. This could be explained by direct insertion of dimethylsilanone into a carbon-oxygen bond to give 379 followed by a beta elimination of silicon and oxygen, or by a bimolecular reaction.



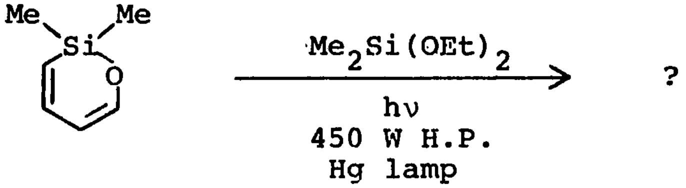


379



In addition, the reaction of the oxasilin 360 with perfluoro-2-butyne was carried out in the presence of each of the following reagents: diethyl ether, ethylene oxide, triethylsilane, tetramethylethylene oxide, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, and <u>trans</u>-cinnamyl methyl ether. In each case a GC mass spectroscopic analysis of the reaction mixture did not result in the identification of any compound that could be construed to have resulted from a reaction of the reagent in question and dimethylsilanone. The same results were obtained for tetramethyl ethylene whether or not the reaction was run in a Teflon or glass vessel.

When a solution of the oxasilin 360 in dimethyldiethoxysilane was degassed and sealed in a quartz NMR tube and irradiated for 175 minutes, it was noticed that the oxasilin had been completely consumed. GC mass spectral analysis revealed that the dimethylsilanone product of dimethyldiethoxysilane was not formed, in fact, no volatile products were formed.



CONCLUSION

It was found that the generation of alpha silylcarbenes (and thus silenes) from thermally induced alpha elimination of chlorine and silicon from carbon did not occur for bis-(trimethylsilyl)dichloromethane. However, silene generation was achieved via a thermally induced (600°C) 1,3-migration of silicon in vinyldisilanes. In the case of 1,2-divinyltetramethyldisilane, the events subsequent to the 1,3-migration are quite complex. Also, the migration was shown not to be general since for 1,1-divinyltetramethyldisilane, alpha elimination is the predominate thermal process.

In light of the fact that alpha silyl carbenes will rearrange to silenes, the analogous rearrangement of alpha silylsilylenes to disilenes was sought; however, the opposite was found. This discovery prompted a mechanistic explanation for the particularly puzzling rearrangement of disilenes to 1,3-disilacyclobutanes that was discovered by Roark and Peddle (144). In the course of providing experimental support for this mechanism, it was discovered that silylenes will undergo intramolecular carbon-hydrogen insertions and that 1,2-disilacyclopropanes will undergo alpha elimination to give beta silylsilylenes.

It was also discovered that 1-disilanylbutadienes will thermally undergo a 1,5-migration of silicon to generate

1-silabutadienes. The generality of this migration was established as it was found that in linear systems this migration occurs at *ca*. 600°C and for cyclic systems (silylsiloles) migration occurs reversibly above 100°C. This reversible 1,5-migration requires an equilibrium concentration of a silene in solution, a fact that should provide for the study of reactions of silenes that have previously been of low yields or unobservable because the reagent of interest could not compete with normal silene dimerization.

The thermal 1,5-migration of silicon in 1-disilanylbutadienes was used synthetically in the construction of a silapyran, which was found to react with perfluoro-2-butyne at room temperature to generate dimethylsilanone. This has proven to be the mildest and most convenient method of silanone generation to date. The first reported examples of silanone insertion into a chlorine-silicon bond and a carbon-oxygen bond are described using this method of generation.

EXPERIMENTAL

Instrumentation

Routine proton NMR spectra were recorded either on a Varian model A-60, EM-360, or a Hitachi R20-B spectrometer. A Varian HA-100 spectrometer was used to record all 100 MHz spectra. Decoupling experiments were performed either on the Varian EM-360 or HA-100 spectrometer. All chemical shifts were reported as parts-per-million (δ scale) using either tetramethylsilane, benzene, or chloroform as internal standards.

C^{13}, F^{19} and Si^{29} NMR spectra were recorded on a Brukker HX-90 NMR spectrometer equipped with a Nicollet 1089 data system.

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

Routine mass spectra were recorded on an Atlas CH-4 Mass Spectrometer. Exact mass measurements were obtained on a MS-902 Mass Spectrometer. Gas Chromatographic Mass Spectra (GCMS) were obtained on either a Perkin-Elmer 270 Mass Spectrometer or a Finnegan Model 4023 Mass Spectrometer.

Ultraviolet spectra (IV) were recorded on a Cary Model 14 spectrophotometer. All melting points (m.p.) were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Gas Chromatographic (GC) data were obtained on a Varian-Aerograph Series 1700 Gas Chromotograph. Column size and packings will be reported as used. High Pressure Liquid Chromatography (HPLC) was performed on a Waters High Pressure Liquid Chromatograph equipped with UV and differential refractomer detectors.

Unless otherwise specified, all GC yields were calculated from predetermined response factors and are based on the amount of starting material used.

Procedures and Results

Synthesis of bis-(trimethylsilyl)dichloromethane 207

The procedure of Bamford and Pant (202) was used to prepare this compound, b.p. 43-45°C (2.0 mm Hg), in 55% yield: NMR (CCl_4) $\delta = 0.25$ (s); IR (neat) 2960, 2910, 1255, 870 and 845 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 230 (4.5), 228 (6), 107 (12), 105 (32), 95 (18), 93 (49), 73 (100), 59 (31).

Vertical flow pyrolysis of 207

Compound 207, which was purified by preparative GC, was dropped through a quartz tube heated to 505°C at a rate of 2.2 ml/hour. A nitrogen flow rate of 60 ml/min was used to sweep the pyrolysis products into a liquid nitrogen trap. The recovered pyrolysate represented a 71% mass recovery. Three major volatile products were indicated by GC analysis.

Trimethylchlorosilane (32% GC yield) was identified by comparison of its GC mass spectrum with that of an authentic sample. The other two products were isolated by preparative GC on a 7' x 1/4" 15% DC-550 on Chromsorb W column at 110°C. The minor product was shown to be bis-(trimethylsilyl)-chloromethane 212 (5.4% GC yield) by comparison of its NMR and mass spectra with those of an authentic sample. The major product of the pyrolysis was 1-trimethyl-1-chloro-dimethylsilylethane 213 (24% GC yield) as identified by its spectra: NMR (CCl_4) $\delta = 0.17$ (s, 9H), $\delta = 0.49$ (s, 6H), $\delta = 6.46$ (AB quartet, 2H, J = 4.5 Hz); ^{13}C NMR ($CDCl_3$) $\delta = 0.3, 3.1, 87.7, 142.9$; IR (neat) 3025, 2965, 1570, 1410, 1258, 1150, 1050, 975, 850 and 785 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 179 (38), 177 (93), 95 (7), 93 (16), 84 (55), 83 (100), 73 (94), 59 (24), 58 (28), 45 (22), 43 (54), calc. for $C_6H_{14}Si_2Cl$ m/e 177.03225, measured 177.02809.

The structure of 213 was also confirmed by treating a THF solution of 213 with methyllithium. After extraction with water, drying with Na_2SO_4 and removal of solvent, it was observed by GC that only one product was formed and it was isolated by preparative GC on a 7' x 1/4" 15% DC-550 on Chromsorb W column at 120°C. This was found to be 1,1-bis-(trimethylsilyl)ethene 214 as identified by its spectra: NMR (CCl_4) $\delta = 0.07$ (s, 18H), $\delta = 6.26$ (s, 2H); GCMS, m/e (% rel. int.) 173 (6), 172 (23), 158 (13), 157 (58), 73 (100). This NMR spectrum was identical to that obtained by Cudlin and coworkers (203).

At 505°C no starting material was recovered and at 380°C virtually none of the starting material had decomposed. The pyrolysis was also performed at 420°C and at 465°C, however, at neither of these temperatures could there be detected by GCMS any product that was isomeric with the starting material. The pyrolysis was unaffected by pretreatment of the pyrolysis tube with concentrated ammonium hydroxide. When the pyrolysis of 207 was carried out at 640°C, only monosilicon-containing products were obtained. These compounds, identified by GCMS via comparison with the mass spectrums of authentic samples, are trimethylsilane, trimethylvinylsilane, chlorodimethylsilane, trimethylchlorosilane, dichlorodimethylsilane and chlorodimethylvinylsilane.

Vertical flow pyrolysis of 207 and triethylchlorosilane

A solution of 207 dissolved in a 9.5 molar excess of triethylchlorosilane was dropped at a rate of 2.2 ml/hour through a quartz tube that was heated to 510°C and through which nitrogen was swept at a rate of 300 ml/min. The triethylchlorosilane had little effect on the pyrolysis of 207 since the same relative amounts of trimethylchlorosilane, 212 and 213, were formed as established by comparison of their retention times and their GC mass spectrum with those of authentic samples. In addition, GCMS analysis indicated that no new major products were formed or that any new product was formed in which a triethylsilylgroup had been incorporated.

Vertical flow pyrolysis of 207 and benzaldehyde

Compound 207 was co-pyrolyzed with a 5 mole excess of benzaldehyde by dropping the mixture at a rate of 6.2 ml/hour into a quartz tube that was heated at 510°C and through which nitrogen was swept at a rate of 60 ml/min. The benzaldehyde was purified by passing through silica gel. The pyrolysate was collected in a liquid nitrogen trap and was found to be a clean mixture of benzaldehyde, benzene, trimethylchlorosilane (16% GC yield), and 213 (31% GC yield). These four compounds were identified by comparison of their retention times and their GC mass spectra with those of authentic samples. GCMS analysis gave no evidence for the presence of hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, or 2-chloro-2-methylstyrene.

Synthesis of bis-(trimethylsilyl)chloromethane 212

To a dry flask that was cooled to 0°C and equipped with a drying tube and a magnetic stirrer was added 6.33 grams (0.0276 moles) of bis-(trimethylsilyl)dichloromethane 207. Tri-*n*-butyltin hydride (8.51 grams, 0.0293 moles) was added over a period of 2 to 3 minutes. After addition, the mixture was stirred at room temperature for 15 minutes. Distillation gave 3.87 grams (72%) of 212 collected at 46-49°C (3 mm Hg): NMR (CCl_4) $\delta = 0.14$ (s, 18H), $\delta = 2.32$ (s, 1H); GCMS, m/e (% rel. int.) 194 (2), 181 (4), 179 (10), 85 (34), 73 (100), 59 (19).

Vertical flow pyrolysis of 212

Compound 212 was purified by preparative GC and was pyrolyzed by dropping it at a rate of 2.2 ml/hour into a vertical quartz tube heated to 630°C. A stream of nitrogen (150 ml/min) swept the products into a liquid nitrogen trap. The pyrolysate represented a 62% mass recovery and was found by GC analysis to be a remarkably clean mixture of two compounds. No starting material remained; however, at 510°C almost all of the starting material was recovered. The two products were isolated by preparative GC on a 7' x 1/4" 15% DC-550 on Chromsorb W column at 100°C. The minor product was shown to be bis-(trimethylsilyl)methane 217 (7% GC yield) on the basis of its spectra: NMR (CCl_4) $\delta = -0.27$ (s, 2H), $\delta = 0.03$ (s, 18H); GCMS, m/e (% rel. int.) 145 (100), 73 (59), 65 (13), 59 (13), 45 (19), 43 (12). These spectra are identical to those of the product of reduction of 212 with tri-*n*-butyltinhydride. The major product was determined to be 1-trimethylsilyl-1-dimethylchlorosilylethane 216 (40% GC yield) on the basis of its spectra: NMR ($CDCl_3$) δ = 0.04 (s, 9H), δ = 0.13 (q, 1H, J = 7.5 Hz), δ = 0.39 (d, 6H, J = 2 Hz), δ = 1.10 (d, 3H, J = 7.5 Hz, hν at 0.13 collapses to a singlet); GCMS, m/e (% rel. int.) 181 (20), 179 (42), 93 (12), 86 (100), 85 (87), 73 (77), 59 (38), 58 (45), 45 (22), 43 (22).

Synthesis of *cis*- and *trans*-1,4-dimethoxy-1,4-dimethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene **233a** and **233b**

The procedure of Atwell and Weyenberg was used to prepare a mixture of **233a** and **233b** in 43% yield (21). They reported that the ratio of the two isomers of **233** was 3:1, but did not make an assignment. The two isomers were separated with a Water's ALC-202 liquid chromatograph on a 4' Porasil A preparative column and a solvent (benzene) flow rate of 5.5 ml/min. Assignment of the isomers was made on the basis of the correlation of the shifts of the methoxyl absorptions in the NMR with the amount of added Euroshift F. The assumption is that for the cis isomer the chelation of the europium by the methoxyl oxygen is preferred due to the proximity of the cis methoxyl oxygen atom. As the Euroshift F is added in aliquots up to the point where a total of one equivalent of shift reagent had been added, it was observed that one of the methoxyl absorptions was shifted to a greater degree than the other and that at the one equivalent point, one of the methoxyls was shifted by 21 Hz and the other by 12 Hz. The methoxyl absorption that was shifted by 21 Hz was assigned to that of the cis isomer 233a.

The same isomer ratio (3:1) that was reported by Atwell and Weyenberg was obtained. The major isomer was the trans isomer 233b which had a m.p. 206-208°C and the following spectra: NMR (CCl_4) $\delta = 0.10$ (s, 6H), $\delta = 3.43$ (s, 6H), $\delta = 6.94$ (s, 20H); IR (CCl_4) 2960, 2935, 2835, 1435, 1250, 1090, 875 and 696 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 505 (43), 504 (100), 489 (17), 311 (39), 281 (30), 104 (22), 58 (22), calc. for $Si_2C_{32}H_{32}O_2$ m/e 504.19409, measured 504.19269. The minor isomer was the cis isomer 233a which had a m.p. 215-217°C and the following spectra: NMR (CCl_4) $\delta = -0.03$ (s, 6H), $\delta = 3.49$ (s, 6H), $\delta = 6.97$ (s, 20H); IR (CCl_4) 2960, 2840, 2830, 1440, 1250, 1095, 1085, 880, 865 and 696 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 505 (38), 504 (75), 489 (11), 311 (21), 281 (17), 179 (38), 104 (10), 77 (100).

Photolysis of 233a and 233b

The photolysis were carried out by dissolving either 233a or 233b in the specified solvent, followed by degassing the solution (unless otherwise specified) in a Pyrex NMR tube by the freeze-thaw method. The NMR tube is sealed and the photolysis performed in a Rayonet RPR-100 photochemical reactor adapted with 2537 Å lamps. The operating temperature of the reactor is 44°C.

When the trans isomer 233b is photolyzed in the above manner with benzene as solvent, no change is discernible by NMR after 5 days. Likewise, no change is observed in the photolysis of 233b after 27 hours with cyclohexane as the solvent. With ether as a solvent and with a quartz reaction vessel, no change is observed for 233b after 20 hours.

However, in CCl_4 233b isomerizes to the cis isomer upon photolysis. Starting with pure trans isomer 233b, a cis:trans ratio of 1:3 is observed after 3 hours, a ratio of 1:1 after 5 hours, and a ratio of 2:1 after 7 hours. Prolonged irradiation results in decomposition to a number of products as indicated by NMR and HPLC. A control experiment establishes that a CCl_4 solution of 233b does not isomerize under the same conditions with the lamps off.

Photolysis of 233a in CCl_4 also results in isomerization with subsequent decomposition as observed by NMR.

Synthesis of cis and trans 1,4-dimethoxy-1,4-dimethyl-1,4-disilacyclohexadiene 234a and 234b

Compounds 234a and 234b were prepared from the pyrolysis of sym-dimethyltetramethoxydisilane (prepared by the method of Childs and Weber (237)) at 350°C in a stream of acetylene according to the procedure of Janzen and coworkers (22).

These workers report the formation of a single isomer: NMR (CCl_4) δ = 0.15 (s, 6H), δ = 3.37 (s, 6H), δ = 6.98 (s, 4H). In contrast to their results, a one-to-one mixture of **234a** and **234b** was obtained in each of four runs in a combined yield of 64%. The compounds **234a** and **234b** were isolated by HPLC on a 4' Porasil A preparative column with a solvent (benzene) flow rate of 7.5 ml/min. Stereochemical assignment was made by comparison of the relative shifts in the NMR with those for compounds **233a** and **233b**. The *cis* isomer **233a** has the following spectra: NMR (CCl_4) δ = 0.16 (s, 6H), δ = 3.38 (s, 6H), δ = 6.95 (s, 4H); mass spectrum (70 eV) m/e (% rel. int.) 200 (11), 185 (100), 155 (74), 59 (26), calc. for $C_7H_{13}Si_2O_2$ m/e 185.04542, measured 185.04521. The *trans* isomer **233b** has the following spectra: NMR (CCl_4) δ = 0.19 (s, 6H), δ = 3.31 (s, 6H), δ = 6.93 (s, 4H); mass spectrum (70 eV) m/e (% rel. int.) 200 (19), 185 (100), 171 (44), 155 (75), 59 (38), calc. for $C_8H_{16}Si_2O_2$ m/e 200.06889, measured 200.06816.

Photolysis of **234a**

A CCl_4 solution of **234a** was degassed by the freeze-thaw method and sealed in a Pyrex NMR tube. The solution was photolyzed in a Rayonet RPR-100 photochemical reactor adapted with 2537 Å lamps. After photolysis for 11 hours, **234a** had isomerized to a one-to-one mixture of **234a** and **234b** as determined by NMR. The same one-to-one ratio was observed after photolysis for 25 hours. After photolysis for 78 hours, the majority of 234a and 234b was consumed and a large number of new peaks were observed in the NMR.

Synthesis of 1,4-dichloro-1,4-dimethyl-1,4-disilacyclohexadiene 235

To a dry flask equipped with a magnetic stirrer and a drying tube was added 1.02 grams (0.0051 moles) of a 1:1 mixture of 234a and 234b and 1.20 grams (0.0153 moles) of acetyl chloride. After stirring for one hour at room temperature, the volatile materials were removed by a roto-evaporator while heating at 60°C. The contents of the flask solidified to a white solid (m.p. 60-65°C) and was found by NMR to be relatively pure 235 (1.00 grams, 94%). The NMR indicated a 3:1 ratio of isomers, but they were not separated. The NMR also indicated a small broad absorption in the methoxyl region. An analytically pure sample of a 3:1 mixture of isomers of 235 could be obtained by sublimation at 25°C and 0.6 mm Hg. After four sublimations the melting point was 86-89°C, and the following spectra obtained: NMR (CCl_4) $\delta = 0.53$ (s, 1.5H), $\delta = 0.58$ (s, 3.5H), $\delta = 6.90$ (s, 4H); IR (CCl_4) 2970, 1340, 1260, 1135, 830, 705 and 650 cm^{-1}; mass spectrum m/e (% rel. int.) 210 (70), 208 (100), 195 (39), 193 (58), 169 (9), 107 (16), 95 (100), 93 (20), calc. for $C_6H_{10}Cl_2Si_2$ m/e 207.9698, measured 207.97522.

Photolysis of 235

A CCl_4 solution of 235 was degassed by the freeze-thaw method and sealed in a Pyrex NMR tube. The solution was irradiated in a Rayonet reactor with 2537 Å light. After 24 hours, no change of any kind had occurred as indicated by NMR. Prolonged irradiation (>50 hours) resulted in the appearance of a large number of new peaks in the NMR.

