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Synthesis and mechanistic studies of silaoxetanes and silanones

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SYNTHESIS AND MECHANISTIC STUDIES OF SILAOXETANES AND SILANONES

Iowa State University PH.D. 1983

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Synthesis and mechanistic studies
of silaoxetanes and silanones

by

Gregory Paul Hussmann

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

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Major: Organic Chemistry

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In Charge of Major Work

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For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1983

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DEDICATION

To Kim and Sarah Marie

INTRODUCTION

Although Friedel and Crafts prepared the first organosilicon compound in 1865, major achievements in the field of organosilicon chemistry did not occur until the early 1900s and the systematic studies of Frederic Stanley Kipping (1, 2). Kipping, whose investigations spanned the first four decades of this century, laid the foundations for modern organosilicon chemistry. His research efforts ranged from the synthesis of simple organosilicon compounds to the investigation of silicone polymer properties.

Kipping's contributions to organosilicon chemistry were magnified with the development of the "Direct Process" in 1945 by Eugene Rochow. This process enabled the profitable large scale synthesis of organohalosilanes from silicon and alkyl halides (3, 4). The availability of inexpensive organohalosilanes facilitated the growth of the silicone industry and afforded easier access to other starting materials. With more readily available starting materials, researchers were able to build on the foundations Kipping had laid, and the scope of organosilicon chemistry was broadened.

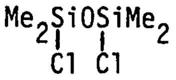
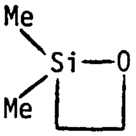
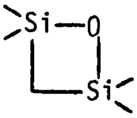
Today there are three major areas of research in the field of organosilicon chemistry: silicone polymers, the use of organosilicon reagents in organic synthesis, and the synthesis and study of silicon-centered reactive intermediates. Significant achievements have recently been reported in this latter area of research. The isolation of a stable species containing a silicon-silicon π bond, disilenes, and a silicon-carbon π bond, silenes, definitively proves the capability of silicon to (p-p) π bond (5, 6).

This dissertation will address the possibility of silicon-oxygen (p-p) π bonding by attempting mild silanone generation from a variety of precursors. The most promising precursor, a maleic anhydride-sila-α-pyran adduct, was shown to be a direct thermal and photochemical source of silanones. The formation and decomposition of 2-silaoxetanes, benzosilaoxetanes, and related cyclic systems was also examined. Although a stable silaoxetane was not isolated, evidence for their formation and decomposition to silanones was obtained. The potential rearrangement of silanones to silylenes and of silylenes to silanones was investigated. Evidence was obtained for a silylene to silanone rearrangement through an intermediate disilaoxetane. Finally, it was serendipitously discovered that silicon substitution has a surprising effect on the photochemically induced rearrangement of furans and pyrroles. The photochemistry of silicon-substituted heteroaromatics and the thermal chemistry of the allenic products were examined.

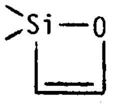
NOMENCLATURE

The nomenclature used in this dissertation will, with the exceptions decribed below, follow the IUPAC convention. Simple organosilicon compounds will be named as derivatives of silane (SiH_4). Saturated and unsaturated four-membered rings containing adjacent silicon and oxygen atoms will be named as derivatives of silaoxetane and silaoxete, respectively. Compounds containing (p-p) π bonded silicon will be named as derivatives of silene ($H_2Si{=}CH_2$) and silanone ($H_2Si{=}O$). Divalent silicon species will be referred to as derivatives of silylene ($H_2Si:$). For the sake of clarity, methyl substituents on silicon will often be represented as a dash emanating from the silicon.

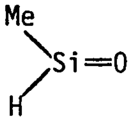
Examples:

$Me_2Si(OMe)H$	dimethylmethoxysilane
 $Me_2Si(Cl)OSi(Cl)Me_2$	1,3-dichlorotetramethyldisiloxane
	2,2-dimethyl-2-silaoxetane
	2,2,4,4-tetramethyl-2,4-disilaoxetane

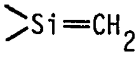
Examples: (continued)



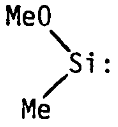
2,2-dimethyl-2-silaoxete



methylsilanone



dimethylsilene



methylmethoxysilylene

HISTORICAL

The purpose of this historical section is to provide the reader with background information pertinent to the contents of this dissertation. The research presented in this dissertation can broadly be classified into three categories: (1) the synthesis and chemistry of silanones, (2) the synthesis and chemistry of silicon-oxygen containing four-membered rings, and (3) the photorearrangement of silicon-substituted heteroaromatics. The first two categories will be reviewed in this section. The photochemistry of silicon-substituted heteroaromatics has received virtually no attention; hence, a review of this area is not warranted. The photochemistry of other heteroaromatics has recently been reviewed by Padwa, and the reader is referred to this work for background information (7).

Silanones

Interest in synthesizing compounds containing a silicon-oxygen (p-p) π bond dates back to the investigations of Friedel and Crafts in 1866 (8). For fifty years following these initial studies, numerous researchers reported the synthesis and isolation of compounds containing a silicon-oxygen π bond (9, 10). These "silanones" were generally synthesized from hydrolysis of dialkoxysilanes or dichlorosilanes and from dehydration of silanediols.

Throughout these early studies it was commonly accepted that silanones were a stable and isolable species. However, as the turn of the century approached, many researchers began to question these early beliefs. They recognized that these free silanones might actually exist as molecular aggregates. This suspicion was eventually confirmed as better analytical methods were developed. It was proven that no silanone had ever been isolated and that only polymeric silicones had been synthesized. The realization of this fact contributed to a growing belief that continued efforts in this area would be futile. Even Kipping stated in 1936, "The prospect of any immediate and important advance in this section of organic chemistry does not seem very hopeful" (2). As a result of these attitudes, interest in synthesizing silanones and other compounds containing π bonded silicon dwindled.

A renewal of interest in the generation of compounds containing π bonded silicon did not occur until the mid-1960s. Since this resurgence, the study of silanone chemistry has grown tremendously. In the past four years, four reviews on the synthesis and chemistry of silanones have appeared (11-14). The most recent review, by Hoekman, offers a critical analysis of the silanone literature. The importance of Hoekman's insights will be addressed later.

Modern synthetic methods used to generate silanones can broadly be classified into three categories: pyrolysis of linear and cyclic siloxanes, silylene oxidation, and decomposition of 2-silaoxetanes. The synthesis of 2-siloxetanes and their decomposition to silanones will only briefly be covered in this section. A thorough historical review on 2-silaoxetanes and other silicon-oxygen containing four-membered rings will be presented in the next section. A review on the former two methods of silanone generation and on other miscellaneous methods of silanone generation will now be presented.

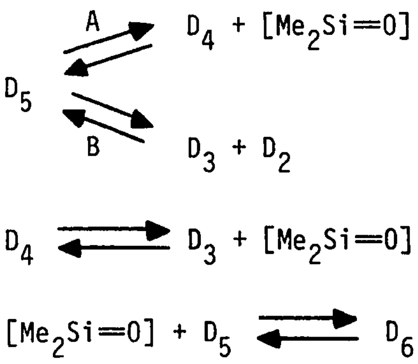
Silanones from siloxane pyrolysis

The pyrolytic decomposition of a siloxane to a silanone was first reported by Andrianov and Sokolov in 1952 (15). They found that pyrolysis of polydimethylsiloxanes at 150°-200°C resulted in new polydimethylsiloxanes that differed from the starting material only in the number of Me_2SiO units. This result was rationalized through the intermediacy of dimethylsilanone. However, as Hoekman states in his review, this data does not demand the intermediacy of dimethylsilanone (14). A bimolecular reaction which results in the transfer of a Me_2SiO unit is an equally valid explanation.

More definitive evidence for silanone intermediacy was obtained by Nametkin and coworkers, who pyrolyzed cyclocarbosiloxanes and cyclosiloxanes at 500°-700°C (16, 17). Their results were similar to the results of Andrianov and Sokolov. The products of the pyrolysis differed from starting material and from each other only in the number of Me_2SiCH_2 and Me_2SiO units.

Nametkin and coworkers also studied the kinetics of the gas phase thermal decomposition of decamethylcyclopentasiloxane (D_5). Their data showed first-order kinetics during the decomposition of D_5, a initial increase followed by a decrease in the concentration of octamethylcyclotetrasiloxane (D_4), a steady increase in the concentration of hexamethylcyclotrisiloxane (D_3), and a small, steady state concentration of dodecamethylcyclohexasiloxane (D_6). From these results, Nametkin and coworkers concluded that the decomposition of D_5 was a unimolecular process that could proceed through two pathways (Scheme 1). An analysis of the product distribution indicated that at least 60% of the reaction proceeded through path A and formation of dimethylsilanone. The decomposition of D_4 to D_3 and dimethylsilanone accounts for the high concentration of D_3 in the final product mixture The origin of D_6 is presumed to be an addition of dimethylsilanone to D_5.

Scheme 1



A similar kinetic study on the gas phase pyrolytic decomposition of D_4 at 500°-650°C was carried out by Davidson and Thompson (18, 19). Their results indicated that during the first 4% of the reaction, the decomposition of D_4 followed first-order kinetics. The only products, D_3 and D_5, were initially formed in equivalent amounts. However, as the reaction progressed, the concentration of D_5 diminished while the concentration of D_3 continually increased. From this data, the following mechanism was postulated (Scheme 2).

Scheme 2

$$D_4 \rightleftarrows D_3 + [Me_2Si{=}O] \qquad (1)\ (-1)$$

$$[Me_2Si{=}O] + D_4 \rightleftarrows D_5 \qquad (2)\ (-2)$$

$$[Me_2Si{=}O] + D_5 \rightleftarrows D_6 \qquad (3)\ (-3)$$

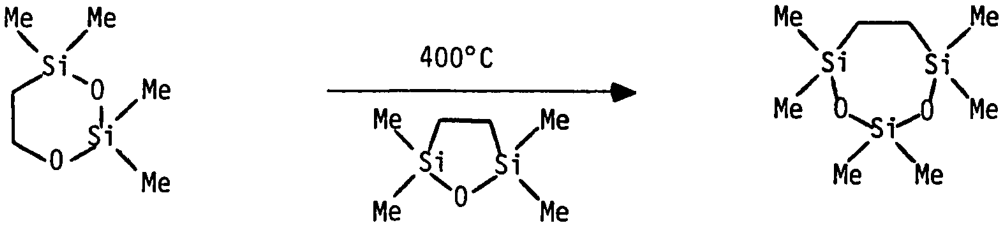
$$D_6 \longrightarrow 2\ D_3 \qquad (4)$$

Davidson and Thompson proposed that the early stages of this decomposition are adequately described by reactions 1, 2, and -2, and that the first order disappearance of D_4 and concomitant formation of D_3 clearly implies dimethylsilanone intermediacy. The ultimate excess of D_3 over D_5 was rationalized by employing reactions 3 and 4 and by polymerization of dimethylsilanone onto the surface of the reactor.

Additional evidence for the intermediacy of dimethylsilanone was acquired by trapping experiments. When D_4 was thermolyzed in the presence of simple alkenes or silicone grease, formation of D_5 was not observed, but formation of D_3 still occurred. Davidson and Thompson suggested that the alkenes and the silicone grease were trapping dimethylsilanone; consequently, the formation of D_5 from D_4 and dimethylsilanone was blocked. Although no trapping products were isolated, evidence for $(Me_2SiO)(C_2H_4)_n$, where n = 1 to 6, was obtained when ethylene was used as the trap.

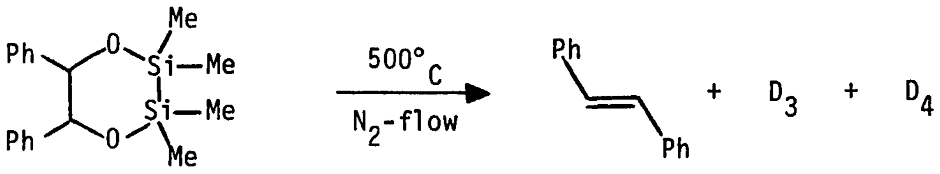
From their kinetic data, Davidson and Thompson were able to calculate the strength of the silicon-oxygen (p-p) π bond. They arrived at a value of 37.8 kcal/mole. This number has recently been substantiated by Kutzelnigg and coworkers who reported results from an <u>ab initio</u> study on the parent silanone, $H_2Si=O$ (20). Using standard basis sets, they calculated a minimum (p-p) π bond strength of 30 ±5 kcal/mole.

Several studies on the thermal decomposition of cyclocarbosiloxanes to silanones have recently been carried out. In one such study, Barton and Tumey observed that pyrolysis of **1** at 400°C in the presence of **2** resulted in the formation of **3** in a 74% yield (21). These authors suggested that **1** decomposed to ethylene and two molecules of dimethylsilanone. Insertion of dimethylsilanone into a Si-O bond of **2** accounted for the final product.



1 **2** **3**

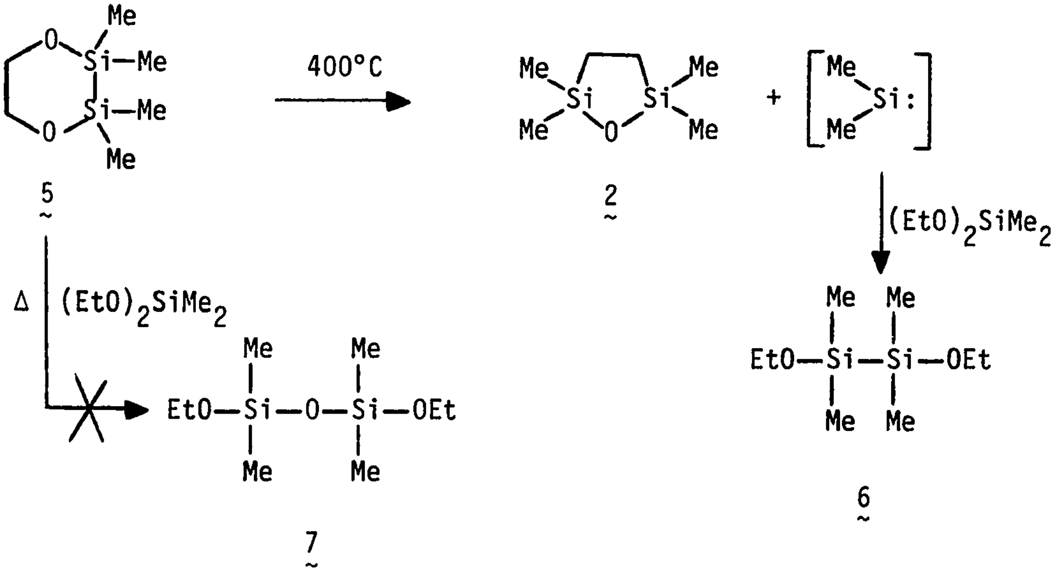
In a similar study, Barton and Kilgour found that pyrolysis of the disiladioxane **4** resulted in the formation of <u>trans</u>-stilbene, D_3, and D_4 (22). The cyclosiloxanes, D_3 and D_4, were postulated to arise from cylooligomerization of dimethylsilanone.



4

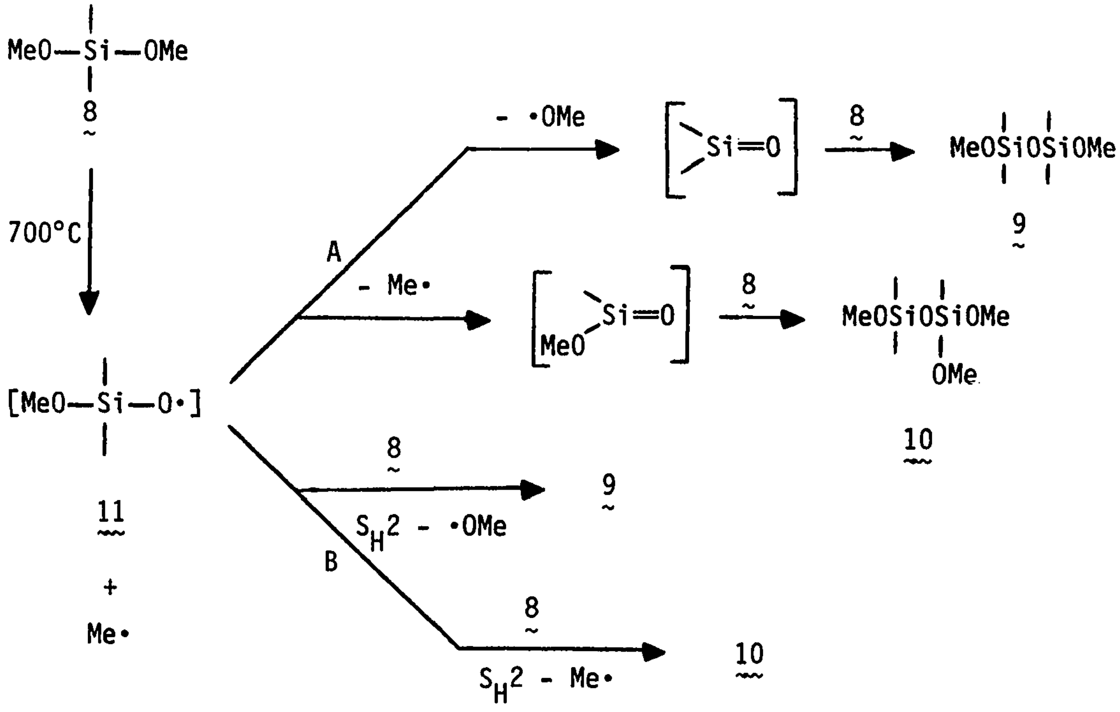
73% 28% 17%

Although 4 appears to thermally generate dimethylsilanone, this mode of ring cleavage is not general for the disiladioxane ring system. Hoekman reported that thermolysis of the disiladioxane 5 resulted in dimethylsilylene extrusion and formation of 2 (14). The dimethylsilylene was trapped with diethoxydimethylsilane to yield the insertion product 6. The expected dimethylsilanone insertion product 7 was not observed. Thus, the use of the disiladioxane ring system as a silanone generator has limited utility.



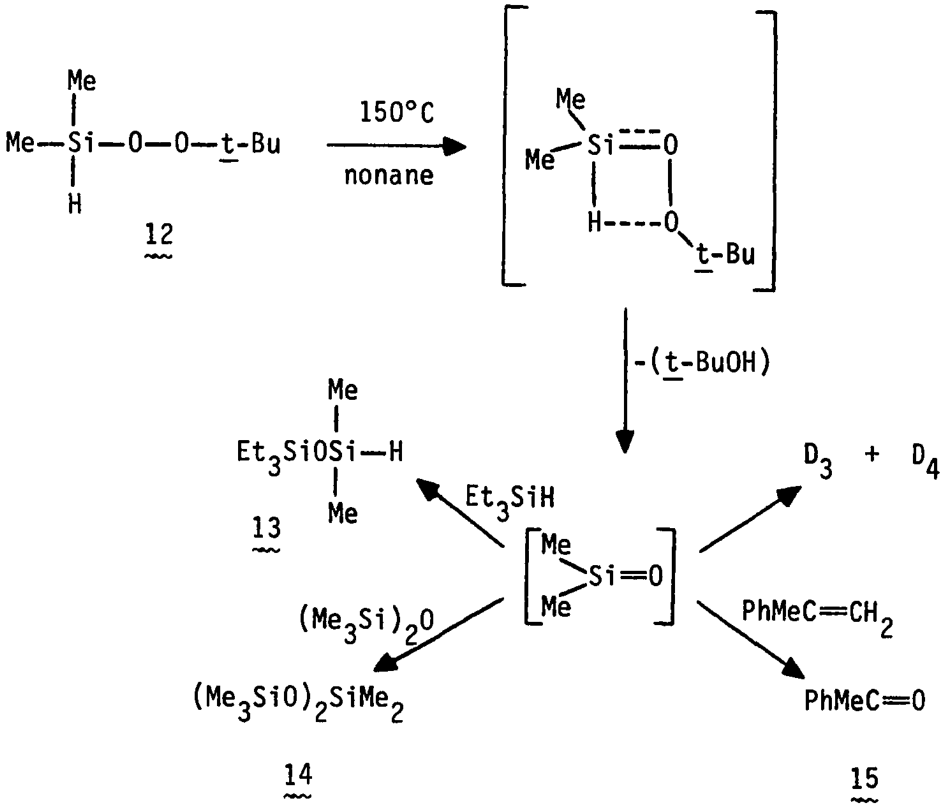
Hoekman has also studied the gas phase high temperature decomposition of simple linear siloxanes (14). In a typical experiment, dimethyldimethoxysilane, 8, was pyrolyzed at 700°C in a N_2-flow system. The major products were 1,3-dimethoxytetramethyldisiloxane, 9, and 1,1,3-trimethoxytrimethyldisiloane, 10 (Scheme 3). Although silanones may have been formed in this reaction, path A, Hoekman preferred to explain his results by a S_H2 attack of the initially formed radical 11 on starting material, path B. Also studied was the thermal behavior of the following silylethers: $Me_2Si(OEt)_2$, $(EtO)_4Si$, Me_3SiO*t*-Bu, Me_3SiO*i*-Pr, Me_3SiOEt, Me_3SiOPh, Me_3SiOCH_2Ph, and Me_2(*t*-Bu)$SiOCH_2Ph$. The decomposition of these silyethers was reported to be similar to the decomposition of dimethyldimethoxysilane. In all cases, products consistent with silanone intermediates were formed. However, a S_H2 radical process was also in agreement with the observed results.

Scheme 3



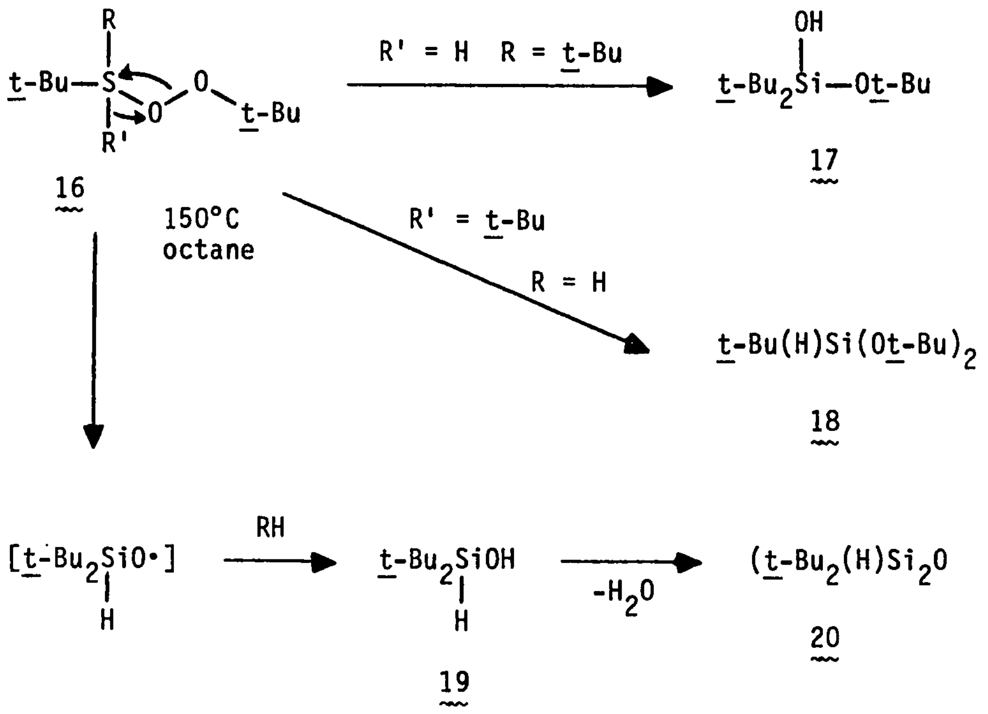
Recently, Yablokov and coworkers reported that the pyrolysis of dimethylsilyl-*t*-butylperoxide resulted in dimethylsilanone formation *via* a four-centered transition state (Scheme 4) (23). The intermediacy of dimethylsilanone was inferred by trapping with triethylsilane, with hexamethyldisiloxane, and with α-methylstyrene. The products of these trapping experiments were 13, 14, and 15, respectively. If no trap was present, D_3 and D_4 were formed.

Scheme 4



In a similar study, Barton, Hoekman, and Burns attempted to generate di-*t*-butylsilanone from di-*t*-butylsilyl-*t*-butylperoxide (24). However, in contrast to Yablokov's results when 16 was pyrolyzed, no evidence for a silanone could be found. The major products of the thermolysis were the silanol 17, the silylether 18, the hydridosilanol 19, and the disiloxane 20. The authors postulated the mechanism shown in Scheme 5.

Scheme 5

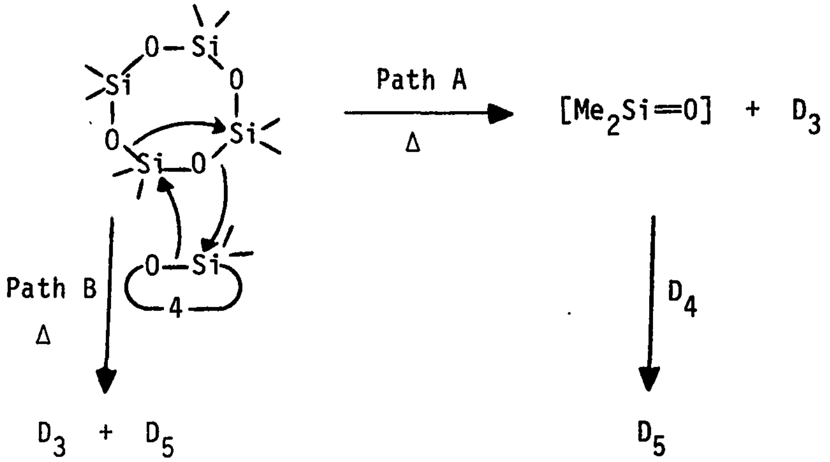


A precedented thermal rearrangement of 16 yields products 17 and 18 (25). Cleavage of the O-O bond followed by radical abstraction yields 19. Condensation of 19 yields the disiloxane 20.

Thermolysis of other hydridosilylperoxides also failed to give products consistent with silanone formation. These failures prompted Barton, Hoekman, and Burns to reexamine Yablokov's results. In a series of elegant experiments, Barton and coworkers systematically refuted Yablokov's claims and interpretations. They concluded that no experimental evidence exists that demands silanone intermediacy from the pyrolysis of hydridosilylperoxides. This conclusion remains unchallenged; consequently, it appears that hydridosilylperoxides are not the convenient thermal source of silanones that was previously reported. Hoekman has indicated, however, that photolysis of bissilylperoxides may result in the formation of small amounts of silanones via O-O bond cleavage and loss of a stable radical (14).

Before continuing with this review, a few comments concerning Hoekman's analysis of the silanone literature are warranted (14). The majority of reports in the literature that claim silanone intermediacy base this claim on the observation of silanone trapped products. Hoekman correctly points out that the mere observation of these trapping products is insufficient evidence for claiming silanone formation. These trapping products may alternatively be formed via a bimolecular silanone-transfer process. These concepts are illustrated in Scheme 6 using D_4 as the source of dimethylsilanone and as the silanone trap. In path A, free dimethylsilanone is generated and trapped with D_4 to give D_5. In path B, a Me_2SiO unit is transferred to D_4 in a bimolecular process to directly yield D_5. Both paths ultimately yield the same products.

Scheme 6



An obvious way to distinguish between path A and path B is a kinetic study of the reaction. In the previously discussed works of Nametkin (16, 17) and Davidson (18, 19), such a study was carried out. Their measured first-order kinetic decomposition of D_5 and of D_4 and their observed product distributions clearly eliminated the bimolecular silanone-transfer process as an alternative to free silanone formation.

Hoekman continued his critical evaluation of the silanone literature by insinuating that Nametkin's and Davidson's results were incorrect. He sought to prove the unreliability of Nametkin's and Davidson's work and substantiate his own belief that there are almost no instances in which a silanone must be invoked by citing inconsistencies between their two studies. These inconsistencies were: different product distributions from the pyrolysis of D_6 and different interpretations of the importance of D_2 intermediacy. The inability of Davidson to observe trapping products from the reaction of dimethylsilanone with ethylene was also noted by Hoekman as a significant problem.

These criticisms of Nametkin's and Davidson's work are unwarranted. Although Nametkin and Davidson did obtain different results from the pyrolysis of D_6, their ultimate conclusion was the same: D_3 is the final formed product. In addition, the kinetic data on which dimethylsilanone intermediacy was based were measured during the initial stages of D_5 and D_4 decomposition: before D_6 was formed. Thus, the decomposition of D_6 is irrelevant to the final conclusion of dimethylsilanone formation.

Davidson addresses Hoekman's second criticism in a subsequent report apparently not seen by Hoekman (19). A close examination of this report and of Nametkin's original report (17) shows that both authors completely agree on the relative importance of D_2 intermediacy during the thermal decomposition of D_5 and of D_4. They conclude that D_5 thermally decomposes to D_4 plus dimethylsilanone or D_3 plus D_2, and that D_4 thermally decomposes to D_3 plus dimethylsilanone. They indicate that the decomposition of D_4 to two molecules of D_2 is unlikely because of the high enthalpy of formation of D_2.

Hoekman's final criticism is also addressed in Davidson's subsequent report. Davidson indicates that he did obtain evidence for trapping products from the reaction of dimethylsilanone with ethylene. It is the conclusion of this author that Nametkin's and Davidson's results stand as convincing evidence for the intermediacy of dimethylsilanone and that the insinuation by Hoekman that these results are unreliable is unsubstantiated.

Nevertheless, Hoekman's original insights unarguably stand. Because most literature reports which claim silanone intermediacy do not eliminate the possibility of a bimolecular silanone-transfer process, these reports must be carefully evaluated.

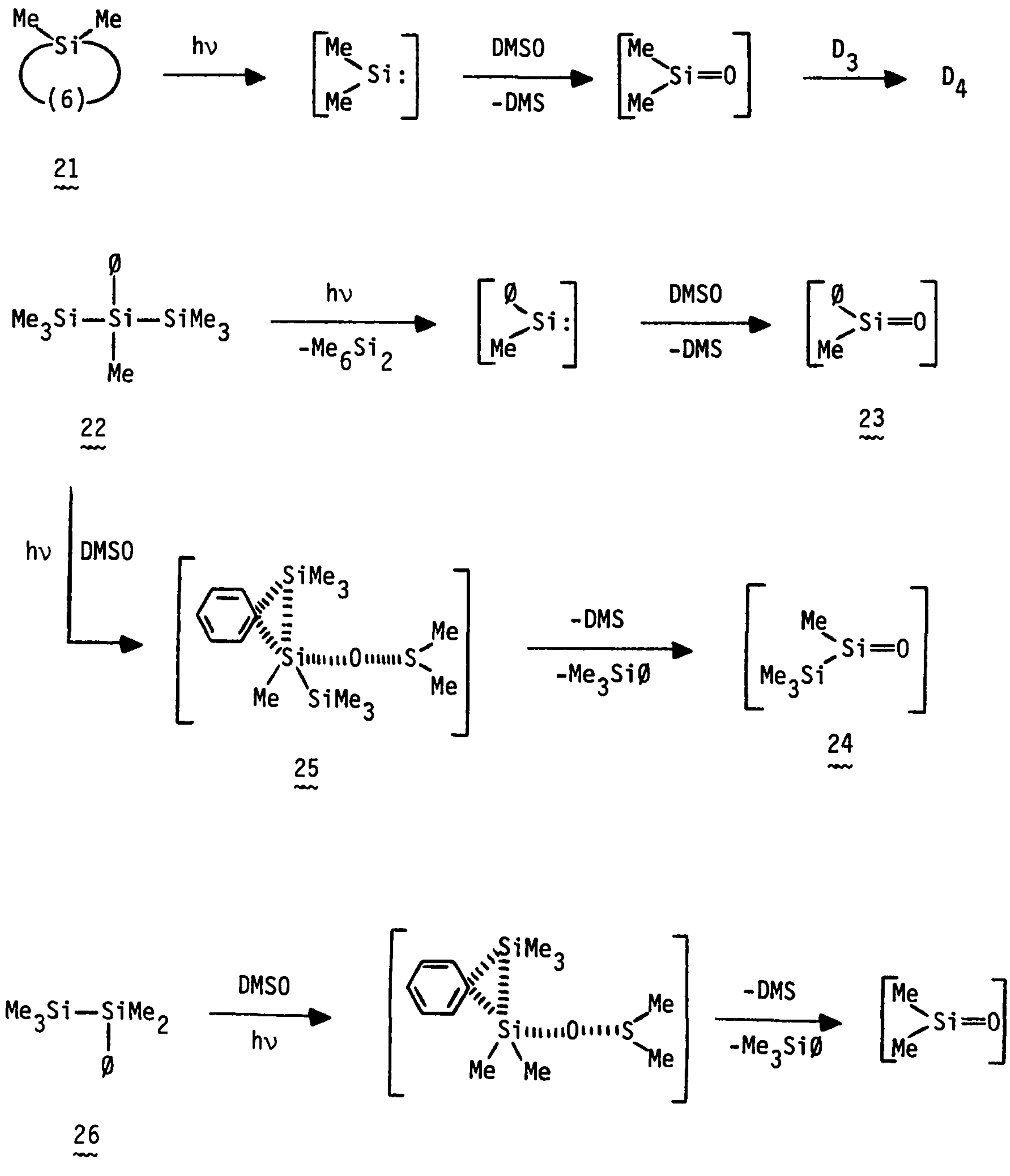
Silanones from silylene oxidation

The second general method of silanone formation is based upon the oxidation of silylenes. The work reported in this area can be classified by the three types of oxidizing agents used: dimethylsulfoxide (DMSO), ketones, and epoxides.

The use of DMSO as an oxidizing agent has been extensively studied by Weber and coworkers (26-29). They found that photolysis of dodecamethylcyclohexasilane, **21**, a known dimethylsilylene generator, in the presence of DMSO and D_3 yielded dimethylsulfide (DMS) and the silanone trapping product, D_4 (Scheme 7). Weber and coworkers attempted to extend this method of silanone formation to silylenes generated from the photolysis of phenyl-substituted disilanes and trisilanes. When the trisilane **22** was photolyzed in the presence of DMSO and a silanone trap, two different silanones were observed: phenylmethylsilanone, **23**, and trimethylsilymethylsilanone, **24**. Both silanones were trapped in low yields. Weber postulated that phenylmethylsilanone was formed from the expected DMSO oxidation of phenylmethylsilylene. The formation of **24** was postulated to occur from the phenyl-bridging intermediate **25**. A similar intermediate was invoked to explain dimethylsilanone formation from the photolysis of **26** in DMSO.

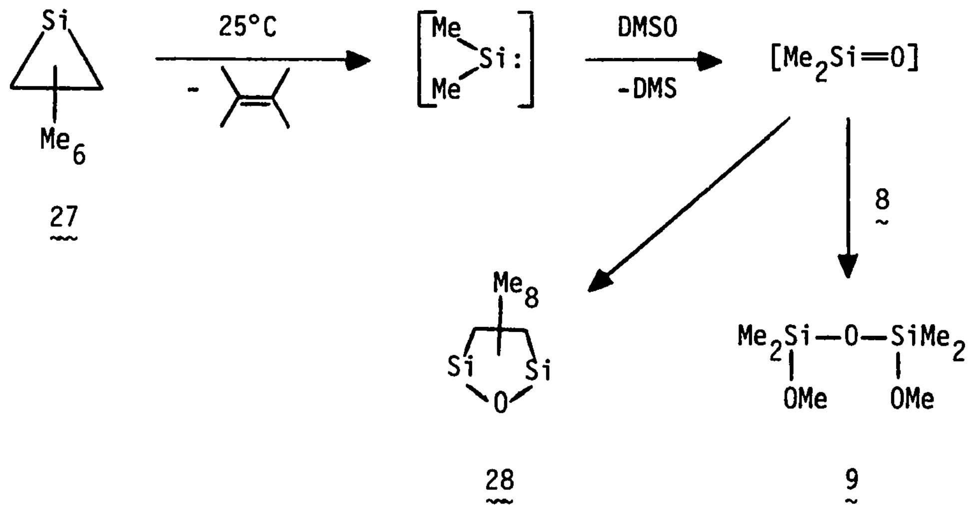
Seyferth and coworkers have also reported that silylenes, generated from the silirane **27**, will react with DMSO to form silanones (Scheme 8) (30). When **27** was thermolyzed at 25°C in the presence of DMSO, the cyclic disiloxane **28** was formed in a 53% yield. The formation of **28** was rationalized by insertion of dimethylsilanone into a Si-C bond of **27**. Additional proof that dimethylsilanone was formed in this reaction was obtained by trapping with **8** to give the insertion product **9** in a 69% yield. Seyferth and coworkers also showed that silylenes could be

Scheme 7


hν
DMSO
-DMS
D_3
D_4
21
$-Me_6Si_2$
22
23
hν
DMSO
25
-DMS
$-Me_3Si\emptyset$
24
26

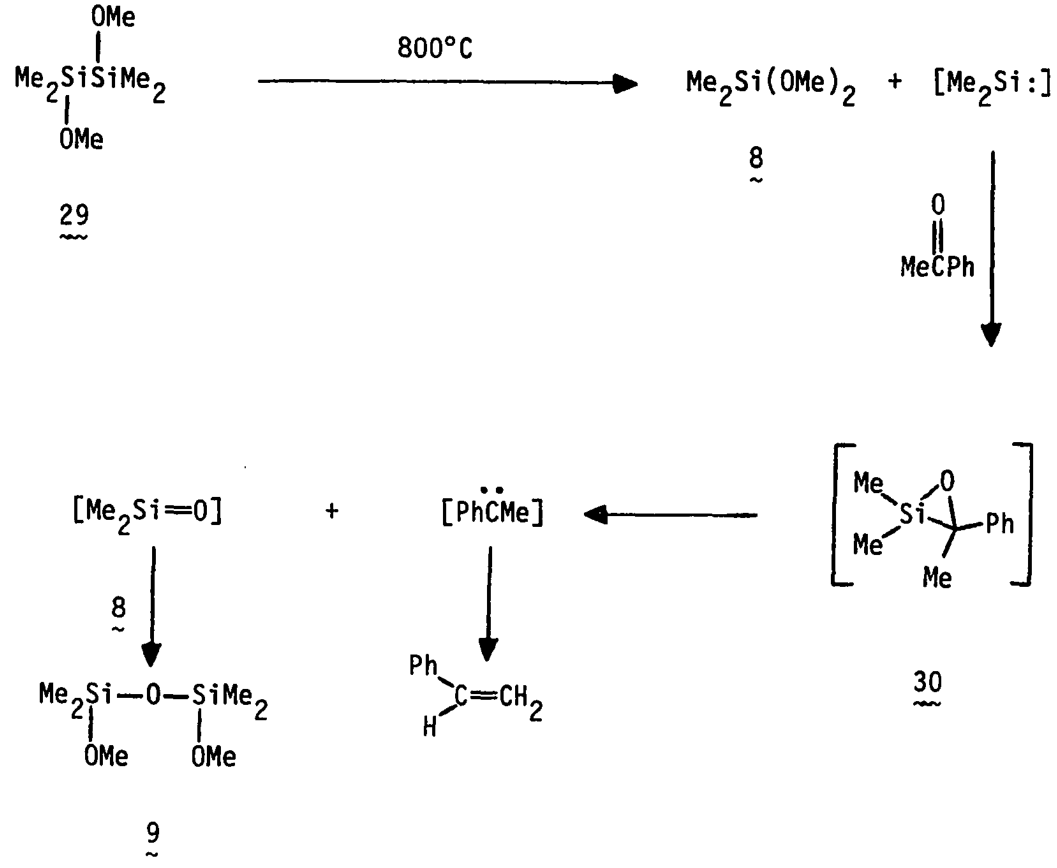
oxidized to silanones with pyridine N-oxide and with trimethylamine N-oxide.

Scheme 8



The oxidation of a silylene to a silanone using a ketone as the oxidizing agent has been reported by Ando and coworkers (31). They pyrolyzed the dimethylsilylene generator 29 at 800°C in the presence of acetophenone and obtained 8, 9, and styrene (Scheme 9). The oxasilacyclopropane 30 was postulated as the initially formed intermediate from the reaction of dimethylsilylene with acetophenone. Decomposition of 30 to phenylmethylcarbene, which can undergo C-H bond insertion to yield styrene, and to dimethylsilanone, which can insert into a Si-O bond of 8 to yield 9, completed Ando's mechanistic proposal.

Scheme 9



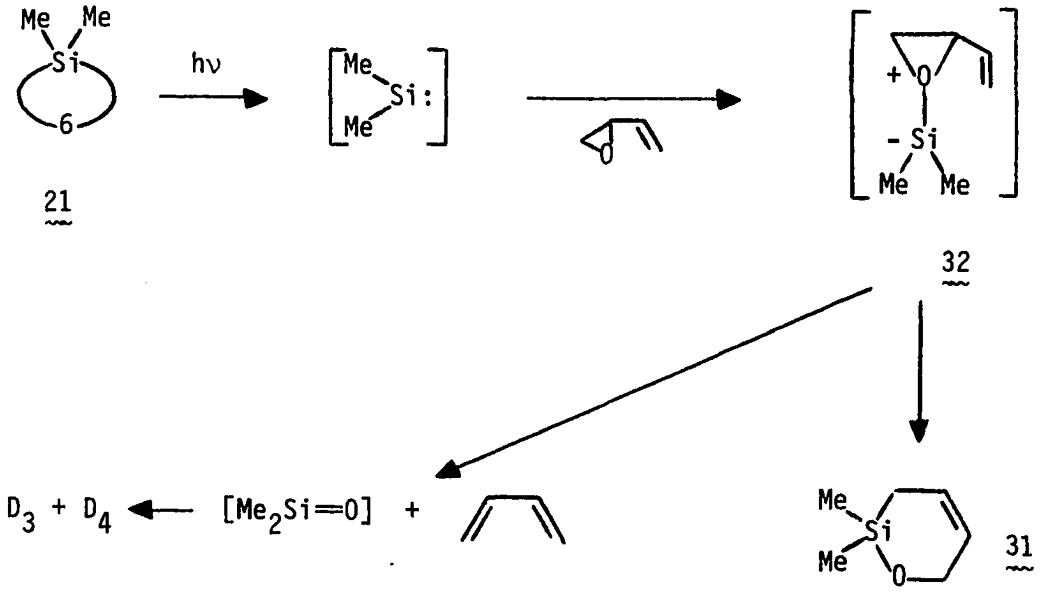
The recently reported preparation of a stable oxysilacyclopropane from the addition of a silylene to a ketone lends precedent for the formation of **30** (32). However, Ando's proposed route to **9** must be regarded with some suspicion. Hoekman has recently shown that pyrolysis of **8** at comparable temperatures yields **9** in equivalent or higher yields (14). This alternative route to **9** prevents a conclusive statement regarding the ability of ketones to oxidize silylenes to silanones.

Several reports on the oxidation of silylenes with epoxides have recently appeared in the literature. In one such report, Weber and coworkers examined the reaction of photochemically generated dimethylsilylene with vinyl epoxides (33). They found that irradiation of 21 in 3,4-epoxy-1-butene yielded butadiene, D_3, D_4, and the cyclosiloxane 31 (Scheme 10). These products were postulated to arise through the intermediacy of the ylid 32. This ylid could rearrange to form 31 or could decompose to butadiene and dimethylsilanone. Dimethylsilanone could then cyclooligermerize to D_3 and D_4. No attempt to trap the free silanone was reported.

Similar results were observed by Barton and Goure (34). They reported that dimethylsilylene, generated thermally from hexamethylsilirane or photochemically from dodecamethylcyclohexasilane, reacted with cyclooctene oxide to yield products that were consistent with the intermediacy of dimethylsilanone (Scheme 11). A mechanism identical to the previously discussed mechanism offered by Weber was postulated. Again, the key intermediate is the ylid 33. Decomposition of this ylid to cyclooctene and dimethylsilanone followed by insertion of dimethylsilanone into 27 or into D_3 resulted in formation of the observed products.

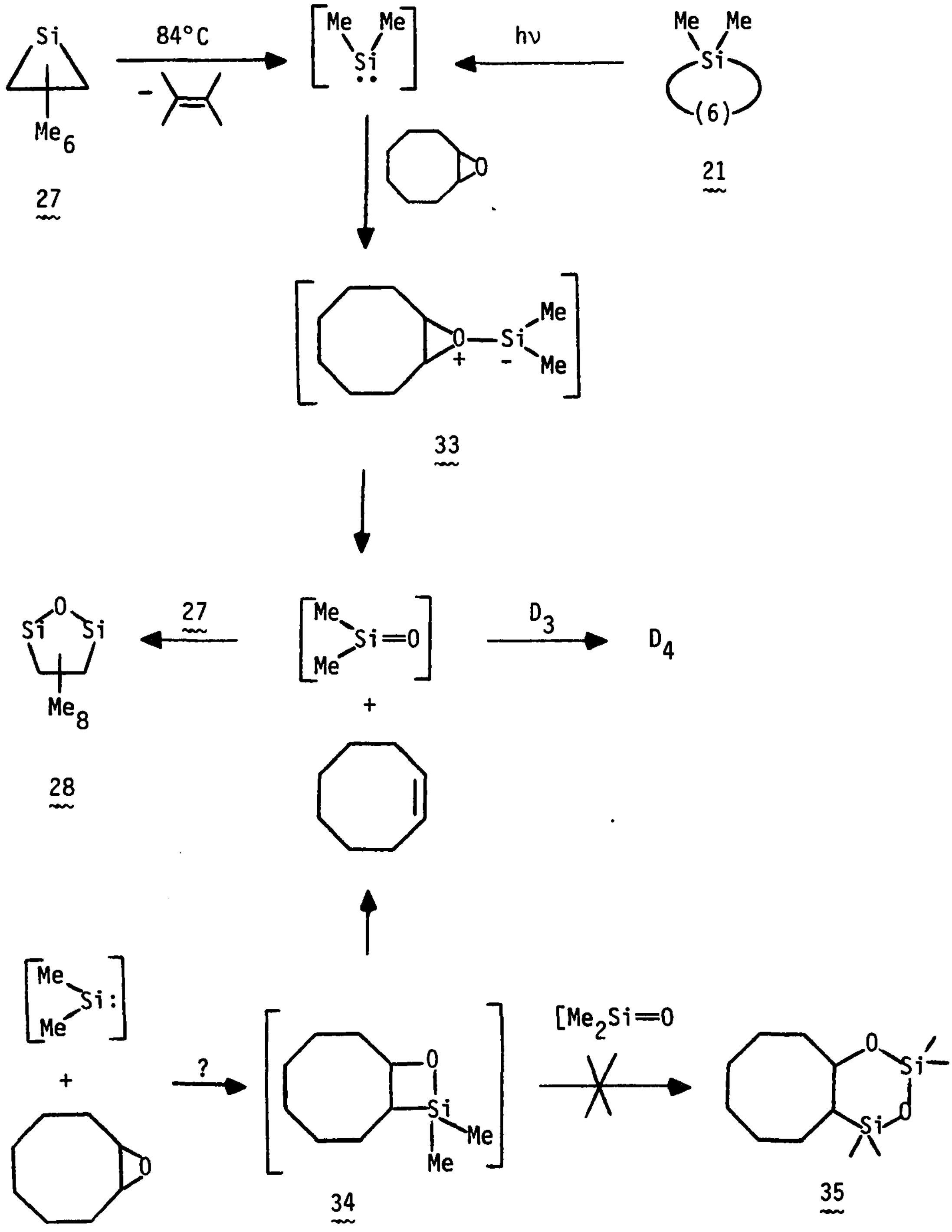
Barton and Goure also considered the 2-silaoxetane 34, formed from dimethylsilylene insertion into a C-O bond of cyclooctene oxide, as an alternative to the ylid intermediate 33. Silaoxetanes are known to decompose to give alkenes and silanones. However, it was expected that dimethylsilanone formed during the decomposition of 34 would insert back into 34 to yield the stable disiloxane 35. No 35 was observed; hence, the proposed formation of the 2-silaoxetane 34 was dismissed.

Scheme 10



Ando and coworkers have utilized an epoxide oxidation of a silylene to synthesize the hindered dimesitylsilanone (35). They reported that irradiation of the trisilane 36 in the presence of propylene oxide resulted in formation of hexamethyldisilane, propene, and the siladioxane 37 (Scheme 12). Ando and coworkers proposed that decomposition of the initially formed ylid yielded propene and dimesitylsilanone. Insertion of dimesitylsilanone into a C-O bond of the starting epoxide gives the siladioxane 37. This is the first reported example of a silanone inserting into a C-O bond. No attempt to capture the free dimesitylsilanone with known trapping agents was reported.

Scheme 11


Si
Me6
27
84°C
-
Me Me
Si
hν
Me Me
Si
(6)
21
0
0—Si
Me
Me
+ -
33
0
Si Si
Me8
28
27
Me
Si=0
Me
D3
D4
+
Me
Si:
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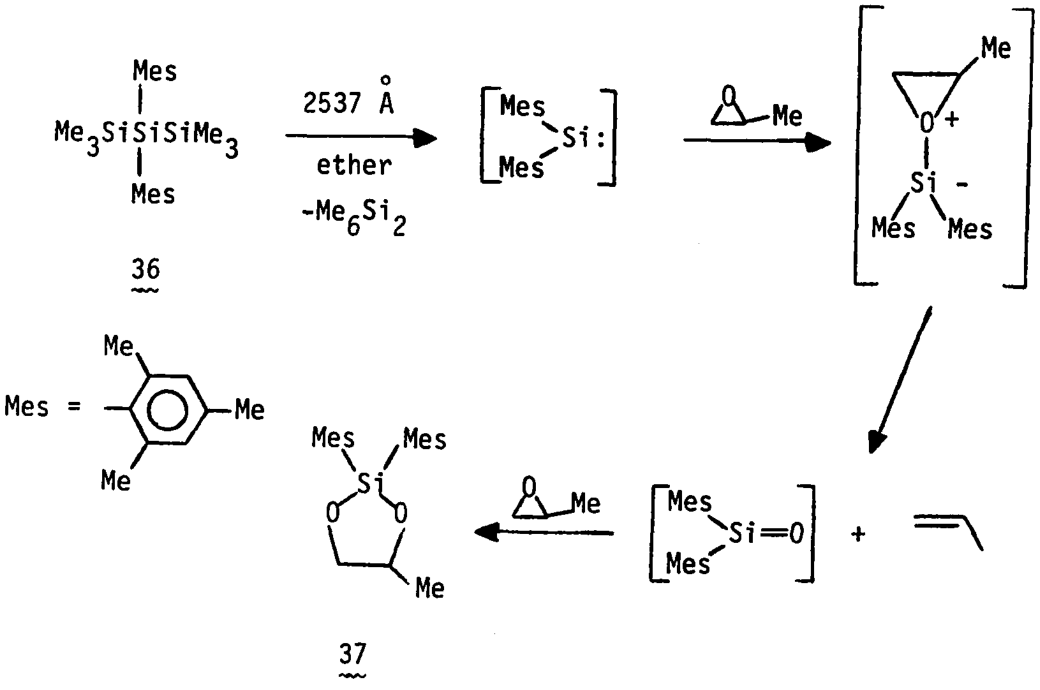
34
[Me2Si=0
0
Si
Si
0
35

Scheme 12

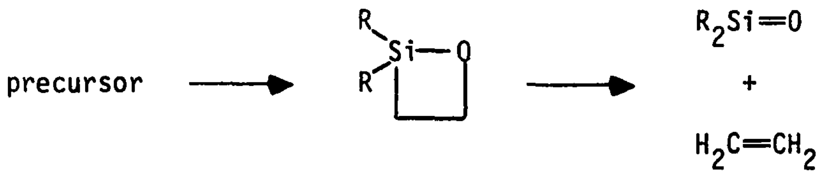


36

37

Silanones from 2-silaoxetanes

The third general method of silanone preparation relies on the initial synthesis of 2-silaoxetanes. These unstable four-membered rings rapidly decompose to give an alkene and a silanone. This process is illustrated below.

