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Synthetic and mechanistic studies of the elusive 2-silaoxetanes

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Synthetic and mechanistic studies of the elusive 2-silaoxetanes

by

Michael Lee Tumey

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

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DEDICATION

This thesis is dedicated to my father

Charles O. Tumey, Sr.

who has given me strength,
honesty, and compassion with
which to live.

INTRODUCTION

Interest in compounds which contain silicon-oxygen (p-p)π double bonds, silanones, dates back three quarters of a century. In 1904 Dilthey and Eduardoff (1) reported that diphenylsilanone was formed in the pyrolysis of diphenylsilanediol. Apparently, a new area had been opened to investigation. However, better methods of chemical structure determination came into existence which proved that these reported silanone monomers were actually oligomers and polymers of these compounds. These early attempts and failures at isolation led to a state of dormancy in this area as an attitude of disbelief concerning the very existence of silicon multiple bonds prevailed.

Gradually, more sensitive analytical methods were developed. However, these advances alone were not enough to reopen this seemingly forbidden area of study. The realization had to be made that compounds might actually exist even though they might not be isolable. Thus, a basic shift from synthesis and isolation was made; a new emphasis was placed upon how the observed products were formed, the mechanism of the reaction. The study and trapping of reactive intermediates became important. As a result, the door to silanone research was reopened finally with the work of Andrianov and Sokolov (2) in 1952; the intermediacy of a silanone had been invoked.

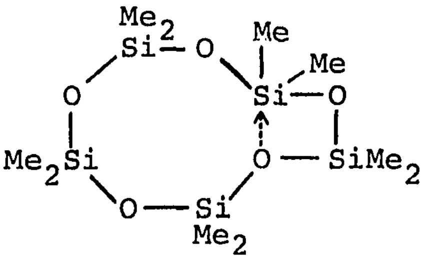
This thesis will consider the use of compounds as potential silanone generators. In particular, interest in the area of 2-silaoxetanes will be stressed: their formation and their mechanism of decomposition. This investigation will be extended to include 2,4-disilaoxetanes. The intermediacy of silanones in the decompositions of both species will be studied. Finally, in a somewhat related area, a study of the potential rearrangement of α-silylcarbenes to silicon-carbon $(p-p)\pi$ doubly bonds species will be made.

HISTORICAL

Silanones

The modern day investigation of silanones began with the studies of Andrianov and Sokolov (2). In these studies polydimethylsiloxanes were pyrolyzed at 150-200 °C to give various new polysiloxanes which differed only in chain length from the starting material in increments of Me_2SiO units. These results led them to suggest that dimethylsilanone, Me_2SiO, was being generated as a reaction intermediate.

Somewhat more substantial evidence of silanone intermediacy was obtained in the area of cyclosiloxane and cyclocarbosiloxane redistributions at 500-700 °C. In a series of articles Nametkin, Gusel'nikov, and coworkers (3-5) described the pyrolyses of a number of cyclosiloxanes and cyclocarbosiloxanes which differed in ring size. The products which they observed from these reactions were new cyclosiloxanes or cyclocarbosiloxanes which were either larger or smaller than the starting materials by units of Me_2SiO or Me_2SiCH_2. A more detailed kinetic study of the thermolysis of the ten-membered decamethylcyclopentasiloxane $\underline{1}$ revealed that its concentration decreased monotonically with time, giving the following Arrhenius dependency: $k = 10^{12.0} \exp(-61{,}000/RT)$ sec^{-1}. In addition, the concentration of the eight-membered octamethylcyclotetrasiloxane $\underline{2}$ which was formed in the reaction was noted to increase initially, pass through a maximum, and decrease finally as the concentration of a second product, hexamethylcyclotrisiloxane 3 increased. These results suggested that these rearrangements were stepwise in nature. Thus, a four-centered transition state similar to that of 4 which resulted in dimethylsilanone extrusion was postulated.



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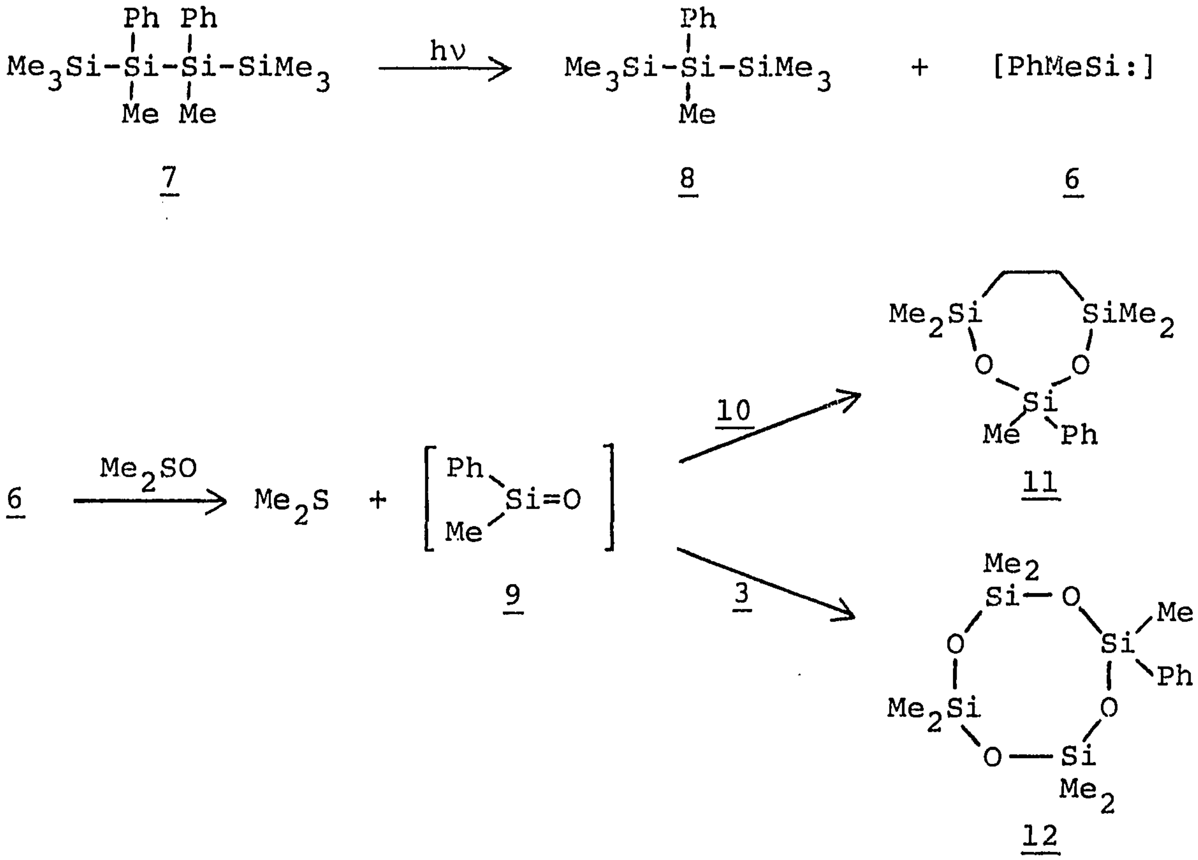
A similar kinetic study of the gas-phase thermal decomposition of octamethylcyclotetrasiloxane was made by Davidson and Thompson (6). Up to approximately 25% decomposition of 2 , the pyrolysis gave only examethylcyclotrisiloxane 3 and decamethylcyclopentasiloxane 1. For the first 4% decomposition the rate of formation of 3 was a simple first-order expression: $\log k = 14.85 \pm 0.39 - (72.0 \pm 1.5)/2.303RT$ (95% confidence limits), where k was in sec^{-1} and the activation energy was in kcal/mole. Additional information regarding the mechanism of this redistribution reaction was obtained from trapping experiments. Ethylene, propylene, 1,3-butadiene, and traces of silicone grease were all found to be effective inhibitors of the formation of cyclopentasiloxane 1 although no mention of any trapping products was made. At the same time these reagents had no effect upon the formation of cyclotrisiloxane 3. These observations tended to give further support to the formation of dimethylsilanone as an intermediate. The kinetic data also allowed the calculation to be made of a minimum value for the silicon-oxygen π bond in dimethylsilanone. This value, 37.8 kcal/mole, led the authors to propose that dimethylsilanone existed as a weak silicon-oxygen doubly bonded species rather than a diradical.

In a different type of experiment Sharp and Margrave (7) studied the low-temperature reaction of thionyl fluoride with silicon difluoride, which is also named as difluorosilylene to indicate a divalent silicon species analogous to carbenes. They observed the formation of three homologous series of fluorosiloxanes: linear polysiloxanes, $Si_nO_{n-1}F_{2n+2}$; asymmetric disiloxanes, $F_3Si(SiF_2)_nOSiF_3$; and cyclosiloxanes, $(F_2SiO)_n$. These compounds were suggested primarily by mass spectrometry and to a lesser extent by fluorine magnetic resonance spectrometry. Similar results were obtained when silicon difluoride was reacted with oxygen or sulfur dioxide. In addition, when silicon difluoride was reacted with 2-propanone, hexafluorodisiloxane was produced with no apparent side reactions of the silicon species with the carbon skeleton. From these observations the authors suggested a stepwise mechanism for the thionyl fluoride reaction, with the first step being an oxygen abstraction to give difluorosilanone, $F_2Si=O$. This resulting species attacked a halogen atom of the remaining SF_2, an oxygen of a second thionylfluoride, a $(SiF_2)_n$ or SiF_4 species, or dimerized to form perfluorocyclosiloxanes. The polysiloxanes resulted then from a linear polymerization of difluorosilanone or a diradical species, $(F_2Si)_nO$.

Oxygen abstraction was also proposed by Weber and coworkers as the first step in the reaction of photochemically generated dimethylsilylene 5 or methylphenylsilylene 6 with dimethylsulfoxide (8,9). For example, when octamethyl-2,3-diphenyltetrasilane 7 was photolyzed through quartz in the presence of dimethylsulfoxide, the major primary process was the formation of heptamethyl-2-phenyltrisilane 8 and methylphenylsilylene 6 which further reacted with dimethylsulfoxide to form dimethylsulfide and the proposed methylphenylsilanone 9. The methylphenylsilanone led to oligomers in the absence of trapping agents. However, when either 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane 10 or hexamethylcyclotrisiloxane 3 was present in the initial reaction mixture, trapping of the silanone intermediate was observed with 2,4,4,7,7-pentamethyl-2-phenyl-1,3-dioxa-2,4,7-trisilacycloheptane 11 or heptamethylphenylcyclotetrasiloxane 12 being formed, respectively.

In addition, a second primary photo-process was observed (Scheme 2). The authors suggested that nucleophilic attack

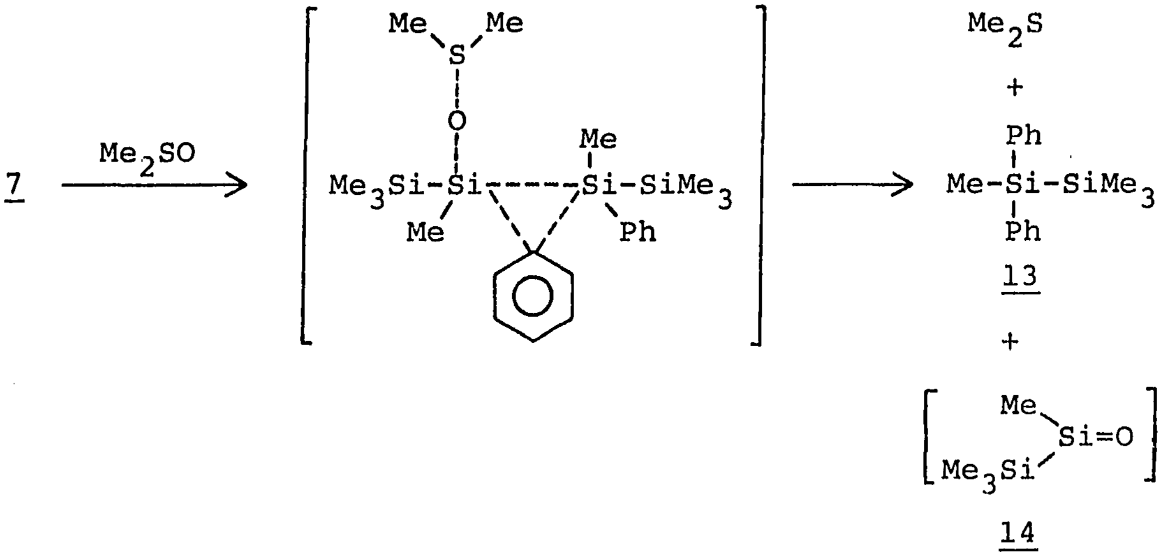
Scheme 1



by the oxygen of dimethylsulfoxide upon one of the phenyl-substituted silicon atoms followed by migration of the phenyl group to an adjacent silicon atom gave the observed tetramethyl-1,1-diphenyldisilane 13, a second molecule of dimethylsulfide, and methyltrimethylsilylsilanone 14. Again, the intermediacy of this second silanone was established from trapping experiments.

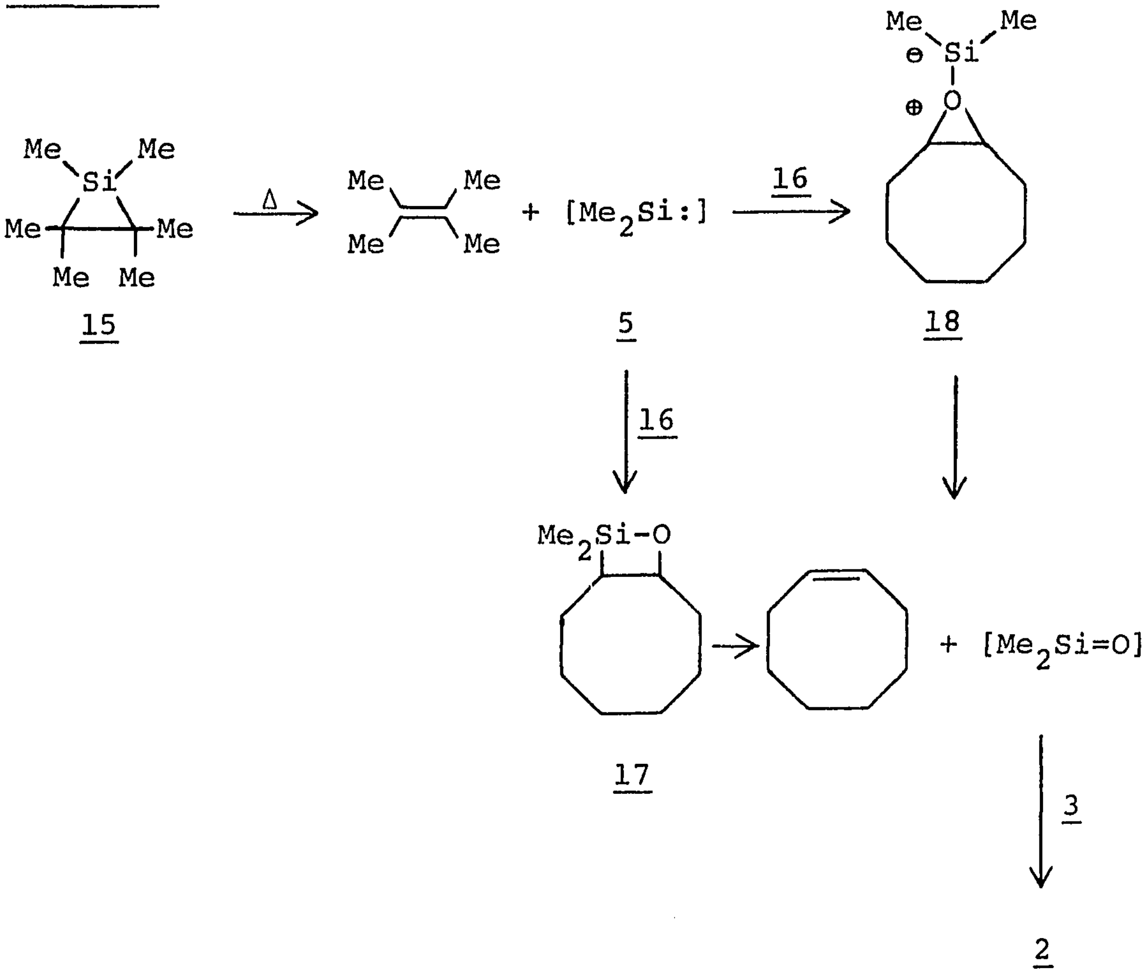
Quite recently the reaction of dimethylsilylene with epoxides has been investigated by Barton *et al.* (10). Hexa-

Scheme 2



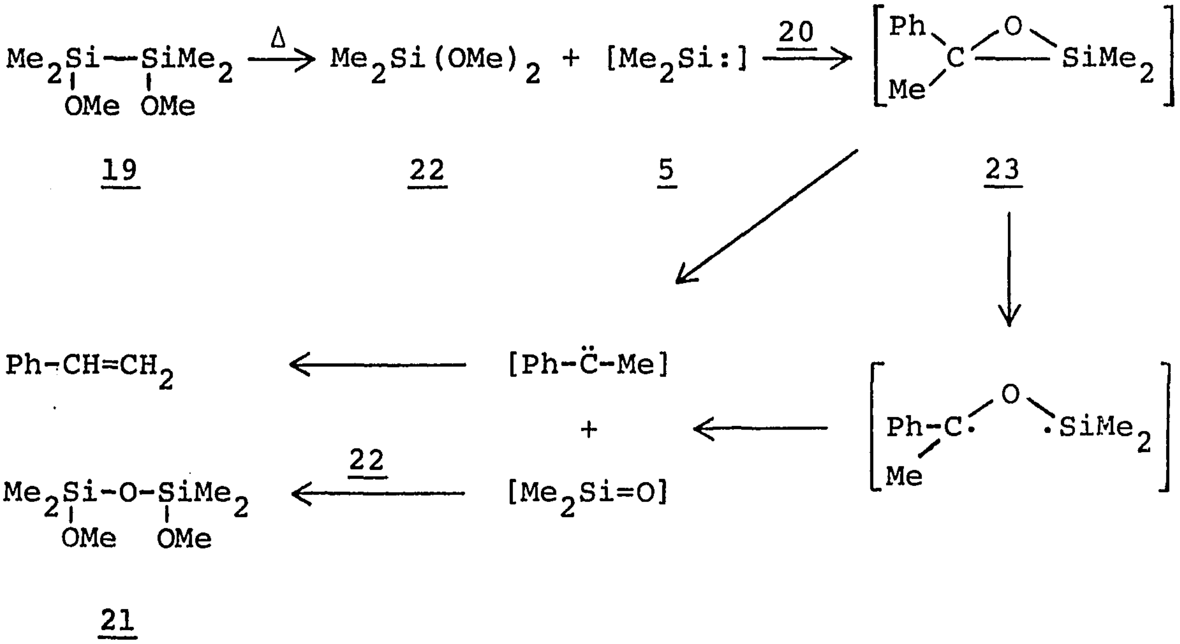
methylsilirane $\underline{15}$ which had been shown by Seyferth and Annarelli (11) to extrude thermally dimethylsilylene $\underline{5}$ was heated to 85-90° in a sealed tube with excess cyclooctene oxide $\underline{16}$ and hexamethylcyclotrisiloxane $\underline{3}$. The major products were 2,3-dimethyl-2-butene, cyclooctene, and octamethylcyclotetrasiloxane $\underline{2}$. To explain these products the authors suggested that dimethylsilylene either inserted into the carbon-oxygen bond of cyclooctene oxide to form the silaoxetane $\underline{17}$ or formed the oxygen ylid $\underline{18}$ (Scheme 3). In both pathways dimethylsilanone was lost to give cyclooctene with the silanone being trapped to yield octamethylcyclotetrasiloxane $\underline{2}$. Very similar results were obtained when dimethylsilylene was generated photochemically from dodecamethylcyclohexasilane (12).

Scheme 3



In a somewhat different experiment Ando and coworkers (13) studied the interaction of thermally generated dimethylsilylene with ketones. Flow pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane 19 (14) with an excess of acetophenone 20 at 800°C gave moderate yields of sym-dimethoxytetramethyldisiloxane 21 and styrene in addition to dimethoxydimethylsilane 22 and some polysilanes. The authors proposed an initial addition of dimethylsilylene 5 to the carbonyl group of acetophenone to give an intermediate silaoxirane 23 which either cleaved in a stepwise fashion or underwent a direct cheletropic fragmentation to give methylphenylcarbene and dimethylsilanone. Finally, the carbene rearranged to

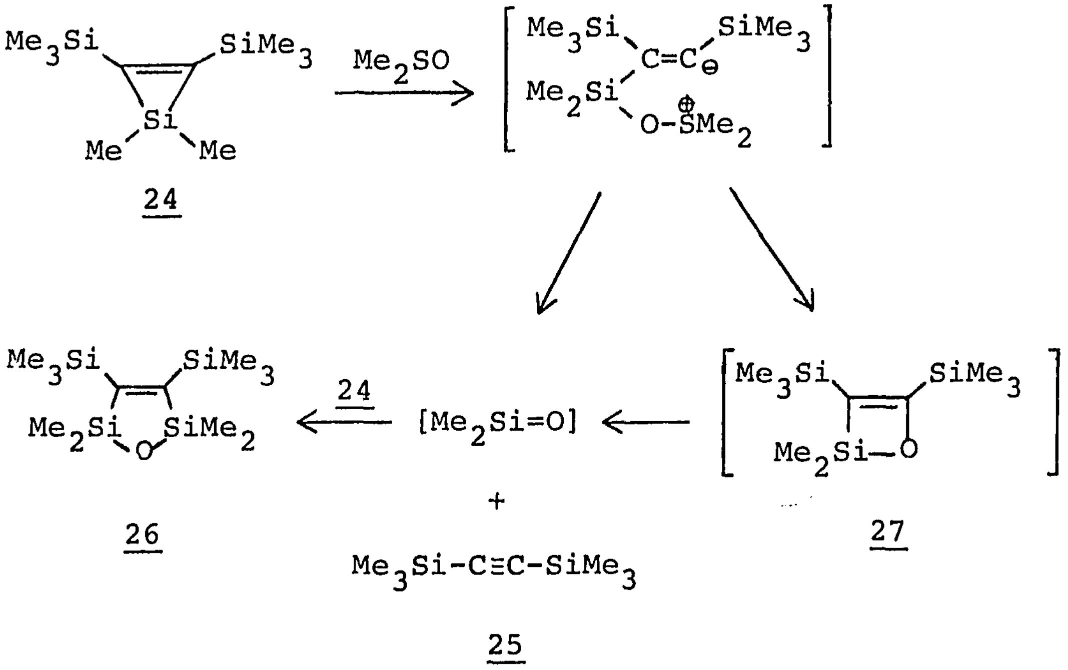
Scheme 4



yield styrene, and dimethylsilanone was trapped by the by-product of the reaction, dimethoxydimethylsilane to form the disiloxane 21.

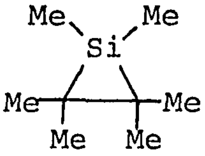
Abstraction of oxygen by silicon-containing species other than silylenes was reported recently by Seyferth and coworkers (15). 1,1-Dimethyl-2,3-bis(trimethylsilyl)-1-silirene 24 reacted with dimethylsulfoxide at 0°C to give dimethylsulfide, bis(trimethylsilyl)acetylene 25, and 3,3,5,5-tetramethyl-1,2-bis(trimethylsilyl)-4-oxa-3,5-disilacyclopentene 26. The mechanism which was suggested by the authors involved an initial insertion of the oxygen of dimethylsulfoxide into the silicon-carbon bond of the silirene to give either an intermediate silaoxetene 27 which decomposed or bis(trimethylsilyl)acetylene and dimethylsilanone directly. Next, the silanone added across the silicon-carbon bond of a second silirene molecule to give the observed product 26 as shown in Scheme 5. The intermediacy of dimethylsilanone was

Scheme 5



confirmed by trapping experiments with hexamethylcyclotrisiloxane and dimethoxydimethylsilane. The possibility of dimethylsilylene 5 extrusion prior to reaction with dimethylsulfoxide was excluded by the authors since the silirene 24 was thermally very stable.

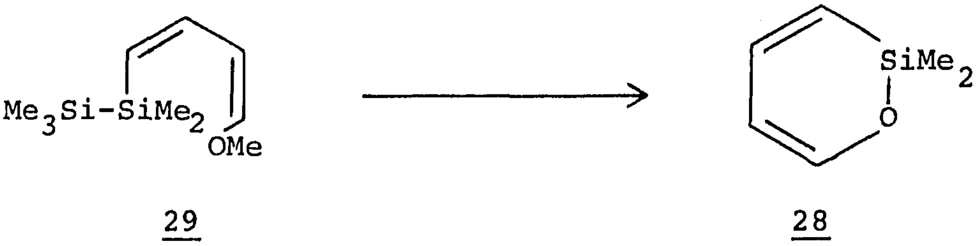
Similar results were obtained when hexamethylsilirane 15 was substituted for the silirene 24, again under conditions where the starting material was thermally stable. In addition, pyridine N-oxide and trimethylamine N-oxide reacted with silirene to generate silanone products although in lower yields than for dimethylsulfoxide.



15

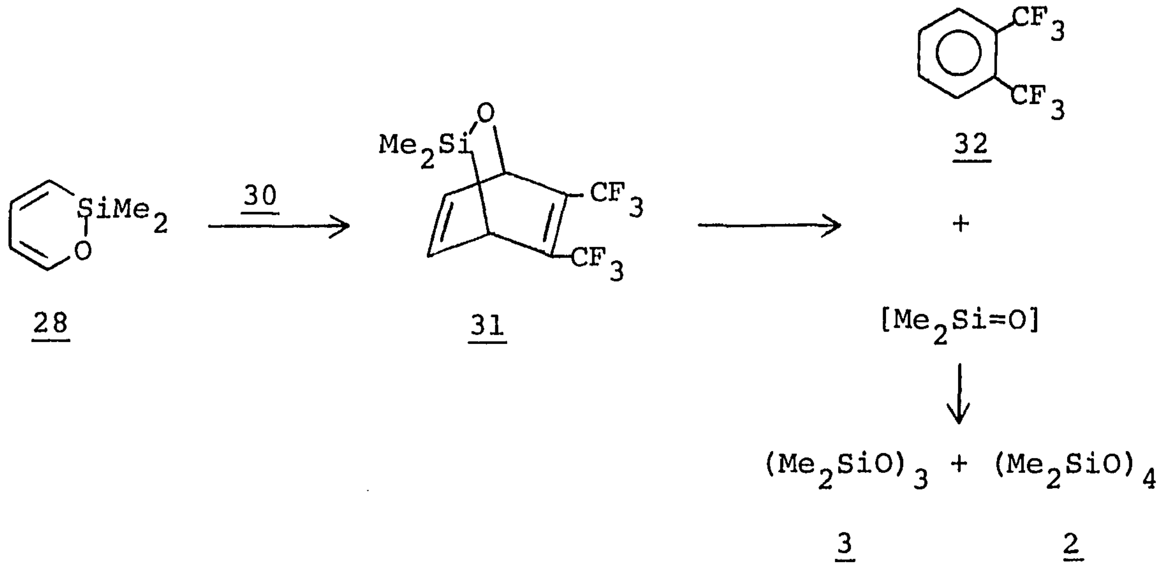
Very recently Barton and Wulff (16) have investigated the reactions of 6,6-dimethyl-6-sila-5-oxa-1,3-cyclohexadiene 28 which was formed as the major product in the vacuum pyrolysis of the disilane 29. When 28 was reacted with 1,1,1,4,4,4-

Scheme 6



hexafluoro-2-butyne 30 even at room temperature, none of the expected Diels-Alder adduct 31 was detected. Instead, the products were 1,2-bis(trifluoromethyl)benzene 32 and small amounts of hexamethylcyclotrisiloxane 3 and octamethylcyclotetrasiloxane 2. These products were explained in terms of the decomposition of the adduct 31 as shown in Scheme 7.

Scheme 7



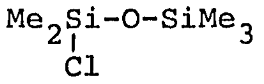
28 31 32

[$Me_2Si=O$]

$(Me_2SiO)_3 + (Me_2SiO)_4$

3 2

Trapping experiments with dimethoxydimethylsilane or chlorotrimethylsilane gave sym-dimethoxytetramethyldisiloxane 21 or 1-chloro-1,1,3,3,3-pentamethyldisiloxane 33, respectively, which were consistent with formation of dimethylsilanone under these very mild conditions.