The reaction of trimethylsilyllithium 240 with silicon tetrachloride

Trimethylsilyllithium (0.0408 moles) was generated from methyllithium and hexamethyldisilane in HMPA at 0°C according to the method by Still (208). The HMPA solution of the silyl anion was added to 2.72 grams (0.016 moles) of $SiCl_4$ in 20 ml of refluxing THF. After addition, the solution was refluxed for 2 hours, after which the solvent and other volatiles were removed by evaporation under reduced pressure. A distillation at 10 mm Hg resulted in the collection of 0.90 grams of distillate in the range of 30-95°C. Analysis by GCMS reveals the presence of three major products, none of which corresponded to the desired coupling product 2,2-dichlorohexamethyltrisilane 245. The major product was isolated by preparative GC on a 12' x 1/4" 15% SE-30 on

Chromsorb W column and identified as octamethyltrisilane 242 on the basis of its spectra: NMR (CCl_4) $\delta = 0.07$ (s); IR (neat) 2960, 2905, 1400, 1245, 830, 790, 720 and 680 cm^{-1}; mass spectrum m/e (% rel. int.) 204 (25), 189 (18), 131 (77), 116 (50), 73 (100), calc. for $C_8H_{24}Si_2$ m/e 204.11859, measured 204.11690. A second product from this mixture was identified as decamethyltetrasilane 243 on the basis of its GC mass spectrum: m/e (% rel. int.) 262 (33), 247 (11), 189 (59), 173 (28), 131 (89), 116 (35), 73 (100). The spectra presented here for 242 and 243 are identical to the corresponding spectra of the respective authentic samples prepared by the method of Gilman and Harrell (238). The third product was isolated by preparative GC in the same manner as was 242 and tentatively identified as tris-(dimethylamino)chlorosilane 244 on the basis of its spectra: NMR (CCl_4) $\delta = 2.53$ (s); mass spectrum m/e (% rel. int.) 197 (17), 195 (45), 152 (31), 151 (29), 136 (15), 108 (25), 43 (100).

The reaction of trimethylsilyllithium 240 with dibromodifluoromethane

Trimethylsilyllithium (0.072 moles) was generated from methyllithium and hexamethyldisilane in HMPA at 0°C according to the method by Still (208). The HMPA solution of 240 was diluted with 350 ml of ether and then cooled to -78°C. After stirring for 45 minutes at -78°C, 6.0 grams

(0.072 moles) of dibromodifluoromethane was added slowly. After stirring for a few minutes, the solution was warmed to room temperature and extracted with pentane and water. The organic phase was washed three times with water and dried with $MgSO_4$. After the volatile materials were removed by a rotoevaporator, approximately 4 grams of a clear liquid remained. Analysis by NMR shows the presence of only silicon methyls. Analysis by GCMS reveals the fact that only three compounds are present and in approximately equal amounts. These compounds were identified as hexamethyldisilane, octamethyltrisilane 242, and decamethyltetrasilane 243 by comparison of their mass spectra with those of authentic samples.

Reactions of trimethylsilyllithium 240 with functionalized silanes

Trimethylsilyllithium 240 was prepared from methyllithium and hexamethyldisilane in HMPA at 0°C according to the method of Still (208). In an attempt to prepare unsymmetrical disilanes, 240 was reacted with the following functionalized silanes.

Triethylchlorosilane An HMPA solution of 240 (0.0015 moles) was diluted with 10 ml of THF and cooled to -78°C. After addition of 0.0015 moles of triethylchlorosilane, the solution was stirred for 5 minutes at -78°C. After warming to room temperature, 50 ml of pentane and 25 ml of water were added. The pentane layer was washed twice with water and dried with sodium sulfate. The pentane was removed to leave 0.39 grams of an oil that by GC analysis *via* comparison with the retention time of an authentic sample did not contain any of the desired coupling product 1,1,1-triethyl-2,2,2-trimethylsilane.

Triethylsilane This reaction was run on the same scale and with the same procedure as for triethylchlorosilane. The major product of the reaction was isolated by preparative GC on a 6' x 1/4" 15% SE-30 on Chromsorb W column at 130°C. This compound was identified as 1,1,1-triethyl-2,2,2-trimethylsilane (41% GC yield) on the basis of its spectra: NMR (CCl_4) δ = 0.10 (s, 9H), δ = 0.51 - 1.18 (m, 15H); IR (neat) 2965, 2930, 2890, 1250, 1020, 860, 835, 725 and 710 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 188 (52), 173 (17), 159 (24), 131 (41), 115 (90), 103 (41), 87 (100), 73 (55), 59 (52), calc. for $C_9H_{24}Si_2$ m/e 188.141663, measured 188.142362.

Triethylbromosilane This reaction was carried out on a 0.0025 mole scale with the same procedure as was used for triethylchlorosilane. The major product of the reaction was isolated by preparative GC on a 10' x 1/4" 15% SE-30 on Chromsorb W column at 140°C, and was identified as 1,1,1-triethyl-2,2,2-trimethyldisilane (39% GC yield) by comparison of its spectra with those of an authentic sample.

Triethylsilylperchlorate (**239**) This reaction was carried out on a 0.0025 mole scale with the same procedure as was used for triethylchlorosilane (239). The major product of the reaction was isolated by preparative GC on a 10' x 1/4" 15% SE-30 on Chromsorb W column at 140°C, and was identified as 1,1,1-triethyl-2,2,2-trimethyldisilane (55% GC yield) by comparison of its spectra with those of an authentic sample.

Diisopropylmethylsilane (**163**) To an HMPA solution of **240** (0.00375 moles) at 0°C was added a solution of 0.348 grams (0.00268 moles) of diisopropylmethylsilane in 2 ml of HMPA. After stirring for 5 minutes, 100 ml of pentane was added. The pentane solution is washed 3 times with 50 ml of water and dried with sodium sulfate. Removal of the pentane left 0.504 grams of a clear oil. The major product was isolated by preparative GC on a 6' x 1/4" 15% SE-30 on Chromsorb W at 130°C and identified as 1,1-diisopropyltetramethyldisilane (32% GC yield) on the basis of its spectra: NMR (CCl_4) δ = 0.00 (s, 3H), δ = 0.16 (s, 9H), δ = 1.05 (s, 14H); IR (neat) 2950, 2890, 2860, 1460, 1245, 992, 880, 852, 828, 770, 730 and 698 cm^{-1}; mass spectrum m/e (% rel. int.) 202 (30), 187 (9), 159 (36), 145 (8), 129 (23), 117 (86), 84 (34), 73 (100), 59 (54), calc. for $C_{10}H_{26}Si_2$ m/e 202.157313, measured 202.155084.

Bromodimethylvinylsilane, dimethylethoxyvinylsilane, and dimethylvinylsilane These reactions were run on the same scale and with the same procedure as for triethylchlorosilane. Removal of the pentane solvent left 0.35-0.44 grams of a yellow oil. GC analysis with a 10' x 1/4" 15% Se-30 on Chromsorb W column at 170°C reveals that the only compound in these oils with a retention less than 50 minutes was THF.

Synthesis of 1-methyl-2,5-diphenylsilacyclopentane 238a

Compound 238a was prepared by the method used by Weyenberg and coworkers for the preparation of 238b (216). Lithium shot (13.9 grams, 2 moles) and one liter of THF were added to a 3 liter flask that was purged with N_2 and cooled to 0°C. A solution of 104 grams of styrene (1 mole) and 57.5 grams of methyldichlorosilane (0.5 mole) in 300 ml of THF was added over a period of one hour. The solution was vigorously stirred for 3 days at 0°C. The solution was filtered and the THF removed by evaporation, then 1.5 l. of benzene was added and the solution filtered again. The gummy residue that remained after the removal of the benzene was distilled at 0.6 mm Hg. Compound 238a was collected (presumably as a mixture of four diastereomers) between 150-215°C (36 grams, 29%): NMR (CCl_4) δ = -0.5 to 0.50 (3 steps of doublets, J = 4 Hz, 3H), δ = 0.8 to 3.0 (m, 6H), δ = 3.8 to 4.4 (m, 1H), δ = 7.25 (s, 10H).

Reaction of 238a with trimethylsilyllithium

Trimethylsilyllithium 240 (0.005 moles) was prepared from methyllithium and hexamethyldisilane in HMPA at 0°C according to the method of Still (208). To this solution of 240 was added a solution of 1.26 grams (0.005 mole) of 238a in 4 ml of HMPA. After stirring for 10 minutes, excess methyl iodide was added. The reaction mixture was extracted with 100 ml of pentane and 50 ml of water. The pentane layer was washed two more times with 50 ml of water and dried with sodium sulfate. After removal of pentane, the residue was heated at 85°C under a vacuum of 1.0 mm Hg for one hour to leave 1.16 grams of a clear oil. Analysis of the NMR (CCl_4) of this oil reveals by integration that the trimethylsilyl groups did not become incorporated. The NMR is most consistent with abstraction of the benzylic hydrogens by trimethylsilyllithium and incorporation of a methyl group when the reaction was quenched with methyl iodide.

Synthesis of 1-methyl-2,5-diphenylsilole (237a)

Compound 237a was prepared by the method used by Atwell and coworkers for the preparation of 237b (212). A solution of 5.00 grams (0.0137 mole) of 1,4-dibromo-*trans*,*trans*-1,4-diphenylbutadiene (212) in 200 ml of ether was cooled to 0°C under N_2. Addition of 0.0275 moles of *n*-butyllithium in hexane was followed by stirring for 30 minutes as the solution warmed to room temperature. A solution of 1.58 grams

(0.0137 mole) of methyldichlorosilane in 100 ml of THF was added rapidly and was followed by stirring for 1 hour. The reaction mixture was hydrolyzed with 1% HCl, washed with saturated sodium chloride solution and dried with sodium sulfate. After removal of solvent, the residue was dissolved in 7.5 ml of hot ethanol. Upon cooling, 2.30 grams (53%) of 237a was collected and dried under vacuum. The yellow fluorescent solid had a melting point of 97-98.5°C and the following spectra: NMR (CCl_4) δ = 0.50 (d, 3H, J = 4 Hz), δ = 4.95 (q, 1H, J = 4 Hz), δ = 7.25 (m, 10H); IR (CCl_4) 3070, 3030, 2995, 2965, 2140, 1595, 1490, 1445, 1250, 930, 870 and 690 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 248 (57), 233 (100), 232 (42), 204 (10), 203 (24), 202 (11), 129 (12), 105 (53), calc. for $C_{17}H_{16}Si$ m/e 248.10213, measured 248.10051.

Reaction of 237a with trimethylsilyllithium

Trimethylsilyllithium 240 (0.001 moles) was prepared from methyllithium and hexamethyldisilane in HMPA at 0°C according to the method of Still (208). After dilution with 10 ml of THF, the solution was cooled to -78°C. A solution of 0.25 grams (0.001 mole) of 237a in 2 ml of THF was added and the resulting green solution was stirred for one hour at -78°C. After warming, the solution was hydrolyzed with 1% HCl and extracted with 20 ml of pentane. The pentane solution was washed twice with water and dried with sodium sulfate. Removal of solvent left 0.26 grams of a yellow solid. Analysis by NMR revealed only the presence of some starting material and a large cluster of absorptions at δ = 0.20 to -0.20. No absorptions were observed at the positions expected for the desired product 218. After the successful synthesis of 218 by a different method, it became clear on the basis of chemical shifts that 218 was not formed in this reaction.

Synthesis of tris-(trimethylsilyl)methylsilane 251

Compound 251 was prepared according to the procedure by Smith (218). To a vigorously stirred mixture of 571 grams (5.26 moles) of trimethylchlorosilane dissolved in 500 ml of THF and 83.0 grams (11.9 moles) of lithium shot was added 50 ml of a solution of 262 grams (1.76 mole) of methyltrichlorosilane in 350 ml of THF. After stirring for one hour at room temperature, the reaction mixture turned brown and became exothermic. The remainder of the methyltrichlorosilane solution was added dropwise over a period of 4 hours and, upon completion, the reaction mixture was stirred for 48 hours at room temperature, or until it was observed that lithium was no longer being consumed. The solution was filtered, the solvent removed by rotoevaporator and the residue distilled to give 300 grams (38%) of 251, b.p. 95-100°C/27mm. NMR (CCl_4) δ = -0.11 (s, 3H), δ = 0.13 (s, 27H);

mass spectrum m/e (% rel. int.) 262 (4.6), 198 (8.2), 174 (27), 159 (10), 131 (11), 129 (11), 115 (9), 99 (5), 73 (100), 59 (11).

Synthesis of 1,1-dichlorotetramethyldisilane 252

Compound 252 was prepared following the procedure described by Harrell (217). A solution of 332 grams (1.78 moles) of tris-(trimethylsilyl)methylsilane 251 in 1.7 l. of CCl_4 was cooled to -25°C with a CCl_4/CO_2 bath. Chlorine gas was bubbled through the solution and the reaction monitored by GC. Addition of chlorine was stopped when the yield of 252 was maximized as indicated by GC. Distillation yielded 83 grams (35%) of 252, b.p. 54-58°C (34 mm Hg), which had the following spectra: NMR (CCl_4) δ = 0.27 (s, 9H), δ = 0.80 (s, 3H); IR (neat) 2960, 2900, 1400, 1250, 860, 840, 780, 715 and 650 cm^{-1}; mass spectrum m/e (% rel. int.) 188 (1.1), 186 (1.6), 173 (1.1), 171 (1.4), 151 (1.1), 95 (2.6), 93 (7.1), 73 (100), calc. for $C_4H_{10}Si_2Cl_2$ m/e 185.98547, measured 185.98404.

Synthesis of 1-trimethylsilyl-1-methyl-2,5-diphenylsilole 218

Compound 218 was prepared according to the method used by Atwell and coworkers (212) for the preparation of 1,1-dimethyl-2,5-diphenylsilole. The 1,4-dibromo-trans,trans-1,4-diphenylbutadiene 253 called for in this procedure was also prepared by the method of Atwell and coworkers (212).

A more recent procedure for the preparation of **253** by Reich and Reich (240) was tried, but found inferior.

To a solution of 12.0 grams (0.033 moles) of **253** in 500 ml of either at 0°C was added 0.066 moles of *n*-butyllithium in hexane. The ice-bath was removed and the solution stirred for 30 minutes. A solution of 6.8 grams (0.036 moles) of **252** in 200 ml of THF was added all at once and the resultant yellow solution stirred for 45 hours. The reaction mixture was hydrolyzed with 500 ml of 1% HCl, washed with saturated sodium chloride, and dried with sodium sulfate. After removal of solvent, the residue was passed through a 3" x 10" silica gel column with hexane. The yellow, blue-fluorescent band was collected and the solvent removed to leave 6.7 grams of a yellow solid that was shown to be a mixture of 218 and *trans*,*trans*-1,4-diphenylbutadiene. The latter could be selectively sublimed away from **218** at 60°C and 0.06 mm Hg. The sublimation was followed by periodically checking by NMR the purity of **218** that was left in the bottom of the sublimation. After 4 days, the material in the bottom of the sublimation was pure **218**, a bright yellow solid 5.4 grams (51%), m.p. 95-96.5°C with the following spectra: NMR (CCl_4) $\delta = 0.0$ (s, 9H), $\delta = 0.68$ (s, 3H), $\delta = 7.1 - 7.6$ (m, 12); ^{29}Si NMR ($CDCl_3$) $\delta = 63.547$, $\delta = 66.851$; IR (KBr) 3080, 3060, 3025, 2950, 2890, 1590, 1488, 1253, 1240, 850, 840, 780, 755, 720 and 688 cm^{-1}; mass spectrum m/e (% rel.

int.) 321 (26), 320 (83), 306 (28), 305 (100), 245 (13), 227 (21), 177 (15), 159 (13), 145 (27), 135 (48), 107 (15), 105 (30), 73 (99), calc. for $C_{20}H_{24}Si_2$ m/e 320.14166, measured 320.14006.

Synthesis of 1,4-diphenyl-2,3-dicarbomethoxy-7-trimethylsila-7-methyl-7-silanorbornadiene 258

To a solution of 0.266 grams (0.00083 moles) of the silole 218 in 6 ml of hexane was added 0.177 grams (0.00125 moles) of dimethylacetylene dicarboxylate 257. After stirring for a few minutes at room temperature, the solution was cooled to -10°C. The solution was filtered, and the white solid washed with hexane to give 0.149 grams (39%) of 258, m.p. 143-147°C (discoloration occurs at 120°C). Compound 258 was characterized on the basis of its spectra: NMR (CCl_4) δ = -0.17 (s, 9H), δ = 0.68 (s, 3H), δ = 3.60 (s, 6H), δ = 7.31 (s, 2H), δ = 7.45 (s, 10H); IR (KBr) 3050, 3020, 2950, 2890, 1720, 1595, 1545, 1490, 1425, 1290, 1240, 1135, 1115, 1050, 855, 825, 770, 735, 715 and 695 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 462 (10), 447 (100), 430 (11), 421 (18), 419 (30), 415 (35), 147 (35), calc. for $C_{26}H_{30}O_4Si_2$ m/e 462.16557, measured 462.16545.

Synthesis of 1,1,1,2,3,3,3-heptamethyltrisilane 259

2-Chloroheptamethyltrisilane 262 was prepared as described by Harrell (217). To a solution of 0.15 grams

(0.00384 moles) of lithium aluminum hydride in 30 ml of diethylether was added 3.0 grams (0.0134 moles) of **262**. The ether solution was stirred for 12 hours at room temperature, hydrolyzed with water, washed with saturated sodium chloride, and dried with sodium sulfate. Removal of solvent left 2.08 grams (82%) of fairly pure **259**. Analytically pure samples of **259** were obtained by preparative GC on a 10' x 1/4" 20% DC-550 on Chromsorb P column at 150°C for the purposes of spectral analysis: NMR (CCl_4) $\delta = 0.09$ (d, 3H, J = 5.5 Hz, collapses to singlet upon $h\nu$ at $\delta = 3.03$), $\delta = 0.14$ (s, 18H), $\delta = 3.03$ (q, 1H, J = 5.5 Hz); NMR (C_6D_6) $\delta = 0.13$ (d, 3H, J = 5.5 Hz), $\delta = 0.17$ (s, 18H), $\delta = 3.45$ (q, 1H, J = 5.5 Hz); IR (neat) 2960, 2900, 2070, 1400, 1240, 835, 765, 740 and 680 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 191 (2), 190 (18), 175 (13), 131 (3), 117 (6), 116 (35), 115 (3), 102 (31), 101 (13), 73 (100), calc. for $C_7H_{22}Si_2$ m/e 190.10294, measured 190.10217. Compound **259** reacts with CCl_4 over a period of a few hours at room temperature. Although this was unexpected, it is in keeping with an increase in reactivity of silylhydrides with increasing numbers of silyl substituents on the silicon bearing the hydrogen. For example, tris-(trimethylsilyl)-chlorosilane has been prepared by the reaction of CCl_4 with tris-(trimethylsilyl)silane (241).

Irradiation of a benzene solution of 260 and trimethylsilane

To 0.4 ml of C_6D_6 was added 2.0 mmole of silole 218 and 2.0 mmole of dimethylacetylene dicarboxylate 257. After 9 hours, the absorptions due to 218 and 257 were almost gone and the absorptions due to the adduct 260 remain constant. Approximately 0.3 ml of trimethylsilane was added and the solution was degassed by the freeze-thaw method and sealed in a quartz NMR tube. Irradiation of this solution was carried out with a Hanovia 450 W high pressure lamp and followed by NMR. After 53 minutes the absorptions due to the adduct 260 were absent. The only volatile product observable by GC was the heptamethyltrisilane 259. which was identified by comparison of its retention time and its GC mass spectrum with those of an authentic sample. The yield was determined to be 5% by comparison of peak areas with a standard solution of 259.