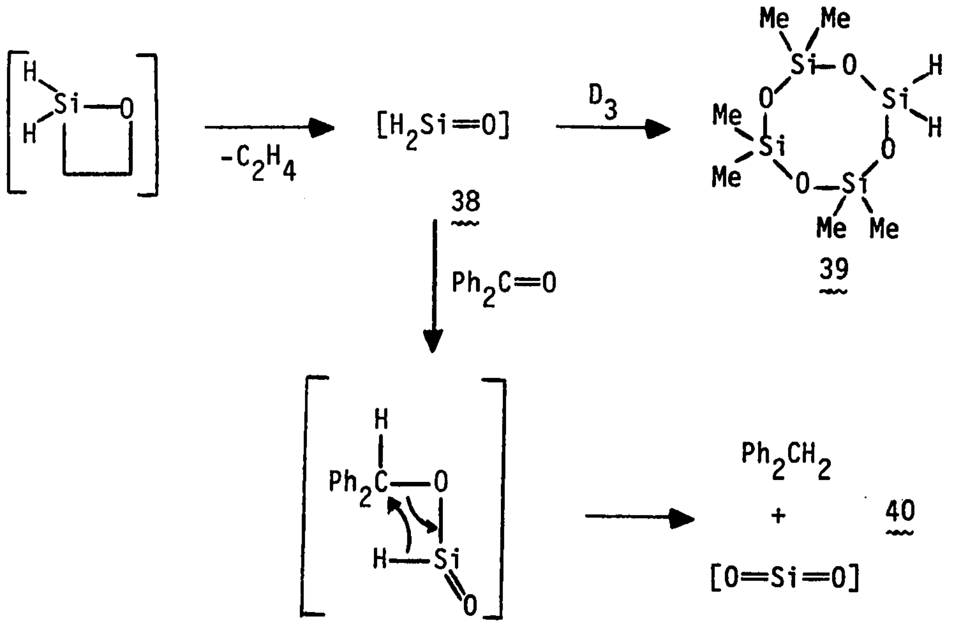


2-silaoxetane

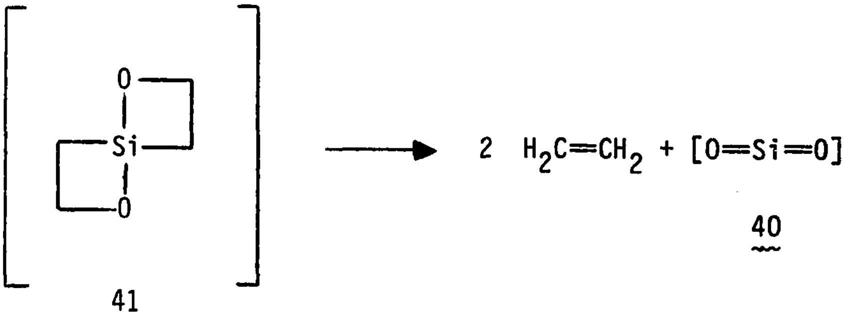
Because a complete historical on 2-silaoxetanes and on other silicon-oxygen containing four-membered rings will be presented in the next section, their synthesis and chemistry will not be discussed here. What will be presented are examples of the more unusual silanones that have been synthesized from 2-silaoxetanes.

Sommer and coworkers reported the synthesis of the parent silanone 38 from decomposition of the parent 2-silaoxetane (36). This is the only reported synthesis of the parent silanone (Scheme 13). Evidence for 38 was obtained by trapping with D_3 to give the insertion product 39. This silanone was also reported to react with benzophenone in an unusual hydrogen migration sequence. The observed product from this reaction was diphenylmethane. Although not observed or trapped, the silane dioxide 40, was also presumed to be formed.

Scheme 13



Mazerolles and coworkers have proposed the formation of silane dioxide from decomposition of a spiro-2-silaoxetane 41 (37). The intermediacy of 40 was based upon the observation of an alkene. No trapping evidence was reported. The data that were obtained from this reaction did not allow Mazerolles to conclusively state that 41 was formed. His results could also be rationalized through the intermediacy of the 2-silaketene 42. A more thorough treatment of Mazerolles's work will be presented in the next section.



41

40

$CH_2{=}Si{=}O$

42

As a conclusion to this historical section on silanones, a brief summary on the different types of silanones that have thus far been proposed as reactive intermediates is presented below (Table 1). The known chemistry of these silanones is limited to insertion reactions and dimerization. Silanones have been shown to insert into Si-O bonds, Si-Cl bonds, Si-C bonds of siliranes and silirenes, and C-O bonds of epoxides. In the absence of traps, silanones dimerize to D_2 which reacts with another silanone unit to form D_3. In a unique reaction, the parent silanone, $H_2Si{=}O$, has been shown to transfer its hydrogens to carbonyl compounds.

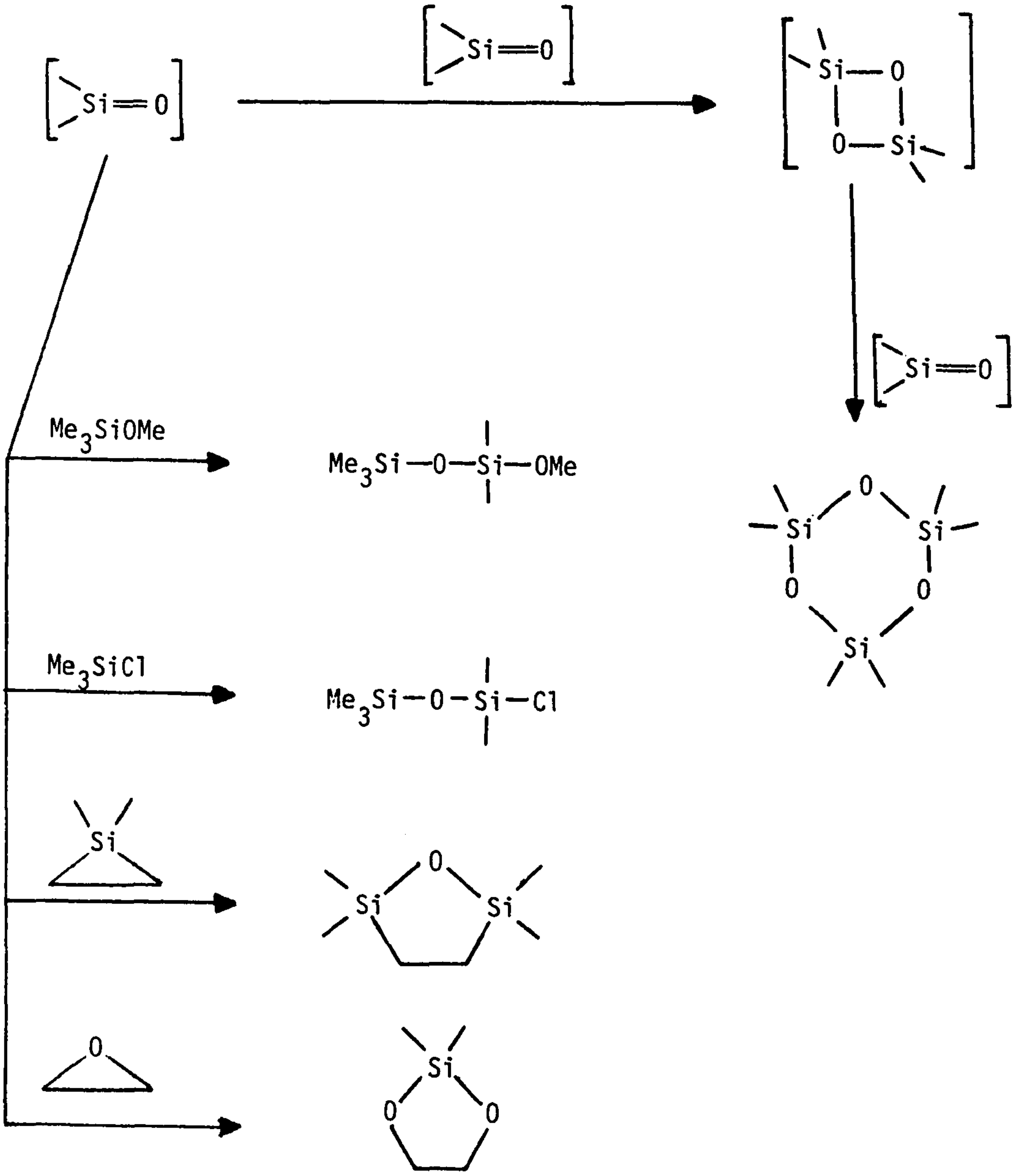
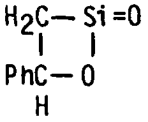
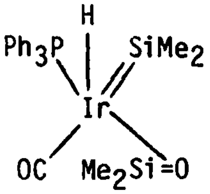


Table 1. Summary of the different types of silanones recently reported in the literature

Silanone	Method of Preparation	References
$Me_2Si{=}O$	A[a], B[b], C[c]	16-19, 26-34
$Me(MeO)Si{=}O$	A	14
t-Bu(H)Si=O	C	14
$Ph_2Si{=}O$	B	29
$Mes_2Si{=}O$	B	35
$Ph(Me)Si{=}O$	B	27, 28
$Me_3Si(Me)Si{=}O$	B	28
$H_2Si{=}O$	C	36
$CH_2{=}Si{=}O$	C	37[d]
	C	37
$O{=}Si{=}O$	C	37
	C	38
$(Me_3Si)_2Si{=}O$	C	39

[a] Pyrolysis of linear or cyclic siloxanes.

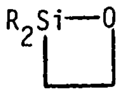
[b] Silylene oxidation.

[c] Silaoxetane decomposition.

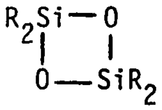
[d] Several unusual silanones were postulated but no trapping evidence was obtained.

Silicon-Oxygen Containing Four-Membered Rings

This review will cover the synthesis and chemistry of silicon-oxygen containing four-membered rings. The ring systems which will be considered are shown below and will be referred to as silaoxetanes. They are individually the 2-silaoxetane **43**, the D_2 analog **44**, the disiladioxetane **45**, the disilaoxetane **46**, and the siladioxetane **47**. All of these systems have in common at least one Si-O bond.



43



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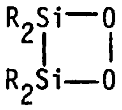

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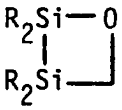

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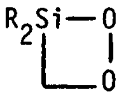


47

Interest in the synthesis of these silaoxetane ring systems stems from their presumed ability to undergo a rapid $2\sigma + 2\sigma$ ring opening to form a silanone and one other π bonded moiety. This decomposition is so facile that despite numerous attempts, only highly hindered silaoxetanes have been undisputably isolated (39, 40).

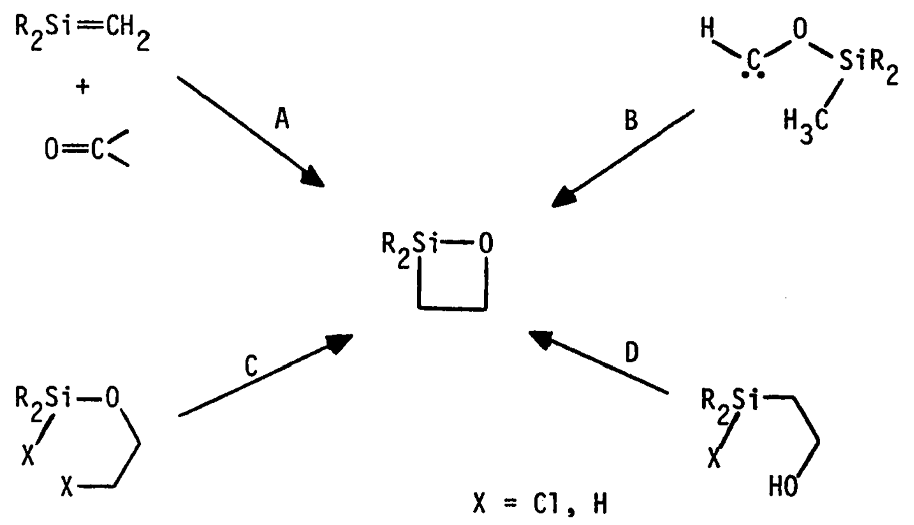
The reasons for this facile decomposition are not immediately obvious. Based on accepted bond energies, the enthalpy of reaction for the decomposition of 2,2-dimethyl-2-silaoxetane to dimethylsilanone and ethylene is calculated to be 58 kcal/mole (14). This value would predict that the 2-silaoxetane should be a stable and isolable compound. Similar calculations performed on other silaoxetane ring systems lead to the same conclusions. An examination of ring-strain energies also leads to the prediction that the silaoxetane systems should be stable (14).

In spite of these predictions of thermodynamic stability, silaoxetanes have remained extremely elusive. This incongruity can be rationalized by two different explanations. One explanation assumes that the calculated thermodynamic stability of silaoxetanes is correct but that silaoxetanes are kinetically unstable towards bimolecular reactions and decompose rapidly. This explanation supports Hoekman's hypothesis that 2-silaoxetanes merely act as silanone-transfer agents in a bimolecular process (14). The second explanation relies on the possibility that the silicon-oxygen (p-p) π bond is stronger than originally believed. If this is the case, then the enthalpy of reaction for the decomposition of silaoxetanes is a lower number than previously calculated. This lower value of ΔH would be in more agreement with the observed instability of silaoxetanes.

Whichever explanation is correct is perhaps most important to the question of silanone intermediacy. Most reports on silaoxetane formation do not address this question or attempt to explain the reasons why silaoxetanes are so reactive.

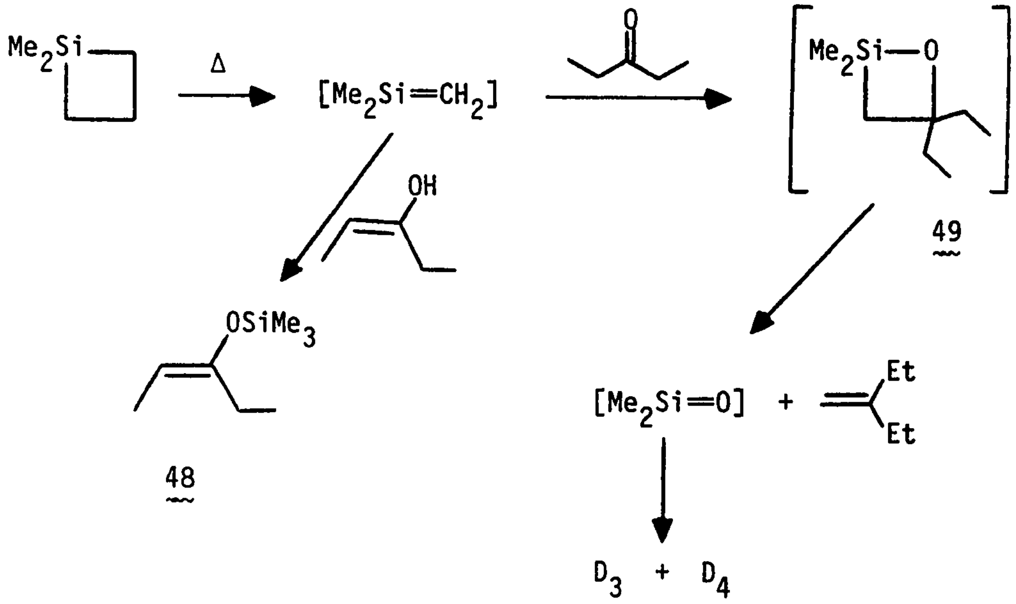
Since silaoxetanes were first proposed as reactive intermediates in the early 1970s, numerous routes to these ring systems have been developed. The majority of work in this area has concentrated on the synthesis of 2-silaoxetanes and to a lesser extent the synthesis of D_2 analogs. Scheme 14 illustrates the four primary methods that have been used to synthesize 2-silaoxetanes. Method A is a $2\pi + 2\pi$ cycloaddition of a silene and a carbonyl compound, method B is a carbene insertion into a C-H bond, method C is Si-C bond formation usually assisted by a metal, and method D is Si-O bond formation from a silyl halide or silyl hydride. Most of these methods are easily extendable to the synthesis of other silaoxetane ring systems. These four general methods of preparing silaoxetanes will be reviewed in order.

Scheme 14



The addition of a silene to a carbonyl compound was first reported by Barton and coworkers in 1972 (41-43). They observed that copyrolysis of 3-pentanone with 1,1-dimethyl-1-silacyclobutane at 600-700°C gave cyclosiloxanes, 2-ethyl-1-butene, and a product with a mass corresponding to an adduct of $Me_2Si{=}CH_2$ and 3-pentanone. This adduct was later identified as the trimethylsilylenolate 48 (Scheme 15). The cyclosiloxanes and the alkene were postulated to arise through the intermediacy of a 2-silaoxetane. This 2-silaoxetane decomposed to the alkene and dimethylsilanone which cyclooligermerized to D_3 and D_4.

Scheme 15

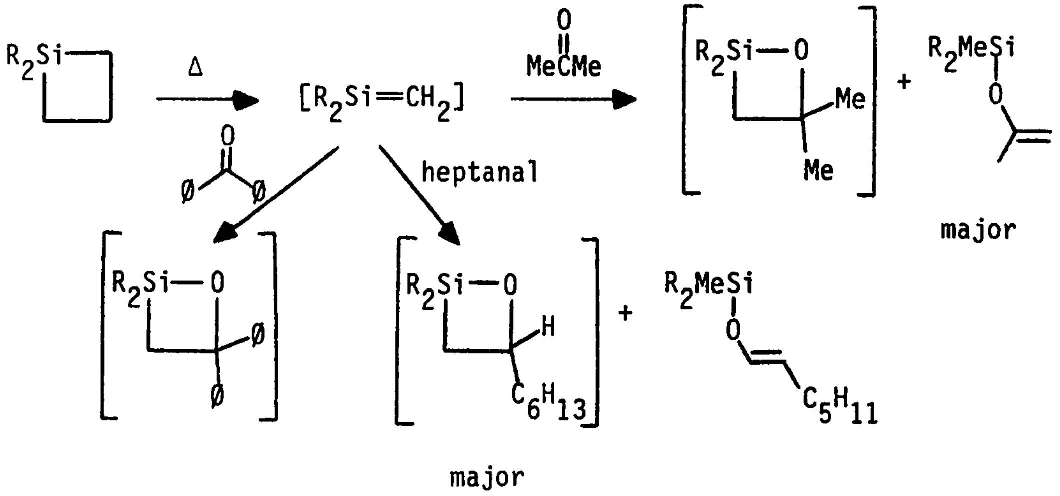


48

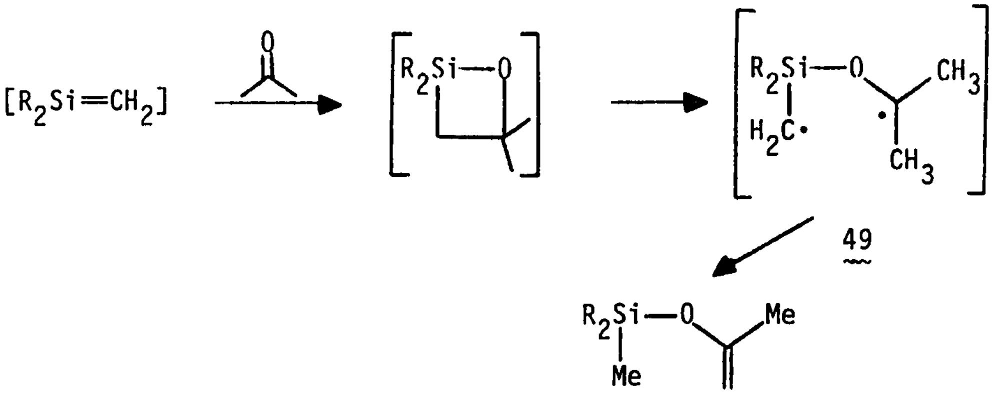
49

Similar chemistry was observed by Sommer and coworkers. In a series of papers, they reported that silenes, generated thermally from silacyclobutanes, reacted with carbonyl compounds to form intermediate 2-silaoxetanes (Scheme 16) (36, 44-47). They observed that the course of the reaction was independent of the functionality on the silicon, except when R = H, but was very dependent on the type of carabonyl compound used. If benzophenone or benzaldehyde were used, the yield of products arising through the intermediacy of a 2-silaoxetane was maximized. If an aldehyde containing enolizable hydrogens was used, significant yields of silyl enol ethers were obtained. Silyl enol ethers were the major products of the reaction when ketones containing two enolizable hydrogens were used. These results were rationalized by postulating that silenes react with carbonyl compounds containing no enolizable hydrogens to form the intermediate 2-silaoxetane. If the carbonyl compound contains enolizable hydrogens, the silene could be trapped by the enol form or could react in a concerted six-electron process to give the silyl enol ether.

Scheme 16



Gusel'nikov and coworkers have also observed silyl enol ethers from the reaction of thermally generated silenes with carbonyl compounds containing α-hydrogens (48). They, however, prefer to explain these silyl enol ethers as arising from 2-silaoxetanes which, under the conditions of the reaction, ring open to diradicals, i.e. 49. The diradicals can intramolecularly abstract a hydrogen to form the observed products.

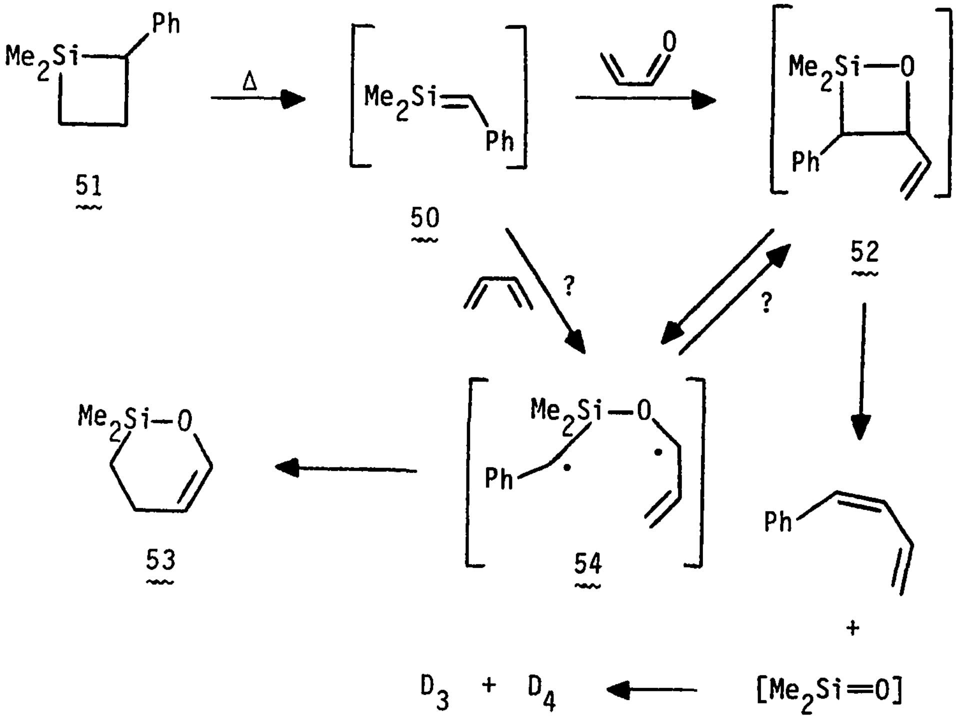


49

Weber and coworkers have studied the reaction of thermally generated 1,1-dimethylphenylsilene with acrolein and have obtained evidence which supports Gusel'nikov's mechanism. They reported that pyrolysis of 51 and acrolein results in formation of D_3, D_4, 1-phenyl-1,3-butadiene, and the siloxycyclohexene 53 (Scheme 17) (49, 50). The silaoxetane 52 was postulated as the initially formed intermediate. This silaoxetane could decompose to dimethylsilanone and 1-phenyl-1,3-butadiene or could, as Gusel'nikov proposed, ring open to the diradical 54. Closure of 54 gives the observed siloxycyclohexene 53.

Although not commented upon by Weber, it is also possible that 53 arises from direct cycloaddition of 50 and acrolein. There is considerable evidence which indicates that the cycloaddition of a silene to a carbonyl compound is not a concerted process. Silicon-oxygen bond formation may precede carbon-carbon bond formation such that a polar or diradical intermediate is formed first, *i.e.* 54. This type of initially formed intermediate can be used to rationalize all the results of Sommer, Gusel'nikov, and Weber.

Scheme 17



51

50

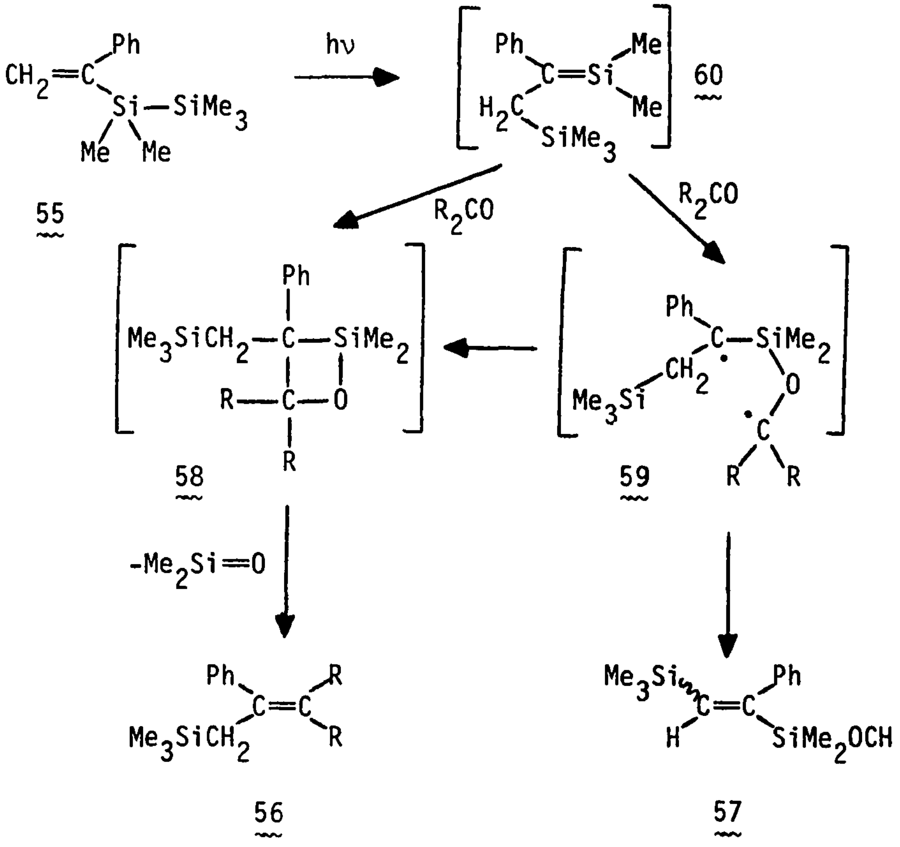
52

53

54

Ishikawa and coworkers, in a series of reports describing the reaction of photochemically generated silenes with carbonyl compounds, substantiate the concept of a nonconcerted cycloaddition (51-53). They found that irradiation of the vinyl disilane 55 in the presence of carbonyl compounds resulted in two different alkenes, 56 and 57 (Scheme 18). They proposed that the silene 60, generated via a 1,3-trimethylsilyl shift, is trapped with a carbonyl compound to directly form the 2-silaoxetane 58 or the diradical 59. The diradical can close to the 2-silaoxetane, which ultimately decomposes to dimethylsilanone and 56, or can abstract a hydrogen to yield 57. The importance of the diradical intermediate is dependent upon the type of carbonyl compound used. If R = Me, formation of 56 via 58 occurs exclusively; however, if R = Ph, the diradical is evidently stabilized and 56 and 57 are formed in comparable yields.

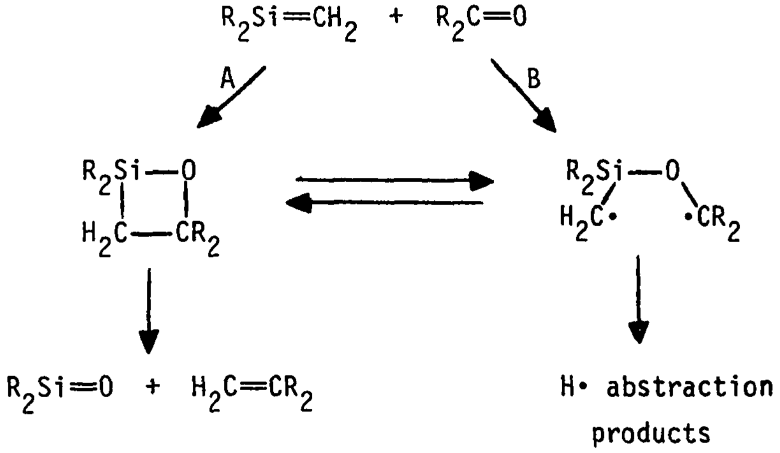
Scheme 18



Interestly, Ishikawa and coworkers reported that reaction of photochemically generated silenes with carbonyl compounds containing enolizable hydrogens did not result in silyl enol ethers. This is in contrast to the results obtained from the reaction of thermally generated silenes with enolizable ketones and aldehydes. No rational was offered for this discrepancy.

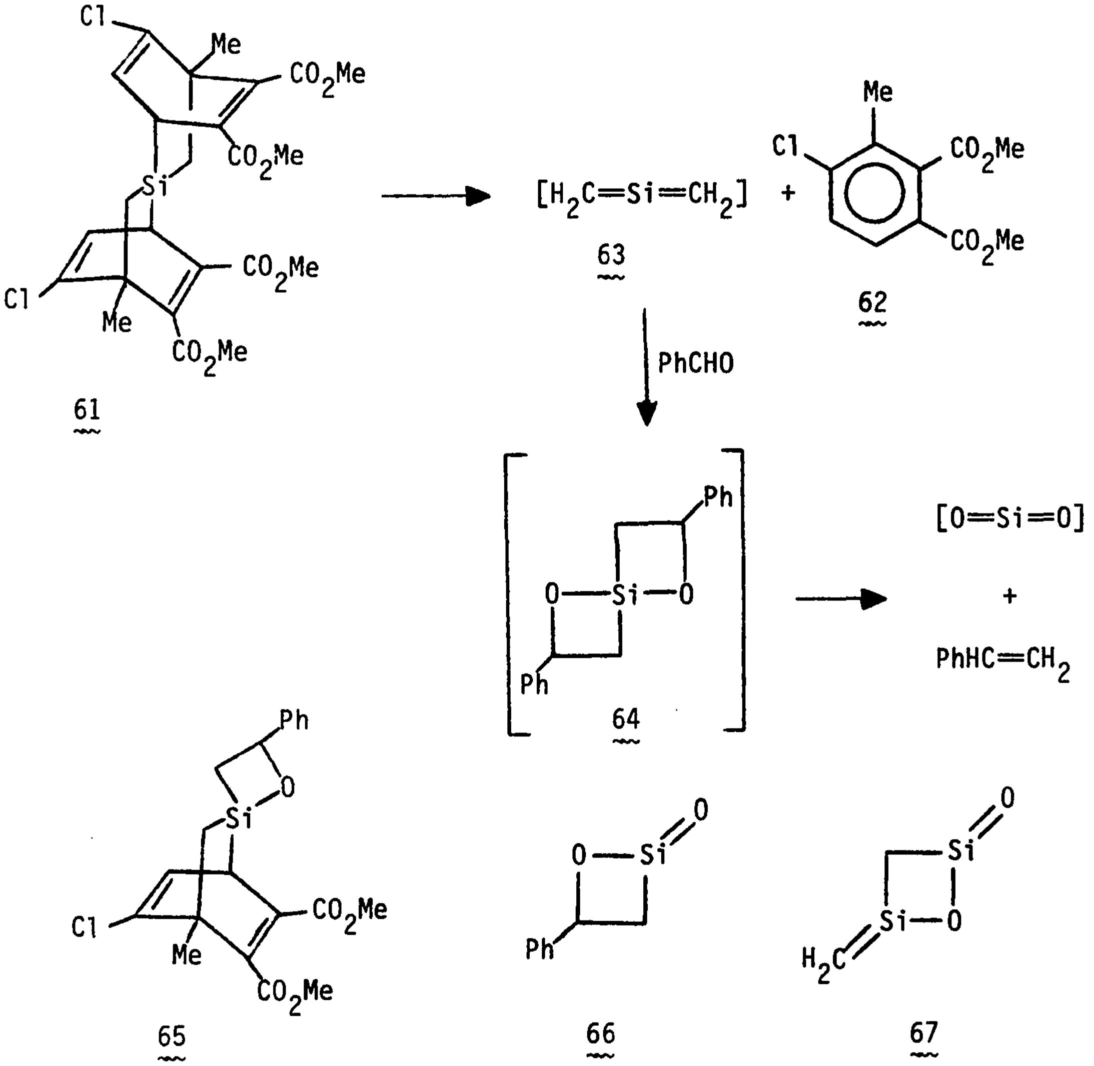
In summary, the available data suggest that silenes can react with carbonyl compounds to directly form a 2-silaoxetane or to form a diradical intermediate (Scheme 19). These two species can be in equilibrium, or the 2-silaoxetane can decompose to a silanone and an alkene, and the diradical can intramolecularly abstract a hydrogen to form a silyl ether or a vinyl silane. The importance of the diradical intermediate is dependent upon the presence of radical stabilizing groups.

Scheme 19



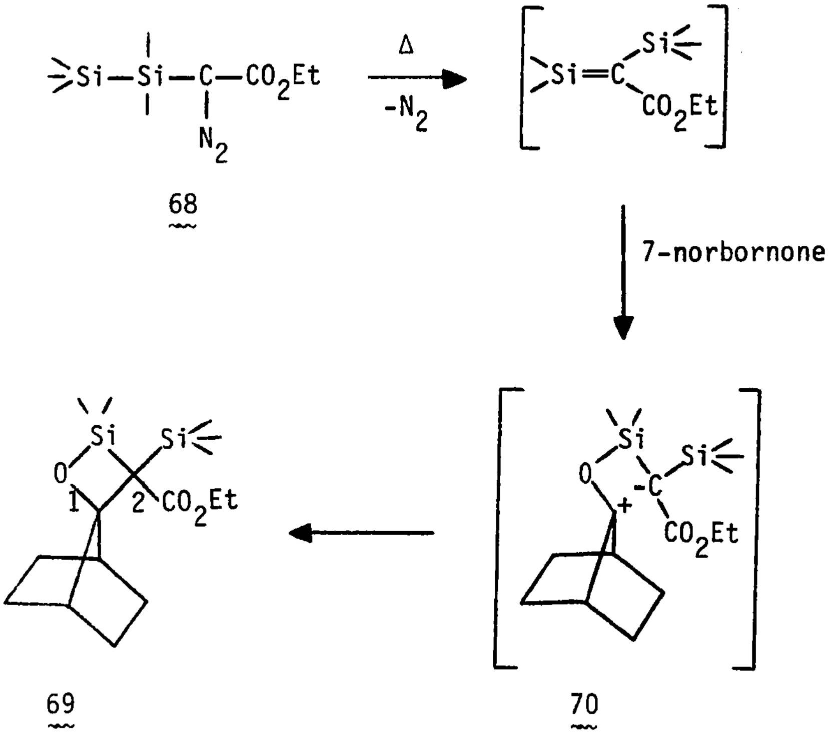
Several unusual 2-silaoxetanes were postulated as reactive intermediates by Mazerolles and coworkers (37). They pyrolyzed 61 at 520°C in the presence of benzaldehyde and obtained styrene and 62 as products (Scheme 20). Drawing analogy from earlier reports on the pyrolysis of disilabicyclooctadienes (54, 55) they postulated the 2-silaallene 63 as the initially formed intermediate. Addition of two molecules of benzaldehyde to 63 affords the spirosilaoxetane 64, which decomposes to silane dioxide and styrene. The possibility of 61 decomposing in a stepwise fashion could not be ruled out. Several different silaoxetanes are then formed: 65, 66, and 67. Although these silaoxetanes were postulated, no evidence for their intermediacy was reported.

Scheme 20



Ando and coworkers have recently reported the synthesis and isolation of a stable 2-silaoxetane. They pyrolyzed the silene precursor 68 in the presence of 7-norbornone and isolated three compounds by preparative gas chromatography. One of these compounds was deduced to be the 2-silaoxetane 69. The structure of 69 was based upon mass spectral, IR, and NMR data. Key NMR and IR absorptions are shown below (Scheme 21) (56).

Scheme 21



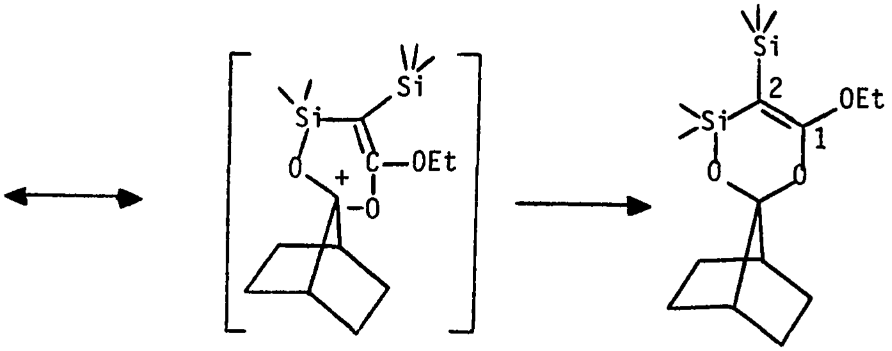
IR: C=O, 1560 cm^{-1}

^{13}C NMR: C_1, δ = 113.8 ppm

C_2, δ = 58.9 ppm

The isolation of a stable silaoxetane that is not sterically hindered is difficult to believe. A reexamination of the results of Ando and coworkers shows that they misassigned structure 69 (57). The spectral data and the observed chemistry for 69 are more consistent with the ketene acetal 71. The formation of this compound is easily rationalized from zwitterion 70. The key IR and NMR absorptions are in better agreement with a structure which contains a silicon-substituted vinyl ether: $\nu_{C=C}$ 1560 cm^{-1}, C_1 $\delta = 113.8$ ppm, C_2 $\delta = 58.9$ ppm. Thus, it appears the claim of a stable 2-silaoxetane by Ando and coworkers is unfounded.

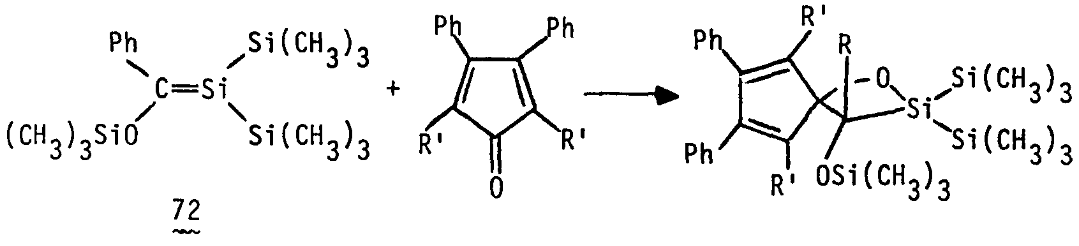
70



71

The reaction of the highly hindered silene 72 with a highly hindered cyclopentadienone has recently been reported by Märkl and Horn to yield stable 2-silaoxetanes (Scheme 22) (39). Unlike in Ando's reported isolation of 69, the spectral features of these 2-silaoxetanes are consistent with their reported structures. These are the first examples of stable 2-silaoxetanes. Undoubtedly, the steric bulk possessed by these 2-silaoxetanes is responsible for their stability. Märkl and Horn also reacted 72 with diphenyl ketone, flourenone, and tetraphenyl pyrone. In no case was a stable 2-silaoxetane obtained. Decomposition to the silanone and alkene was observed.

Scheme 22



72

73

$R' = Ph$

$R' = C_2H_5$

$R' = COOCH_3$

$R = R' = Ph$

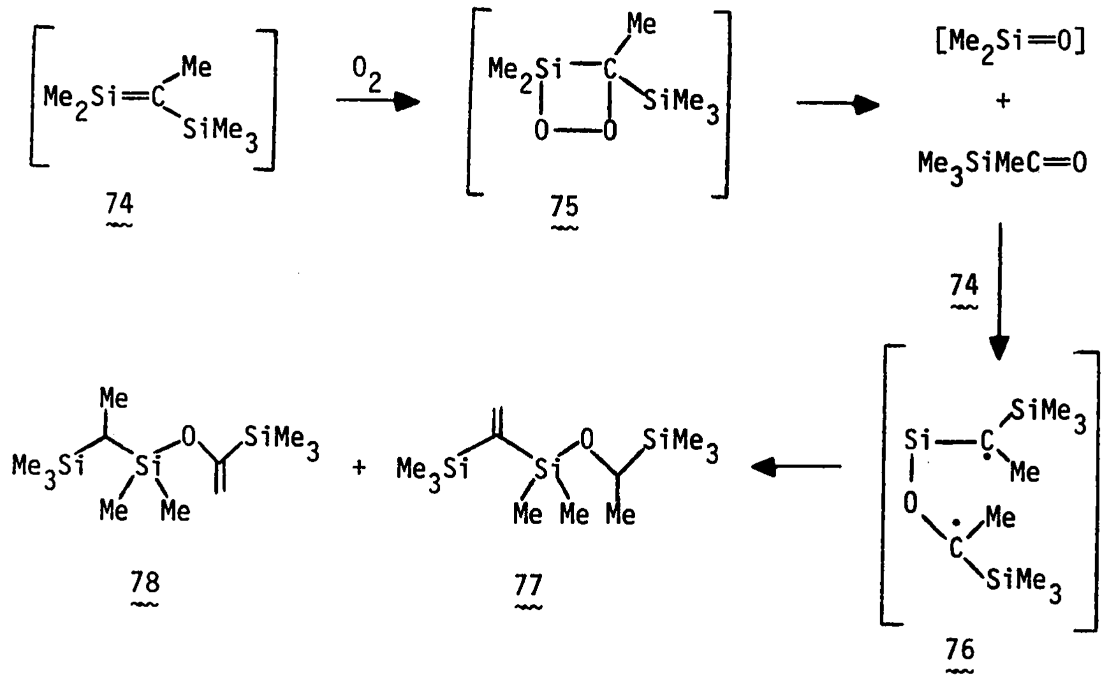
$R = Ph;\ R' = C_2H_5$

$R = Ph;\ R' = COOCH_3$

$R = C(CH_3)_3;\ R' = Ph$

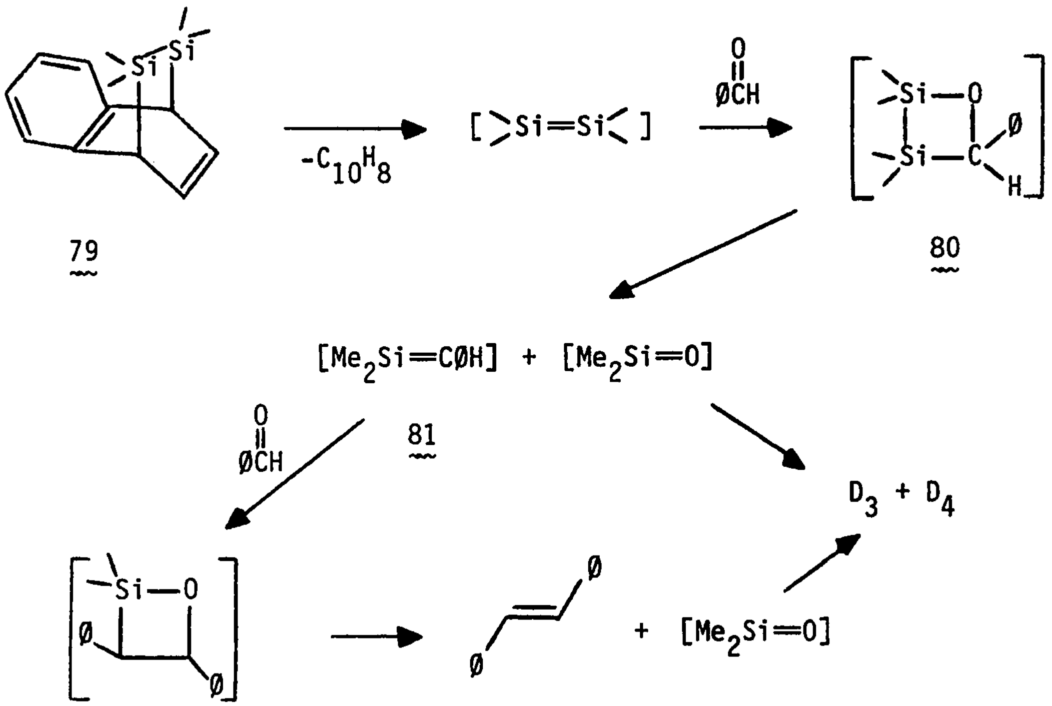
The $2\pi + 2\pi$ cycloaddition route to 2-silaoxetanes has been extended to the synthesis of other silaoxetane ring systems. Hoekman reported that silene 74, generated from bistrimethylsilyldiazomethane, reacted with O_2 to form the siladioxetane 75 (Scheme 23) (14). This unstable ring system decomposed rapidly to dimethyldisilanone and trimethylsilylmethylketone. The observed products from this reaction, 77 and 78, were postulated to arise through the intermediacy of diradical 76.

Scheme 23



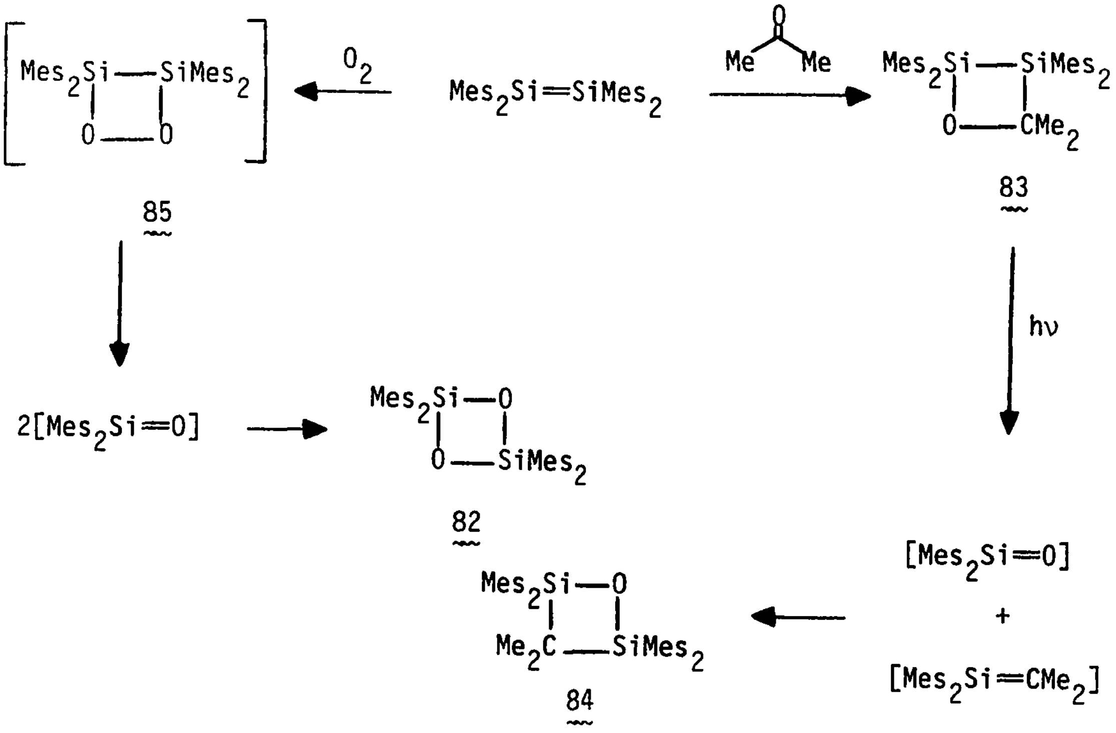
The intermediacy of a disilaoxetane has been postulated by Barton and Kilgour (22). They reported that pyrolysis of 79 in the presence of benzaldehyde resulted in the formation of D_3, D_4, and stilbene (Scheme 24). These products were rationalized by invoking the intermediacy of the disilaoxetane 80. This unstable ring system could rapidly decompose to dimethylsilanone and the silene 81. The observed products were then formed from cyclooligermerization of dimethylsilanone and cycloaddition of 81 with benzaldehyde. An alternative diradical mechanism not involving the intermediacy of 80 is also consistent with the observed results.