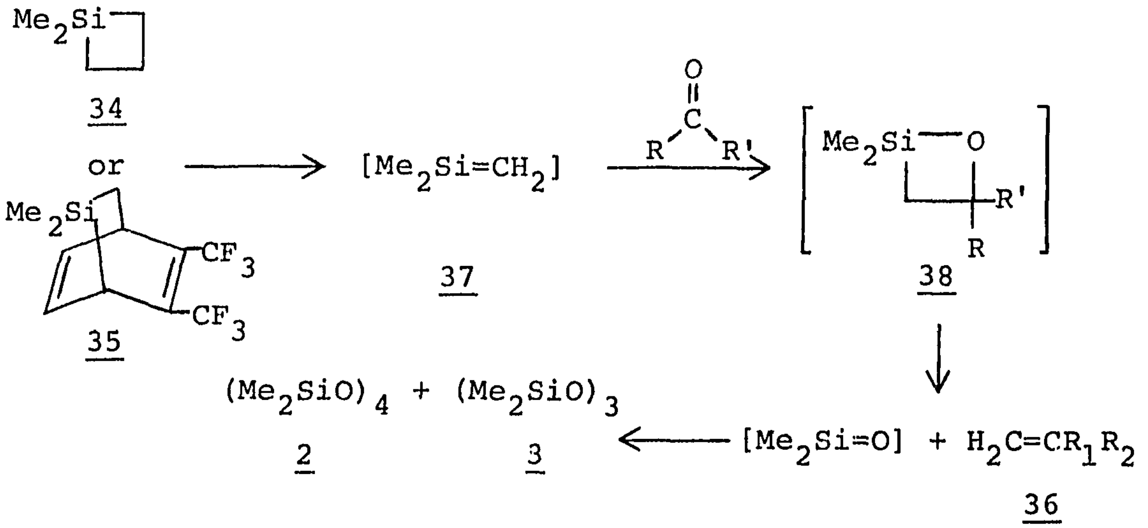


$Me_2Si(Cl)\text{-}O\text{-}SiMe_3$

33

Perhaps the most frequently encountered examples of proposed silanone intermediates have been in the attempted trappings of silicon-carbon (p-p)π doubly bonded species, silenes. In 1972 Barton and coworkers (17) reported the co-pyrolysis of ketones and aldehydes with both 1,1-dimethyl-1-silacyclobutane 34 and 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,8-diene 35. The products which were observed were the cyclosiloxanes 2 and 3 and the alkene 36 which would result from a Wittig type addition of methylene to the carbonyl compound (Scheme 8). The authors proposed

Scheme 8

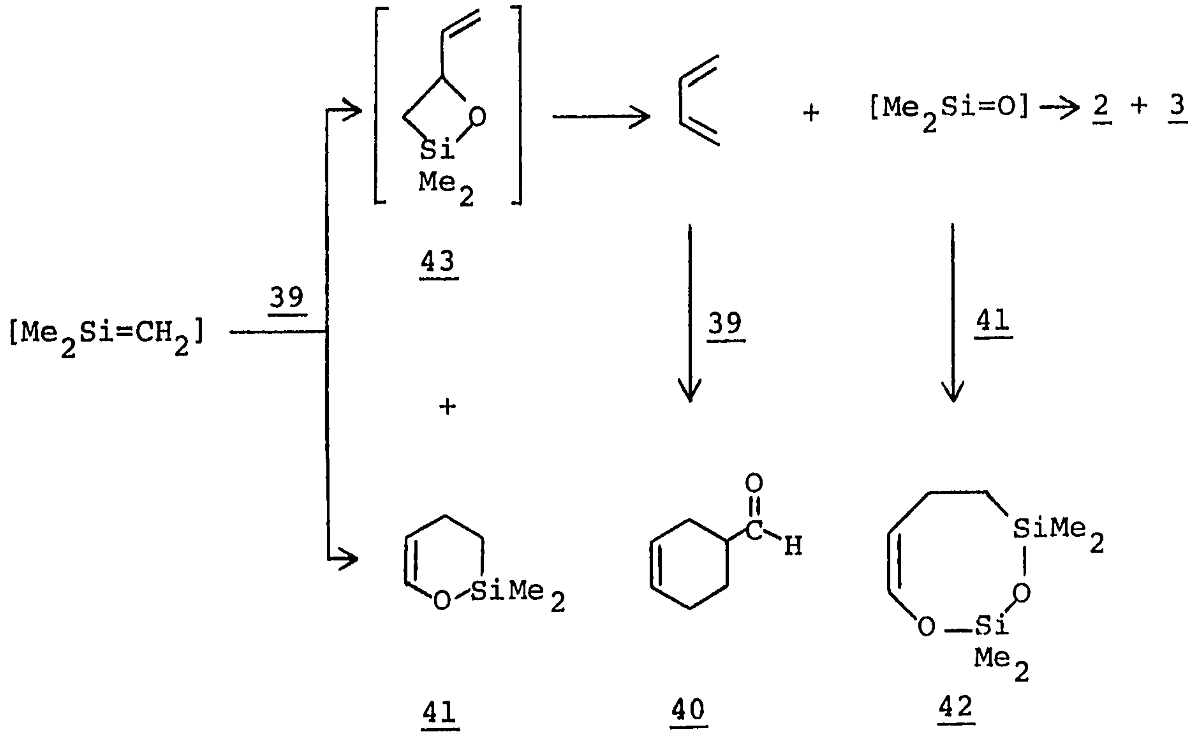


that an initially generated silene 37 added to the carbonyl group to give an intermediate 2-silaoxetane 38. Under the conditions of the flow pyrolysis 38 cleaved to give the corresponding alkene 36 and dimethylsilanone which underwent cyclic oligomerization to form the cyclosiloxanes 2 and 3.

In a similar investigation Sommer and coworkers studied the thermolysis reactions of several silacyclobutanes with a series of aldehydes and ketones. Again, the alkenes which might be expected to arise from the proposed 2-silaoxetane intermediate were observed. In general, higher yields of alkenes were obtained for aromatic aldehydes and ketones than for aliphatic ones. In addition, cyclosiloxanes were isolated which supported the proposed intermediacy of a silanone (18-20).

Comparable results were obtained by Valkovich and Weber (21,22) in the copyrolysis of 1,1-dimethyl-1-silacyclobutane 34 (or the 2-phenyl derivative) and acrolein 39 at 600°C. The products which were isolated included ethylene, 1,3-butadiene, 3-cyclohexene-1-carboxaldehyde 40, hexamethylcyclotrisiloxane 3, octamethylcyclotetrasiloxane 2, 4,4-dimethyl-3-oxa-4-silacyclohexene 41, and 4,4,6,6-tetramethyl-3,5-dioxa-4,6-disilacyclooctene 42. Again, a 2-silaoxetane intermediate 43 which decomposed to dimethylsilanone was suggested to explain the formation of several of the products as shown in Scheme 9. In addition to the 1,3-butadiene and cyclosiloxanes, the cyclooctene 42 which the authors proposed was formed from an

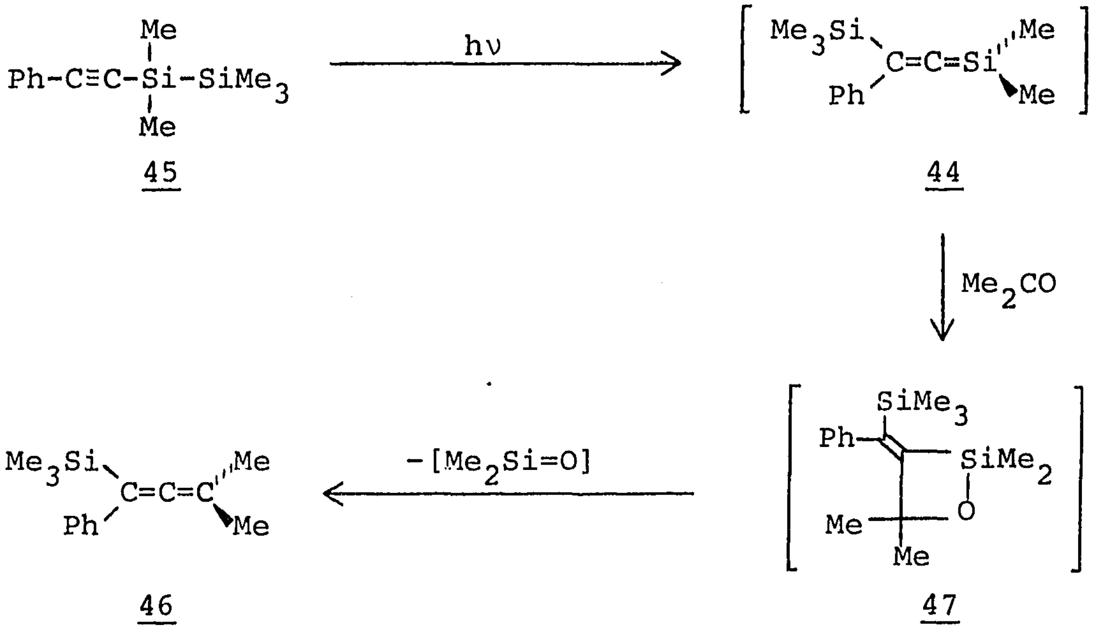
Scheme 9



insertion of dimethylsilanone into cyclohexene 41 seemed to be consistent with the mechanism.

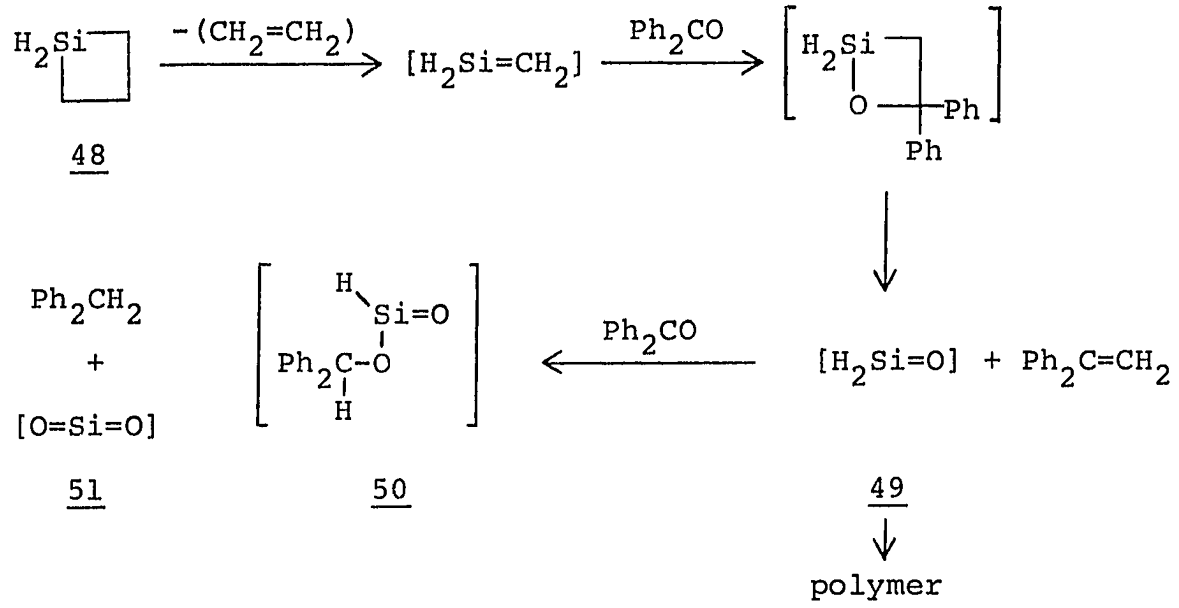
In 1976 Ishikawa et al. (23) reported the trapping of a proposed 1-silaallene intermediate 44 by acetone. In the photolysis of (pentamethyldisilanyl)phenylacetylene 45 in benzene with acetone present as a trap, 3-methyl-1-phenyl-1-trimethylsilyl-1,2-butadiene 46 was isolated as a minor product. An initial 1,3-migration of silicon followed by trapping with acetone was proposed (Scheme 10). The resulting 2-silaoxetane 47 then lost dimethylsilanone to give the observed product 46. Interestingly no cyclosiloxanes were reported in this case.

Scheme 10



An absence of cyclosiloxanes was also noted by Golino and coworkers (24) in the flow pyrolysis of silacyclobutane 48 with benzophenone at 560°C. The only isolated products were 1,1-diphenylethylene and a small amount of diphenylmethane which by using 1,1-dideuterio-1-silacyclobutane was shown to result at least in part from reduction of benzophenone by a $H_2Si{=}X$ species ($X = CH_2$ or O). The mechanism which the authors proposed is shown in Scheme 11. They suggested that the intermediate silanone 49 either polymerized or added to a second molecule of benzophenone via the silicon-hydrogen bond and that this intermediate 50 decomposed to diphenylmethane and a silicon dioxide species 51. The absence of

Scheme 11



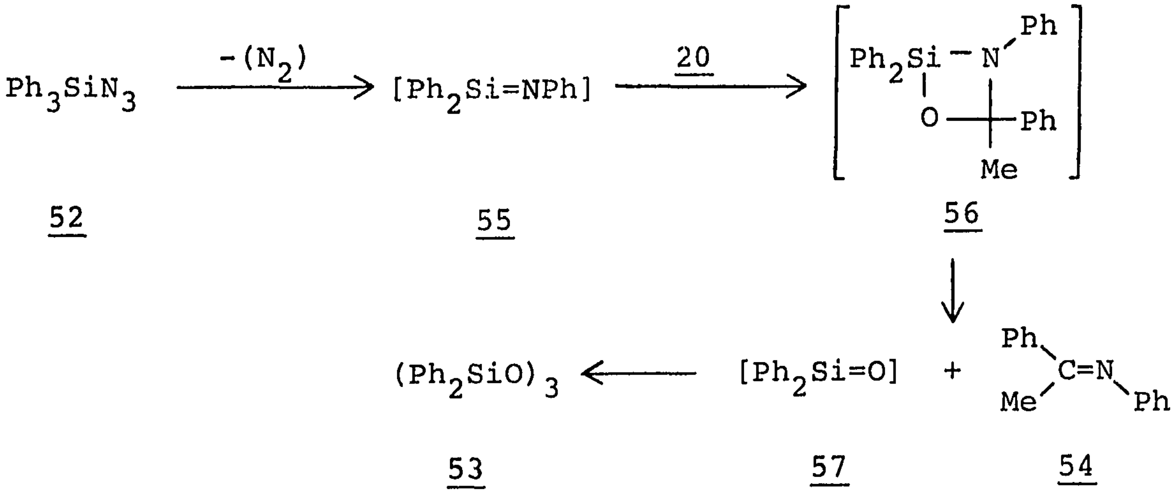
cyclosiloxanes, $(H_2SiO)_n$ was rationalized by noting that the cyclic trimer had never been reported and that the cyclic tetramer had been reported to decompose at room temperature (25). Therefore, such species were not expected to survive under the reaction conditions. However, silanone formation was established by trapping with added hexamethylcyclotrisiloxane to give 1,1,3,3,5,5-hexamethylcyclotetrasiloxane.

Several other examples of trapping experiments of silenes with carbonyl compounds have been described (26-29).

Silanones have also been postulated in reactions of aldehydes and ketones with multiply bonded silicon species other than silenes. For example, Sommer and coworkers (30,31) have reported the trapping of thermally generated silaimines,

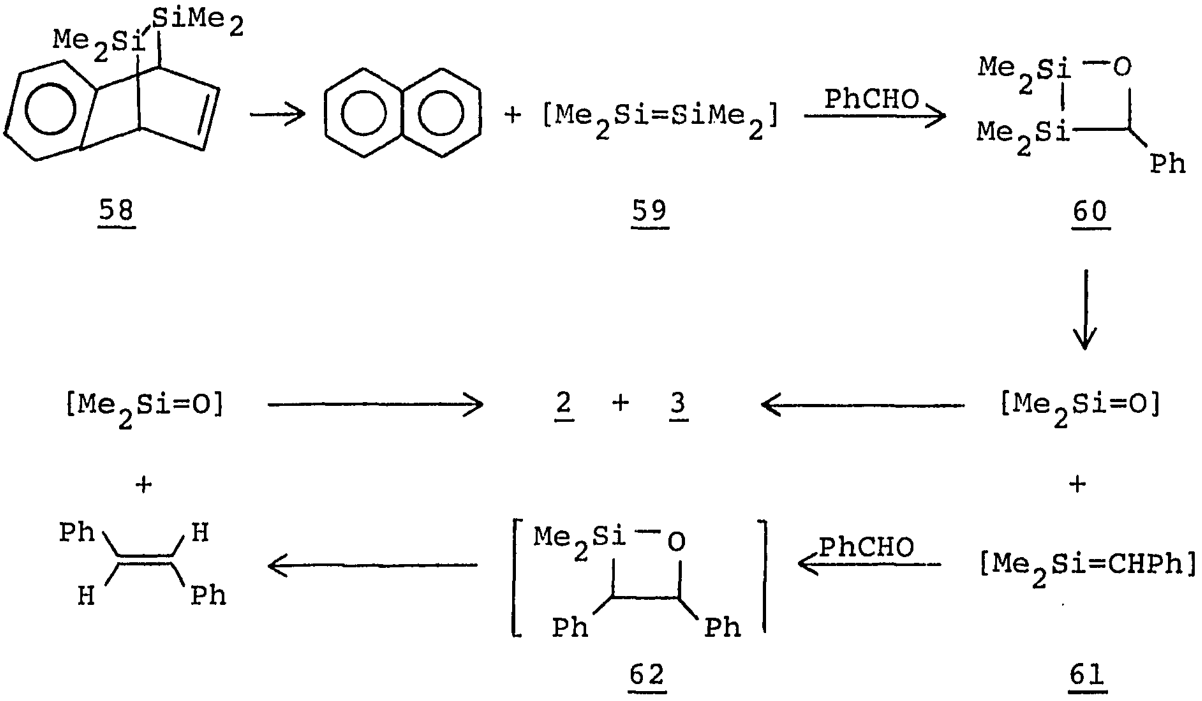
$R_2Si{=}NR$. When triphenylsilylazide 52 was pyrolyzed with acetophenone 20, hexaphenylcyclotrisiloxane 53 and (N-phenyl)-methylphenylimine 54 were isolated. The proposed mechanism involved an initial extrusion of nitrogen to give the triphenylsilaimine 55 which added to acetophenone to give the four-centered intermediate 56 (Scheme 12). Decomposition of 56 gave the imine 54 and diphenylsilanone 57 which led to the cyclosiloxane 53.

Scheme 12



Barton and Kilgour (32,33) reported the formation of dimethylsilanone from the reaction of benzaldehyde with compounds containing silicon-silicon (p-p)π double bonds, disilenes. When 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene 58 was pyrolyzed in the presence of an excess of benzaldehyde, the products were naphthalene, trans-stilbene, hexamethylcyclotrisiloxane 3, and octamethylcyclotetrasiloxane 2. Since Roark and Peddle (34) had already rather conclusively established the thermal extrusion of tetramethyldisilene 59 from 58, the authors suggested two possible mechanisms to explain the products after eliminating dimethylsilylene 5 and phenylcarbene as intermediates. The first of these mechanisms was reminiscent of the reaction of silenes with carbonyl compounds as shown in Scheme 13. The

Scheme 13

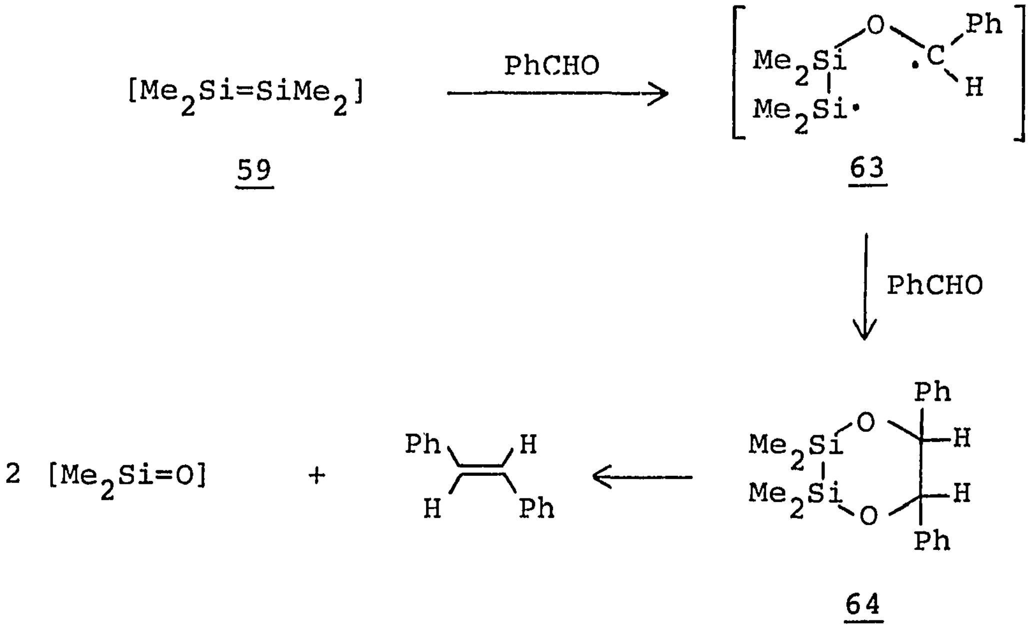


first step involved formation of a 2,3-disilaoxetane 60 followed by cleavage to give dimethylsilanone and the silene

61. This silene was trapped subsequently by a second molecule of benzaldehyde to give the 2-silaoxetane 62 which decomposed to give a second molecule of dimethylsilanone and *trans*-stilbene.

However, the absence of any dimer of silene 61, *cis*- or *trans*-1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane even when only a small excess of benzaldehyde was used led the authors to suggest an alternative mechanism (Scheme 14).

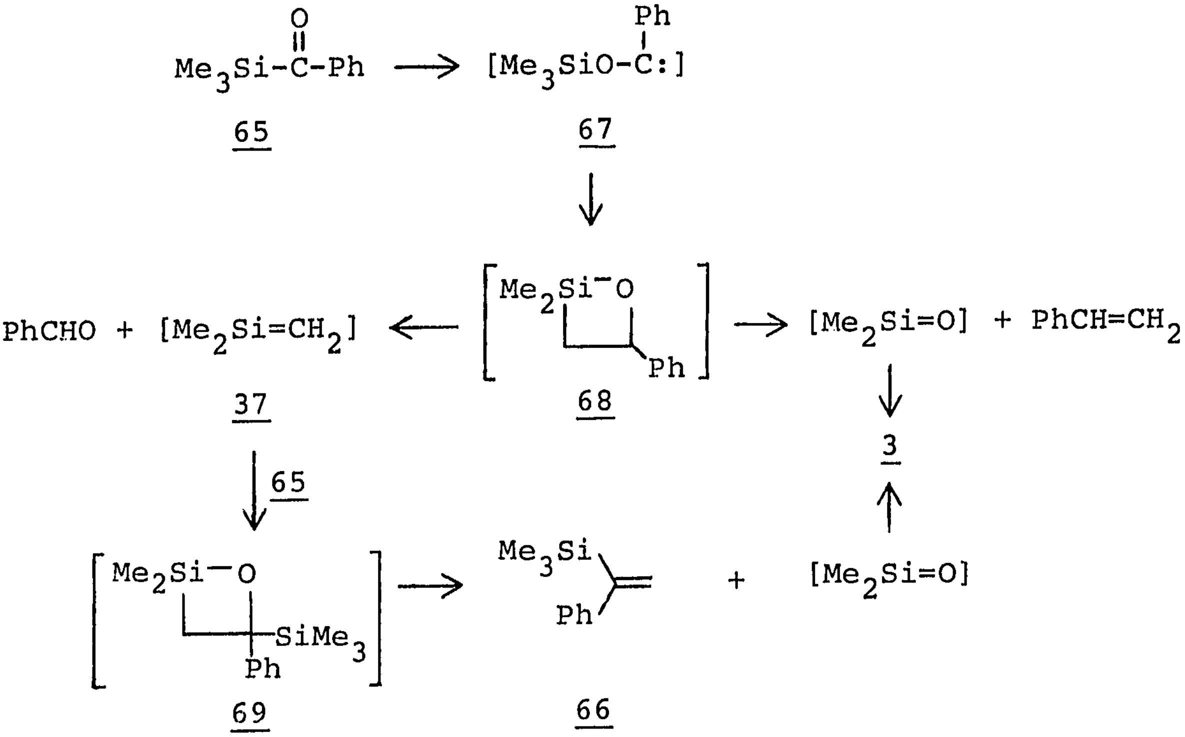
Scheme 14



In this proposed pathway disilene 59 reacted with benzaldehyde to give the 1,4-diradical 63 which added a second molecule of benzaldehyde to produce the 2,3-disila-1,4-dioxane 64. Then, this dioxane underwent a six-electron decomposition to give *trans*-stilbene and two molecules of dimethylsilanone. Indeed, when independently synthesized dioxane 64 was pyrolyzed under the reactions conditions, the products were again *trans*-stilbene and cyclosiloxanes 2 and 3. Thus, the second mechanism was certainly consistent with the results although the first mechanism could not be totally excluded.

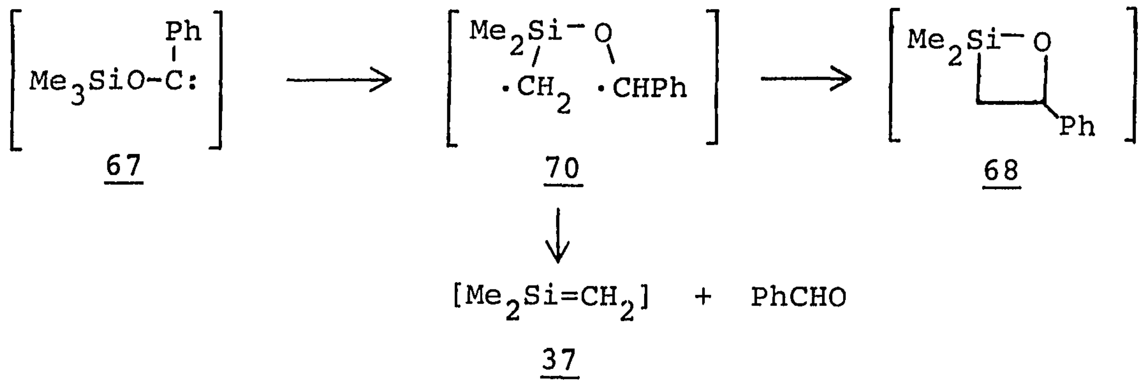
Central to all the mechanisms describing carbonyl trapping of multiply bonded silicon species was the initial formation of a 2-silaoxetane intermediate. It was proposed that this intermediate then cleaved to produce an alkene and a silanone. Recently, however, evidence was presented by Ando and coworkers (35,36) which suggested, according to the authors, that 2-silaoxetanes might undergo silicon-oxygen bond cleavage to give a silene and a carbonyl compound. Flow pyrolysis of phenyl(trimethylsilyl)ketone 65 at 500°C gave hexamethylcyclotrisiloxane 3, styrene, benzaldehyde, and α-trimethylsilyl styrene 66. Brook and coworkers had previously shown that several silylketones rearranged photochemically (37-41) and thermally (42) to give siloxycarbenes which either reacted with various added trapping reagents or underwent intramolecular reactions. Therefore, these authors proposed an initial rearrangement to the siloxycarbene 67 followed by an insertion into a carbon-hydrogen bond of one of the silyl methyl groups to produce the 2-silaoxetane 68 (Scheme 15). The next step involved cleavage of silaoxetane 68 in two different directions. Rupture of the silicon-

Scheme 15



carbon bond led to styrene and dimethylsilanone which oligomerized to the cyclosiloxane 3. Cleavage in the opposite direction gave benzaldehyde and the silene 37. It was suggested by the authors that this silene added to the carbonyl group of a second molecule of starting ketone 65 to give a second 2-silaoxetane 69. Finally, this silaoxetane cleaved to give α-trimethylsilylstyrene and a second molecule of dimethylsilanone. Thus, some question of reversibility of the silene addition to carbonyl compounds was raised. However, the authors failed to consider an alternative mechanism which might explain the formation of benzaldehyde and α-trimethylsilylstyrene 66 without the intermediacy of 2-silaoxetane 68. If the siloxycarbene 67 were generated at least in part in the triplet state or underwent intersystem crossing from an initial singlet to triplet which might be facilitated by the aryl group (43), hydrogen abstraction might occur to give the 1,4-diradical 70 (Scheme 16). This diradical might close to give the 2-silaoxetane 68 or might simply cleave at the silicon-oxygen bond to produce benzaldehyde and silene 37 which could react as shown previously in Scheme 15. Therefore, the silaoxetane cleavage to benzaldehyde might not be necessary. Still, this work has brought to light the need to actually study the reactivity of other 2-silaoxetanes.

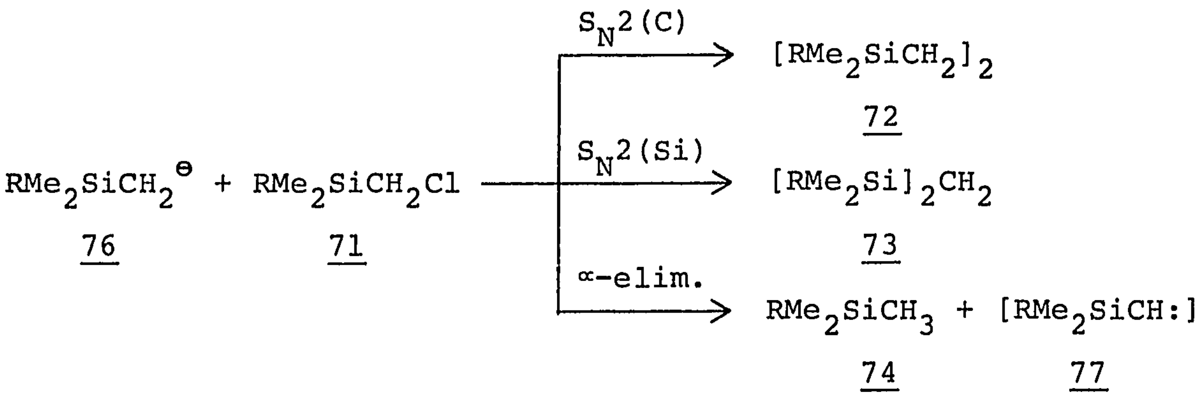
Scheme 16



α-Silylcarbenes

Interest in the intermediacy and reactivity of α-silylcarbenes was generated by the early work of Connolly and Urry (44) and Connolly (45). These authors studied the Wurtz reaction of a series of alkyl(chloromethyl)dimethylsilanes 71 with alkali metals. The products which they observed consistently included 1,2-bis(alkyldimethylsilyl)ethane 72, bis(alkyldimethylsilyl)methane 73, alkyltrimethylsilane 74, and 2,4-dialkyl-2,4-dimethyl-disilahexane 75. These products were explained by an initially formed α-(alkyldimethylsilyl)carbanion 76 reacting with starting silane 71 by one of the three pathways shown in Scheme 17. The α-silylcarbene 77 underwent

Scheme 17



a 1,3-insertion to give 1-alkyl-1-methyl-1-silirane which was attacked by anion 76 with ring opening to produce the disilahexane 75 (Scheme 18). The intermediacy of α-(alkyldimethylsilyl)carbene 77 was suggested by the isolation of the 1,5-

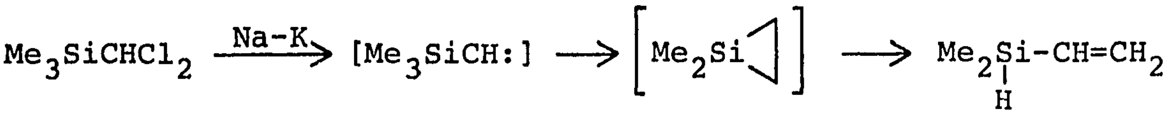
Scheme 18

76 75

insertion product, 1,1-dimethyl-1-silacyclopentane when chloromethyldimethyl-*n*-propylsilane was used as the starting material.