Synthesis of 2-chloroheptamethyltrisilane 262

Compound 262 was prepared from tris-(trimethylsilyl)-methylsilane 251 as described by Harrell (217). A solution of 75 grams (0.286 moles) of 251 in 450 ml of CCl_4 was cooled to -25°C in a CCl_4/CO_2 bath. Chlorine gas was bubbled through the solution and the reaction was followed by NMR. When the amount of product reached a maximum, the addition of chlorine was stopped and the product isolated by distillation with a 25 cm vacuum jacketed column packed with glass helices:

yield 16 grams (25%), b.p. 84.5-86°C at 21 mm Hg; NMR (CCl_4) δ = 0.25 (s, 18H), δ = 0.52 (s, 3H); ^{29}Si NMR ($CDCl_3$) δ = 66.770 (2Si), δ = 92.085 (1Si); IR (neat) 2960, 2900, 1400, 1245, 835, 780 and 695 cm^{-1}; mass spectrum m/e (% rel. int.) 226 (2.3), 224 (5.5), 211 (2.2), 209 (5.2), 138 (3.2), 136 (8.4), 131 (15), 118 (7), 117 (13), 116 (68), 115 (6), 101 (29), 73 (100), 59 (14), 45 (41), 43 (23).

Pyrolysis of 262 at reduced pressure

Compound 262 was distilled slowly (0.15 mm Hg, 25°C) through a horizontal quartz tube that was packed with quartz chips and heated to 700°C. The pyrolysate was collected in a liquid nitrogen trap and represented an 83% mass recovery. Four major products were obtained. Trimethylsilane was the minor product and was identified by comparison of its GC mass spectrum with that of an authentic sample. The three major products were isolated by preparative GC on a 12' x 1/4" 20% DC-550 on Chromsorb P column at 80°C. Trimethylchlorosilane (42% GC yield) was identified by comparison of the NMR and GC mass spectrum with those of the authentic material. The second major product (28% GC yield) was identified as 1,1-dimethyl-1,3-disilacyclobutane 143 on the basis of its spectra: NMR (CCl_4) δ = 0.19 (T, 4H, J = 4.6 Hz, collapses to singlet upon hν at 4.50), δ = 0.30 (s, 6H), δ = 4.50 (quintet, 2H, J = 4.6 Hz, collapses to a singlet upon hν at 0.19); IR (neat) 2960, 2900, 2130, 1245, 950, 870, 835, 805 and 685 cm^{-1}; mass spectrum (24 eV) m/e (% rel. int.) 117 (16), 116 (100), 115 (22), 101 (89), 99 (11), 73 (24), 59 (17), 43 (3), calc. for $C_4H_{12}Si_2$ m/e 116.04776, measured 116.04541. The remaining product was identified as 1,3-dimethyl-1,3-disilacyclobutane 142 (15% GC yield) on the basis of its spectra: NMR (CCl_4) δ = 0.19 (T, 4H, J = 4.0 Hz, collapses to singlet upon hν at 4.75), δ = 0.40 (d, 6H, J = 3.7 Hz, collapses to singlet upon hν at 4.75), δ = 4.75 (m, 1H); IR (neat) 2960, 2900, 2110, 1345, 1250, 945, 880, 860 and 710 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 117 (16.5), 116 (95), 115 (27), 102 (14), 101 (100), 100 (12), 99 (22), 73 (33), 69 (11), 59 (23). The spectra of 142 and 143 compare well with those in the literature (25). The NMR spectrum for 142 is consistent with that expected for the trans isomer and weak absorption in the NMR may be due to the cis isomer. 1,1,3-Trimethyl-1,3-disilacyclobutane 149 is not a product of this reaction as indicated by a comparison of the GC retention times of the products of the pyrolysis with that of the authentic material.

Co-pyrolysis of 262 and 2-butyne

A mixture of 1.55 grams (0.0069 mole) of 262 and 3.73 grams of 2-butyne (0.0691 moles) was added dropwise to a vertical quartz tube that was packed with quartz chips and heated to 600°C. A 60 ml/minute sweep of nitrogen carried the products into a liquid nitrogen trap. Five compounds were identified from the pyrolysate. Trimethylchlorosilane (61% GC yield) was identified by comparison of its GC mass spectrum with that from an authentic sample. Three compounds were isolated by preparative GC on a 10' x 1/4" 20% DC-550 on Chromsorb P column at 100°C. One of these was identified as starting material **262** (28% GC yield) on the basis of its NMR and mass spectra. The second was determined to be 1,1,3,4,5-pentamethyl-1,3-disilacyclopentene **146** on the basis of its spectra: NMR (C_6D_6) δ = -0.48 (d of d, 1H, J = 15 Hz, J = 2.5 Hz, collapses to doublet upon hν at 4.70), δ = -0.06 (d of d, 1H, J = 15 Hz, J = 4 Hz, collapses to a doublet upon hν at 4.70), δ = 0.10 (s, 6H), δ = 0.17 (d, 3H, J = 4 Hz, collapses to a singlet upon hν at 4.70), δ = 1.74 (broad s, 6H), δ = 4.70 (m, 1H); IR (neat) 2950, 2900, 2850, 2090, 1245, 970, 930, 880, 850, 825, 780 and 730 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 170 (10), 156 (17), 155 (100), 131 (7), 127 (8), 116 (6), 73 (12), calc. for $C_8H_{18}Si_2$ m/e 170.09406, measured 170.09471, calc. for $C_5H_{11}Si_2$ m/e 127.03994, measured 127.04033. The spectra for **146** are the same as those for the same compound in the literature (95). The third product isolated from this pyrolysis has been tentatively identified as 3-exo-trimethylsilylmethylene-1-methyl-1-silacyclobutane **263** on the basis of its spectra: NMR (C_6D_6) δ = 0.01 (d, 3H, J = 4 Hz), δ = 0.07

(s, 9H), δ = 1.42 (AB quartet of multiplets, 4H), δ = 4.44 (m, 1H), δ = 6.27 (m, 1H, collapses to broad singlet upon hν at 1.42); IR (neat) 3010, 2960, 2900, 2130, 1580, 1245, 1140, 1090, 1000, 890, 835, 775 and 740 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 170 (17), 156 (16), 155 (100), 129 (10), 127 (18), 95 (13), 73 (42), 59 (14), calc. for $C_8H_{18}Si_2$ m/e 170.09471, measured 170.09187. The yields are based on the amount of reacted starting material. The yield of **263** was determined assuming that its response factor was the same as that of **146**. The co-pyrolysis of **262** and 2-butyne at 500°C resulted only in the recovery of starting materials. Hexamethyl-2-oxo-1,3-disilacyclopentene **38** was determined to be present in the pyrolysate by comparison of its GC mass spectrum with that of an authentic sample; however, its yield is less than 1% assuming that its response factor is the same as that of **146**.

Co-pyrolysis of **262** and benzaldehyde

A mixture of 0.00145 moles of **262** and 0.0145 moles of benzaldehyde was dropped into a vertical quartz tube that was packed with quartz chips and heated to 610°C. The pyrolysis products were swept into a liquid nitrogen trap with a nitrogen carrier gas at a rate of 45 ml/minute. The benzaldehyde was purified by passing through silica gel. *Trans*-stilbene (17% GC yield) was isolated by preparative GC on a 10' x 1/4" 20% DC-550 on Chromsorb P column at 220°C and was identified by comparison of its NMR and GC mass spectrum with those of an authentic sample. The cyclosiloxanes **151** and **152** (D_3 and D_4) were determined not to be present in the pyrolysate as determined by GCMS and by comparison of the retention times of the products of the pyrolysate with those of authentic samples of D_3 and D_4 on a 27' x 1/4" 15% SE-30 on Chromsorb W column at 120°C and on a 12' x 1/4" 20% DC-550 on Chromsorb P column at 97°C.

Co-pyrolysis of **262** with trimethylsilane and trimethyldeuterosilane

A 1.00 gram sample of **262** was dropped into a vertical quartz tube that was packed with quartz chips and heated to 630°C and through which a stream of trimethylsilane was swept at 60 ml/minute. The pyrolysate (1.04 grams) was collected in a liquid nitrogen trap. Trimethylchlorosilane (25% GC yield) and recovered starting material **262** (42% GC yield) were identified in the pyrolysate by comparison of their retention times and GC mass spectra with those of authentic samples. Five compounds, **259** and **264**-**267** were isolated by preparative GC on a 12' x 1/4" 20% SE-30 on Chromsorb W column at 67°C with retention times of 150, 160, 186, 201 and 204 minutes, respectively. All five compounds were found to be isomeric and correspond to adducts of trimethylsilylmethylsilylene and trimethylsilane. The yields are based on unrecovered starting material. The yields of **264**, **266** and **267** were calculated using the response factor for **265**. The spectra of these five compounds from both the pyrolysis with trimethylsilane and trimethyldeuterosilane are given below.

*1,1,1,2,3,3,3-Heptamethyltrisilane **259** (10% GC yield)*

The NMR, IR and mass spectra match those of an authentic sample. For **259D** obtained from the pyrolysis with Me_3SiD, the absorption at $\delta = 3.03$ in the NMR (C_6D_6) is absent. In the IR, the absorption at 2070 cm^{-1} is reduced by greater than 90% and a new absorption at 1505 cm^{-1} is observed. Compound **259D** has the following GC mass spectrum: (70 eV) m/e (% rel. int.) 191 (10), 191 (1), 176 (10), 131 (5), 116 (34), 103 (30), 101 (17), 73 (100), 59 (9).

*Compound **264** (4% GC yield)* This compound was not isolated from the pyrolysis with Me_3SiH; however, a GC mass spectrum was obtained: (70 eV) m/e (% rel. int.) 190 (3), 189 (2), 175 (13), 131 (7), 117 (13), 116 (14), 102 (30), 101 (14), 73 (100), 59 (12). Compound **264D** was isolated from the pyrolysis with Me_3SiD and was found to have the following spectra: NMR (C_6D_6) $\delta = -0.37$ (broad singlet, 2H), $\delta = 0.07$ (s, 9H), $\delta = 0.11$ (s, 9H); mass spectrum (70 eV) m/e (% rel. int.) 192 (5), 177 (17), 132 (7), 119 (8), 117 (9), 104 (41), 73 (100), 60 (9). In the NMR spectrum of **265**, a small triplet at $\delta = 3.75$ was noticed that was not due to 265. This could be from 264 since 264 and 265 overlap in the GC. This triplet collapses to a singlet upon irradiation at δ = -0.27. On the basis of the above data, compound 264 is tentatively assigned as 2,2,5,5-tetramethyl-2,3,5-trisilahexane.

2,2,3,5-Tetramethyl-2,3,5-trisilahexane 265 (17% GC yield The structure of 265 was assigned on the basis of the following spectra: NMR (C_6D_6) δ = -0.27 (m, 2H), δ = 0.13 (s, 9H), δ = 0.12 (d, 6H, J = 4.5 Hz), δ = 0.24 (d, 3H, J = 4.8 Hz), δ = 4.01 (sextet, 1H, J = 4.8 Hz), δ = 4.27 (nonet, 1H, J = 4.5 Hz); IR (neat) 2950, 2890, 2100, 2070, 1242, 1035, 885, 825, 795 and 680 cm^{-1}; mass spectrum (24 eV) m/e (% rel. int.) 190 (6), 189 (3), 175 (16), 131 (5), 118 (9), 117 (36), 116 (100), 115 (5), 102 (7), 101 (17), 73 (31), calc. for $C_7H_{21}Si_3$ m/e 189.09512, measured 189.09687. The absorptions at δ = 4.01 and 4.27 in the NMR were enhanced by averaging 16 scans on a Varian HA-100 NMR spectrometer with a Nicolet 535 signal averager with and without double irradiation at δ = -0.27. Without double irradiation, the absorption at 4.01 was found to consist of six lines with the relative intensities of 1.5:5.5:10:10:5.5:1.0 (1:5:10:10:5:1 expected for a sextet) and the absorption at δ = 4.27 was found to consist of seven lines with the relative intensities of 7.3:26:57:70:57:26:7.3 (for a nonet nine lines are expected with the relative intensities of 1:8:28:56:70:56:28:8:1).

With double irradiation at δ = -0.27, the absorption at δ = 4.01 was found to consist of four lines with relative intensities of 1.1:3:3:1.1 (1:3:3:1 expected for a quartet) and the absorption at δ = 4.27 was found to consist of seven lines with the relative intensities of 0.8:4.3:15:20:15:4.3: 0.8 (1:6:15:20:15:6:1 expected for heptet).

For 265D isolated from the pyrolysis with Me_3SiD, the sextet at δ = 4.01 was found to be less than 10% of the intensity of the nonet at δ = 4.27. In addition, the absorption at δ = 0.24 is now a singlet. In the IR, the absorption at 2070 cm^{-1} is absent, while that a 2100 cm^{-1} remains, and a new absorption at 1515 cm^{-1} is observed. Compound 256D was found to have the following mass spectrum: (70 eV) m/e (% rel. int.) 191 (5), 190 (6), 176 (12), 132 (7), 118 (50), 117 (94), 116 (93), 102 (34), 101 (37), 73 (100).

Compound 266 (4% GC yield) The spectra of 266 isolated from the pyrolysis with Me_3SiH are: NMR (C_6D_6) δ = -0.26 (m, 4H), δ = 0.08 (m, 15H), δ = 4.22 (m, 3H); GC mass spectrum (70 eV) m/e (% rel. int.) 189 (2), 175 (43), 131 (12), 117 (9), 116 (10), 115 (20), 101 (18), 73 (100), 59 (20). Compound 266D was not isolated from the pyrolysis with Me_3SiD; however, a GC mass spectrum was obtained: m/e (% rel. int.) 178 (26), 177 (37), 176 (21), 132 (11), 131 (28), 116 (19), 115 (11), 103 (8), 74 (58), 73 (100), 60 (10), 59 (12).

2,4,6-Trimethyl-2,4,6-trisilaheptane 267 (7% GC yield)

The structural assignment for 267 was made on the basis of the following spectra: NMR (C_6D_6) δ = -0.26 (T, 4H, J = 3.9 Hz), δ = 0.09 (d, 12H, J = 3.9 Hz), δ = 0.14 (d, 3H, J = 4.3 Hz), δ = 4.30 (m, 3H); mass spectrum (70 eV) m/e (% rel. int.) 189 (4), 188 (3), 175 (33), 173 (10), 129 (6), 117 (33), 115 (29), 101 (17), 73 (100), 59 (24). Spectra were obtained for 267D that were isolated from the pyrolysis with Me_3SiD: NMR (C_6D_6) the absorption at δ = 4.30 integrates to one hydrogen, indicating that two deuteriums have been incorporated; however, the silicon-methyl region is consistent with a mixture of isomers; IR (neat) 2950, 2890, 2100, 1530, 1245, 1040, 885, 825 and 795 cm^{-1}; GC mass spectrum (70 eV) m/e (% rel. int.) 191 (5), 190 (8), 189 (8), 188 (5), 178 (10), 177 (21), 176 (23), 175 (12), 130 (5), 129 (5), 119 (27), 118 (32), 117 (20), 116 (20), 115 (19), 102 (11), 101 (9), 74 (42), 73 (100), 60 (24), 59 (23).

Co-pyrolysis of 138 and trimethylsilane

Compound 138 was prepared according to the procedure published by Roark and Peddle (144), involving the addition of sodium naphthalide to 1,2-dichlorotetramethyldisilane. Compound 138 could not be completely separated from the excess naphthalene. A mixture of 0.426 grams of 138 and naphthalene that was 52% 138 by weight was dissolved in 0.2 ml of benzene and the resultant solution was dropped into a vertical quartz tube that was heated to 600°C and through which a stream of trimethylsilane was passed at a rate of 60 ml/minute. A liquid nitrogen trap contained 0.521 grams of a light yellow oil. The amount of naphthalene in the pyrolysate over that which was in the starting material represents a 66% yield of naphthalene as determined by GC. Five products were observed that by GCMS were all isomeric and that correspond to an adduct of trimethylsilane and tetramethyldisilene. These compounds were observed to have the same GC mass spectrums as the same five isomeric compounds obtained from the co-pyrolysis of **262** and Me_3SiH: **259** and **264**-**267**. The two major products were isolated by preparative GC on a 12' x 1/4" 15% SE-30 on Chromsorb W column at 72°C and were identified as **259** (17% GC yield) and **265** (17% GC yield) by comparison of their IR, NMR and mass spectra with those of authentic samples. The third major product was isolated by preparative GC under the same conditions and was identified as **267** (6% GC yield) by comparison of its NMR and mass spectra with those of an authentic sample. The two minor products were identified as **264** (3% GC yield) and **266** (3% GC yield) by observing that their GC mass spectra were the same as the corresponding products obtained from the pyrolysis of **262** and Me_3SiH. The yields are based on the amount of naphthalene formed and those for 264, 266 and 267 were calculated using the response factor determined for 265.

Co-pyrolysis of 262 and isoprene

Compound 262 was dissolved in a 10 mole excess of isoprene and the solution was dropped into a vertical quartz tube that was heated to 640°C and was being swept by a stream of nitrogen at 30 ml/minute. The pyrolysate was collected in a liquid nitrogen trap and represented a 78% mass recovery. Some starting material was recovered as determined by GCMS. GCMS also indicated that three products were formed, 270-272, in the relative ratios of 14:3.5:1.0 (assuming identical R_f's), that were all isomeric and that correspond to adducts of isoprene and $C_4H_{12}Si_2$. These three isomers were isolated by preparative GC on a 10' x 1/4" 20% DC-550 on Chromsorb P column at 120°C. Compound 270 was identified as 1-methyl-1-trimethylsilyl-2,3-dimethyl-1-silacyclopentene on the basis of its spectra: NMR (CCl_4) δ = 0.08 (s, 9H), δ = 0.16 (s, 3H), δ = 1.33 (m, 4H), δ = 1.79 (m, 3H), δ = 5.50 (m, 1H); GC mass spectrum (70 eV) m/e (% rel. int.) 184 (9), 170 (8), 169 (47), 141 (7), 116 (43), 111 (35), 110 (24), 109 (21), 101 (14), 95 (12), 85 (8), 83 (11), 73 (100), 59 (25). Compound 271 was identified as 1-methyl-1-dimethylsilylmethyl-2,3-dimethyl-1-silacyclopentene on the basis of the following spectra: NMR (CCl_4) δ = -0.10 (d, 2H, J = 4.4 Hz, collapses to singlet upon hν at 3.98), δ = 0.10 (d, 6H, J = 4.0 Hz, collapse to a singlet upon hν at 3.98), δ = 0.17 (s, 3H), δ = 1.24 (m, 4H), δ = 1.76 (m, 3H), δ = 3.98 (m, 1H), δ = 5.48 (m, 1H); GC mass spectrum (70 eV) m/e (% rel. int.) 184 (20), 169 (62), 156 (34), 143 (16), 142 (61), 141 (100), 129 (50), 127 (40), 116 (49), 115 (25), 113 (11), 111 (19), 109 (16), 101 (75), 99 (14), 95 (12), 85 (22), 83 (16), 73 (100), 71 (18), 69 (17), 59 (68). The NMR spectra of compound 272 was weak and possibly contaminated; however, the pattern of the silicon methyl absorptions and the absence of the appropriate allylic methylene absorption demonstrates that it is not 1,1,2,2,4-pentamethyl-1,2-disilacyclohex-4-ene 273, the NMR of which has been published (95). The NMR is most consistent with an acyclic butadienyl silane. Compound 272 has the following GC mass spectrum (70 eV) m/e (% rel. int.) 184 (16), 169 (66), 156 (30), 143 (16), 142 (56), 141 (100), 129 (34), 127 (36), 117 (33), 116 (38), 115 (18), 113 (12), 111 (16), 109 (15), 101 (54), 85 (24), 83 (15), 73 (100), 59 (62).