Scheme 24

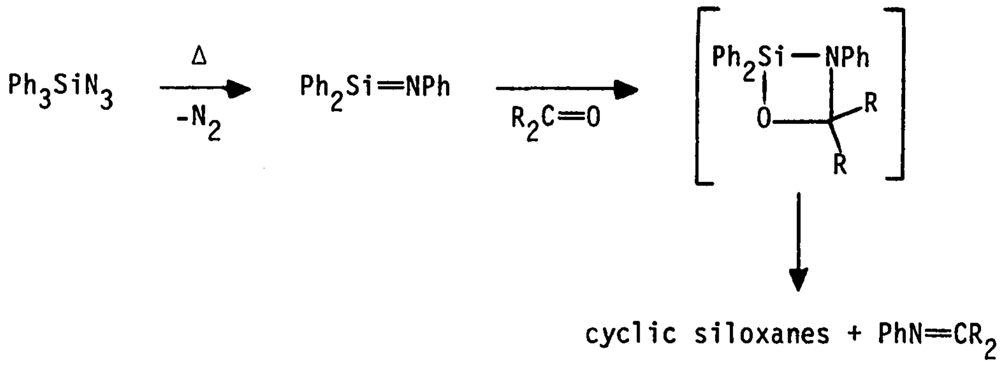


Recently, West and coworkers reported the synthesis of three stable silaoxetane ring systems: the D_2 analog 82, the 1,2-disilaoxetane 83, and the 1,3-disilaoxetane 84 (39). All of these silaoxetanes were prepared from cycloaddition of O_2 or of acetone to the stable tetramesityldisilene (Scheme 25). Addition of O_2 to tetramesityldisilene was originally reported to give the stable disiladioxetane 85 (5). However, upon careful examination of its chemical and physical properties, the structure of this adduct was deduced to be the D_2 analog 82. The formation of 82 is presumed to occur through the intermediacy of 85, followed by its decomposition to dimesitylsilanone and head-to-tail recombination. Addition of acetone to tetramesityldisilene gives the stable 1,2-disilaoxetane 83. West and coworkers observed that upon irradiation this 1,2-disilaoxetane underwent rearrangement to the 1,3-disilaoxetane 84. They postulated this rearrangement occurred through the intermediacy of dimesitysilanone and 1,1-dimesityl-2,2-dimethyl-1-silene. Similar to the stability of 73, the stability of these silaoxetanes is undoubtedly due to their steric bulk.

Scheme 25



One final report of a silaoxetane synthesis *via* a cycloaddition route deserves mention. Sommer and coworkers have reported that pyrolysis of triphenylsilylazide in the presence of ketones resulted in products that were consistent with the intermediacy of azasilaoxetanes (58, 59).

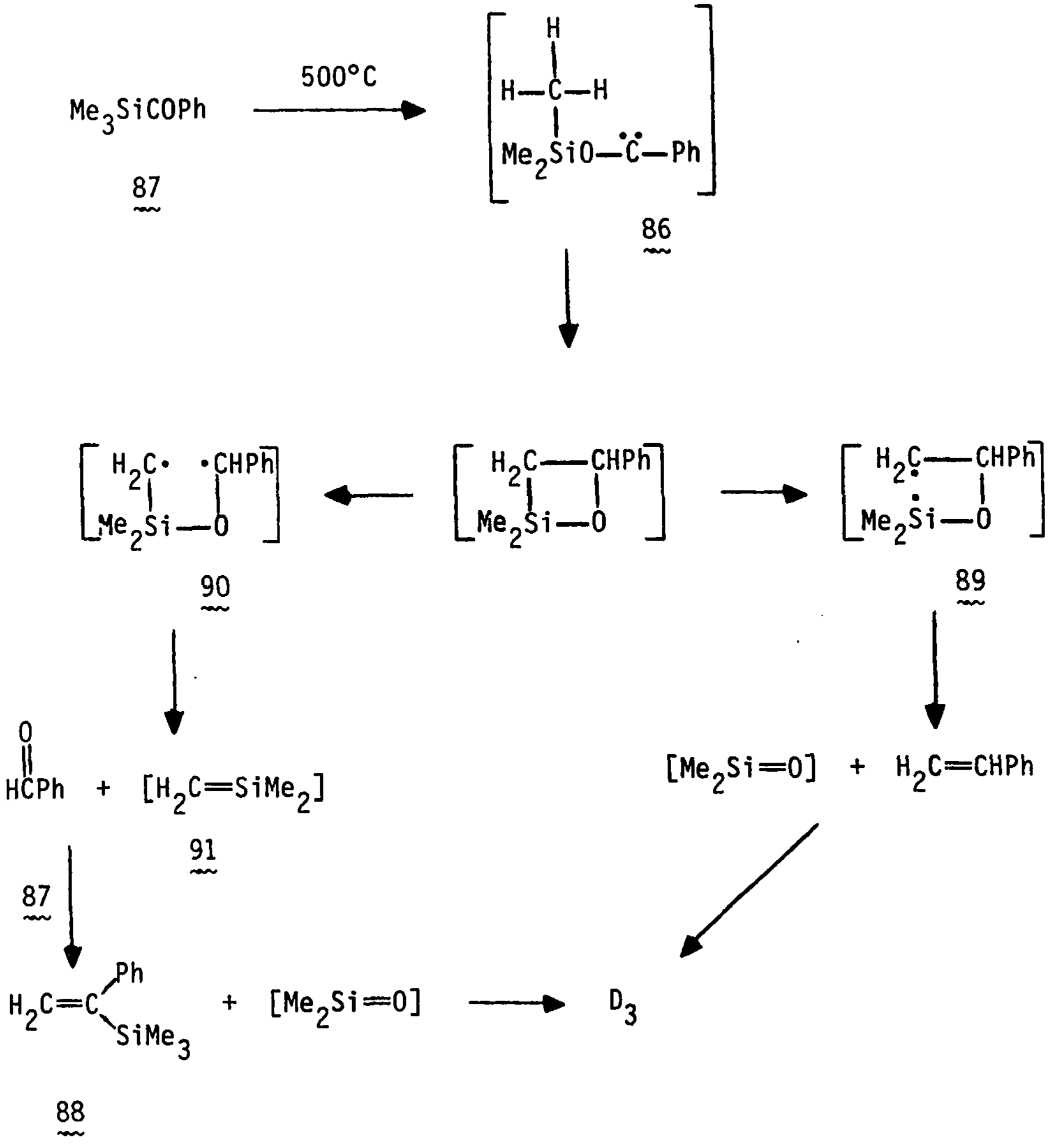


The second general method of preparing silaoxetanes is based upon ring closure *via* C-H bond insertion of a carbene. The work reported in this area has been carried out by Ando and coworkers (60, 61). In a typical experiment, the siloxy carbene **86** was generated from a thermally induced Brook rearrangement on the α-silyl ketone **87** (Scheme 26). This siloxy carbene was postulated to intramolecularly insert into a silicon-methyl C-H bond to form the intermediate 2-silaoxetane. The observed products from this reaction were benzaldehyde, the vinyl silane **88**, D_3, and styrene. Ando and coworkers proposed that these products were formed from initial decomposition of the 2-silaoxetane to diradical **89** or diradical **90**. Diradical **89** reacted further to form dimethylsilanone and styrene: the predicted decomposition products from the 2-silaoxetane. Diradical **90** was presumed to decompose to benzaldehyde and silene **91**, which reacted with **87** to ultimately yield the vinyl silane **88**.

Although the decomposition of a 2-silaoxetane to a diradical of type **90** is precedented, the further decomposition of such a radical to a silene and a carbonyl compound is without precedent. Previous studies indicate that diradical **90** should undergo intramolecular hydrogen abstraction to yield a silyl enol ether or a vinyl silane (Scheme 19).

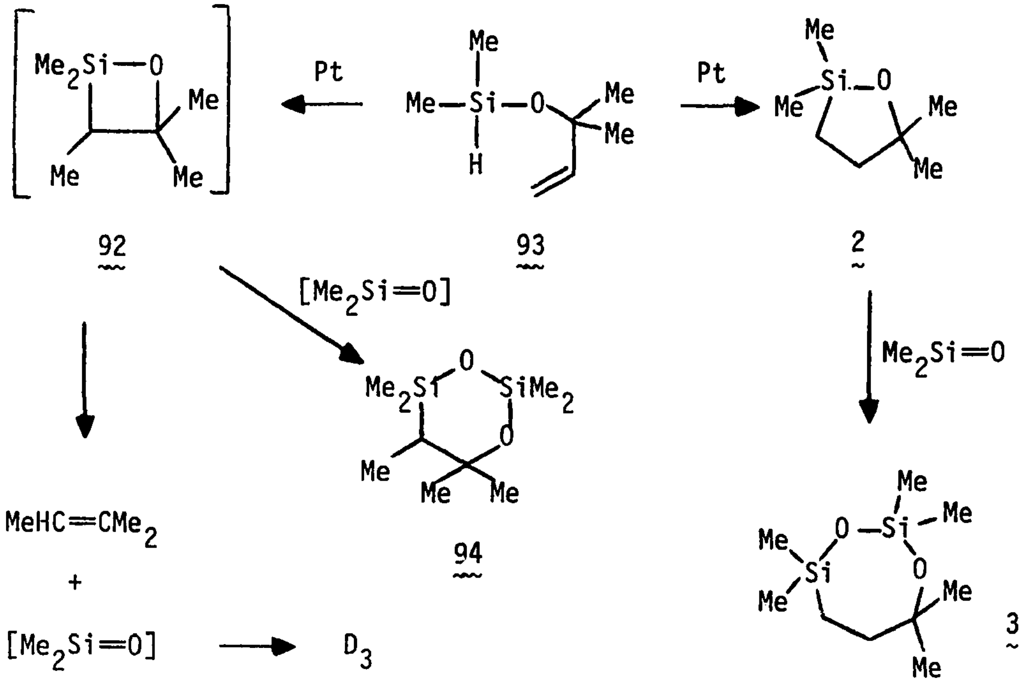
The conclusion of Ando and coworkers that 90 decomposes to a silene and a carbonyl compound suggests that path B in Scheme 19 should be an equilibrium; hence, the addition of a silene to a carbonyl compound may be a reversible process.

Scheme 26

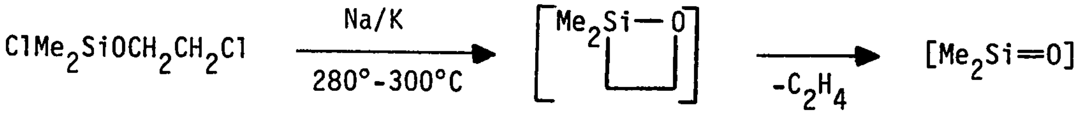


The third general method of silaoxetane preparation is based upon ring closure by formation of a silicon-carbon bond. In 1979, Frye and Lane claimed intermediacy of the 2-silaoxetane 92 in the platinum catalyzed intramolecular hydrosilation of 93 (Scheme 27) (62). They observed the formation of five major products from this reaction: D_3, 2-methyl-2-butene, 94, 2, and 3. The presence of D_3 and 2-methyl-2-butene suggests that 93 closed directly to the 2-silaoxetane 92. Product 94 was postulated to arise from dimethylsilanone insertion into the 2-silaoxetane. Evidently, the steric hindrance provided by the methyl groups enables 92 to have a sufficiently long lifetime for dimethylsilanone insertion to occur. This is the first reported example of a silanone inserting into a 2-silaoxetane ring system.

Scheme 27



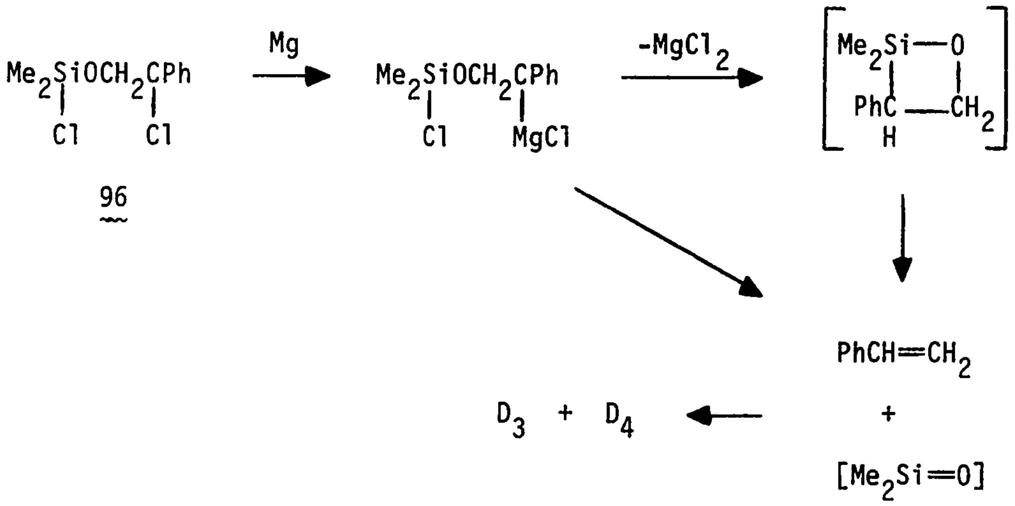
Recently, Gusel'nikov and coworkers reported the synthesis of a 2-silaoxetane from the alkali metal assisted ring closure of chloro(2-chloroethoxy)dimethylsilane 95 (63). The proposal of a 2-silaoxetane intermediate was based upon the observation of cyclic siloxanes and ethylene.



95

In a similar but more detailed study, Tumey reported that 95 or chloro(2-chloro-2-phenylethoxy)dimethylsilane 96 reacted with magnesium to give cyclic siloxanes and ethylene or styrene, respectively. Tumey commented that these products are consistent with the intermediacy of a 2-silaoxetane but are not demanding of it. The Grignard reagent could also undergo a six-electron fragmentation to directly yield styrene and dimethylsilanone (Scheme 28) (12).

Scheme 28

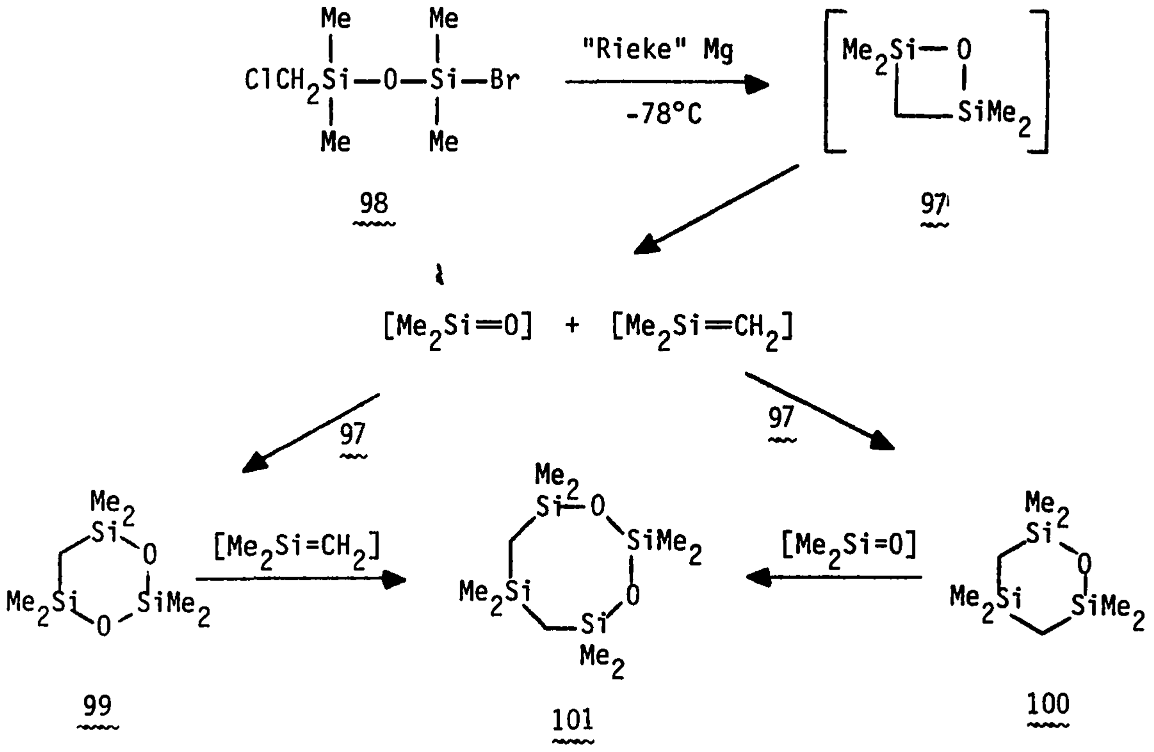


96

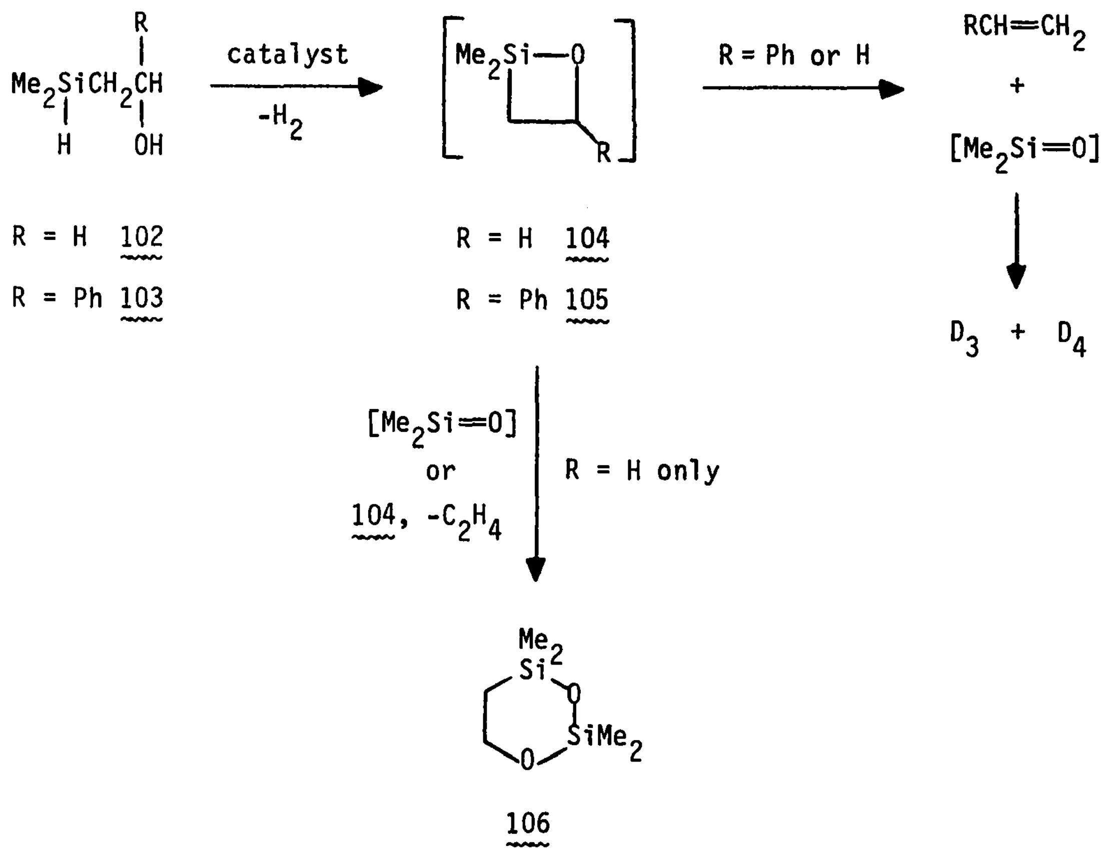
Tumey has attempted to extend this method of silaoxetane formation to the synthesis of the 2,4-disilaoxetane 97 (Scheme 29) (12). He reported that reaction of 1-bromo-3-(chloromethyl)-1,1,3,3-tetramethyldisiloxane with Rieke magnesium at -78°C resulted in three products, 99, 100, and 101. The siloxycyclohexanes, 99 and 100, could be formed from dimethylsilanone or 1,1-dimethylsilene insertion, respectively, into a Si-O bond of 97. The third major product, 101, is formed from 99 or 100 in similar fashion. Although these products strongly suggest the intermediacy of 97, it is also possible that this reaction proceeds through a direct fragmentation of the initially formed Grignard reagent to dimethylsilanone and 1,1-dimethylsilene. Insertion of dimethylsilanone or 1,1-dimethylsilene into a Si-O bond of starting material, followed by Rieke magnesium induced cyclization, affords the observed products.

The fourth general method of preparing silaoxetanes utilizes Si-O bond formation to complete ring closure. The majority of work in this area has been carried out by Barton and Tumey (21). They attempted to effect Si-O bond formation by treatment of 2-(dimethylsilyl)ethanol or 2-(dimethylsilyl)-1-phenylethanol with Wilkinson's catalyst or with Raney nickel (Scheme 30). The products of these reactions were postulated to arise through the intermediacy of 2-silaoxetane 104 or 105. The product distribution is surprisingly dependent on R. When R equals H, the 1,3-dioxane 106 is the major product of the reaction. Barton and Tumey suggested that 106 was formed by insertion of dimethylsilanone into a Si-O bond of the 2-silaoxetane 104 or by a bimolecular silanone transfer process involving two molecules of 104. When R equals phenyl, however, none of the corresponding 1,3-dioxane is obtained. The only products are D_3, D_4, and styrene. This observation suggests that 2-silaoxetane 105 is less stable than 2-silaoxetane 104. The phenyl substituent evidently contributes to this instability by stabilizing a diradical intermediate if decomposition of 105 occurs stepwise or by formation of a conjugated double bond if decomposition is concerted.

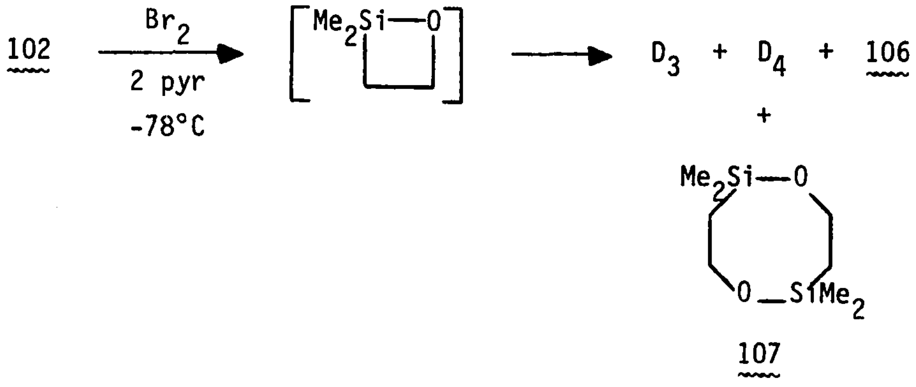
Scheme 29



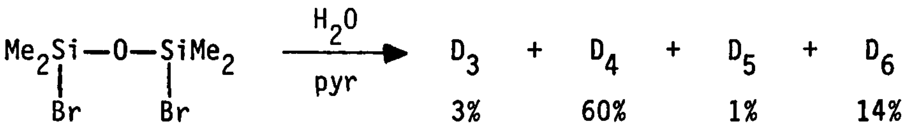
Scheme 30



Barton and Tumey also reported the possibility of a 2-silaoxetane intermediate when 102 is treated with Br$_2$ in pyridine at -78°C. Again, the observed products were D$_3$, D$_4$, and the 1,2-dioxane 106. The mechanism utilized to explain these products is identical to the previously discussed mechanism. Also formed, presumably in an intermolecular reaction involving two molecules of 102, was the cyclosiloxane 107.



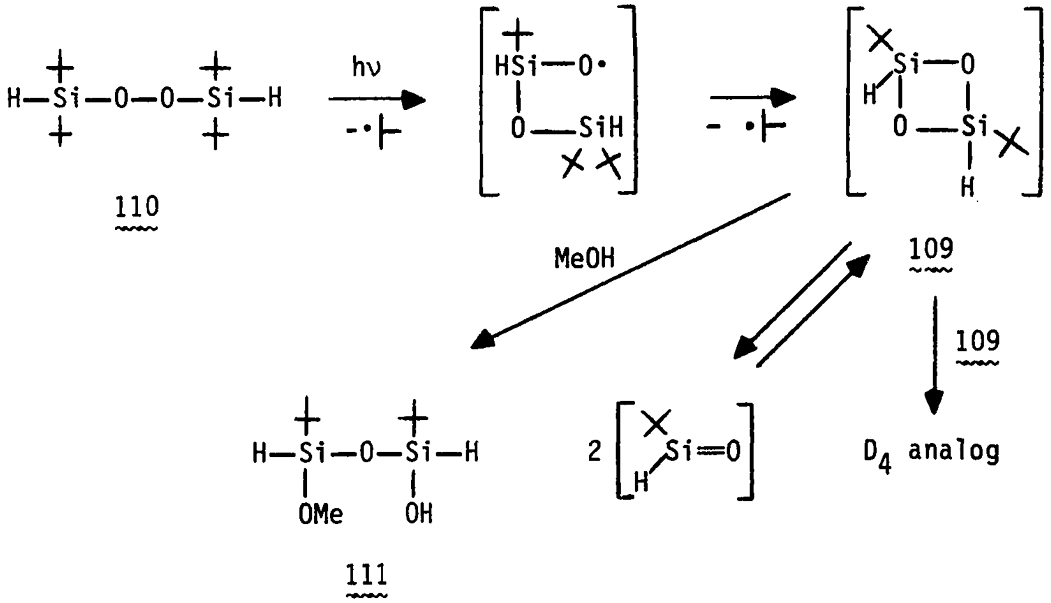
An unsuccessful attempt to generate D_2 from a slow controlled hydrolysis of 108 has been reported by Hoekman (14). The major product of this reaction, D_4, was probably formed in an intermolecular condensation of two molecules of starting material. No conclusive evidence for the intermediacy of D_2 was obtained.



108

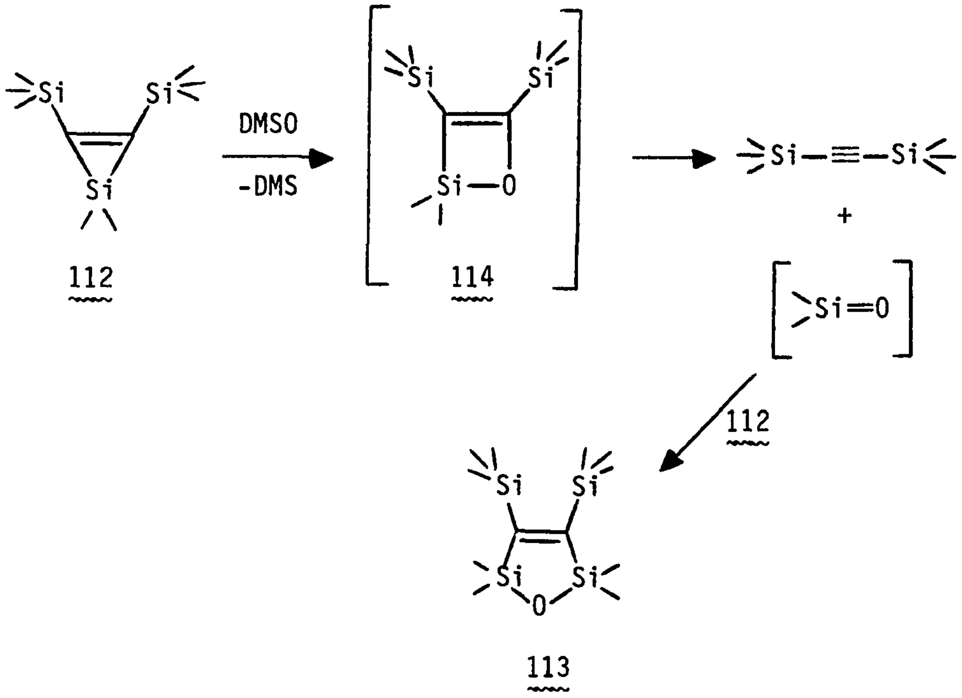
Several miscellaneous methods of silaoxetane formation deserve mention. Hoekman has reported the intermediacy of the D_2 analog 109 from photolysis of bis(di-t-butylsilyl)peroxide. Formation of 109 was postulated to occur via rearrangement of 110, loss of a t-butyl radical, and radical ring closure (Scheme 31) (14). Evidence for 109 was obtained by trapping with MeOH to give 111. This is the first reported example of trapping a silaoxetane ring system with an alcohol. In the absence of a trap, 109 dimerized to the D_4 analog or decomposed to *t*-butylsilanone.

Scheme 31

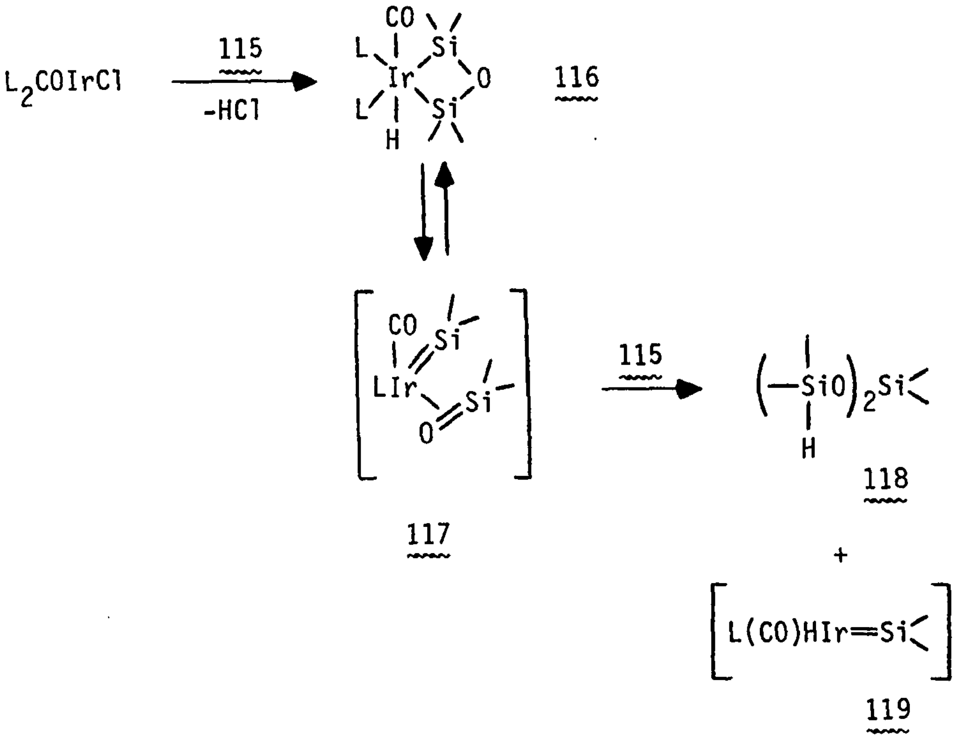


The intermediacy of a silaoxetene has been postulated by Seyferth and coworkers (30). They observed that DMSO reacted with silarene 112 to give bis(trimethylsilyl)acetylene, DMS, and 113 (Scheme 32). The intermediate 2-silaoxetene 114, formed by either a stepwise or concerted mechanism, decomposed to the acetylene and dimethylsilanone. Insertion of dimethylsilanone into a Si-C bond of 112 accounts for the final formed product.

Scheme 32



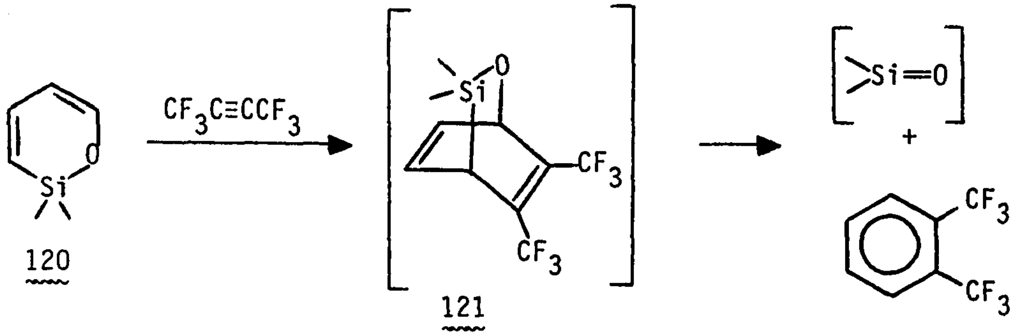
Several transition metal containing silaoxetanes have been prepared and isolated (38). The synthesis of these unusual metallocycles is usually effected by reaction of halo metals with 1,1,3,3-tetramethyldisiloxane 115. The chemistry of these metallosilaoxetanes is surprisingly similar to the chemistry of silaoxetanes. Complex 116 is believed to rearrange to 117, which transfers a silanone unit to 1,1,3,3-tetramethyldisiloxane to form 118 and 119.


L2COIrCl
115
-HCl
CO
L
Ir
L
H
Si
O
Si
116
CO
LIr
Si
Si
O
117
115
SiO
H
2Si
118
+
L(CO)HIr=Si
119

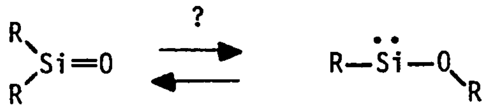
RESULTS AND DISCUSSION

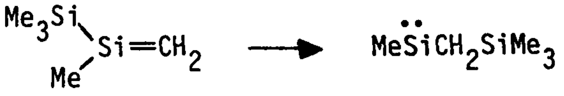
The original goals of this work were threefold: (1) develop a mild, high yielding, direct synthetic route to silanones, (2) utilize this route to examine silanone chemistry, and (3) obtain unambiguous evidence for silanone intermediacy. The pursuit of these goals has resulted in four primary areas of study.

The first area of study examined the potential of the the 7-oxa-8-silabicyclo[2.2.2]octane ring system to serve as a direct source of silanones. Interest in this system stems from the investigations of Barton and Wulff, who serendipitously synthesized the dimethylsila-α-pyran 120 (64). Barton and Wulff noted that treatment of 120 with perfluoro-2-butyne resulted in products consistent with dimethylsilanone formation. Presumably the 7-oxa-8-silabicyclooctadiene 121 is the first formed intermediate.



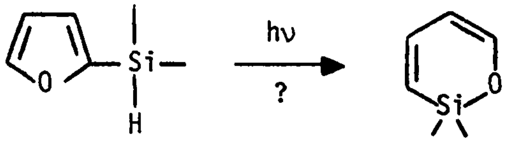
The second area of study utilized chemistry developed in the previous area of study to examine the potential rearrangement of a silanone to a silylene or of a silylene to a silanone. This work was precipitated by the recently reported observation of silene 122 undergoing a 1,2-trimethylsilyl shift to the silylene 123 (65, 66).





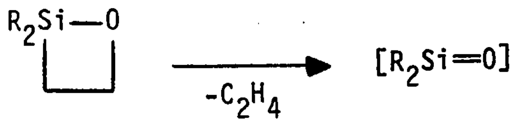
122 123

The third area of investigation has as its origin the desire to develop an alternative synthetic route to the sila-α-pyran ring system 120. The route that was examined was based upon the known photochemistry of alkyl-substituted furans; hence, the photochemistry of silicon-substituted furans was studied.



120

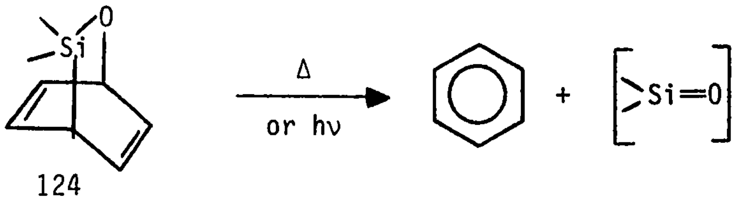
The final area of study sought to synthesize silanones from silaoxetane ring systems. Silaoxetanes are believed to undergo rapid decomposition to silanones under extremely mild conditions (see Historical section). The synthesis of several novel silaoxetane systems was attempted.



Direct Thermal and Photochemical Generation of Dimethylsilanone from the 7-Oxa-8-silabicyclo[2.2.2]octene Ring System

Since silanones were first postulated as reactive intermediates in 1952 by Andrianov and Sokolov (15), three basic methods for their synthesis have been developed: (1) the high temperature thermolysis of linear and cyclic siloxanes, (2) the initial synthesis and subsequent decomposition of silaoxetane ring systems, and (3) the oxidation of silylenes with DMSO. One of the goals of this work was to develop an alternative synthetic route to silanones which was mild, high yielding, and could be used to obtain unambiguous evidence for the existence of this highly reactive species. The problems with the previously discussed methods of generating silanones are that they either utilize extremely high temperatures or the synthesis of another reactive intermediate, such as a silene, silylene or silaoxetane, must first be accomplished. These harsh conditions and the presence of other reactive intermediates greatly inhibits the ability to study the chemistry of silanones or the kinetics of their formation. These types of studies are important in view of the current debate concerning the very existence of silanones. As discussed in the historical section of this dissertation, except for the debatable kinetic studies of Davidson and coworkers and of Nametkin and coworkers, the only evidence for silanone intermediacy is the observation of silanone trapping products (16-19). Although in past studies this was sufficient evidence for claiming silanone formation, it is now recognized that silanone trapping products may also be formed in a bimolecular process which does not involve a free silanone.

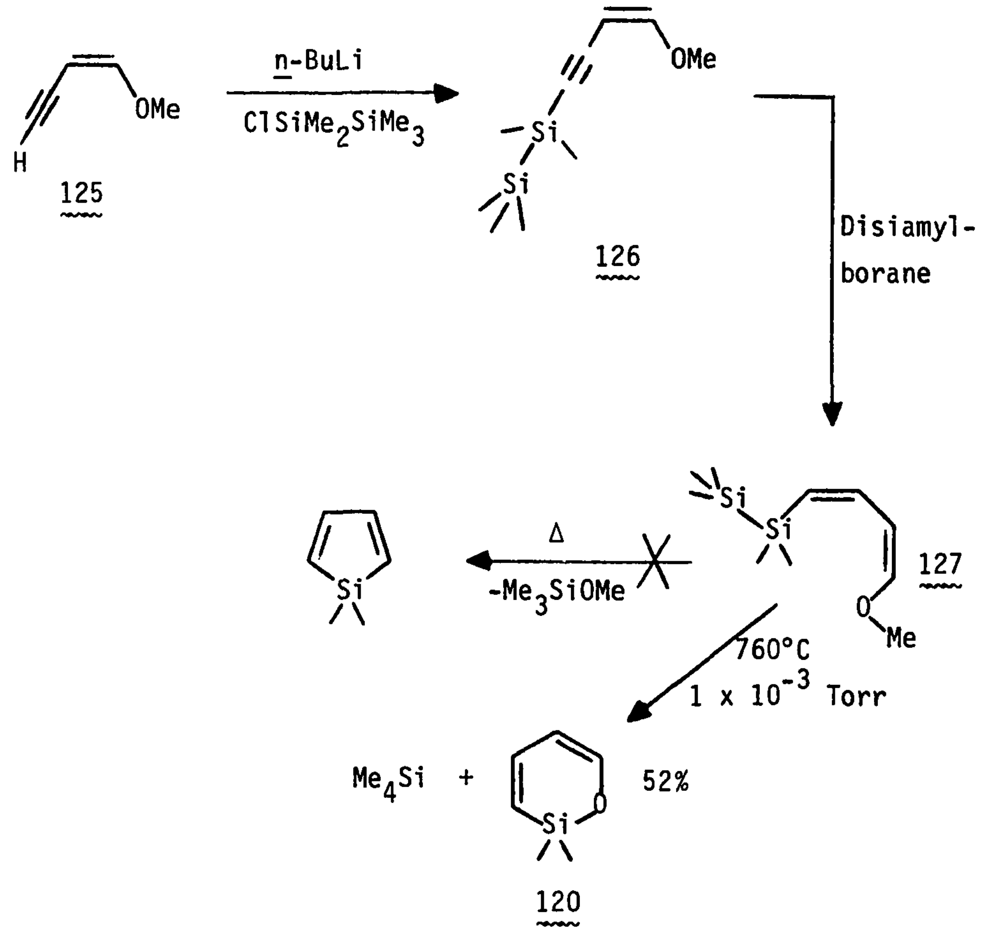
The solution to these problems and the attainment of the goals of this work were clearly dependent upon the development of a precursor that would *directly* decompose to a silanone. Such a precursor would be amenable to kinetic studies which would hopefully provide conclusive evidence for silanone intermediacy. A precursor which appeared to meet these criteria was the 7-oxa-8-silabicyclo[2.2.2]octadiene ring system 124. Extrusion of the siloxy bridge in a retro-Diels-Alder reaction would be expected to directly yield a silanone and benzene. Similar chemistry has been observed with 7-silabicyclo[2.2.2]octadienes and 7,8-disilabicyclo[2.2.2]octadienes (54, 55).



124

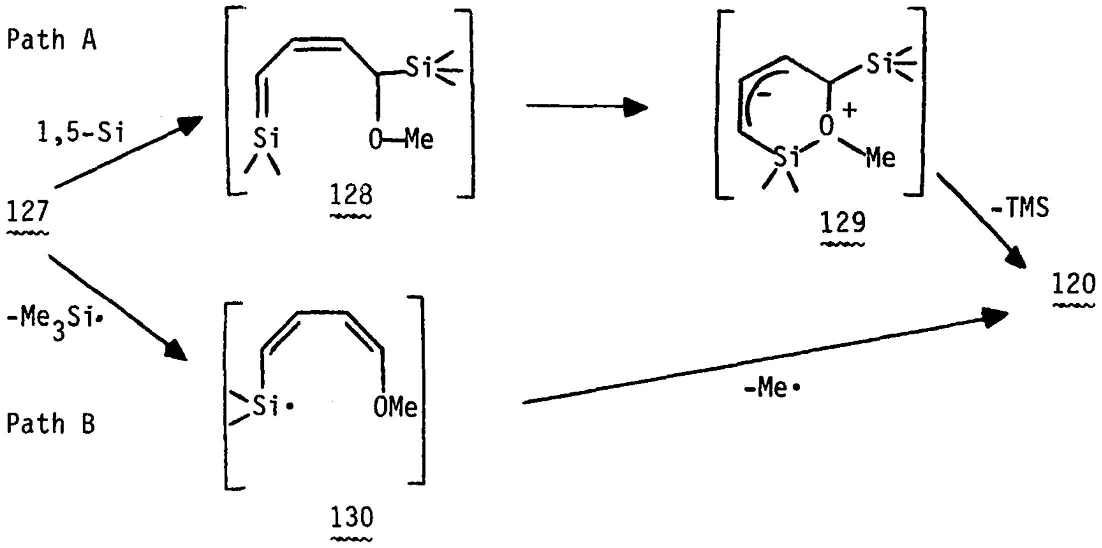
The synthesis of systems such as 124 was made possible by Barton and Wulff, who serendipitously prepared the sila-α-pyran 120 (64). Their synthetic approach to 120 is illustrated in Scheme 33. (Subsequent work by this author showed that the reduction of 126 could be affected more efficiently and more generally using diisobutylaluminum hydride (DIBAH) and N-methylpyrrolidine.) It was initially predicted that pyrolysis of 127 would result in loss of trimethylmethoxysilane and formation of dimethylsilacyclopentadiene. Instead, when 127 was pyrolyzed at 760°C and 1 X 10^{-3} torr, the 2,2-dimethyl-1-oxa-2-silacyclohexa-3,5-diene 120 (a sila-α-pyran) and tetramethylsilane (TMS) were formed.

Scheme 33



Two mechanistic proposals were offered to explain these unexpected products (Scheme 34). In path A, a precedented 1,5-trimethylsilyl shift yields the intermediate silene 128, which can cyclize by Si-O bond formation to the zwitterion 129. A loss of TMS in a β-elimination affords the observed product. The second mechanism considered, especially probable under the high temperature conditions of reaction, was path B. In path B, initial Si-Si bond cleavage yields the silyl radical 130. Cyclization of 130, followed by loss of a methyl radical, also yields the dimethylsila-α-pyran. At the time Barton and Wulff completed their studies, both path A and path B remained viable mechanistic rational for formation of 120.

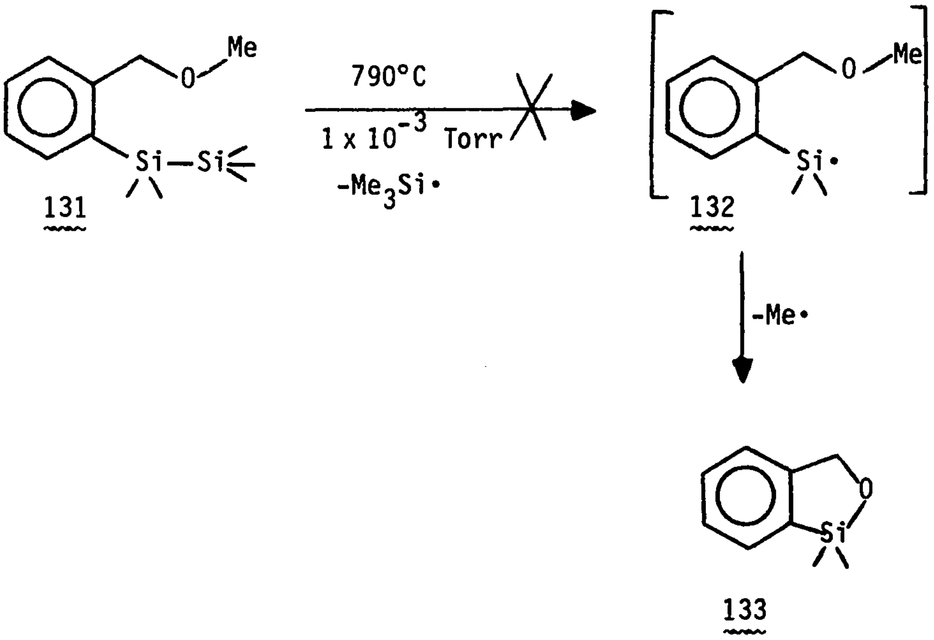
Scheme 34



In an effort to distinguish between path A and path B, the thermal chemistry of *o*-pentamethyldisilybenzyl methyl ether, 131, was examined. In this system, a 1,5-silicon shift is not possible; however, cleavage of the Si-Si bond should be just as favorable as the proposed similar cleavage in 127 (Scheme 35). If this occurs, closure of the resulting radical 132 would be expected to give the siloxyindane 133. This compound is a known, thermally stable system (14). Pyrolysis of 131 at

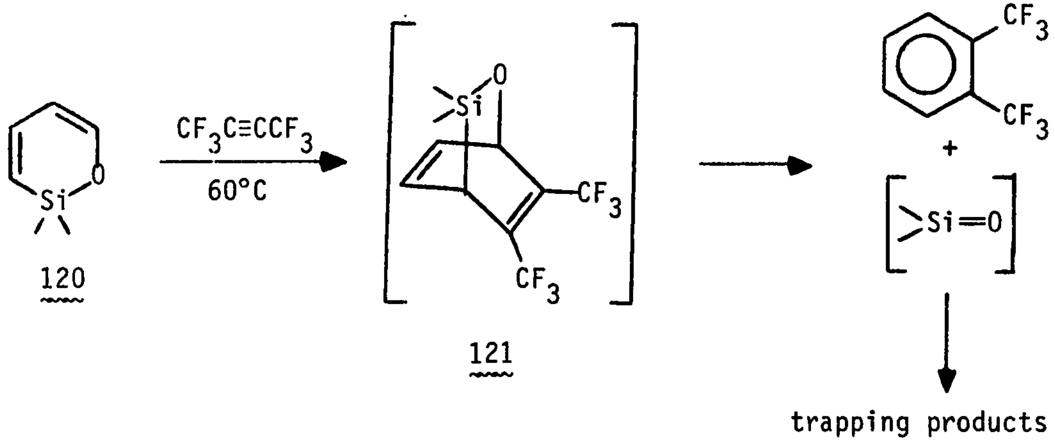
790°C, 1 X 10^{-3} torr yielded no products that were consistent with Si-Si bond cleavage. In fact, analysis of the pyrolysate revealed greater than 90% recovered starting material. Thus, path B in Scheme 34 appears to be an unlikely mechanism for formation of 120 from the pyrolysis of 127.

Scheme 35



In addition to their synthesis of the dimethylsila-α-pyran, Barton and Wulff reported that it reacted with perfluoro-2-butyne in the presence of various silanone traps to afford dimethylsilanone trapped products in almost quantitative yields (Scheme 36). Unfortunately, the presumed initially formed intermediate 121 was not isolated nor could it be identified in any spectroscopic fashion. Although the trapping experiments of Barton and Wulff suggest that 121 decomposes to dimethylsilanone, their inability to isolate it or observe it prohibits conclusive mechanistic interpretation. It is also possible, however unlikely, that 121 acts as a silanone transfer agent. The observed products are then formed in a bimolecular process not involving free dimethylsilanone. In order to distinguish between these mechanistic alternatives, a direct synthesis of silanone, thus, a stable adduct, was required.

Scheme 36

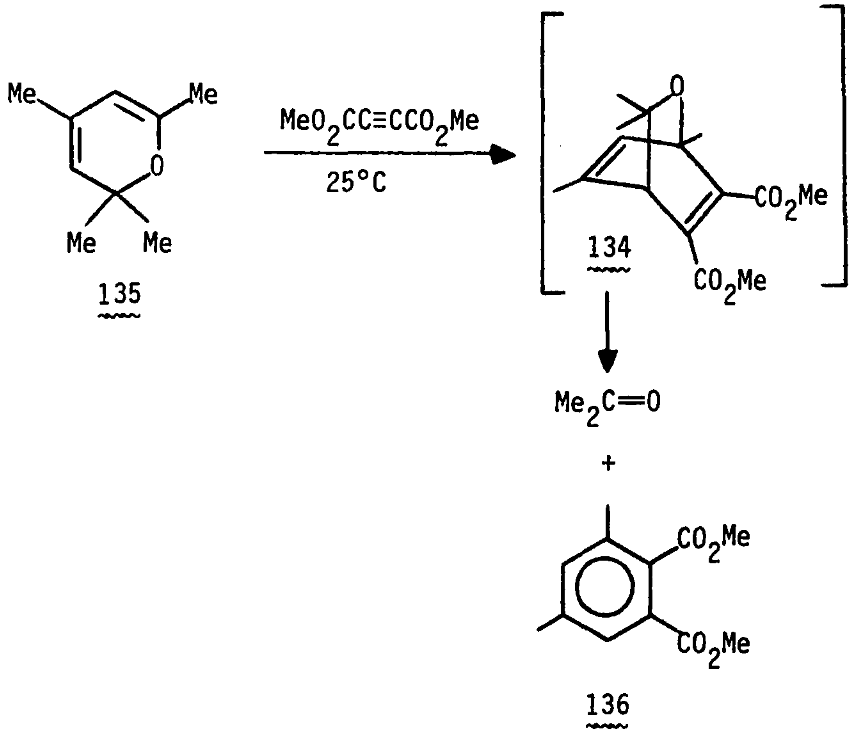


The inability to isolate 121 is, on first examination, puzzling. Similar compounds, such as 7-silabicyclo[2.2.2]octadiene, 7,8-disilabicyclo[2.2.2]octadiene and bicyclo[2.2.2]octadiene require temperatures greater than 150°C before retro-Diels-Alder reactions occur (54, 55, 67). Drawing assumptions from these systems, one would incorrectly predict that 121 should be isolable. Fortunately, examination of the analogous carbon system 134 offers a solution to this puzzle.