At roughly the same time Skell and Goldstein (46) reported that the flow pyrolysis of dichloromethyltrimethylsilane 78 in a sodium-potassium vapor atmosphere gave dimethylvinylsilane 79 as a product. The authors proposed that α-trimethylsilyl)carbene 80 was formed initially and that this carbene inserted into a carbon-hydrogen bond to produce 1,1-dimethylsilirane 81 (Scheme 19). Finally, the silirane rearranged to give the observed dimethylvinylsilane.

Scheme 19



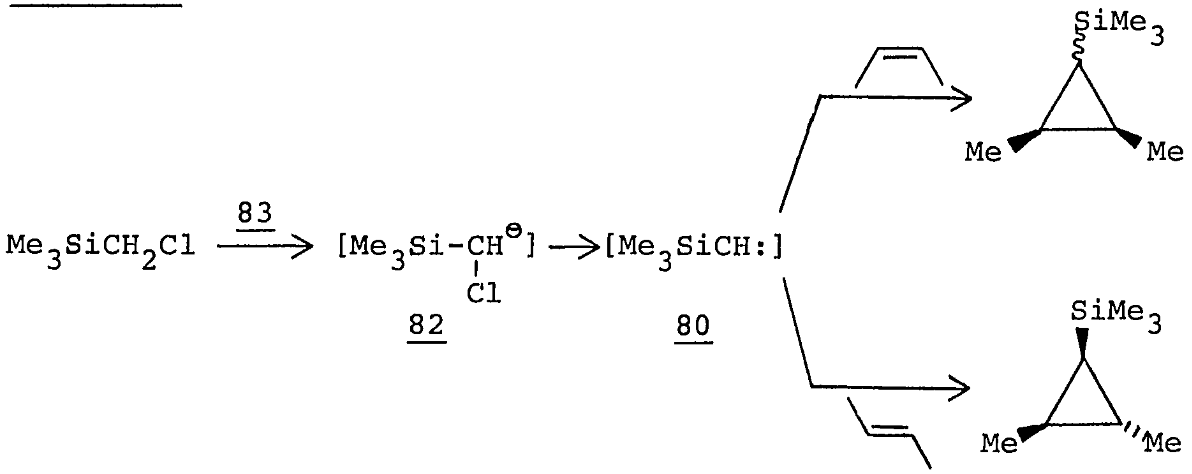
78 80 81 79

In a somewhat different experiment Dyakonov and coworkers (47) reacted chloromethyltrimethylsilane with *n*-butyllithium. The products which they isolated included *n*-butyltrimethylsilane, trimethyl-*n*-pentylsilane, *trans*-1,2-bis(trimethylsilyl)ethylene, and 1-*n*-butyl-1,2-bis-(trimethylsilyl)ethane. The authors claimed that α-chloro-α-(trimethylsilyl)carbanion **82** was formed initially and that **82** lost lithium chloride to give α-(trimethylsilyl)carbene **80**. Then, the reaction of the carbene with α-chloro-α-(trimethylsilyl)carbanion was to produce *trans*-1,2-bis(trimethylsilyl)-ethylene which reacted subsequently with *n*-butyllithium to give 1-*n*-butyl-1,2-bis(trimethylsilyl)ethane. Interestingly, when the reaction was performed with an excess of added cyclohexene, none of the 7-(trimethylsilyl)norcarane which was expected from trapping of the proposed carbene intermediate was observed.

In a related report Burford and coworkers (48) generated the α-chloro-α-(trimethylsilyl)carbanion **82** at -78°C by reaction of *sec*-butyllithium with chloromethyltrimethylsilane in tetrahydrofuran and one equivalent of hexamethylphosphoramide. The anion was found to be stable up to approximately -40°C where it began to decompose. No products from an α-elimination to give carbene were observed, however.

In a slightly modified experiment Olofson and coworkers (49) reported recently the reaction of chloromethyltrimethylsilane with lithium 2,2,6,6-tetramethylpiperidide **83** in hexane solution. When an excess of olefin was added to the original reaction mixture, the products which were isolated in moderate yields were the cyclopropanes which were postulated by the authors as arising from the addition of α-(trimethylsilyl)carbene 80 to the olefin (Scheme 20). The reaction was found to be stereospecific when cis- and trans-olefins were used. This led the authors to suggest that the carbene was in the singlet state.

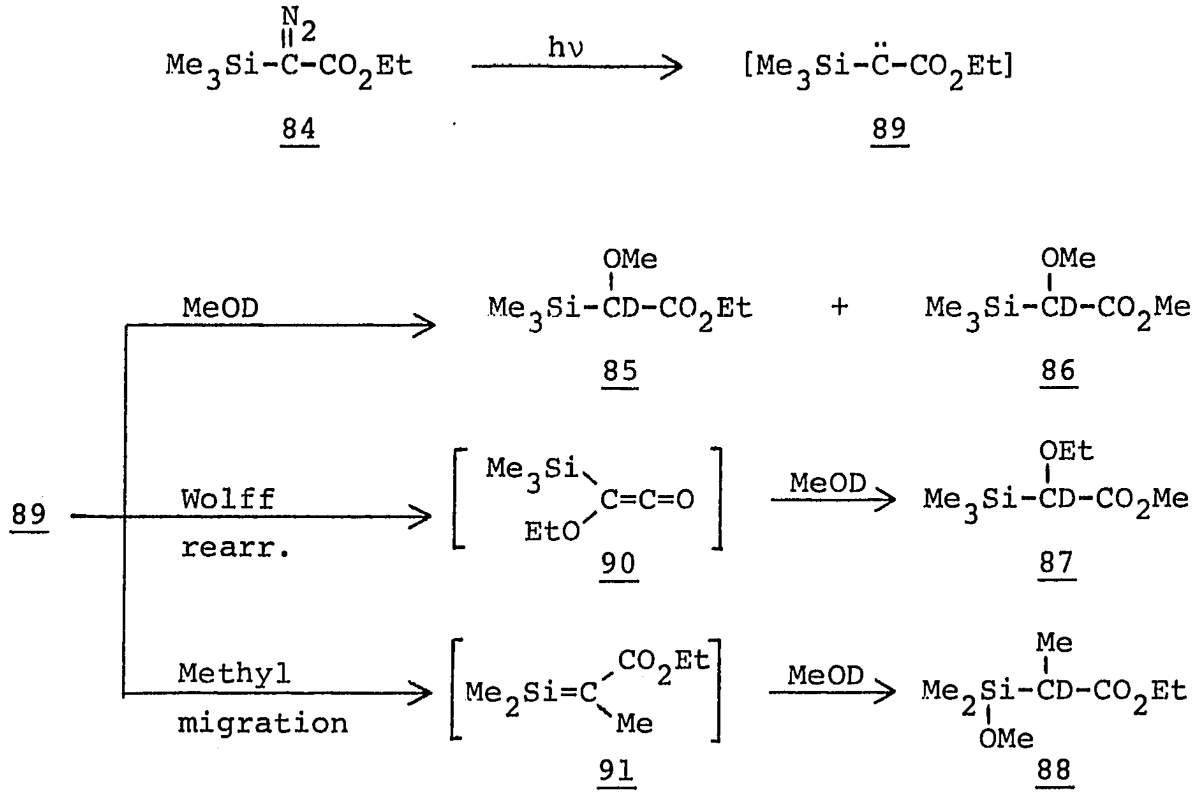
Scheme 20



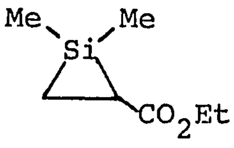
Seyferth and Hanson (50) have reported the use of the mercurials $(Me_3SiCCl_2)_2Hg$, $(Me_3SiCBr_2)_2Hg$, and $(Me_3SiCHBr)_2Hg$ as thermal precursors of the carbenes $Me_3SiCCl:$, $Me_3SiCBr:$, and $Me_3SiCH:$, respectively in the reaction with olefins to give cyclopropanes.

A large portion of the research in α-silylcarbenes has centered around the synthesis (51-53) of silyldiazocompounds and their decomposition (54-58) in the presence of olefins to give cyclopropanes. Recently, however, reports of rearrangement products from these decompositions have begun to appear. Ando and coworkers (59) studied the photochemical decomposition of ethyl(trimethylsilyl)diazoacetate 84 in the presence of various alcohols. With methanol-d_1 the products which were isolated were ethyl-α-deuterio-α-methoxy-α-trimethylsilylacetate 85, methyl-α-deuterio-α-methoxy-α-trimethylsilylacetate 86, methyl-α-deuterio-α-ethoxy-α-trimethylsilylacetate 87, and ethyl-α-deuterio-α-(methoxydimethylsilyl)propionate 88. Products 85 and 86 were rationalized as simply arising from trapping of α-silylcarbene 89 by alcohol (Scheme 21). Compound 87 was explained by reaction of alcohol with the ketene 90 which was formed by a Wolff rearrangement of the carbene 89. The remaining product, 88 was perhaps the most intriguing of those isolated. The authors suggested that this product resulted from trapping by methanol-d_1 of an intermediate silene 91 which might be stabilized through resonance. They proposed that this silene came from a methyl migration in the intermediate α-silylcarbene 89. The fact that the deuterium from methanol-d_1 was found only at the α-carbon of the ester 88 tended to eliminate any intermediacy of 2-carboethoxy-1,1-dimethyl-1-silirane 92. In addition, a carboethoxy(trimethylsilyl)carbonium ion 93 was ruled out as an intermediate by reacting the starting diazocompound 84 with methanol in the

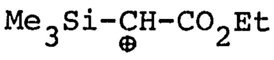
Scheme 21



presence of a catalytic amount of hydrochloric acid. No methyl migration product was observed.



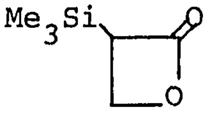
92



$Me_3Si\text{-}\underset{\oplus}{C}H\text{-}CO_2Et$

93

Ando and coworkers (60) found that vacuum pyrolysis of methyl(trimethylsilyl)diazoacetate followed by quenching of the pyrolysate with methanol gave somewhat different results. Again, the methanol trapping product of the ketene which resulted presumably from the Wolff rearrangement of α-carbomethoxy-α-(trimethylsilyl)carbene was observed. There was a new type of product, β-lactone 94 which was postulated by the authors as arising from the insertion of the carbene into the carbon-hydrogen bond of the methoxy group.

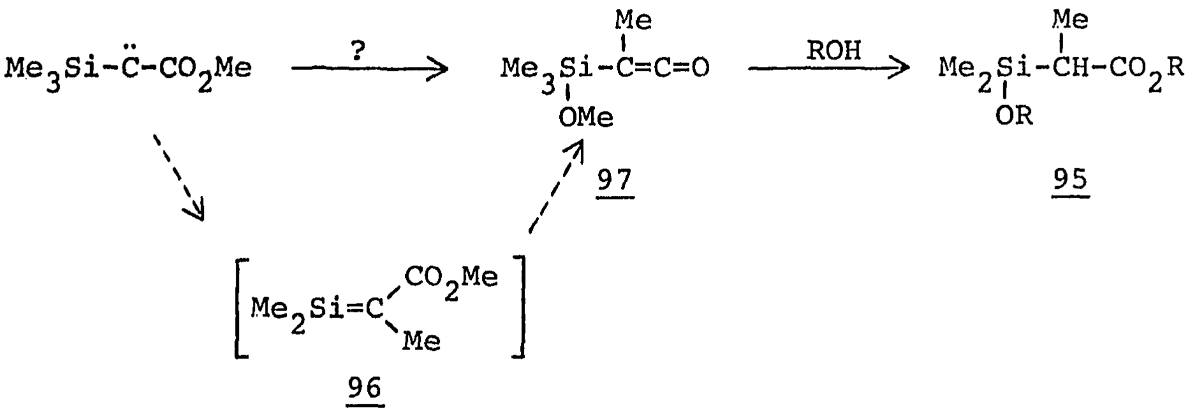


94

In addition, a product 95 (where R=Me) which appeared to come from methanol trapping of an intermediate silene 96 was isolated. However, trapping experiments with alcohols other than methanol revealed that both alkoxy groups in compound 95 came from the added alcohol. When the pyrolysate was examined prior to quenching with alcohol, the methoxyketene 97 was observed. This ketene was found to lead quantitatively to the twice-exchanged product 95 (Scheme 22). Therefore, the authors concluded that silene 96 was not the immediate precursor of compound 95, although the silene might be involved in the formation of methoxyketene 97. The exact origin of the ketene was not clearly determined, however.

Ando et al. (61,63,64) and Barton et al. (62) investigated the flow pyrolysis of phenyl(trimethylsilyl)diazomethane 98 at 500°C. The products which were isolated

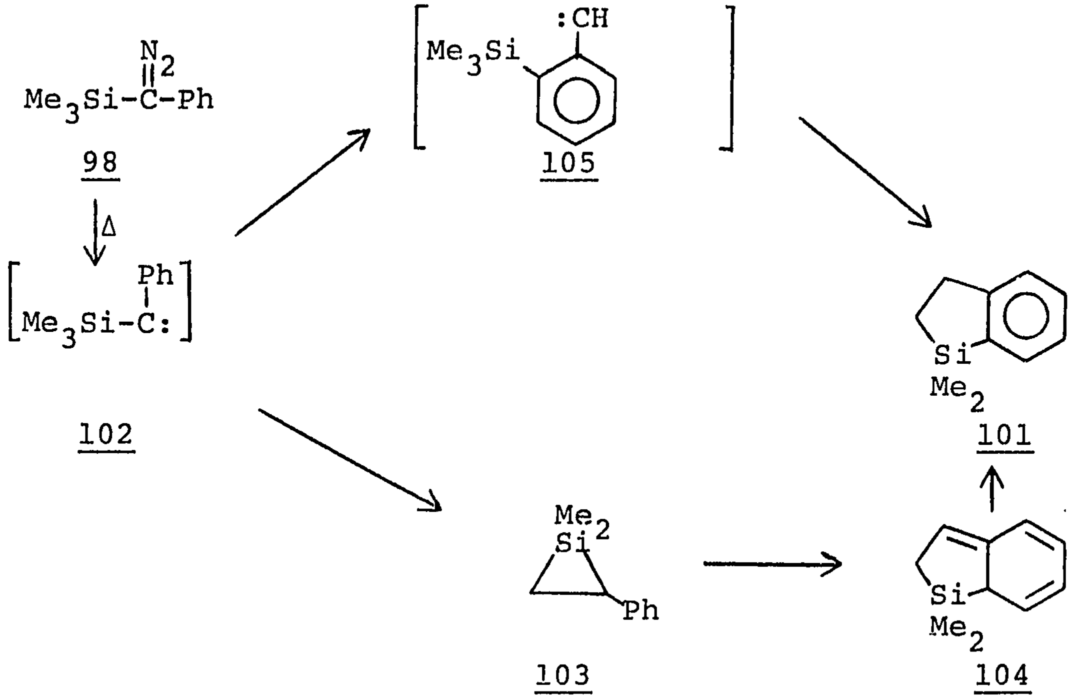
Scheme 22



included E-bis(trimethylsilyl)stilbene 99, benzyltrimethylsilane 100, 3,3-dimethyl-3-silabenzocyclopentene 101, and styrene. It was suggested that the stilbene 99 was formed either by direct dimerization of the α-silylcarbene 102 or by reaction of that carbene with unreacted diazocompound 98. Benzyltrimethylsilane was the product which would result from hydrogen abstraction by the α-silylcarbene. The 3,3-dimethyl-3-silabenzocyclopentene was not so simply explained. Initially, Ando and coworkers (61) suggested that the benzocyclopentene 101 was formed by insertion of the α-silylcarbene 102 into a carbon-hydrogen bond of a methyl group to give the silirane 103. Then, the silirane rearranged to the triene 104 which underwent rearomatization to produce the observed compound (Scheme 23).

However, Barton, Jones, and coworkers (62) showed by labelling experiments that this mechanism was incorrect. They proposed that the initially formed α-silylcarbene 102 underwent

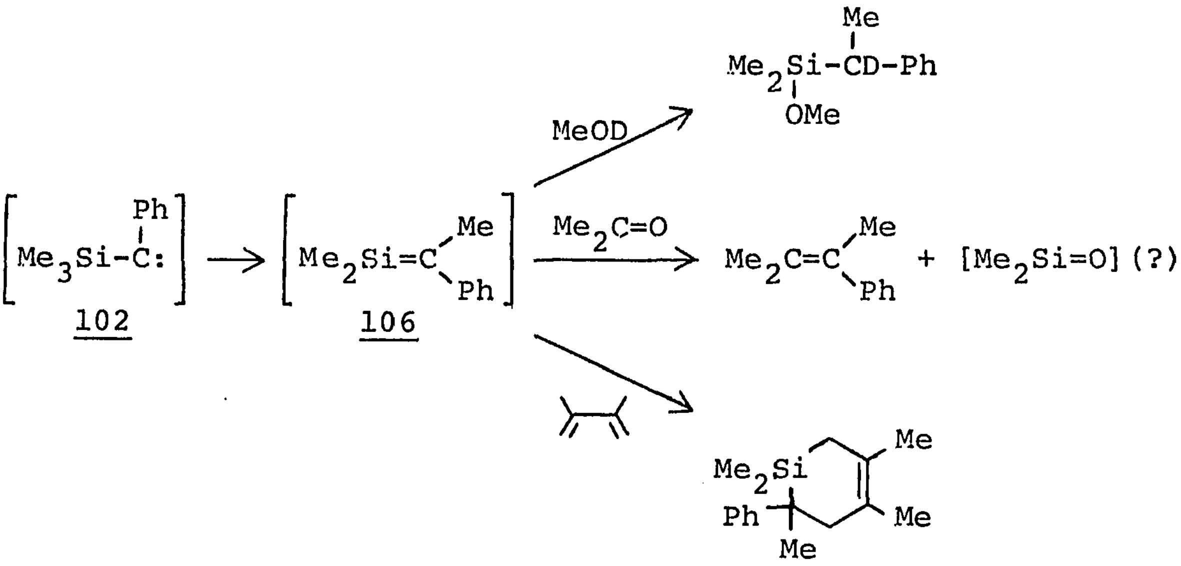
Scheme 23



a carbene-carbene rearrangement to the new carbene 105 which inserted into a carbon-hydrogen bond of a methyl group to give the benzocyclopentene 101 as shown in Scheme 23. Still, silirane 103 was postulated via extrusion of dimethylsilylene to explain the formation of styrene (11).

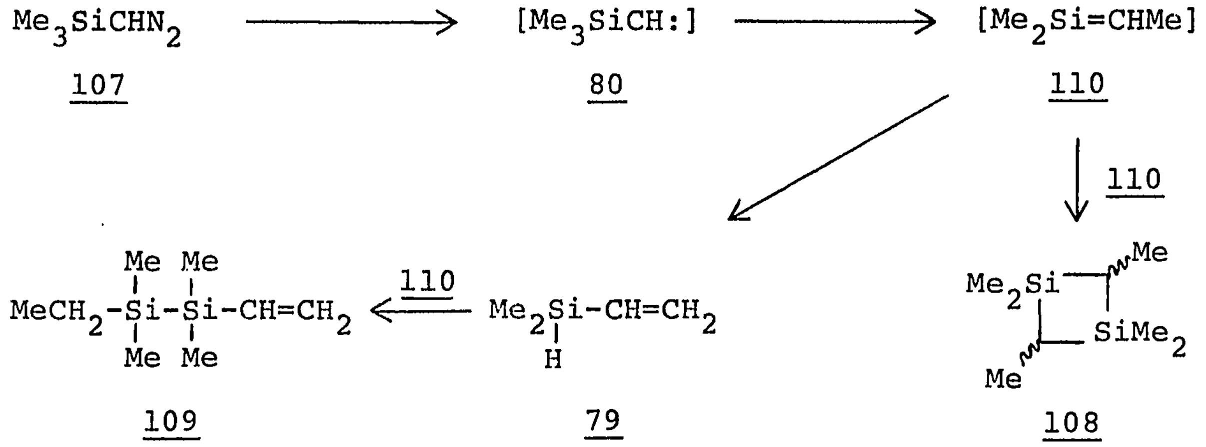
In addition to products resulting from carbon-hydrogen insertion, α-silylcarbene 102 gave products which were consistent with insertion into a silicon-carbon bond to give a silene 106. The intermediacy of this silene was suggested by the copyrolyses of diazocompound 98 and methanol-d_1 (64), acetone (63,64), or 2,3-dimethylbutadiene (63,64) to give the expected trapping products as shown in Scheme 24.

Scheme 24



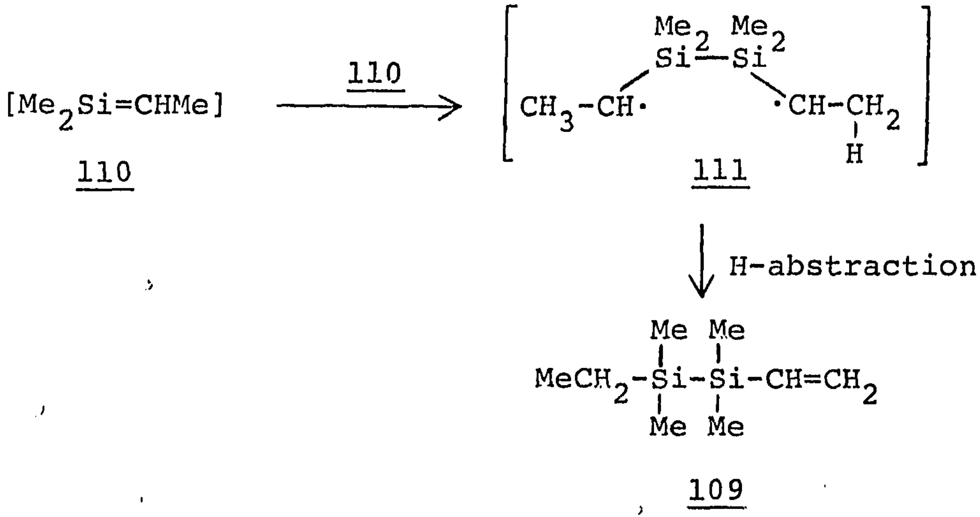
In studying the photolysis of trimethylsilyldiazomethane 107 in the presence of various reagents Haszeldine and co-workers (65) noted the formation of an unidentified dimer of α-(trimethylsilyl)carbene 80. Kreeger and Shechter (66) reexamined this system. Vacuum pyrolysis of trimethylsilyldiazomethane at 440°C yielded as the major products cis- and trans-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes 108 and as the minor products dimethylvinylsilane 79, trimethylvinylsilane, and 3,3,4,4-tetramethyl-3,4-disila-1-hexene 109. The formation of the 1,3-disilacyclobutanes 108 was suggestive of the intermediacy of the silene, 2-methyl-2-sila-2-butene 110 (Scheme 25). This was confirmed by copyrolysis of trimethylsilyldiazomethane with 2-propanol or benzaldehyde which gave ethyldimethyl-2-propoxysilane or cis- and trans-1-phenyl-1-propenes, respectively.

Scheme 25



An attempt was made by the authors to answer the question of whether 1,1-dimethyl-1-silirane 81 was formed initially from α-silylcarbene 80 and then rearranged to either the silene 110 or dimethylvinylsilane 79 as was suggested earlier in the work of Skell and Goldstein (46). When α-deuterio(trimethylsilyl)-diazomethane was used as the starting material, the pyrolysis produced cis- and trans-2,4-dideuterio-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes. No deuterium was detected in the methyl groups. Thus, a direct methyl migration from silicon to carbon in carbene 80 to give silene 110 was indicated. In addition a second product, 2,5-dideuterio-3,3,4,4-tetramethyl-3,4-disila-1-hexene was isolated. Since deuterium was found only at the 2 and 5 positions, the authors suggested that the silene 110, and not 1,1-dimethyl-1-silirane, was the precursor to dimethylvinylsilane 79. This conclusion was based upon the assumption that disilane 109 was formed by addition of dimethylvinylsilane to the intermediate silene 110 as shown in Scheme 25. However, work by Brook and Harris (67) with sterically hindered silenes has opened the door to a very important alternative mechanism which is consistent with the labelling results (Scheme 26). The intermediate silene 110 might

Scheme 26



dimerize in a head-to-head manner to produce the diradical 111. Hydrogen abstraction would give the observed disilane 109. Thus, the intermediacy of 1,1-dimethyl-1-silirane to explain the formation of dimethylvinylsilane need not be excluded since vinylsilane 79 may not be involved in formation of 109.

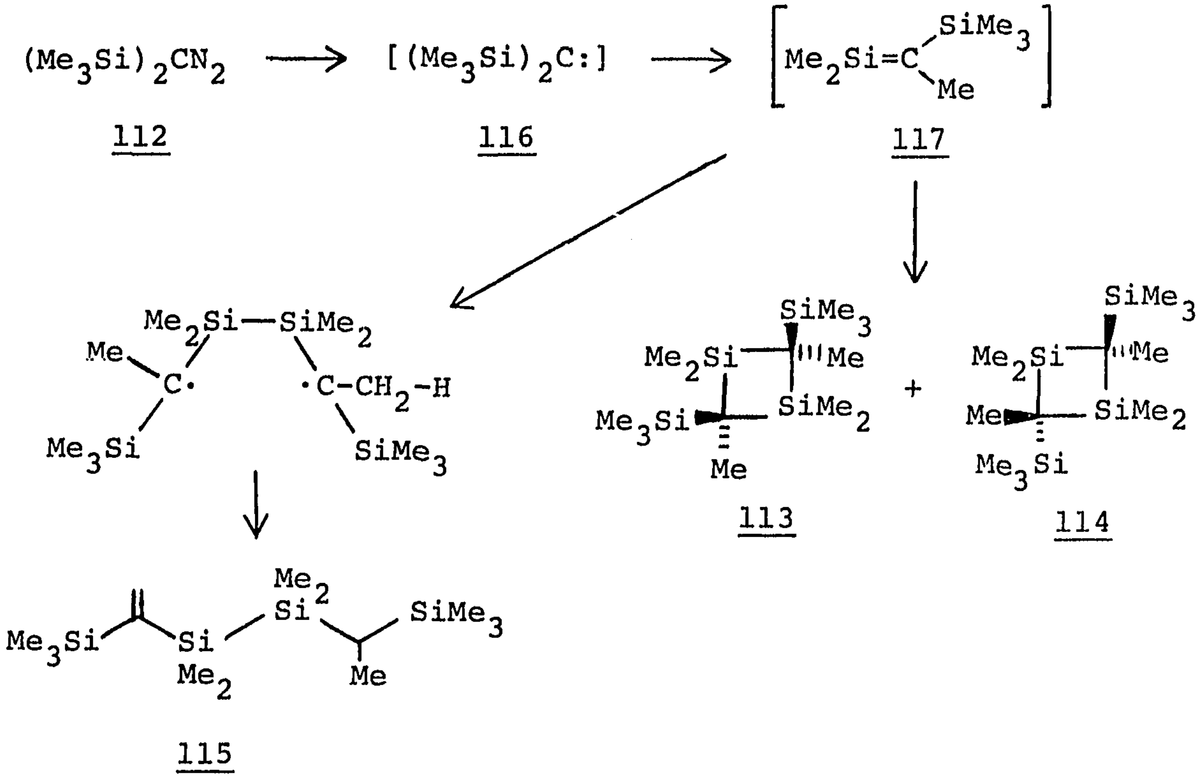
The photolysis of trimethylsilyldiazomethane in various alcohols and diethylamine was also studied by Kreeger and

Shechter (66). Again products were observed which were consistent with trapping of 2-methyl-2-sila-2-butene 110. Thus, the methyl migration was observed in both thermally and photochemically generated α-(trimethylsilyl)carbene.

Subsequently, Chedekel, Shechter, and coworkers (68) determined by electron spin resonance spectroscopy that at least some of the α-(trimethylsilyl)carbene was in the triplet state when formed by irradiation of trimethylsilyldiazomethane in an argon matrix. Warming of the matrix gave the products previously observed in the vacuum pyrolysis of trimethylsilyldiazomethane.