Synthesis of 3-chloro-2,2,3,5,5-pentamethyl-2,3,5-trisilahexane 274 (242)

A suspension of 7.97 grams (0.065 mole) of chloromethyldimethylsilane and 0.45 grams (0.065 mole) of lithium dispersion in ether was stirred at -20°C for 2.5 hours. The solution was warmed to room temperature and 10.0 grams

(0.053 mole) of 1,1-dichlorotetramethyldisilane 252 in ether was added and the solution stirred for 3 hours. Hexane was added and the resulting solution was filtered and stripped of solvent. GC analysis of the resulting oil revealed it to be a 1:1 mixture of 252 and 274. Compound 274 was isolated by preparative GC on a 10' x 1/4" 15% DC-550 on Chromsorb W column at 140-210°C at 6°C/minute, and the following spectra taken: NMR (CCl_4) δ = 0.11 (d, 20H), δ = 0.48 (s, 3H), the methylene H's fall under the Si-Me absorptions; mass spectrum (70 eV) m/e (% rel. int.) 238 (0.5), 235 (9), 233 (20), 203 (78), 189 (27), 167 (6), 165 (17), 147 (12), 145 (22), 130 (100), 115 (68), 73 (82), 59 (15).

Pyrolysis of 274 (242)

The pyrolysis of 0.97 grams of 274 is carried out by dropping it through a vertical quartz tube that is packed with quartz chips and heated to 600°C and through which a nitrogen carrier gas is passed at 30 ml/minute. The pyrolysate was collected in a liquid nitrogen trap and represents a 54% mass recovery. GC analysis indicates that all starting material is gone and that only two products are cleanly formed. These were isolated by preparative GC on a 10' x 1/4" 15% DC-550 on Chromsorb W column at 70°C. The more volatile product was identified as trimethylchlorosilane (48% GC yield) by comparison of its spectra with those from an authentic sample. The other product was identified as 1,1,3-trimethyl-1,3-disilacyclobutane 149 (39% GC yield) on the basis of its spectra: NMR (CCl_4) δ = -0.12 (m, 4H), δ = 0.06 (s, 6H), δ = 0.12 (d, 3H, J = 4.0 Hz, collapses to singlet upon hν at δ = 4.43), δ = 4.43 (m, 1H, J = 4.0 Hz, collapses to quartet upon hν at δ = -0.12); the GC mass spectrum is identical to that in the literature (25).

Synthesis of 1,2-divinyltetramethyldisilane 276

1,2-Dichloro-1,1,2,2-tetramethyldisilane was prepared by the photochemical coupling of dimethylchlorosilane (29). To a refluxing solution of vinylmagnesium bromide (200 ml THF, 0.24 mole Grignard reagent) was added, at a rate sufficient to maintain reflux, 20 g (0.107 mole) of the dichlorodisilane in 350 ml hexane. After completion of addition, the solution was cooled to 0°C, hydrolyzed with 5% HCl, the organic layer separated, washed with water and dried over Na_2SO_4. After removal of solvents, distillation yielded 8.5 g (51%) of 1,2-divinyl-1,1,2,2-tetramethyldisilane 276: b.p. 63-65° (35 mm); NMR (CCl_4) δ = 0.13 (s, 12H), 5.2 - 6.7 (vinyl mult., 6H); mass spectrum (m/e, % rel. int.) 156 (12), 155 (46), 127 (10), 95 (12), 85 (53), 73 (43), 71 (12), 59 (100), 58 (10).

Pyrolysis of **276**

The pyrolysis was conducted in a vertical one foot quartz tube filled with quartz chips and enclosed in a tube furnace. Disilane **276** was mechanically added at a rate of 2.2 ml/hour concomitant with a nitrogen flow of 26 ml/minute. With the temperature at 460°C there was no reaction, at 525°C there was *ca*. 20% conversion of **276**, and at 630°C only 4.4% of **276** remained in the product mixture. A single, sealed-tube pyrolysis at 238°C (7 hours) afforded no reaction. Analysis of the product mixture was conducted on a Varian Model 920 gas chromatograph with all products being isolated on a 12 ft, 20% DC-550/Chromsorb P column at 95°C. Yields were determined by gas chromatography using undecane as a standard. Response factors (RF) were determined for products **277**-**280** and **283**. For products **281** and **282**, the RF of **279** was assumed, for **284** the RF of **283** was used, and for **285**-**289** the RF of **276** was assumed valid. Products were largely identified by NMR spectra and gas chromatographic-mass spectra (GCMS). The instruments used respectively were a Varian HA-100 and a Finnegan Model 2000 quadrapole mass spectrometer.

Dimethylvinylsilane **277** NMR (CCl_4) δ = 0.15 (d, 6H, J = 7 Hz), 4.08 (m, 1H), 5.4 - 6.4 (vinyl m, 3H), spectrum identical to that of authentic sample prepared from $LiAlH_4$ reduction of dimethylethoxyvinylsilane; GCMS, m/e (% rel.

int.) 86 (11), 71 (37), 59 (32), 58 (100), 45 (37), 43 (37); yield, 2.4%.

Trimethylvinylsilane 278 NMR (CCl_4) δ = 0.06 (s, 9H), 5.4 - 6.4 (vinyl m, 3H); GCMS, m/e (% rel. int.) 100 (9), 85 (100), 73 (13), 59 (84), 43 (47), matched with spectrum of authentic material; yield, 2.8%.

Dimethyldivinylsilane 279 NMR (CCl_4) δ = 0.13 (s, 6H), 5.4 - 6.4 (vinyl m, 6H); GCMS, m/e (% rel. int.) 112 (<1), 97 (100), 59 (31), 43 (21); yield, 2.4%.

1,1,3,3-Tetramethyl-1,3-disilacyclobutane 280 NMR (CCl_4) δ = -0.02 (s, 4H), 0.27 (s, 12H); GCMS, m/e (% rel. int.) 144 (23), 130 (15), 129 (100), 101 (20), 73 (13), 59 (25), calc. for $C_6H_{16}Si_2$ m/e 144.07906, measured 144.07841; the IR spectrum matched the published spectrum (243), yield, 13.9%.

3,3-Dimethyl-3-silacyclopentene 281 NMR ($DCCl_3$) δ = 0.03 (s, 6H), 0.57 (m, 2H, CH_2 in ring α to Si), 2.38 (m, $2H_C$, allylic), 5.87 (d of t, $1H_A$, vinyl α to Si, J_{AB} = 11 Hz, J_{AC} = 2 Hz), 6.76 (d of t, $1H_B$, vinyl β to Si, J_{BC} = 3 Hz); GCMS, m/e (% rel. int.) 112 (12), 98 (11), 97 (100), 95 (26), 69 (10); yield, 1.7%.

4,4-Dimethyl-4-silacyclopenten 282 NMR ($CDCl_3$) δ = 0.02 (s, 6H), 1.17 (broad s, 4H), 5.82 (broad s, 2H); GCMS, m/e (% rel. int.) 112 (31), 98 (11), 97 (100), 95 (26), 71 (13), 59 (15), 58 (30), 55 (11); yield, 2.5%.

3,3,5,5-Tetramethyl-3,5-disilacyclopentene **283** NMR ($CDCl_3$) δ = -0.38 (s, 2H), 0.16 (s, 12H), 7.15 (s, 2H); GCMS, m/e (% rel. int.) 156 (29), 143 (13), 141 (100), 113 (15), 73 (25), 63 (17), 59 (17), 45 (14), 43 (23); yield, 3.5%. Both the NMR and mass spectra match those published by Fritz and coworkers (244).

1,1,3,3-Tetramethyl-1,3-disilacyclopentane **284** NMR (CCl_4) δ = -0.48 (s, 2H), 0.08 (s, 12H), 0.63 (s, 4H); GCMS, m/e (% rel. int.) 158 (25), 144 (14), 143 (85), 130 (34), 115 (100), 73 (27), 59 (33); yield, 0.8%. Both the NMR and mass spectrum match those published by Fritz and Götz (245).

1,1,3,3-Tetramethyl-1,3-disila-2-methylidenecyclopentane **285** NMR ($CDCl_3$) δ = -0.02 (s, 12H), 0.65 (s, 4H), 6.34 (s, 2H); GCMS, m/e (% rel. int.) 171 (11), 170 (61), 155 (91), 142 (28), 129 (24), 127 (100), 97 (25), 96 (21), 95 (31), 85 (27), 83 (23), 73 (87), 59 (63), 45 (26), 43 (50); IR (neat) 3040, 2955, 2910, 1590, 1240, 830 and 775 cm^{-1}; yield, 2.1%.

3,3,4,5,5-Pentamethyl-3,5-disilacyclopentene **286** NMR ($CDCl_3$) δ = -0.27 (q, $1H_A$, J_{AB} = 8 Hz), -0.06 (s, 6H), 0.00 (s, 6H), 0.92 (d, $3H_B$, Me, hν at -0.27 collapses to singlet), 7.02 (s, 2H); GCMS, m/e (% rel. int.) 170 (32), 156 (17), 155 (100), 127 (49), 95 (50), 73 (47), 59 (50), 45 (16), 43 (31); IR (neat) 2960, 1250, 830 and 785 cm^{-1}; yield, 2.0%.

3,3,6,6-Tetramethyl-3,6-disilacyclohexene 287 NMR ($CDCl_3$) δ = 0.05 (s, 12H), 0.82 (s, 4H), 6.84 (s, 2H); GCMS, m/e (% rel. int.) 170 (45), 156 (12), 155 (90), 142 (20), 129 (28), 128 (18), 127 (100), 97 (62), 96 (74), 95 (61), 73 (83), 59 (72), 58 (20), 55 (16), 45 (25), 43 (59); IR (neat) 2950, 2920, 2900, 1410, 1245, 1050, 820, 780 and 685 cm^{-1}; ^{13}C-NMR, δ = -2.27, 7.74, 150.68; yield, 1.9%.

3,3,5,5-Tetramethyl-3,5-disilacyclohexene 288 NMR ($CDCl_3$) δ = -0.19 (s, 2H), 0.06 (s, 6H), 0.08 (s, 6H), 1.32 (d of d, 2 H_C, allylic CH_2), 5.51 (d of t, 1 H_A, $=CH_A-Si$, J_{AC} = 1.4 Hz), 6.73 (d of t, 1 H_B, $CH_B = CH_A-Si$, J_{BC} = 5.4 Hz, J_{AB} = 15 Hz), hν at δ 1.32 collapses both H_A and H_B to doublets, J = 15 Hz; GCMS, m/e (% rel. int.) 170 (37), 156 (25), 155 (100), 142 (23), 129 (24), 128 (10), 127 (68), 95 (33), 73 (40), 59 (44), 45 (21), 43 (36); both NMR and mass spectra match those published by Fritz and Götz (245); IR (neat) 3040, 2960, 2900, 1580, 1245, 1020, 860, 830, 805 and 785 cm^{-1}; yield, 2.1%.

3,3-Dimethyl-3-sila-4-dimethylsilylcyclopentene 289 NMR (C_6D_6) δ = 0.07 (d, 6H, J = 4 Hz), 0.20 (s, 6H), 2.47 (m, 2 H_B, allylic CH_2, J_{AB} = 9 Hz, H_A methine H is hidden by SiMe's as hν at 0.10 reduces $H_{BB'}$ to AB quartet of triplets), 4.22 (m, 1H, Si-H_E, J_{E-SiMe} = 4 Hz), 6.08 (d of t, 1 H_D, $CH_C=CH_D-Si$, J_{CD} = 10 Hz, J_{BD} = 3 Hz, hν at 2.47 collapses both H_D and H_C to doublets J = 10 Hz), 6.85 (d of t, 1 H_C,

J_{BC} = 2 Hz, J_{CD} = 10 Hz); GCMS, m/e (% rel. int.) 170 (10), 156 (19), 155 (100), 129 (36), 128 (7), 127 (43), 97 (24), 96 (80), 95 (77), 73 (68), 59 (84); IR (neat) 3040, 2970, 2920, 2110, 1570, 1250, 1035, 990, 890, 845 and 775 cm^{-1}; yield, 1.4%.

Co-pyrolysis of **276** and benzaldehyde

A solution of **276** dissolved in a six-molar excess of benzaldehyde was pyrolyzed, as described above, with an addition rate of 2.2 ml/hour, a nitrogen flow of 20 ml/min, and a furnace temperature of 630°C. Gas chromatographic analysis was performed as described above and response factors (RF) were obtained for all products. Yields are based on unrecovered **276** and an assumed 1:1 stoichiometry. The products and yield were **277** (2.0%), **278** (1.5%), **279** (7.9%), **280** (3.9%), hexamethylcyclotrisiloxane (3.6%), **276** (11.9%), octamethylcyclotetrasiloxane (4.3%) and styrene (20.2%). An undetermined amount of benzene from decarbonylation of benzaldehyde was also observed. All peaks in the GC trace matched the retention times of authentic samples. Only styrene was actually isolated for NMR analysis.

Co-pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane and 3,3-dimethyl-3-silacyclobutene

Dimethylsilete (prepared by the method of Block and Revelle (117) was dissolved in a three-fold molar excess of dimethoxytetramethyldisilane (223) and pyrolyzed in a vertical-flow system (2.2 ml/hr, N_2-flow 25 ml/min, 620°C). Mass recovery was 82%. Only one peak in the GC trace was near the retention time of 283 and this compound was shown by NMR not to be 283.

Synthesis of ethynylmethylsilane 301

To 100 ml of THF at 0°C that was saturated with acetylene was added 0.216 moles of ethyl magnesium bromide in THF. Acetylene was bubbled through the solution during addition and the resulting ethynyl Grignard solution was added to a solution of 0.60 moles of $MeSiCl_3$ in 200 ml of THF at 0°C. The solution was stirred for a few hours at room temperature, then 150 ml of toluene was added and all of the volatiles collected up to 110°C. These volatiles were redistilled through a 25 cm column packed with glass helices and a fraction collected from 75-85°C that by NMR is a mixture of 4.4 grams (15%) of methyldichloroethynylsilane and 1.8 grams of THF. This fraction has the following spectral absorptions due to methyldichloroethynyl silane: NMR (CCl_4) $\delta = 0.93$ (s, 3H), $\delta = 2.90$ (s, 1H); IR (CCl_4) 3280, 3190 and 2040 cm^{-1}.

A solution of 1.45 grams of the fraction, 3 ml of THF and 0.27 grams of lithium aluminum hydride was mixed at 0°C in a flask that was connected *via* a closed system to an NMR tube containing CCl_4 at -78°C. After 2 hours, 0.5 ml of water was added *via* septum, and after the pressure was released, the flask was warmed to 40°C. Ethynylmethylsilane was collected in the NMR tube over a period of 4 hours and the following spectra obtained: NMR (CCl_4) $\delta = 0.35$ (t, 3H, J = 4.5 Hz, collapses to a singlet upon hν at $\delta = 4.05$), $\delta = 2.35$ (t, 1H, J = 1 Hz, collapses to a singlet upon hν at $\delta = 4.05$), $\delta = 4.05$ (quartet of doublets, 2H, J = 4.5 Hz, J = 1 Hz, collapses to quartet upon hν at $\delta = 2.35$); IR (CCl_4) 3295, 2970, 2155, 2025 (weak), 1250, 1060, 940, 890, 700, 670 and 600 cm^{-1}; GC mass spectrum (70 eV) m/e (% rel. int.) 70 (38), 69 (33), 68 (10), 55 (100), 54 (25), 53 (60), 45 (27), 44 (54), 43 (40).

Synthesis of 1,1-divinyltetramethyldisilane 295

To a refluxing solution of 0.12 moles of vinyl magnesium bromide in 100 ml of THF was added 10.0 grams (0.0535 moles) of 1,1-dichlorotetramethyldisilane 252 in 150 ml of hexane at a rate sufficient to maintain reflux. The solution was maintained at reflux for 5 hours after addition, then cooled and hydrolyzed with 5% HCl, washed with water and dried with sodium sulfate. After removal of solvent, distillation gave 4.1 grams (45%) of 252 collected at 74-77.5°C/57 mm and with the following spectra: NMR (CCl_4) $\delta = 0.08$ (s, 9H), $\delta = 0.18$ (s, 3H), $\delta = 5.4 - 6.6$ (m, 6H); IR (neat) 3050, 3005, 2950, 2895, 1625, 1580, 1400, 1240, 1005, 940, 855, 830, 775 and 715 cm^{-1}; GC mass spectrum (70 eV) m/e

(% rel. int.) 170 (1), 156 (11), 155 (100), 97 (16), 95 (12), 85 (42), 73 (77), 71 (19), 59 (39).

Pyrolysis of 295

A 0.500 gram sample of 295 was evaporated (25°C, 5×10^{-4} torr) through a horizontal quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a liquid nitrogen trap and analysis by GCMS revealed that only two products were formed. These were identified as trimethylvinyl silane and trimethylsilane (3:1 ratio) by comparison of their mass spectra with those of authentic samples. An NMR spectrum of the pyrolysate reveals the presence of a weak triplet at $\delta = 2.35$ and a weak quartet of doublets at $\delta = 4.05$ consistent with the presence of a trace amount of ethynylmethylsilane 301. In a pyrolysis of 295 at 635°C in a vertical quartz tube swept with nitrogen, the major products are also trimethylsilane and trimethylvinylsilane and in the same ratio; however, no evidence for 301 was obtained.

Photolysis of 295

A solution of 0.50 grams of 295 in 2.5 ml of methanol (distilled from BaO) and 2.5 ml of benzene was degassed in a quartz tube by purging with argon. The solution was irradiated with a 450 Watt high pressure mercury lamp and the reaction followed by GC. After 21 hours, 50% conversion of starting material is observed with formation of only two products, 307 and 308 (2:5 ratio), in near quantitative yield as indicated by NMR. Both products were isolated by preparative GC on a 10' x 1/4" 20% DC-550 on Chromsorb P column at 190°C. Compound 308 was identified as 1-trimethylsilyl-2-methylmethoxyvinylsilylethane on the basis of the following spectra: NMR (CCl_4) $\delta = 0.0$ (s, 9H), $\delta = 0.15$ (s, 3H), $\delta = 0.49$ (broad singlet, 4H), $\delta = 3.44$ (s, 3H), $\delta = 5.6 - 6.2$ (m, 3H); GC mass spectrum (70 eV) m/e (% rel. int.) 188 (18), 187 (100), 175 (4), 174 (4), 159 (7), 157 (5), 155 (7), 133 (9), 129 (19), 101 (65), 97 (19), 89 (37), 75 (27), 73 (48), 71 (23), 59 (76). Compound 307 was identified as 1-trimethylsilyl-1-methylmethoxyvinylsilylethane on the basis of the following spectra: NMR (CCl_4) $\delta = -0.05$ to 0.25 (m, 13H), $\delta = 1.07$ (d of d, 3H, $J = 8$ Hz, $J = 2$ Hz), $\delta = 3.42$ (s, 3H), $\delta = 5.6 - 6.2$ (m, 3H); GC mass spectrum (70 eV) m/e (% rel. int.) 202 (1), 187 (23), 174 (4), 173 (3), 159 (6), 101 (100), 89 (24), 86 (12), 75 (23), 73 (42), 71 (16), 59 (36).