The precursor to 134, 2,2,4,6-tetramethylpyran 135, was prepared according to the method of Safieddine and coworkers (Scheme 37) (68).

Similar to the reaction of dimethylsila-α-pyran with perfluoro-2-butyne, the reaction of 135 with dimethyl acetylene dicarboxylate does not result in a stable adduct. Monitoring the reaction progress by hydrogen NMR revealed no peaks attributable to 134. Instead, acetone and 136 were directly formed. Similar results from other pyran-acetylene reactions have been reported by Salomon and coworkers (69). Thus, the carbon analogs of the 7-oxy-8-silabicyclo[2.2.2]octadiene ring system are equally unstable and the inability to isolate or observe 121 is not so surprising.

Scheme 37

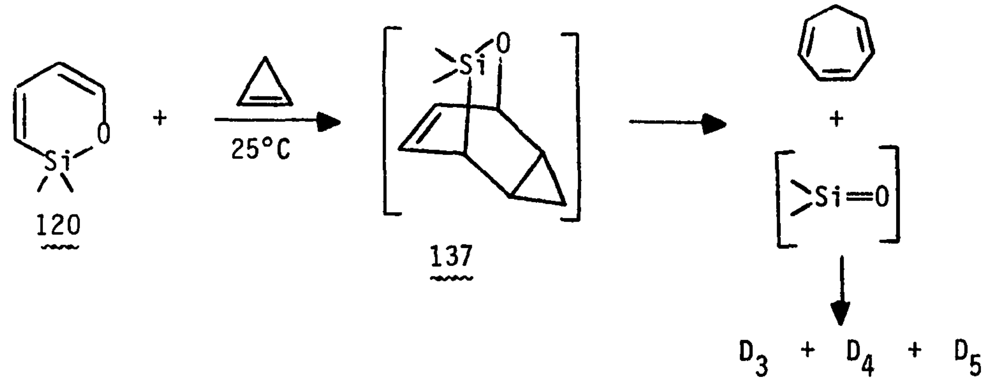


The instability of 121 is presumably due, in part, to direct formation of an aromatic ring. If this aromatic driving force could be eliminated, a stable adduct may be obtained. The use of an alkene, instead of an alkyne, as the dienophile should yield an adduct which could not directly undergo a retro-Diels-Alder reaction to an aromatic system.

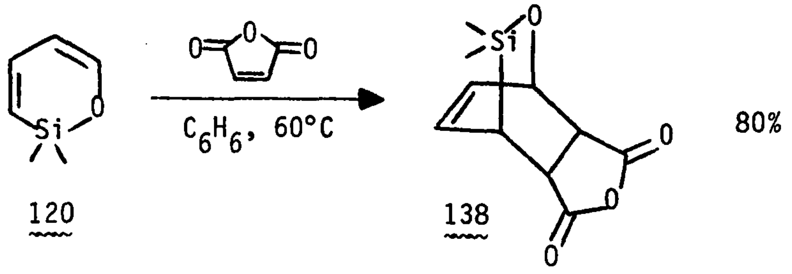
Cyclopropene was initially chosen as the dienophile. It is conveniently generated, as a gas, by the reaction of allyl chloride and sodium amide. Thus, freshly prepared cyclopropene was passed into a solution of dimethylsila-α-pyran in CCl_4 and the reaction progress was monitored by hydrogen NMR. Considerable product formation was observed; however, no peaks clearly attributable to the expected adduct 137 were seen. All attempts to isolate 137 by distillation and chromatography failed. Analysis of the reaction mixture by gas chromatography-mass spectroscopy (GC-MS) revealed that unreacted dimethylsila-α-pyran, cyclopropene oligomers, cycloheptatriene, D_3, D_4, and D_5 were formed. These latter products indicate that formation of the desired adduct did occur (Scheme 38). Evidently, under the conditions of reaction or under the conditions of attempted isolation, 137 underwent a retro-Diels-Alder reaction to cycloheptatriene and dimethylsilanone which then cyclooligomerized to the observed cyclosiloxanes.

It was obvious from the preceding attempt at forming a stable Diels-Alder adduct of 120 that mild conditions of reaction and methods of isolation were necessary for success. One of the mildest methods of isolation is recrystallization, and crystalline Diels-Alder adducts can virtually be insured if maleic anhydride is used as the dienophile. The reaction of 120 with maleic anhydride at 60°C in benzene did indeed afford a stable crystalline adduct 138, which could be isolated in 80% yield (Scheme 39). It next needed to be determined if this adduct would serve as the direct thermal or photochemical source of silanone that was desired. (Wulff has reported that the reaction of 120 with maleic anhydride afforded an adduct which he identified as 138 by hydrogen NMR. Wulff did not report the successful isolation of this adduct (13).)

Scheme 38

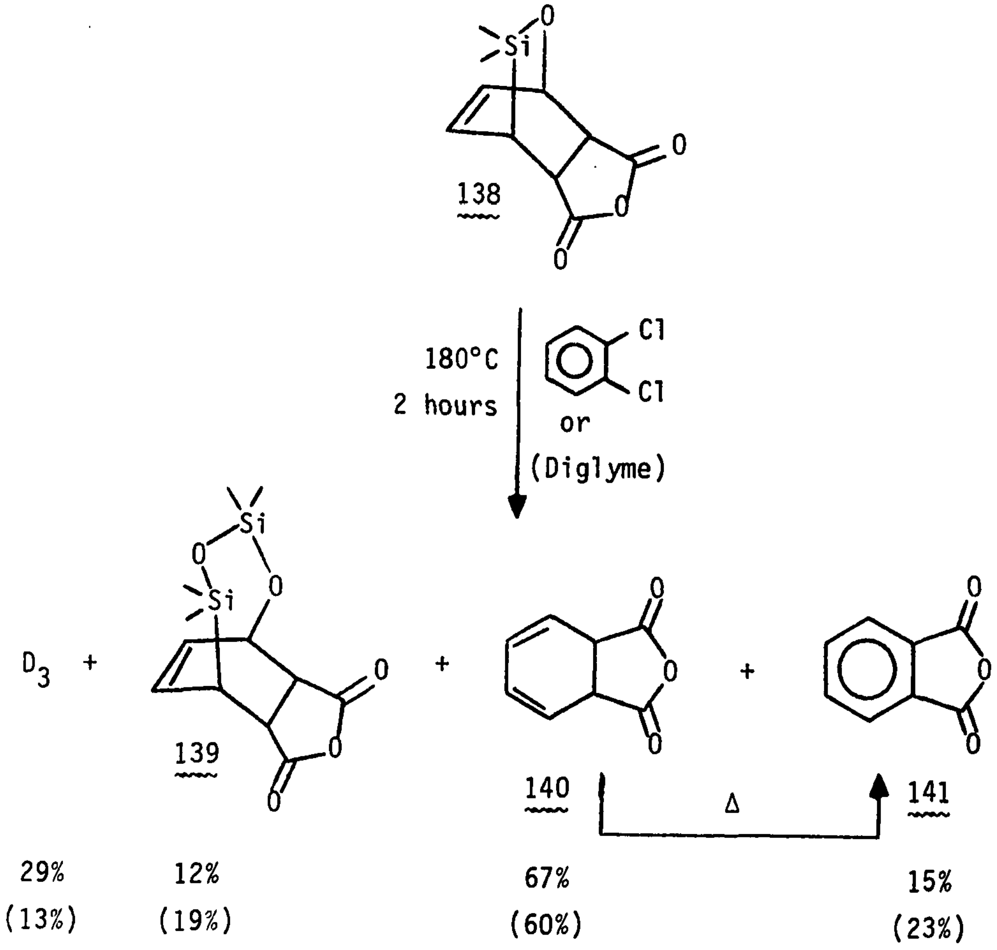


Scheme 39



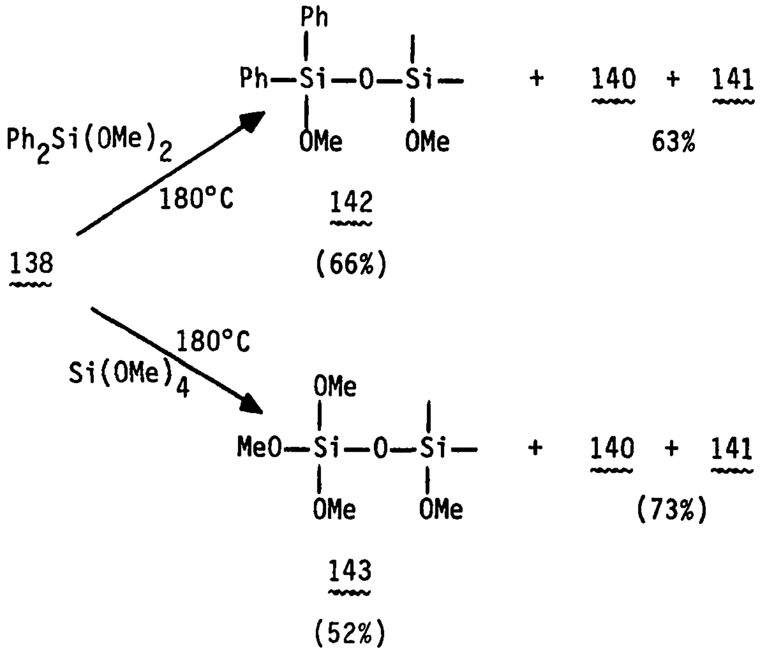
Heating 138 in *o*-dichlorobenzene or in diglyme for 2 hours at 180°C yielded four major products: D_3, the disiloxane 139, 1,2-dihydrophthalic anhydride 140, and phthalic anhydride 141 (Scheme 40). Phthalic anhydride presumably arises from aromatization of 1,2-dihydrophthalic anhydride. Indeed, in an independent experiment, phthalic anhydride was formed when 1,2-dihydrophthalic anhydride was heated in solution at 180°C. The formation of 140, 139, and D_3 are suggestive of dimethylsilanone extrusion from 138. Dimethylsilanone can cyclooligermerize to D_3 or can insert into a Si-O bond of starting material to yield 139.

Scheme 40



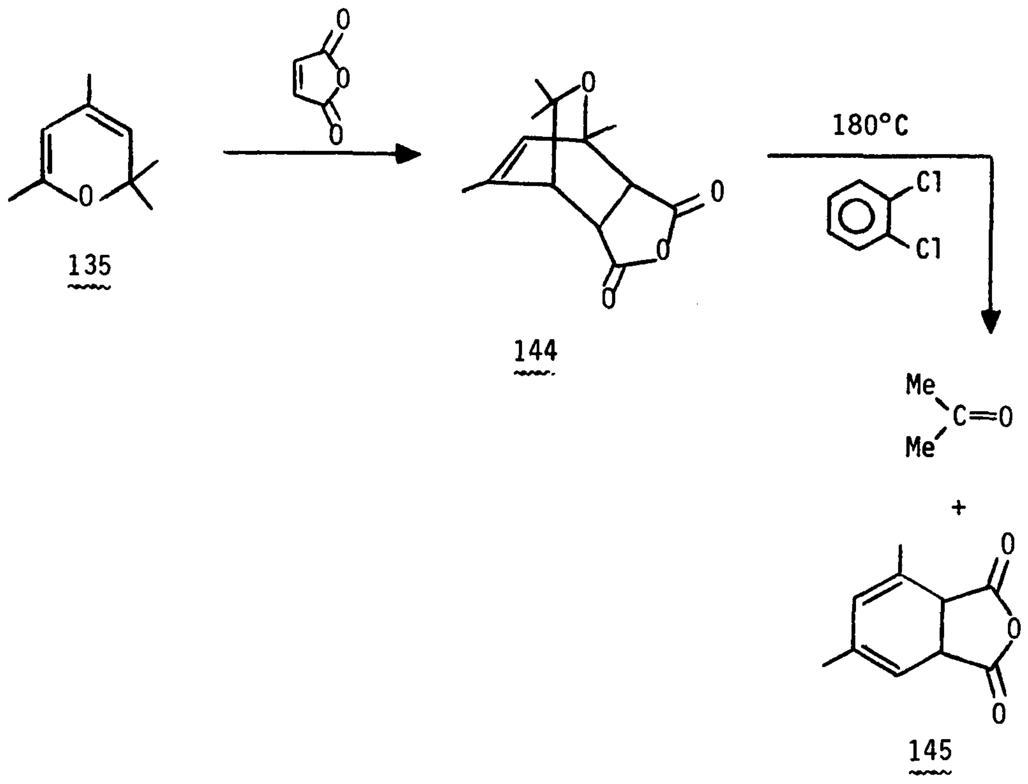
Additional evidence that dimethylsilanone is being generated was obtained from trapping experiments. Thermolysis of 138 in diphenyldimethoxysilane yielded, in addition to the anhydrides 140 and 141, the dimethylsilanone insertion product 1,1-diphenyl-3,3-dimethyldimethoxydisiloxane 142 (66%) (Scheme 41). Trapping of dimethylsilanone was also achieved with tetramethoxysilane. The insertion product 143 was formed in 52% yield.

Scheme 41



Supportive evidence that 138 is undergoing a retro-4+2-cycloaddition and extrusion of the siloxy bridge was obtained from thermolysis of the analogous carbon system 144 (Scheme 42). Reaction of 2,2,4,6-tetramethyl pyran with maleic anhydride yielded the Diels-Alder adduct 144. Thermolysis of 144 in *o*-dichlorobenzene at 180°C resulted in a retro-4+2-cycloaddition and formation of 145 and acetone.

Scheme 42



It appears from the trapping experiments and from the thermal chemistry of the analogous carbon system 144 that 138 decomposes directly to dimethylsilanone. However, none of these data rigorously eliminates the possibility of a silanone transfer mechanism. Decomposition of 138 may occur in a bimolecular process where a dimethylsilanone unit is transferred to the trapping agents giving rise to the observed products. In an effort to distinguish between this silanone transfer mechanism and unimolecular decomposition to free dimethylsilanone, the influence of added silanone traps on the rate of decomposition was examined. If decomposition of 138 is unimolecular and dimethylsilanone is generated in the rate determining step, the addition of silanone traps should have no affect on the rate of reaction. However, if decomposition of 138 occurs in a bimolecular or silanone transfer mechanism, the addition of silanone traps should increase the rate of reaction.

In theory, the affect of added trap on the rate of decomposition of 138 can easily be determined. In practice, however, several problems were encountered. The dimethylsila-α-pyran-maleic anhydride adduct 138 was not stable to liquid chromatography (LC) or gas chromatography (GC) conditions. Thus, these two methods could not be used to follow the decomposition of 138. Ideally, the rate of decomposition of 138 could be quantified by following the appearance of the diene moiety in 1,2-dihydrophthalic anhydride with the ultraviolet (UV) spectroscopy. However, under the conditions of reaction, 1,2-dihydrophthalic anhydride slowly aromatizes to phthalic anhydride, and the more intense, overlapping absorptions of phthalic anhydride prevent any useful observations. Rate data were ultimately acquired by following the decomposition of 138 with hydrogen NMR spectroscopy. This method was not without its problems. In order to obtain reliable integrations, relatively high concentrations of 138 were necessary. In addition, reliable data are dependent upon the clean appearance or disappearance of the peak being integrated. Although the silicon-methyl hydrogens of 138 provided a readily integratable peak, the products of decomposition absorb in the same region. In addition, reproducible results were difficult to achieve due to minor, uncontrollable concentration changes that occurred during degassing of the sample. To the extent that reliable data could be obtained, it was apparent that very complex processes were occurring. Figure 1 and Figure 2 illustrate the effect of added diphenyldimethoxysilane and tetramethoxysilane on the rate of decomposition of 138. For convenience, first-order kinetics are assumed.

These data indicate that the rate of decomposition of 138 is dependent on both the amount and type of silanone trap added. At low concentrations of $Ph_2Si(OMe)_2$, decomposition of 138 occurs at a slower rate than in the absence of the trap. As the amount of added $Ph_2Si(OMe)_2$ is increased, the rate of decomposition of 138 increases. At any concentration of added $Si(OMe)_4$, the rate of decompositon of 138 is always slower than if no trap was added. To further complicate this matter, there is an apparent solvent affect on the rate of decomposition. Decomposition is fastest in o-dichlorobenzene ($t_{1/2}$ = 100±10 min, 170°C), slower in diphenylether ($t_{1/2}$ = 130±10 min, 170°C), and slower still in diglyme ($t_{1/2}$ = 150±10 min, 170°C).

The sensitivity of 138 to decomposition conditions is also illustrated when 1,3-dibromopropane is used as the solvent. The rate of decompositon of 138 is at least five times faster than in any of the previously mentioned solvents. In additon, the products formed when 138 is thermolyzed in 1,3-dibromopropane are not consistent with dimethylsilanone intermediacy (Scheme 43). In the absence of added trap, D_4 is formed in higher yields than D_3. When a silanone trap is added, D_3, only a small amount of dimethylsilanone trapped product is observed.

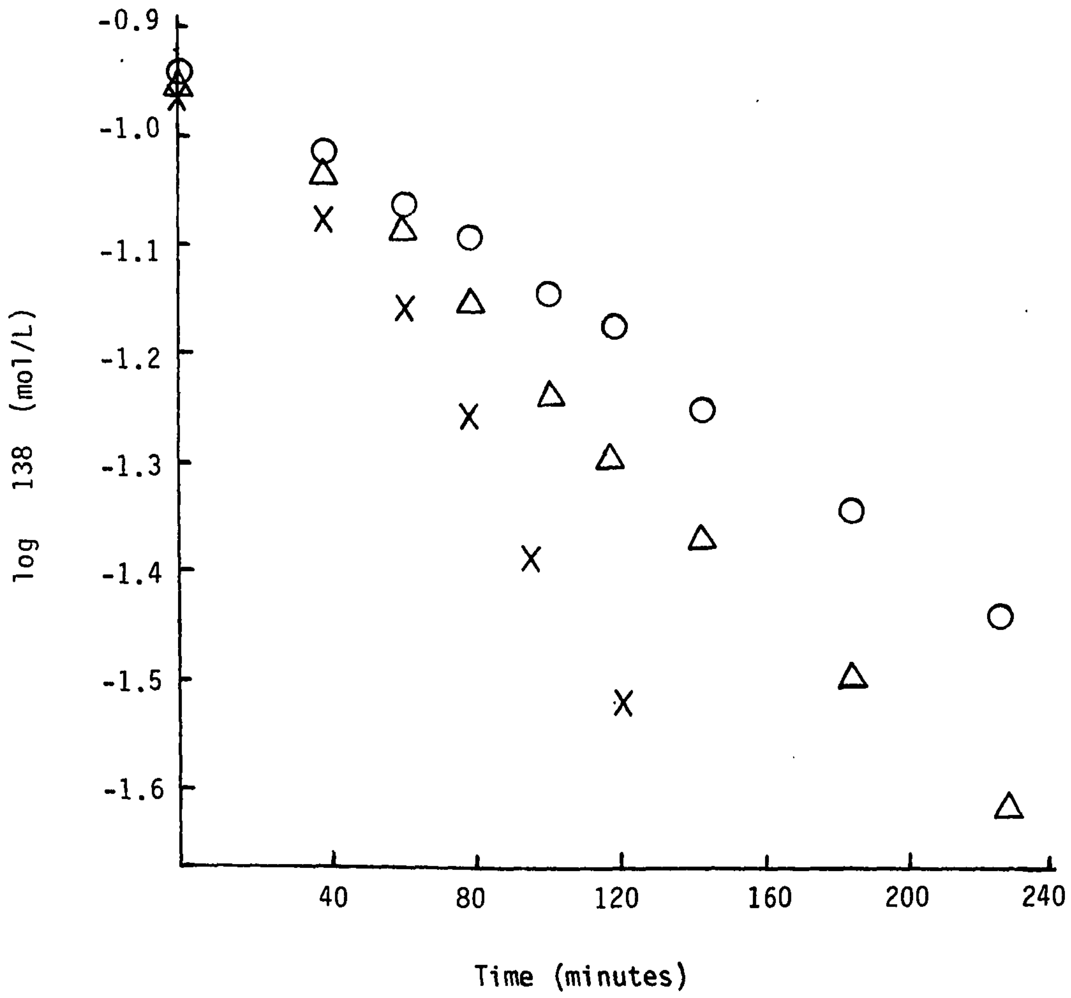


Figure 1. Decomposition of 138 with (O) 4.5-fold excess $Ph_2Si(OMe)_2$, without (Δ) added $Ph_2Si(OMe)_2$, and with (X) 9.1-fold excess $Ph_2Si(OMe)_2$ at 165°C in *o*-dichlorobenzene

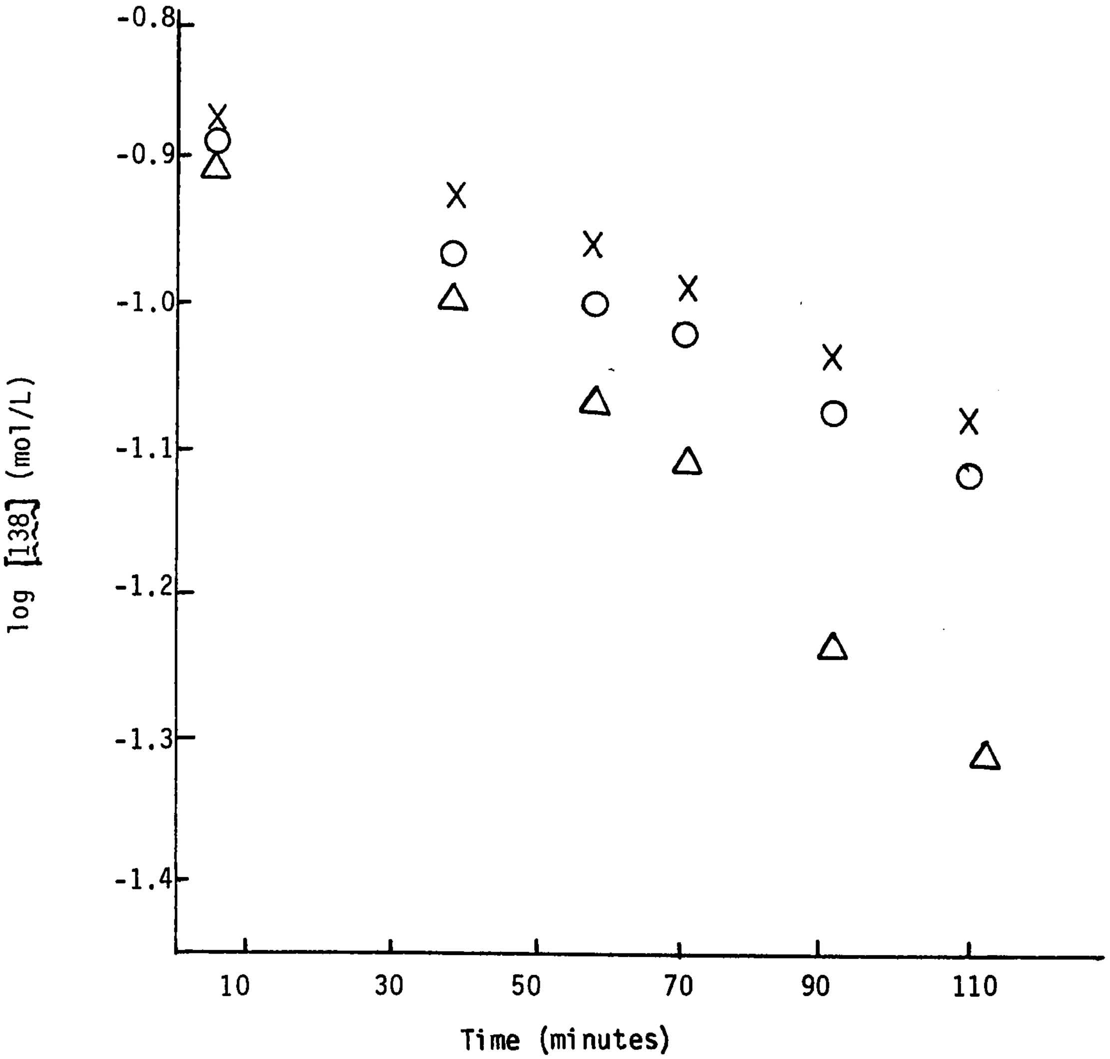
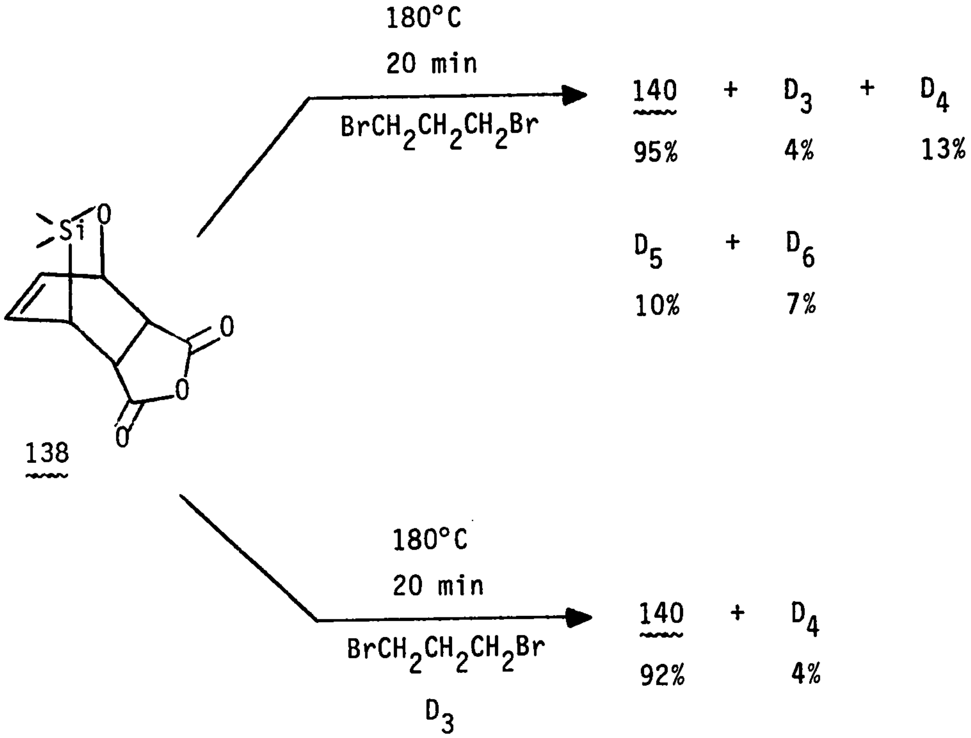


Figure 2. Thermal decomposition of 138 with (X) 9.0-fold excess $Si(OMe)_4$, with (O) 20.1-fold excess $Si(OMe)_4$, and without (Δ) added $Si(OMe)_4$ at 165°C in *o*-dichlorobenzene

Scheme 43



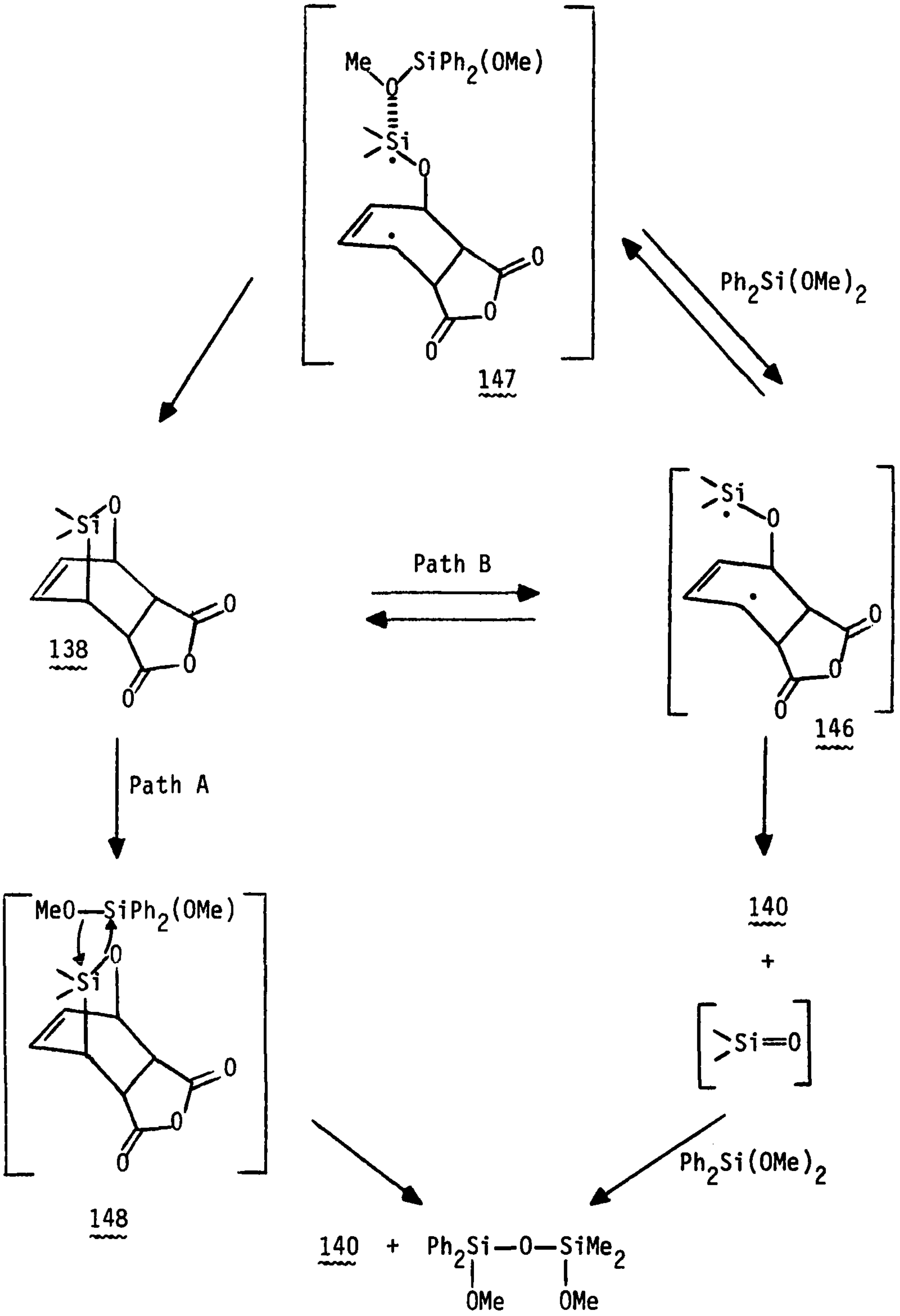
It is impossible to offer a simple rationalization for these results and observations. It was initially believed that many of these seemingly inexplicable results were due to experimental inconsistencies. However, all of the previously discussed observations and trends proved reproducible. The unusual results obtained when 138 is thermolyzed in 1,3-dibromopropane are, perhaps, easiest to rationalize. A close examination of the GC-MS obtained on the crude reaction mixture indicated the presence of allyl bromide. Thermolysis of 1,3-dibromopropane evidently results in formation of allyl bromide by loss of HBr. Acid catalyzed decomposition of 138 would then account for the rapid rate of reaction and unusual product distribution.

The peculiar relative rate data obtained upon thermolysis of 138 in the presence or absence of $Ph_2Si(OMe)_2$ and $Si(OMe)_4$ may also be a consequence of acid catalysis. However, the trapping products obtained from these thermolyses, unlike the thermolysis of 138 in 1,3-dibromopropane, are consistent with dimethylsilanone intermediacy. In addition, precautions such as base washed glassware and distillation of solvents from calcium hydride prior to their use should have prohibited any acid catalysis. Assuming the relative rate data are not due to a catalyzed process, it is apparent from their complexity that at least two mechanisms for the decomposition of 138 in the presence of trap are required: one mechanism, where the addition of silanone trap inhibits complete decomposition of 138 and, another mechanism, in which added silanone trap accelerates the decomposition of 138. These two mechanisms would necessarily be in competition with each other, and the dominance of one mechanism over the other would be dependent upon the trap used.

It is difficult to speculate as to the exact nature of these mechanisms. Only a guess can be offered (Scheme 44). The mechanism in which added silanone trap accelerates decomposition of 138 could conceivably be a simple bimolecular silanone-transfer reaction, path A. The mechanism in which added silanone trap inhibits decomposition of 138 is perhaps radical in nature, path B. Cleavage of the Si-C bond in 138 would result in diradical 146, which could undergo additional bond cleavage to yield dimethylsilanone and 140. Silanone traps or oxygen containing solvents may affect "stabilization" of diradical 146 by coordination of the silyl radical to an oxygen, *i.e.* 147. This "stabilization" would necessarily be sufficient to inhibit additional bond cleavage of 146 to form 140 and dimethylsilanone, and rapid intramolecular radical recombination to reform starting material would occur. Although no precedent for this type of silyl radical stabilization exists, the affinity of silicon-centered reactive intermediates for oxygen is well known. In addition, the more oxygens available for coordination the more important this process should be. Hence, this mechanism is consistent with the observed slow rate of decomposition of 148 in $Si(OMe)_4$ and in solvents such as diglyme. The observed results also require that decomposition by path A is less important in the presence of $Si(OMe)_4$ than in the presence of $Ph_2Si(OMe)_2$. This would be expected assuming formation of transition state 148 is dependent upon initial coordination of silicon and oxygen. The silicon in $Si(OMe)_4$ is less electrophilic than the silicon in $Ph_2Si(OMe)_2$; hence, coordination to 138 and subsequent bond cleavage would be less likely.

It should be stressed that the above explanation for the effect of added silanone trap on the decomposition of 138 is merely a conjecture based on little precedent and somewhat dubious data. Whatever the explanation for these results is, it is clear that 138 did not cleanly decompose in a unimolecular fashion. In spite of the suggestion of dimethylsilanone intermediacy from the trapping experiments and from the thermochemistry of the analogous carbon system 144, no definitive statement regarding dimethylsilanone formation from thermolysis of 138 can be made.

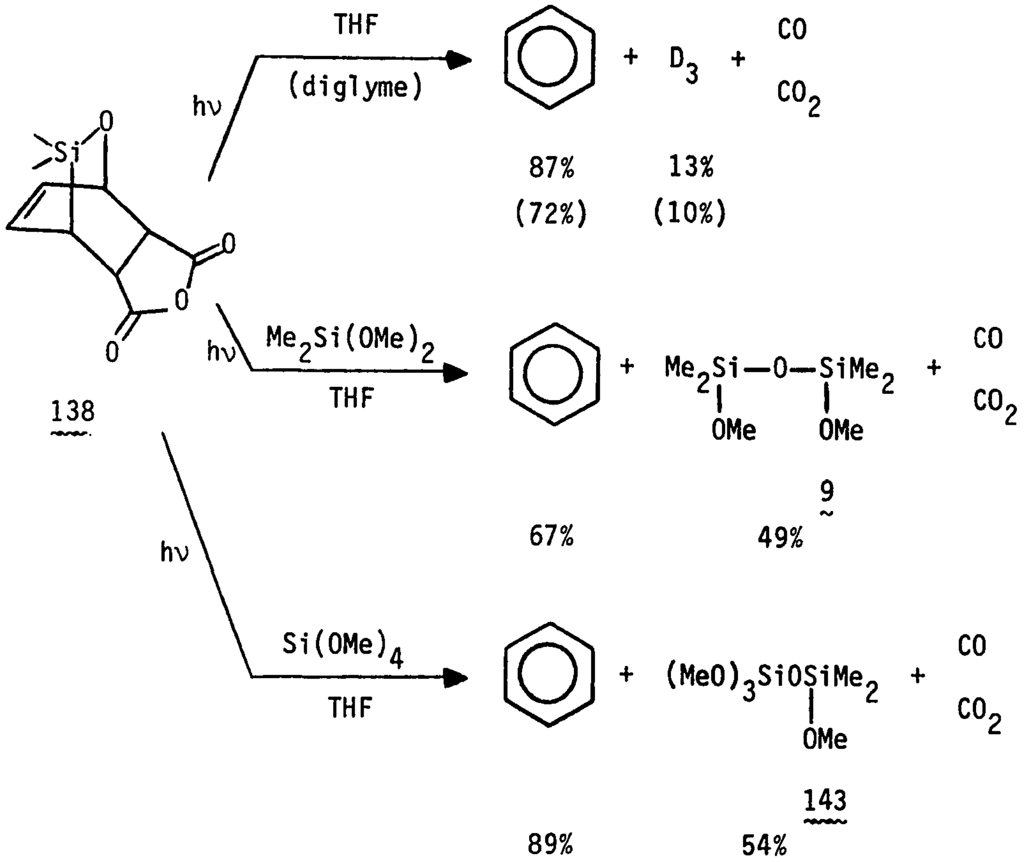
Scheme 44


147
Ph$_2$Si(OMe)$_2$
138
Path B
146
Path A
148
140
+
Ph$_2$Si(OMe)$_2$
140 + Ph$_2$Si—O—SiMe$_2$
OMe
OMe

Thermolysis of 138 was also performed in the gas phase. Sublimation of 138 through a horizontal, quartz chip packed tube, contained in a 30 cm hot zone at 520°C (1 X 10^{-5} torr), resulted in formation of 140 (59%), D_3 (4.2%), and D_4 (2.6%). These products were trapped in a liquid nitrogen cooled trap approximately 20 cm from the hot zone. An attempt was made to trap free dimethylsilanone by addition of a silanone trap, diphenyldimethoxysilane, to the liquid nitrogen cooled trap. In this manner, dimethylsilanone, generated in the hot zone, would necessarily have a long enough lifetime to travel from the hot zone to the cold trap. If successful silanone trapping could be achieved, decomposition of 138 to free dimethylsilanone must have occurred. Unfortunately, no products arising from dimethylsilanone insertion into diphenyldimethoxysilane were observed. Only 140 (50%), D_3 (6%), and D_4 (3%) were formed. If formed, dimethylsilanone must react very rapidly with itself or with a Si-O bond in the starting material or in the glass.

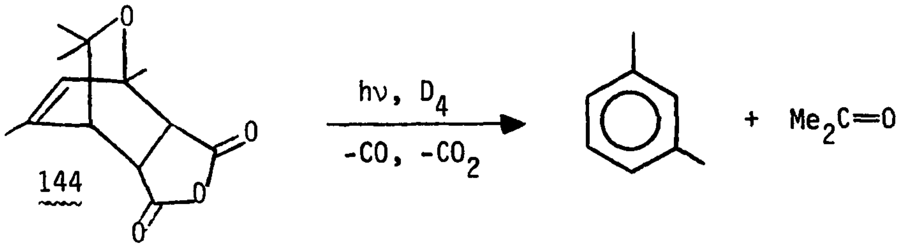
Past studies on the synthesis and chemistry of silicon-centered reactive intermediates have often shown that interesting comparisons can be made between thermally induced and photochemically induced rearrangements and decompositions. Thus, the photochemistry of 138 was examined. Interestingly, the photolysis of 138 in THF or in diglyme with a 450 watt, high pressure Hg lamp, resulted in rapid evolution of gas and clean formation of benzene and cyclosiloxanes (Scheme 45). The formation of cyclosiloxanes is suggestive of dimethylsilanone intermediacy. Further evidence of dimethylsilanone intermediacy was obtained from trapping experiments. Photolysis of 138 in the presence of dimethyldimethoxysilane or tetramethoxysilane resulted in the dimethylsilanone insertion products 9 and 143, respectively.

Scheme 45



Additional supportive evidence that dimethylsilanone is being extruded in the photolysis of 138 comes from the similar extrusion of acetone from photolysis of the analogous carbon system 144 (Scheme 46). Also observed in the photolysis of 144 is formation of m-xylene and gas evolution.

Scheme 46



These results, like the similar results from thermolysis of 138, are suggestive of dimethylsilanone intermediacy. However, a bimolecular silanone-transfer process cannot be excluded. To distinguish between these two possibilities, the effect of added silanone traps on the rate of decomposition of 138 was examined. The relative rate of decomposition was determined by following the appearance of benzene with hydrogen NMR or gas chromatography. As Figure 3 and Figure 4 illustrate, the addition of silanone trap has no effect on the rate of benzene formation. To some extent, the relative rate of reaction could also be determined by following the disappearance of 138. Again, no effect from the addition of trap on the rate of decomposition was indicated. Thus, this rate data would appear to eliminate the possibility of 138 photochemically decomposing *via* a silanone-transfer mechanism.

The rate data just presented, the trapping experiments, and the extrusion of acetone from photodecomposition of 144 all apparently indicate that 138 photochemically decomposes in a unimolecular fashion with free dimethylsilanone formation. However, the elusive silanone does not concede capture so easily. The rate data and the trapping experiments are consistent with two decomposition pathways and one of

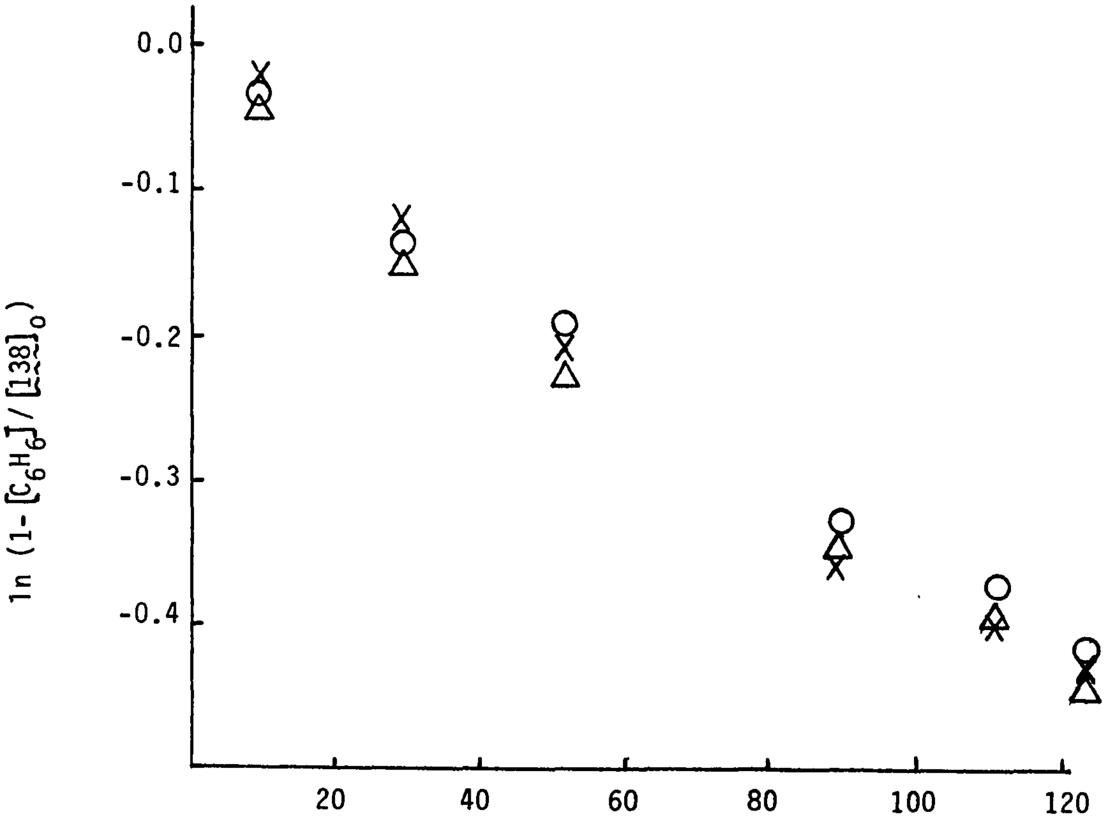


Figure 3. Photochemical decomposition of 138 with (X) no trap, with (O) 2.3-fold excess of $Si(OMe)_4$, and with (Δ) 8.3-fold excess of $Si(OMe)_4$ in diglyme

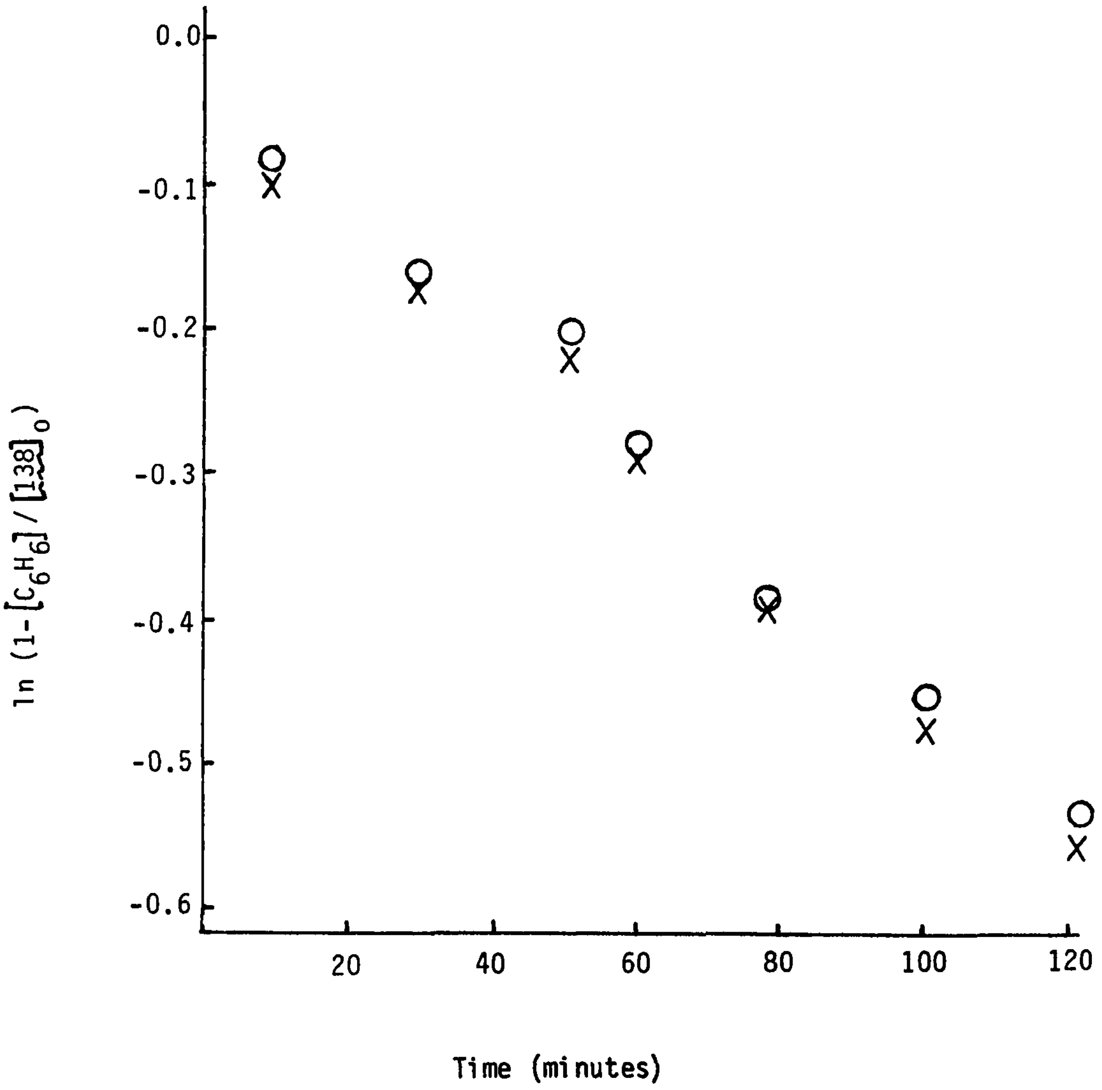
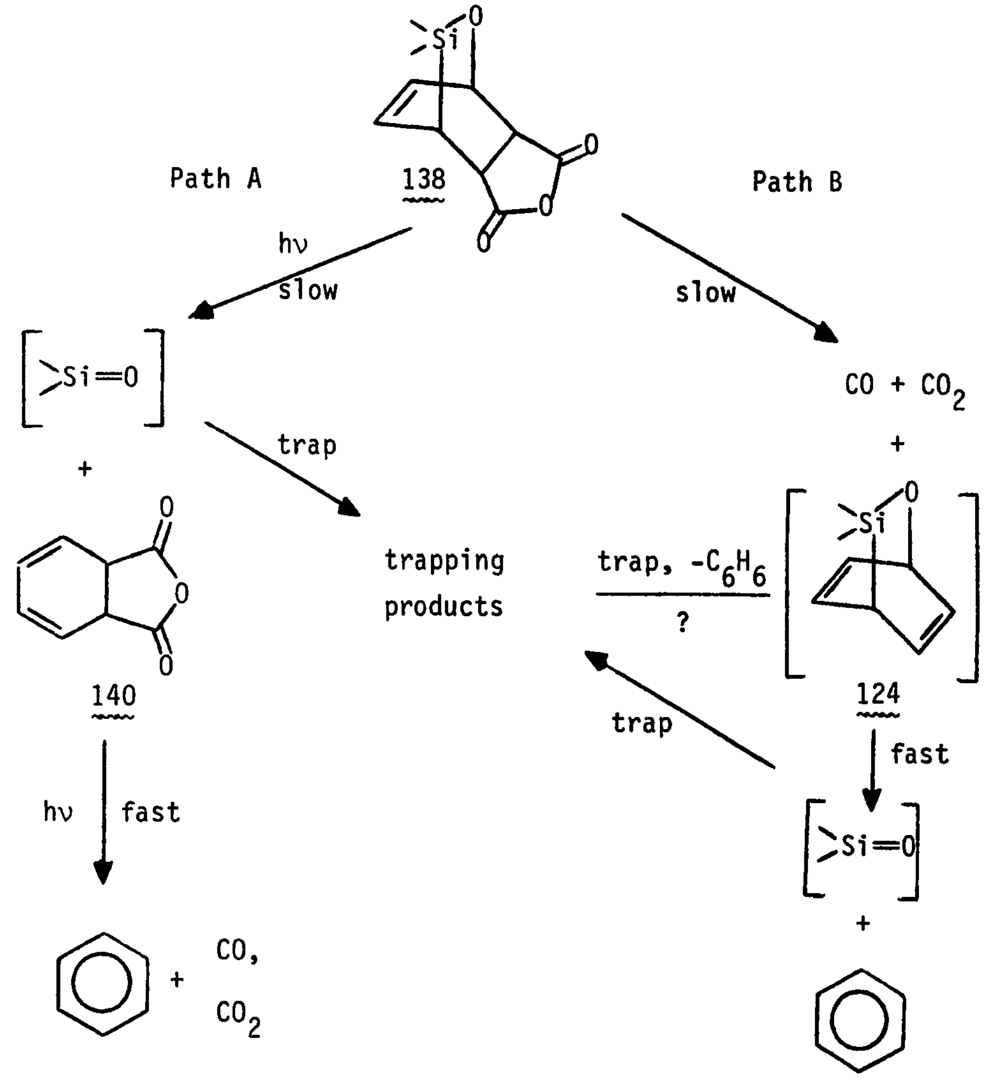


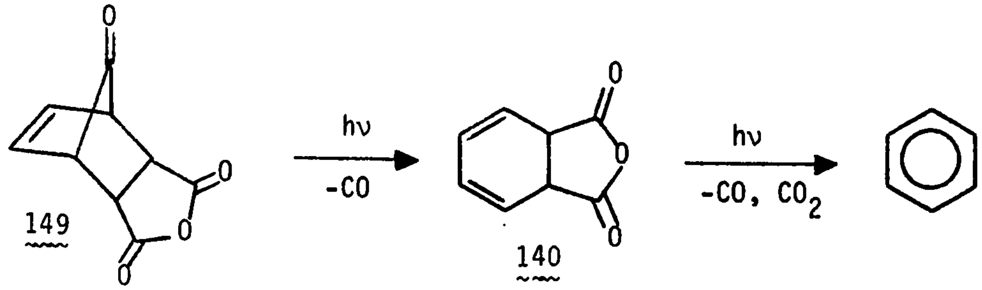
Figure 4. Photochemical decomposition of 138 with (X) no trap, and with (O) 7.0-fold excess of $Me_2Si(OMe)_2$ in diglyme

these pathways does not rigorously require the intermediacy of dimethylsilanone (Scheme 47). To be consistent with the relative rate data, the rate determining step of decomposition cannot be dependent upon a silanone trap. In path A, the rate determining step is extrusion of free dimethylsilanone and formation of 140. Although 140 was not isolated or observed, its photodecomposition to benzene, CO, and CO_2 was independently shown to occur much faster than photodecomposition of 138. Thus, 140 reacts faster than it is formed, and its lack of observation is not unexpected. Path A is also consistent with the reported initial photoextrusion of CO from 149 (70). In path B, the rate determining step is extrusion of CO and CO_2 with formation of 7-oxa-8-silabicyclo[2.2.2]-octadiene 124. Most probably, 124 rapidly decomposes to benzene and dimethylsilanone, but this is not a necessity. This intermediate can also function as a silanone-transfer agent, and in a bimolecular reaction with added traps, transfer the dimethylsilanone unit to form the observed products.