Quite recently, Barton and Hoekman (69) extended studies of this type to the thermal and photochemical decomposition of bis(trimethylsilyl)diazomethane 112. Flow pyrolysis of the diazocompound gave as the major products the *cis*- and *trans*-2,4-bis(trimethylsilyl)-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes 113 and 114 and 2,2,4,4,5,5,6,7,7-nonamethyl-3-methylidene-2,4,5,7-tetrasilaoctane 115. It was postulated that an initially formed carbene 116 rearranged to 2,3,4,4-tetramethyl-2,4-disila-2-pentene 117. Then, silene 117 dimerized in a head-to-tail fashion to give the 1,3-disilacyclobutanes 113 and 114 or in a head-to-head fashion followed by hydrogen abstraction to give the disilane 115 (Scheme 27). Copyrolysis of bis(trimethylsilyl)diazomethane and benzaldehyde gave *E*- and *Z*-β-methyl-β-(trimethylsilyl)styrene and small amounts of hexamethylcyclotrisiloxane 3 and octamethylcyclotetrasiloxane 2

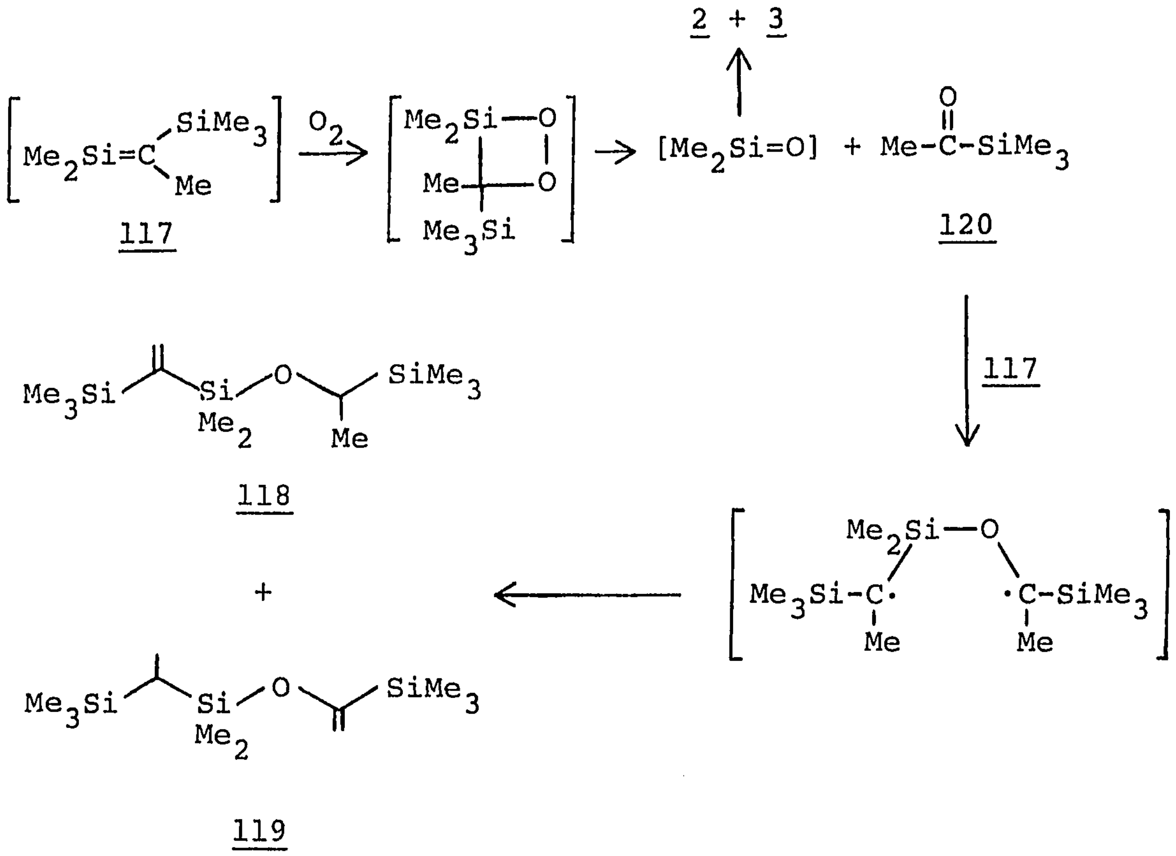
Scheme 27



which were consistent with carbonyl trapping of the intermediate silene 117.

It was also found that oxygen trapped the silene 117 to produce 2,2,3,5,5,7,7-heptamethyl-6-methylidene-4-oxa-2,5,7-trisilaoctane 118, 2,2,5,5,6,7,7-heptamethyl-3-methylidene-4-oxa-2,5,7-trisilaoctane 119, and small amounts of acetyltrimethylsilane 120 and cyclosiloxanes 2 and 3. The mechanism which they suggested to explain these products is shown in Scheme 28. The plausibility of acetyltrimethylsilane 120 as an intermediate was confirmed by copyrolysis of 120 with the starting diazocompound 112 to give a nearly quantitative yield of compounds 118 and 119.

Scheme 28



Similar results were obtained in the photochemical decomposition of bis(trimethylsilyl)diazomethane, again adding support for the rearrangement of ∝-silylcarbenes to silenes. Thus, the reactivity of ∝-silylcarbenes has become of growing interest in the studies of silicon (p-p)π bonded species (70).

EXPERIMENTAL

General Information

Infrared spectra (ir) were recorded on a Beckman IR-4250 or Beckman 18A spectrophotometer. Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer. Routine proton magnetic resonance spectra (nmr, 60MHz) were determined on a Varian Model A-60, Varian EM-360, or Hitachi R20-B spectrometer, and chemical shifts were reported as parts per million (δ scale) from tetramethylsilane (TMS). 100MHz spectra were determined on a Varian Model HA-100 spectrometer using chloroform or tetramethylsilane as an internal lock-standard and trifluoroacetic acid (TFA) as an external lock-standard. Fourier transform proton magnetic resonance spectra (90MHz) were recorded on a Bruker HX-90 using acetone-d_6 as an internal standard. Routine mass spectra were obtained on an Atlas CH-4 or MS902 spectrometer. High resolution mass spectra were determined on the MS902 spectrometer. Gas chromatography/mass spectral (GCMS) analyses were performed on a Perkin-Elmer 270 spectrometer or a Finnigan 4023 spectrometer with INCO data system. Routine analytical gas chromatography (G.C.) was done on a Varian Model 920, F&M 500, Varian Model 1700, Tracor 550, or Varian Model 3700 gas chromatograph.

All yields were obtained by gas chromatographic analysis unless otherwise stated. A known amount of an internal standard was added to a given amount of sample. Response factors for each component relative to the internal standard were experimentally determined.

Chloro-(2-chloroethoxy)dimethylsilane 120

12.1 g (0.150 mol) of ethylene chlorohydrin in 100 ml of anhydrous benzene were added dropwise with stirring over 2 hours to 58.1 g (0.450 mol) of dichlorodimethylsilane and 11.9 g (0.150 mol) of pyridine in 150 ml of benzene at 0°C under nitrogen. After a total reaction time of 3 hours the mixture was filtered under nitrogen. Distillation of the filtrate gave 10.5 g (40.7%) of chloro-(2-chloroethoxy)dimethylsilane.

b.p. 134-138°C [lit. 85°C/74 torr (71)]

nmr (CCl_4) 3.92 (2H, t, J=5.5 Hz), 3.52 (2H, t, J=5.5 Hz), 0.51 (6H, s)

mass spectrum (70 eV) m/e (rel. intensity) 157(82)($P-CH_3$), 137(52)(P-Cl), 123(100)($P-CH_2Cl$), 113(94), 93(96) (Me_2ClSi), 63(54)(C_2H_4Cl); all ions contain chlorine.

exact mass (P-15) 156.96421 (meas.), 156.96542 (calc. for $C_3H_7Cl_2OSi$)

Reaction of chloro-(2-chloroethoxy)dimethylsilane 120 with magnesium powder

A solution of 2.06 g (0.0120 mol) of chloro-(2-chloroethoxy)dimethylsilane in 25 ml of anhydrous hexamethylphosphoramide (HMPA) was added dropwise with mechanical stirring to 0.584 g (0.0240 mol) of magnesium powder in 35 ml of HMPA under nitrogen. After a total reaction time of 22.5 hours the mixture was vacuum distilled (0.03 torr) at room temperature and all volatile components were collected. A proton magnetic resonance spectrum (neat) of the crude distillate showed some HMPA, a peak at approximately 4.9 ppm, and two peaks at approximately 0.2 ppm. Analysis by gas chromatography (16 ft. x 0.25 in. 4% SE-30/6% QF-1 on chromasorb W) revealed only two components. One of these was HMPA. The other component was isolated by preparative gas chromatography. The proton magnetic resonance spectrum for the component (in CCl_4) showed only a singlet at approximately 0.08 ppm. By comparison of retention time with an authentic sample the component was octamethylcyclotetrasiloxane 2 (22.3%).

Reaction of chloro-(2-chloroethoxy)dimethylsilane 120 with Rieke magnesium at room temperature

Rieke magnesium was prepared according to the procedure of Rieke and Bales (72) using 5.10 g (0.0535 mol) of anhydrous magnesium chloride, 3.75 g (0.0960 mol) of potassium and 4.00 g (0.0240 mol) of potassium iodide in 125 ml of anhydrous tetrahydrofuran. 4.18 g (0.0240 mol) of chloro-(2-chloroethoxy)dimethylsilane in 20 ml of tetrahydrofuran were added dropwise with stirring to the Rieke magnesium under nitrogen at room temperature. After a total reaction time of 6 hours the mixture was filtered under nitrogen. Carbon tetrachloride was added to the filtrate to precipitate out any remaining salts. The liquid layer was separated and distilled under vacuum (17-19 torr) at room temperature to remove the excess tetrahydrofuran and carbon tetrachloride. Analysis of the remaining 3.87 g of solution by gas chromatography (16 ft. x 0.25 in. 4% SE-30/6% QF-1 on chromasorb W) revealed the presence of hexamethylcyclotrisiloxane 3 (0.3%), octamethylcyclotetrasiloxane 2 (18.2%), and decamethylcyclopentasiloxane 1 (2.2%). These were confirmed by retention times and low resolution mass spectral patterns of authentic samples.

Reaction of chloro-(2-chloroethoxy)dimethylsilane 120 with Rieke magnesium at 0°C

4.02 g (0.0231 mol) of chloro-(2-chloroethoxy)dimethylsilane in 20 ml of tetrahydrofuran were added dropwise with stirring to Rieke magnesium [from 5.10 g (0.0535 mol) of anhydrous magnesium chloride, 3.75 g (0.0960 mol) of potassium, and 4.00 g (0.0240 mol) of potassium iodide in 125 ml of tetrahydrofuran] under nitrogen at 0°C. After 6 hours of total reaction time the mixture was filtered under nitrogen and the excess tetrahydrofuran was removed *in vacuo* (0.03 torr) at 0°C. Carbon tetrachloride was added to the remaining mixture and the liquid layer was separated from the salts. The excess solvents were again removed *in vacuo*. These distillates contained no silicon compounds by proton magnetic resonance spectroscopy. The gas chromatogram (16 ft. x 0.25 in. 4% SE-30/6% QF-1 on chromasorb W; Injector 76°C, Column 47°C, Detector 78°C) of the remaining solution revealed trace amounts of cyclosiloxanes 2 and 3 and an unidentified component coming through the column before carbon tetrachloride. This component was collected by preparative gas chromatography. A proton magnetic resonance spectrum of the component (in CCl_4) was too dilute for an exact interpretation; however, a weak signal at approximately 3.5-4.0 ppm and a stronger signal at 0.1-0.3 ppm were detectable. A low resolution mass spectrum of the component gave only peaks which were cyclosiloxanes 1, 2, and 3 with 2 being present in a much higher amount. The component showed signs of decomposition to cyclosiloxanes 2 and 3 when re-injected into the gas chromatograph (injector 202°C). Unfortunately, numerous attempts to reproduce this exact procedure failed to give any detectable amounts of this unidentified compound.

2-Chloro-2-phenylethanol 121

2-Chloro-2-phenylethanol was prepared according to the procedure of Knipe (73) using 48.0 g (0.400 mol) of styrene oxide in chloroform and hydrogen chloride gas. Vacuum distillation gave 31.5 g (50.4%) of the product.

b.p. 78-82°C/0.02 torr [lit. 86°C/1 torr (73)] nmr ($CDCl_3$) 7.32 (5H, m), 4.90 (1H, t, J=7 Hz), 3.82 (2H, d, J=7 Hz), 2.76 (1H, s)

ir (thin film) 3390 (s, broad), 1497(m), 1458(s), 1058(s) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 156 (25)(Parent), 125(71)(P-CH_2OH), 104(61), 91(100)(C_7H_7), 77(32)(C_6H_5), 44(55)(C_2H_4O); (P+2) ion indicative of chlorine.

Chloro-(2-chloro-2-phenylethoxy)dimethylsilane 122

25.2 g (0.160 mol) of 2-chloro-2-phenylethanol and 12.6 g (0.160 mol) of pyridine in 150 ml of anhydrous ether were added dropwise with stirring over 8 hours to 82.6 g (0.650 mol) of dichlorodimethylsilane in 100 ml of ether under nitrogen. After an additional 16 hours of stirring the mixture was filtered under nitrogen. The filtrate was vacuum distilled to give 26.6 g (66.5%) of chloro-(2-chloro-2-phenylethoxy)dimethylsilane.

b.p. 87-90°C/0.03 torr

nmr (CCl_4) 7.29 (5H, s), 4.83 (1H, t, J=7 Hz), 4.01 (2H, d, J=7 Hz), 0.39 (3H, s), 0.33 (3H, s)

ir (thin film) 3058(m), 3015(m), 2958(m), 2920(m), 2870(m), 1444(s), 1251(vs), 1110(vs), 814(vs), 795(vs) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 248(20)(Parent), 233(8)(P-CH_3), 213(12)(P-Cl), 212(20)(P-HCl), 187(16), 123(100)(P-C_6H_5CHCl), 113(44), 104(60)($C_6H_5CHCH_2$), 93(60)(Me_2SiCl), 91(44)(C_7H_7), 77(24)(C_6H_5), 36(36)(HCl) exact mass (p) 248.01805 (meas.), 248.01911 (calc. for $C_{10}H_{14}Cl_2OSi$) (P-125) 123.00234 (meas.), 123.00330 (calc. for C_3H_8ClOSi)

Reaction of chloro-(2-chloro-2-phenylethoxy)dimethylsilane 122 with magnesium turnings

3.74 g (0.0150 mol) of 122 in 10 ml of anhydrous ether were added dropwise with stirring to 0.364 g (0.0150 mol) of magnesium turnings in 20 ml of ether under nitrogen. After 26 hours at reflux in ether very little reaction was noted. Tetrahydrofuran was exchanged for ether as the solvent. At reflux in tetrahydrofuran reaction was noted within 15 minutes. After an additional 1.5 hours the mixture was filtered under nitrogen. The tetrahydrofuran was removed *in vacuo* to give a viscous material. Carbon tetrachloride was added and the newly precipitated salts were removed by filtration. After removing the excess carbon tetrachloride *in vacuo* a proton magnetic resonance spectrum of the remaining solution revealed signals for styrene and cyclosiloxanes 1, 2, and 3. The presence of the components was confirmed by gas chromatography/mass spectral analysis by comparison to authentic samples.

Reaction of chloro-(2-chloro-2-phenylethoxy)dimethylsilane 122 with Rieke magnesium

Rieke magnesium was prepared from 3.18 g (0.0334 mol) of anhydrous magnesium chloride, 2.35 g (0.0600 mol) of potassium, and 2.49 g (0.0150 mol) of potassium iodide in 80 ml of anhydrous tetrahydrofuran by the method of Rieke and Bales (72). After cooling the mixture to -78°C, 3.74 g (0.0150 mol) of chloro-(2-chloro-2-phenylethoxy)dimethylsilane in 35 ml of tetrahydrofuran were added dropwise with stirring over 3.5 hours under nitrogen. After 3 additional hours of stirring 100 ml of anhydrous ether were added and the resulting mixture was vacuum filtered under nitrogen. The excess ether and tetrahydrofuran were removed *in vacuo*. A preliminary proton magnetic resonance spectrum of the remaining solution (neat) gave peaks for styrene and cyclosiloxanes 1, 2, and 3 by comparison to known samples. In addition, peaks in the aldehyde region (9.6 ppm), at approximately 3.7 ppm, and in the phenyl region (7.3 ppm) which were not from styrene by integration were observed. Analysis of the solution by gas chromatography (16 ft. x 0.25 in. 15% SE-30 on chromasorb W) revealed the following components by comparison of retention times: styrene, cyclosiloxanes 1, 2, and 3, and a major component which was isolated by preparative gas chromatography and proved to be phenylacetaldehyde 123.

nmr (CCl_4, 90 MHz, Fourier Transform) 9.670 (1H, t, J=2.35 Hz), 7.260 (5H, d, J=2.35 Hz), 3.658 (2H, d, J=2.35 Hz)

ir(CCl_4) 3040(m), 2831(m), 2735(m), 1732(vs), 1503(s), 1459(s), 1086(m), 1035(m), 702(vs)

The phenylacetaldehyde was found to arise from essentially quantitative thermal decomposition of starting material 122 under the gas chromatographic conditions (Injector 200°C). Thus, the yield of styrene and the combined yield of cyclosiloxanes 1, 2, and 3 were determined to be 89% and 49% respectively, based upon unreacted starting material as calculated from the amount of phenylacetaldehyde obtained at the end of the reaction.

Tri-n-butylmethoxystannane 124

Tri-n-butylmethoxystannane was prepared by the method of Valade and Pereyere (74) using 8.58 g (0.327 mol) of sodium in 250 ml of absolute methanol to generate sodium methoxide which was reacted with 98.0 g (0.301 mol) of tri-n-butylchlorostannane.

The yield of tri-n-butylmethoxystannane was 80.4 g (83.2%).

b. p. 60-61°C/0.02 torr [lit. 117°C/2 torr (74)]

nmr (CCl_4) 3.44 (3H, s), 1.86-0.70 (27H, m)

Methyl-α-(tri-n-butylstannyl)acetate 125

Methyl-α-(tri-n-butylstannyl)acetate was prepared according to a similar procedure of Lutsenko and Ponomarev (75) by bubbling 5.80 g (0.138 mol) of ketene (from pyrolysis of diketene from Aldrich) through a solution of 20.0 g (0.0623 mol) of tri-n-butylmethoxystannane in 50 ml of anhydrous ether at 0-5°C. Vacuum distillation gave 19.5 g (86.3%) of methyl-α-(tri-n-butylstannyl)acetate.

b.p. 92-95°C/0.02 torr

nmr (neat) 3.49 (3H, s), 1.87 (2H, s), 1.73-0.66 (27H, m)

Preparation of 2-(dimethylsilyl)ethanol 126 from methyl-α-(tri-n-butylstannyl)acetate 125

10.0 g (0.0275 mol) of methyl-α-(tri-n-butylstannyl)-acetate were added dropwise with stirring to 7.00 g (0.0543 mol) of dichlorodimethylsilane (under nitrogen) and the resulting mixture was heated 16 hours at 80-90°C according to the procedure of Lutsenko and coworkers (76,77). The mixture was vacuum distilled to remove the unreacted dichlorodimethylsilane and the expected product, methyl-α-(chlorodimethylsilyl)acetate 127. The distillate was dissolved in 10 ml of anhydrous ether and added dropwise to a suspension of 1.89 g (0.0499 mol) of lithium aluminum hydride in 100 ml of refluxing ether. After 1.5 hours the reaction mixture was worked up at 0-5°C by addition of moist ether followed by water. Vacuum distillation of the organic layer (90-95 torr) at room temperature removed the excess ether. The remaining liquid showed peaks in its proton magnetic resonance spectrum (neat) which were consistent for the desired 2-(dimethylsilyl)ethanol: 3.9(m), 3.3(m), 0.7(m), and 0.1(d) (approximate values). After removing the water and ether which were still present in the sample only 0.172 g of crude material remained. The OH and SiH stretchings were observable in the infrared spectrum of the crude material.

Ethyl-α-(dimethylsilyl)acetate 128

This procedure was based upon similar types of reactions by Fessenden and Fessenden (78). A solution of 4.73 g (0.0500 mol) of chlorodimethylsilane and 10.4 g (0.0625 mol) of ethyl-α-bromoacetate in 25 ml of a 50:50 (by volume) mixture of anhydrous benzene and ether was added dropwise over 40 minutes to a suspension of 4.09 g (0.0625 mol) of zinc powder in 60 ml of benzene under nitrogen. A mildly exothermic reaction was noted. The mixture was heated at 60-70°C for a total reaction time of 5 hours. The mixture was filtered and distilled to remove the ether and benzene. Removal of approximately half of the benzene resulted in the settling out of solution of a reddish brown oil. The oil was treated with 10 ml of a 5% HCl solution to dissolve any salts and extracted twice with ether. Removal of the ether *in vacuo* gave 5.78 g of a rather viscous reddish liquid. The proton magnetic resonance spectrum (in $CDCl_3$) of the liquid showed the following peaks: 5.0 (6 units, quartet), 4.3-3.3 (44 units, multiplet), 2.0 (8 units, "two singlets"), 1.5-1.0 (57 units, multiplet), and 0. 3-0.1 (52 units, "two singlets") (approximate values). Comparison with the spectra of authentic samples revealed that the sample contained unreacted ethyl-α-bromoacetate and possibly ethylacetate. Analysis by gas chromatography (16 ft. x 0.25 in. 15% SE-30 on chromasorb W) confirmed the presence of ethyl-α-bromoacetate and ethylacetate by comparison of retention times. The presence of sym-tetramethyldisiloxane was also noted.

Ethyl-α-(dimethylsilyl)acetate 128

This procedure was based upon similar reactions of Gold, Sommer and Whitmore (79). 5.44 g (0.0500 mol) of chloromethyldimethylsilane were added dropwise with stirring to 1.78 g (0.0525 mol) of magnesium turnings in 60 ml of anhydrous tetrahydrofuran under nitrogen. After 8 additional hours of stirring 5.42 g (0.0500 mol) of ethylchloroformate in 50 ml of anhydrous ether were added dropwise to the Grignard reagent. Salt formation was noted within 10 minutes. After 10 additional hours the mixture was quenched with cold saturated ammonium chloride solution. The organic layer was separated and dried over sodium sulfate. The excess ether and tetrahydrofuran were removed *in vacuo* (120 torr). Vacuum distillation (40-42 torr) gave a liquid which boiled at 50-54°C. Analysis by gas chromatography (6 ft. x 0.25 in. 20% DC-550 on chromasorb W) revealed three major components and three minor ones. Gas chromatography/mass spectral analysis of the samples showed only one major peak with m/e 145, 131, and 73 which might be expected for the desired ethyl-α-(dimethylsilyl)acetate 128. However, a proton magnetic resonance spectrum of the mixture showed no signal for the silyl hydrogen although peaks at 4.18 (quartet, J=7 Hz), 1.29 (triplet, J=7 Hz), 1.19 ("doublet", J=6 Hz), and several peaks at 0.21 to -0.23 ppm were observed. Attempted separation of the major component of the mixture by high pressure liquid chromatography (1 ft. μ-porasil, $CHCl_3$ eluant, 1.0 ml/min) failed as shown by essentially no change in the proton magnetic resonance spectrum. Again, no silyl hydrogen or any apparent coupling of the silyl methyls with a silyl hydrogen was observed.

Chloroethoxydimethylsilane 129

21.2 g (0.460 mol) of absolute ethanol in 15 ml of anhydrous toluene were added dropwise with mechanical stirring to 60.0 g (0.465 mol) of dichlorodimethylsilane and 36.4 g (0.460 mol) of pyridine in 55 ml of toluene at 0°C under nitrogen. After 5.5 hours the mixture was filtered under nitrogen. The filtrate was distilled to give 9.75 g (15.3%)

of chloroethoxydimethylsilane. (The amount of product was calculated from its proton magnetic resonance spectrum due to contamination by toluene.)

b.p. 93-95°C [lit. 94-95°C (80)]

nmr (neat) 3.84 (2H, quartet, J=7 Hz), 1.28 (3H, t, J=7 Hz), 0.49 (6H, s) (plus peaks for toluene)

Ethyl-α-(ethoxydimethylsilyl)acetate 130

This procedure was based upon similar types of reactions by Andrianov and Makarova (81). A mixture of 9.75 g (0.704 mol) of chloroethoxydimethylsilane and 11.74 g (0.0704 mol) of ethyl-α-bromoacetate was added dropwise with mechanical stirring to 3.50 g (0.152 mol) of sodium in 100 ml of anhydrous ether under nitrogen. After 18.5 hours the mixture was filtered under a nitrogen atmosphere. The reddish-brown filtrate was distilled and two fractions were collected at boiling points 94-96°C and 104-108°C. The proton magnetic resonance spectra of these two fractions were virtually identical.

nmr (neat) 3.15 (4H, quartet, J=7 Hz), 0.63 (6H, t, J=7 Hz), -0.40 (6H, s) (plus peaks for toluene from starting material)

The gas chromatogram (16 ft. x 0.25 in. 15% SE-30 on chromasorb W) of the sample showed peaks for toluene and a second major component. By comparison of the retention time of this component with authentic sample, from the proton magnetic resonance spectrum, and from the boiling point (104-108°C) of the fraction, the component was determined to be diethoxydimethylsilane 131 [literature b.p. 113.8°C (82)].

Hydroboration-oxidation of ethoxydimethylvinylsilane 132

180 ml of a 1.0 M solution of borane-tetrahydrofuran (0.180 mol) solution was added dropwise with stirring to 62.5 g (0.480 mol) of ethoxydimethylvinylsilane in 150 ml of tetrahydrofuran at 0°C under nitrogen. After gradual warming to room temperature the mixture was stirred an additional 18 hours. 37.6 g (0.500 mol) of anhydrous trimethylamine oxide were added slowly to the mixture (83). A vigorous reaction was noted. After 24 additional hours of reaction the mixture was extracted three times with saturated sodium chloride solution. The organic layer was dried over sodium sulfate. Excess tetrahydrofuran was removed *in vacuo*. Vacuum distillation (0.03 torr) resulted in the majority of the mixture polymerizing into a jelly-like mass. A small amount of distillate was collected over the range 61-81°C. A proton magnetic resonance spectrum of the distillate (in $CDCl_3$) showed the following peaks: 4.08 (triplet, J=6 Hz), 3.66 (quartet, J=7 Hz), 1.17 ("triplet", J=7 Hz) with messlets in the regions 1.45-0.70 and 0.37-0.02 ppm. Column chromato-

graphy (10 in. silica gel) of the sample failed to remove any of the "impurities" from the rather complex mixture. Gas chromatographic analysis (16 ft. x 0.25 in. 15% SE-30 on chromasorb W) showed only two broad peaks which overlapped.

2-(Dimethylphenylsilyl)ethanol 133

2.14 g (0.0110 mol) of α-(dimethylphenylsilyl)acetic acid in 50 ml of anhydrous ether were added dropwise with stirring over 1 hour to a suspension of 0.418 g (0.0110 mol) of lithium aluminum hydride in 80 ml of ether under nitrogen. After 4.5 additional hours the mixture was cooled to 0-5°C and moist ether followed by water was added slowly. The ether layer was separated and dried over magnesium sulfate. The ether was removed *in vacuo* to give 1.49 g (73.4%) of 2-(dimethylphenylsilyl)ethanol.

b.p. 121-124°C/10 torr [lit. 120-122°C/8 torr (84)]

nmr ($CDCl_3$) 7.40 (5H, m), 3,72 (2H, t, J=8 Hz), 2.21 (1H, s), 1.20 (2H, t, J=8 Hz), 0.38 (6H, s). These values were consistent with those in the literature (85).

Reaction of 2-(dimethylphenylsilyl)ethanol 133 with bromine

A solution of 1.27 g (0.00796 mol) of bromine and 0.630 g (0.00796 mol) of pyridine in 40 ml of dichloromethane was added dropwise with stirring to 1.44 g (0.00796 mol) of 2-(dimethylphenylsilyl)ethanol in 20 ml of dichloromethane under nitrogen. After 5 hours the light orange solution was stored at -10°C for 36 hours. The newly formed precipitate was filtered off under nitrogen. The filtrate was vacuum distilled (40-50 torr) at 0°C to remove the dichloromethane. Further distillation (0.1 torr) at room temperature yielded a colorless liquid. The proton magnetic resonance spectrum (in CCl_4) of the distillate showed the following peaks: 7.55-6.97 (identical to the pattern for authentic bromobenzene), 5.17 (CH_2Cl_2), and a small peak at 0.05 (singlet with "shoulder"). Gas chromatographic separation (16 ft. x 0.25 in. 15% SE-30 on chromasorb W) of the mixture confirmed the presence of bromobenzene, dichloromethane, a small amount of hexamethylcyclotrisiloxane 3, and a trace amount of octamethylcyclotetrasiloxane 2.