Reaction of 1-trimethylsilyl-1-methyl-2,5-diphenylsilole 218 and diphenylacetylene

A mixture of 0.162 grams (0.506 mmole) of 218 and 0.090 grams (0.506 mmole) of diphenylacetylene was heated in an NMR tube that had been flushed with argon and sealed with a septum for 12 hours at 150°C. CCl_4 was added and the NMR indicated only the presence of 324 and starting materials. The CCl_4 was removed and the residue was dissolved in hexane and chromatographed on silica gel. Unreacted starting materials quickly eluted with hexane. The product was eluted with 5% Et_2O/hexane, and after removal of solvent a colorless oil was obtained that had a striated appearance. Spectral analysis revealed that this oil was pure 324 (0.165 gram, 63%). The product could also be isolated and purified from the crude reaction mixture by two crystallizations from hexane to give a white solid (31%, m.p. 164-168°C) that had the following spectra: NMR (CCl_4) δ = -0.07 (s, 9H), δ = 1.01 (s, 3H), δ = 4.67 (d, J = 5.6 Hz, collapses to singlet upon hν at 7.75 and vice versa), δ = 6.5 - 7.4 (m, 20H), δ = 7.75 (d, J = 5.6 Hz); ^{29}Si NMR ($CDCl_3$) δ = 82.636, δ = 88.671; IR (KBr) 3090, 3070, 3060, 3030, 2950, 1605, 1500, 1490, 1445, 1250, 955, 890, 840, 760 and 700 cm^{-1}; mass spectrum (70 eV) (% rel. int.) 498 (18), 320 (50), 305 (50), 247 (22), 205 (13), 177 (12), 172 (71), 157 (12), 145 (38), 143 (10), 135 (33), 129 (100), 128 (30), 127 (19), 105 (55), 73 (76), calc. for $C_{34}H_{34}Si_2$ m/e 498.21992, measured 498.22007. Based on the above spectra, the white solid was tentatively identified as 1-methyl-2,3,6,7-tetraphenyl-7-trimethylsilyl-1-silanorbornadiene 324. This was confirmed by E. V. Arnold and J. Clardy at Cornell University when they carried a single crystal x-ray determination of the product from this reaction (229). When 218 and diphenylacetylene are heated for 2 hours at 150°C, a 3:3:2 mixture of 218:324:328 was obtained.

Thermolysis of siloles 218, 237a, and 237b

A Pyrex tube containing 0.406 grams of 218 was degassed and sealed. The tube was heated for 42 hours at 110°C. An NMR spectrum was taken of the contents of the tube and found to be consistent with a 1:2 mixture of silole 218 and a dimer of 218. The CCl_4 was removed and the residue chromatographed on silica gel. The column was eluted with hexane which after evaporation left a yellow oil. Crystallization from methanol gave 0.158 grams of a white solid (m.p. 186.5-188°C) that had the following spectra: NMR (CCl_4) $\delta = -0.78$ (s, 9H), $\delta = -0.24$ (s, 9H), $\delta = 0.03$ (s, 3H), $\delta = 1.18$ (s, 3H), $\delta = 4.02$ (t, overlapped d of d, H_B, $J_{AB} = J_{BX} = 5$ Hz), $\delta = 4.35$ (d of d, H_A, $J_{AY} = 2.5$ Hz, $h\nu$ at $\delta = 6.59$ collapses to d), $\delta = 5.9$-7.35 (m, 22H, ArH + H_X + H_Y); mass spectrum (70 eV) m/e (% rel. int.) 640 (2), 321 (32), 320 (100), 306 (24), 305 (79), 247 (11), 227 (12), 145 (20), 135 (23), 105 (19), 73 (59), calc. for $C_{40}H_{48}Si_4$ m/e 640.28333, measured 640.28233. On the basis of the above spectra, and by analogy to the structure of the diphenylacetylene adduct 324 (known from x-ray diffraction), the dimer of 218 was assigned the structure 328 (see page 168 of this thesis).

If silole 218 is heated (neat) at 150°C for 9 hours, a 1.1:1.0 ratio of 218:328 is obtained that remains unchanged with continued heating. Equilibrium was established by heating separately samples of 218 and 328 for 24 hours at 150°C (both were heated briefly at 190°C to allow 328 to melt) and finding that both gave a 1.1:1.0 mixture of 218:328 as determined by NMR. The equilibrium ratio of 218:328 was found to be reached after heating 218 for 65 minutes at 150°C. After heating 218 for 10 minutes at 150°C, the ratio of 218:328 was 4.5:1.0. A solution of 0.122 grams of 218 in diphenylether was degassed and sealed in an NMR tube. Equilibration was followed in the NMR at 160°C and all of the absorptions observed were attributable to either 218 or 328. Thermal dimerization was not observed for 1,1-dimethyl-2,5-diphenylsilole 237b or for 1-methyl-2,5-diphenylsilole 237a. When either 237a or 237b were heated in a degassed, sealed tube for 16 hours at 150°C, no change could be observed by NMR.

Reaction of 1,1-dimethyl-2,5-diphenylsilole 237b with diphenylacetylene

Diphenylacetylene (0.679 grams, 0.0038 moles) and 237b (1.00 grams, 0.0038 moles) were degassed and sealed in a tube which was heated at 150°C for 7 days. The contents of the tube was crystallized from $CHCl_3$/hexane to give 0.117 grams of a light yellow solid which had an NMR spectrum consistent with that published for 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene 325 (21). The solvent was removed and the residue was crystallized from acetone to give 0.503 grams (30%) of a white solid (m.p. 175-188°C) that was identified as 1,2,3,4-tetraphenyl-7,7-dimethyl-7-silanorbornadiene 326: NMR (CCl_4) δ = 0.17 (s, 3H), δ = 0.64 (s, 3H), δ = 6.4 - 7.1 (m, 20H), δ = 7.41 (s, 2H). The NMR spectrum of the crude reaction mixture is devoid of absorptions between δ = 0.64 and 6.40, and is consistent with a 4:1:8 mixture of 237b:325:326.

Reaction of silole 218 with benzaldehyde

A solution of 0.225 grams of 218 (0.703 mmole) and 0.074 grams (0.703 mmole) of benzaldehyde (purified by passing through silica gel) in 2.5 ml of dry benzene was degassed and sealed in a tube which was heated at 150°C for 16 hours. The tube was opened and the solvent replaced by CCl_4. The NMR spectrum is consistent with quantitative formation of 1-methyl-2-oxo-3,6,7-triphenyl-7-trimethylsilyl-1-silanorborn-5-ene 329: NMR (CCl_4) δ = -0.10 (s, 9H), δ = 1.12 (s, 3H), δ = 4.02 (d of d, 1H, collapses to doublet (J = 5.6 Hz) upon hν at δ = 5.09, collapses to a doublet (J = 2.6 Hz) upon hν at δ = 6.54), δ = 5.09 (d, 1H, J = 2.6 Hz, hν at δ = 4.02 gives a singlet), δ = 6.54 (d, 1H, J = 5.6 Hz, hν at δ = 4.02 gives a singlet), δ = 6.8 - 7.3 (m, 15H). Adduct 329 decomposed when exposed to silica gel and resisted attempts at crystallization. If the reaction is carried out with a large excess of benzaldehyde, the NMR spectrum of the reaction mixture becomes exceedingly complex.

Reaction of silole 218 with benzophenone

A solution of 0.152 grams (0.475 mmole) of 218 and 0.086 grams (0.475 mmole) of benzophenone in 2 ml of dry benzene was degassed and sealed in a tube which was heated at 150°C for 10 hours. The solvent was removed and the residue crystallized from hexane to give 0.145 grams (61%) of a white solid (m.p. 188-189.5°C) that was identified as 1-methyl-2-oxo-3,3,6,7-tetraphenyl-7-trimethylsilyl-1-silanorborn-5-ene 330 on the basis of the following spectra: NMR (CCl_4) δ = -0.23 (s, 9H), δ = 1.4 (s, 3H), δ = 4.77 (d, 1H, J = 5 Hz, hν at δ = 6.83 gives a singlet), δ = 6.3 - 7.5 (m, 21H, ArH + H_X); IR (KBr) 3080, 3050, 3020, 2990, 2950, 1595, 1490, 1440, 1245, 885, 830, 755 and 695 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 502 (100), 429 (13), 247 (9), 227 (31), 105 (13), 77 (9), 73 (83), calc. for $C_{33}H_{34}OSi_2$ m/e 502.21483, measured 502.21658. The NMR spectrum of the crude reaction indicates a near quantitative formation of 330. The assignment of the stereochemistry of the trimethylsilyl group was made assuming it would be the same as in the diphenylacetylene adduct 324 for which it is known from x-ray diffraction studies.

Synthesis of 1-methyl-1-trimethylsilyldibenzosilole 331

To a solution of 11.64 grams (0.0373 moles) of α,α'-dibromobiphenyl (246) in 125 ml of ether at 0°C was added 0.0746 moles of n-butyl lithium. After stirring for 4 hours at room temperature, 6.98 grams (0.0373 moles) of 1,1-dichlorotetramethyldisilane in 50 ml of ether was added quickly. The organic solution was stirred for one hour, hydrolyzed with 1% HCl, washed with saturated sodium chloride solution and dried with sodium sulfate. After removal of solvent, the residue was chromatographed on silica gel. After elution with hexane, the solvent was removed to leave 8.9 grams (90%, m.p. 56-62°C) of 331: NMR (CCl_4) $\delta = 0.04$ (s, 9H), $\delta = 0.41$ (s, 3H), $\delta = 6.9 - 7.8$ (m, 8H); mass spectrum (20 eV) m/e (% rel. int.) 268 (31), 253 (13), 195 (100), 165 (14), 73 (39), calc. for $C_{16}H_{20}Si_2$ m/e 268.11036, measured 268.10794.

Reaction of silole 331 with benzaldehyde

A small amount of 331 and an excess of benzaldehyde (purified by passing through silica gel) were put in an NMR tube and the solution flushed with argon and then heated to 150°C for 22 hours. An NMR spectrum of the contents of the tube indicated that no reaction had occurred.

Reaction of silole 218 with methanol

A solution of 0.196 grams (0.613 mmoles) of 218 and 0.158 grams (4.94 mmoles) of methanol (distilled from BaO) in 2 ml of benzene (distilled from LAH) was degassed and sealed in a tube which was heated to 146°C for 4 hours. The tube was opened and the solvent replaced by CCl_4. The NMR spectrum indicated a 1.25:1.0 ratio of two methanol adducts of 218 which resisted all attempts at crystallization. Separation was effected by HPLC on a C-18 μ-Bondapak column with 85% aqueous methanol. The major product was identified as 1-methyl-1-methoxy-2,5-diphenyl-2-trimethylsilylsilacyclopent-3-ene 333 on the basis of its spectra: NMR (CCl_4) δ = -0.03 (s, 9H), δ = 0.06 (s, 3H), δ = 2.89 (s, 3H), δ = 3.42 (m, 1H, collapses to singlet upon hν at δ = 6.33, absent when MeOD is employed as reactant), δ = 6.33 (center of two overlapped d of d, 2H, J_{AB} = J_{BX} = 1.7 Hz, J_{AB} = 8 Hz, collapses to AB quartet upon hν at δ = 3.42 or when MeOD is employed as reactant), δ = 7.01 - 7.24 (m, 10H); mass spectrum (70 eV) m/e (% rel. int.) 352 (20), 337 (6), 278 (10), 264 (9), 249 (24), 248 (100), 247 (7), 234 (10), 233 (8), 145 (8), 105 (8), 89 (6), 75 (11), 73 (58), calc. for $C_{21}H_{28}Si_2O$ m/e 352.16788, observed 352.16673; IR (CCl_4) 3090, 3070, 3030, 2970, 2850, 1595, 1495, 1250, 1185, 1090, 925, 840 and 700 cm^{-1}. The minor product was identified as

1-methyl-1-methoxy-2,5-diphenyl-2-trimethylsilylsilacyclopent-4-ene **334** on the basis of its spectra: NMR (CCl_4) δ = -0.08 (s, 9H), δ = 0.60 (s, 3H), δ = 2.80 (s, 3H), δ = 3.10 (m, 2H, collapses to apparent doublet J = 0.8 Hz upon $h\nu$ at δ = 7.08, with MeOD as reactant is observed as a broad doublet J = 2.0 Hz which collapses to a broad singlet upon $h\nu$ at δ = 7.08), δ = 7.0 - 7.45 (m, 11H); mass spectrum (70 eV) m/e (% rel. int.) 352 (15), 337 (4), 278 (15), 249 (24), 248 (100), 234 (9), 233 (10), 145 (5), 121 (6), 105 (6), 89 (6), 75 (8), 73 (55), 59 (19), calc. for $C_{21}H_{28}Si_2O$ m/e 352.16788, observed 352.1652; IR (CCl_4) 3080, 3060, 3030, 2965, 2840, 1595, 1490, 1265, 1250, 1085, 840 and 700 cm^{-1}.

The relative amounts of **333** and **334** were found to be dependent upon the concentration of methanol. A series of reactions of **218** and methanol were carried out in which a constant amount of the silole **218** (0.090 grams, 0.281 mmole) and varying amounts of methanol were reacted. The concentration of **218** was held constant in each case by dilution to a total solution volume of 2.0 ml with benzene. For each run the solution was degassed and sealed in a heavy walled glass tube which was heated at 145°C for 8 hours. The ratio of **333**:**334** was determined from the crude reaction mixture by integration of the methoxyl absorptions at δ = 2.80 and δ = 2.89. The following ratios of **333**:**334** were observed:

1 equiv. of MeOH, 2.6:1.0; 5 equiv. of MeOH, 1.3:1.0; 8 equiv. of MeOH, 1.25:1.0; 12 equiv. of MeOH, 1.2:1.0; 25 equiv. of MeOH, 1.5:1.0; 125 equiv. of MeOH, 2.4:1.0.

Adducts **333** and **334** were shown not to interconvert by the following experiments. A solution of 0.061 grams (0.19 mmole) of 218 and 0.0486 grams (1.52 mmoles) of methanol in 1.0 ml of diphenyl ether was degassed and sealed in an NMR. The tube was heated at 146°C and was periodically removed and cooled to room temperature and the NMR spectrum recorded. The absorptions due to **334** and **333** were observed to grow simultaneously throughout the course of the reaction (complete in 2 hours). In a different experiment, a 2.4:1.0 mixture of **333**:**334** was heated with 8 equivalents of methanol at 145°C for 3 hours and the resultant ratio of **333**:**334** remained unchanged.

Reaction of **328**, the thermal dimer of silole **218**, with methanol

A solution of 0.046 grams of **328**, 2 ml of methanol, and 1 ml of benzene was degassed and sealed in a heavy walled tube. Likewise, a tube was sealed containing 0.046 grams of **218** in 2 ml of methanol and 1 ml of benzene. The tubes were heated at 140°C for 5 hours. After replacing the solvent by CCl_4, the NMR spectrum of each reaction indicated the formation of a 2.0:1.0 mixture of **333**:**334**.

The reaction of silole 218 with cis-stilbene

A mixture of 0.119 grams (0.372 mmole) of 218 and 0.067 grams (0.372 mmole) of cis-stilbene was degassed and sealed in a tube which was heated at 148°C for 27 hours. The reaction mixture was chromatographed on silica gel. Upon elution with hexane, small amounts of unreacted starting materials were removed from the column. Further elution with hexane gave (after removal of solvent) 0.128 grams (69%) of oil that proved to be a pure sample of the adduct 341. This oil was crystallized from ethanol/water to give white crystals (m.p. 117.5-119°C). These crystals were identified as 1-methyl-2,3,6,7-tetraphenyl-7-trimethylsilyl-1-silanorborn-5-ene 341 on the basis of its spectra: NMR (CCl_4) δ = -0.11 (s, 9H), δ = 0.85 (s, 3H), δ = 3.01 (d, H_A, J = 11 Hz, collapses to singlet upon hν at 7.5), δ = 4.17 (m, H_B and H_C, simultaneous irradiation at δ = 3.01 and δ = 7.50 produces an AB quartet, J_{BC} = 3.5 Hz), δ = 6.39 - 7.57 (m, 21H, ArH + d at δ = 7.5, H_X, J_{CX} = 5 Hz, collapses to singlet when hν at δ = 4.25); mass spectrum (70 eV) m/e (% rel. int.) 500 (0.2), 321 (32), 320 (100), 306 (16), 305 (53), 247 (12), 145 (18), 135 (19), 105 (24), 73 (64), calc. for $C_{34}H_{36}Si_2$ m/e 500.23557, measured 500.23530; IR (KBr) 3070, 3050, 3020, 2960, 2940, 2930, 2900, 1590, 1485, 1440, 1255, 1240, 1180, 1070, 1025, 950, 880, 860, 820, 740 and 690 cm^{-1}. The stereochemistry of the trimethylsilyl group was assumed to be the same as that for the diphenylacetylene adduct 324. The coupling constant of 11 Hz for the olefin derived hydrogens is most consistent with that expected for exo-cis hydrogens (231). The absence of any absorption at δ = 2.62 in the NMR indicates that the trans-adduct 340 was not formed in this reaction. The NMR spectrum of the crude reaction mixture indicates a near quantitative formation of only one isomer of 341.

The reaction of silole 218 with trans-stilbene

The reaction was carried out in accordance with the procedure described for the reaction of 218 with cis-stilbene. An NMR spectrum of the reaction mixture was taken; (CCl_4) δ = -0.17 (s, 9H), δ = 0.80 (s, 3H), δ = 2.62 (d, 1H, J = 7 Hz), δ = 3.99 (m, 2H), δ = 6.34 (m. 1H), δ = 6.8-7.8 (m, 20H). This spectrum is consistent with the formation of 1-methyl-2,3,6,7-tetraphenyl-7-trimethylsilyl-1-silanorborn-5-ene 340. The coupling constant of 7 Hz for the olefin hydrogens is consistent with that expected for a trans-relationship (231). The absence of any absorption at δ = 3.01 in the NMR indicates that the cis-adduct 341 is not formed in this reaction.

Irradiation of 218 with and without methanol

A solution of 0.138 grams (0.43 mmole) of 218 and 0.079 grams (2.47 mmole) of methanol in 1.0 ml of C_6D_6 was degassed in an NMR tube by purging with argon. The photolysis of this solution with a 450 Watt high pressure mercury lamp was followed by NMR and was observed to be complete after 93 minutes. The NMR indicated that several products were formed and the major product was isolated (0.033 grams, 24%) by crystallization from hexane as a white solid (m.p. 209-211°C). This solid was identified as **342**, the 2+2 cyclodimer of 218, on the basis of its spectra: NMR (CCl_4) δ = -0.52 (s, 18H), δ = 0.42 (s, 6H), δ = 4.29 (d, 2H, J = 4 Hz), δ = 6.7-7.4 (m, 22H); mass spectrum (70 eV) m/e (% rel. int.) 625 (0.4), 320 (100), 305 (60), 177 (8), 145 (15), 135 (18), 105 (11), 73 (25), calc. for $C_{39}H_{45}Si_4$ m/e 625.25984, measured 625.26168. The NMR spectrum of **342** is quite similar to that for the 2+2 cyclodimer of 1,1-dimethyl-2,5-diphenylsilole (232). When irradiation of **218** was carried out in a similar manner without methanol, it was found that the NMR spectrum of the crude reaction mixture matched that from the photolysis with methanol. No products were identified from the photolysis of **218** under dilute conditions (0.11 grams in 200 ml of benzene or cyclohexane) with or without added methanol. The residue from these photolysis was an entractable material that was not soluble in common solvents.