In conclusion, a considerable accumulation of evidence: trapping experiments, relative rate data, and analogous carbon chemistry suggest that the maleic anhydride-sila-α-pyran adduct 138 photoextrudes dimethylsilanone. This is the first reported example of direct photogeneration of a silanone. However, the possibility of product formation through a bimolecular silanone-transfer process, which does not involve free dimethylsilanone, cannot be eliminated. Nevertheless, the ability of 138 to function as a mild, convenient, high yielding silanone synthon, has definitively been demonstrated. (Currently Chapman and

Scheme 47


Path A
138
Path B
hν
slow
slow
Si=O
CO + CO$_2$
+
+
trap
trapping
products
trap, -C$_6$H$_6$
?
140
124
trap
fast
hν
fast
Si=O
+
+
CO,
CO$_2$

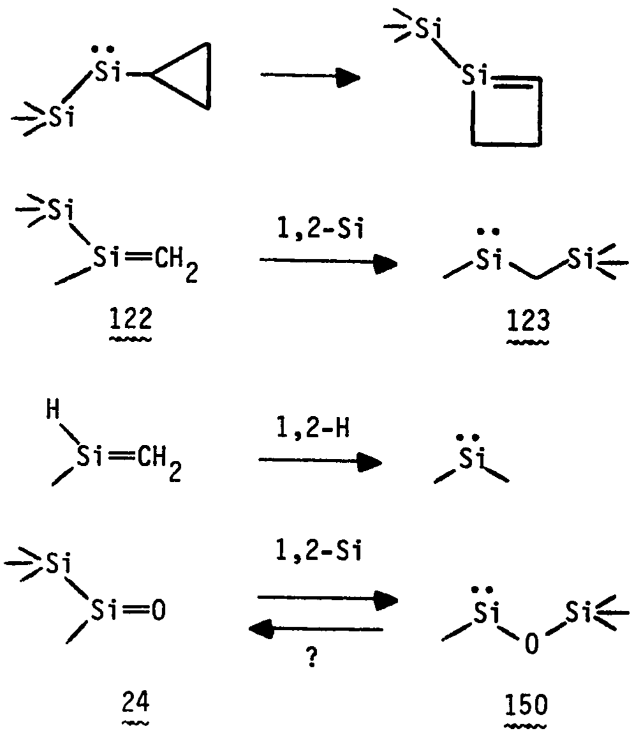

149
hν
-CO
140
hν
-CO, CO$_2$

coworkers (UCLA) are attempting direct observation of dimethylsilanone from the low temperature matrix photolysis of **138**.)

Examination of the Silanone to Silylene and Silylene to Silanone Rearrangements

Silene to silylene and silylene to silene rearrangements have recently been the focus of considerable research efforts. A silylene to silene isomerization has been reported by Barton and coworkers to occur upon high temperature generation of methyl(cyclopropyl)silylene (Scheme 48) (71). In addition, Barton and coworkers have shown that the high temperature generation of 1-silyl substituted silenes results in 1,2-silyl migration to afford silylenes (66, 72). Conlin and coworkers and Michl and coworkers have independently reported that silene to silylene isomerization can also occcur *via* a 1,2-hydrogen migration (73, 74). Although these latter reports have recently been questioned (72), it is clear that silenes and silylenes can occupy the same energy surface. In an effort to expand the limited knowledge of silanone chemistry and to determine if silanones and silylenes can occupy the same energy surface, the chemistry of methyl(trimethylsilyl)silanone was examined. Based on silicon's migratory aptitude and simple bond energy analysis, the isomerization of methyl(trimethylsilyl)silanone to methyl(trimethylsiloxy)silylene should be a facile process with a ΔH_{rxn} of at least 17 kcal/mole (75). Thus, the rearrangement of **24** to **150** should occur just as readily as the analogous rearrangement of **122** to **123**.

Scheme 48

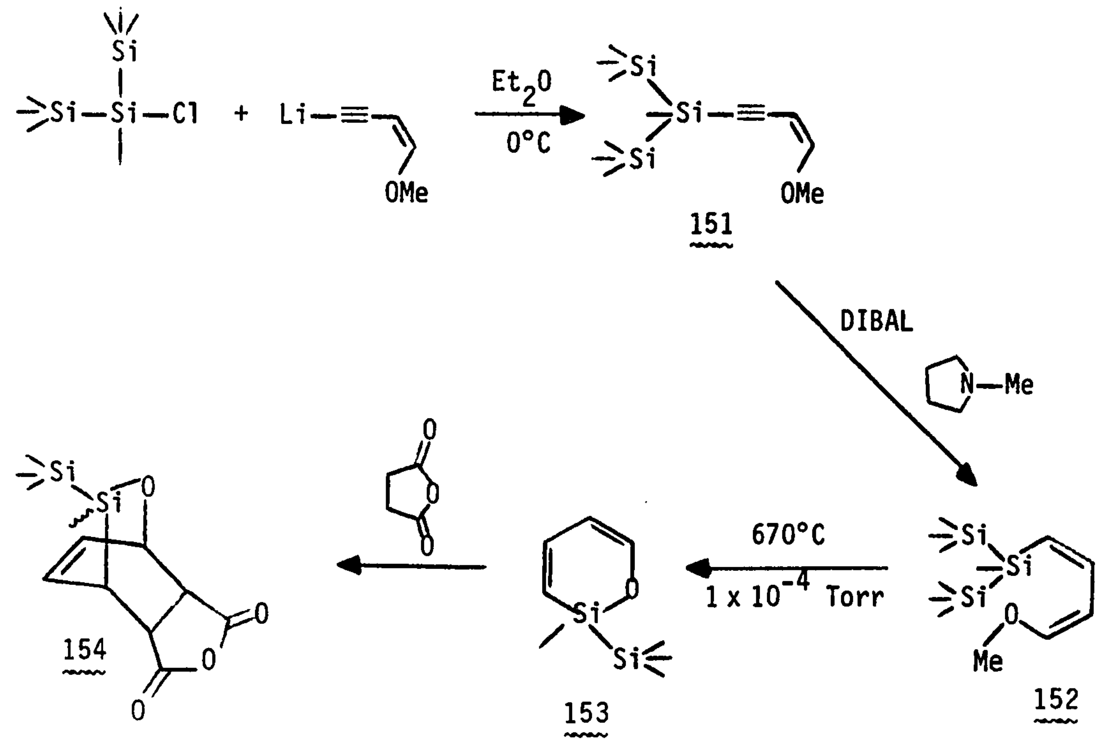


The generation of methyl(trimethylsilyl)silanone, in less than 5% yield, has been reported by Weber and Okinoshima in the reaction of DMSO with 2-phenylheptamethyltrisilane. Weber did not report, nor was he probably searching for, any isomerization of methyl(trimethylsilyl)-silanone (28). The low yields obtained in this reaction precluded its use in this study. To probe the possibility of isomerization of 24 to 150, or *vice versa*, a convenient reliable synthetic route to both intermediates was required. As described in the previous section of this dissertation, 1,1-dimethylsila-α-pyran or its maleic anhydride adduct are convenient thermal and photochemical precursors to dimethylsilanone. Methyl(trimethylsilyl)silanone should be available using similar methodology; consequently, the preparation of 1-methyl-1-trimethylsilylsila-α-pyran was undertaken (Scheme 49). Addition of bis(trimethylsilyl)methylchlorosilane to the anion of cis-4-methoxybut-1-yne-3-ene afforded a 67% yield of the coupling product 151. Unlike the reduction of 126 (Scheme 33), the carbon-carbon triple bond in 151 could not be reduced with disiamylborane. Surprisingly, treatment of 151 with disiamylborane resulted in hydrogenation of the double bond. The steric bulk around the triple bond apparently prohibits addition of the borane reagent. Using the greater affinity of aluminum reagents for carbon-carbon triple bonds offered a solution to this problem. Indeed, treatment of 151 with DIBAL furnished the desired diene 152 in 48% yield. Pyrolysis of 152 (650°C, 1 X 10^{-3} torr) resulted in a mixture of products from which 1-methyl-1-trimethylsilylsila-α-pyran was isolated by preparative gas chromatography. Addition of maleic anhydride to 153 afforded a 33% isolated yield of the crystalline adduct 154 as a mixture of syn and anti isomers.

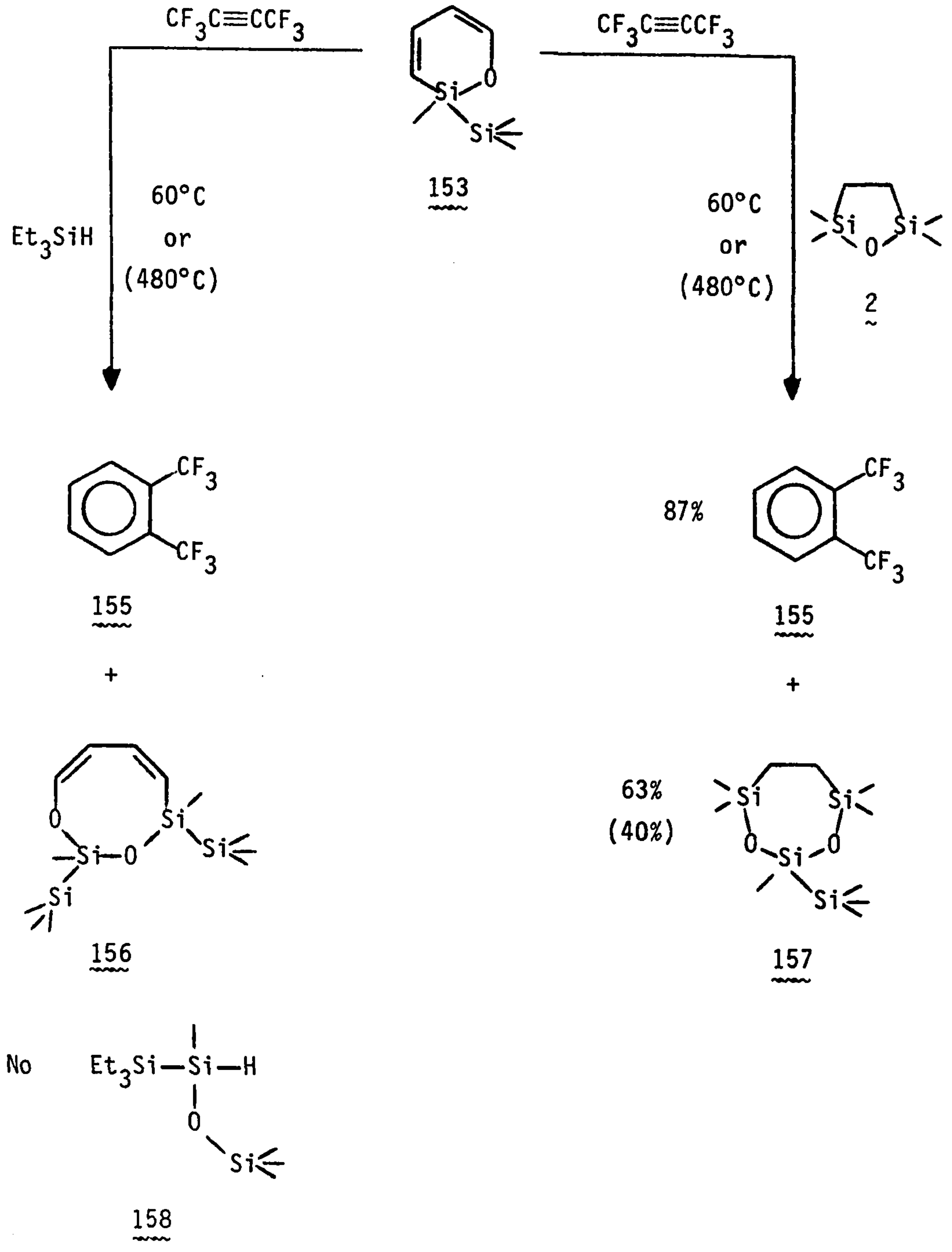
Barton and Wulff have previously shown that the addition of perfluoro-2-butyne to 1,1-dimethylsila-α-pyran resulted in products consistent with dimethylsilanone extrusion from an intermediate Diels-Alder adduct (Scheme 36) (64). In a similar fashion, the generation of methyl(trimethylsilyl)silanone from 153 was envisioned. To determine if methyl(trimethylsilyl)silanone underwent a 1,2-trimethylsilyl migration to methyl(trimethylsiloxy)silylene, Et_3SiH, a known silylene trap, was added to the reaction mixture (76-78). If silanone to silylene rearrangement occurred, insertion of the silylene into the Si-H bond of

Et_3SiH would afford 1,3,3,3-tetramethyl-1-triethylsilyldisiloxane. Thus, a solution of 153, excess perfluoro-2-butyne, and Et_3SiH was sealed in an NMR tube and heated at 60°C for 10 hours. Analysis of this reaction mixture by GC-MS revealed the presence of two major volatile products, 155 and 156 (Scheme 50). Disappointingly, no evidence for a product consistent with silylene trapping was obtained. It is apparent from the formation of 155 and 156 that methyl(trimethylsilyl)silanone was indeed generated. This was confirmed by repeating the reaction in identical fashion except Et_3SiH was replaced with the silanone trap 2. Again, two major volatile products were formed: 155 (87%) and 157 (63%), the expected product arising from insertion of 24 into a Si-O bond of 2.

Scheme 49



Scheme 50


CF3C≡CCF3
CF3C≡CCF3
153
Et3SiH
60°C
or
(480°C)
60°C
or
(480°C)
2
155
87%
155
+
+
156
63%
(40%)
157
No
Et3Si—Si—H
158

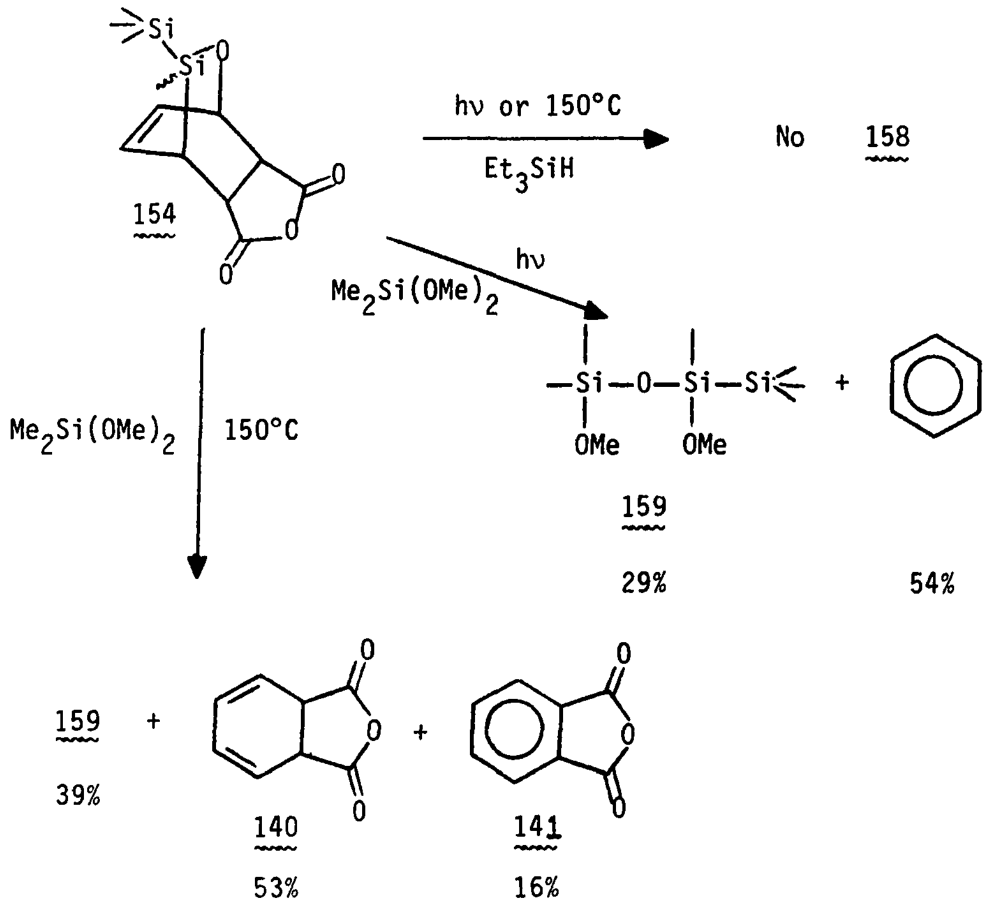
The apparent high temperature requirements of the silene to silylene isomerization observed by Barton and coworkers suggested that attempted isomerization of 24 to 150 be repeated at higher temperatures (66, 72). Thus, copyrolysis of 153 and Et_3SiH at 480°C with perfluoro-2-butyne as the carrier gas was performed. Analysis of the pyrolysate by GC-MS revealed that, in addition to unreacted starting material (approximately 20%), two major volatile components, 155 and 156, were formed. As before, no evidence for any silylene formation could be found. Repeating the pyrolysis in 2 once again confirmed that methyl(trimethylsilyl)-silanone had been generated (Scheme 50).

It is not clear from the literature that Et_3SiH is an efficient silylene trap in the gas phase. Thus, it was desired to repeat the pyrolysis of 153 in the presence of a proven gas phase silylene trap: a butadiene or an acetylene (79, 80). In a sense, this reaction had already been performed. A diene moiety and an acetylene were both present during the pyrolysis of 153 in perfluoro-2-butyne. Unfortunately, no evidence for trapping of 150 by the diene portion of 153 or by perfluoro-2-butyne was obtained. It is possible, however, that 153 and perfluoro-2-butyne are inefficient silylene traps, and it was deemed necessary to repeat the pyrolysis with an electron rich acetylene. Thus, a solution of 153 in benzene was pyrolyzed at 500°C with acetylene as the carrier gas. This experiment proved fruitless as at least twenty volatile products, none formed in significant yield, were observed by GC.

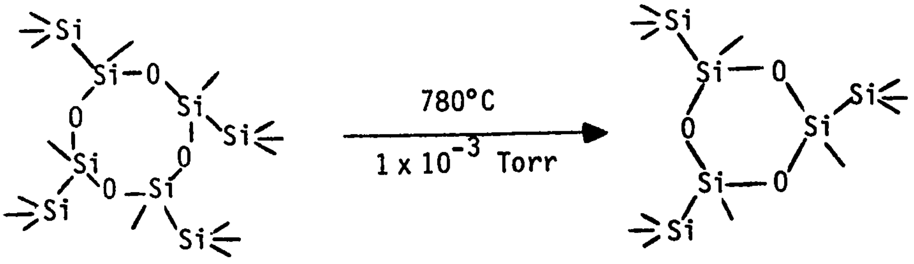
The potential isomerization of 24 to 150 was also examined by generation of 24 from photolysis or thermolysis of the Diels-Alder adduct 154. Evidence that 154 extrudes methyl(trimethylsilyl)silanone was obtained by chemical trapping. Irradiation of 154 in degassed dimethyldimethoxysilane afforded two major products: benzene (54%) and the silanone insertion product 159 (29%) (Scheme 51). Thermolysis of 154 in dimethyldimethoxysilane at 150°C also afforded 159 in 39% yield. In addition, 1,2-dihydrophthalic anhydride (53%) and phthalic anhydride (16%) were formed. To determine if the photolysis or thermolysis of 154 resulted in formation of methyl(trimethylsiloxy)silylene from isomerization of methyl(trimethylsilyl)silanone, both reactions were repeated in the presence of Et_3SiH. Analysis of the photolysate by GC-MS and NMR provided no evidence for the expected silylene trapping product 158. The major products from the photolysis of 154 in Et_3SiH were identified as benzene and 1,3,5-trimethyl-1,3,5-tris(trimethylsilyl)-cyclotrisiloxane 160. Similar results from thermolysis of 154 in Et_3SiH at 150°C were obtained. The major products, identified by GC only, were 1,2-dihydrophthalic anhydride and 160.

It is clear from trapping experiments that pyrolysis of 154 with perfluoro-2-butyne at 480°C did result in methyl(trimethylsilyl)silanone formation. It was desired to generate methyl(trimethylsilyl)silanone at still higher temperatures in the hope of coercing an isomerization to methyl(trimethylsiloxy)silylene. Unfortunately, the use of 153 as a source of 24 at temperatures greater than 500°C led to reduced yields and complex reaction mixtures. Generation of 24 from the adduct 154 at high temperatures also led to complex product mixtures. Pyrolysis of 154 in a benzene solution at 600°C in the presence of dimethyldimethoxysilane or with butadiene as a carrier gas afforded neither methyl(trimethylsilyl)-silanone or methyl(trimethylsiloxy)silylene trapping products as determined by GC-MS. Thus, a different high temperature method of generating methyl(trimethylsilyl)silanone was required.

Scheme 51

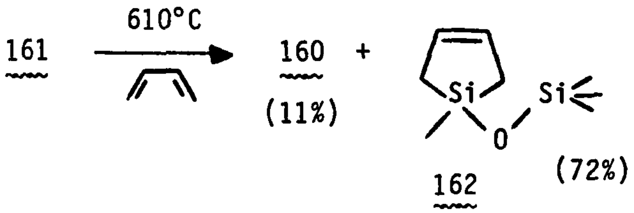


The high temperature decomposition of D_4 to D_3 and dimethylsilanone has previously been reported by Davidson and Thompson (18, 19). Drawing analogy from this work generation of 24 should be possible by thermal decomposition of its D_4 analog. 1,3,5,7-Tetramethyl-1,3,5,7-tetrakis-(trimethylsilyl)cyclotetrasiloxane, 161, was prepared in 44% yield by a slow hydrolysis of 1,1-dichlorotetramethyldisilane. Pyrolysis of 161 (780°C, 1 X 10^{-4} torr) resulted in a complex reaction mixture from which 161, the D_3 analog 160, and several isomers of 161 and 160 were identified by GC-MS as the major products. Similar results were obtained upon pyrolysis of 161 (610°C) in a N_2 flow.



161 160

The observance of 160 is suggestive of methyl(trimethylsilyl)-silanone extrusion from 161. The potential isomerization of 24 to methyl(trimethylsiloxy)silylene was examined by repeating the pyrolysis of 161 in the presence of butadiene. Thus, 161, dissolved in benzene, was pyrolyzed at 610°C using butadiene as the carrier gas. Surprisingly, analysis of the pyrolysate by GC-MS revealed only three major silicon containing components: recovered starting material (67% completion), the D_3 analog 160 (11%), and 1-methyl-1-trimethylsiloxy-1-silacyclopent-3-ene 162 (72%, based on 161 decomposing to one equivalent of 150). Isolation of 162 by preparative gas chromatography enabled complete structural identification.



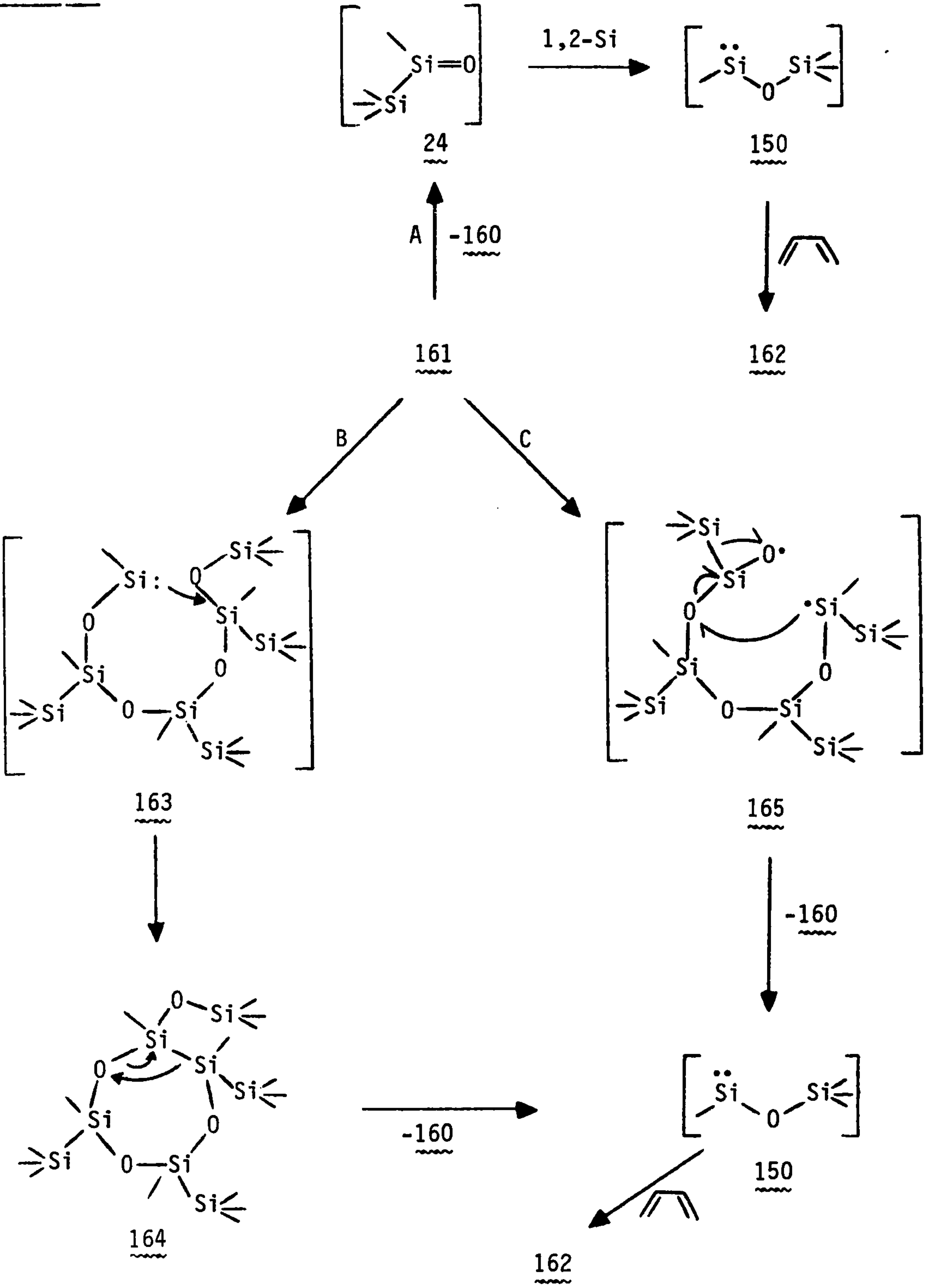
In an independent experiment, it was shown that an identical pyrolysis of 160 (610°C, butadiene flow, 91% completion) afforded, among numerous unidentified products, an 11% yield of 162. Thus, the low yield of 160 obtained in the pyrolysis of 161 can be attributed to its instability under the conditions of reaction. In addition, the high yield of 162 obtained in the pyrolysis of 161 is somewhat misleading and should more correctly be calculated based on 161 decomposing to more than one equivalent of methyl(trimethyl(siloxy)silylene.

The formation of the silacyclopentene 162 in the pyrolysis of 161 is strong evidence for the intermediacy of methyl(trimethylsiloxy)-silylene. Assuming 161 initially decomposed to methyl(trimethylsilyl)-silanone, it appears that a silanone to silylene isomerization *via* a 1,2-silyl migration has occurred. Unfortunately, trapping of methyl(trimethylsilyl)silanone could not be achieved. Pyrolysis of 161 (610°C, N_2 flow) in the presence of dimethyldimethoxysilane did not furnish any of the expected silanone insertion product. Although this result can be explained by 24 intramolecularly isomerizing to 150 faster than intermolecular insertion into dimethyldimethoxysilane, it compels consideration of alternative mechanisms.

Based on literature precedent, three mechanisms warrant consideration (Scheme 52). In path A, an elimination of methyl(trimethylsilyl)-silanone from 161, in a fashion analogous to that previously reported for D_4 (18, 19), followed by 1,2-silyl migration to 150 and subsequent trapping, affords 162. In path B, initial α-elimination affords silylene 163, which undergoes intramolecular insertion into a Si-O bond to yield 164. A second α-elimination then furnishes 150, which is again trapped by butadiene. Athough α-eliminations and Si-O bond silylene insertions are precedented, it seems unlikely that the silylene 163 would insert preferentially into the Si-O bond required to form the 7-membered ring 164 or that the silylene 163 would not be intercepted by butadiene. In path C, initial cleavage of a Si-O bond affords diradical 165 which can undergo 1,2-silyl migration and concomitant ring closure to yield 150 and 160. This path is similar to an alternative mechanism offered by Barton and coworkers for the silene to silylene isomerization (72). However, this path requires the initial cleavage of a Si-O bond, the strongest bond in the molecule, and can, therefore, be eliminated.

Although path A, path B, and path C cannot be rigorously distinguished with the available data, it appears most likely that the decomposition of 161 to 150 does indeed occur *via* path A and initial formation of methyl(trimethylsilyl)silanone. Thus, these results would provide the first example of a silanone to silylene isomerization. The complex pyrolysates obtained upon pyrolysis of 161 in the absence of butadiene suggest that methyl(trimethylsiloxy)silylene reacts further to afford numerous products. This suggestion is verified in the following study.

Scheme 52

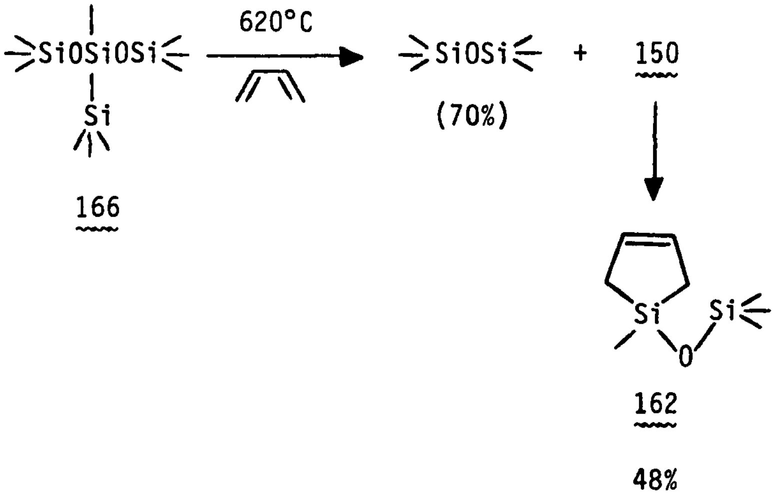


The potential isomerization of methyl(trimethylsiloxy)silylene to methyl(trimethylsilyl)silanone *via* a 1,2-silyl migration was also investigated. This isomerization is formally an insertion of a silylene into a Si-O bond. Although such insertions are well-precedented, this particular intramolecular insertion has not been reported (26). The preparation of methyl(trimethylsiloxy)silylene by a thermally induced α-elimination of hexamethyldisiloxane from bis-(trimethylsiloxy)trimethylsilylmethylsilane **166** was envisioned. Thermal α-elimination of a silyl alkoxide from a silicon center has become a standard method of preparing silylenes (81). Slow addition of H_2O to a stirring solution of 1,1-dichlorotetramethyldisiloxane and excess trimethylchlorosilane afforded a 31% yield of **166** which was isolated by preparative gas chromatography.

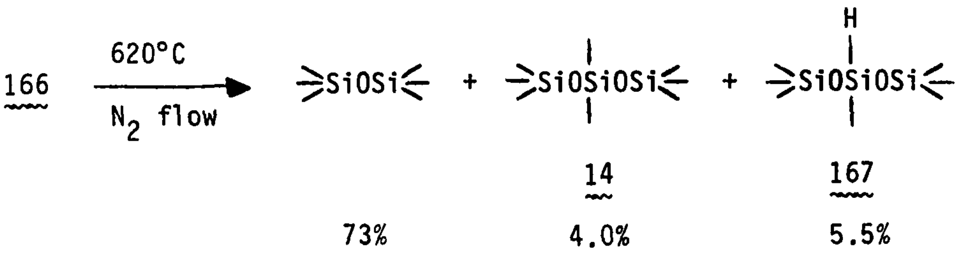
To determine that **166** would generate the desired silylene, its pyrolysis was initially carried out in the presence of a silylene trap: butadiene. At 620°C (N_2 flow), the pyrolysis of **166** resulted in two major silicon containing products which were isolated by preparative gas chromatography and identified as hexamethyldisiloxane (70%) and the silylene addition product **162** (48%) (Scheme 53). Thus, it appears that **166** does indeed afford methyl(trimethylsiloxy)silylene.

To search for the possible isomerization of **150** to **24**, pyrolysis of **166** (620°C, N_2 flow) was carried out in the absence of a silylene trap. This pyrolysis proved to be a much more complex reaction. Although hexamethyldisiloxane was formed in 73% yield, only small amounts of other volatile silicon containing products were produced. The two highest yielding products could be isolated and were identified as octamethyltrisiloxane 14 (4.0%) and 1,1,1,3,5,5,5-heptamethyltrisiloxane 167 (5.4%) (Scheme 54). The yield of 14 and 167 was increased slightly to 10% and 14%, respectively, by flash vacuum pyrolysis (850°C, 1 X 10^{-4} torr) of 166 in excess hexamethyldisiloxane. In either pyrolysis, no evidence of methyl(trimethylsilyl)silanone intermediacy was obtained.

Scheme 53



Scheme 54



Although there was no indication of 150 rearranging directly to 24, the formation of 14 and 167 suggested that an indirect rearrangement to a silanone may have occurred. The origin of 14 and 167 is most easily rationalized from dimethylsilanone and methylsilanone insertion into hexamethyldisiloxane. Barton and coworkers have recently reported that the β-silyl silylene 123 undergoes γ-C-H bond insertion to yield the 1,3-disilacyclobutane 168 (Scheme 55) (82). If a similar γ-C-H bond insertion occurred with 150, the 1,2-disilaoxetane 169 would result (Scheme 56). Decomposition of 169 could occur along two pathways: path A, with formation of dimethylsilanone and 1-methylsilene, or path B, with formation of methylsilanone and 1,1-dimethylsilene. Insertion of dimethylsilanone and methylsilanone into a Si-O bond of hexamethyldisiloxane then yields the observed disiloxanes 14 and 167, respectively.

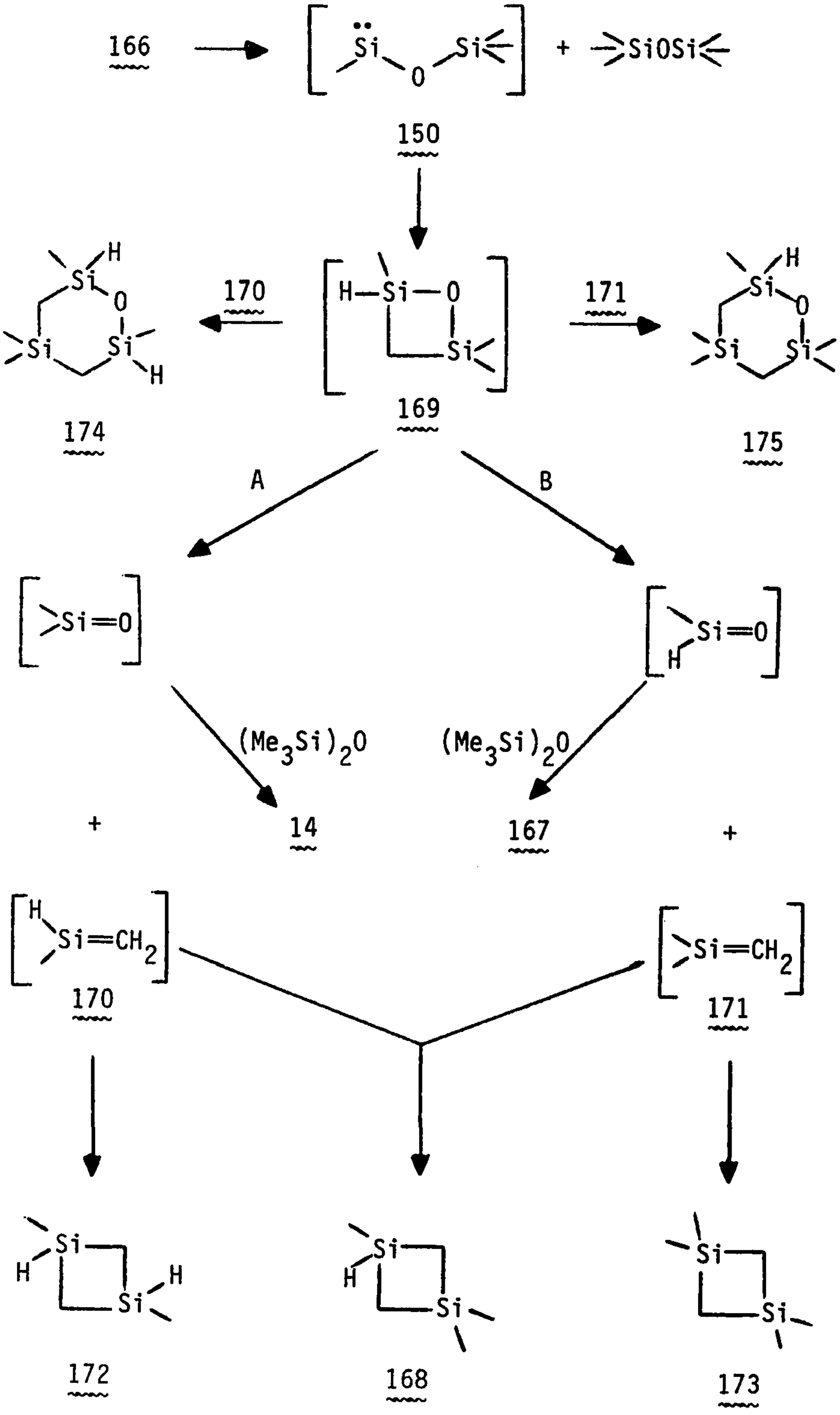
Scheme 55

123

168

The fate of silenes 170 and 171 is presumably dimerization to the three possible 1,3-disilacyclobutanes: 172, 168, and 173 (83). The volatility of these dimers made their detection in the previously performed pyrolyses difficult. However, by slow vacuum pyrolysis of 166 (850°C, 1 X 10^{-4} torr), the formation of all three dimers (albeit in trace amounts) was confirmed by comparative GC-MS. This experiment also

Scheme 56


166
150
+
169
170
171
174
175
A
B
(Me$_3$Si)$_2$O
(Me$_3$Si)$_2$O
+
14
167
+
170
171
172
168
173

provided evidence for the intermediacy of 169. Tumey has previously reported that 2,2,4,4-tetramethyl-2,4-disilaoxetane trapped 1,1-dimethylsilene by Si-O bond insertion to yield 2,2,4,4,6,6-hexamethyl-2,4,6-trisilapyran (Scheme 29) (14). In similar fashion, 170 and 171 were trapped by the 2,4-disilaoxetane 169 to yield 174 and 175. Because 174 and 175 were formed in trace amounts, their structures were deduced solely from GC-MS data.

In summary, it is apparent that methyl(trimethylsiloxy)silylene does not isomerize to methyl(trimethylsilyl)silanone. This is not unexpected considering the large positive enthalpy of isomerization. The fate of methyl(trimethylsiloxy)silylene appears to be γ-C-H bond insertion to yield a 1,3-disilaoxetane which decomposes to silanones and silenes. Thus, an indirect silylene to silanone and silene rearrangement was observed. The formation of these four types of reactive intermediates readily explains the low yields and complex pyrolysates observed in this study.

Attempted Generation of Dimethylsila-α-pyran: Photochemistry of Silicon Substituted Furans, Pyrroles, and Thiophenes

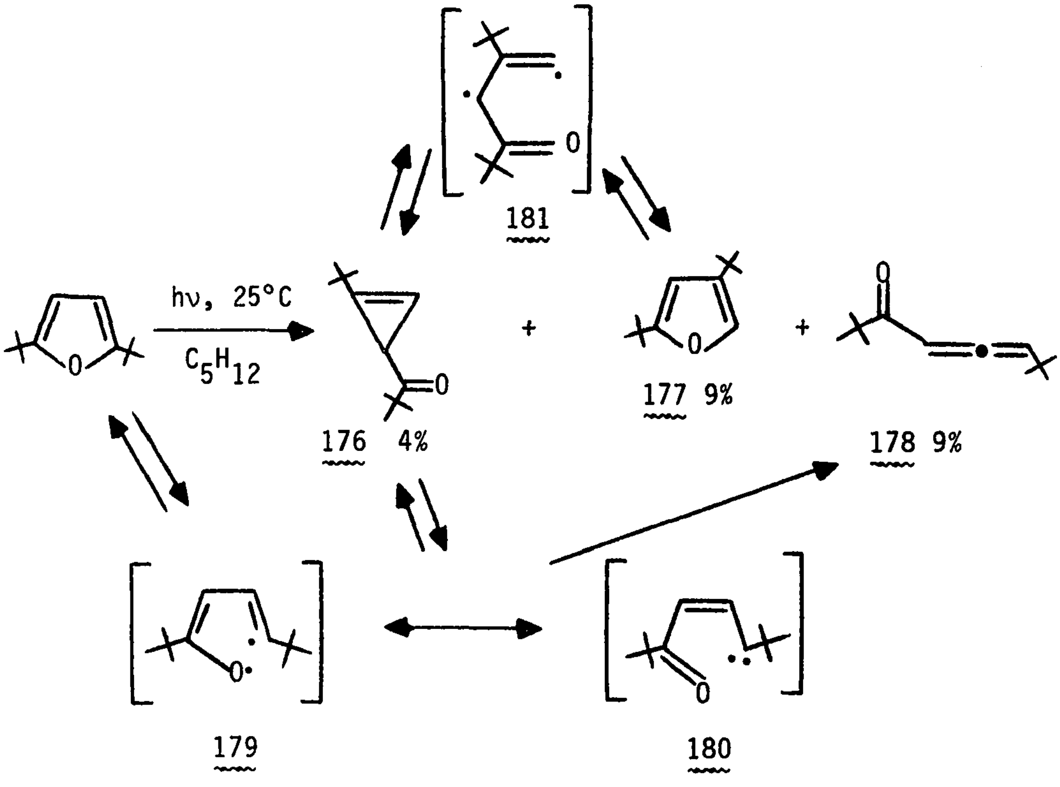
Before describing the goals and results of this section, a brief summary on furan photochemistry is warranted.

The majority of work in furan photochemistry was completed in the late 1960s and early 1970s principally by two research groups (84-95). A complete historical discussion on this work is beyond the scope of this dissertation (7). Fortunately, all important concepts in furan photochemistry can conveniently be illustrated with one example. In 1971, van Tamelen and Whitesides reported that irradiation of 2,5-di-*t*-butylfuran in pentane with a medium pressure mercury lamp resulted in considerable amounts of polymer and three volatile products isomeric with starting material: **176**, **177**, and **178** (Scheme 57) (85). Similar to other reported furan photolyses, these products are throught to arise from initial C-O bond cleavage and formation of 1,5-diradical **179**. This diradical is a resonance structure of the vinyl carbene **180**. Closure of the diradical, or a vinyl carbene rearrangement, yields directly the 3-acylcyclopropene **176**. Under the conditions of irradiation, **176** is unstable, and cleavage of the cyclopropene ring occurs. Thus, starting material is reformed through **179**, or 2,4-di-*t*-butylfuran is formed through diradical **181**. The allenyl ketone **178** arises from either a 1,2-hydrogen migration in **179** or from a C-H bond insertion in **180**.

Other generalizations on furan photochemistry not apparent from this example can be made. The irradiation of monosubstituted furans, *i.e.* 2-methyl furan, always results in C-O bond cleavage at the carbon which bears the substituent. In addition to the previously discussed ring cleavage reactions of acylcyclopropenes, aldehydic acylcyclopropenes can undergo decarbonylation to cyclopropenes. The low yield of volatile products obtained in the irradiation of 2,5-di-*t*-butylfuran is common to all furan photolyses. Finally, it should be stated that the vinyl carbene resonance form **180** is not often considered. Evidence for the carbene comes from formation of allenes in the photolysis of 2,5-

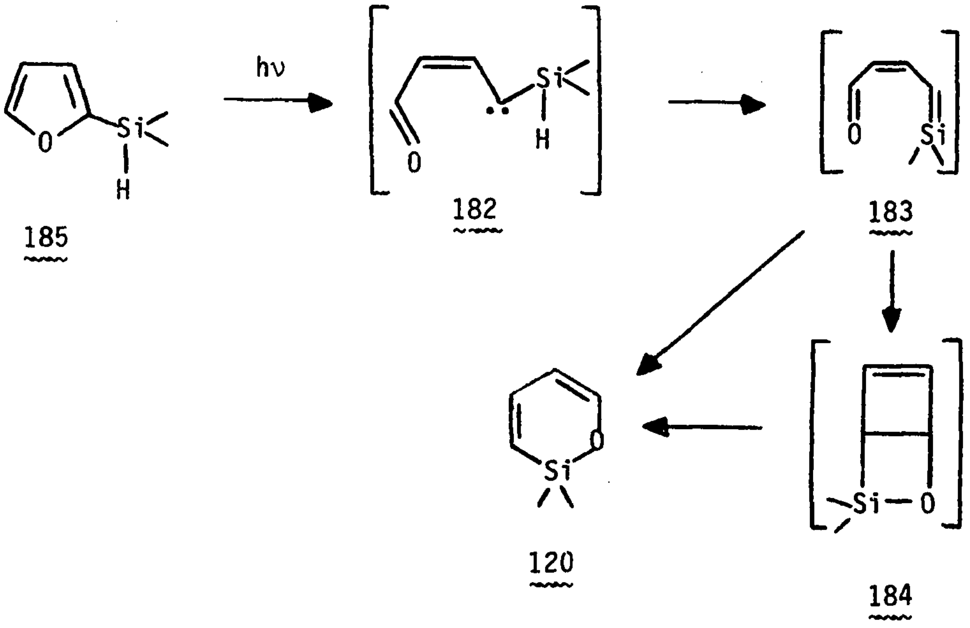
disubstituted furans and other examples of apparent intramolecular C-H insertion products. No evidence for intermolecular trapping of the carbene has been reported.

Scheme 57



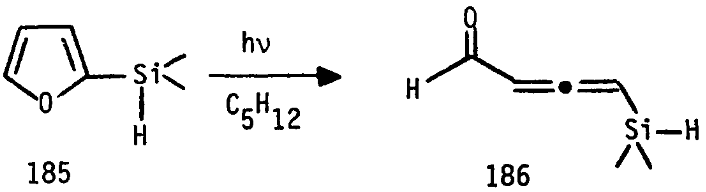
In spite of the low yields and complex product mixtures, it was desired to utilize furan photochemistry for synthetic purposes. By intramolecular trapping of the initially formed intermediate, an alternate route to the sila-α-pyran ring system was envisioned (Scheme 58). Irradiation of 2-(dimethylsilyl)furan was predicted, based on literature precedent, to yield vinyl carbene 182. Intramolecular insertion of this carbene into the adjacent Si-H bond would then afford silene 183. Although this specific reaction is unprecedented, the insertion of carbenes into Si-H bonds is well known (96). Once formed, the silene 183 would be expected to rapidly close to dimethylsila-α-pyran. Closure of 183 to silaoxetane 184, followed by ring opening, would also yield 120.

Scheme 58



2-(Dimethylsilyl)furan 185 was readily prepared by lithiation of furan with *n*-butyllithium followed by the addition of dimethylchlorosilane. The photolysis of a 1% solution of 185, in pentane using a high pressure mercury lamp, was carried out under an argon atmosphere. The reaction progress was followed by hydrogen NMR and IR. After 2 hours of irradiation, considerable polymer formation had occurred. However, an examination of the crude reaction mixture by NMR surprisingly showed only one volatile product had been formed. This product proved impossible to isolate, but, based on the following partial spectral data, a structure was tentatively assigned as 186 (Scheme 59): NMR (pentane) δ 9.1 (m, 1H, CHO, hν at 5.2 collapses to s), 5.2 (m, 2H); IR (pentane) 2120 (SiH), 1930 (C=C=C), and 1690 cm^{-1} (C=O). Assuming the allene 186 was the product of this reaction, its formation in a remarkable 53% yield, based on starting material consumed, was calculated. The extreme cleanness, the relative high yield, and the formation of only one volatile product in this photolysis are unprecedented in previously reported furan photochemistry. Although it was evident that the desired dimethylsila-α-pyran had not been formed, the novel features of this reaction dictated further investigation.