(Ethoxydimethylsilyl)oxirane 134

59.5 g (0.456 mol) of ethoxydimethylvinylsilane 132 in 150 ml of dichloromethane were added dropwise with stirring to 100 g of m-chloroperbenzoic acid (85% from Aldrich) in 700 ml of dichloromethane. After 12 hours the reaction mixture was cooled to 0-5°C and filtered. The cold filtrate was extracted twice with cold saturated sodium bicarbonate solution, twice with cold saturated sodium bicarbonate solution, and dried over sodium sulfate. The organic layer was distilled to give 34.9 g (52.3%) of (ethoxydimethylsilyl)oxirane.

b.p. 37-38°C/27 torr

nmr ($CDCl_3$, 100 MHz) 3.63 (2H, quartet, J=7 Hz), 2.76-1.94 (3H, m), 1.11 (3H, t, J=7 Hz), 0.06 (3H, s), 0.03 (3H, s)

ir (thin film) 2995(s), 2950(m), 1261(s), 1114(vs), 1088(vs), 957(s) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 146(6)(Parent), 131(53)(P-CH_3), 115(44)($C_2H_3SiMeOC_2H_5$), 103(89) ($Me_2SiOC_2H_5$), 101(39)(P-OC_2H_5), 87(67)($C_2H_3SiMeOH$), 75(100)(Me_2SiOH), 73(25)(Me_3Si), 61(78)(MeHSiOH), 59(67) (Me_2SiH)

exact mass (P-15) 131.05318 (meas.), 131.05284 (calc. for $C_5H_{11}O_2Si$)

2-(Dimethylsilyl)ethanol 126

This approach was suggested by the work of Eisch and Trainor (86) with silyl epoxides. 5.10 g (0.0349 mol) of (ethoxydimethylsilyl)oxirane in 50 ml of anhydrous ether were added dropwise with stirring over 6 hours to a suspension of 0.992 g (0.0261 mol) of lithium aluminum hydride in 130 ml of ether under nitrogen. After a total reaction time of 21 hours the mixture was cooled to 0-5°C and cold water was slowly added to just decompose the unreacted lithium aluminum hydride. The organic layer was separated and dried over sodium sulfate. Vacuum distillation gave 3.24 g (89.0%) of 2-(dimethylsilyl)-ethanol.

b.p. 65-66°C/10-12 torr [lit. 79-80°C/96 torr (77)]

nmr ($CDCl_3$, 100 MHz) 3.83 (1H, "septet", J=3 Hz), 3.68 (2H, t, J=8 Hz), 2.80 (1H, s), 1.00 (2H, triplet of doublets, J=8 Hz, J'=3 Hz), 0.06 (6H, d, J=3 Hz)

ir (thin film) 3360(s), 2130(vs), 1263(s), 1050(s) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 80(6)($P-CH_3$), 75(65)($P-H-C_2H_4$, Me_2SiOH), 61(100)($P-CH_3-C_2H_4$, MeHSiOH), 59(24)(Me_2SiH), 45(18)(CH_2CH_2OH), 43(42)(MeSi), 31(6) (CH_2OH)

exact mass (P-15) 89.04235 (meas.), 89.04227 (calc. for C_3H_9OSi)

Reaction of 2-(dimethylsilyl)ethanol 126 with bromine

5.67 ml of a 0.909 M solution of bromine (0.00515 mol) in dichloromethane were dissolved in 10 ml of dichloromethane. The resulting solution was added dropwise with stirring to 0.537 g (0.00515 mol) of 2-(dimethylsilyl)ethanol and 0.815 g (0.0103 mol) of pyridine in 70 ml of dichloromethane in a closed system at -78°C under argon. After 3 hours of reaction time an evacuated gas collection tube was opened to the system still at -78°C to collect all volatile components. Analysis of the collected vapor by high resolution mass spectrometry revealed no ethylene present. After allowing the reaction mixture to warm to 0°C the procedure was repeated. Still no ethylene could be detected. The reaction mixture was slowly distilled to remove the excess dichloromethane. The remaining mixture was filtered to remove the salts. Analysis of the filtrate by gas chromatography (12 ft. x 0.25 in. 15% SE-30 on chromasorb W) showed hexamethylcyclotrisiloxane 3 (1.1%), octamethylcyclotetrasiloxane 2 (0.6%), and two unidentified components. These compounds were isolated by preparative gas chromatography. Spectra of these compounds proved them to be 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135 (31.8%) and 2,2,6,6-tetramethyl-1,5-dioxa-2,6-disilacyclooctane 136 (46.1%). The cyclosiloxanes were confirmed by gas chromatography/mass spectral analysis.

2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135

nmr ($CDCl_3$, 100 MHz) 4.09 (2H, t, J=6 Hz), 0.94 (2H, t, J=6 Hz), 0.15 (6H, s), 0.10 (6H, s)

ir (CCl_4) 2966(m), 2930(m), 1657(m), 1258(s), 979(s) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 176(19)(Parent), 161(7)(P-CH_3), 133(100)(P-CH_3-C_2H_4, $Me_2SiOSiMeO$), 119(4)($Me_2SiOSiHO$), 103(7)($HSiOSiMe_2$), 89(3)(Me_3SiO), 75(5)($Me_2Si{=}OH$), 73(5)(Me_3Si)

exact mass (P) 176.06893 (meas.), 176.06889 (calc. for $C_6H_{16}O_2Si_2$)

2,2,6,6-tetramethyl-1,5-dioxa-2,6-disilacyclooctane 136

nmr ($CHCl_3$, 100 MHz) 3.94 (4H, t, J=6 Hz), 0.95 (4H, t, J=6 Hz), 0.15 (12H, s) ir (CCl_4) 2958(m), 1256(s), 1071(s), 976(s) cm^{-1} (weak spectrum)

mass spectrum (70 eV) m/e (rel. intensity) 176(15)($P-C_2H_4$), 161(10)($P-C_2H_4-CH_3$), 133(100)($Me_2SiOSiMeO$), 119(5) ($Me_2SiOSiHO$), 103(10)($HSiOSiMe_2$), 75(8)($Me_2Si{=}OH$), 73(6)(Me_3Si)

exact mass (P-28) 176.06895 (meas.), 176.06889 (calc. for $C_6H_{16}O_2Si_2$)

Reaction of 2-(dimethylsilyl)ethanol with bromine; methanol quench

5.96 ml of a 0.865 M solution of bromine (0.00515 mol) in dichloromethane were dissolved in a mixture of 5 ml of pentane and 5 ml of dichloromethane. The resulting solution was added dropwise with stirring to 0.537 g (0.00515 mol) of 2-(dimethylsilyl)ethanol and 0.815 g (0.0103 mol) of pyridine in a mixture of pentane (35 ml) and dichloromethane (20 ml) at -78°C under nitrogen. After 2 additional hours the mixture was filtered into 1.82 g (0.00567 mol) of absolute methanol at -78°C. Pyridinium bromide (1.55 g, 94% based upon two equivalents of HBr generated) was isolated upon filtration. The filtrate and methanol were gradually warmed to room temperature over 5 hours. Excess pentane and dichloromethane were removed *in vacuo* (240 torr) to give 0.814 g of solution. Analysis by gas chromatography (12 ft. x

0.25 in. 15% SE-30 on chromasorb W) revealed only four products: hexamethylcyclotrisiloxane 3 (10.5%), octamethylcyclotetrasiloxane 2 (1.6%), 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135 (29.8%), and 2,2,6,6-tetramethyl-1,5-dioxa-2,6-disilacyclooctane 136 (46.6%). Gas chromatography/mass spectral analysis confirmed the presence of these components and the absence of any methanol trapping product.

Reaction of 2-(dimethylsilyl)ethanol 126 with Wilkinson's catalyst

This procedure was based upon the types of reactions of Corriu and coworkers (87). 0.486 g (0.00466 mol) of 2-(dimethylsilyl)ethanol in 10 ml of anhydrous benzene was added dropwise with stirring over 2 hours to a mixture of 0.0043 g (4.65×10^{-6} mol) of tris(triphenylphosphine)rhodium chloride (Wilkinson's catalyst) in 5 ml of benzene under nitrogen. After 56 additional hours 30 ml of pentane were added and the resulting mixture was filtered. Excess pentane was removed from the mixture *in vacuo* (200 torr) at 35°C to leave 2.36 g of solution. Analysis of the solution by gas chromatography/mass spectrometry and gas chromatography (12 ft. x 0.25 in 15% SE-30 on chromasorb W) revealed the presence of hexamethylcyclotrisiloxane 3 (6.4%) and 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135 (56.6%) by comparison with authentic samples.

Reaction of 2-(dimethylsilyl)ethanol 126 with Raney nickel

This procedure was based upon the types of reactions of Barrau *et al.* (88) and Massol *et al.* (89). 0.208 g (0.00200 mol) of 2-(dimethylsilyl)ethanol in 2 ml of freshly distilled pentane was added dropwise with stirring to 0.0587 g (0.00100 mol) of Raney nickel (90) in 5 ml of pentane at 0-5°C under nitrogen. After 12 hours at 0-5°C the mixture was stirred at room temperature for an additional 12 hours. The reaction mixture was filtered under nitrogen. Gas chromatography/mass spectral analysis of the filtrate showed the presence of hexamethylcyclotrisiloxane 3 and 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135 by comparison with authentic samples. The excess pentane was removed from the filtrate *in vacuo* (230 torr) to give 0.197g of material. Analysis of the sample by gas chromatography (12 ft. x 0.25 in 20% DC-550 on chromasorb P) gave peaks for a small amount of pentane, cyclosiloxane 3 (trace), and dioxane 135 (42.2%) as the only products observed.

E-Methoxydimethyl-(1,2-diphenylvinyl)silane

A mixture of 3.78 g (0.0400 mol) of chlorodimethylsilane, 5.12 g (0.0400 mol) of diphenylacetylene, and a catalytic amount chloroplatinic acid (Speier's catalyst) was irradiated with a sun lamp for 1.5 hours. The original slurry became a liquid within 0.5 hour of irradiation. 12.0 g (0.160

mol) of trimethylorthoformate were added in one aliquot. After 76 hours at room temperature the mixture was filtered. Excess trimethylorthoformate was removed *in vacuo* (0.1-0.2 torr) to leave 6.59 g (61.6%) of *E*-methoxydimethyl-(1,2-diphenylvinyl)silane

nmr (CCl_4) 7.29-6.85 (11H, m), 3.44 (3H, s), 0.18 (6H, s)

ir (thin film) 3065(m), 3030(m), 2970(s), 1606(s), 1501(s), 1453(m), 1257(vs), 1088(vs) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 268(79)(Parent), 253(63)(P-CH_3), 221(36)(P-CH_3-CH_3OH), 178(16)(Ph-C≡C-Ph), 151(32)($C_6H_5\underset{\text{Me}}{\text{Si}}OMe$), 89(100)($Me_2SiOMe$), 75(17)($Me_2Si{=}OH$)

exact mass (P) 268.12835 (meas.), 268.12748 (calc. for $C_{17}H_{20}OSi$)

E- and *Z*-1-(Methoxydimethylsilyl)-1,2-diphenyloxirane 138

1.34 g (0.00500 mol) of *E*-methoxydimethyl-(1,2-diphenylvinyl)silane in 10 ml of chloroform were added dropwise with stirring to 1.16 g (0.00574 mol) of m-chloroperbenzoic acid (85% from Aldrich) in 60 ml of chloroform at 55-60°C under nitrogen. After 24 hours the mixture was stirred an additional 4 hours at room temperature. Excess chloroform was removed *in vacuo* to leave a yellowish slurry. Pentane was added and the resulting mixture was filtered. Pentane was removed *in vacuo* to give a viscous, deep yellow liquid which was "filtered" through 3 inches of silica gel with pentane as eluting solvent. Pentane was removed to give 0.757 g (53.4%) of faint yellow liquid, E- and Z-1-(methoxydimethyl)-1,2-diphenyloxirane. (Perhaps the heating for 24 hours in the peracid may have equilibrate the starting vinylsilane 137).

nmr (CCl_4) 7.48-6.95 (10H, m), 4.29 and 4.22 (1H, 2 singlets, 3:1 ratio), 3.48 (3H, s), 0.23 and 0.18 and 0.09 (6H, 3 singlets, 1.5:1.5:1 ratio)

Reduction of E- and Z-1-(methoxydimethylsilyl)-1,2-diphenyloxirane 138 with lithium aluminum hydride

0.750 g (0.00265 mol) of oxirane 138 in 10 ml of anhydrous ether was added dropwise with stirring to a suspension of lithium aluminum hydride in 20 ml of ether under nitrogen. After a total reaction time of 24 hours the mixture was cooled to 0-5°C and cold water was slowly added to decompose the unreacted lithium aluminum hydride. The organic layer was separated and dried over sodium sulfate. Excess ether was removed *in vacuo* (150 torr) at 30-35°C. A proton magnetic resonance spectrum of the remaining liquid showed only trace amounts of silicon-containing compounds and large peaks for *cis*- and *trans*-stilbene. The presence of the stilbenes was confirmed by gas chromatographic analysis (12 ft. x 0.25 in. 15% SE-30 on chromasorb W) of the liquid.

trans-β-(Methoxydimethylsilyl)styrene 139

14.2 g (0.150 ml) of chlorodimethylsilane were added dropwise with stirring over 8 hours to 15.3 g (0.150 mol) of phenylacetylene and a catalytic amount of chloroplatinic acid (Speier's catalyst) under nitrogen. After an additional 16 hours 47.7 g (0.450 mol) of trimethylorthoformate were added at one time. The resulting mixture was stirred at room temperature for 84 hours. Vacuum distillation of the reaction mixture gave 23.8 g (84.2%) of trans-β-(methoxydimethylsilyl)-styrene (91).

b.p. 130-132°C/4 torr

nmr (CCl_4) 7.62-6.85 (6H, m), 6.70 (2H, AB quartet, J=20 Hz), 3.45 (3H, s), 0.25 (6H, s)

ir (thin film) 3065(w), 3030(w), 2962(s), 2835(m), 1606(m), 1574(m), 1251(s), 1087(vs), 990(s), 842(vs) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 192(24)(Parent), 177(97)($P-CH_3$), 145(100)($P-CH_3-CH_3OH$), 89(19)(Me_2SiOMe), 75(37)($Me_2Si=OH$), 59(35)(Me_2SiH)

exact mass (P) 192.09641 (meas.), 192.09705 (calc. for $C_{11}H_{16}OSi$)

trans-β-(Methoxydimethylsilyl)styrene oxide 140

12.0 g (0.0624 mol) of trans-β-(methoxydimethylsilyl)-styrene in 40 ml of dichloromethane were added dropwise with stirring to 13.5 (0.0628 mol) of m-chloroperbenzoic acid (80-90% from Aldrich) in 120 ml of dichloromethane. After 16 hours the mixture was cooled to 0-5°C and filtered. The cold filtrate was extracted twice with cold 5% sodium bicarbonate solution and dried over sodium sulfate. Dichloromethane was removed *in vacuo* to give cleanly 10.9 g (83.9%) of *trans*-β-(methoxydimethylsilyl)styrene oxide.

nmr (CCl_4) 7.18 (5H, s), 3.63 (1H, d, J=3 Hz), 3.46 (3H, s), 2.13 (1H, d, J=3 Hz), 0.22 (3H, s), 0.19 (3H, s)

2-(Dimethylsilyl)-1-phenylethanol 141

3.50 g (0.0168 mol) of *trans*-β-(methoxydimethylsilyl)-styrene oxide 138 in 40 ml of anhydrous ether were added dropwise with stirring to a suspension of 0.638 g (0.0168 mol) of lithium aluminum hydride in 180 ml of ether under nitrogen. After 44 hours the mixture was cooled to 0-5°C and cold water was added dropwise to just decompose the unreacted lithium aluminum hydride. The mixture was filtered and the filtrate was dried over sodium sulfate. Ether was removed *in vacuo* to give 2.02 g (66.7%) of 2-(dimethylsilyl)-1-phenylethanol.

b.p. 122°C/2 torr

nmr (CCl_4, 100 MHz, TFA external lock) 4.82 (1H, t, J=7 Hz), 3.92 (1H, "septet", J=4 Hz), 3.04 (1H, broad singlet), 1.25 (2H, 2:4:3:4:2 "quintet", 0.13 (3H, d, J=4 Hz), 0.06 (3H, d, J=4 Hz)

(Irradiation at 4.82 produced 1:3:3:1 quartet at 1.25; irradiation at 3.92 produced an "AB quartet" at 1.25.)

ir (thin film) 3361 (s, broad), 3060(m), 3027(m), 2952(m), 2109(s), 1601(m), 1244(s), 1035(s), 1018(s), 880(vs) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 180(1)(Parent), 165(3)($P-CH_3$), 162(10)($P-H_2O$), 147(29)($P-H_2O-CH_3$), 145(11), 121(10)($C_6H_5-\underset{H}{Si}-Me$), 104(100)($C_6H_5CHCH_2$), 91(10) ($C_7H_7$), 78(26)($C_6H_6$), 77(20)($C_6H_5$), 75(36)($Me_2Si=OH$)

exact mass (P) 180.09620 (meas.), 180.09705 (calc. for $C_{10}H_{16}OSi$)

Reaction of 2-(dimethylsilyl)-1-phenylethanol 141 with Wilkinson's catalyst

0.620 g (0.00344 mol) of 2-(dimethylsilyl)-1-phenylethanol in 10 ml of anhydrous benzene was added dropwise over 4 hours with stirring to 0.0032 g (3.44×10^{-6} mol) of tris(triphenylphosphine)rhodium chloride (Wilkinson's catalyst) in 8 ml of benzene under nitrogen. After an additional 44 hours the reaction mixture was placed under vacuum (0.07 torr) and all volatile materials were collected at -78°C. The excess benzene was removed from the distillate *in vacuo* (105 torr) to leave 1.027 g of solution. Analysis of the solution by gas chromatography (12 ft. x 0.25 in. 20% DC-550 on chromasorb P) revealed by comparison of retention times with authentic samples the presence of styrene (30.0%), ethylbenzene (15.8%, from reduction of styrene under the reaction conditions), hexamethylcyclotrisiloxane 3 (8.1%), and octamethylcyclotetrasiloxane 2 (10.8%). Gas chromatography/mass spectral analysis confirmed the presence of all four components.

Reaction of 2-(dimethylsilyl)-1-phenylethanol 141 with Wilkinson's catalyst in the presence of dimethoxydimethylsilane 22

A solution of 0.352 g (0.00195 mol) of 2-(dimethylsilyl)-1-phenylethanol and 0.470 g(0.00391 mol) of dimethoxydimethylsilane in 8 ml of anhydrous benzene was added dropwise with stirring to 0.0036 g (3.91×10^{-6} mol) of tris(triphenylphosphine)rhodium chloride (Wilkinson's catalyst) in 5 ml of benzene under nitrogen. After a total reaction time of 42 hours the mixture was filtered to remove the rhodium catalyst. Separation of the mixture by gas chromatography (12 ft. x 0.25 in. 20% SE-30 on chromasorb W or 12 ft. x 0.25 in. 20% DC-550 on chromasorb P) gave styrene (39.9%), ethylbenzene (12.1%), hexamethylcyclotrisiloxane 3 (6.0%), octamethylcyclotetrasiloxane 2 (6.8%), sym-dimethoxytetramethyldisiloxane 21 (22.6%), and sym-1,5-dimethoxy-hexamethyltrisiloxane 142 (12.5%, assuming the response factor for 142 to be the same as 21). The components were confirmed by gas chromatography/mass spectral analysis and, in the case of the di- and trisiloxanes, by the spectra of pure materials isolated by preparative gas chromatography.

sym-dimethoxytetramethyldisiloxane **21**

nmr (CCl_4, 100 MHz, TFA external lock) 3.56 (6H, s), 0.25 (12H, s)

ir (CCl_4) 2970(m), 2839(m), 1261(s), 1097(s), 1060(s) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 179(83)(P-CH_3), 149(100)[$Me_2SiOSi(OMe)O$], 133(12)($Me_2SiOSiMeO$), 119(25)($Me_2SiOSiHO$), 89(6)(Me_2SiOMe), 75(7)($Me_2Si{=}OH$), 73(6)(Me_3Si)

exact mass (P-15) 179.05584 (meas.), 179.05598 (calc. for $C_5H_{15}O_3Si_2$)

sym-1,5-dimethoxyhexamethyltrisiloxane **142**

nmr (CCl_4, 100 MHz, TFA external lock) 3.55 (6H, s), 0.28 (6H, s), 0.25 (12H, s)

ir (CCl_4) 2964(m), 1260(s), 1091(s), 1042(s)

mass spectrum (70 eV) m/e (rel. intensity) 253(100)(P-CH_3), 223(55)[$Me_2SiOSiMe_2OSi(OMe)O$], 207(30)($Me_2SiOSiMe_2OSiMeO$), 193(19)($Me_2SiOSiMe_2OSiHO$), 133(15)($Me_2SiOSiMeO$), 119(22)($Me_2SiOSiHO$), 104(25), 89(31)(Me_2SiOMe), 73(32)(Me_3Si), 59(25)(Me_2SiH)

Reaction of 2-(dimethylsilyl)ethanol 126 with Wilkinson's catalyst in the presence of dimethoxydimethylsilane 22

0.480 g (0.00461 mol) of 2-(dimethylsilyl)ethanol and 2.21 g (0.0184 mol) of dimethoxydimethylsilane in 8 ml of anhydrous benzene were added dropwise with stirring over 3 hours to 0.0043 g (4.61×10^{-6} mol) of tris(triphenylphosphine)rhodium chloride (Wilkinson's catalyst) in 8 ml of benzene under nitrogen. After an additional 43 hours 25 ml of pentane were added and the resulting mixture was filtered. Removal of the pentane from the filtrate *in vacuo* (200 torr) gave 2.03 g of material. This mixture contained hexamethylcyclotrisiloxane 3 (1.5%), octamethylcyclotetrasiloxane 2 (<1%), *sym*-dimethoxytetramethyldisiloxane 21 (1.6%), and 2,2,4,4-tetramethyl-2,4,-disila-1,3-dioxane 135 (26.0%) as shown by comparison with authentic samples using gas chromatographic (12 ft. x 0.25 in. 20% DC-550 on chromasorb P) and gas chromatography/mass spectral analyses.

2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane 10

2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane was prepared according to the procedure of Piccoli, Haberland, and Merker (92). 6.94 g (0.0732 mol) of chlorodimethylsilane were added dropwise with stirring over 2.5 hours to 8.84 g (0.0732 mol) of chlorodimethylvinylsilane at 75°C under nitrogen. The mixture was then stirred for 10 hours at room temperature.

Distillation of the mixture gave 13.1 g (83.5%) of 1,2-bis(chlorodimethylsilyl)ethane 143.

b.p. 199°C/763 torr [lit. 198°C/734 torr (92)]

m.p. 37°C [lit. 37°C (92)]

8.61 g (0.0400 mol) of 1,2-bis(chlorodimethylsilyl)ethane was added dropwise with vigorous stirring over 1 hour to 20 ml of water at 0-5°C. The resulting mixture was extracted with ether. The ether solution was washed with 5% sodium bicarbonate solution and dried over sodium sulfate. The ether was removed *in vacuo* (200 torr) at 35-40°C. The remaining rather viscous liquid was heated with 0.1 g of potassium hydroxide. The product, 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (2.52 g) distilled from the mixture.

b.p. 120-124°C [lit. 124°C/735 torr (92)]

nmr ($CDCl_3$) 0.76 (4H, s), 0.15 (12H, s)

Thermolysis of 2,2,6,6-tetramethyl-1,5-dioxa-2,6-disilacyclooctane 136

An investigation of the thermal stability of 2,2,6,6-tetramethyl-1,5-dioxa-2,6-disilacyclooctane was made by injection of 0.2 microliter aliquots of 136 into the injector port of a gas chromatograph at various injector temperatures (12 ft. x 0.25 in. 15% SE-30 on chromasorb W). At injector temperatures of 210°C there was approximately 1-2 percent decomposition to ethylene and 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135. The formation of 135 was confirmed by retention time and gas chromatography/mass spectral analysis. The formation of ethylene was established by trapping with bromine and detection of 1,2-dibromoethane. At temperatures of 270°C approximately 50 percent decomposition was noted. Finally, at 370°C 136 decomposed quantitatively to ethylene, 135, and a trace amount of hexamethylcyclotrisiloxane 3 (presumably from decomposition of 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane).

Co-pyrolysis of 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135 and 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane 10

0.0500 g (0.283 mmol) of 135 and 0.340 g (2.08 mmol) of 10 were degassed and heated in a sealed tube at 400°C for 7 hours. The resulting mixture upon analysis by gas chromatography (12 ft. x 0.25 in 15% SE-30 on chromasorb W) revealed three components: the starting oxadisilacyclopentane 10, hexamethylcyclotrisiloxane 3 (trace), and an unidentified compound. The unknown component was isolated by preparative gas chromatography and proved to be the trapping product for dimethylsilanone, 2,2,4,4,7,7-hexamethyl-1,3-dioxa-2,4,7-trisilacycloheptane 144 (73.6%, assuming the response factor for 144 to be the same as starting 10).

nmr ($CHCl_3$, 100 MHz) 0.73 (4H, s), 0.15 (6H, s), 0.08 (12H, s) mass spectrum (70 eV) m/e (rel. intensity) 234(54)(Parent), 219(100)(P-CH_3), 206(33)(P-C_2H_4), 191(67)(P-CH_3-C_2H_4), 147(12)($CH_2SiMe_2OSiMeO$), 133(16)($Me_2SiOSiMeO$), 89(10) (Me_3SiO), 74(14)(Me_2SiO), 73(54)(Me_3Si)

exact mass (P) 234.09274 (meas.), 234.09277 (calc. for $C_8H_{22}O_2Si_3$)

Co-pyrolysis of 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135 and dimethoxydimethylsilane 22

0.0230 g (0.130 mmol) of 135 and 0.160 g (1.27 mol) of dimethoxydimethylsilane were degassed and heated in a sealed tube at 420°C for 9 hours. Analysis of the pyrolysate by gas chromatography/mass spectrometry and gas chromatography (12 ft. x 0.25 in. 20% DC-550 on chromasorb P) revealed the presence of hexamethylcyclotrisiloxane 3 (19.0%), sym-dimethoxytetramethyldisiloxane 21 (40.8%), and sym-1,5-dimethoxyhexamethyltrisiloxane 142 (2.3%, assuming the response factor for 140 to be the same as 21).

Bis(chloromethyldimethylsilyl)amine 145

Bis(chloromethyldimethylsilyl)amine was prepared according to the procedure of Schmidt and Wieber (93) using 142 g (0.992 mol) of chloro(chloromethyl)dimethylsilane and 32 ml of liquid ammonia. 33.0 g (29.0%) of 145 were isolated. b.p. 105-107°C/12 torr [lit. 103-105°C/10 torr (92)] nmr ($CDCl_3$) 2.68 (4H, s) 0.17 (12H, s) (no amine proton observed)

ir (thin film) 3365(s), 2970(s), 2936(s), 1400(s), 1260(vs), 1079(s), 948(vs) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 182(25), 180(55) (P-CH_2Cl), 154(38), 152(100), 145(11), 137(20), 131(18), 116(60), 102(10), 100(30), 81(17), 79(26), 75(42), 73(23)

exact mass (P-49) 180.04335 (meas.), 180.04316 (calc. for $C_5H_{15}ClNSi_2$)

1-(Chloromethyl)-1,1,3,3-tetramethyldisiloxane 146

19.1 g (0.0830 mol) of bis(chloromethyldimethylsilyl)-amine in 100 ml of anhydrous ether at 0-5°C was hydrolyzed with 1 M hydrochloric acid to chloromethyldimethylsilanol 147 by the procedure of Wieber and Schmidt (94). The ether layer was separated and dried over anhydrous sodium carbonate. 94 ml (0.166 mol) of methyllithium-lithium bromide solution (1.8 M in ether from Aldrich) were added dropwise under nitrogen to the dried ether solution of chloromethyldimethylsilanol at 0°C to generate lithium chloromethyldimethylsilanolate 148 (95). Next, 15.7 g (0.166 mol) of chlorodimethylsilane were added dropwise to the mixture at 0°C. After gradual warming to room temperature over 5 hours the mixture was filtered. The filtrate was extracted twice with saturated sodium chloride solution and dried over sodium sulfate. Ether was removed *in vacuo* (180 torr) at 35°C. Distillation of the remaining liquid gave 18.2 g (59.8%) of 1-(chloromethyl)-1,1,3,3-tetramethyldisiloxane.

b.p. 134-136°C/746 torr [lit. 140.5°C/750 torr (96)]

nmr ($CDCl_3$, 100 MHz) 4.68 (1H, septet, J=3 Hz), 2.73 (2H, s), 0.22 (6H, s), 0.21 (6H, d, J=3 Hz)

ir (thin film) 2967(s), 2932(m), 2128(s), 1255(s), 1063(s), 904(s) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 183(1), 181(3) (P-H), 169(4), 167(10)($P-CH_3$), 155(3), 153(9) [$Me_2Si(H)OSi(Cl)Me$], 133(100)($P-CH_2Cl$), 75(2)($Me_2Si{=}OH$), 73(15)(Me_3Si)

exact mass (P-1) 181.02650 (meas.), 181.02718 (calc. for $C_5H_{14}ClOSi_2$) (P-15) 167.01091 (meas.), 167.01153 (calc. for $C_4H_{12}ClOSi_2$)

1-Bromo-3-(chloromethyl)-1,1,3,3-tetramethyldisiloxane 149

24.7 ml of a 1.82 *M* solution of bromine (0.0450 mol) in carbon tetrachloride were added dropwise with stirring over 6 hours to 8.23 g (0.0450 mol) of 1-(chloromethyl)-1,1,3,3-tetramethyldisiloxane and 3.56 g (0.0450 mol) of pyridine in 50 ml of carbon tetrachloride at 0°C under nitrogen. After warming to room temperature the mixture was stirred an additional 8 hours. The mixture was filtered under nitrogen. The filtrate was vacuum distilled to give 7.92 g (67.1%) of product 149.

b.p. 67-69°C/5 torr; 176-178°C/750 torr

nmr ($CDCl_3$, 100 MHz) 2.45 (2H, s), 0.44 (6H, s), 0.28 (6H, s)

mass spectrum (70 eV) m/e (rel. intensity) 247(5), 245(4), ($P-CH_3$), 219(21), 217(15), 213(100), 211(95)($P-CH_2Cl$), 183(9), 181(14)(P-Br), 169(7), 167(14)($Me_2SiOSiMe_2Cl$), 155(11), 153(28), 139(14), 137(17)(Me_2SiBr), 75(4) (Me_2SiOH), 73(25)(Me_3Si)

exact mass (P-15) 244.92147 (meas.), 244.922035 (calc. for $C_4H_{11}BrClOSi_2$)

Reaction of 1-bromo-3-(chloromethyl)-1,1,3,3-tetramethyldisiloxane 149 with Rieke magnesium

Rieke magnesium (72) was prepared using 1.71 g (0.0180 mol) of anhydrous magnesium chloride, 1.25 g (0.0320 mol) of potassium, and 1.34 g (0.00800 mol) of potassium iodide in 50 ml of anhydrous tetrahydrofuran. After cooling the mixture to -78°C 2.13 g (0.00814 mol) of 1-bromo-3-(chloromethyl)-1,1,3,3-tetramethyldisiloxane in 20 ml of tetrahydrofuran were added dropwise with stirring over 2 hours under nitrogen. The mixture was stirred at -78°C an additional 2 hours and allowed to gradually warm to room temperature over 9 hours. All volatile materials were distilled (0.03 torr, 40-50°C) from the mixture and collected at -78°C. Excess tetrahydrofuran was removed from the volatile materials by distillation at atmospheric pressure to leave 2.77 g of solution. Analysis of the solution by gas chromatography (6 ft. x 0.125 in. 3% OV-1 on chromasorb W) revealed a very complex mixture of three major components and numerous unidentified minor components. Gas chromatography/mass spectral analysis showed these components to be 2,2,4,4,6,6-hexamethyl-2,4,6-trisila-1,3-dioxane 150 (5.5%), 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaoxane 151 (6.5%), and 2,2,4,4,6,6,8,8-octamethyl-1,3-dioxa-2,4,6,8-tetrasilacyclooctane 152 (6.3%). These three components were isolated by preparative gas chromatography and their structures were confirmed.