Reaction of silole **218** with iron pentacarbonyl

A mixture of 0.108 grams of **218** and a five-fold excess of iron pentacarbonyl was degassed and sealed in a tube that was heated at 148°C for 12 hours. The reaction mixture was passed through a silica gel column with hexane. The red band was collected and the solvent removed to leave 0.219 grams of a red semi-solid which was crystallized from alcohol to give 0.092 grams of bright red crystals (59%, m.p. 128.5-129.5°C) that were identified as 344, the iron tricarbonyl diene complex of silole 218, on the basis of its spectra: NMR (CCl_4) δ = -0.12 (s, 9H), δ = 1.20 (s, 3H), δ = 6.07 (s, 2H), δ = 7.14 (m, 10H); IR (CCl_4) 3060, 3030, 2960, 2900, 2045, 1978, 1595, 1495, 1255, 1245, 1035, 860 and 695 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 460 (2.8), 432 (6), 376 (49), 336 (31), 320 (57), 305 (67), 263 (42), 219 (27), 161 (30), 145 (30), 117 (34), 105 (44), 91 (32), 73 (100), calc. for $C_{23}H_{24}O_3Si_2Fe$ m/e 460.06131, measured 460.0606. The chemical shift (δ = 1.20) for the ring-silicon methyl is consistent with it being endo according to known shifts of endo methyls for similar complexes (233). Compound 344 could also be isolated from the reaction of 218 and an equimolar amount of nonacarbonyl diiron in degassed benzene at 55°C *via* chromatography on silica gel with hexane followed by sublimation. In this latter reaction, however, considerable starting material was recovered, which was the reason for the difficulty in purification of 344.

Synthesis of octamethyltrisilane 242

Octamethyltrisilane was prepared according to the procedure of Gilman and Harrell (238). To a flask containing 629 grams (4.98 mole) of trimethylchlorosilane, 50 grams (7.2 mole) of lithium shot and 900 ml of THF, was added 13 grams (0.10 mole) of dimethyldichlorosilane. After 30 minutes, the solution became warm and a solution of 170 grams (1.32 moles) of dimethyldichlorosilane in 500 ml of THF was added over a period of 8 hours. The solution was stirred until the lithium was no longer consumed (2½ days). Hexane was added to the organic solution which was filtered, washed with water and saturated sodium chloride and dried with sodium sulfate. Distillation gave 384 grams (75%) of 242 (b.p. 165-170°C): NMR (CCl_4) $\delta = 0.08$ (s); IR (neat) 2960, 2910, 1400, 1245, 830, 785, 725, 685 and 615 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 204 (25), 189 (18), 131 (77), 116 (50), 73 (100).

Synthesis of pentamethylchlorodisilane 353

A solution of 142 grams (0.696 mole) of octamethyltrisilane 242 in 650 ml of methylene chloride was cooled to -25°C with a CO_2/CCl_4 bath. Chlorine gas was bubbled through the solution and was stopped when the amount of product 353 was maximized as indicated by GC. Distillation through a 25 cm column packed with glass helices gave

86.5 grams (75%) of 353 (b.p. 133 - 133.5°C). NMR (CCl_4) $\delta = 0.16$ (s, 9H), $\delta = 0.45$ (s, 6H); IR (neat) 2960, 2900, 1395, 1245, 830, 785, 685 and 660 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 168 (2.2), 166 (5.0), 153 (2.1), 151 (5.2), 131 (5.2), 95 (1.1), 93 (3.3), 73 (100), calc. for $C_5H_{15}Si_2Cl$ m/e 166.04009, measured 166.03828.

Synthesis of 3-methyl-1-pentamethyldisilanylbut-3-ene-1-yne 345

To a solution of 1.95 grams (0.0295 moles) of 3-methylbut-3-ene-1-yne in 125 ml of THF was added 0.0295 moles of n-butyllithium. The solution was stirred for 10 minutes, then cooled to 0°C. To this solution was added 5.0 grams (0.030 moles) of pentamethylchlorodisilane. After stirring for 30 minutes, the organic solution was quenched with saturated ammonium chloride, washed with saturated sodium chloride and dried over sodium sulfate. Distillation yielded 4.04 grams (69%) of 345 (b.p. 49-51°C at 4 mm): NMR (CCl_4) $\delta = 0.12$ (s, 9H), $\delta = 0.20$ (s, 6H), $\delta = 1.88$ (broad singlet, 3H), $\delta = 5.28$ (m, 2H, collapses to AB quartet, J = 1.1 Hz, upon $h\nu$ at $\delta = 1.88$); IR (neat) 3110, 2960, 2905, 2150, 1620, 1275, 1250, 980, 900, 855, 830, 800 and 775 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 197 (12), 196 (53), 182 (17), 181 (86), 155 (19), 141 (18), 123 (83), 97 (15), 73 (100), calc. for $C_{10}H_{20}Si_2$ m/e 196.11036, measured 196.11056.

Synthesis of cis-3-methyl-1-pentamethyldisilanyl butadiene 346

A mixture of 0.1 grams of Lindlar's catalyst, 0.1 ml of quinoline and 15 ml of hexane was saturated with hydrogen in a hydrogenation apparatus. After 3.0 grams (0.0153 mole) of the eneyne 345 was added, it was observed that one equivalent of hydrogen was taken up in 73 minutes at which point the reaction was stopped. After filtration and removal of solvent, a GC analysis of the crude reaction mixture indicated the presence of four compounds. The three major compounds of this mixture were isolated by preparative GC on a 12' x 1/4" 20% DC-550 on Chromsorb P column at 150°C. One of these was determined to be starting material (17.0%, GC yield). The second compound was determined to be isopropylpentamethyldisilanyl acetylene (17.9%, GC yield) on the basis of its spectra: NMR (CCl_4) $\delta = 0.10$ (s, 9H), $\delta = 0.15$ (s, 6H), $\delta = 1.18$ (d, 3H, J = 8 Hz), $\delta = 2.58$ (heptet, 1H, J = 8 Hz, collapses to a singlet upon hν at $\delta = 1.18$); IR (neat) 2950, 2890, 2160, 1310, 1240, 1195, 960, 830, 790 and 760 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 198 (44), 183 (15), 155 (71), 147 (29), 141 (20), 127 (11), 126 (28), 125 (71), 124 (46), 83 (28), 75 (16), 73 (100), 59 (14), calc. for $C_{10}H_{22}Si_2$ m/e 198.12601, measured 198.12502. The third compound was determined to be the desired product 346 (18.3%, GC yield) on the basis of its spectra: NMR (CCl_4) $\delta = 0.06$ (s, 9H), $\delta = 0.16$ (s, 6H), $\delta = 1.86$ (broad singlet, 3H), $\delta = 4.94$ (broad singlet, 2H), $\delta = 5.57$ (d, 1H, J = 16 Hz), $\delta = 6.83$ (d, 1H, J = 16 Hz); IR (neat) 3080, 2950, 2890, 1630, 1240, 890, 830, 795 and 680 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 198 (1.2), 183 (2), 110 (50), 109 (11), 73 (100), 58 (16), calc. for $C_{10}H_{22}Si_2$ m/e 198.12601, measured 198.12484.

Pyrolysis of 346

The pyrolysis of 346 was carried out by evaporating it (0.07 torr, 25°C) through a horizontal quartz that was packed with quartz chips and heated to 635°C. The pyrolysate (0.146 grams) was trapped in liquid nitrogen. Four products were obtained that were isolated by preparative GC on a 12' x 1/4" 20% DC-550 on Chromsorb P column at 125°C. The major product, 347 (36.8%, GC yield) was identified as the trans isomer of the starting material on the basis of its spectra: NMR (CCl_4) $\delta = 0.07$ (s, 9H), $\delta = 0.15$ (s, 6H), $\delta = 1.87$ (broad singlet, 3H), $\delta = 5.05$ (broad singlet, 2H), $\delta = 5.82$ (d, 1H, J = 20 Hz), $\delta = 6.65$ (d, 1H, J = 20 Hz); IR (neat) 3080, 2950, 2890, 1580, 1245, 985, 890, 835, 820 and 795 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 198 (4), 183 (3), 110 (52), 109 (9), 73 (100), 59 (18), calc. for $C_{10}H_{22}Si_2$ m/e 198.12601, measured 198.12547. One of the products was determined to be trans-3-trimethylsilylmethyl-1-dimethylsilylbutadiene 349 (11% GC yield) on the basis of its spectra: NMR (CCl_4) δ = -0.03 (s, 9H), δ = 0.20 (d, 6H, J = 3.5 Hz), δ = 1.78 (broad singlet, 2H), δ = 4.05 (m, H_X, J_{AX} = 3.5 Hz), δ = 4.82 (H_C and H_D, collapses to AB quartet, J = 2 Hz, upon hν at δ = 1.78), δ = 5.62 (d of d, H_A, J_{AX} = 3.5 Hz, J_{AB} = 19 Hz), δ = 6.51 (d, H_B, J = 19 Hz); IR (neat) 3075, 2950, 2890, 2110, 1575, 1245, 980, 885, 850, 830 and 795 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 198(3), 183 (1), 124 (10), 109 (22), 74 (8), 73 (100), 59 (100). Also identified from this reaction was 1-cis-3-trans-4-dimethylsilyl-2-methyl-1-trimethylsilylbutadiene 350 (18.1%, GC yield): NMR (CCl_4) δ = 0.13 (s, 9H), δ = 0.16 (d, 6H, J = 3.9 Hz), δ = 1.86 (sharp singlet, 3H), δ = 4.09 (m, 1H), δ = 5.53 (broad singlet, 1H), δ = 5.71 (d of d, H_A, J_{AB} = 19 Hz, J_{AX} = 3.9 Hz), δ = 6.54 (d, H_B, J = 19 Hz); IR (neat) 2980, 2950, 2890, 2110, 1565, 1245, 985, 890, 865, 830, 785 and 685 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 198 (0.3), 183 (2), 110 (35), 109 (14), 73 (100), 59 (20), calc. for $C_{10}H_{22}Si_2$ m/e 198.12601, measured 198.12539. The last product from this pyrolysis was identified as 1-trans-3-trans-4-dimethylsilyl-2-methyl-1-trimethylsilylbutadiene 351 (12.7%, GC yield) on the basis of the following spectra: NMR (CCl_4) δ = 0.15 (s, 9H), δ = 0.19 (d, 6H, J = 3.8 Hz), δ = 1.93 (d, 3H, J = 1 Hz), δ = 4.15 (m, 1H), δ = 5.59 (broad singlet, 1H, J = 1 Hz), δ = 5.84 (d of d, 1H, J = 19 Hz, J = 3.8 Hz), δ = 6.89 (d, 1H, J = 19 Hz); IR (neat) 2950, 2890, 2110, 1600, 1555, 1250, 1150, 980, 890, 870 and 840 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 183 (0.7), 110 (45), 109 (8), 83 (6), 73 (100), 59 (21), calc. for $C_{10}H_{22}Si_2$ m/e 198.12601, measured 198.12503. On the basis of GC retention times, it was determined that when a solution of **346** in diphenylether was heated at 226°C for 90 minutes, **346** isomerized to 347.

Synthesis of *cis*-1-pentamethyldisilanyl-4-methoxybut-1-yne-3-ene **354**

cis-4-Methoxybut-1-yne-3-ene **352** is commerically available from Aldrich Chemical Company in the form of a 50% aqueous methanol solution. Compound **352** was purified by extraction of the methanol solution with water and ether, drying the ether layer with sodium sulfate followed by distillation (b.p. 122-125°C). A solution of 49.3 grams (0.601 mole) of **352** in 1.5 liter of THF was cooled to 0°C. To this solution was added 0.601 mole of *n*-butyllithium in hexane over a period of 20 minutes. This was followed by rapid addition (10 minutes) of 100.0 grams (0.601 mole) of pentamethylchlorodisilane. The organic solution was stirred for 1 hour, quenched with saturated ammonium chloride, washed with water and saturated sodium chloride, and dried with sodium sulfate. After removal of solvent, distillation gave 97.0 grams of **354** (76%, b.p. 85-87°C/4 mm): NMR (CCl_4) δ = 0.07 (s, 9H), δ = 0.18 (s, 6H), δ = 3.81 (s, 3H), δ = 4.46 (d, 1H, J = 7 Hz), δ = 6.23 (d, 1H, J = 7 Hz); IR (neat) 2970, 2905, 2105, 1635, 1390, 1275, 1250, 1115, 955, 835, 800, 765, 730, 695, 665 and 620 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 212 (9), 211 (3), 198 (11), 197 (74), 171 (70), 169 (10), 167 (59), 143 (12), 141 (50), 139 (52), 109 (31), 89 (53), 83 (11), 73 (100), 59 (22), calc. for $C_{10}H_{19}OSi_2$ m/e 211.09745, measured 211.097689.

Synthesis of *cis,cis*-1-pentamethyldisilanyl-4-methoxy-1,3-butadiene **355**

The *cis*-reduction of **354** was carried out with disiamylborane according to the general method for the *cis*-reduction of conjugated acetylenes that has been reported by Zweifel and Polston (234).

Disiamylborane (0.260 mole) was prepared by adding 0.260 mole of BH_3:THF complex to a solution of 36.4 grams (0.52 mole) of 2-methyl-2-butene in 125 ml of THF at 0°C, followed by stirring for 2 hours at 0°C.

The solution of disiamylborane was added to a solution of 50 grams (0.236 mole) of *cis*-1-pentamethyldisilanyl-4-methoxybut-1-yne-3-ene **354** in 250 ml of THF at 0°C, and the resultant solution was stirred for 3 hours at 0°C. After addition of 63 ml of glacial acetic acid, the reaction mixture was heated at 55°C for 5 hours. The solution was cooled to room temperature and 220 ml of 20% aqueous sodium hydroxide and 65 ml of 30% H_2O_2 were added slowly and concurrently. After addition, stirring was continued for 30 minutes and then the aqueous layer was drained off and washed with hexane. The combined organic phase was washed twice with saturated sodium chloride and dried with magnesium sulfate. After removal of solvent, distillation gave 18.7 grams of slightly impure 355 (37%, b.p. 80-89°C/3 mm). An analytically pure sample was obtained by preparative GC on a 12' x 1/4" 20% SE-30 on Chromsorb W column at 100°C for the purpose of obtaining the following spectra: NMR (CCl_4) $\delta = 0.03$ (s, 9H), $\delta = 0.15$ (s, 6H), $\delta = 3.63$ (s, 3H), $\delta = 5.05$ (d of d of d, H_C, $J_{BC} = 12$ Hz, $J_{CD} = 6.5$ Hz, $J_{AC} = 1.0$ Hz), $\delta = 5.32$ (d of t, H_A, $J_{AB} = 14$ Hz, $J_{AD} = 1.0$ Hz), $\delta = 5.84$ (d of t, H_D, $J_{BD} = 0.5$ Hz), $\delta = 7.01$ (d of d of d, H_B); mass spectrum (70 eV) m/e (% rel. int.) 199 (11), 111 (54), 89 (21), 73 (100), calc. for $C_9H_{19}OSi_2$ m/e 199.0975, measured 199.0971. Attempted *cis*-reduction of the triple bond with hydrogen and Lindlar's catalyst afforded only mixtures of randomly reduced 354.

Pyrolysis of *cis*,*cis*-1-pentamethyldisilanyl-4-methoxy-1,3-butadiene 355

Compound 355 (6.30 grams) was pyrolyzed by evaporating (100°C, 10^{-3} torr) through a horizontal quartz tube that was packed with quartz chips and was heated to 760°C. The pyrolysate was collected in a liquid nitrogen trap and represented an 84% mass recovery. The two major products of the pyrolysis were identified. One of these was identified as tetramethylsilane (30% GC yield) by comparison of its GC retention time and its GC mass spectrum with those of an authentic sample. Distillation of the pyrolysate yields a fraction (80-95°C, 3.14 grams) that is about 60% by weight the major product. The major product was purified for spectral analysis and for all chemical reactions by preparative GC on a 12' x 1/4" 15% SE-30 on Chromsorb W column at 80°C. The major product was assigned the structure of 2,2-dimethyl-1-oxo-2-silacyclohexa-3,5-diene 360 (52% GC yield) on the basis of its spectra: NMR (CCl_4) $\delta = 0.29$ (s, 6H), $\delta = 5.07$ (t of d, H_C, $J_{CD} = J_{CB} = 6$ Hz, $J_{AC} = 1.0$ Hz), $\delta = 5.54$ (d of t, H_A, $J_{AB} = 14$ Hz, $J_{AD} \sim J_{AC}$), $\delta = 6.54$ (overlapped with H_B, H_D), $\delta = 6.71$ (d of d of d, H_B, $J_{BD} \sim 1$ Hz); mass spectrum (70 eV) m/e (% rel. int.) 126 (20), 111 (100), 85 (14), calc. for $C_6H_{10}OSi$ m/e 126.0501, measured 126.0498; IR (neat) 3065, 3015, 2975, 1620, 1535, 1360, 1270, 1090, 1025, 940, 900, 855, 810, 785, 740 and 705 cm^{-1}.

If the pyrolysis of 355 is carried out by dropping through a vertical quartz tube with a nitrogen sweep, the yield of 360 decreases, and the number of minor products increases dramatically.

Reaction of the oxasilin 360 with maleic anhydride

An NMR tube containing 0.195 grams (1.55 mmole) of 360 and 0.152 grams (1.55 mmole) of maleic anhydride in 1.5 ml of $CDCl_3$ was heated at 65°C for 4½ hours. Analysis of the subsequent NMR spectrum revealed a near quantitative formation of the 4+2 cycloadduct 366. Compound 366 was not isolated and was identified only by its NMR spectrum: $\delta = 0.02$ (s, 3H), $\delta = 0.22$ (s, 3H), $\delta = 2.68$ (m, 1H, collapses to a doublet, $J = 2.5$ Hz, upon $h\nu$ at $\delta = 6.48$), $\delta = 3.28$ (d of d, 1H, $J = 2.5$ Hz, $J = 9$ Hz), $\delta = 3.75$ (d of d, 1H, $J = 4$ Hz, $J = 9$ Hz), $\delta = 4.95$ (m, 1H, collapses to a doublet, $J = 4$ Hz, upon $h\nu$ at 6.48), $\delta = 6.48$ (m, 2H).

Reaction of the oxasilin 360 with perfluoro-2-butyne 370

A CCl_4 solution of 0.10 grams of 360 and a large excess of 370 (∿0.4 ml) of 370 was degassed and sealed in a NMR tube. After 20 minutes at room temperature, no change had occurred. After 10 hours at room temperature, the presence of the very characteristic absorption for 1,2-bis(trifluoromethyl)benzene 364 was observed at $\delta = 7.60$ (360:364 is 4:1). No absorptions were observed that could be attributed to the Diels-Alder adduct of 360 and 370. According to GC retention times, if D_3 or D_4 are formed it would only be in small amounts. When the solution of 360 and 370 was heated at 55°C for 5 hours, all of the oxasilin was consumed. It was found that bis(trimethylsilyl)acetylene did not react with **370** when heated at 65°C for 7 hours.