Scheme 59



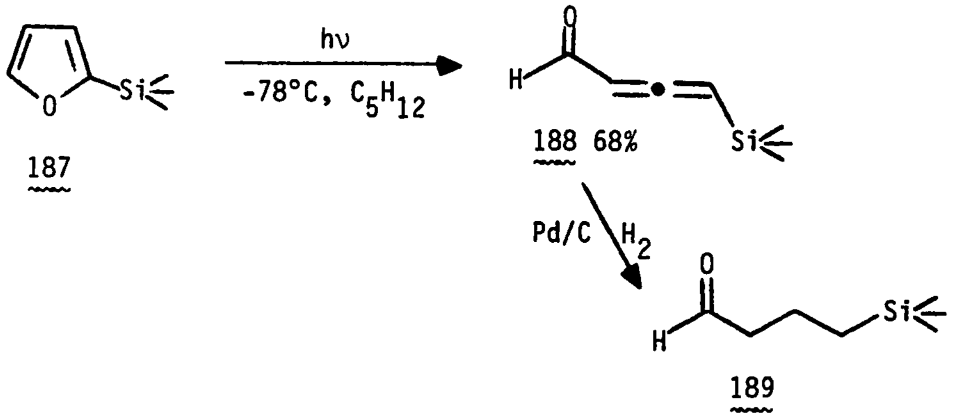
185

186

53%

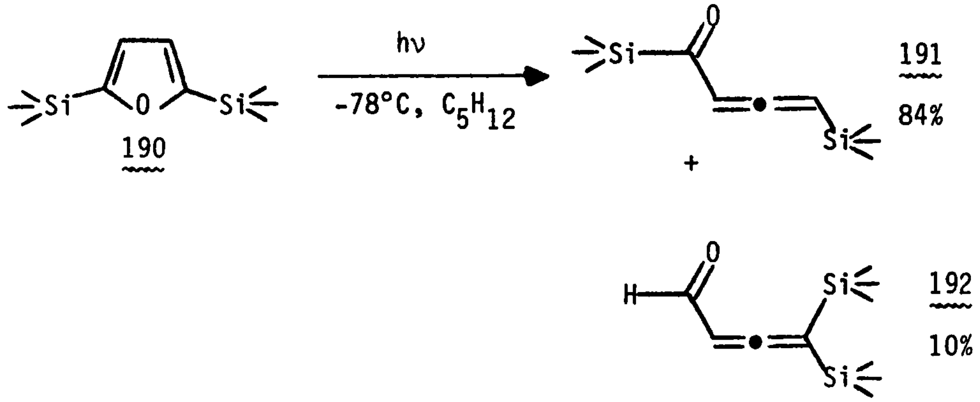
In order to examine the generality of this photochemistry, several other silicon-substituted furans were photolyzed. It became evident after a few attempts that polymer formation and secondary thermal reactions could be thwarted if lower irradiation temperatures were used. Thus, the photolysis of 2-(trimethylsilyl)furan 187 was performed at -78°C. Similar to the photolysis of 185, irradiation of 187 for 2 hours resulted in only one volatile product which was identified as 4-trimethylsilyl-2,3-butadienal 188 (Scheme 60). Based on unreacted starting material (13%), a 68% yield of 188 was obtained. 4-Trimethylsilyl-2,3-butadienal was initially identified on the basis of its IR and NMR only. Like the allene 186, all attempts to isolate 188 resulted in polymer formation and decomposition. This is not surprising since previously reported allenyl aldehydes and allenyl ketones are also unstable and polymerize readily (97-99). The structure of 188 was finally confirmed by *in situ* hydrogenation to 4-(trimethylsilyl)-butanal 189, which was isolated and completely characterized.

Scheme 60



Photolysis of 2,5-bis(trimethylsilyl)furan 190 at -78°C in pentane also resulted in clean product formation. After 2 hours of irradiation, 65% of 190 had reacted, and only two volatile products had formed: 1,4-bis(trimethylsilyl)-2,3-butadienone, 191, (84%) and 4,4-bis(trimethylsilyl)-2,3-butadienal, 192, (10%) (Scheme 61). The structure of 192 was deduced from spectral data obtained on the crude reaction mixture: NMR (pentane) δ 9.42 (d, 1H, J = 8 Hz), 5.15 (d, 1H, J = 8 Hz); IR (pentane) 1910 and 1675 cm^{-1}. After considerable effort, 191 was isolated and purified by repeated low temperature crystallization from pentane. Complete structural characterization was then possible: NMR (CCl_4) δ 5.59 (d, 1H, J = 7 Hz), 5.32 (d, 1H, J = 7 Hz), 0.22 (s, 9H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 235.4, 216.8, 96.9, 87.6, -1.0, -1.5; IR (neat) 1942 and 1595 cm^{-1}; calculated for $C_{10}H_{20}OSi_2$ (M^+) m/e 212.1053, measured m/e 212.1059.

Scheme 61



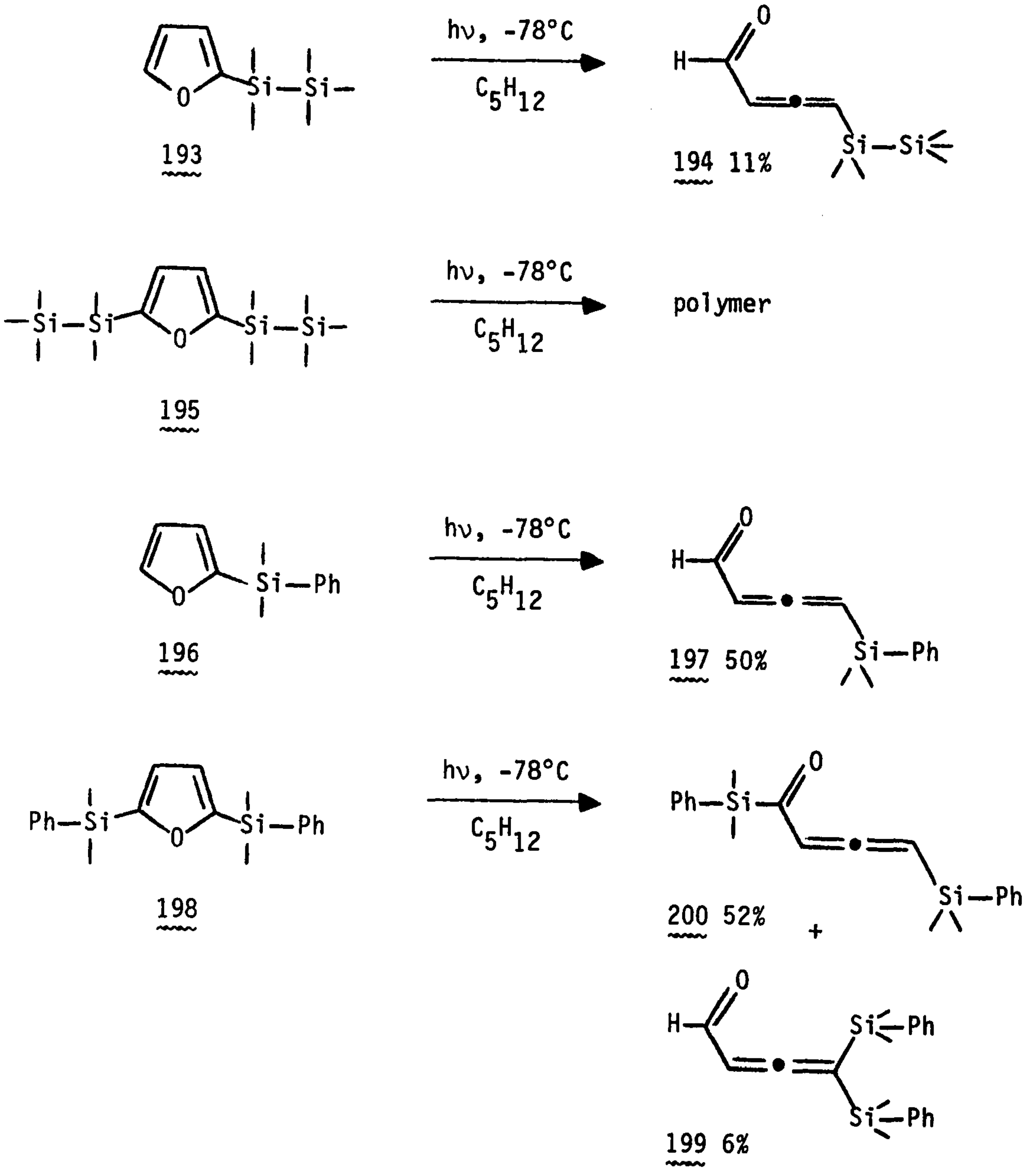
Before 191 was isolated by low temperature crystallization, several other more common methods of isolation and characterization were attempted. Distillation, preparative chromatography, or catalytic hydrogenation of impure 191 did not result in successful identification, but novel isomerizations occurred. These rearrangements prompted an investigation into the thermal chemistry of 191. The results of this investigation will be presented in the following section.

It is obvious from the preceding results that silicon substitution has a remarkable effect on the photochemistry of furans. This effect is dramatically seen by comparison of 2,5-di-*t*-butylfuran photochemistry (Scheme 57) with the photochemistry of the analogous silicon substituted furan, 2,5-bis(trimethylsilyl)furan (Scheme 61). In order to probe for the cause of this effect, several other silicon-substituted furans were photolysed. The results from these photolyses are presented in Scheme 62.

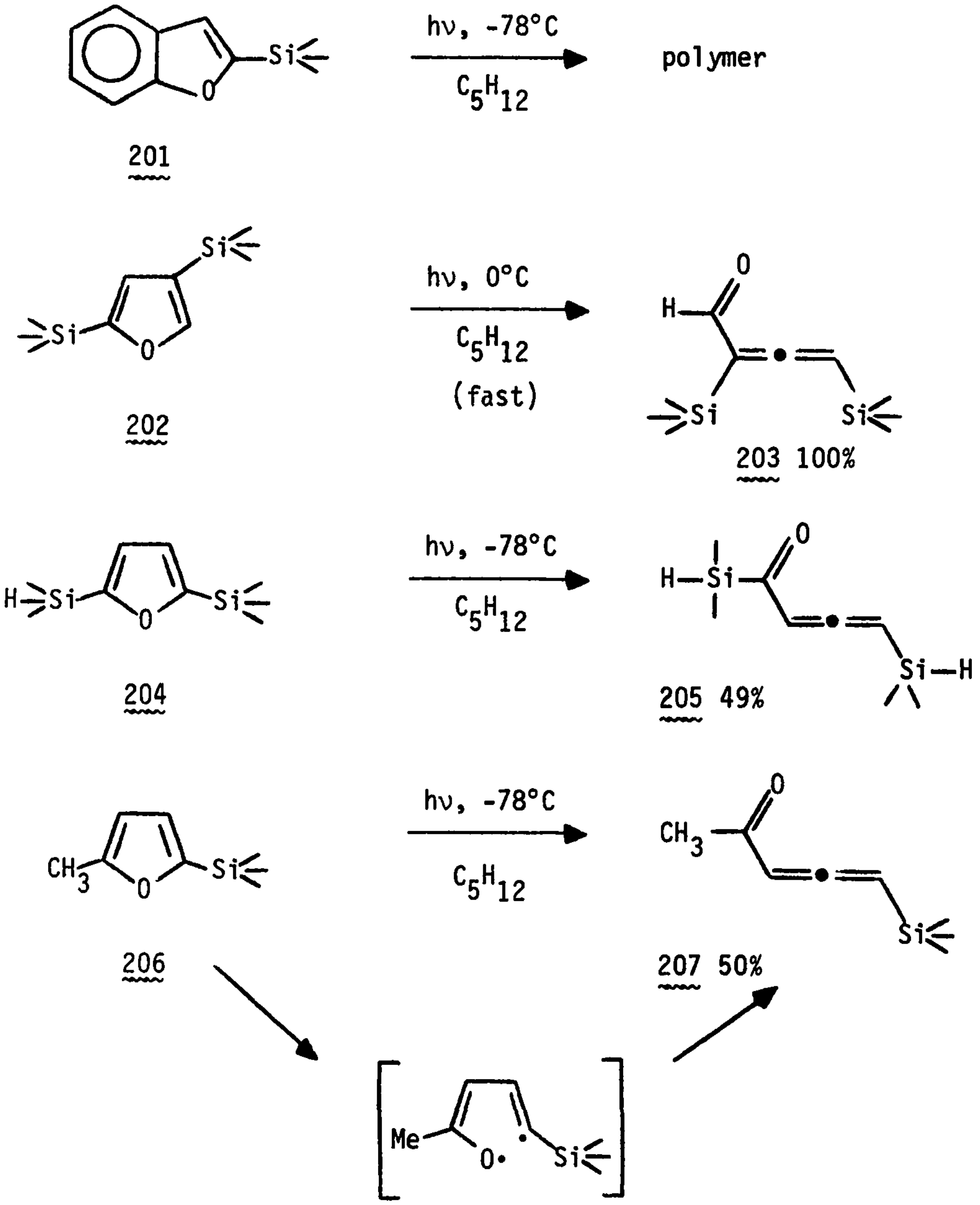
Irradiation of 2-(pentamethyldisilyl)furan **193** afforded, in low yield, the expected allenyl aldehyde **194**. Unlike the irradiation of **187** and **190**, however, considerable polymer formation was observed. Irradiation of 2,5-bis(pentamethyldisilyl)furan **195** also yielded considerable amounts of polymer, and only a trace amount of an allene could be detected. These results can be attributed to apparent facile Si-Si bond cleavage in **193** and **195**. The silyl radicals formed from this cleavage may then undergo polymerization. Evidence that Si-Si bond cleavage occurs was obtained by repeating the irradiation of **193** in the presence of MeOH. Analysis of this photolysate by GC-MS revealed the presence of the silyl radical trapped products: 2-(dimethylsilyl)furan and 2-(dimethylmethoxysilyl)furan.

The addition of a phenyl chromaphore to the system does not drastically alter the course of the photolysis. Irradiation of 2-(dimethylphenylsilyl)furan **196** yielded the corresponding allenyl aldehyde **197**, and irradiation of 2,5-bis(dimethylphenylsilyl)furan **198** afforded the corresponding allenyl aldehyde **199** and allenyl

Scheme 62



Scheme 62 (continued)



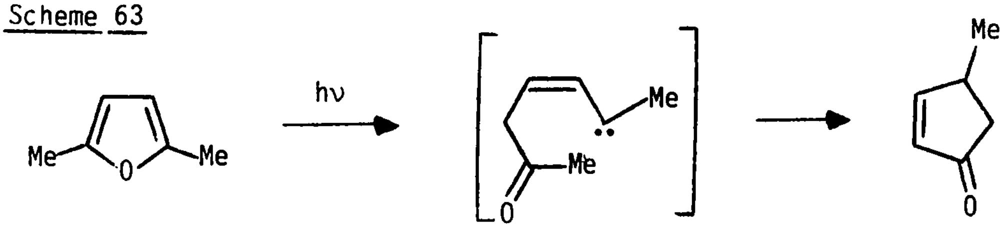
ketone 200. Thus, 196 and 198 react similarly to 187 and 190, although slightly lower yields are obtained.

2-(Trimethylsilyl)benzofuran 201, predictably, did not lose aromaticity and rearrange to an allenyl ketone upon photolysis. Indeed, analysis of the photolysate by NMR and gas chromatograph showed no volatile product had been formed.

A surprisingly rapid and high yielding reaction ensued upon irradiation of 2,4-bis(trimethylsilyl)furan 202. 2,4-Bis(trimethylsilyl-2,3-butadienal, 203, was formed in quantitative yield as determined by NMR.

The photolysis of 2,5-bis(dimethylsilyl)furan 204 and 2-trimethylsilyl-5-methylfuran 206 were run in an attempt to intramolecularly trap a presumed vinyl carbene intermediate. One of the most convincing pieces of evidence that vinyl carbenes are formed in the irradiation of alkyl-substituted furans was reported by Srinivasan and Boué (100). Photolysis of 2,5-dimethylfuran (12% conversion) afforded a 26% yield of 4-methylcyclopent-2-enone 208 (Scheme 63). Srinivasan and Boué suggested that 208 arose by insertion of the vinyl carbene 209 into a methyl C-H bond. It was hoped that similar Si-H bond or C-H bond insertion would occur upon photolysis of 204 and 206, respectively. Unfortunately, irradiation of either 204 or 206 did not yield any products analogous to 208. Photolysis of 204 afforded 1,4-bis(dimethylphenylsilyl)-2,3-butadienone 205 (49%) and polymer. Photolysis of 206 yielded 1-methyl-4-trimethylsilyl-2,3-butadienone 207 (50%) as the only observable volatile product. The exclusive formation of 207 in this reaction suggests that initial C-O bond cleavage in **206** occurred only at the silicon substituted carbon. Hence, silicon substitution has a strong directive influence on the photoinduced furan rearrangement.

Scheme 63



209 **208**

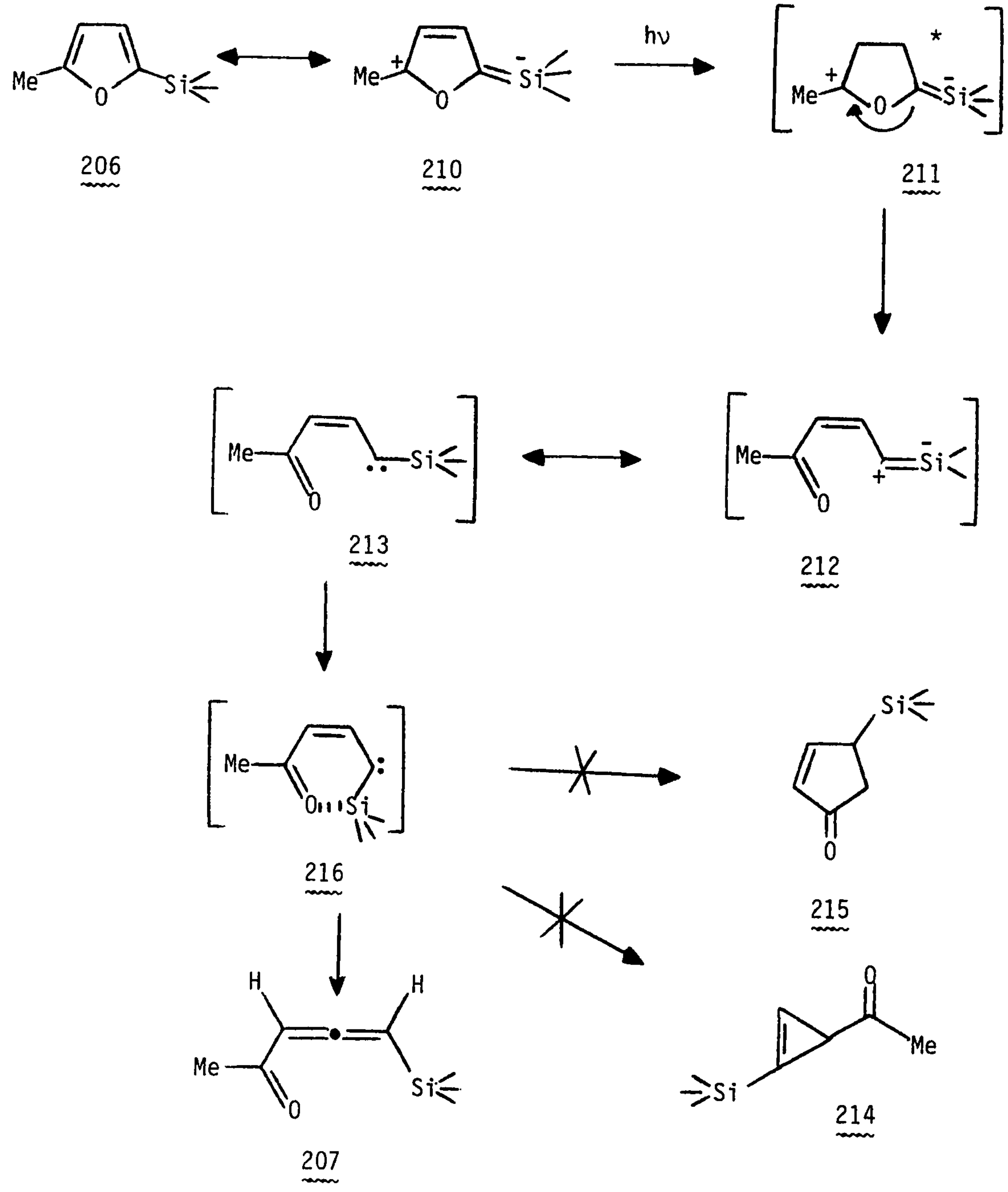
Intermolecular trapping of the presumed vinyl carbene intermediate was attempted by photolysis in MeOH or in Et_3SiH. Irradiation of 2-(trimethylsilyl)furan in either MeOH or Et_3SiH yielded no O-H bond or Si-H bond insertion products. As in the photolysis of **187** with no added trap, 4-trimethylsilyl-2,3-butadienal was the only volatile product observed. The addition of oxygen to the photolysis of 2,5-bis(trimethylsilyl)furan also did not alter the course of its previously described isomerization. Formation of 1,4-bis(trimethylsilyl)-2,3-butadienone still occurred in similar yields.

The inability to detect any intermediate in the photolysis of these silyl-substituted furans hinders definitive mechanistic interpretation. It is clear that the seemingly subtle change of silicon substitution on the furan ring results in cleaner photolyses, exclusive formation of allenes, and selective ring opening. However, it does not appear probable that mere silicon substitution could drastically alter the previously accepted mechanism of photoinduced furan rearrangement.

Silicon-substituted furans and alkyl-substituted furans have virtually indentical ultraviolet absorption spectra and extinction coefficients: 190 λ max (CH_3CN) 233 (17,588); 2,5-di-*t*-butylfuran λ max (CH_3CN) 220 (10,000). Thus, it would appear likely that, similar to alkyl-substituted furans, the irradiation of silicon-substituted furans results in initial C-O bond cleavage. A mechanism, illustrated with the photolysis of 2-trimethylsilyl-5-methylfuran, that is consistent with the previously discussed results is offered in Scheme 64. Rational for this mechanism is presented below.

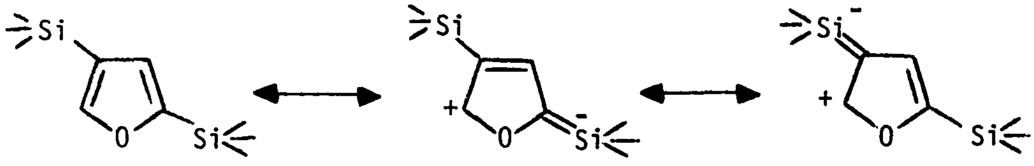
It is well documented, and easily observed by NMR, that silicon exhibits a strong electron withdrawing effect when directly bonded to furan rings (101, 102). Hence, resonance structures such as 210 are important in the ground state and also, perhaps, in the initial photo-excited state 211. Through such a polar excited state, silicon can facilitate and control the direction of ring opening to directly yield the silicon stabilized carbene 212. The problem with this mechanism is that previous experiments yielded no evidence for carbene 213 or its resonance diradical form. In addition, if the carbene is generated, literature precedent predicts it should react to form the acyl cyclopropene 214 or the cyclopentenone 215. Neither of these products were observed. This discrepancy can be rationalized by invoking coordination of silicon to oxygen in carbene 214 to yield a six-membered cyclic intermediate 216. The geometrical constraints of this intermediate would not allow the carbene to insert into a methyl C-H bond to yield 215 or to add to the C-C double bond to yield 214. Thus, the carbene is forced to

Scheme 64



insert into a vinyl C-H bond to yield the observed allene. Similar rational is extendable to the photochemistry of the other silicon-substituted furans.

This polar excited state mechanism is also consistent with the rapid and quantitative formation of 2,4-bis(trimethylsilyl)-2,3-butadienal upon irradiation of 2,4-bis(trimethylsilyl)furan (Scheme 62.). The addition of a second trimethylsilyl group at the 4 position offers increased stabilization of the polar excited state through inclusion of resonance hybrids 217 and 218. Thus, ring opening is facilitated to a greater extent, and a faster, higher yielding reaction ensues.



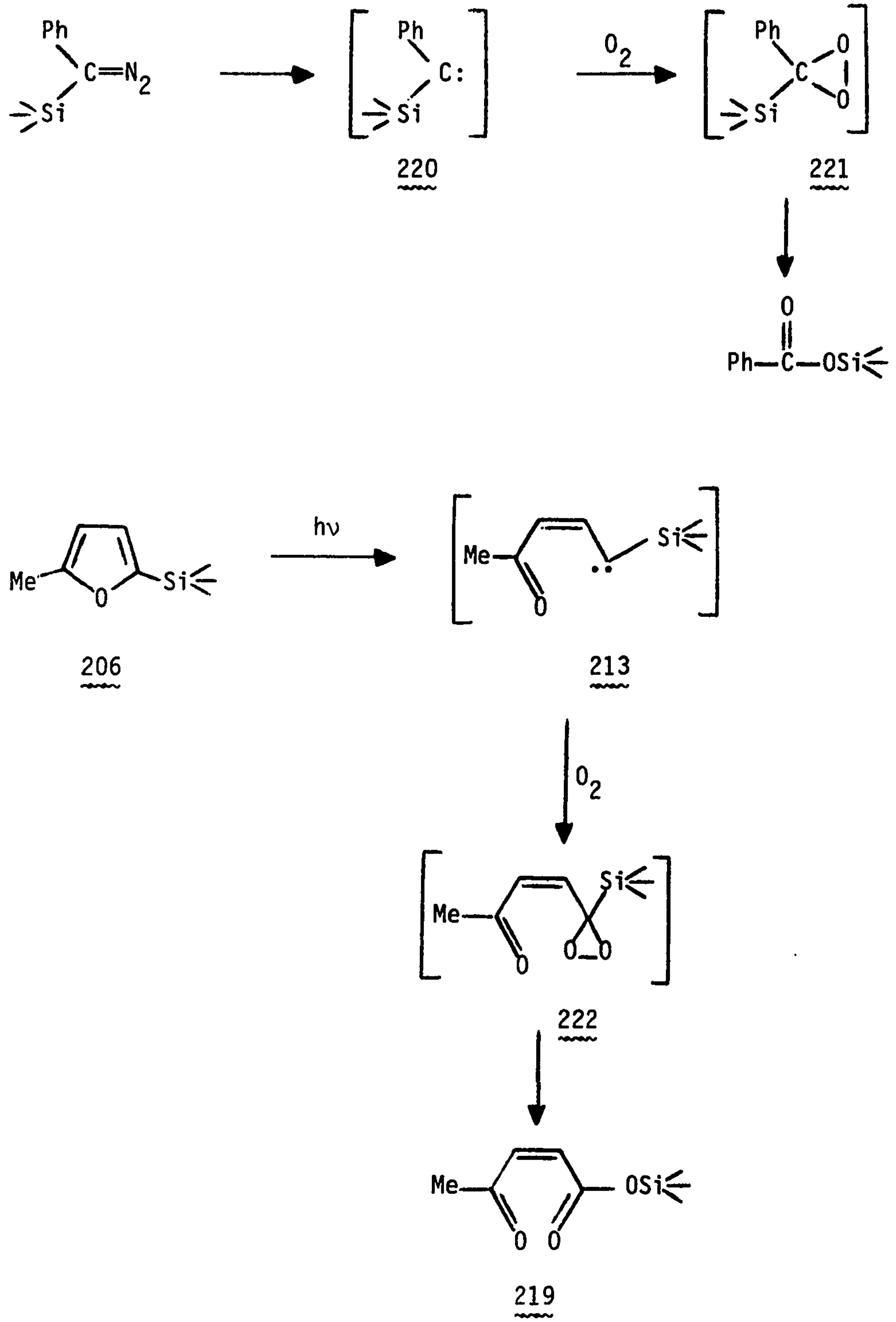
202 217 218

The proposal that silicon substitution facilitates ring opening of furans by electron withdrawal necessarily predicts that other electron withdrawing groups would have a similar effect. This prediction is verified by the reported irradiation of 2-cyanofuran (94, 95). The major product from this irradiation is 2-cyanocyclopropene-3-carboxaldehyde, which was trapped with MeOH in 20% yield. Compared to yields obtained from silicon-substituted furan photolyses, this yield is low. However, compared to yields obtained from alkyl-substituted furan photolyses, this yield is remarkably high. Thus, similar to silicon substitution, substitution with an electron withdrawing cyano group increases yields and reduces the number of products formed. Unlike silicon-substituted furans, irradiation of 2-cyanofuran did not yield an allene. This difference can be attributed to the previously discussed unique ability of silicon to coordinate to oxygen, forming a geometrically constrained carbene intermediate.

Supportive evidence that photoinduced ring opening of silicon-substituted furans to a carbene occurs is found in the work of Adam and Rodriguez (103). They reported that the irradiation of 2-trimethylsilyl-5-methyfuran 206, in the presence of singlet oxygen, afforded a quantitative yield of the silyl ester 219 (Scheme 65). This is the only literature report of a silicon-substituted furan photolysis. α-Silyl carbenes, 220, are known to react with singlet oxygen to yield a siladioxirane, 221, which rapidly decomposes to a silyl ester (104). The results of Adam and Rodriguez are conveniently rationalized through a similar sequence. Addition of singlet oxygen to the initially generated carbene and decomposition of the resulting dioxirane, 222, yields the silyl ester 219. Although Adam and Rodriguez recognized the intermediacy of 222, they did not suggest it arose from a carbene.

Before concluding, brief mention should be made as to the origin of 4,4-bis(trimethylsilyl)-2,3-butadienal 192 and 4,4-bis(dimethylphenylsilyl)-2,3-butadienal 199 from the photolysis of 2,5-bis(trimethylsilyl)furan and 2,5-bis(dimethylphenylsilyl)furan, respectively. The inability to isolate either 192 or 199 precludes definitive structural assignment; hence, any proposed mechanism accounting for their formation would be speculative. It is clear that 192 and 199 are not secondary

Scheme 65



products arising from the allenyl ketones, and that their formation necessarily involves both a silyl and a hydrogen migration. The exact nature of these migrations remains a mystery.

In summary, the irradiation of silicon-substituted furans leads to unprecedented exclusive formation of allenes in high yield. These results are most conveniently explained by: ring opening facilitated by a silicon induced polarization of the initial excited state, generation of a silicon stabilized carbene, coordination of silicon to oxygen forming a constrained cyclic carbene, and finally C-H bond insertion of the carbene. The synthetic potential of this photochemistry is obvious. Silicon-substituted furans are easily prepared, and irradiations can be carried out on gram quantity scales to give good yields of the allenyl carbonyl compounds. Only a few inefficient methods of preparing allenyl aldehydes and ketones have been previously reported (98, 99). Recent results from Reich and Kelly have shown that systems similar to the allenyl carbonyl compounds are useful synthetic intermediates (105).

The effect of silicon substitution on the photochemistry of thiophenes and pyrroles was also examined. Similar to the photochemistry of furans, the photochemistry of thiophenes and pyrroles is generally a complex process affording low yields of numerous products. A detailed review has recently been published by Padwa (7).

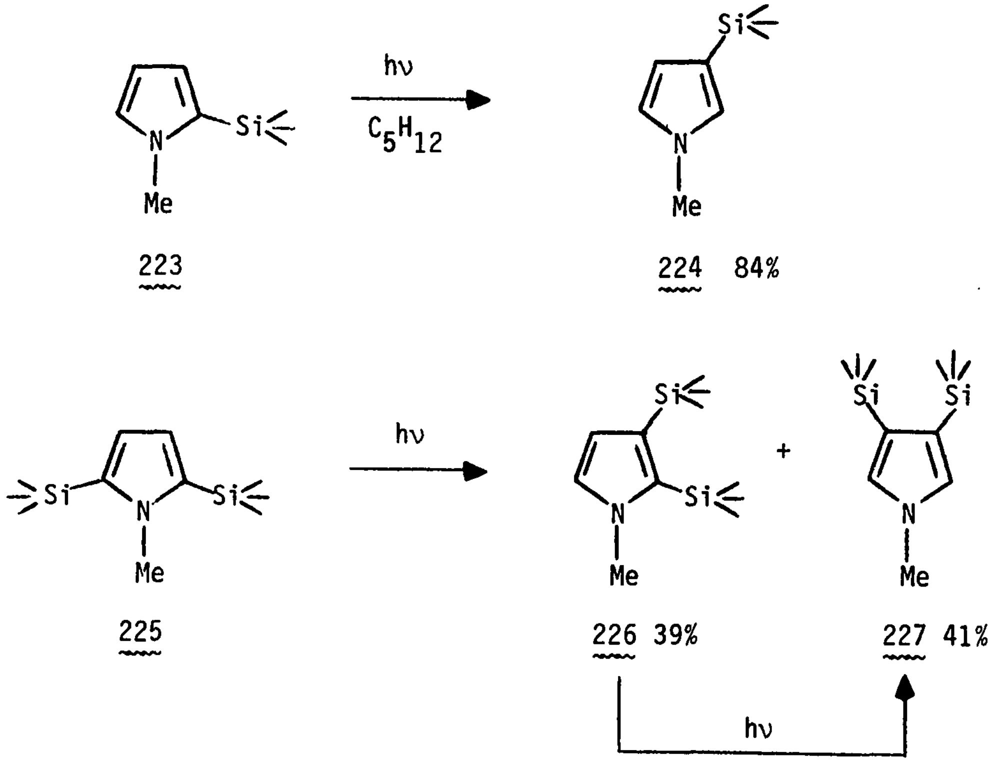
Silicon substitution has no apparent positive effect on the photochemistry of thiophenes. Irradiation of either 2-(trimethylsilyl)-

thiophene or 2,5-bis(trimethylsilyl)thiophene in degassed pentane at -78°C yielded only intractable polymer.

In contrast to these unremarkable results, photolysis of silicon-substituted pyrroles affords a high yield of rearranged starting material. Irradiation of 2-trimethylsilyl-N-methylpyrrole 223 in degassed pentane with a medium pressure mercury lamp yielded 3-trimethylsilyl-N-methyl pyrrole 224 (84%) as the only volatile product (Scheme 66). A similar irradiation of 2,5-bis(trimethylsilyl)-N-methylpyrrole 225 afforded intially two products: 2,3-bis(trimethylsilyl)-N-methylpyrrole 226 (39%) and 3,4-bis(trimethylsilyl)-N-methylpyrrole 227 (41%). Continued irradiation of this reaction mixture, or irradiation of 226, resulted in exclusive formation of 227. An explanation for these results is offered in Scheme 67. This mechanism is based on the mechanism offered by Day and coworkers who observed formation of 3-cyano-N-methylpyrrole upon photolysis of 2-cyano-N-methylpyrrole (106, 107).

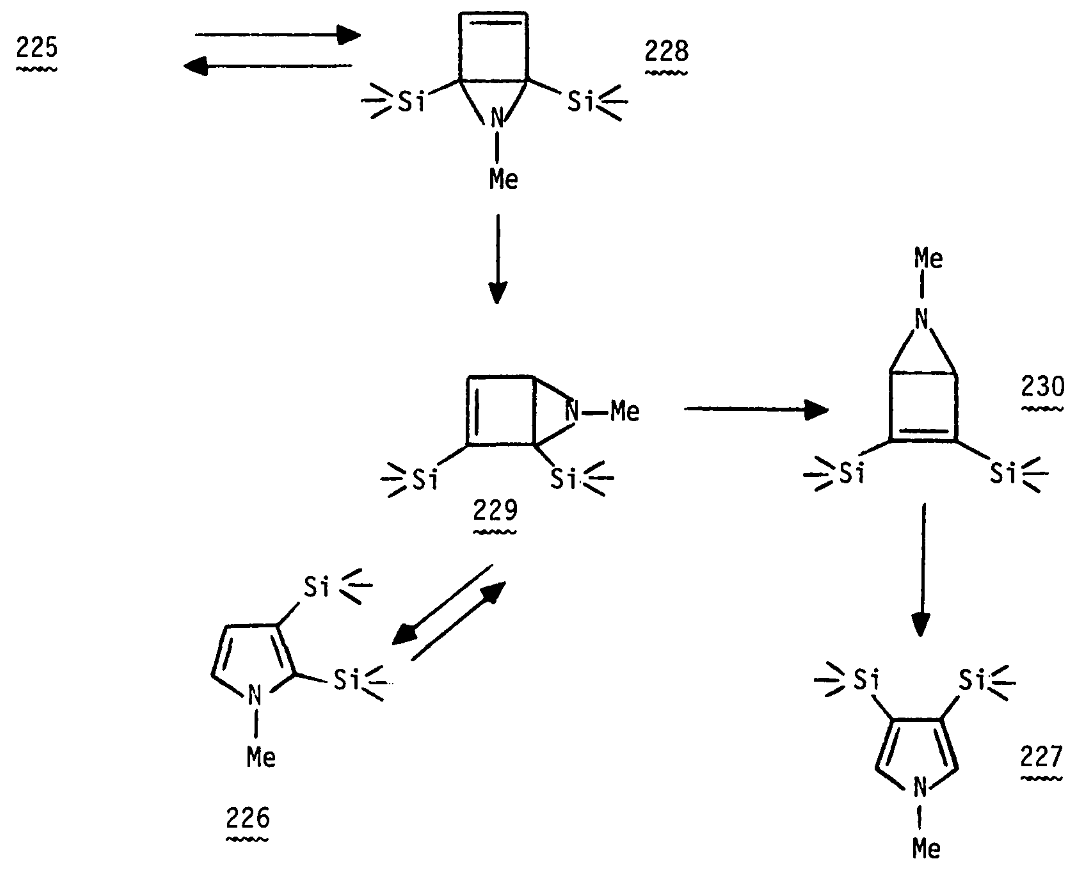
As Scheme 67 shows, photolysis of 225 results in a 4-electron electrocyclic ring closure to the 5-azabicyclo[2.2.1]pent-2-ene 228. A 1,3-nitrogen migration, or a nitrogen ring walk, affords 229, which reversibly ring opens to 226. Intermediate 229 can also undergo an additional 1,3-nitrogen shift to yield 230, which irreversibly ring opens to the final formed product, 3,4-bis(trimethylsilyl)-N-methylpyrrole. Evidence of an azabicyclopentene intermediate in the photolysis of 2-cyano-N-methylpyrrole was obtained by trapping with furan to yield a Diels-Alder adduct. Similar trapping of 229 was attempted without success. Presumably, the C-C double bond in 229 is too electron rich to react. The formation of 224 upon photolysis of 223 can occur through a similar sequence of events.

Scheme 66



It is not immediately obvious why 224 and 227 do not react further under the conditions of irradiation. Similar chemistry is observed with cyano-substituted pyrroles; however, no explanation has been put forth. Interestingly, alkyl-substituted pyrroles do not show similar photochemical behavior. Irradiation of 2,5-dimethylpyrrole in the gas phase yielded H_2, CH_4, C_2H_6, and polymer (108). Based on these observations, it is apparent that electron withdrawing substituents at the 2-position of the pyrrole ring are necessary for isomerization to occur. Thus, similar to the role silicon plays in furan photochemistry, the role of silicon in pyrrole photochemistry appears to be electron withdrawal into its empty d-orbitals. The role of silicon may also be steric in nature. A subsequent 1,3-nitrogen shift in intermediate 230 may be hindered by the bulky trimethylsilyl groups. Thus, once the 3-substituted and 3,4-substituted isomers are formed, further isomerization by a 1,3-nitrogen shift to the silicon-substituted carbon is prevented.

Scheme 67



Like silicon-substituted furan photolysis, the photolysis of silicon-substututed pyrroles can be performed with gram quantities and taken to 100% conversion. Pyrroles substituted at the 3 and 4 positions are not readily accessible. The route presented here offers high yields of 3-substituted and 3,4-substituted functionalized pyrroles from easily prepared starting materials.

Thermal chemistry of 1,4-disilyl-2,3-butadienones

As discussed in the previous section, considerable difficulties were encountered in the isolation of 1,4-bis(trimethylsilyl)2,3-butadienone 191 from the photolysis of 2,5-bis(trimethylsilyl)furan 190. Before 191 was successfully isolated by low temperature crystallization, isolation was attempted by preparataive gas chromatography and distillation. In addition, characterization of 191 was attempted by catalytic hydrogenation. Surprisingly, these methods of isolation and characterization resulted in rearrangement of 191 to two different isomers. The course of events is described below.

Analysis of the crude reaction mixture from the photolysis of 190 by gas chromatography revealed that one major product had been formed. This was consistent with NMR analysis of the crude photolysate. Isolation of this major product by preparative gas chromatography was then, apparently, achieved. Surprisingly, the NMR and IR spectra of this isolated product did not correspond to the NMR and IR of the major product in the crude reaction mixture. Isomerization of 191 on the gas chromatograph column had occurred. This isomerized product was identified as 2,4-bis(trimethylsilyl)furan 202. At this point, characterization of the major product from the photolysis of 190 was attempted by in situ catalytic hydrogenation. Treatment of the crude photolysate with Pd/C and H_2, and analysis of the resulting reaction mixture by NMR, revealed isomerization to 2,4-bis(trimethylsilyl)furan had once again occurred.

Vacuum distillation of the major product from the crude photolysate was then attempted. Although clean separation could not be achieved, it was evident that the major product from photolysis of 190 was completely unstable towards distillation. In fact, NMR analysis of the pot residue suggested isomerization had again occurred. The exact nature of this isomerization was not clear; however, it could be determined that 2,4-bis(trimethylsilyl)furan was not formed.

The results of this isomerization by distillation were ultimately clarified after the major product from the photolysis of 190 was isolated by low temperature crystallization and identified as 1,4-bis(trimethylsilyl)-2,3-butadienone 191. Distillation conditions were then mimicked by heating a concentrated solution of 191 in CCl_4 or D_6-benzene at 70°C. Under these conditions, quantitative isomerization of 191 was achieved. The product of this isomerization proved too unstable for isolation; however, the following spectral features were observed: NMR (CCl_4) δ 0.18 (s, 9H), 0.28 (s, 9H), 5.0 (s, 1H), 6.3 (s, -O$\underline{H}$); IR (CCl_4) 3440 (OH), and 2120 cm^{-1} (C≡C). These data suggested a stable enol functional group 231. This was verified by the addition of trimethylchlorosilane to the reaction mixture and isolation of silyl enol ether

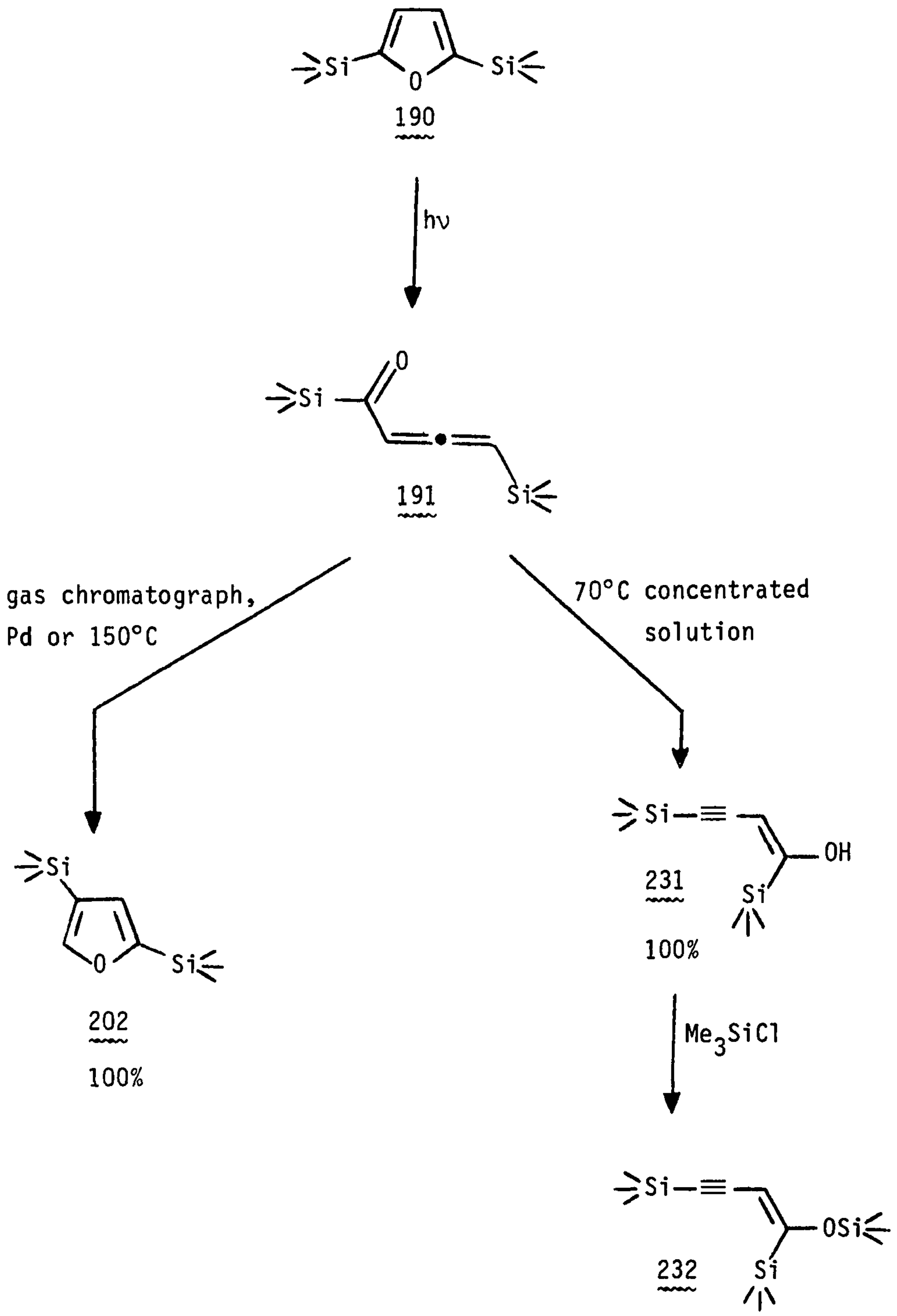
232: NMR ($CDCl_3$) δ 0.18 (s, 9H), 0.25 (s, 9H), 0.39 (s, 9H), 5.20 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -2.3, 0.1, 1.5, 98.8, 102.0, 102.2, 173.0; IR (neat) 2140 (C≡C) and 1565 cm^{-1} (C=C-O); calculated for $C_{13}H_{28}OSi_3$ (M^+) m/e 284.1448, measured m/e 284.1445.

Interestingly, heating a dilute solution of 191 in CCl_4 at 150°C for 30 minutes led to quantitative formation of 2,4-bis(trimethylsilyl)-furan. This is the identical isomerization observed when isolation of 191 by preparative gas chromatography and characterization by catalytic hydrogenation were attempted. Scheme 68 summarizes these observed isomerizations.

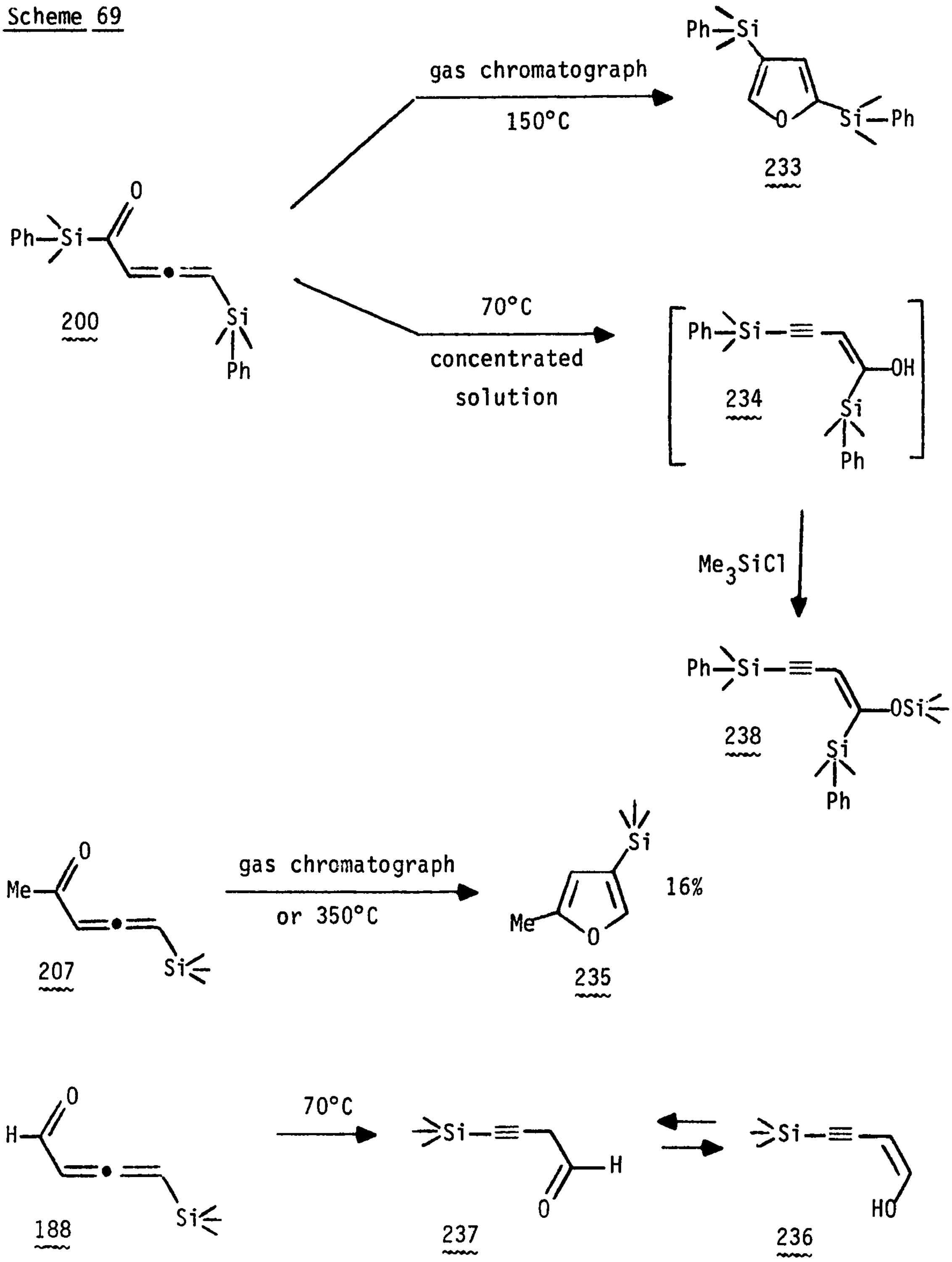
Similar to these isomerizations of 191, 1,4-bis(dimethylphenylsilyl)2,3-butadienone 200 isomerizes to 2,4-bis(dimethylphenylsilyl)-furan 233 upon attempted isolation by preparative gas chromatography, or to the enynol 234 upon heating a concentrated solution of 200 in CCl_4 at 70°C (Scheme 69). Isomerization of 1-methyl-4-trimethylsilyl-2,3-butadienone 207 to 2-methyl-4-trimethylsilylfuran 235 also occurs. However, a higher temperature was required and a lower yield was obtained. The propensity of allenyl aldehydes to polymerize prohibited their isolation; hence, their potential isomerization to furans and enynols was difficult to determine. To the extent that such an experiment was possible, it was determined that 4-trimethylsilyl-2,3-butadienal isomerized upon heating in a concentrated solution to 4-trimethylsilyl-3-butynal 236 the keto form of enynol 237.