2,2,4,4,6,6-Hexamethyl-2,4,6-trisila-1,3-dioxane 150

nmr (CCl_4) 0.16 (12H, s), 0.07 (6H, s), -0.03 (2H, s)

ir (CCl_4) 2970(m), 1255(s), 1024(vs), 976(m) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 220(1)(Parent), 205(100)($P-CH_3$), 189(18)($P-CH_3-CH_4$), 175(4) ($Me_2SiSiMe_2OSiMe$), 133(6)($Me_2SiOSiMeO$), 131(11) (Me_2SiCH_2SiMeO), 117(7)($Me_2SiOSiMe$), 75(7)($Me_2Si{=}OH$), 73(23)(Me_3Si)

exact mass (P) 220.07769 (meas.), 220.07713 (calc. for $C_7H_{20}O_2Si_3$)

2,2,4,4,6,6-Hexamethyl-2,4,6-trisilaoxane 151

nmr (CCl_4, 100 MHz, TFA external lock) 0.10 (18H, s), -0.18 (4H, s)

[The spectrum which was reported in the literature (97) for neat 149 using cyclohexane as an internal reference and a 60 MHz instrument showed peaks at 0.11 (6H, s), 0.09 (12H, s), and -0.19 (4H, s).]

ir (CCl_4) 2905(m), 2896(m), 1259(s), 1251(s), 1026(vs) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 203(100)(P-CH_3), 187(13(P-CH_3-CH_4), 175(7)($Me_2SiSiMe_2OSiMe$), 133(7) ($Me_2SiOSiMeO$), 131(8)(Me_2SiCH_2SiMeO), 117(5)($Me_2SiOSiMe$), 115(5)(Me_2SiCH_2SiMe), 94(17)(P-2CH_3, doubly charged ion), 75(5)(Me_2SiOH), 73(20)(Me_3Si)

exact mass (P-15) 203.07384 (meas.), 203.07438 (calc. for $C_7H_{19}OSi_3$)

2,2,4,4,6,6,8,8-Octamethyl-1,3-dioxa-2,4,6,8-tetrasilacyclooctane 152

nmr (CCl_4) 0.13 (12H, s), 0.10 (6H, s), 0.07 (6H, s), -0.08 (4H, s)

ir (CCl_4) 2954(s), 2895(m), 1256(vs), 1048(vs) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 277(100)(P-CH_3), 261(4)(P-CH_3-CH_4), 245(3)(P-CH_3-2CH_4), 205(3)(P-CH_3-Me_2SiCH_2), 203(2)(P-CH_3-Me_2SiO), 189(7)(P-CH_3-Me_4Si), 133(2)($Me_2SiOSiMeO$), 131(3)(Me_2SiCH_2SiMeO), 73(13)(Me_3Si)

exact mass (P-15) 277.09189 (meas.), 277.09318 (calc. for $C_9H_{25}O_2Si_4$)

Reaction of 1-bromo-3-(chloromethyl)-1,1,3,3-tetramethyldisiloxane 149 with Rieke magnesium in the presence of dimethoxydimethylsilane 22

1.66 g (0.00634 mol) of 1-bromo-3-(chloromethyl)-1,1,3,3-tetramethyldisiloxane and 4.08 g (0.0340 mol) of dimethoxydimethylsilane in 40 ml of anhydrous tetrahydrofuran were added dropwise with stirring over 5 hours to a suspension of Rieke magnesium (72) [magnesium chloride (3.42 g, 0.0360 mol), potassium (2.50 g, 0.0640 mol), and potassium iodide (2.68 g, 0.0160 mol) in 120 ml of tetrahydrofuran] at ~78°C under nitrogen. After gradual warming to room temperature over 18 hours the mixture was vacuum filtered under nitrogen. Excess tetrahydrofuran was removed from the filtrate by simple distillation to give 2.60 g of solution. Gas chromatographic analysis (6 ft. x 0.125 in. 3% OV-1 on chromasorb W) of the solution revealed the presence of 2,2,4,4,6,6-hexamethyl-2,4,6-trisila-1,3-dioxane 150 (2.0%), 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaoxane 151 (36.5%), *sym*-dimethoxytetramethyldisiloxane 21 (16.9%), *sym*-1,5-dimethoxyhexamethyltrisiloxane 140 (8.2% assuming the response factor for 140 to be the same as 21), and a major unidentified component in addition to some unidentified minor components. Gas chromatography/mass spectral analysis confirmed the presence of the previously named components and suggested that the unidentified major component was an adduct of dimethoxydimethylsilane and some reaction intermediate of formula $C_5H_{14}OSi_2$. Isolation of this component by preparative gas chromatography identified the compound as 2,6-dimethoxy-2,4,4,6-tetramethyl-3-oxa-2,4,6-trisilaheptane <u>153</u> (27.9%).

nmr (CCl_4) 3.40 (3H, s), 3,36 (3H, s), 0.13 (6H, s), 0.10 (6H, s), 0.03(6H, s), -0.05 (2H, s)

ir (CCl_4) 2962(s), 2904(m), 2833(m), 1257(s), 1190(m), 1028(vs) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 251(100)($P-CH_3$), 221(20), 205(13)($OSiMe_2CH_2SiMe_2OSiMe$), 163(7), 133(5) ($Me_2SiOSiMeO$), 131(5)(Me_2SiCH_2SiMeO), 89(17)(Me_3SiO), 75(2)(Me_2SiOH), 73(10)(Me_3Si)

exact mass (P-15) 251.09534 (meas.), 251.09551 (calc. for $C_8H_{23}O_3Si_3$)

The trisilaheptane <u>153</u>, as well as the other isolated products, was found to be thermally stable under the gas chromatographic conditions.

(Aminomethyl)trimethylsilane 154

(Aminomethyl)trimethylsilane was prepared according to the procedure of Noll, Daubert, and Speier (98) by heating

24.5 g (0.200 mol) of chloromethyltrimethylsilane and 119 g (7.00 mol) of liquid ammonia in an autoclave at 85-90°C. 9.78 g (47.4%) of (aminomethyl)trimethylsilane were isolated.
b.p. 83-85°C [lit. 83°C/736 torr (98)]
nmr (CCl_4) 2.10 (2H, s), 0.91 (2H, broad singlet), 0.02 (9H, s)

N-(trimethylsilylmethyl)-N-nitrosourea 155

The preparation of N-(trimethylsilylmethyl)-N-nitrosourea was based upon the procedures of Matjeka (99) and Bachmann and Struve (100). 3.14 ml of concentrated hydrochloric acid (0.0484 mol) were added to 5.00 g (0.0484 mol) of (aminomethyl)trimethylsilane to form the ammonium salt. 8.74 g (0.145 mol) of urea and 30 ml of water were added. The resulting solution was refluxed for 8 hours. Upon cooling two layers formed with the upper layer solidifying. Absolute ethanol was added to just dissolve the solid layer. 6.67 g (0.0968 mol) of sodium nitrite were dissolved in the reaction mixture. The resulting solution was added slowly to a solution of 2.15 ml of concentrated sulfuric acid dissolved in a mixture of 17 ml of absolute ethanol and 17 ml of water at 0°C *via* a funnel extending beneath the surface of the acid solution. Foaming was noted and a pale yellow solid floated to the surface of the mixture. After 10 hours at 0°C the impure solid was collected by suction filtration. The product was isolated by eluting the impure solid with chloroform, collecting the eluant, and removing the chloroform *in vacuo*. 5.19 g (61.1%) of *N*-(trimethylsilylmethyl)-*N*-nitrosourea were collected as pale yellow platelike crystals.

m.p. 93-94°C [lit. 95.5-96°C (55,56)]

nmr ($CDCl_3$) 3.53 (2H, s), 0.03 (9H, s) (The nitrogen protons were not observed.)

Trimethylsilyldiazomethane 107

Trimethylsilyldiazomethane was prepared according to the procedure of Seyferth and co-workers (55,56) using 2.00 g (0.0114 mol) of *N*-(trimethylsilylmethyl)-*N*-nitrosourea. 0.708 g (31.4%) of trimethylsilyldiazomethane was isolated by preparative gas chromatography (5 ft. x 0.25 in. 20% XF-1150 on chromasorb P).

nmr (neat) 2.65 (1H, s), 0.18 (9H, s)

ir (thin film) 2962(s), 2070(vs), 1266(s), 843(s) cm^{-1}

UV λ_{max} (pentane) 237, 400 nm

Photolysis of trimethylsilyldiazomethane 107 in dodecane

0.437 g (3.82 mmol) of trimethylsilyldiazomethane was dissolved in 100 ml of dodecane. The solution was degassed and sealed inside a 500-ml pyrex tube. The pale yellow green solution was irradiated through a filter (400 nm) for 160 hours at room temperature using a Hanovia 450L medium pressure lamp. Vacuum distillation (0.07 torr) of the solution followed by preparative gas chromatography of the distillate (5 ft. x 0.25 in. 20% XF-1150 on chromasorb P; Injector 43°C, Column 20°C, and Detector 55°C) gave 72.0 mg (16.5%) of trimethylsilyldiazirine 156.

nmr ($CDCl_3$, 100 MHz), -0.03 (9H, s), -0.53 (1H, s)

UV λ_{max} (in pentane) 311, 319, 325, 333, 340 nm

Photolysis of trimethylsilyldiazomethane 107 with acetone in pentane

0.287 g (0.00251 mol) of trimethylsilyldiazomethane and 2.92 g (0.0503 mol) of acetone (freshly distilled from K_2CO_3) were dissolved in 400 ml of pentane and the solution degassed with a small, continuous flow of nitrogen. The solution was irradiated through quartz with a Hanovia 450L medium pressure lamp for 2.5 hours at room temperature with a small flow of nitrogen bubbling through the solution. The excess pentane and acetone were removed from the solution by distillation at atmospheric pressure. Preparative gas chromatography (5 ft. x 0.25 in. 20% XF-1150 on chromasorb P) gave 0.0205 g of material. This material appeared to be an adduct of acetone and a reaction intermediate of formula $C_4H_{10}Si$ from the low resolution mass spectrum. Subsequent spectra of the material were consistent with 2,4,4-trimethyl-3-oxa-4-sila-1-hexene 157.

nmr ($CHCl_3$, 100 MHz) 4.12 (2H, "singlet"), 1.86 (3H, s), 1.44-0.68 (5H, m), 0125 (6H, s)

mass spectrum (70 eV) m/e (rel. intensity) 144(13)(Parent), 129(65)($P-CH_3$), 116(42)($P-C_2H_4$, $Me_2SiOCMe_2$), 115(100) ($P-C_2H_5$), 101(16)($MeSiOCMe_2$), 86(13), 75(81)(Me_2SiOH), 73(29)(Me_3Si), 61(23)(MeHSiOH), 59(38)(Me_2SiH)

exact mass (P) 144.09593 (meas.), 144.09704 (calc. for $C_7H_{16}OSi$), (P-15) 129.07295 (meas.), 129.07356 (calc. for $C_6H_{13}OSi$), (P-69) 75.02666 (meas.), 75.02662 (calc. for C_2H_7OSi)

Photolysis of matrix-isolated trimethylsilyldiazomethane 107 (101)

Trimethylsilyldiazomethane was isolated in an argon matrix at 8°K. Irradiation (>355 nm) of the matrix produced a photostationary state involving trimethylsilyldiazomethane [λ_{max} (in 3-methylpentane at 77°K) 400 nm] and trimethylsilyldiazirine [λ_{max} (in 2-methyltetrahydrofuran at 77°K) 309, 317, 324, 332, 340 nm]. This mixture was also obtained upon irradiation of pure trimethylsilyldiazirine 156. Continued irradiation of the mixture led to a new compound, 2-methyl-2-sila-2-butene 110. The infrared spectrum of 110 at 8°K in the argon matrix showed the following peaks: 3020, 2980, 2965, 2940, 2900, 2870, 1450, 1410, 1370, 1315, 1255, 1120, 978, 883, 808, 795, 712, 708, 645, 608, and 358 cm^{-1}. Upon warming the matrix above 45°K the disappearance of bands for 110 and simultaneous formation of bands for the head-to-tail dimers of 110, *cis*- and *trans*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutane 108, was observed. [This was confirmed by comparison to authentic samples of 108 prepared by the vacuum pyrolysis of trimethylsilyldiazomethane according to the procedure of Kreeger and Shechter (66)].

Ethoxy(trimethylsilyl)acetylene 158

This procedure was based upon that of Shchukovskaya and Pal'chik (102). 23.3 g (0.214 mol) of ethyl bromide in 30 ml of anhydrous ether were added dropwise with stirring to 5.20 g (0.214 mol) of magnesium turnings in 20 ml of ether under nitrogen. After 2 hours 15.0 g (0.214 mol) of ethoxyacetylene (from Farchan Chemicals) in 20 ml of ether were added dropwise at 0-5°C. After 6 hours 21.7 g(0.200 mol) of chlorotrimethylsilane in 35 ml of ether were added dropwise over 3 hours. The mixture was stirred at room temperature for 8 hours and at reflux for 2 additional hours. Filtration and distillation of the filtrate gave 5.81 g (19.0%) of 158.

b.p. 53-55°C/32 torr [lit. 57.2°C/34 torr (102)]

nmr ($CDCl_3$) 4.04 (2H, quartet, J=7 Hz), 1.24 (3H, t, J=7 Hz), -0.03 (9H, s)

ir (thin film) 2968(m), 2184(vs), 1254(s), 1207(m), 991(m), 843(vs) cm^{-1}

Trimethylsilylketene 159

Trimethylsilylketene was prepared according to the procedure of Shchukovskaya, Pal'chik, and Lazarev (103) by heating 5.80 g (0.0408 mol) of ethoxy(trimethylsilyl)-acetylene at 120-130°C and collecting the distillate (4.10 g, 88.0%).

b.p. 80-82°C

nmr ($CDCl_3$) 1.72 (1H, s), 0.11 (9H, s)

ir (thin film) 3050(m), 2972(s), 2914(m), 2115(vs), 1275(s), 1258(s), 1057(m), 845(s) cm^{-1}

Photolysis of trimethylsilylketene 159

1.08 g (0.00948 mol) of trimethylsilylketene were dissolved in 125 ml of pentane and the resulting solution was degassed. The solution was irradiated through quartz (2537 Å) in a Rayonet photochemical reactor for 24 hours at 30-35°C. The solution was distilled under nitrogen to remove excess pentane. The remaining solution showed only starting ketene 159 and some pentane by proton magnetic resonance spectroscopy and by gas chromatographic analysis (12 ft. x 0.25 in. 15% SE-30 on chromasorb W).

Pyrolysis of trimethylsilylketene 159

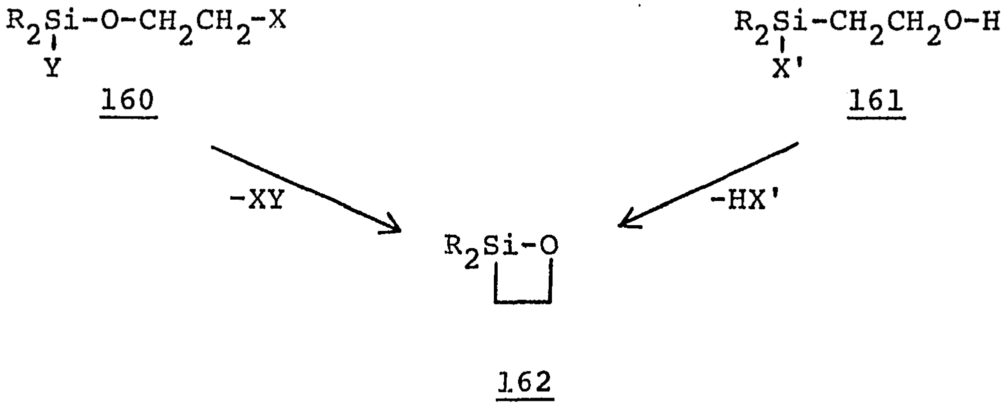
0.255 g (0.00233 mol) of trimethylsilylketene was dissolved in 2 ml of anhydrous benzene. The resulting solution was slowly dripped into a vertical tube furnace at 480°C with a nitrogen flow (30 ml/min). The pyrolysate was collected at -196°C. A proton magnetic resonance spectrum of the pyrolysate revealed only the starting ketene 159 and minor impurities which were present before pyrolysis.

RESULTS AND DISCUSSION

2-Silaoxetanes

Up to this time no isolated 2-silaoxetanes have been reported although such species have been proposed as key intermediates in numerous mechanisms (28,29,35,36). The bulk of this research has been directed toward the synthesis of 2-silaoxetane systems under conditions where these compounds might be stable enough to isolate or at least to observe spectroscopically. Two general approaches were utilized in these attempts (Scheme 29). The first of these involved ring closure with the silicon-carbon bond being formed in the last step. In the second approach the final step was the coupling of the silicon and oxygen atoms to give the desired product.

Scheme 29



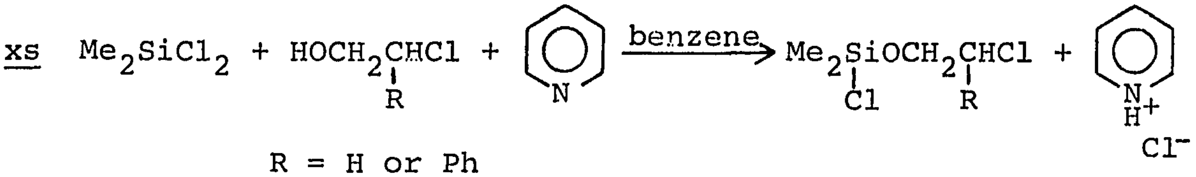
Silicon-carbon bond formation

The first of these approaches was based upon the general reaction of Grignard reagents with halosilanes to give silicon-carbon bonds (104). Thus, applying this reaction in an intramolecular process, one might hope to synthesize 2,2-dimethylsilaoxetane systems from compounds such as 160 where X and Y were halogens.

Synthesis and reactions of chloro-(2-chloroethoxy)dimethylsilane 120

Chloro-(2-chloroethoxy)dimethylsilane was prepared in 41% isolated yield from the reaction of ethylene chlorohydrin with an excess of dichlorodimethylsilane as shown in Scheme 30. Silane 120 was reacted with Rieke magnesium (72) in tetrahydrofuran at room temperature in an attempt to affect ring closure to give 2,2-dimethyl-2-silaoxetane 163. However, a proton magnetic resonance spectrum of the product mixture revealed only a large, rather broad singlet in the silyl

Scheme 30



R = H or Ph

120 R=H (41%)

122 R=Ph (67%)

methyl region in addition to solvent peaks. Separation by gas chromatography gave two peaks whose retention times corresponded exactly for those of authentic samples of hexamethylcyclotrisiloxane 3 (<1%), octamethylcyclotetrasiloxane 2 (18%), and decamethylcyclopentasiloxane 1 (2%). A low resolution mass spectrum of the mixture also showed peaks which were consistent with a mixture of the three cyclosiloxanes (105). The formation of these cyclosiloxanes strongly suggested the formation of dimethylsilanone during the course of the reaction.

Thinking that the dimethylsilanone might be arising from decomposition of 2,2-dimethyl-2-silaoxetane under the reaction conditions the reaction was repeated at 0°C. A gas chromatogram of this new reaction mixture revealed the presence of small amounts of cyclosiloxanes 2 and 3 and an unidentified component which came off the column (47°C) before the solvent. The very small amount of this unidentified compound which was obtained by preparative gas chromatography decomposed to a small extent upon the gas chromatograph at injector temperatures of approximately 200°C to give cyclosiloxanes 2 and 3. A low resolution mass spectrum of the component showed only peaks for octamethylcyclotetrasiloxane 2 and small amounts of cyclosiloxanes 1 and 3. A proton magnetic resonance spectrum of the component was too weak for a definitive analysis although a peak in the silyl methyl region and a weak signal at approximately 3.5-4.0 ppm were present. Numerous attempts to reproduce these results failed to give any detectable amounts of this unidentified compound. Instead, only cyclosiloxanes 1, 2, and 3 were observed in combined yields of 40-50% depending upon the individual reaction. Similar results were obtained when Rieke magnesium was replaced by magnesium powder in hexamethylphosphoramide.

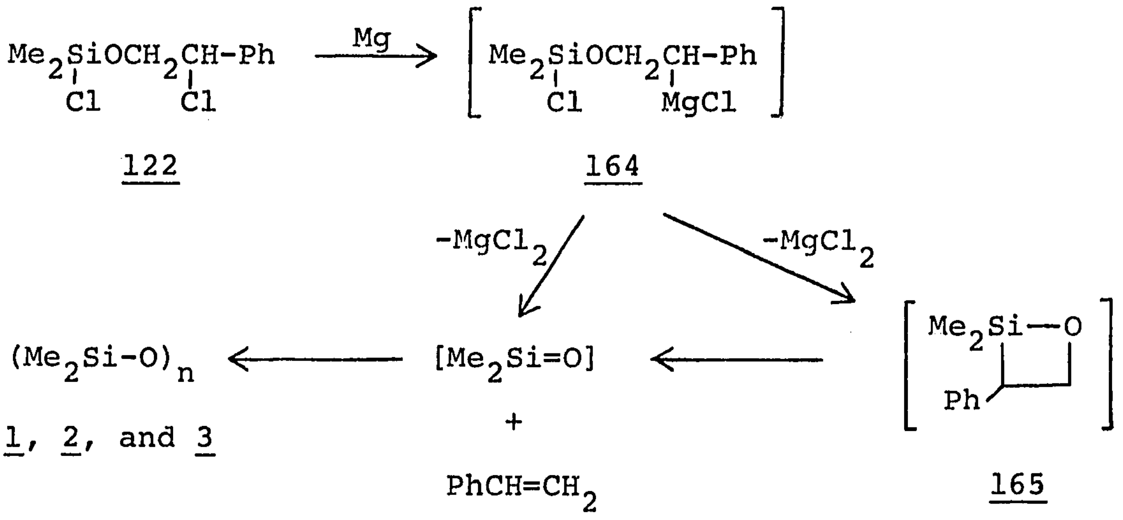
These results were all consistent with a dimethylsilanone intermediate. However, if a silanone were being produced in the reaction, ethylene would be expected as a by-product. To simplify detection of any by-product olefin the phenyl-substituted derivative 122 was used. It was also hoped that this benzyl chloride derivative might react at lower temperatures and as a result, lower the probability of any thermal decomposition of the 2-silaoxetane which might be formed in the reaction.

Synthesis and reaction of chloro-(2-chloro-2-phenylethoxy)-dimethylsilane 122

Chloro-(2-chloro-2-phenylethoxy)dimethylsilane was prepared in 67% isolated yield from 2-chloro-2-phenylethanol and excess dichlorodimethylsilane (Scheme 30). Silane 122 was reacted with Rieke magnesium in tetrahydrofuran at -78°C. The resulting product mixture showed the presence of styrene and cyclosiloxanes 1, 2, and 3 by proton magnetic resonance spectropy. The presence of these compounds was confirmed by comparison of gas chromatographic retention times with authentic samples. The styrene was produced in 89% yield and the cyclosiloxanes 1, 2, and 3 were produced in 52% combined yield based upon unreacted starting material.

These observations and those for the reactions of chloro-(2-chloroethoxy)dimethylsilane 120 suggest two possible pathways for formation of dimethylsilanone and styrene as shown in Scheme 31. The initially formed Grignard reagent 164 could close to give 2,2-dimethyl-3-phenyl-2-silaoxetane 165 which decomposed to styrene and dimethylsilanone. Alternatively, the Grignard reagent could undergo a direct

Scheme 31



six-electron fragmentation to give the products. Such eliminations have been reported recently by Fostein and Pommier (106) for systems in which the halogen on silicon was replaced by an alkyl group. Of course, their systems had no possibility for ring closure. The results from these reactions do not allow for the immediate distinction between the two pathways since dimethylsilanone and styrene would be produced in either case.

Silicon-oxygen bond formation

Two well-precedented reactions were utilized in an effort to synthesize 2-silaoxetane systems by formation of a silicon-oxygen bond as the final step (Scheme 32). First, alcohols are known to react with halosilanes by cleavage of the silicon-halogen bond to form a silicon-oxygen bond (104). Second, alcohols have been shown to undergo a dehydrocondensation with silyl hydrides in the presence of a catalyst (87-89) to produce silicon-oxygen bonds. Therefore, pre-

Scheme 32

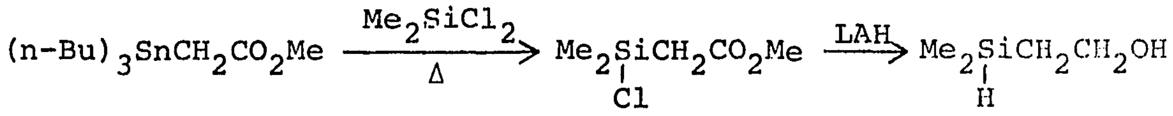
$$\begin{tikzcd}
\begin{array}{c} R_3Si\text{-}X \ + \ R'OH \\ (X=\text{halogen}) \end{array} \arrow[r] & R_3Si\text{-}OR' \ + \ HX \\
R_3Si\text{-}H \ + \ R'OH \arrow[u, "X_2"'] \arrow[r, "\text{catalyst}"] & R_3Si\text{-}OR' \ + \ H_2
\end{tikzcd}$$

cursors such as the (2-hydroxyethyl)silanes 161 (Scheme 29) where X=H or halogen were needed. This task was somewhat simplified by the fact that silyl hydrides may be converted easily to the corresponding silyl chloride or bromide by reaction with elemental chlorine or bromine, respectively. Thus, 2-(dimethylsilyl)ethanol 126 might serve as a central precursor for both methods of attack.

Synthesis of 2-(dimethylsilyl)ethanol 126

The preparation of 2-(dimethylsilyl)ethanol was reported earlier by Lutsenko and coworkers (76,77) using the sequence of reactions shown in Scheme 33 with a reported overall yield of 35% for the two steps. This route required the synthesis

Scheme 33

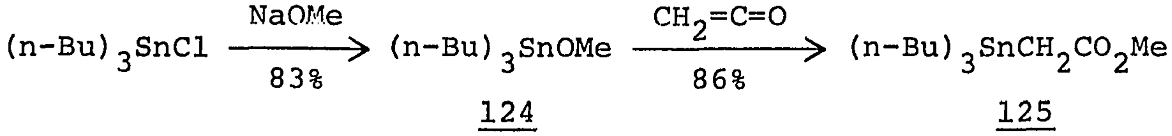


$$(n\text{-Bu})_3SnCH_2CO_2Me \xrightarrow[\Delta]{Me_2SiCl_2} Me_2\underset{\substack{|\\ Cl}}{Si}CH_2CO_2Me \xrightarrow{LAH} Me_2\underset{\substack{|\\ H}}{Si}CH_2CH_2OH$$

125 127 126

of the methyl-α-(tri-n-butylstannyl)acetate 125. This was accomplished in an overall 72% isolated yield as shown in Scheme 34. First, tri-n-butylmethoxystannane 124 was prepared by reacting tri-n-butylchlorostannane with sodium methoxide (74). Tri-n-butylmethoxystannane was then reacted at 0°C with ketene to give the starting ∝-stannylester <u>125</u> (75). However, the conversion of <u>125</u> to 2-(dimethylsilyl)-

Scheme 34

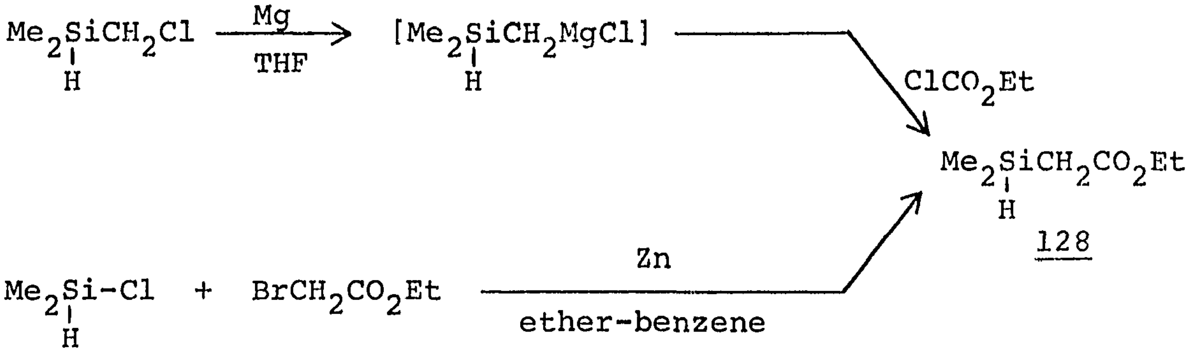


$$(n\text{-Bu})_3SnCl \xrightarrow[83\%]{NaOMe} \underset{\underline{124}}{(n\text{-Bu})_3SnOMe} \xrightarrow[86\%]{CH_2=C=O} \underset{\underline{125}}{(n\text{-Bu})_3SnCH_2CO_2Me}$$

ethanol in our hands was not as successful. Methyl-∝-(tri-n-butylstannyl)acetate was reacted with an excess of dichlorodimethylsilane at 80-90°C and the resulting mixture was added directly to an ethereal suspension of lithium aluminum hydride (LAH). From this reaction mixture only a 6% yield of crude product was obtained which by proton magnetic resonance spectroscopy was consistent with 2-(dimethylsilyl)-ethanol. While this reaction sequence did apparently produce the alcohol <u>126</u>, it had the disadvantage of a low overall yield (4%). Since larger quantities of <u>126</u> were desired, an alternative reaction sequence was sought.