Reaction of the oxasilin **360** with perfluoro-2-butyne **370** in the presence of dimethyldimethoxysilane

A solution of 0.108 grams (0.857 mmole) of **360** and a large excess (~0.4 ml) of **370** in 1.0 ml of dimethyldimethoxysilane was degassed and sealed in a tube under vacuum. The tube was heated at 65°C for 6 hours. The tube was cooled and opened, then allowed to warm to remove the excess **370**. All of the oxasilin **360** had reacted as determined by GCMS. The two major products were isolated by preparative GC on a 12' x 1/4" 15% SE-30 column on Chromsorb W at 82°C. The more volatile compound was identified as 1,2-bis(trifluoromethyl)benzene **364** (72% GC yield) on the basis of its spectra: NMR (CCl_4) $\delta = 7.86$, multiplet; mass spectrum (70 eV) 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). These spectra match those of an authentic sample of **364**, particularly the pattern of the multiplet in the NMR. The other major product was identified as *sym*-tetramethyldimethoxydisiloxane **371** (76% GC yield) on the basis of its spectra: NMR (CCl_4) $\delta = 0.08$ (s, 6H), $\delta = 3.74$ (s, 3H); mass spectrum (70 eV) m/e (% rel. int.) 180 (12), 179 (81), 149 (100), 133 (16), 119 (28), 82 (13), 75 (10), 59 (21), 43 (13). These spectra match those of an authentic sample of 371. The yield of 371 is based on the amount of 364 formed. No cyclosiloxanes were observed by GCMS.

Reaction of the oxasilin 360 with perfluoro-2-butyne 370 in the presence of trimethylsilyl-3-butenyl ether

A solution of 0.147 grams (1.17 mmole) of 360 and a large excess (~0.3 ml) of 370 in 1.0 ml of trimethylsilyl-3-butenyl ether was degassed and sealed under vacuum in a tube that was heated at 64°C for 6½ hours. The tube was cooled and opened, and the excess 370 allowed to escape. 1,2-Bis-(trifluoromethyl)benzene 364 (61% GC yield) was identified by comparison of its GC mass spectrum with that of an authentic sample. The other two major products were isolated by preparative GC on a 12' x 1/4" 15% SE-30 on Chromsorb W column at 100°C. The more volatile of these was identified as 3-butenyloxypentamethyldisiloxane 373 (67% GC yield) on the basis of its spectra: NMR (CCl_4) $\delta = 0.04$ (s, 6H), $\delta = 0.15$ (s, 9H), $\delta = 1.26$ (d, 3H, J = 3 Hz), $\delta = 4.46$ (m, 1H), $\delta = 5.19$ (m, 2H), $\delta = 5.98$ (m, 1H); mass spectrum (70 eV) m/e (% rel. int.) 218 (10), 203 (24), 149 (100), 147 (41), 73 (10), 55 (44), calc. for $C_9H_{22}O_2Si_2$ m/e 218.1158, measured 218.1158; IR (neat) 3080, 2960, 1640, 1255, 1045, 960, 920, 860, 840, 810, 790, 750 and 680 cm^{-1}. The other major product is tentatively assign the structure of 2,2,4,4-tetramethyl-1,3-dioxo-2,4-disilacycloocta-5,7-diene **372** (10% GC yield) on the basis of its spectra: NMR (CCl_4) δ = 0.46 (s, 12H), δ = 5.61 (d of d, 1H, J = 7 Hz, J = 4 Hz, collapses to a doublet, J = 7 Hz, upon $h\nu$ at δ = 6.84), δ = 6.00 (d, 1H, J = 15 Hz), δ = 6.53 (d, 1H, J = 7 Hz, collapses to singlet upon $h\nu$ at δ = 5.61), δ = 6.84 (d of d, 1H, J = 15 Hz, J = 4 Hz, collapses to a doublet, J = 15 Hz upon $h\nu$ at δ = 5.61); mass spectrum (70 eV) m/e (% rel. int.) 200 (11), 186 (12), 185 (71), 159 (27), 135 (14), 134 (16), 133 (100), 119 (11), 85 (11), 73 (12). A minor product was tentatively identified as 1-butenyloxyheptamethyltrisiloxane **374** (5.4% GC yield) on the basis of its mass spectrum: m/e (% rel. int.) 292 (0.1), 277 (1.6), 233 (32), 221 (40), 206 (49), 191 (11), 103 (14), 73 (23), 55 (100). The yields of **372**, **373** and **374** are based upon the amount of **364** formed. The yield of **374** takes into account the fact that two moles of dimethylsilanone is incorporated. The yields of **372** and **374** were calculated assuming response factors identical to that of **373**.

Reaction of the oxasilin **360** with perfluoro-2-butyne 370 in the presence of triethyl orthoacetate

A solution of 0.120 grams of **360** and a large excess of 370 (∿0.5 ml) in 1.0 ml of triethyl orthoacetate was degassed and sealed under vacuum in a tube that was heated at 62°C for

7 hours. The tube was cooled and opened and the excess 370 allowed to escape. 1,2-Bis(trifluoromethyl)benzene 364 (74% GC yield) was identified by comparison of its GC mass spectrum with that of an authentic sample. Along with 364, the major products of this reaction were determined to be ethyl acetate 377 (65% GC yield) and dimethyldiethoxysilane 378 (60% GC yield). Compounds 377 and 378 were identified by isolation via preparative GC on a 12' x 1/4" 20% SE-30 on Chromsorb W column at 80°C and comparison of their NMR and mass spectra with those of authentic samples. The yields of 377 and 378 are based on the amount of 364 formed.

Reaction of the oxasilin 360 with perfluoro-2-butyne 370 in the presence of trimethylchlorosilane

A solution of 0.0934 grams of 360 and a large excess of 370 (∿0.5 ml) in 1.0 ml of Me_3SiCl, that had been purged with argon, was degassed and sealed under vacuum in a tube that was heated for 8 hours at 65°C. The tube was cooled and opened and the excess 370 allowed to escape. The solution was decanted from a light green precipitate and was found to contain three reaction products. 1,2-Bis(trifluoromethyl)benzene 364 (36%, GC yield) was identified by comparison of its GC mass spectrum with that of an authentic sample. The major product was identified as pentamethylchlorodisiloxane 375 (37%, GC yield) on the basis of its spectra: NMR (CCl_4) δ = 0.15 (s, 9H), δ = 0.42 (s, 6H); mass spectrum m/e (% rel. int.) 169 (43), 167 (100), 147 (10), 76 (13), 73 (14). The third major product of this reaction was identified as 1-chloroheptamethyltrisiloxane 376 (34%, GC yield) on the basis of its spectra: NMR δ = 0.10 (s, 15H), δ = 0.42 (s, 6H); mass spectrum m/e (% rel. int.) 243 (29), 241 (68), 221 (4), 133 (11), 113 (11), 73 (100). The yields of 375 and 376 are based on the amount of 364 formed. The yield of 376 was calculated assuming the response factor of 375 and taking into account that two moles of dimethylsilanone are incorporated.

Reaction of the oxasilin 360 with perfluoro-2-butyne 370 in the presence of reagents which failed to react with dimethylsilanone

The reaction of 360 with 370 was carried out in the presence of each of the following reagents according to the procedure described for the same reaction in the presence of dimethyldimethoxysilane: diethyl ether, ethylene oxide, triethylsilane, tetramethylethylene oxide, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, and trans-cinnamylmethyl ether. In each case a GC mass spectroscopic analysis of the reaction mixture did not result in the identification of any compound that could be construed to have resulted from a reaction of the reagent in question and dimethylsilanone. The same results were obtained for tetramethylethylene whether or not the reaction was run in a glass or Teflon vessel.

Photolysis of the oxasilin 360 in the presence of dimethyldiethoxysilane

A solution of 0.0585 grams of 360 in 0.8 ml of dimethyldiethoxysilane was degassed and sealed in a quartz NMR tube. NMR was used to follow the irradiation in a 450 Watt high pressure mercury lamp, and it was noticed that after 175 minutes, 360 had been completely consumed. GC mass spectral analysis revealed that the dimethylsilanone trapping product of dimethyldiethoxysilane was not formed, in fact, no volatile products were formed.

BIBLIOGRAPHY

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

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

3. W. H. Atwell and D. R. Weyenberg, J. Organometal. Chem. 5, 594 (1966).

4. D. N. Roark and G. J. D. Peddle, J. Amer. Chem. Soc. 94, 5837 (1972).

5. H. Sakurai, Y. Kamiyama and Y. Nakadaira, Angew. Chem. Internat. Ed. 17, 674 (1978).

6. A. Kasdan, E. Herbst and W. C. Lineberger, J. Chem. Phys. 62, 541 (1975).

7. I. Dubois, Can. J. Phys. 46, 2485 (1966).

8. P. P. Gaspar, in Reactive Intermediates, Vol. 1, edited by M. Jones, Jr. and R. A. Moss (Wiley-Interscience, New York, N.Y., 1978) pp. 229-279.

9. P. P. Gaspar and B. J. Herold, in Carbene Chemistry, 2nd ed., by W. Kirmse (Academic Press, New York, N.Y., 1971) pp. 504-536.

10. W. H. Atwell and D. R. Weyenberg, Angew. Chem. Internat. Ed. 8, 469 (1969).

11. E. A. Chernyshev, N. G. Komalenkova and S. A. Bashkirova, Russian Chemical Reviews 45, 913 (1976).

12. O. M. Nefedov, S. P. Kolesnikov and A. I. Ioffe, in Journal of Organometallic Chemistry Library, Vol. 5, edited by D. Seyferth (Elsevier, New York, N.Y., 1977) pp. 181-217.

13. P. S. Skell and P. W. Owen, J. Amer. Chem. Soc. 94, 5434 (1972).

14. P. P. Gaspar, B. D. Pate and W. Eckelman, J. Amer. Chem. Soc. 88, 3878 (1966).

15. P. P. Gaspar and P. Markusch, J. Chem. Soc. Chem. Commun., 1331 (1970).

16. P. P. Gaspar, P. Markusch, J. D. Holten, III, and J. J. Frost, J. Phys. Chem. 76, 1352 (1972).

17. P. P. Gaspar, R. J. Hwang and W. C. Eckelman, J. Chem. Soc. Chem. Commun., 242 (1974).

18. P. P. Gaspar and R. J. Hwang, J. Amer. Chem. Soc. 96, 6198 (1974).

19. R. J. Hwang and P. P. Gaspar, J. Amer. Chem. Soc. 100, 6626 (1978).

20. C. Friedel and A. Ladenburg, Liebigs Ann. Chem. 203, 241 (1880).

21. W. H. Atwell and D. R. Weyenberg, J. Amer. Chem. Soc. 90, 3438 (1968).

22. E. G. Janzen, J. B. Pickett and W. H. Atwell, J. Amer. Chem. Soc. 90, 2719 (1968).

23. M. E. Childs and W. P. Weber, J. Org. Chem. 41, 1799 (1976).

24. M. E. Childs and W. P. Weber, Tetrahedron Lett., 4033 (1974).

25. R. T. Conlin and P. P. Gaspar, J. Amer. Chem. Soc. 98, 868 (1976).

26. R. T. Conlin and P. P. Gaspar, J. Amer. Chem. Soc. 98, 3715 (1976).

27. W. H. Atwell and D. R. Weyenberg, Intrascience Chem. Rept. 7, 139 (1973).

28. W. H. Atwell and J. G. Uhlman, J. Organometal. Chem. 52, C21 (1973).

29. T. J. Barton and D. S. Banasiak, J. Organometal. Chem. 157, 255 (1978).

30. W. Ando, M. Ikeno and A. Sekiguchi, J. Amer. Chem. Soc. 99, 6447 (1977).

31. D. R. Weyenberg and W. H. Atwell, Pure Applied Chem. 19, 343 (1969).

32. H. Sakurai, the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 14, 1978, ORGN7S.

33. E. A. Chernyshev, N. G. Komalenkova and S. A. Bashkirova, Pokl. Akad. Nauk SSSR 205, 868 (1972).

34. E. A. Chernyshev, N. G. Komalenkova and S. A. Bashkirova, Zh. Obshch. Khim. 41, 1175 (1971).

35. E. A. Chernyshev, N. G. Komalenkova, S. A. Bashkirova, A. V. Kisin and V. I. Pchelintsev, Zh. Obshch. Khim. 45, 2221 (1975).

36. E. A. Chernyshev, N. G. Komalenkova, S. A. Bashkirova and T. A. Zhavoronkova, Zh. Obshch. Khim. 46, 1278 (1976).

37. E. A. Chernyshev, N. G. Komalenkova and S. A. Bashkirova, Zh. Obshch. Khim. 46, 1286 (1976).

38. E. A. Chernyshev, N. G. Komalenkova, S. A. Bashkirova, N. A. Batygino and A. V. Kisin, Zh. Obshch. Khim. 47, 1196 (1977).

39. E. A. Chernyshev, N. G. Komalenkova, S. A. Bashkirova and V. V. Sokolov, Zh. Obshch. Khim. 48, 830 (1978).

40. E. A. Chernyshev, N. G. Komalenkova, S. A. Bashkirova, N. S. Fedotov, G. F. Evert and V. F. Mironov, Zh. Obshch. Khim. 48, 633 (1978).

41. M. Schmeisser and K. P. Ehlers, Angew. Chem. 76, 781 (1962).

42. R. L. Jenkins, A. J. Vanderwiclon, S. P. Ruis, S. R. Gird and M. A. Ring, Inorg. Chem. 12, 2968 (1973).

43. T. J. Barton and D. S. Banasiak, J. Amer. Chem. Soc. 99, 5199 (1977).

44. W. D. Wulff, W. F. Goure and T. J. Barton, J. Amer. Chem. Soc. 100, 6336 (1978).

45. M. D. Sefcik and M. A. Ring, J. Amer. Chem. Soc. 95, 5168 (1973).

46. H. Sakurai, A. Hosomi and M. Kumada, J. Chem. Soc. Chem. Commun., 4 (1969).

47. R. J. Hwang, R. T. Conlin and P. P. Gaspar, J. Organometal. Chem. 94, C38 (1975).

48. R. L. Jenkins, R. A. Kedrowski, L. E. Elliot, D. C. Tappen and M. A. Ring, J. Organometal. Chem. 86, 347 (1975).

49. H. Gilman, S. G. Cottis and W. H. Atwell, J. Amer. Chem. Soc. 86, 1596 (1964).

50. H. Gilman, S. G. Cottis and W. H. Atwell, J. Amer. Chem. Soc. 86, 5584 (1964).

51. A. Laporterie, J. Dubac, P. Mazerolles and M. Lesbre, Tetrahedron Lett., 4653 (1971).

52. E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler and E. Staude, Angew. Chem. Internat. Ed. 2, 507 (1963).

53. L. Rösch, Angew. Chem. Internat. Ed. 16, 480 (1977).

54. D. Seyferth and D. C. Annarelli, J. Amer. Chem. Soc. 97, 7162 (1975).

55. D. Seyferth, D. C. Annarelli and S. C. Vick, J. Amer. Chem. Soc. 98, 6382 (1976).

56. D. Seyferth and D. C. Annarelli, J. Organometal. Chem. 117, C51 (1976).

57. D. Seyferth and S. C. Vick, J. Organometal. Chem. 125, C11 (1977).

58. D. Seyferth and D. C. Annarelli, J. Amer. Chem. Soc. 97, 2273 (1975).

59. D. Seyferth and D. P. Duncan, J. Amer. Chem. Soc. 100, 7734 (1978).

60. D. Seyferth, S. C. Vick and M. L. Shannon, J. Organometal. Chem. 135, C37 (1977).

61. M. Ishikawa and M. Kumada, J. Chem. Soc. Chem. Commun., 612 (1970).

62. M. Ishikawa, K. I. Nakagawa and M. Kumada, J. Organometal. Chem. 131, C15 (1977).

63. M. Ishikawa, K. I. Nakagawa and M. Kumada, J. Organometal. Chem. 135, C45 (1977).

64. M. Ishikawa and M. Kumada, J. Chem. Soc. Chem. Commun., 489 (1971).

65. I. N. Jung and W. P. Weber, J. Organometal. Chem. 114, 257 (1976).

66. M. Ishikawa, T. Takaoka and M. Kumada, J. Organometal. Chem. 42, 333 (1972).

67. M. Ishikawa and M. Kumada, J. Organometal. Chem. 81, C3 (1974).

68. M. Ishikawa, K. I. Nakagawa, M. Ishiguro, F. Ohi and M. Kumada, J. Organometal. Chem. 152, 155 (1978).

69. M. Ishikawa, F. Ohi and M. Kumada, J. Organometal. Chem. 86, C23 (1975).

70. M. Ishikawa, M. Ishiguro and M. Kumada, J. Organometal. Chem. 49, C71 (1973).

71. M. Ishikawa, F. Ohi and M. Kumada, Tetrahedron Lett., 645 (1975).

72. H. Okinoshima and W. P. Weber, J. Organometal. Chem. 155, 165 (1978).

73. H. Okinoshima and W. P. Weber, J. Organometal. Chem. 150, C25 (1978).

74. H. Sakurai, Y. Kobayashi and Y. Nakadaira, J. Amer. Chem. Soc. 93, 5272 (1971).

75. H. Sakurai, Y. Kobayashi and Y. Nakadiara, J. Amer. Chem. Soc. 96, 2656 (1974).

76. M. Kumada, M. Ishikawa, H. Okinoshima and K. Yamamoto, Ann. N. Y. Acad. Sci. 239, 32 (1974).

77. H. Sakurai and M. Murakami, J. Amer. Chem. Soc. 94, 5080 (1972).

78. H. S. D. Soysa, H. Okinoshima and W. P. Weber, J. Organometal. Chem. 133, C17 (1977).

79. W. Ando, M. Ikeno and A. Sekiguchi, J. Amer. Chem. Soc. 100, 3613 (1978).

80. M. Ishikawa and M. Kumada, J. Organometal. Chem. 42, 325 (1972).

81. H. Sakurai, Y. Kamiyama and Y. Nakadaira, J. Amer. Chem. Soc. 99, 3879 (1977).

82. H. Sakurai, Y. Kobayashi and Y. Nakadaira, J. Organometal. Chem. 120, C1 (1976).

83. R. Balasubramanian and M. V. George, J. Organometal. Chem. 85, 131 (1975).

84. P. S. Skell and E. J. Goldstein, J. Amer. Chem. Soc. 86, 1442 (1964).

85. H. Sakurai, T. Kobayashi and Y. Nakadaira, J. Organometal. Chem. 162, C43 (1978).

86. J. C. Thompson, J. L. Margrave and P. L. Timms, J. Chem. Soc. Chem. Commun., 566 (1966).

87. C. S. Liu and T. L. Hwang, J. Amer. Chem. Soc. 100, 2577 (1978).

88. R. A. Ferrieri, E. E. Siefert, M. J. Griffin, O. F. Zeck and Y. N. Tang, J. Chem. Soc. Chem. Commun., 6 (1977).

89. O. F. Zeck, Y. Y. Su, G. P. Gennaro and Y. N. Tang, J. Amer. Chem. Soc. 98, 3474 (1976).

90. J. C. Thompson and J. L. Margrave, Inorg. Chem. 11, 913 (1972).

91. T. J. Barton and M. Juvet, Tetrahedron Lett., 3893 (1975).

92. M. E. Volpin, Yu D. Koreshkov, V. G. Dulova and D. N. Kursanov, Tetrahedron 18, 107 (1962).

93. R. West and R. E. Bailey, J. Amer. Chem. Soc. 85, 2871 (1963).

94. T. J. Barton and J. A. Kilgour, J. Amer. Chem. Soc. 96, 7150 (1974).

95. T. J. Barton and J. A. Kilgour, J. Amer. Chem. Soc. 98, 7746 (1976).

96. H. Sakurai, Y. Kamiyama and Y. Nakadaire, J. Amer. Chem. Soc. 99, 3879 (1977).

97. M. Ishikawa, T. Fuchikami and M. Kumada, J. Amer. Chem. Soc. 99, 245 (1977).

98. M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem. 142, C45 (1977).

99. D. L. Perry and J. L. Margrave, J. Chem. Educ. 53, 696 (1976).

100. C. H. Haas and M. A. Ring, Inorg. Chem. 14, 2253 (1975).

101. L. E. Gusel'nikov, N. S. Nametkin and V. M. Vdovin, Acc. Chem. Res. 8, 18 (1975).

102. D. Seyferth and T. F. O. Lim, J. Amer. Chem. Soc. 100, 7074 (1978).

103. H. Okinoshima and W. P. Weber, J. Organometal. Chem. 149, 279 (1978).

104. C. J. Attridge, Organometal. Chem. Rev. A5, 323 (1970).

105. J. A. Kilgour, Ph.D. Dissertation, Iowa State University, 1975 (unpublished).

106. D. S. Banasiak, Ph.D. Dissertation, Iowa State University, 1977 (unpublished).

107. A. G. Brook, J. W. Harris, J. Lennon and M. E. Sheikh, J. Amer. Chem. Soc. 101, 83 (1979).

108. H. Sakurai, Y. Kamiyama and Y. Nakadaire, J. Amer. Chem. Soc. 98, 7453 (1976).

109. O. L. Chapman, C. C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton and M. L. Tumey, J. Amer. Chem. Soc. 98, 7844 (1976).