The isomerization of allenyl ketones to furans has been previously described (100, 109). Srinivasen and coworkers reported 1,4-dimethyl-

Scheme 68


Si
O
Si
190
hν
Si
O
Si
191
gas chromatograph,
Pd or 150°C
70°C concentrated
solution
Si
O
Si
202
100%
Si
OH
Si
231
100%
Me$_3$SiCl
Si
OSi
Si
232

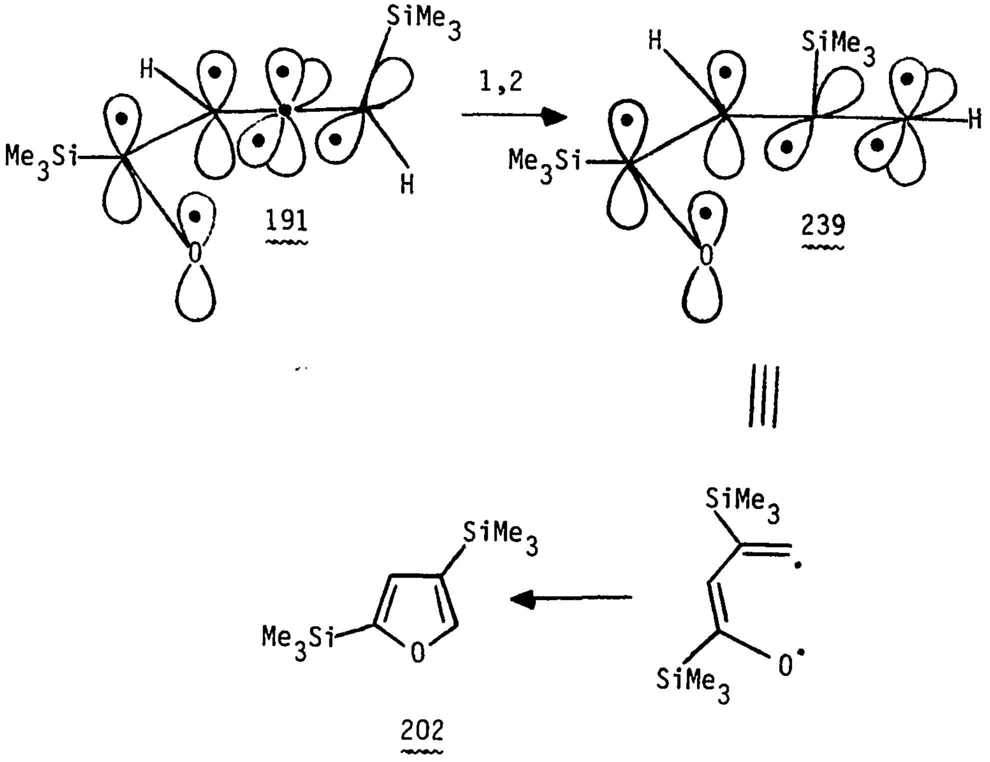
Scheme 69


gas chromatograph
150°C
233
200
70°C
concentrated solution
234
Me_3SiCl
238
gas chromatograph
or 350°C
207
235
16%
70°C
188
237
236

2,3-butadienone rearranged in the injection port of a gas chromatograph to 2,5-dimethylfuran. No mechanism was offered. Jullien and coworkers reported the low yield isomerization of several allenyl ketones to 2,5-disubstituted furans upon gas phase pyrolysis at 750°C. A one-step ring closure and hydrogen migration through a bent allene was the proposed mechanism. Comparison of these results with the isomerization of silyl-substituted allenyl ketones to furans reveals two significant differences. Isomerization of silyl-substituted allenyl ketones occurs at lower temperature, and 2,4-disubstituted furans, not 2,5-disubstituted furans, are the products of isomerization.

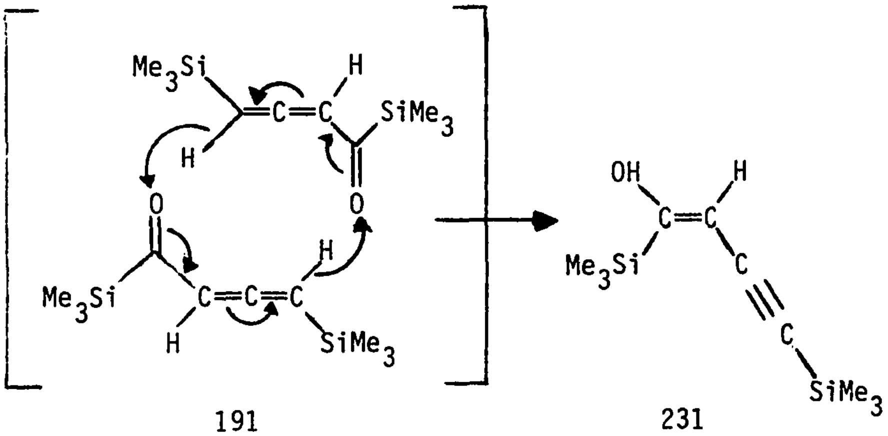
It is obvious that at some point in the rearrangement of silyl allenyl ketones to furans, silicon migration must occur. The isomerization of **207** to **235** suggests that migration from the terminal allene carbon takes place. An examination of the p-orbitals of **191** (Scheme 70) shows that a 1,2-silyl migration from the terminal allene carbon is geometrically direct and results immediately in a resonance stabilized diradical **239**. This diradical needs only to close to give the observed furan. Thus, the migratory aptitude of silicon and direct stabilization of the intermediate diradical accounts for the facility of isomerization of silyl-substituted allenyl ketones to furans. That **191** and **200** isomerize at lower temperature and in higher yield than **207** suggests that silicon substitution at the carbonyl carbon also facilitates their isomerization to furans. The exact role of silicon substitution at this position is not clear. It is known that silicon functions as an electron withdrawing group when attached to sp^2 hybridized carbons (101). This effect is most pronounced in silyl ketones (110). Hence, the facile isomerization of 191 and 200 may be, in part, due to polarization of the diradical intermediate, *i.e.* 239, by electron withdrawal.

Scheme 70



The formation of stable enynols 231 and 234, from heating concentrated solutions of 191 and 200, respectively, was initially difficult to believe. There is no literature precedent for such an isomerization nor is there any reason to expect that the enol forms of 231 and 234 would be stable. However, their spectral features and isolation of silyl enol ethers 232 and 238 prove that 232 and 234 were indeed formed and are stable in solution. Subsequent experiments indicated that this isomerization is concentration dependent. Formation of enynols occurs exclusively in concentrated solutions at 70°C. As the concentration of starting silyl allenyl ketone is decreased, and/or the temperature is increased, competitive formation of 2,4-disubstituted furans occurs. This concentration dependence suggests that formation of 231 and 234 is a bimolecular process. Such a process is illustrated in Scheme 71. Examination of molecular models shows that exchange of hydrogens between two molecules of 231 is geometrically favorable. This exchange is facilitated by electron withdrawal from the carbonyl group with the adjacent silicon. Thus, in a 12-electron rearrangement, two molecules of the enynol 231 are formed. The stability of the enol form of 231 and 234 can be attributed to conjugation with the triple bond, electron delocalization by silicon, and intramolecular hydrogen bonding in the concentrated solutions. Upon extended heating of the enynol 231, the keto form was observable.

Scheme 71



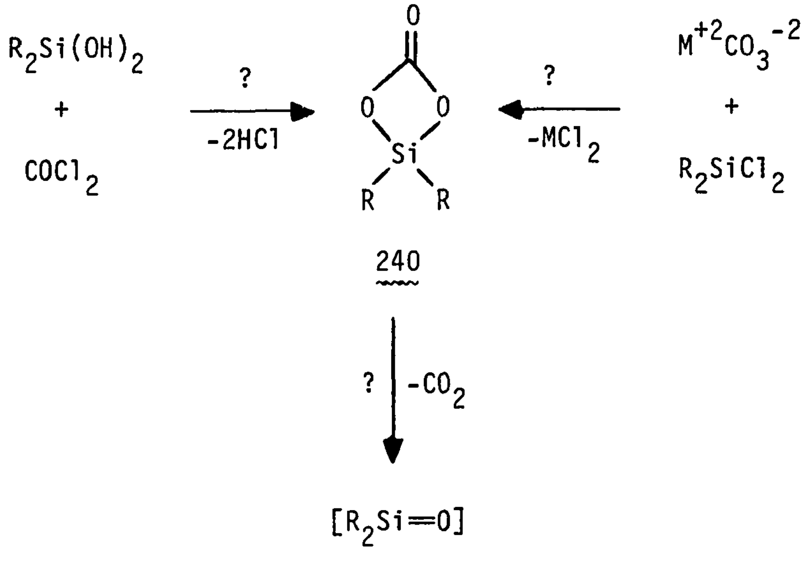
191 231

Before concluding this section, brief mention should be made on the original interpretation of the results from the photolysis of silyl-substituted furans. As discussed previously, the photolysis of 2,5-bis(trimethylsilyl)furan resulted in almost quantitative formation of 1,4-bis(trimethylsilyl)-2,3-butadienone, which underwent thermal isomerization to 2,4-bis(trimethylsilyl)furan. Based on literature precedent, in particular the photolysis of 2,5-di-t-butylfuran (Scheme 57), 2,4-bis(trimethylsilyl)furan should have been a primary photoproduct from the irradiation of 2,5-bis(trimethylsilyl)furan. Yet, it was clearly formed in a secondary thermal reaction. The only difference between the irradiation of **190** and 2,5-di-t-butylfuran, other than the silicon substitution, was the lower temperatures used in the photolysis of **190**. This raised the possibility that the complex reaction mixtures and low yields obtained in the photolysis of alkyl-substituted furans were primarily due to secondary thermal processes. Thus, previously reported furan photochemistry was possible in error. To probe this possibility, the photolysis of 2,5-di-t-butylfuran was repeated at -78°C. No improvement in yields or number of products was obtained. The three major volatile products were formed in yields similar to those previously reported by van Tamelen and Whitesides (85) [**176** (9.5%), **177** (2.6%), **178** (11%)]. Hence, silicon substitution is definitively the parameter responsible for the cleanliness and high yields obtained upon photolysis of silicon substituted furans.

Synthesis and Chemistry of Silaoxetanes and Silaoxetes

Attempted formation of silaoxetanes *via* nucleophilic oxygen attack

Although stable silaoxetanes have recently been prepared by a number of workers (see Historical section), at the time this study was begun a stable silaoxetane was unknown. However, silaoxetanes had been proposed numerous times as reactive intermediates which undergo spontaneous decomposition to silanones. The desire to prepare a stable silaoxetane which would serve as a direct silanone source prompted the work reported in this section. The initial target silaoxaetane was the silacyclocarbonate ring system **240**. This ring system was chosen primarily because of the simplicity envisioned in its synthesis. Two routes were examined in an attempt to synthesize **240**: the reaction of a silane diol with phosgene and the reaction of a carbonate salt with a silyl dihalide.



240

The addition of dimethyldichlorosilane to K_2CO_3 or to $CaCO_3$ in benzene in the presence of crown ethers resulted in no observable reaction after stirring at reflux for 48 hours. Repeating the reaction in more polar solvents, such as tetrahydrofuran (THF) or acetonitrile, gave similar results. This lack of reaction can be attributed to the insolubility of carbonate salts, even in the presence of crown ethers, in aprotic solvents (111).

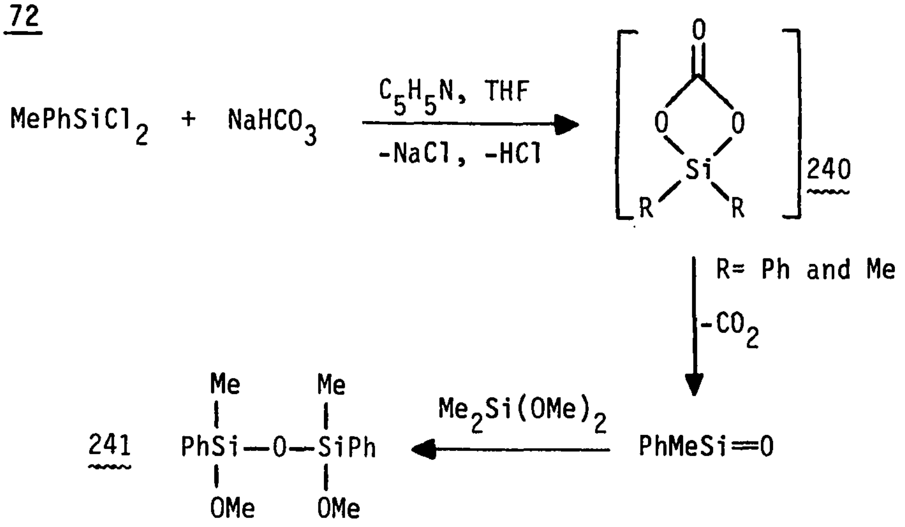
The problem of carbonate dianion insolubility was solved by the use of a bicarbonate salt. The addition of dimethyldichlorosilane to $NaHCO_3$ and triethylamine in THF resulted in gas evolution and formation of D_3, D_4, and D_5 as the only volatile products. The observation of these cyclic siloxanes is suggestive of dimethylsilanone intermediacy. To test for this possibility, the reaction was repeated in the presence of dimethyldimethoxysilane. Interestingly, the only observable product was identified as 1,3-dimethoxytetramethyldisiloxane (89%); the expected product from dimethylsilanone insertion into dimethyldimethoxysilane.

Although these results are consistent with silacyclocarbonate formation and its decomposition to dimethylsilanone, an alternative explanation which does not demand the intermediacy of either 240 or dimethylsilanone appears more likely. The reaction of dimethyldichlorosilane with $NaHCO_3$ undoubtedly results in HCl production. Although triethylamine is present to neutralize this HCl, some HCl may also react with $NaHCO_3$ to generate H_2O and CO_2. Thus, gas evolution is observed. The observed products can then be formed by hydrolysis and oligermerization of dimethyldichlorosilane and by aqueous acid promoted cleavage and recombination reactions. These cleavage-recombination reactions are well documented and can occur under thermal, acid, or base catalyzed conditions (3, 4).

Evidence which supports this acid promoted cleavage-recombination mechanism was obtained from the reaction of phenylmethyldichlorosilane with $NaHCO_3$ in the presence of dimethyldimethoxysilane. Four major products were observed: 1,3-dimethoxytetramethyldisiloxane **9**, 1-phenyl-1,3-dimethoxytrimethyldisiloxane **241** (18%), phenylmethyldimethoxysilane **242** (27%), and 1,3-diphenyl-1,3-dimethoxydimethyldisiloxane **243** (36%). If the silacyclocarbonate **240** was formed in this reaction, its predicted decomposition to CO_2 and phenylmethylsilanone should have ultimately afforded the trapping product **241** (Scheme 72). Indeed, this product was observed and was, perhaps, formed through the intermediacy of **240** and phenylmethylsilanone. However, the formation of the other products suggests that the reaction proceeded through an acid promoted cleavage-recombination mechanism (Scheme 73). In this mechanism, initially produced HCl reacts with $NaHCO_3$ to generate H_2O and CO_2. The observed products are then formed by aqueous acid promoted cleavage of **8** which affords MeOH and **244**. Condensation of **244** yields **9**, and reaction of MeOH with phenylmethyldichlorosilane affords **242**. Acid cleavage of **242** yields the silanol **245**, which can condense with itself or with **244** to give **243** and **241**, respectively.

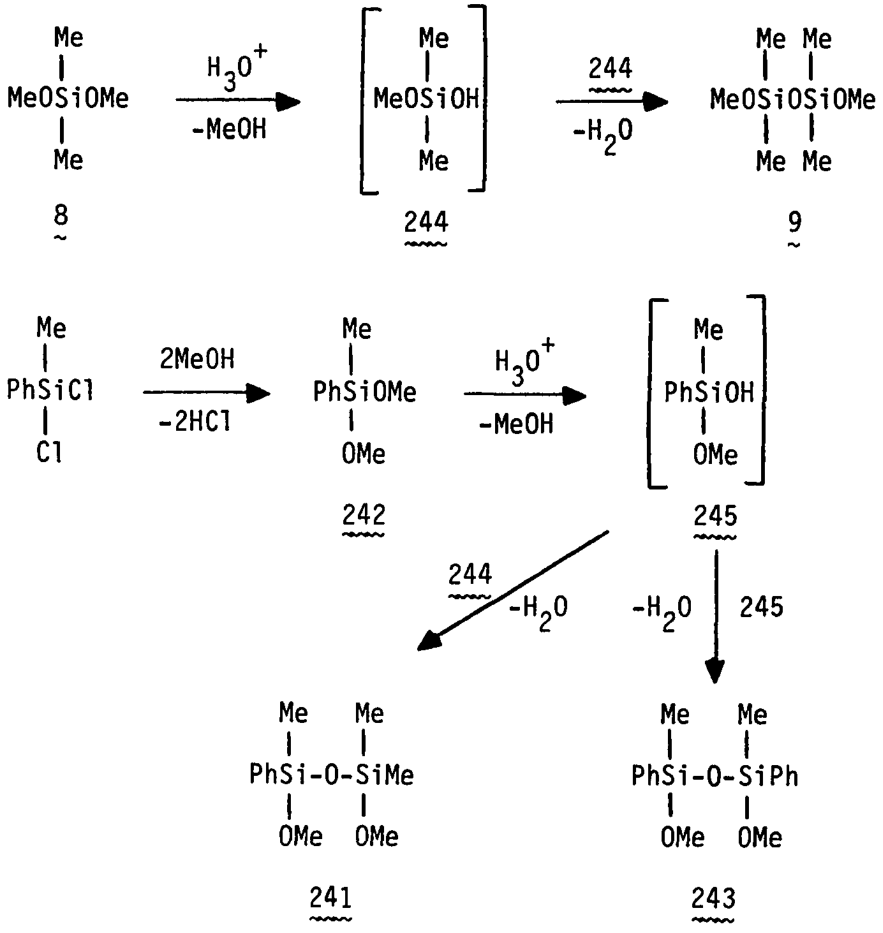
In conclusion, although the reaction of silyl dihalides with bicarbonate may proceed through the intermediacy of silacyclocarbonates and silanones, the products most likely arise from an aqueous acid cleavage-recombination process.

Scheme 72



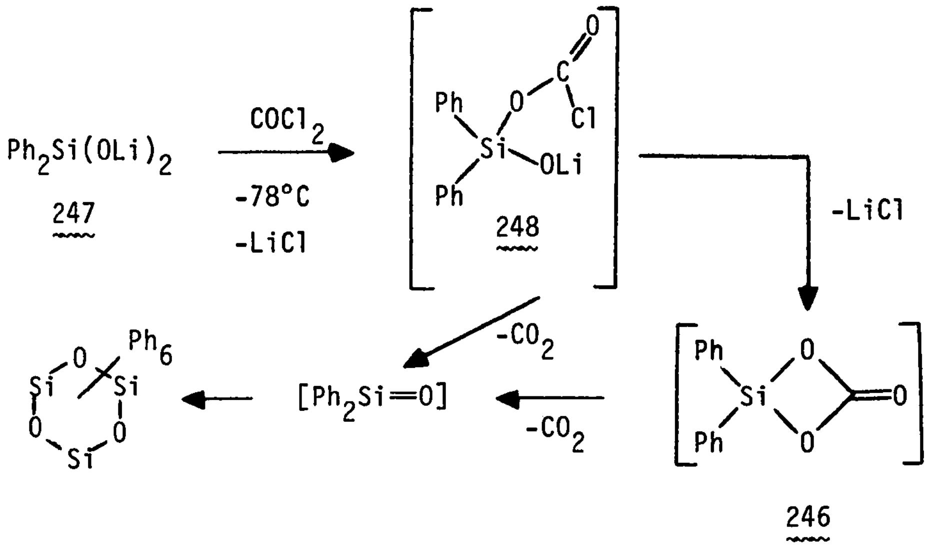
The second synthetic approach to the silacyclocarbonate ring system was based upon carbonate formation by reaction of a silane diol with phosgene. Literature precedent for this reaction comes from the work of Mironov and coworkers who reported that triethylsilanol or triethylsilanolate reacted with phosgene to yield bis(triethylsilyl)carbonate (112). Thus, diphenylsilane diol was reacted with phosgene in the presence of triethylamine. Only one silicon containing product was isolated from this reaction: hexaphenylcyclotrisiloxane in 75% yield. The formation of hexaphenylcyclotrisiloxane was consistent with the intermediacy of diphenylsilanone and 1,1-diphenyl-1-silacyclocarbonate 246. However, silane diols are known to condense to cyclosiloxanes in the presence of acid. Because HCl was formed in the reaction, this mechanistic alternative could not be discounted.

Scheme 73



To eliminate HCl formation and the possibility of acid catalyzed condensation, the dilithium salt of diphenylsilane diol was prepared. Reaction of dilithium diphenyldisilanolate 247 with phosgene at -78°C again resulted in hexaphenylcyclotrisiloxane. With the possibility of acid catalyzed condensation eliminated, it appears that formation of hexaphenylcyclotrisiloxane must have occurred through the intermediacy of diphenylsilanone. Diphenylsilanone could arise from either decomposition of the silacyclocarbonate 246 or direct fragmentation of intermediate 248 (Scheme 74). Gas evolution was not visibly observed.

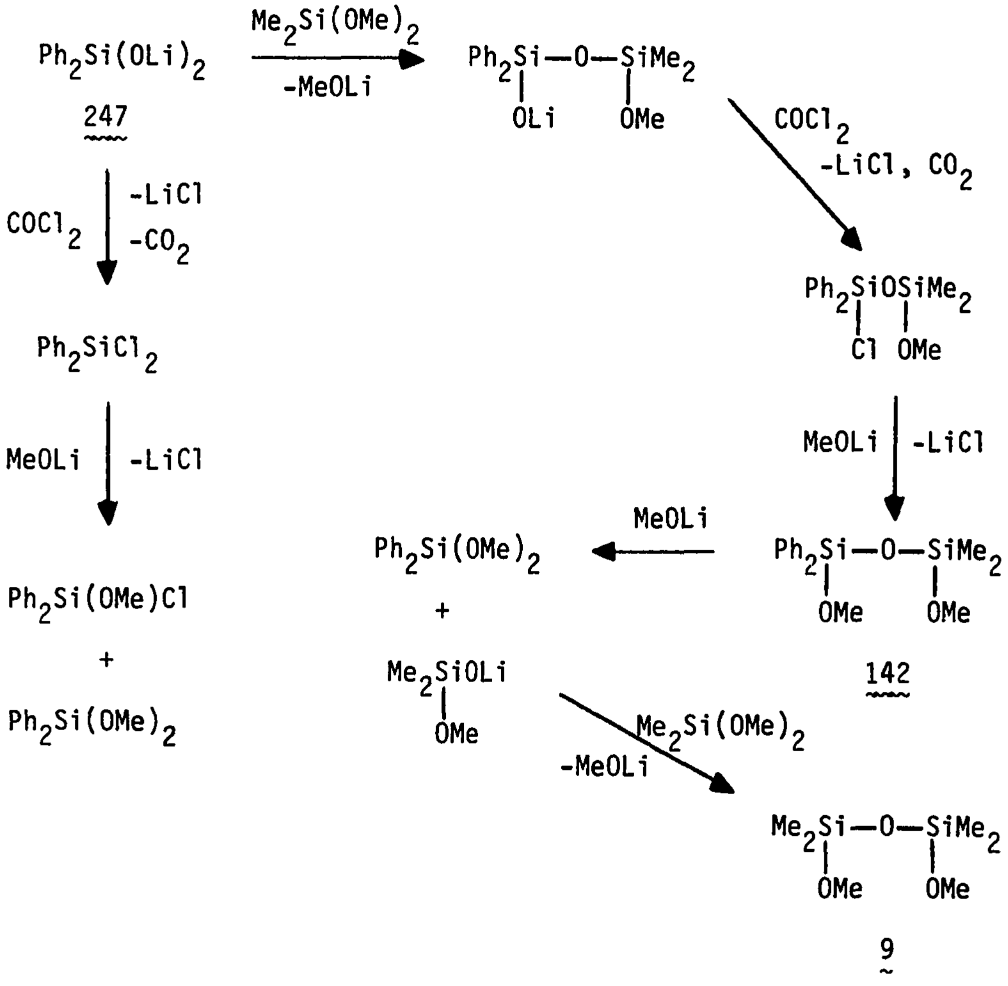
Scheme 74



To further test for diphenylsilanone intermediacy, the above reaction was repeated in the presence of a silanone trap: dimethyldimethoxysilane. Surprisingly, this resulted in a very complex mixture of products. The four major products were identified as diphenyldimethoxysilane, 1,1-diphenyl-3,3-dimethyldimethyldisiloxane 142, diphenylchloromethoxysilane, and 1,3-dimethoxytetramethyldisiloxane 9. These products were formed in a 4:2:2:3 ratio, respectively.

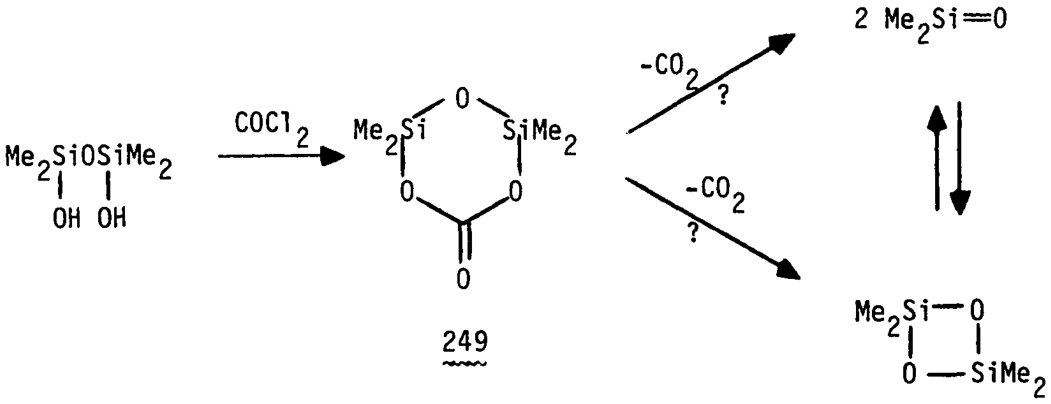
The formation of 142, the expected diphenylsilanone insertion product, is certainly consistent with diphenylsilanone intermediacy. However, the formation of the other products from any conceivable silanone mechanism is unlikely. These products are most consistent with a base induced redistribution mechanism. Silanolates or metal alkoxides are known to cleave Si-O bonds to form new silanolates or new metal alkoxides (3). In addition, phosgene has been reported to react with silanols or silyl alkoxides to form silyl halides (112). Thus, using these known processes, the following mechanism may be postulated which accounts for all the observed products formed from the reaction of 247 with $COCl_2$ and 8 (Scheme 75).

Scheme 75



A similar series of reaction also accounts for the formation of hexaphenylcyclotrisiloxane from the previously discussed reaction of phosgene with dilithium diphenyldisilanolate. Because the reaction of silane diols or disilanolates with phosgene has the potential of proceeding via a phosgene, base induced, or acid catalyzed cleavage mechanism, further attempts to generate silacyclocarbonates and silanones from this route were not made.

An attempt was made to synthesize the tetramethyldisiloxycyclocarbonate ring system 249 from the reaction of phosgene with tetramethyldisiloxane-1,3-diol. This ring system was desired because of its potential to serve as a source of D_2 or dimethylsilanone.

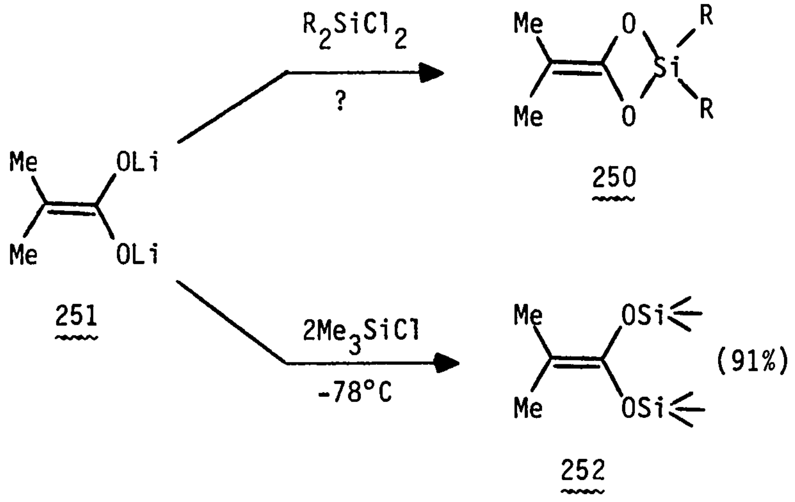


The reaction of phosgene with tetramethyldisiloxane-1,3-diol in the presence of triethylamine afforded the cyclic siloxanes D_3 (3%), D_4 (63%), and D_6 (18%). No carbonate carbonyl was detected by IR. Although these results are consistent with formation of 249, followed by its decomposition to D_2 which dimerizes to D_4 or extrudes dimethylsilanone, a more probable explanation is acid catalyzed dimerization and cleavage of the starting diol. Further attempts to form **249** were not pursued.

The problems encountered in the attempted synthesis of the silacyclocarbonate and disiloxycyclocarbonate ring systems are illustrative of the general problems faced when trying to synthesize silanone precursors or to unambiguously determine silanone intermediacy. Silanone precursors, such as silaoxetanes, are generally unstable systems, hence, difficult to isolate. Their isolation is even more difficult when they are synthesized in the presence of an acid or a base. Either an acid or a base can promote cleavage of Si-O bond resulting in destruction of the silanone precursor. Attempting to determine silanone intermediacy is also extremely difficult if the potential for acid or base formation exists. Silanone intermediacy is usually suggested by the formation of silanone trapping products. Unfortunately, these silanone trapping products can often be rationalized as arising from an acid or base promoted cleavage or condensation of the silanone precursor. Thus, the potential presence of an acid or a base makes isolation of the silanone precursor unlikely and unambiguous determination of silanone formation virtually impossible. This statement is certainly applicable to the previously discussed attempts at forming silacyclocarbonates and silanones from nucleophilic substitution of silyl dihalides with bicarbonate and of phosgene with silane diols.

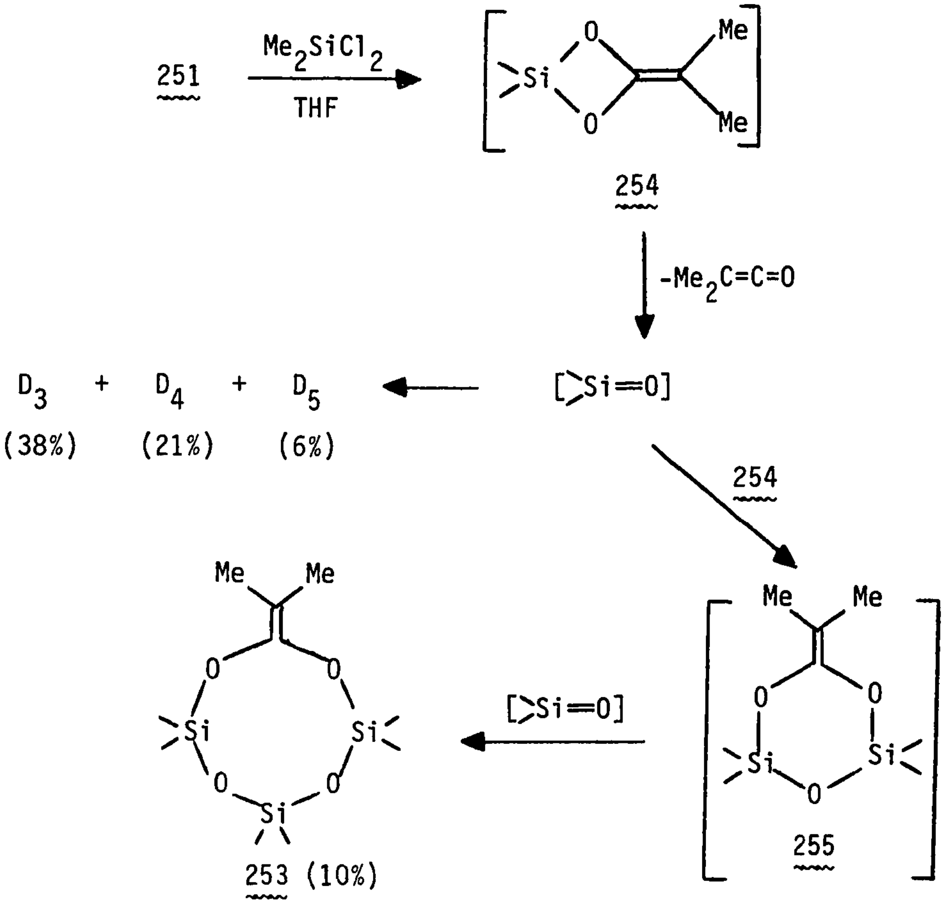
A nucleophilic oxygen substitution reaction was also utilized in an attempt to synthesize the siladioxetane **250**. The synthesis of **250** was visualized to occur by reacting the dioxyanion **251**, generated from isobutyric acid and two equivalents of lithium diisopropylaminde (LDA), with a dichlorosilane. To insure that 251 could be prepared and would react with silyl halides at both oxygens, the reaction was initially run by quenching with two equivalents of trimethylchlorosilane. An almost quantitative yield of the bis(trmethylsilyl)ketene acetal 252 was obtained (Scheme 76).

Scheme 76



Synthesis of a siladioxetane was attempted by reaction of 251 with dimethyldichlorosilane. Several products were identified from this reaction: D_3, D_4, D_5, and the eight-membered ring 253. The observation of these cyclosiloxanes was suggestive of the intermediacy of both dimethylsiladioxetane 254 and dimethylsilanone (Scheme 77). The initially formed dimethylsiladioxetane may decompose to dimethylsilanone, which cyclooligermerizes to D_3, D_4, and D_5 or inserts into a Si-O bond of 254 to ultimately afford 253.

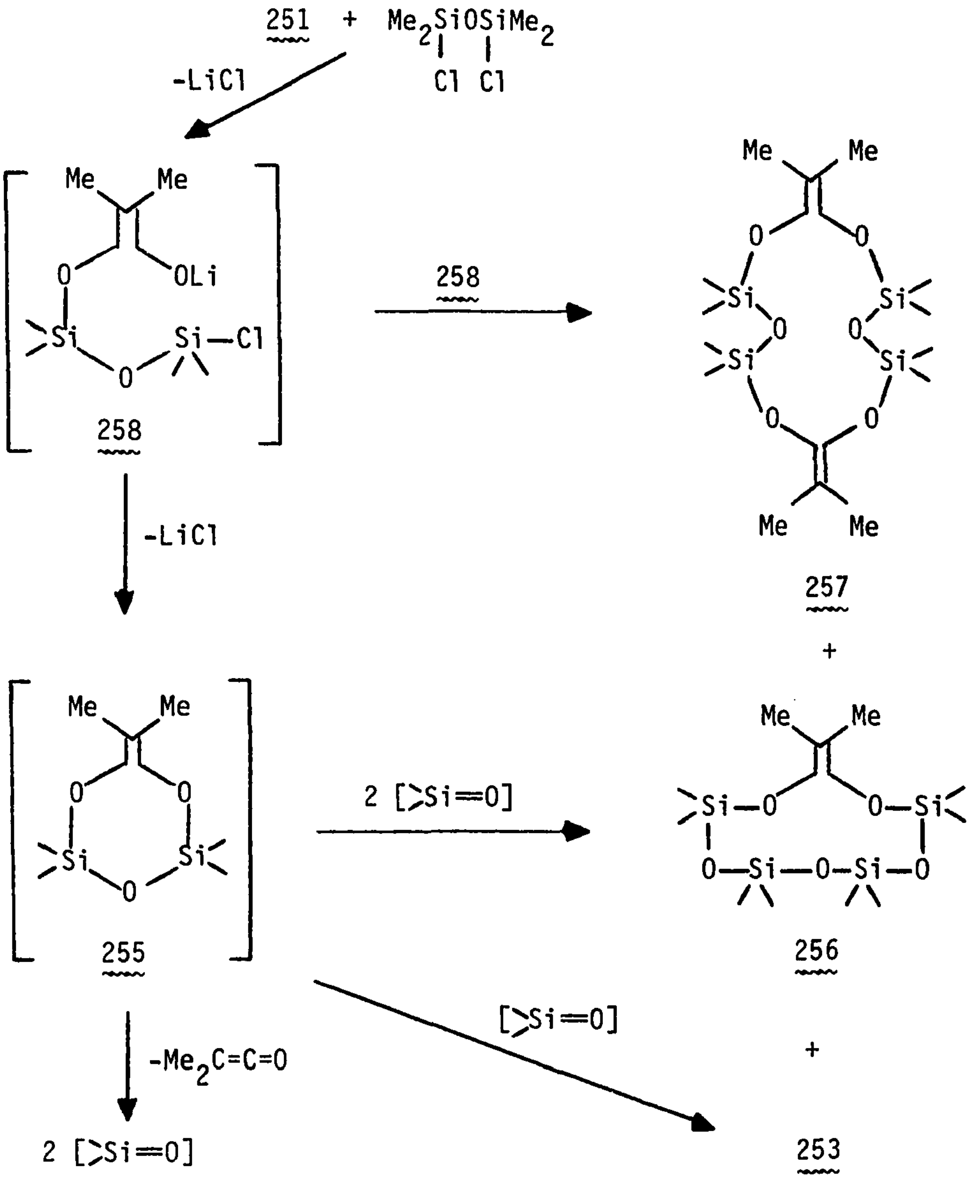
Scheme 77



Several criticisms of this mechanism are evident. Because diisopropyl amine, generated from the reaction of LDA with isobutyric acid, or residual isobutyric acid can react with dimethyldichlorosilane to generate HCl, all results can potentially be explained by an acid catalyzed mechanism. Indeed, the difficulty encountered when attempting to consistently reproduce these results may be a consequence of acid involvement. In addition, one must explain the peculiar absence of the expected by-product of dimethylsilanone formation: dimethylketene. No evidence for either dimethylketene or its dimer could be found by MS or IR analysis of the crude reaction mixture. However, a careful analysis of the GC-MS obtained on the crude reaction mixture revealed the presence of N,N-diisopropylisobutyramide. The formation of an amide from the reaction of a 1° or 2° amine with a ketene is well documented (113). Diisoproplylamine, two equivalents of which were present in the reaction mixture, may have reacted with dimethylketene to afford N,N-diisopropylisobutyramide. Thus, the lack of direct observation of dimethylketene is not unexpected.

Another product which is notably absent is the cyclodisiloxane 255, the presumed intermediate, which inserts dimethylsilanone to form 253. Although no similar ring system has been reported in the literature, six-membered rings containing a Si-O bond are generally stable. The instability of 255 is difficult to rationalize. An independent synthesis of 255 was attempted by reaction of the dioxyanion 251 with 1,3-dichlorotetramethyldisiloxane. As in the previously discussed reactions of 251, this reaction proved difficult to consistently reproduce. Among the numerous products formed were the cyclotrisiloxane 253, the cyclotetrasiloxane 256, and the twelve-membered ring 257. The expected cyclodisiloxane 255 was not isolated or observed. However, the formation of 253 and 256 are suggestive of the intermediacy of 255 (Scheme 78). 1,3-Dichlorotetramethyldisiloxane and 251 may react to initially form 258 which can dimerize to afford 257 or undergo ring closure to furnish the expected product 255. The cyclodisiloxane 255 then decomposes to dimethylsilanone which inserts into a Si-O bond of 255 to afford 253 and, ultimately, 256. The cyclosiloxanes 253 and 256 may also be formed in a silanone transfer reaction between two molecules of 255.

Scheme 78

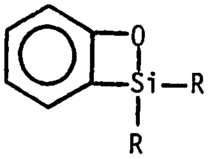


As stated previously, diisopropyl amine, formed from the reaction of LDA with isobutyric acid, can react with the chlorosilanes to generate HCl or can react with isobutyric acid to generate H_2O. Thus, the elusive nature of 255 and the observed products may be a consequence of HCl or H_2O promoted reactions. In an effort to eliminate this problem caused by diisopropyl amine, alternative methods of forming dioxyanion 251 were examined. Unfortunately, no methods which gave satisfactory yields of 251 and eliminated the potential for HCl or H_2O production were found.

In conclusion, the results obtained from the reaction of dioxyanion 251 with dimethyldichlorosilane or with 1,3-dichlorotetramethyldisiloxane are consistent with formation of siladioxetane 254, cyclodisiloxane 255, and dimethylsilanone. However, the necessity for postulating these intermediates is prevented by the posibility of HCl promoted reactions.

Synthesis and reactions of 2-sila-3,4-benzooxetes

In the previous section, it became evident that the successful synthesis of a silaoxetane and unambiguous determination of silanone intermediacy are virtually impossible goals to achieve in the presence of an acid or a base. In addition, it became clear that the high reactivity and instability of sterically unhindered silaoxetanes limited their use as a stable direct source of silanones. Thus, a pH neutral route towards a stable silicon-oxygen containing four-membered ring was desired. A system that appeared to satisfy these criteria was the benzosilaoxete 259.



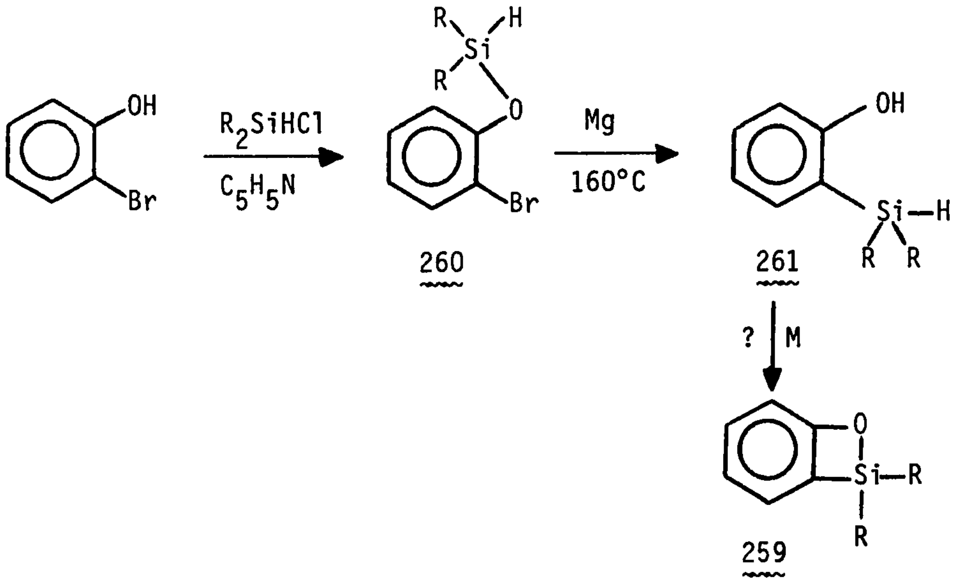
259

Benzosilaoxetes have not been previously reported in the literature. Silaoxetes, in general, have received only limited attention. The only report of a siloxete is from Seyferth and coworkers who postulated the intermediacy of 3,4-bis(trimethylsilyl)-2,2-dimethyl-2-silaoxete in the DMSO oxidation of 2,3-bis(trimethylsilyl)-1,1-dimethylsilarene (Scheme 32) (30). This silaoxete reacted similarly to saturated silaoxetanes by decomposing rapidly to bis(trimethylsilyl)acetylene and dimethylsilanone. A potential advantage of benzosilaoxetes over other silicon-oxygen containing four-membered rings is that rapid decomposition to silanones should occur less readily because two highly reactive, unstable intermediates, benzyne and a silanone, would necessarily be generated. Hence, benzosilaoxetes are a potential stable direct source of silanones.

The primary synthetic route to benzosilaoxetes was based upon ring formation by a metal catalyzed dehydrocondensation of a silyl hydride and an alcohol. The formation of Si-O bonds using this methodology has ample precedent (114-116). In fact, Tumey has shown that silaoxetanes may be formed by similar dehydrocondensation reactions (12). The obvious advantage of using this method is that no acid or base is generated.

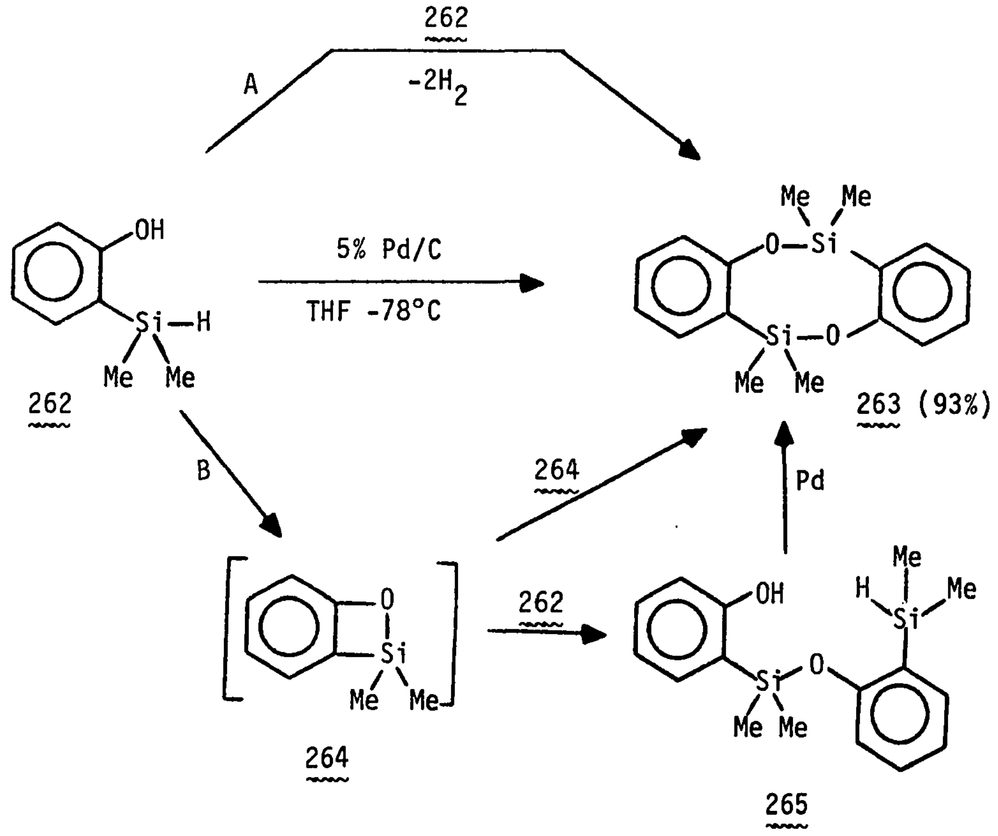
The precursors to the benzosilaoxetes were readily prepared according to the procedure of Mironov *et al.* (Scheme 79) (116, 117). This two step synthesis generally afforded the desired *o*-silylphenol in 50-60% overall yield. The thermal rearrangement of 260 to 261 is formally analogous to the Speier rearrangement.

Scheme 79



The initial system examined was the *o*-dimethylsilylphenol 262. Treatment of a dilute THF solution containing 262 at -78°C with 5% palladium on charcoal afforded a 93% yield of the eight-membered ring 263 (Scheme 80). None of the expected benzosilaoxete 264 was observed. The formation of 263 could conceivably occur by two mechanistically different paths: path A or path B. In path A, 263 is formed in a simple bimolecular dehydrocondensation involving two molecules of starting material. In path B, the benzosilaoxete 264 is initially formed. The benzosilaoxete may either dimerize with itself to yield 263 or may react with the O-H bond in starting material to yield 265 which dehydrocondenses to 263.

Scheme 80

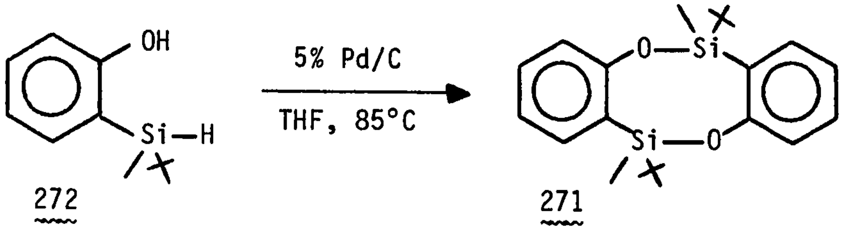


Although path A cannot rigorously be eliminated, a bimolecular reaction between two molecules of 262 seems unlikely under the high dilution conditions. Path B has precedent in the work of Hoekman, who reported that the D_2 analog, 2,4-di-*t*-butylcyclodisiloxane, could dimerize to the D_4 analog or could add MeOH across a Si-O bond to afford a linear siloxanol (Scheme 31 in the Historical section). Hoekman also reported that the D_2 analog could be trapped by the Si-O bond in D_3 (14).