First, attempts were directed toward the synthesis of ∝-silylacetates which might be reduced conveniently to the alcohol <u>126</u>. The preparation of ethyl-∝-(dimethylsilyl)-acetate <u>128</u> was attempted by two different routes (Scheme 35).

Scheme 35

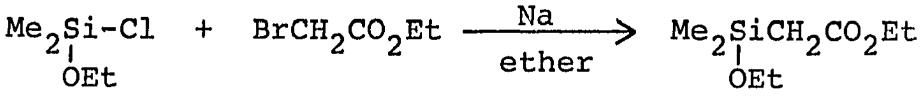


In the first reaction, which was fashioned after the reactions of Gold and coworkers (79), chloromethyldimethylsilane was reacted with magnesium turnings in tetrahydrofuran (THF) followed by addition of ethylchloroformate. Aqueous workup gave none of the desired ester as shown by the proton magnetic resonance spectrum. There was no evidence of any silyl hydride: neither a multiplet for the silyl hydrogen itself, nor a doublet in the silyl methyl region indicative of coupling to the silyl hydrogen. Instead, a very complex mixture of silicon-containing compounds was observed.

In the second reaction which was based upon the reactions of Fessenden and Fessenden (78), chlorodimethylsilane and ethyl-α-bromoacetate were added to zinc powder in a benzene-ether solution. Although a reaction of some type was indicated by the liberation of heat during the addition, after aqueous workup the proton magnetic resonance spectrum failed to show the presence of the α-silylester 128. The products which were observed were unreacted ethyl-α-bromoacetate, ethylacetate, and small amounts of benzene and *sym*-tetramethyldisiloxane, the latter of which presumably arising from hydrolysis of unreacted chlorodimethylsilane. These components were also indicated by comparison of gas chromatographic retention times with those of authentic samples.

A third attempted method of synthesis of an α-silylester which was based upon the types of reactions of Andrianov and Makarova (81) is shown in Scheme 36. Chloroethoxydimethylsilane 129 was prepared from dichlorodimethylsilane and ethanol in approximately 15% isolated yield. A small amount of toluene which had been used as solvent was also present in the product by the proton magnetic resonance spectrum. A mixture of this chloroethoxydimethylsilane and ethyl-α-bromoacetate was added to sodium metal in ether. Filtration of the reaction mixture followed by distillation gave two volatile fractions of boiling point ranges 94-96°C and 104-108°C and a brown polymeric residue. The proton magnetic

Scheme 36



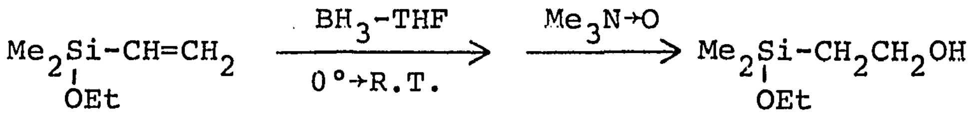
$$\underset{\displaystyle OEt}{Me_2Si}\text{-}Cl + BrCH_2CO_2Et \xrightarrow[\text{ether}]{Na} \underset{\displaystyle OEt}{Me_2Si}CH_2CO_2Et$$

129 130

resonance spectra of the two fractions were virtually identical and revealed two components: toluene and what appeared to be diethoxydimethylsilane [nmr (neat) 3.15 (4H, quartet, J=7 Hz), 0.63 (6H, t, J=7 Hz), -0.40 (6H, s)]. The compounds were confirmed by comparison of gas chromatographic retention times with those of authentic samples. The reported boiling point of 113.8°C for diethoxydimethylsilane 131 (82) was also consistent. The exact origin of this diethoxydimethylsilane was not clear, however.

At this point the method for synthesis of 2-(dimethylsilyl)ethanol was changed. An attempt was made to prepare a 2-silylethanol which might be converted into 2-(dimethylsilyl)ethanol. Thus, the hydroboration-oxidation of ethoxydimethylvinylsilane 132 was attempted as shown in Scheme 37. The "direct" method using dimethylvinylsilane was not used due to the instability of silicon-hydrogen bonds toward oxidation. A borane-tetrahydrofuran solution was added to

Scheme 37



$$\underset{\text{OEt}}{\mathrm{Me_2Si}}\text{-CH=CH}_2 \xrightarrow[0°\rightarrow \text{R.T.}]{\text{BH}_3\text{-THF}} \xrightarrow{\text{Me}_3\text{N}\rightarrow\text{O}} \underset{\text{OEt}}{\mathrm{Me_2Si}}\text{-CH}_2\text{CH}_2\text{OH}$$

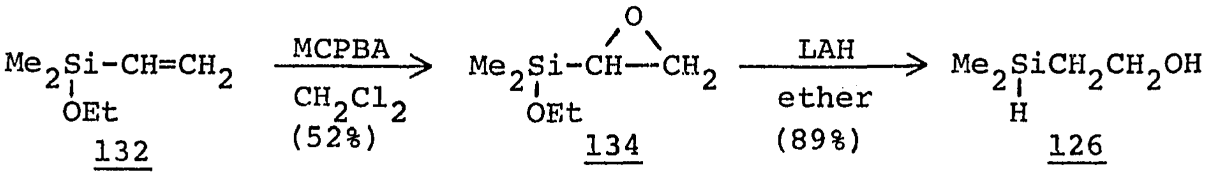
132 166

silane 132 in tetrahydrofuran (THF) at 0°C. In an effort to reduce the possibility of cleavage at the silicon atom during the oxidation of the intermediate organoborane, anhydrous trimethylamine oxide (83) was used at room temperature. A rather vigorous reaction was noted upon addition of the amine oxide. Aqueous workup followed by distillation resulted in the majority of the reaction mixture decomposing into intractable polymeric material. However, a small amount of distillate was collected over the boiling point range 61-81°C/0.03 torr. In addition to the presence of an ethoxy group, the proton magnetic resonance spectrum of the distillate revealed a "triplet" at approximately 4.1 ppm, several peaks at 0.8-1.4 ppm, and several peaks in the silylmethyl region 0.05-0.35 ppm. The position and number of the peaks suggested that the distillate was perhaps a mixture of the desired 2-(ethoxydimethylsilyl)ethanol 166, the isomeric 1-(ethoxydimethylsilyl)ethanol 167, and other silicon-containing compounds. Attempted separation of the mixture by column chromatography failed as shown by the proton magnetic resonance spectrum. Since that time Lim and coworkers (107) have reported that the hydroboration of chlorodimethylvinylsilane gave a 36:64 mixture of boron addition to the α- and β- positions, respectively, with respect to silicon. No oxidation was attempted upon the chlorosilylborane.

From these results it was clear that a different approach to the synthesis of 2-(dimethylsilyl)ethanol was still needed if sizeable quantities were to be produced. Earlier work by

Eisch and Trainor suggested such a route. These authors reported that reduction of various (trialkyl- and triarylsilyl)oxiranes with lithium aluminum hydride went regiospecifically to produce only the 2-silylethanol. It was suggested by the authors that this result was due to the interaction of the empty d-orbitals on silicon with the incoming hydride. With these results in mind the two-step sequence of reactions in Scheme 38 was undertaken.

Scheme 38



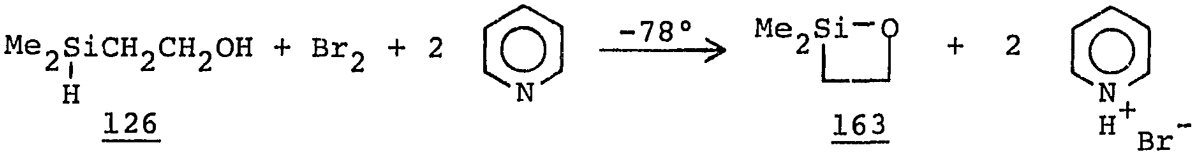
Addition of ethoxydimethylvinylsilane 132 to *m*-chloroperbenzoic acid (MCPBA) (85% from Aldrich) gave upon distillation (ethoxydimethylsilyl)oxirane 134 in 52% isolated yield. The epoxide 134 was then reduced with lithium aluminum hydride (LAH) to give exclusively upon distillation 2-(dimethylsilyl)ethanol 126 in 89% isolated yield. Thus, a convenient synthesis of 2-(dimethylsilyl)ethanol was obtained from commercially available ethoxydimethylvinylsilane in a 46% overall yield.

Reactions of 2-(dimethylsilyl)ethanol 126

As was shown earlier in Scheme 32 silyl halides react with alcohols with elimination of hydrogen halide to give alkoxysilanes. Thus, if the silyl hydrogen in 2-(dimethylsilyl)ethanol were converted to the corresponding silyl halide, one might hope for an intramolecular ring closure to give the desired 2,2-dimethyl-2-silaoxetane 163 as was depicted in Scheme 29 where R=Me.

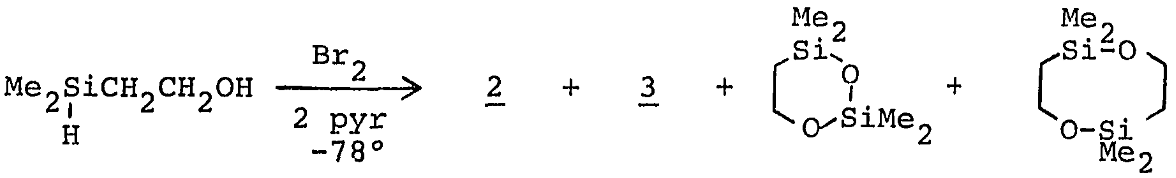
Using this approach, bromine in dichloromethane was reacted with 2-(dimethylsilyl)ethanol at -78°C as shown in Scheme 39. Two equivalents of pyridine were used to trap the expected hydrogen bromide: one equivalent from formation of the intermediate silylbromide 168 and a second equivalent from an intramolecular ring closure to give 163. Reaction of bromine was virtually instantaneous under the conditions of a very slow addition of bromine. Filtration of the mixture gave an isolated yield of 94% of pyridinium hydrobromide based upon two equivalents of hydrogen bromide being produced.

Scheme 39



None of the expected 2-silaoxetane 163 was observed, however. Instead, hexamethylcyclotrisiloxane 3 (1%), octamethylcyclotetrasiloxane 2 (<1%), 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135 (32%), and 2,2,6,6-tetramethyl-1,5-dioxa-2,6-disilacyclooctane 136 (46%) were isolated (Scheme 40).

Scheme 40



126 135 136

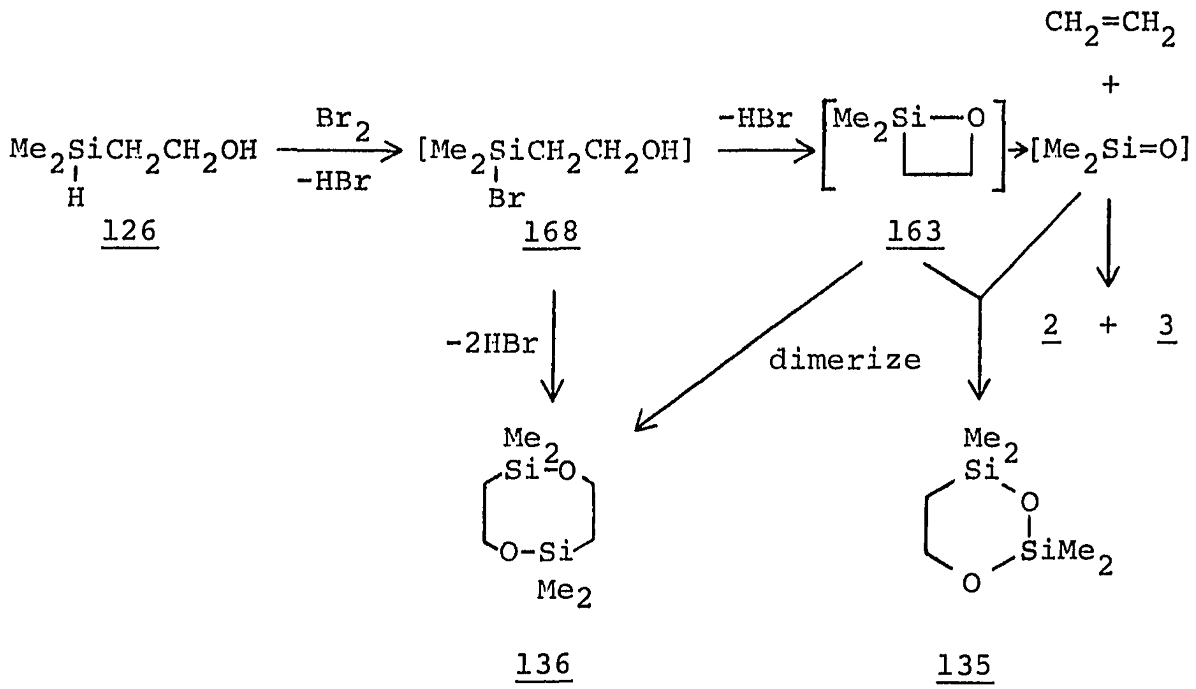
(<1%) (1%) (32%) (46%)

Although the reaction had been run in a closed system under argon, no ethylene which would be expected from decomposition of the 2,2-dimethyl-2-silaoxetane was detectable in the vapors above the reaction mixture, even at 0°C, by analysis with high resolution mass spectrometry. Attempted trapping of any intermediate 2-silaoxetane 163 by addition of the reaction mixture at -78°C to methanol was unsuccessful. No adducts of 2,2-dimethyl-2-silaoxetane and methanol were observed by gas chromatography/mass spectral analysis. Again, the cyclosiloxanes 2 (2%) and 3 (11%), the 1,3-dioxane 135 (29%) and the 1,5-dioxacyclooctane 136 (47%) were isolated.

Of these products perhaps the most interesting was the 1,3-dioxane 135. The possibility that 135 might come from loss of ethylene from the 1,5-dioxacyclooctane 136 was suggested when an attempted high resolution mass spectrum of 136 revealed no ions for the parent molecule or for the loss of a methyl group from silicon. The ion of highest mass which was observed was for a loss of ethylene, the parent ion of 135. Indeed, it was found that 136 did begin to decompose upon the gas chromatograph at injector temperatures of 210°C or greater. In fact, by 370°C the decomposition of 136 to 135 and ethylene (identified as its dibromide) was essentially quantitative. However, at injector temperatures of less than 200°C very little or no decomposition was observed. In addition, the presence of 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135 in the crude reaction mixture was detected by proton magnetic resonance spectroscopy and high pressure liquid chromatography. These observations suggested that 135 was being formed not by thermal decomposition of 136 but by an alternative pathway. A possible mechanism which is consistent with the products is shown in Scheme 41.

The initially formed silylbromide 168 might react intermolecularly to give 136 or intramolecularly to give 2,2-dimethyl-2-silaoxetane 163. The 2-silaoxetane could then dimerize in a head-to-tail fashion to give 136 or decompose

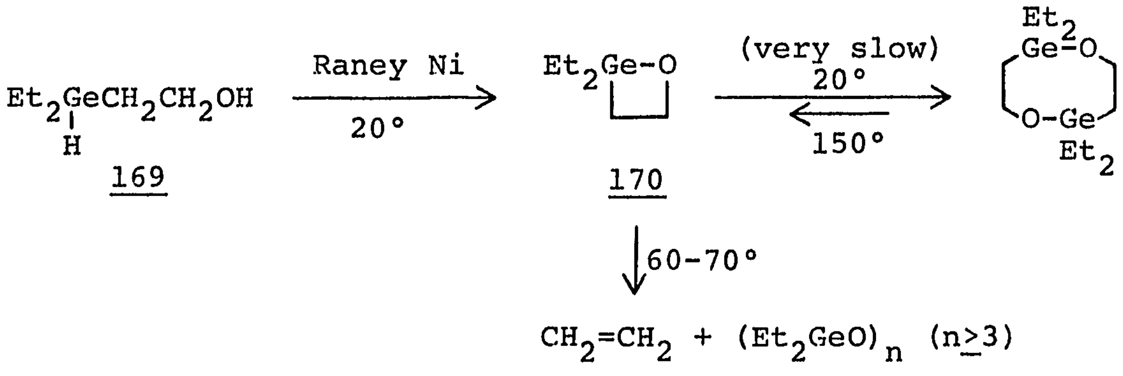
Scheme 41



to ethylene and dimethylsilanone which could oligomerize to cyclosiloxanes 2 and 3. The 1,3-dioxane 135 could result from trapping of dimethylsilanone by 2,2-dimethyl-2-silaoxetane. Such a species as the 2-silaoxetane 163 might be expected to be a good trap for silanone based upon the previous reports that hexamethylcyclotrisiloxane 3 adds silanones in solution to give the cyclotetrasiloxanes (8,9,10,15). Of course, this mechanism would require that the 2-silaoxetane 163 have a significant half-life such that sufficient quantities were present to trap dimethylsilanone before the silanone could oligomerize to cyclosiloxanes.

In an effort to determine whether the products of the bromine reaction were of a general nature and not simply characteristic of the particular reaction conditions, a catalytic approach to the formation of 2,2-dimethyl-2-silaoxetane was investigated. Satgé and coworkers (88,89) had reported earlier that 2-(diethylgermyl)ethanol 169 reacted in the presence of Raney nickel to produce 2,2-diethyl-2-germaoxetane 170 (Scheme 42). Thus, 2-(dimethylsilyl)ethanol

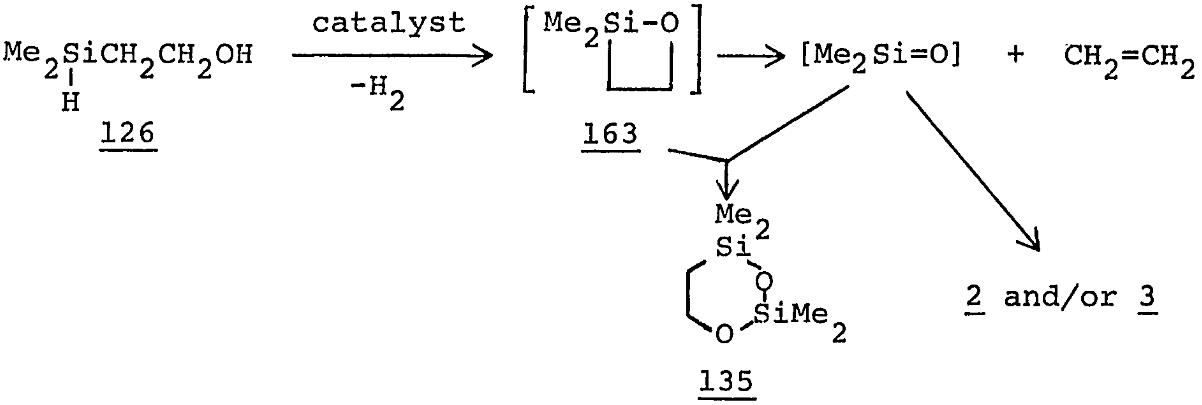
Scheme 42



126 was added in an analogous fashion to Raney nickel in pentane at 0°C. No 2,2-dimethyl-2-silaoxetane 163 was obtained. Instead, hexamethylcyclotrisiloxane 3 (<1%) and 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135 (42%) were formed as the only products which were detectable by gas chromatographic and gas chromatography/mass spectral analyses.

These results were apparently independent of the particular catalyst which was used. Corriu and Moreau (87) had shown in previous work that Wilkinson's catalyst tris-(triphenylphosphine)rhodium chloride promoted the dehydrocondensation between alcohols and silylhydrides. Therefore, 2-(dimethylsilyl)ethanol was added slowly to 0.001 equivalent of Wilkinson's catalyst in benzene at room temperature. The only detectable products were hexamethylcyclotrisiloxane 3 (6%) and 1,3-dioxane 135 (57%). When a known silanone trap, dimethoxydimethylsilane was present during the reaction, a small amount of trapping was observed: cyclosiloxanes 2 (<1%) and 3 (2%), 1,3-dioxane 135 (26%) and *sym*-dimethoxytetramethyldisiloxane 21 (2%). These results and those from the Raney nickel experiments allowed a general mechanism to be written (Scheme 43). The noted absence of 1,5-dioxacyclo-

Scheme 43



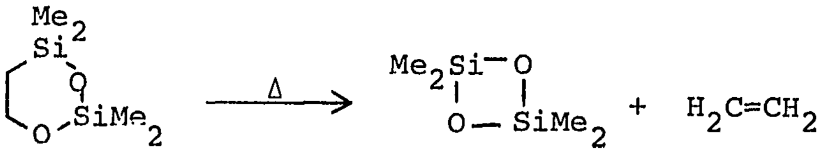
octane 136 in the catalytic reactions tends to suggest that its formation in the bromine reactions (Scheme 41) very likely resulted from an intermolecular reaction of silyl bromide 168. In addition, the absence of 1,3-dioxane 135 in the earlier reactions of chloro-(2-chloroethoxy)dimethylsilane 120 with magnesium suggests that the initially formed Grignard reagent may be undergoing direct fragmentation rather than ring closure to 2,2-dimethyl-2-silaoxetane (Scheme 31).

The results from the reactions of 2-(dimethylsilyl)-ethanol with bromine and with the two different catalysts appear to be quite similar. In both cases the 1,3-dioxane 135 is formed as a major product. The formation of this compound is strongly suggestive of an intermediate 2-silaoxetane 163 being formed and that this intermediate exists in a high enough concentration to function as a trap for its own decomposition product, dimethylsilanone. It should be noted that no products from cleavage of a 2-silaoxetane via the silicon-oxygen bond were observed as suggested by the pyrolysis experiments of Ando and coworkers (35,36).

Reactions of 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane 135

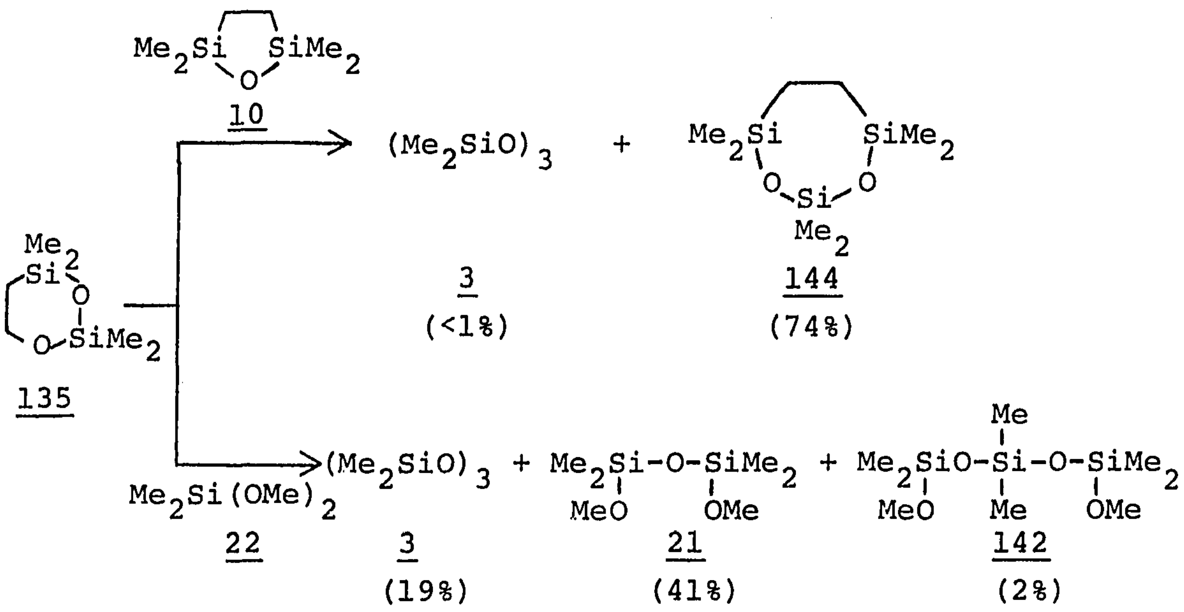
As was mentioned previously 136 decomposed thermally to 135 and ethylene. This result suggested a rather interesting possibility. Would 135 decompose by an analogous extrusion of ethylene to give the previously unknown tetramethylcyclodisiloxane 171 (Scheme 44)? This cyclodisiloxane was of

Scheme 44

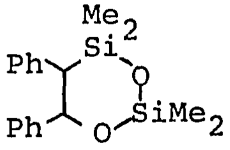

135 171

interest as a possible low temperature generator of dimethylsilanone. Such a system would be particularly well-suited for attempts at spectroscopic observation of a silanone since a unimolecular decomposition of 171 would lead only to dimethylsilanone. Thus, an initial investigation of the thermal stability of 1,3-dioxane 135 was made by gas chromatography. At injector temperatures up to 370°C less than 5% decomposition could be detected as determined by the appearance of hexamethylcyclotrisiloxane 3. In an attempt to lower this decomposition temperature 135 was pyrolyzed in a sealed tube. No significant decomposition was noted until approximately 400°C. In the presence of added 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane 10 there were produced hexamethylcyclotrisiloxane 3 (<1%) and 2,2,4,4,7,7-hexamethyl-1,3-dioxa-2,4,7-trisilacycloheptane 144 (74%). With dimethoxydimethylsilane 22 as a trap the products were hexamethylcyclotrisiloxane 3 (19%), *sym*-dimethoxytetramethyldisiloxane 21 (41%) and *sym*-1,5-dimethoxyhexamethyltrisiloxane 142 (2%) (Scheme 45). These trapping experiments indicated that indeed dimethylsilanone was being produced. This dimethylsilanone could be coming from a direct six-electron fragmentation of 135 or from decomposition of the intermediate tetramethylcyclodisiloxane 171. None of the cyclosiloxane 171 was observed. However, such an intermediate would not be expected to survive at 400°C which is of course far above the desired decomposition range for a low temperature silanone generator. The 1,3-dioxane 135 needed

Scheme 45



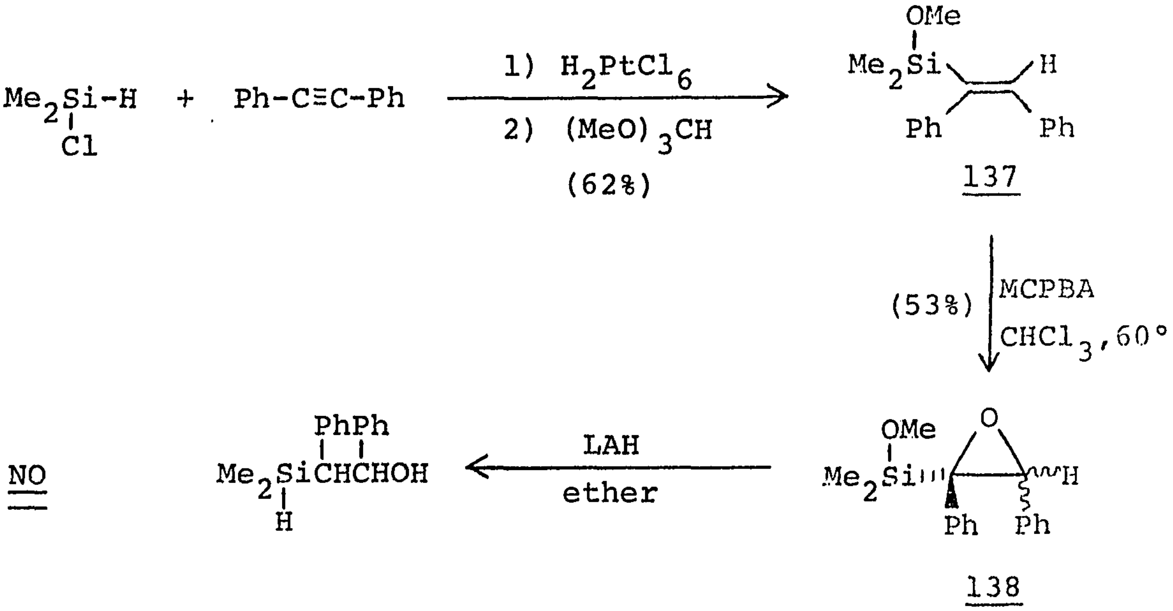
to be modified in order to lower this decomposition temperature. One possible modification might be to attach phenyl substituents to the carbon atoms at the 5- and 6-positions of the ring as in compound 172. Therefore, an attempt to



172

synthesize 1,3-dioxane 172 by a route analogous to that of 135 was made (Scheme 46). The alcohol 173 would be needed.