110. M. R. Chedekel, M. Skoglund, R. L. Kreeger and H. Shechter, J. Amer. Chem. Soc. 98, 7846 (1976).

111. R. Walsh, J. Organometal. Chem. 38, 245 (1972).

112. R. Ahlrichs and R. Heinzman, J. Amer. Chem. Soc. 99, 7452 (1977).

113. N. S. Nametkin, L. F. Gusel'nikov, R. L. Ushakova and V. M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., 1840 (1971).

114. N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova and V. M. Vdovin, Dokl. Akad. Nauk SSSR 201, 1365 (1971).

115. J. Slutsky and H. Kwart, J. Org. Chem. 38, 3659 (1973).

116. T. J. Barton and E. Kline, J. Organometal. Chem. 42, C21 (1972).

117. E. Block and L. K. Revelle, J. Amer. Chem. Soc. 100, 1630 (1978).

118. T. J. Barton and G. T. Burns, J. Amer. Chem. Soc. 100, 5246 (1978).

119. R. L. Kreeger and H. Schechter, Tetrahedron Lett., 2061 (1975).

120. W. Ando, A. Sekiguchi, A. J. Rothschild, R. R. Gallucci, M. Jones, Jr., T. J. Barton and J. A. Kilgour, J. Amer. Chem. Soc. 99, 6995 (1977).

121. P. B. Valkovich and W. P. Weber, Tetrahedron Lett., 2153 (1975).

122. Y. Nakadaira, S. Kanuchi and H. Sakurai, J. Amer. Chem. Soc. 96, 5621 (1974).

123. M. Ishikawa, T. Kuchikami and M. Kumada, J. Organometal. Chem. 117, C58 (1976).

124. M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem. 149, 37 (1978).

125. M. Ishikawa, T. Fuchikami, T. Sugaya and M. Kumada, J. Amer. Chem. Soc. 97, 5923 (1975).

126. P. R. Jones and T. F. O. Lim, J. Amer. Chem. Soc. 99, 8447 (1977).

127. N. Wiberg and G. Preiner, Angew. Chem. Internat. Ed. 16, 328 (1977).

128. T. J. Barton and S. K. Hoekman, submitted for publication to J. Amer. Chem. Soc.

129. (a) T. J. Barton, E. A. Kline and P. M. Garvey, 3rd Internat. Symposium on Organosilicon Chem., Madison, Wisc., 1972. (b) E. A. Kline, Ph.D. Thesis, Iowa State University, 1973 (unpublished).

130. D. N. Roark and L. H. Sommer, J. Chem. Soc. Chem. Commun., 167 (1973).

131. C. M. Golino, R. D. Bush, D. N. Roark and L. H. Sommer, J. Organometal. Chem. 66, 29 (1974).

132. C. M. Golino, R. D. Bush and L. H. Sommer, J. Amer. Chem. Soc. 98, 914 (1974).

133. L. H. Sommer and J. McLick, J. Organometal. Chem. 101, 171 (1975).

134. P. B. Valkovich and W. P. Weber, J. Org. Chem. 40, 229 (1975).

135. C. M. Golino, R. D. Bush, P. On and L. H. Sommer, J. Amer. Chem. Soc. 97, 1957 (1975).

136. R. D. Bush, C. M. Golino and L. H. Sommer, J. Amer. Chem. Soc. 96, 7105 (1974).

137. Y. Nakadaira, S. Kanouchi and H. Sakurai, J. Amer. Chem. Soc. 96, 5623 (1974).

138. R. L. Ushakova, Ph.D. Thesis, Institute of Petrochemical Synthesis, Moscow (1972).

139. G. Bertrand, G. Manuel and P. Mazerolles, Tetrahedron Lett., 2149 (1978).

140. T. J. Barton and G. T. Burns, Iowa State University, unpublished results.

141. M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem. 118, 155 (1976).

142. G. J. D. Peddle, D. N. Roark, A. M. Good and S. G. McGeachin, J. Amer. Chem. Soc. 91, 2807 (1969).

143. C. L. Smith and J. Pounds, J. Chem. Soc., Chem. Commun., 910 (1975).

144. D. N. Roark and G. J. D. Peddle, J. Amer. Chem. Soc. 94, 5837 (1972).

145. T. J. Barton and J. A. Kilgour, J. Amer. Chem. Soc. 98, 7231 (1976).

146. M. J. S. Dewar, D. H. Lo and C. A. Ramsden, J. Amer. Chem. Soc. 97, 1311 (1975).

147. P. H. Blustin, J. Organometal. Chem. 105, 161 (1976).

148. M. D. Curtis, J. Organometal. Chem. 60, 63 (1973).

149. K. Triplett and M. D. Curtis, J. Organometal Chem. 107, 23 (1976).

150. L. C. Snyder, The Pauling Award Symposium, November 5, 1977, Eugene, Ore.

151. J. L. Margrave and P. W. Wilson, Acc. Chem. Res. 4, 145 (1971).

152. J. L. Margrave and D. L. Perry, Inorg. Chem. 16, 1820 (1977).

153. M. L. Tumey, Ph.D. Dissertation, Iowa State University, 1979 (unpublished).

154. K. A. Andrianov and N. N. Sokolov, Dokl. Akad. Nauk SSSR 82, 909 (1952).

155. N. S. Nametkin, R. Kh. Islamov, L. E. Gusl'nikov, A. A. Sobitov and V. M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., 90 (1971).

156. L. E. Gusel'nikov, N. S. Nametkin, T. Kh. Islamov, A. A. Sobitov and V. M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., 84 (1971).

157. N. S. Nametkin, L. E. Gusel'nikov, T. Kh. Islamov, M. V. Shishkina and V. M. Vdovin, Dokl. Akad. Nauk SSSR 175, 136 (1967).

158. N. S. Nametkin, R. Kh. Islamov, L. E. Gusel'nikov and V. M. Vdovin, Usp. Khim. 41, 203 (1972).

159. I. M. T. Davidson and J. F. Thompson, J. Chem. Soc., Chem. Commun., 251 (1971).

160. T. J. Barton and M. L. Tumey, Iowa State University, unpublished results.

161. C. M. Golino, R. D. Bush and L. H. Sommer, J. Amer. Chem. Soc. 97, 7371 (1975).

162. D. R. Parker and L. H. Sommer, J. Organometal. Chem. 110, C1 (1976).

163. T. J. Barton and W. F. Goure, submitted for publication to J. Organometal. Chem.

164. D. Seyferth, T. F. O. Lim, and D. P. Duncan, J. Amer. Chem. Soc. 100, 1626 (1978).

165. J. Slutsky and H. Kwart, J. Amer. Chem. Soc. 95, 8678 (1973).

166. A. G. Brook, Acc. Chem. Res. 7, 77 (1974).

167. A. G. Brook, D. M. MacRae and A. R. Bassindale, J. Organometal. Chem. 86, 185 (1975).

168. H. Kwart and W. E. Barnette, J. Amer. Chem. Soc. 99, 614 (1977).

169. I. F. Lutsenko, Y. I. Baukov, G. S. Burlachenko and B. N. Khasapov, J. Organometal. Chem. 5, 20 (1966).

170. K. Itoh, M. Katsuda and Y. Ishii, J. Chem. Soc. (B), 302 (1970).

171. K. Itoh, T. Katsuura, A. Matsuda and Y. Ishii, J. Organometal. Chem. 34, 63 (1972).

172. J. Pump and E. G. Rochow, Chem. Ber. 97, 627 (1964).

173. O. J. Scherer and R. Schmitt, Tetrahedron Lett., 6235 (1968).

174. N. Wiberg and H. J. Pracht, Chem. Ber. 105, 1388 (1972).

175. R. H. Neilson, R. D. Jacobs, R. W. Scheirman and J. C. Wilbur, Inorg. Chem. 17, 1880 (1978).

176. I. A. Duncan and C. Glidewell, J. Organometal. Chem. 97, 51 (1975).

177. O. J. Scherer and G. Schnabl, J. Organometal. Chem. 52, C18 (1973).

178. O. J. Scherer and R. Schmitt, J. Organometal. Chem. 16, P11 (1969).

179. H. Schmidbaur and W. Malisch, Chem. Ber. 102, 83 (1969).

180. H. J. Reich and S. K. Shah, J. Org. Chem. 42, 1773 (1977).

181. K. Itoh, K. Matsuzaki and Y. Ishii, J. Chem. Soc. (C), 2709 (1968).

182. A. E. Kouya, J. Dunogues, N. Duffaut and R. Calas, J. Organometal. Chem. 148, 225 (1978).

183. S. J. Harris and D. R. M. Walton, J. Chem. Soc. Chem. Commun., 1009 (1976).

184. R. West and G. A. Gornowicz, J. Organometal. Chem. 25, 385 (1970).

185. G. A. Gornowicz and R. West, J. Amer. Chem. Soc. 93, 1714 (1971).

186. R. M. Coates, L. O. Sandefur and R. D. Smillie, J. Amer. Chem. Soc. 97, 1619 (1975).

187. T. J. Pinnavaia, W. T. Collins and J. J. Howe, J. Amer. Chem. Soc. 92, 4544 (1970).

188. I. K. Kusnezowa, K. Ruhlmann and E. Grundemann, J. Organometal. Chem. 47, 53 (1973).

189. T. J. Pinnavaia and J. A. McClarin, J. Amer. Chem. Soc. 96, 3012 (1974).

190. H. J. Reich and D. A. Murcia, J. Amer. Chem. Soc. 95, 3418 (1973).

191. R. B. Larrabee, J. Organometal. Chem. 74, 313 (1974).

192. A. J. Ashe III, J. Amer. Chem. Soc. 92, 1233 (1970).

193. J. C. Pommier and D. Lucas, J. Organometal. Chem. 57, 139 (1973).

194. D. H. O'Brien and C. P. Hrung, J. Organometal. Chem. 27, 185 (1971).

195. V. N. Torocheshnikov, N. M. Sergeyev, N. A. Viktorov, G. S. Goldin, V. G. Poddubny and A. N. Koltsova, J. Organometal. Chem. 70, 347 (1974).

196. L. Birkofer and P. Wegner, Chem. Ber. 99, 2512 (1966).

197. W. H. Atwell, D. R. Weyenberg and J. G. Uhlmann, J. Amer. Chem. Soc. 91, 2025 (1969).

198. A. G. Brook and P. J. Dillon, Can. J. Chem. 47, 4347 (1969).

199. W. I. Bevan, R. N. Haszeldine and J. C. Young, Chem. Ind. (London), 789 (1961).

200. A. R. Bassindale, A. G. Brook, P. F. Jones and J. M. Lennon, Can. J. Chem. 53, 332 (1975).

201. W. I. Bevan, R. N. Haszeldine, J. Middleton and A. E. Tipping, J. Organometal. Chem. 23, C17 (1970).

202. W. R. Bamford and B. C. Pant, J. Chem. Soc. (C), 1470 (1967).

203. J. Cudlin, J. Schraml and V. Chvalovsky, Czech. Chem. Commun. 29, 1476 (1964).

204. C. Eaborn, Organosilicon Compounds (Academic Press Inc., London, 1960) p. 434.

205. D. D. Davis and C. E. Gray, Organometal. Chem. Rev. A 6, 283 (1970).

206. H. Sakurai and F. Kondo, J. Organometal. Chem. 92, C46 (1975).

207. H. Sakurai, A. Okada, M. Kira and K. Yonezawa, Tetrahedron Lett., 1511 (1971).

208. W. C. Still, J. Org. Chem. 41, 3063 (1976).

209. H. Sakurai, M. Kira and H. Umino, Chem. Lett., 1265 (1977).

210. H. Watanabe, K. Higuchi, M. Kobayashi and Y. Nagai, J. Chem. Soc. Chem. Commun., 1029 (1978).

211. H. Watanabe, K. Higuchi, M. Kobayashi, M. Hara, Y. Koike, T. Kitahara and Y. Nagai, J. Chem. Soc. Chem. Commun., 534 (1977).

212. W. H. Atwell, D. R. Weyenberg and H. Gilman, J. Org. Chem. 32, 885 (1967).

213. E. Krochmal, Jr., D. H. O'Brien and P. S. Mariano, J. Org. Chem. 40, 1137 (1975).

214. T. H. Koch, J. A. Soderquist and T. H. Kinstle, J. Amer. Chem. Soc. 96, 5576 (1974).

215. H. Sakurai and A. Okada, J. Organometal. Chem. 35, C13 (1972).

216. D. R. Weyenberg, L. H. Toporcer and A. E. Bey, J. Org. Chem. 30, 4096 (1965).

217. R. L. Harrell, Ph.D. Dissertation, Iowa State University, 1966 (unpublished), p 84.

218. C. L. Smith, Ph.D. Dissertation, Iowa State University, 1966 (unpublished), p 51.

219. M. V. George and R. Balusubramanian, in Journal of Organometallic Chemistry Library, Vol. 2, edited by D. Seyferth (Elsevier, New York, N.Y., 1976).

220. H. Sakurai, in Free Radicals, Vol. 2, edited by J. K. Kochi (John Wiley & Sons, New York, N.Y., 1973) pp 741-809.

221. D. Seyferth and D. P. Duncan, J. Organometal. Chem. 111, C21 (1976).

222. Thesis work of W. F. Goure, Iowa State University, unpublished work of T. J. Barton.

223. P. P. Gaspar, Washington University, St. Louis, Missouri, private communication.

224. T. J. Barton, G. Marquardt and J. A. Kilgour, J. Organometal. Chem. 85, 317 (1975).

225. M. Ishikawa, T. Fuchikami and M. Kumada, Tetrahedron Lett., 1299 (1976).

226. R. C. Kippenhan, Jr., Ph.D. Dissertation, Iowa State University, 1973 (unpublished), p 126.

227. R. Maruca, J. Org. Chem. 36, 1626 (1971).

228. J. Clardy and T. J. Barton, J. Chem. Soc., Chem. Commun., 690 (1972).

229. All crystallographic calculations were done on a Prime 400 computer operated by the Materials Science Center and the Department of Chemistry, Cornell University. The principal programs used were: REDUCE and UNIQUE, data reduction programs, M. E. Leonowicz, Cornell University, 1978; BLS, block diagonal least squares refinement, K. Hirotsu, Cornell University, 1978; ORFLS (modified), full matrix least squares, W. R. Busing, K. O. Martin and H. S. Levy, Oak Ridge, ORNL-TM-305; ORTEP, crystallographic illustration

program, C. Johnson, Oak Ridge, ORNL-3794; BOND, structural parameters and errors, K. Hirotsu, Cornell University, 1978; MULTAN-76, direct methods and fast fourier transform, G. Germain, P. Main and M. Woofson, University of York.

230. P. G. Gassman, Acc. Chem. Res. 4, 128 (1971).

231. A. J. Gordon and R. A. Ford, The Chemist's Companion, (John Wiley and Sons, New York, N.Y., 1972) p 274.

232. T. J. Barton and A. J. Nelson, Tetrahedron Lett., 5037 (1969).

233. H. Sakurai, J. Hayashi and T. Kobayashi, J. Organometal. Chem. 110, 303 (1976).

234. G. Zweifel and N. L. Polston, J. Amer. Chem. Soc. 92, 4068 (1970).

235. A. A. Byovets, M. O. Labartkava, T. L. Krasnova and E. A. Chernyshev, Zh. Obshch. Khim. 48, 930 (1978).

236. R. G. Salomon, J. R. Burns and W. J. Dominic, J. Org. Chem. 41, 2918 (1976).

237. M. E. Childs and W. P. Weber, J. Organometal. Chem. 86, 169 (1975).

238. H. Gilman and R. L. Harrell, J. Organometal. Chem. 5, 201 (1966).

239. T. J. Barton and C. R. Tully, J. Org. Chem. 43, 3649 (1978).

240. H. J. Reich and I. L. Reich, J. Org. Chem. 40, 2248 (1975).

241. R. L. Harrell, Ph.D. Dissertation, Iowa State University, 1966 (unpublished), p 95.

242. These experiments performed by W. F. Goure, Iowa State University, under the direction of T. J. Barton.

243. W. A. Kriner, J. Org. Chem. 29, 1601 (1964).

244. G. Fritz, D. Kummer and G. Sonntag, Z. Anorg. Allg. Chem. 342, 113, 121 (1966).

245. G. Fritz and N. Götz, Z. Anorg. Allg. Chem. 375, 171 (1970).

246. H. Gilman and R. D. Gorsich, J. Amer. Chem. Soc. 77, 6380 (1955).

ACKNOWLEDGEMENTS

I would like to express thanks to my colleagues in the Barton group for their support and many helpful discussions. A special thanks is due to Bill Goure for his collaboration in the silylsilylene work and for his efforts in assembling this manuscript.

This work was accomplished under the leadership of Dr. Thomas J. Barton, and made easier by his ability to inspire and persuade. I would also like to thank Dr. Barton for ensuring that I obtained the educational experience that I wanted and needed at Iowa State University.

I would like to thank my family, my father, my late mother, my sisters, my father-in-law and my mother-in-law for their personal support during the period in which this work was done.

Above all, I would like to thank my wife, Mary, for her love, encouragement, and sacrifice, all of which make this dissertation as much hers as mine.