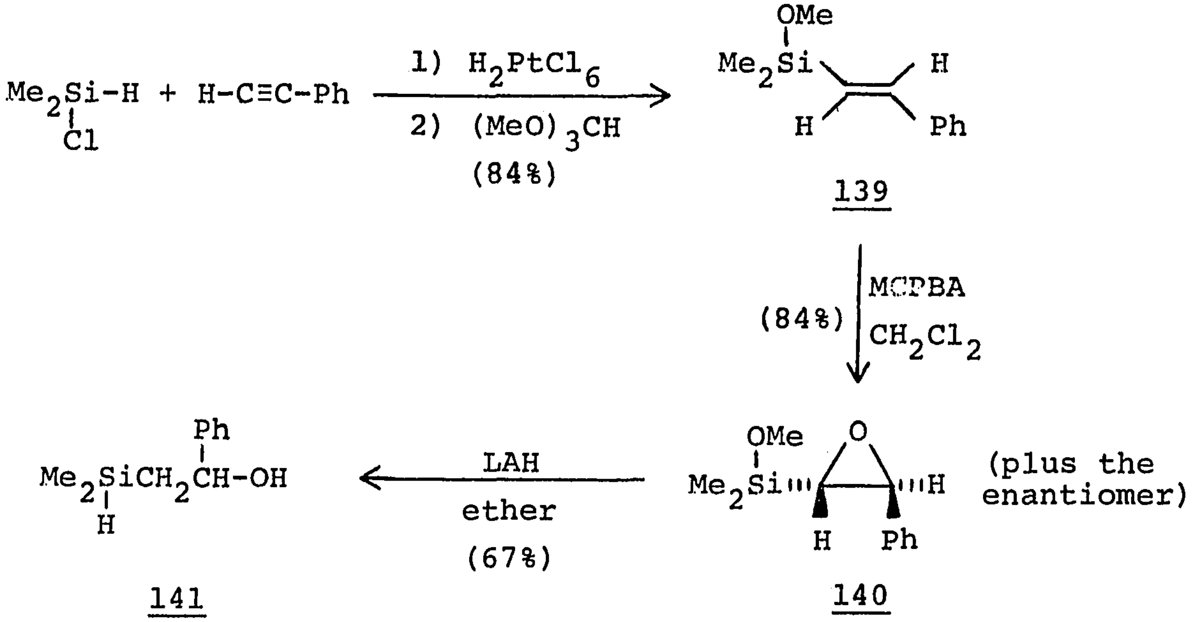
Scheme 46



The hydrosilation and methoxylation steps followed by epoxidation with m-chloroperbenzoic acid (MCPBA) gave E- and Z-1-

(methoxydimethylsilyl)-1,2-diphenyloxirane 138 in 33% overall yield. However, reduction of the epoxide with lithium aluminum hydride did not give the expected alcohol 173 upon aqueous workup. Only trace amounts of unidentifiable silicon-containing compounds were observed. The only detectable major products were *cis*- and *trans*-stilbene. Apparently, the phenyl substituent alpha to the silicon facilitated the cleavage of the silicon-carbon bond. This conclusion was strongly suggested by the successful synthesis of 2-(dimethylsilyl)-1-phenylethanol 141 as shown in Scheme 47.

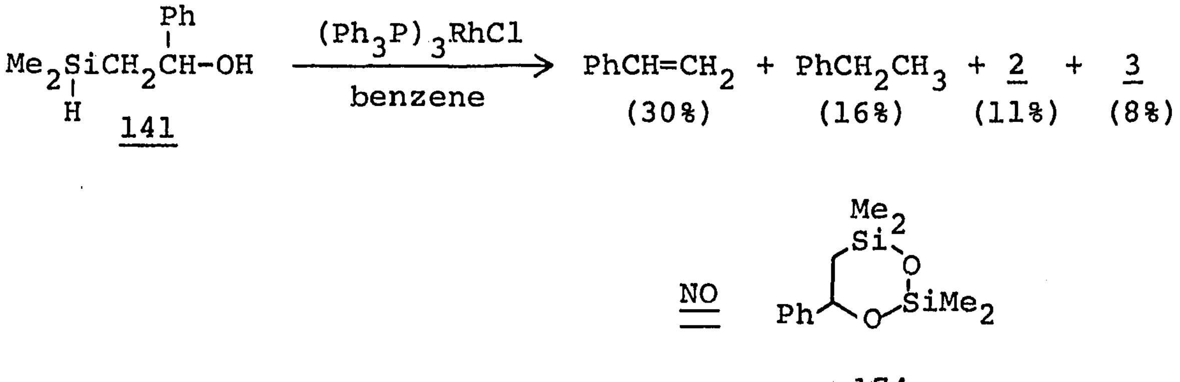
Scheme 47



2-(Dimethylsilyl)-1-phenylethanol 141 was isolated in 47% overall yield from commercially available phenylacetylene and chlorodimethylsilane.

2-(Dimethylsilyl)-1-phenylethanol was reacted with 0.001 equivalent of Wilkinson's catalyst in benzene in the expectation of producing 2,2,4,4-tetramethyl-6-phenyl-2,4-disila-1,3-dioxane 174. However, none of this product was detected by gas chromatography/mass spectrometry or proton magnetic resonance spectroscopy. The observed products included styrene (30%), ethylbenzene from hydrogenation of styrene (16%), and cyclosiloxanes 2 (11%) and 3 (8%) (Scheme 48). Again no products from cleavage of a silicon-oxygen

Scheme 48



$$\underset{\mathrm{H}}{\mathrm{Me_2Si}}\mathrm{CH_2}\overset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{-OH} \xrightarrow[\text{benzene}]{(\mathrm{Ph_3P})_3\mathrm{RhCl}} \underset{(30\%)}{\mathrm{PhCH{=}CH_2}} + \underset{(16\%)}{\mathrm{PhCH_2CH_3}} + \underset{(11\%)}{\underline{2}} + \underset{(8\%)}{\underline{3}}$$

141

NO

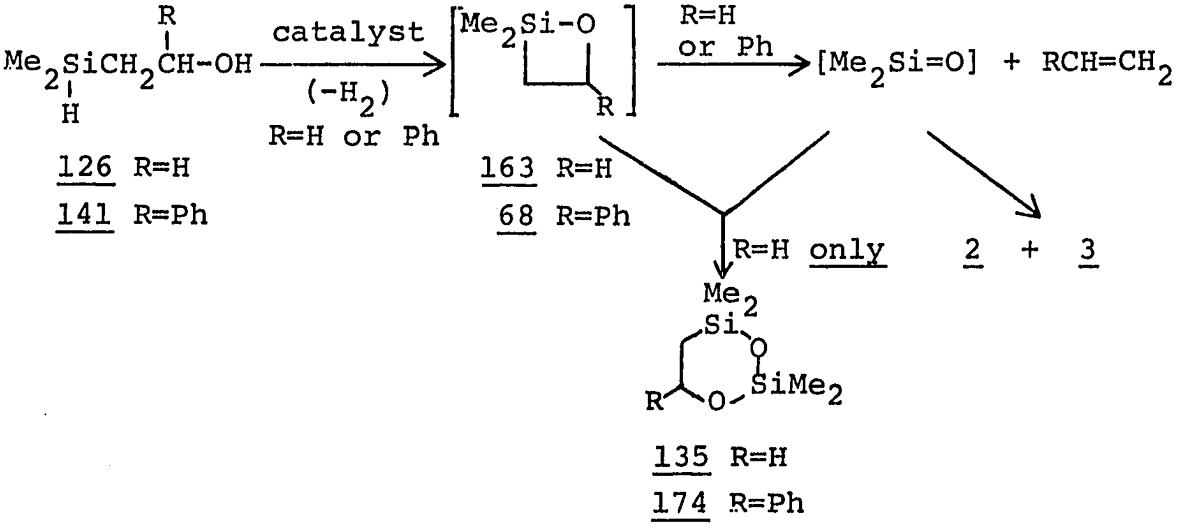
174

bond of an intermediate 2-silaoxetane were detected (35,36). When the reaction was repeated with two equivalents of dimethoxydimethylsilane 22 present, the products were again styrene (40%), ethylbenzene (12%), and cyclosiloxanes 2 (7%) and 3 (6%). In addition, the products for trapping of dimethylsilanone, *sym*-dimethoxytetramethyldisiloxane 21 (23%)

and sym-1,5-dimethoxyhexamethyltrisiloxane 142 (13%) were formed.

These results pointed out some important differences in the chemistries of the 1-phenylethanol 141 and the unsubstituted 2-(dimethylsilyl)ethanol 126. First, when dimethoxydimethylsilane 22 was added to the reaction mixtures, extensive silanone trapping (36%) was observed for 141 while very little trapping (2%) was observed for 126. This would imply that dimethylsilanone was being trapped more efficiently by some other species, perhaps 2,2-dimethyl-2-silaoxetane 163. This would seem to be confirmed by the second important difference between the two systems. The 1,3-dioxane 174 is not observed for 141, but the corresponding 135 is formed from 126 even in the presence of added trap (Scheme 49).

Scheme 49

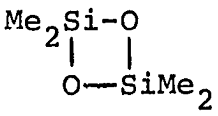


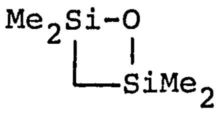
Indeed, if the same mechanism is operative in both systems, there are two likely explanations for these observed differences. The first would be that the 1,3-dioxane is produced in both systems but that the phenyl substitution has lowered the decomposition temperature from approximately 400°C for the unsubstituted 135 to room temperature or below for 174. Such a dramatic decrease seems highly unlikely. An alternative explanation would be that the stabilities of the two initially formed 2-silaoxetanes 163 and 68 differ. If the 2,2-dimethyl-4-phenyl-2-silaoxetane 68 were to decompose much more rapidly than the 2,2-dimethyl-2-silaoxetane 163, the concentration of 68 at any given time might not be adequate to trap dimethylsilanone. In other words, the differences which were observed might arise from a difference in the half-lives of the 2-silaoxetanes 163 and 68. Of course, these arguments are based upon the assumption that dimethylsilanone does not add across the carbon-oxygen or carbon-carbon bond of the 2-silaoxetane ring. In the case of 68 the phenyl substituent might sterically hinder such an addition and produce the observed results. Such an assumption appears to be correct based upon the recent findings of Barton and Wulff (16) that dimethylsilanone gives no detectable adducts with ethylene oxide. Thus, a 2-silaoxetane intermediate would explain the results.

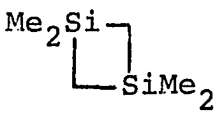
This leaves the question of why the 2,2-dimethyl-4-phenyl-2-silaoxetane 68 should decompose more rapidly than the unsubstituted 163. A possible explanation is that the decomposition of the 2-silaoxetane is a concerted four-electron process with the transition state coming late in the reaction pathway. In this way the effect of conjugation with the phenyl group of 68 may be felt in the transition state and a lowering of the activation energy relative to that for the decomposition of the unsubstituted 2-silaoxetane 163 may occur. The similar, alternative argument is that silanone extrusion begins with homolytic cleavage of the C-O bond. Thus, the relative stabilities of 68 and 163 simply reflect the stability of a benzyl versus a secondary radical. The results which were obtained do not allow a definitive statement on the subject at this time.

2,4-Disilaoxetane

A rather interesting extension of the 2-silaoxetane investigation has been the attempted synthesis of 2,2,4,4-tetramethyl-2,4-disilaoxetane 175. This system is interesting not only as a possible low temperature generator of silanone but also as a generator of silene; from one molecule one might have a direct route into both of these silicon (p-p)π doubly bonded species. Since no previous work has been reported in this area, the stability and reactivity of such a system is unknown. One might guess, however, that the stability of 175 would lie somewhere between that of the thermally quite stable 1,1,3,3-tetramethyl-1,3-disilacyclobutane 176 and that of the unknown, apparently quite reactive tetramethylcyclodisiloxane 171.

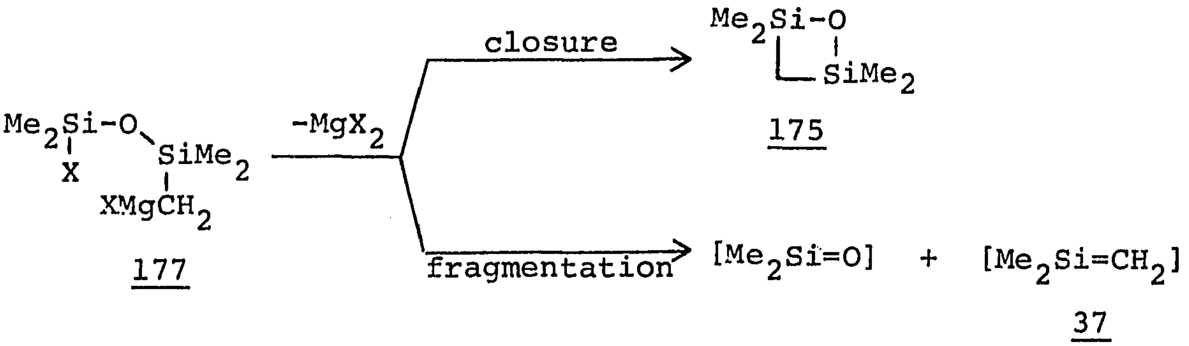

171


175


176

The synthetic approach to 2,2,4,4-tetramethyl-2,4-disilaoxetane was based upon the intramolecular ring closure of the Grignard reagent 177 as shown in Scheme 50. It was hoped that a direct fragmentation which was suggested for the Grignard reagent of the carbon system, chloro-(2-chloro-2-phenylethoxy)-

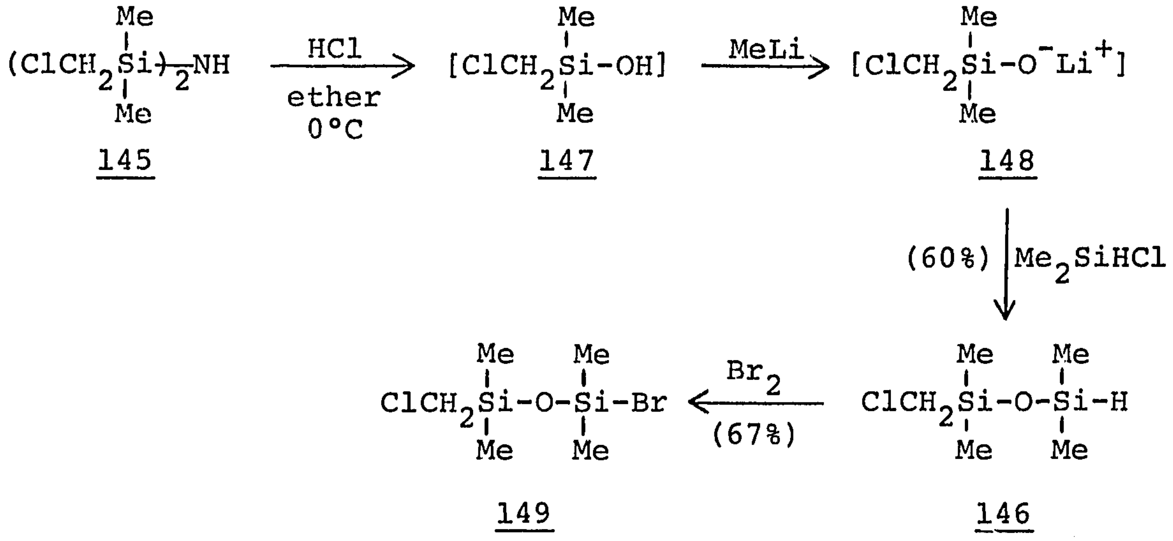
Scheme 50



dimethylsilane 122 (Scheme 31) would be less favorable since the initial cleavage would produce a silene rather than a simple olefin.

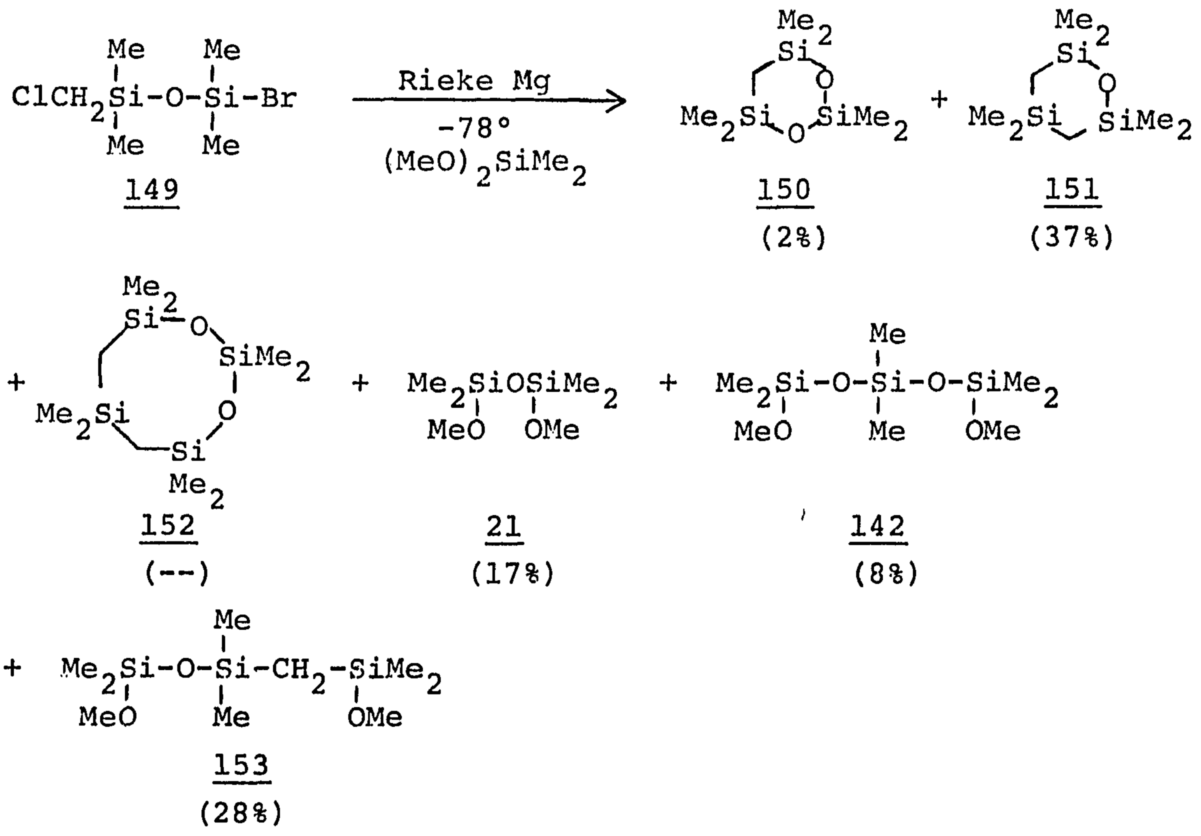
The necessary starting material 1-bromo-3-(chloromethyl)-1,1,3,3-tetramethyldisiloxane 149 was prepared in 40% overall isolated yield by the reaction sequence shown in Scheme 51.

Scheme 51



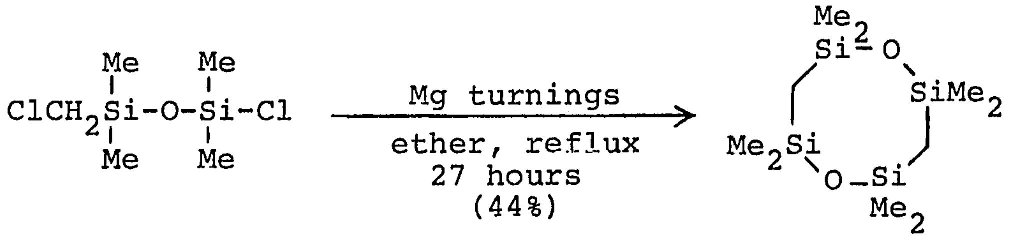
Reaction of 149 with Rieke magnesium (72) at -78°C gave a rather complex mixture of products. However, no detectable amount of the desired 2,2,4,4-tetramethyl-2,4-disilaoxetane 175 was indicated by gas chromatography/mass spectral analysis or by proton magnetic resonance spectroscopy. Three major products were observed: 2,2,4,4,6,6-hexamethyl-2,4,6-trisila-1,3-dioxane 150 (6%), 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaoxane 151 (7%), and 2,2,4,4,6,6,8,8-octamethyl-1,3-dioxa-2,4,6,8-tetrasilacyclooctane 152 (6%). When the reaction was repeated in the presence of a silanone trap, dimethoxydimethylsilane 22, the products were 150 (2%), 151 (37%), *sym*-dimethoxytetramethyldisiloxane 21 (17%), *sym*-1,5-dimethoxyhexamethyltrisiloxane 142 (8%), and 2,6-dimethoxy-2,4,4,6-tetramethyl-3-oxa-2,4,6-trisilaheptane 153 (28%) plus some very minor unidentified components (Scheme 52). None of the 1,3-dioxacyclooctane 152 was observed. In addition, all of the products were found to be thermally stable during gas chromatographic analysis.

Scheme 52



It should be noted that these results were considerably different from those previously reported by Mironov and coworkers (96). In that work 1-chloro-3-(chloromethyl)-1,1,3,3-tetramethyldisiloxane 178 was reacted with magnesium turnings in refluxing ether to give 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-2,4,6,8-tetrasilacyclooctane 179 as the only reported product (Scheme 53). Of course, the reaction conditions were also considerably different in terms of temperature, concentration, and reactivity of the magnesium.

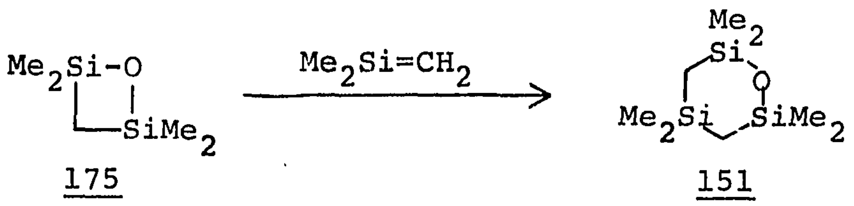
Scheme 53



178 179

A simple interpretation of the results from the reaction of 149 with Rieke magnesium is impossible. The complexity of the product mixture tends to suggest a direct fragmentation of the Grignard reagent 177 to give dimethylsilanone and 2-methyl-2-silapropene 37 (Scheme 50) followed by a somewhat random recombination to give the observed products. Indeed, the trapping experiment does confirm the intermediacy of dimethylsilanone. The formation of the trisilaheptane 153 may also be indicative of the intermediacy of silene 37 assuming that disiloxane 21 can function as a silene trap. However, one of the products, the trisilaoxane 151 does appear to implicate the intermediacy of 2,2,4,4-tetramethyl-2,4-disilaoxetane 175 in light of a recent finding by Barton and Wulff (16). They found that 1,1,3,3-tetramethyl-1,3-disilacyclobutane 176 did not trap to any detectable amount dimethylsilanone at room temperature in solution. Thus, if one discounts a rather improbable ternary complex of two silenes and one silanone in the transition state, it appears that the 2,4-disilaoxetane 175 is trapping silene to form 151 (Scheme 54). In fact, the absence of the silene dimer, 1,1,3,3-tetramethyl-1,3-disilacyclobutane 176 itself tends to argue for a reactive species being present in high enough concentration to function as a silene trap. This would imply that either 2,4-disilaoxetane 175 is formed to some extent from ring closure of the Grignard reagent 177 (Scheme 50) or dimethylsilanone reacts with silene much more rapidly than

Scheme 54

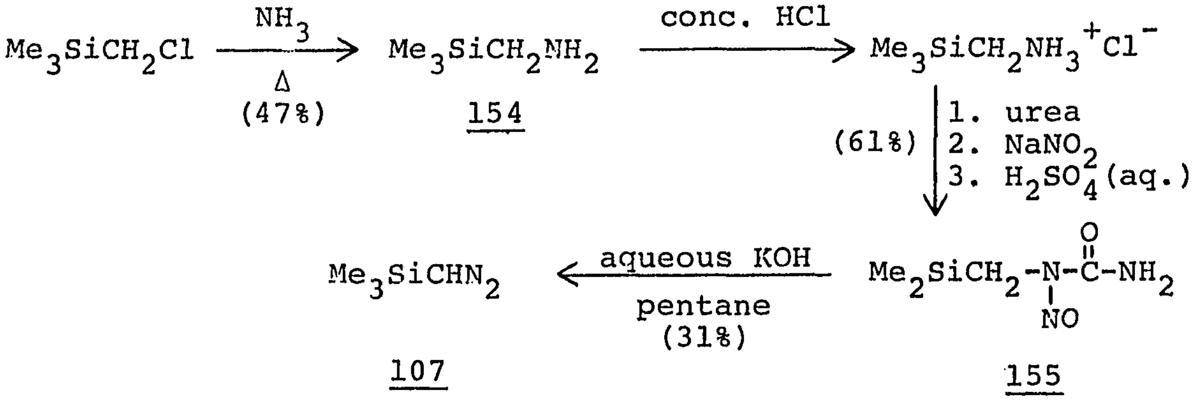


silene itself can dimerize in which case the 2,4-disilaoxetane, or some diradical (or zwitterionic) form of 175, would result. In either case the formation of 2,2,4,4-tetramethyl-2,4-disilaoxetane at some point during the reaction is suggested from these preliminary studies.

α-(Trimethylsilyl)carbene

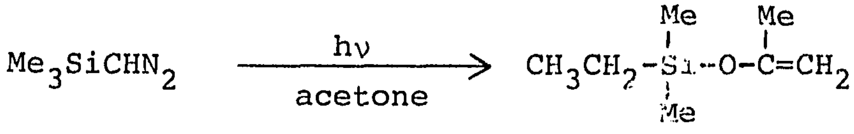
Interest in α-silylcarbenes has increased recently (69,70) as a result of the report by Haszeldine and coworkers (65) that irradiation of trimethylsilyldiazomethane 107 produced an unidentified carbene dimer. The possibility had to be considered that an initially formed α-(trimethylsilyl)carbene 80 might be rearranging to the silene, 2-methyl-2-sila-2-butene 110 followed by dimerization. Thus, in an attempt to study this possible rearrangement trimethylsilyldiazomethane was prepared by the reaction sequence in Scheme 55 in an overall isolated yield of 9%.

Scheme 55



An initial investigation of the photochemistry of 107 in the presence of acetone gave a small amount (6% isolated) of the adduct 2,4,4-trimethyl-3-oxa-4-sila-1-hexene 157 (Scheme 56). This adduct was consistent with an intermediate

Scheme 56



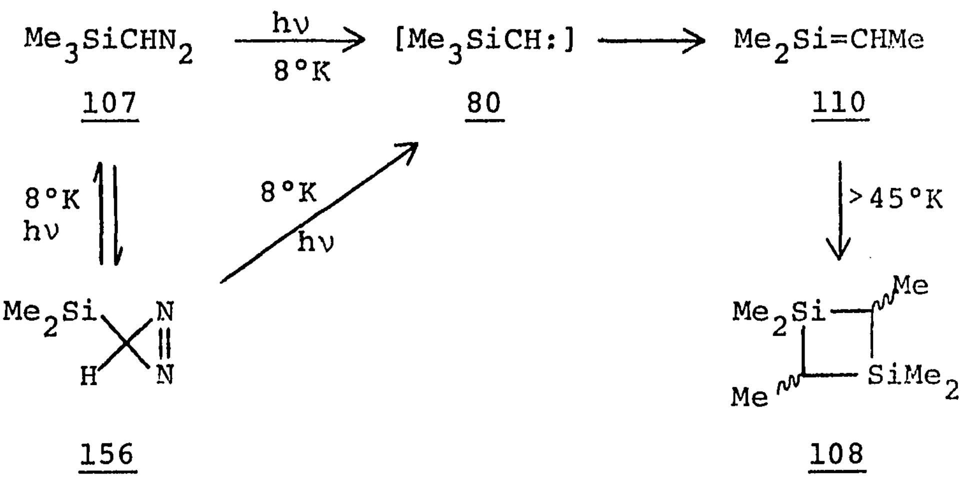
$$Me_3SiCHN_2 \xrightarrow[\text{acetone}]{h\nu} CH_3CH_2-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{C}=CH_2$$

107 157

silene 110 being trapped either by acetone in a stepwise manner followed by hydrogen abstraction or by the enol form of acetone directly.

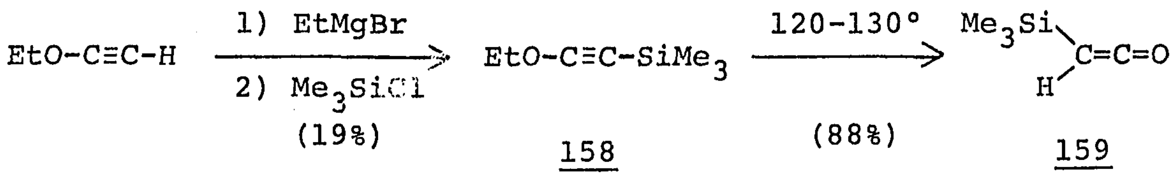
In an effort to observe the intermediate silene spectroscopically trimethylsilyldiazomethane 107 was isolated in an argon matrix at 8°K. Irradiation (λ>355 nm) of the matrix produced initially a photostationary state between the starting diazocompound 107 and trimethylsilyldiazirine 156. This same equilibrium was obtained when starting with pure trimethylsilyldiazirine. (Trimethylsilyldiazirine 156 was isolated in 16.5% yield from irradiation (λ>400 nm) of 107 in dodecane at room temperature.) Continued irradiation of the matrix resulted in the disappearance of 107 and 156 and the formation of a new compound which showed the following infrared spectrum: 3020, 2980, 2965, 2940, 2900, 2870, 1450, 1410, 1370, 1315, 1255, 1120, 978, 883, 808, 795, 712, 708, 645, 608, and 358 cm^{-1}. The olefinic stretch (3020 cm^{-1}) and deformation modes (795 and 645 cm^{-1}) which are characteristic of a trisubstituted olefin led to the assignment of 2-methyl-2-sila-2-butene 110 for the new compound. The formation of the silene dimers, cis- and trans-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes 108 with simultaneous disappearance of the new compound upon warming of the matrix above 45°K confirmed this assignment (101) (Scheme 57). Thus, trimethylsilyldiazomethane could be used for the generation of silenes.

Scheme 57



In an effort to extend this investigation from diazocompounds to ketenes which were more easily prepared, trimethylsilylketene 159 was synthesized in 17% overall isolated yield from commercially available ethoxyacetylene (Scheme 58). Unfortunately, trimethylsilylketene was found to be

Scheme 58



quite stable toward loss of carbon monoxide. Neither irradiation (λ=2537 Å) of 159 nor flow pyrolysis of 159 at 480°C led to any detectable amounts of decomposition products. Thus, trimethylsilylketene failed to be an α-silylcarbene, and consequently a silene, generator.

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