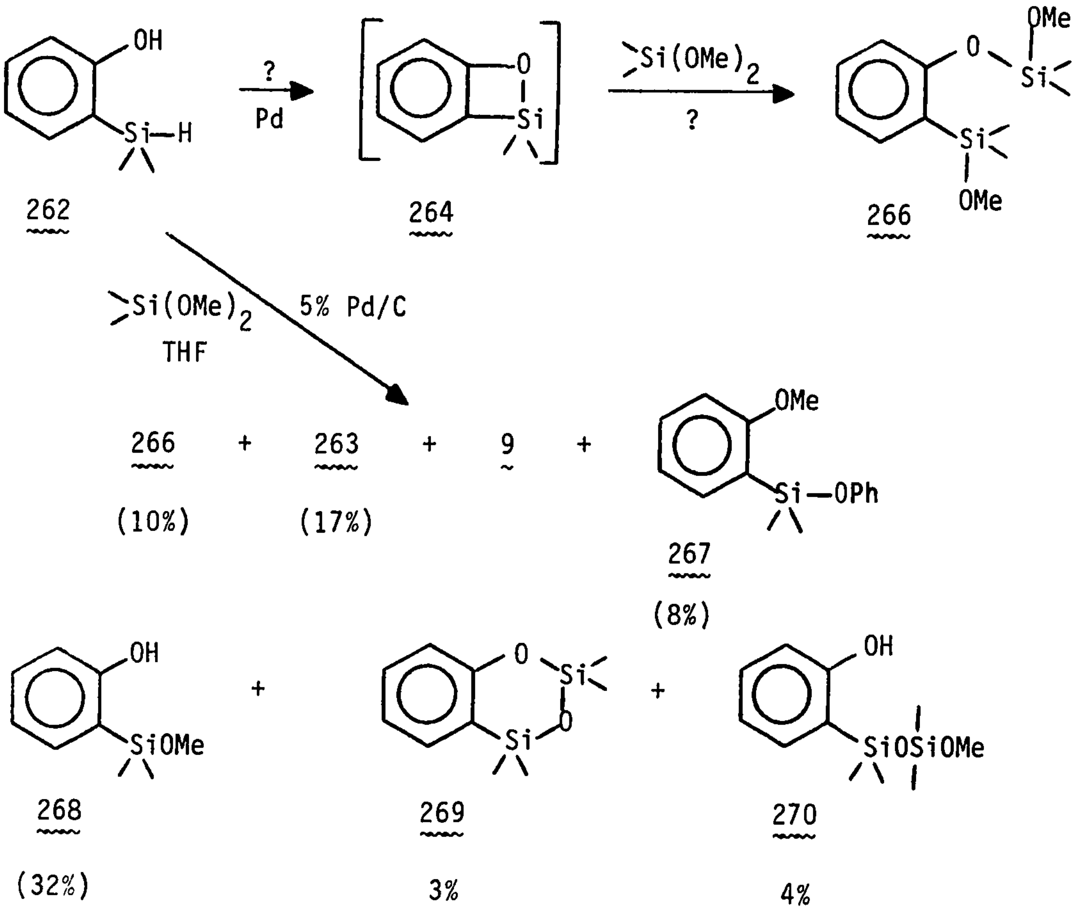
This latter trapping experiment by Hoekman suggests that path A and path B in Scheme 80 may be differentiated by attempting to trap the benzosilaoxete 264 with a Si-O bond. Thus, the reaction of 262 with 5% palladium on charcoal was repeated in the presence of dimethyldimethoxysilane. If the benzosilaoxete is formed, it could conceivably be trapped to afford the dimethoxydisiloxane 266 (Scheme 81). Indeed, analysis of the reaction mixture by GC-MS revealed the presence of 266. However, numerous other products were also formed. The complexity of reaction mixture prohibited isolation of these products; hence, their identification was based solely on mass spectral data. The indicated yields were deduced from relative peak areas.

A simple mechanistic interpretation of this reaction is impossible. The product mixture suggests that a metal catalyzed redistribution process may be occurring (3). This possibility prevents any conclusive statement regarding the entrapment of benzosilaoxete 264 with dimethyldimethoxysilane. Thus, both path A and path B in Scheme 80 remain mechanistic possibilities.

In an additional attempt to distinguish between path A and path B, the palladium catalyzed dehydrocondensations of *o*-(*t*-butylmethylsilyl)-phenol and *o*-(di-*t*-butylsilyl)phenol were examined. An increase in steric bulk around the silicon would be expected to inhibit the bimolecular dehydrocondensation reaction : path A. Treatment of *o*-(*t*-butylmethylsilyl)phenol with 5% Pd/C in refluxing THF afforded only a trace amount of the eight-membered ring 271. The majority of starting material was recovered unchanged. Refluxing o-(di-t-butylsilyl)phenol in a THF solution containing 6% Pd/C for 24 hours yielded only recovered starting material.



Scheme 81

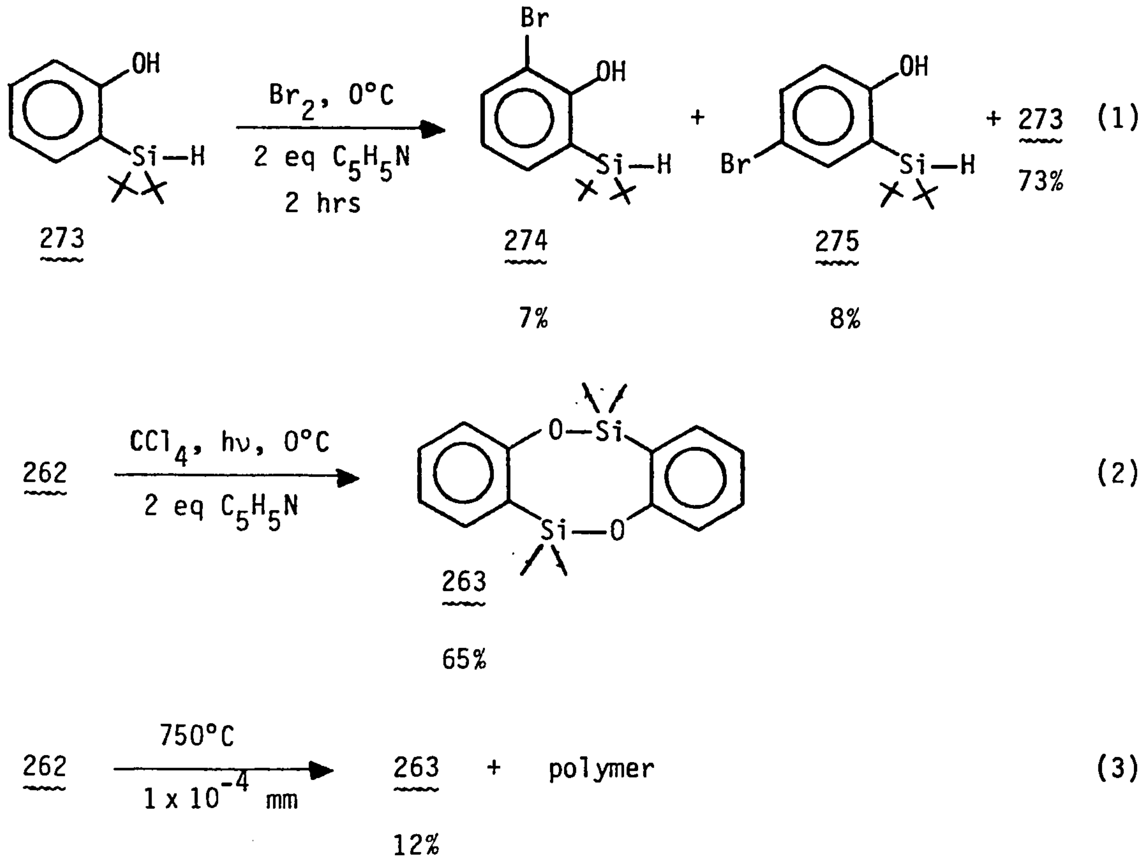


Unfortunately, it appears that the increased steric bulk around silicon inhibited oxidative-addition of the silyl hydride to the metal, thus, preventing the occurrence of any bimolecular or intramolecular dehydrocondensation reaction (118). Thus, path A in Scheme 80 still remains a viable mechanistic alternative for formation of 263 from 262.

Several other routes to a benzosilaoxete were examined. At best, these routes were only equivalent to the previously discussed dehydrocondensation route in both product formation and mechanistic alternatives. Scheme 82 illustrates these other attempts at preparing benzosilaoxetes.

Tumey has previously suggested that 2-dimethylsilylethanol reacts with bromine to afford an intermediate 2,2-dimethylsilaoxetane *via in situ* conversion of the silyl hydride to a silyl bromide and subsequent Si-O bond formation (12). In similar fashion, 273 was reacted with bromine in the hope of forming a stable benzosilaoxete (reaction 1, Scheme 82). Surprisingly, bromine failed to react with the Si-H bond. Instead, bromination of the aromatic ring occurred. Apparently, conversion of 273 to the corresponding silyl bromide is sterically inhibited. Similar results were observed when 272 was treated with bromine. Treatment of 262 under somewhat milder halogenation conditions (CCl_4, hν) (reaction 2, Scheme 82) afforded a 65% yield of 263. As stated before, the observance of 263 is consistent with either a bimolecular condensation mechanism or benzosilaoxete intermediacy.

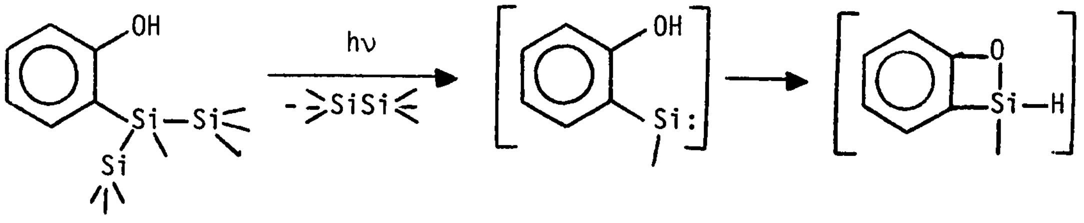
Scheme 82



The mass spectrum of 262 shows a substantial M^+-2 fragment, suggesting the formation of 264 by electron impact. Thus, 262 was pyrolyzed (750°C, 1 X 10^{-4} torr) in an attempt to duplicate this reaction. The pyrolysate (70% mass recovery) contained no starting material and one volatile product, 263, formed in 12% yield. Analysis of the nonvolatile portion of the pyrolysate by ^1H NMR revealed that only silicon-methyl and aromatic hydrogens were present, indicative of a polymer whose structure resembles 263 (reaction 3, Scheme 82). These results are consistent with either benzosilaoxete intermediacy or a bimolecular reaction. Presumably, the Si-H bond in 262 is initially cleaved to afford a silyl radical. This silyl radical could undergo intramolecular homolytic substitution to afford the benzosilaoxete, which dimerizes to 263 or oligermerizes to polymer, or intermolecular homolytic substitution, followed by additional Si-H bond cleavages and radical substitutions, to ultimately afford the observed products.

The synthesis of a benzosilaoxete was also attempted by an intramolecular O-H bond silylene insertion reaction (Scheme 83). The predicted course of this reaction was silylene formation, from irradiation of 276 and loss of hexamethyldisilane, followed by O-H bond insertion. Both of these steps are well-precedented in intermolecular examples (119, 120).

Scheme 83

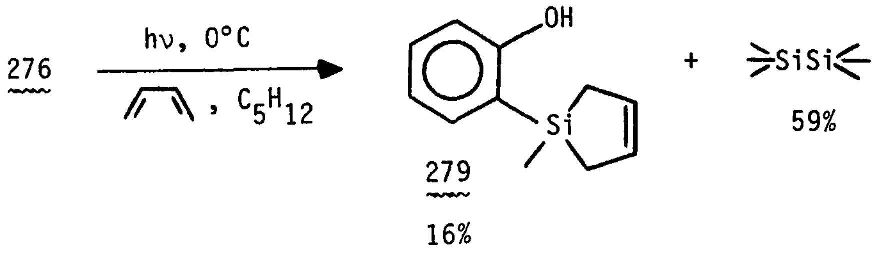


276 277 278

Irradiation of a solution of 276 with a 450 watt mercury arc lamp did indeed afford a high yield of hexamethyldisilane. Unfortunately, no products predicted to arise from the presumed silylene intermediate were observed. Analysis of the photolysate by GC-MS and GC-IR revealed that at least eleven volatile products were formed in low yields; none of which contained a Si-H bond or corresponded to 278 or its dimer. Because of the complexity of the photolysate and the obvious lack of desired products, no further structural identification of the minor products was attempted.

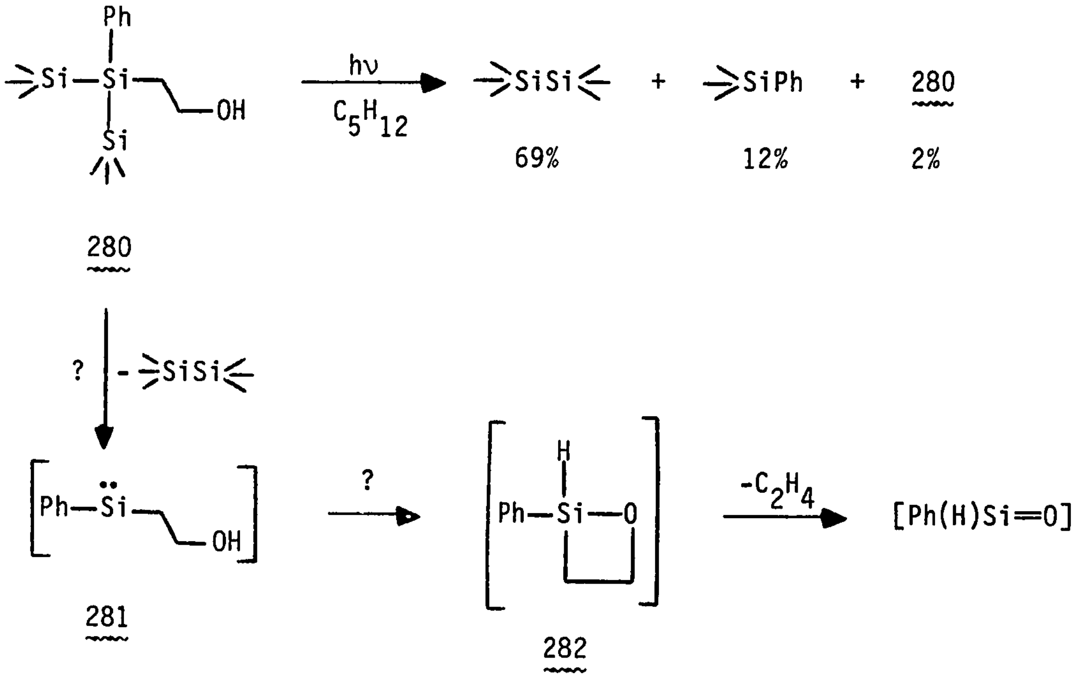
The complexity of this irradiation was surprising. The silylene 277 would appear to have little choice but to react with an O-H bond to form 278 or its dimer. To insure that silylene 277 was being generated, the reaction was repeated in the presence of butadiene, a highly efficient silylene trap. Surprisingly, only a 16% yield of trapped silylene was obtained (Scheme 84). This low trapping yield suggests that the generation of silylene 277, by irradiation of 276, does not cleanly occur. Thus, the complex reaction observed when 277 was photolyzed is not so unexpected.

Scheme 84



This method of attempted benzosilaoxete formation was also utilized in an attempt to generate a 2-silaoxetane. Preparation of the required starting material 2-phenyl-2-(β-ethanol)hexamethyltrisilane 280 was achieved in 31% yield by hydroboration-oxidation of 2-phenyl-2-vinylhexamethyltrisilane. Photolysis of 280 gave results similar to the previously discussed photolysis of 276. The only volatile products observed were hexamethyldisilane, trimethylphenylsilane and recovered starting material (Scheme 85). Hexamethyldisilane is the expected α-elimination product leading to the generation of silylene 281. Trimethylphenylsilane presumably also arises in an α-elimination process. Weber has reported the photolysis of 2-phenylheptamethyltrisilane yields small amounts of trimethylphenylsilane (28).

Scheme 85



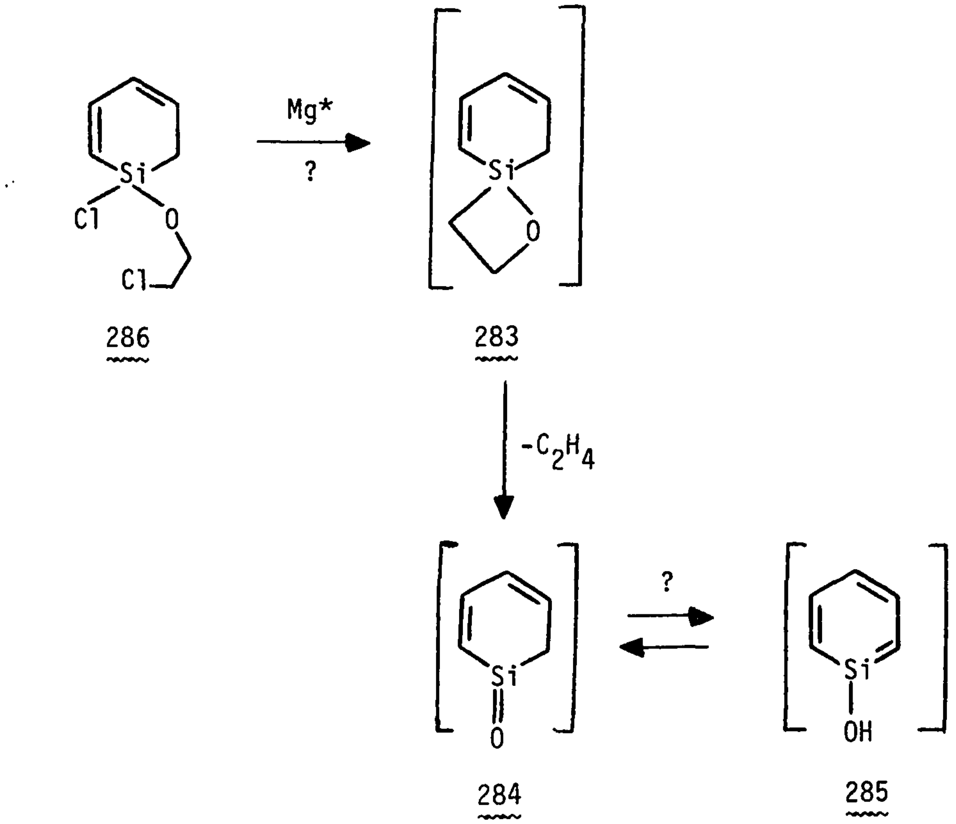
Attempts to trap the presumed silylene intermediate 281 and phenylsilanone, expected from decomposition of 282, with Et_3SiH and $Me_2Si(OMe)_2$, respectively, met with failure. Because no evidence indicating silylene, 2-silaoxetane, or silanone formation was obtained, further studies on this system were not pursued.

To conclude this section, evidence for the intermediacy of a benzosilaoxete in the previously discussed reactions is the observation of benzosilaoxete dimers and, in one case, trapping of the benzosilaoxete with dimethyldimethoxysilane. However, a definitive claim of benzosilaoxete generation cannot be made. The available evidence does not eliminate the possibility of product formation by routes which do not involve benzosilaoxete intermediacy. No evidence that the presumed benzosilaoxetes decompose to dimethylsilanone and benzyne, in anolgy to the decomposition of silaoxetanes, was obtained.

Attempted 2-silaoxetane formation *via* magnesium induced silicon-carbon bond formation

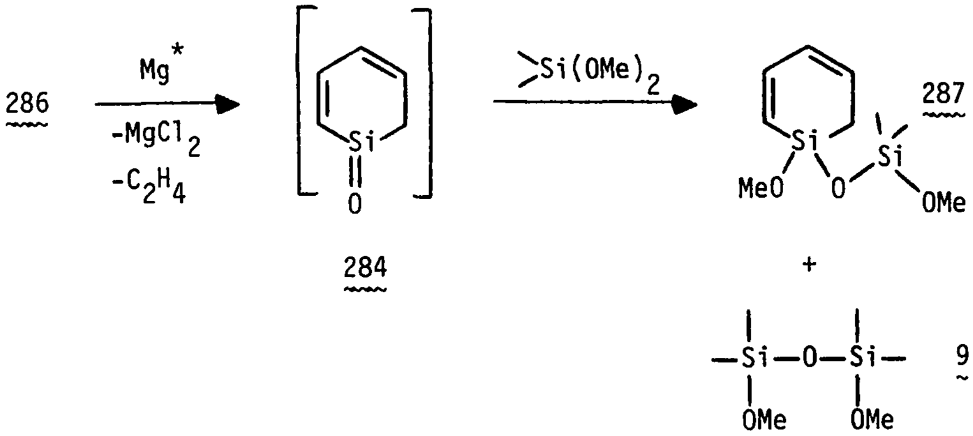
Tumey has recently reported that the reaction of magnesium with chloro-(2-chloroethoxy)dimethylsilane, chloro-(2-chloro-2-phenylethoxy)-dimethylsilane or 1-bromo-3-(chloromethyl)-1,1,3,3-tetramethyldisiloxane resulted in Si-C bond formation and products consistent with silaoxetane intermediacy (Scheme 29) (12). This method of silaoxetane formation was utilized in an attempt to generate the novel spirosilacyclohexadiene-oxetane 283. Interest in this system stems from a desire to examine the importance of a silenol to silanone equilibrium. The silaoxetane 283 should rapidly decompose to silacyclo-2,4-hexadiene-1-one 284 (Scheme 86). If this silanone has a sufficiently long lifetime, formation of the 1-silaphenol 285, by a formal 1,3-hydrogen shift may occur. Thus, a keto-enol type equilibrium involving a silanone and silenol might be observed.

Scheme 86



The starting material for this experiment, 1-chloro-1-(2-chloroethoxy)silacyclo-2,4-hexadiene 286, was prepared from 1,1-dichlorosilacyclo-2,4-hexadiene and 2-chloroethanol. Treatment of 286 with Rieke magnesium (121) in THF at -78°C gave a complex reaction mixture which, by GC, consisted of at least seven components, all formed in low yield. Analysis of the reaction mixture by TLC indicated considerable polymer formation. Analysis by GC-MS showed that no starting material remained and no products consistent with cyclooligermerization of silanone 284 or dimerization of silene 285 were formed.

Evidence that the silanone 284 was formed was obtained by repeating the reaction in dimethyldimethoxysilane. Again, a complex reaction mixture was obtained; however, formation of the silanone insertion product 287 was indicated by GC-MS analysis. Also formed was a considerable amount of 1,3-dimethoxytetramethyldisiloxane.



In retrospect, the complex results obtained from these magnesium induced ring closure reactions are not unexpected. Three highly reactive intermediates, 283, 284, and 285, are predicted to be generated. Each one of these species can ultimately lead to a host of different products. In addition, the reaction conditions used evidently resulted in considerable Si-O bond cleavage. The formation of 1,3-dimethoxytetramethyldisiloxane suggests that Rieke magnesium can promote the redistribution of dimethyldimethoxysilane. Thus, the necessity of using activated magnesium also contributed to the complexity of the reaction. (The use of unactivated magnesium resulted in unreacted starting material.)

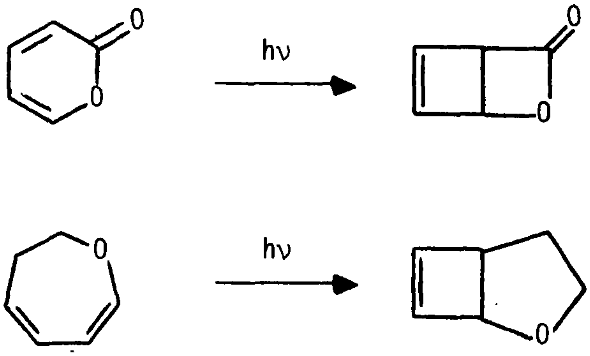
One note of interest, Tumey, in his study of Rieke magnesium induced silaoxetane formation, also reported complex reaction mixtures (12). However, Tumey does not indicate that he observed cleavage of Si-O bond and recombination, a process which appears to be significant in this work. Because many of Tumey's results can be explained by this process, his conclusions should be carefully regarded.

The importance of a silanone-silenol equilibrium is difficult to judge from the sparse data gathered in this study. Trapping experiments suggest the silanone 284 was formed, but no products were observed which indicated the presence of the silene 285. Further work in this area is certainly warranted.

Photolysis of dimethylsila-α-pyran: attempted formation of a 2-silaoxetane

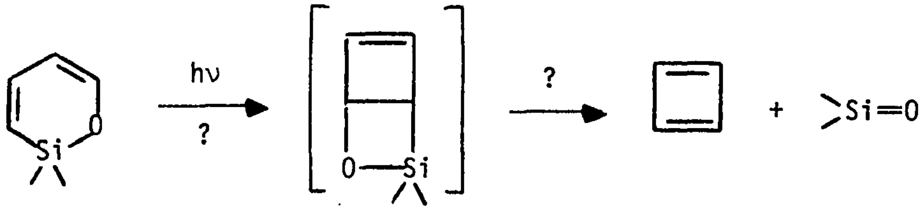
The photochemically induced disrotatory ring closure of cyclic dienes is well precedented (122, 123). A few examples are illustrated below in Scheme 87.

Scheme 87



It was desired to utilize this ring closure method in preparing a 2-silaoxetane from the readily available dimethylsila-α-pyran 120 (Scheme 33). Thus, photolysis of 120 was predicted to yield the bicyclosilaoxetane 288 (Scheme 88). The normal mode of 2-silaoxetane decomposition should be inhibited in 288 because two highly reactive, unstable species, dimethylsilanone and cyclobutadiene, would be generated. It was, therefore, hoped that 288 might exhibit unusual stability. Even if decomposition to dimethylsilanone occurred, a relatively simple route to cyclobutadiene would result.

Scheme 88

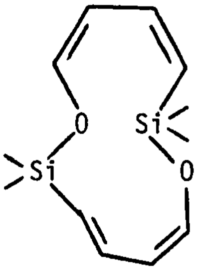


120 288

Wulff had previously reported that the photolysis of 120 through quartz in the presence of dimethyldiethoxysilane for 175 minutes yielded no volatile products (13). In spite of this unfavorable precedent, the reaction was repeated. Irradiation of 120 in degassed pentane through quartz with a 450 watt Hanovia lamp resulted in rapid consumption of starting material. After 45 minutes, 95% of 120 had reacted. Analysis of the reaction mixture by GC-MS revealed that one major volatile product whose molecular weight corresponded to a dimer of 120 had been formed.

This product was isolated by preparative GC (27% yield) and total spectral analysis was obtained.

As of this date, conclusive structural identification has not been achieved. The important spectral features are listed below. Complete spectral data are given in the experimental section. Exact mass measurements indicated a molecular formula of $C_{12}H_{20}O_2Si_2$, a dimer of 120. Hydrogen NMR showed two different silicon-methyl groups, twelve total hydrogens, and multiple peaks from 5.3 ppm to 7.0 ppm, eight total hydrogens. Carbon 13 NMR showed eight different vinyl carbons and two different silicon-methyl carbons. A 300 MHz hydrogen NMR indicated two separate diene units with coupling constants that ranged from 0.5 Hz to 19 Hz. A conjugated diene unit was also consistent with ultraviolet-visible spectral data: λ max equals 238 nm. Obviously, these data eliminate any symmetrical dimer. The 19 Hz coupling constant suggests a trans double bond. A possible structure for the dimer 120 is shown below.



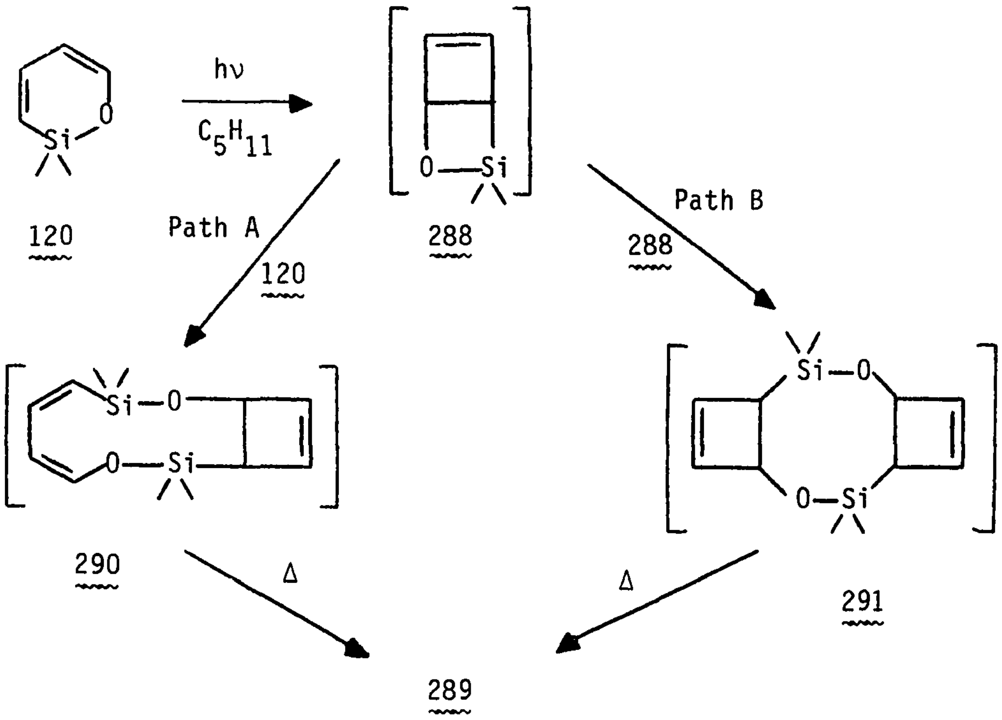
289

Attempts to obtain a crystalline adduct of the dimer with maleic anhydride failed. The dimer 289 is relatively unstable, and the long reaction times necesary for adduction formation evidently led to isomerization and decomposition.

Because conclusive structural proof has not been obtained, the formulation of a mechansim for the formation of 289 must be purely speculative. Nevertheless, one is presented in Scheme 89. Based on literature precedent, irradiation of 120 affords the 2-silaoxetane 288. As predicted, this 2-silaoxetane does not decompose to dimethylsilanone and cyclobutadiene but reacts with 120 or with itself to afford 290 or 291. Similar trapping of silaoxetanes with Si-O bond has been previously reported (14). A thermally induced cyclobutene ring opening, either concerted or radical in nature, affords the observed dimer containing a trans double bond. If ring opening occurs in a concerted, disrotatory fashion, with the bulky dimethylsilyl group rotating to avoid steric interaction, the expected product from intermediate 290 would be 289. Because the ring opening reaction may be radical in nature and may proceed from two different intermediates, 290 or 291, several isomers of 289 may be expected. Indeed, a careful examination of the GC-MS obtained on the photolysate showed, in addition to the isolated dimer 289, that at least three other dimers were formed in trace amounts.

It would appear from subsequent experiments that path A in Scheme 89 is not very important. This path would predict that other Si-O bonds should also trap the 2-silaoxetane 288. However, photolysis in the presence of dimethyldimethoxysilane yielded only the dimer 289. No trapping of 288 was observed. Photolysis of 120 in MeOH resulted in numerous adducts of 288 and MeOH as determined by GC-MS. Unfortunately, this trapping experiment proved fruitless as 120 is unstable towards protic reagents and can react with MeOH by totally different processes not involving a 2-silaoxetane. Until the dimer 289 can conclusively be identified, the importanace of any 2-silaoxetane intermediate in the irradiation of 120 cannot be determined. It would be interesting to irradiate 120 in an argon matrix, inhibiting any thermal reactions, and perhaps obtaining direct spectral evidence for the 2-silaoxetane 288.

Scheme 89



CONCLUSION

Based on the inert thermal behavior of o-(pentamethyldisilyl)benzyl methyl ether, the previously reported formation of 1,1-dimethylsila-α-pyran from thermolysis of Z,Z-1-(pentamethyldisila)-4-methoxy-1,3-butadiene does not proceed via direct elimination of tetramethylsilane (13). Instead, an initial 1,5-silyl shift, followed by ring closure and β-elimination of tetramethylsilane, was determined to be the mechanism of choice.

Reaction of 1,1-dimethylsila-α-pyran with maleic anhydride afforded a stable adduct which was isolated in high yield. Thermolysis (170°C) or photolysis (450 watt mercury arc lamp) of this adduct furnished dimethylsilanone, which was trapped with siloxanes, and 1,2-dihydrophthalic anhydride or benzene, CO, and CO_2, repectively. Relative rate studies on the photodecomposition of the adduct indicated that dimethylsilanone formation was not dependent on added siloxanes. Although this suggested that free dimethylsilanone was formed, a silanone-transfer mechanism could not rigorously be eliminated.

1-Methyl-1-trimethylsila-α-pyran and its maleic anhydride adduct were prepared and shown to be efficient thermal and/or photochemical generators of methyl(trimethylsilyl)silanone. The potential isomerization of methyl(trimethylsilyl)silanone to methyl(trimethylsiloxy)silylene via a 1,2-silicon migration was examined using these methods of generation. At temperatures as great as 480°C, no evidence for isomerization was found. Evidence for this isomerization was obtained by generation of methyl(trimethylsilyl)silanone from pyrolysis of its D_4 analog, in similar fashion to the reported generation of dimethylsilanone from pyrolysis of D_4 (18, 19). Copyrolysis of 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(trimethylsilyl)cyclotetrasiloxane with butadiene (610°C) afforded a high yield of trapped methyl(trimethylsiloxy)silylene.

The independent generation of methyl(trimethylsiloxy)silylene (620°C) was found, in the absence of silylene traps, to afford an intermediate 2,4-disilaoxetane via a γ-C-H bond insertion mechanism. This 2,4-disilaoxetane underwent decomposition to methylsilanone and dimethylsilene or dimethylsilanone and methylsilene.

In contrast to the complexity of alkyl furan photochemistry, the photolysis of silicon-substituted furans resulted in clean isomerization to allenyl aldehydes and ketones. A silicon-stabilized carbene was postulated as the key intermediate. The allenyl carbonyl compounds were found to be thermally unstable. The allenyl ketones derived from 2,5-disilyl-substituted furans underwent thermal isomerization to 2,4-disilyl-substituted furans or to stable enynols.

The irradiation of 2-silyl-substituted pyrroles afforded rapid and quantitative isomerization to 3-silyl-substituted pyrroles. 2,5-Disilyl-substituted pyrroles were found to photoisomerize to 2,3-disilyl and then to 3,4-disilyl-substituted pyrroles. An electrocyclic ring closure to an azabicyclo[2.2.1]pent-2-ene, followed by a nitrogen ring walk and electrocyclic ring opening, was postulated as the mechanism of isomerization.

The preparation of several silaoxetanes and silaoxetes was attempted by a variety of methods: nucleophilic substitution, metal catalyzed dehydrocondensation, silylene O-H bond insertion, and photoinduced electrocyclic ring closure. In no case was a stable silaoxetane or silaoxete isolated; however, indirect evidence for their formation was obtained.

EXPERIMENTAL

Instrumentation

Routine ^1H NMR spectra were recorded on either a Varian model A-60, EM-360, EM-360L or a Hitachi-Perkin Elmer R-20B spectrometer. High resolution ^1H NMR was obtained on a Bruker WM-300 spectrometer. All chemical shifts are reported as parts-per-million (δ scale) from tetramethylsilane using either tetramethylsilane, chloroform, methylene chloride, or benzene as an internal standard. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer using $CDCl_3$ or C_6D_6 as an internal standard.

Infrared (IR) spectra were recorded on either a Beckman IR-4250 or a Beckman Acculab-2 spectrometer. The 2000 cm^{-1} grating change was used as a reference mark. Gas chromatograph-infrared spectra (GC-IR) were obtained using an IBM-IR 98 spectrometer coupled to a Hewlett Packard 5880A gas chromatograph.

Gas chromatograph-mass spectra (GC-MS) were recorded on a Finnegan Model 4023 mass spectrometer. Exact mass measurements were obtained on a MS-902 spectrometer. All mass spectra, unless otherwise noted, were recorded at 70 eV.

Ultraviolet (UV) spectra were obtained on a Perkin Elmer 320 spectrophotometer. Irradiations were performed with a 450 W Hanovia high-pressure mercury arc lamp. Unless otherwise noted, all irradiations were carried out in a standard, water-cooled, quartz immersion well or in quartz NMR tubes.

Gas chromatographic (GC) data were obtained on a Varian-Aerograph model 3700, 1700, 920 or Fischer/Victoreen series 4400 gas chromatograph. Column size and packing will be described as used. Unless otherwise stated, all GC yields were determined with internal standards and predetermined response factors.

All melting points (mp) were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

Procedures and Results

Synthesis of chloropentamethyldisilane

Chloropentamethyldisilane was prepared according to the procedure of Sakurai and coworkers from $AlCl_3$ and hexamethyldisilane (124).

Synthesis of hexamethyldisilane

Hexamethyldisilane was prepared in a manner identical to the procedure of Gilman and Harrell except Li wire was substituted for Li sand (125).

Synthesis of *cis*-1-(pentamethyldisilanyl)-4-methoxybut-1-yn-3-ene **126**

cis-4-Methoxybut-1-yn-3-ene **125**, commercially available from Aldrich Chemical Co., was purified by extraction with H_2O and ether, drying of the ether layer with Na_2SO_4, and distillation (bp 122-125°C). To a stirring solution of 49.3 g (0.601 mol) of **125** in 1.5 L of THF cooled to 0°C was added *n*-butyllithium (0.601 mol) contained in hexane. After 20 min, 100.0 g (0.601 mol) of chloropentamethyldisilane were rapidly added and stirring continued for 1 h. Following extraction with saturated aqueous ammonium chloride, water, and saturated aqueous sodium chloride, the organic layer was dried with magnesium sulfate. After removal of solvent, distillation at 85-87°C and 4 torr afforded 97.0 g (76%) of **126**. The spectral characteristics of **126** were identical to those previously reported by Wulff (13).

Synthesis of *cis,cis*-1-(pentmethyldisilanyl)-4-methoxy-1,3-butudiene **127**

Borane reduction The general method previously described by Zweifel and Polston was utilized (126). Diisamylborane (0.260 mol) was prepared by adding 0.260 mol of BH_3•THF complex to a solution of 36.4 g (0.52 mol) of 2-methyl-2-butene in 125 mL of THF at 0°C. After stirring for 2 h at 0°C, this solution was added to a solution of 50 g (0.236 mol) of **126** in 250 mL of THF and stirring was continued for 3 h at 0°C. After addition of 63 mL of glacial acetic acid, the reaction mixture was heated at 55°C for 5 h. This solution was cooled to room temperature, and 220 mL of 20% aqueous sodium hydroxide followed by 65 mL of 30% H_2O_2 were added slowly. After stirring for an additional 30 min, the aqueous layer was removed and washed with hexane. The combined organic phase was washed with saturated aqueous sodium chloride and dried with $MgSO_4$. After removal of the solvent, distillation at 80-89°C and 3 torr afforded 18.7 g (37%) of slightly impure **127**. The spectral characteristics of **127** were identical to those previously reported by Wulff (13).

DIBAL reduction The reduction of 126 was alternatively carried out using the method previously described by Eisch and Foxton (127). N-Methylpyrrolidine (15.0 g, 0.18 mol) was added to 180 mL of diisobutylaluminum hydride (1 M in heptane) at 0°C. After stirring at 25°C for 20 min, 126 (31.8 g, 0.15 mol) was added and stirring was continued at 60°C for 14 h then 90°C for 3 h. The solution was cooled to 25°C and slowly poured into 200 mL of a H_2O/ice slurry. The organic layer was separated, extracted with saturated sodium chloride, and dried over Na_2SO_4. Removal of the solvent and distillation (80°-85°C, 3 torr) afforded 19.3 g (60%) of 127.

Synthesis of 1,1-dimethylsila-α-pyran; pyrolysis of 127

Compound 127 (6.30 g) was pyrolyzed by evaporating (100°C, 1×10^{-3} torr) through a horizontal quartz tube packed with quartz chips heated to 760°C. The pyrolysate was collected in a liquid nitrogen cooled trap and represented an 84% mass recovery. The two major products were identified as tetramethylsilane (30% GC yield), by comparison of its GC retention time and GC mass spectrum with an authentic sample, and 1,1-dimethylsila-α-pyran (52% GC yield), by comparison of its NMR, IR, and GC mass spectra to those previously reported by Wulff (13). 1,1-Dimethylsila-α-pyran was purified by preparative GC on a 12' 15% SE-30 column. Distillation of the pyrolysate and collection of the fraction boiling between 25°C and 55°C at 7 torr to 0.1 torr afforded 120 in 75% purity. If the pyrolysis of 127 is carried out by dropping through a vertical quartz tube with a nitrogen sweep, the yield of 120 decreases and the number of minor products increase.

Synthesis of o-bromobenzyl methyl ether

o-Bromobenzyl methyl ether was prepared from α,o-dibromotoluene and sodium methoxide according to the procedure of Supniewsky and Adams (128).

Synthesis of o-(pentamethyldisilyl)benzyl methyl ether 131

To a stirring solution of o-bromobenzyl methyl ether (4.4 g, 0.022 mol) in 150 mL of ether at 0°C was added 8.8 mL of 2.5 M n-butyllithium in hexane. After 1 h, 4.0 g (0.024 mol) of chloropentamethyldisilane was added and stirring was continued overnight. Addition of 500 mL of pentane, filtration of the precipitated salts, and concentration by rotary evaporation afforded a yellow oil containing mostly 131. Disilane 131 was isolated and purified by preparative GC (10' 15% SE-30): NMR (CCl_4) δ 0.01 (s, 9H), 0.31 (s, 6H), 3.28 (s, 3H), 4.32 (s, 2H), 7.18 (m, 4H); mass spectrum, m/e (% relative intensity) 237 (0.9), 179 (40), 149 (100), 73 (38); calculated for $C_{12}H_{21}OSi_2$ (M^+-CH_3) 237.11310, measured 237.11303.

Pyrolysis of o-(pentamethyldisilyl)benzyl methyl ether 131

Pyrolysis of 131 was performed by slowly dropping 0.196 g through a vertical quartz tube, packed with quartz chips, swept with N_2 at 30 mL/min, and heated to 790°C. The pyrolysate (0.165 g) was analyzed by

GC-MS and was composed of greater than 90% unreacted **131** with no tetramethylsilane or isomers of **133** detectable.

Synthesis of 2,2,4,6-tetramethylpyran 135

2,2,4,6-Tetramethylpyran was prepared by slight modification of the procedure of Safieddine and Dreux (68). 2,4,6-Trimethylpyrylium perchlorate (6.4 g, 0.029 mol), freshly prepared and recrystallized (129), was carefully added to 150 mL of ether at -78°C. Methyl lithium (0.030 mol) was then added at such a rate as to maintain a reaction temperature of -25°C or below. Following extraction with saturated sodium chloride, the organic layer was dried with Na_2SO_4 and kept at 0°C. After removal of the solvent, analysis of the residue by NMR indicated the presence of **135** which was isolated and purified by preparative GC (8' 12% OV101). The identity of **135** was established by comparison of its NMR spectrum to that originally published by Safieddine and Dreux (68). It was found necessary to freshly prepare **135** prior to its use. When allowed to stand, **135** rapidly decomposes by isomerization to the acyclic dienone.

Reaction of 135 and dimethyl acetylenedicarboxylate

To 0.25 g (0.0018 mol) of freshly prepared 2,2,4,6-tetramethylpyran was added 0.25 g (0.0017 mol) of dimethyl acetylenedicarboxylate in CCl_4. The progress of the reaction was monitored by ^1H NMR. After several hours at 25°C, acetone and dimethyl 3,5-dimethylphthalate **136** were observed in considerable, but undetermined, amounts, along with previously observed products from decomposition of 135. Compound 136 was identified by comparison of its NMR and mass spectrum to those previously reported (130).

Reaction of cyclopropene and 1,1-dimethylsila-α-pyran

Cyclopropene was prepared according to the method of Closs and Krantz (131). To 0.105 g (8.3×10^{-4} mol) of 1,1-dimethylsila-α-pyran contained in CCl_4 was bubbled an excess of freshly prepared cyclopropene until no remaining silapyran could be detected by ^1H NMR. Analysis of the reaction mixture by ^1H NMR and GC-MS revealed no evidence for adduct 137. As determined by comparison of mass spectra to authentic samples, cycloheptatriene, D_3, D_4, and D_5 were the major products of reaction. No yields were determined. All attempts to isolate the presumed initially formed adduct by trap to trap distillation, column chromatography (silica gel, hexane), or preparative GC (10' 10% OV101) were unsuccessful.

Synthesis of 1,1-dimethylsila-α-pyran/maleic anhydride adduct 138

To a benzene solution containing 2.1 g (0.017 mol) of 120 was added 1.5 g (0.015 mol) of freshly sublimed maleic anhydride. The solution was stirred at 60°C for 20 h or until 120 could no longer be detected by GC. Adduct 138 was isolated and purified by repeated crystallization from benzene/pentane: 2.7 g (80%); mp 124-125°C; NMR ($CDCl_3$) δ 6.40 (m, 2H), 4.90 (m, 1H), 3.67 (d of d, 1H, J_{AB} = 9 Hz), 3.18 (d of d, 1H), 2.63 (m, 1H), 0.19 (s, 3H), 0.01 (s, 3H); UV (THF) λ max 222 nm (1787); IR

(KBr) 2980, 1880, 1790 cm^{-1}; mass spectrum, m/e (% relative intensity) 209 (0.4), 152 (61), 137 (88), 78 (90), 75 (100); calculated for $C_9H_9O_4Si$ (M^+-15) 209.02701, measured 209.02770. Adduct 138 proved unstable to GC (5' 3% OV101), HPLC (30 cm Porasil, hexane/$CHCl_3$), or column chromatography (silica gel, hexane). Partial decomposition of 138 to several unidentified products occurred in every case.

General procedure for solution thermolysis of 138

Adduct 138 (50-100 mg) was added to 2-3 mL of solvent (freshly distilled from CaH_2) contained in a 10 mL thick wall ampule. After freeze-thaw degassing, the mixture was sealed under vacuum and heated at 180°C for 2 h. This procedure was utilized with the following solvents.

o-Dichlorobenzene Analysis of the reaction mixture by GC-MS revealed four major products: D_3 (29%), 139 (12%), 1,2-dihydrophthalic anhydride (67%), and phthalic anhydride. The identity of D_3, 1,2-dihydrophthalic anhydride, and phthalic anhydride were established by comparison of their spectral data to authentic samples (70). The identity of 139 was based solely upon its mass spectrum: m/e (% relative intensity) 283 (0.10), 255 (0.12), 177 (7.0), 1491 (25), 133 (39), 105 (23), 78 (100). The yield of 139 was calculated assuming its response factor was equivalent to 1,2-dihydrophthalic anhydride.

Diglyme Analysis of the reaction mixture again revealed four major products: D_3 (13%), 139 (19%), 1,2-dihydrophthalic anhydride (60%), and phthalic anhydride (23%).

Diphenyldimethoxysilane Analysis of the reaction mixture by GC revealed that three major products had been formed: 1,2-dihydrophthalic anhydride (53%), phthalic anhydride (10%), and the dimethylsilanone insertion product, 1,1-dimethyl-1,2-dimethoxy-3,3-diphenyldisiloxane 143 (66%). The insertion product 143 was isolated and purified by preparative GC (8' 10% SE-30): NMR ($CDCl_3$) δ 0.20 (s, 6H), 3.42 (s, 3H), 3.59 (s, 3H), 7.20 (m, 10H); IR (neat) 3060, 2955, 1590, 1260, 1110 cm^{-1}; mass spectrum, m/e (% relative intensity) 303 (16), 241 (61), 211 (13), 181 (18), 165 (23), 105 (23), 91 (100); calculated for $C_{15}H_{19}Si_2O_3$ (M^+-15) 303.08728, measured 303.08692.

Tetramethoxysilane The thermolysis of 138 in tetramethoxysilane was carried out similar to the previously described thermolyses except 6 additional hours of heating were required. Analysis of the crude reaction mixture revealed three major products: 1,2-dihydrophthalic anhydride (45%), phthalic anhydride (28%), and 1,1-dimethyl(tetramethoxy)disiloxane 143 (52%). The insertion product 143 was identified by spectral comparison to an independently prepared sample: NMR ($CDCl_3$) δ 0.01 (s, 6H), 3.40 (s, 12H); IR (neat) 2950, 1265, 1080 cm^{-1}; mass spectrum, m/e (% relative intensity) 226 (0.02), 211 (99), 181 (100), 151 (89); calculated for $C_5H_{15}O_5Si_2$ (M^+-15) 211.04581, measured 211.04614.

Synthesis and thermolysis of 1,2-dihydrophthalic anhydride

The adduct 138 (100 mg) in 100 µL of $CHCl_3$ was pyrolysed by injection onto a GC (injection port temperature 250°C, 12' 15% SE-30).

Collection of the major peak afforded pure 1,2-dihydrophthalic anhydride: mp 98°-100°C (literature 99°-100°C (69)); NMR ($CDCl_3$) δ 3.98 (m, 2H), 5.90 (m, 4H); mass spectrum, m/e (% relative intensity) 150 (10), 148 (3.3), 104 (14), 78 (100). 1,2-Dihydrophthalic anhydride (30 mg) and 200 μL of diglyme were charged into a NMR tube. After freeze-thaw degassing, the tube was sealed under vacuum, and the contents were heated at 180°C. The reaction progress was monitored with ^{1}H NMR. After 1 h, a considerable, but undetermined, amount of phthalic anhydride had been formed. No other products were observed by ^{1}H NMR.

Synthesis of 2,2,4,6-tetramethylpyran-maleic anhydride adduct 144

To a THF solution of freshly prepared 135 (0.77 g, 0.0056 mol) was added 0.51 g (0.0052 mol) of maleic anhydride. After stirring for 10 h at room temperature, the reaction mixture was percolated through a Florisil column with a hexane/ether eluent. Adduct 144 was isolated and purified by recrystallization from ether: 0.43 g (35%); mp 91-92°C; NMR ($CDCl_3$) δ 1.00 (s, 3H), 1.21 (s, 3H), 1.59 (s, 3H), 1.81 (d, 3H, J = 1 Hz), 2.80 (d of d, 1H, J = 2 and 4 Hz), 3.10 (d, 1H, J = 9 Hz), 3.65 (d of d, 1H, J = 9 and 4 Hz), 5.76 (m, 1H); UV (THF) λ max 223 nm (487); IR (KBr) 2970, 2925, 1860, 1775, 1645, 1090, 1070, 910 cm^{-1}; mass spectrum, m/e (% relative intensity) 236 (0.3), 138 (30), 123 (100); calculated for $C_{13}H_{16}O_4$ 236.10490, measured 236.10505.

Thermolysis of 144

A solution of 144 (50 mg) in 3 mL of freshly distilled o-dichlorobenzene was placed in a 10 mL thick wall tube, degassed by the freeze-thaw method, and sealed under vacuum. After heating for 2 h at 180°C, analysis by NMR and GC-MS showed that no 144 remained. Formed in considerable, but undetermined, yield were acetone, identified by NMR and GC-MS comparison to an authentic sample, and 3,5-dimethyl-1,2-dihydrophthalic anhydride 145, tentatively identified by its mass spectrum: m/e (% relative intensity) 178 (M^+, 20), 150 (M^+-CO, 4), 106 (M^+-CO+CO_2, 67), 91 (100).

Relative rate analysis of the thermal decomposition of 138 with and without added silanone trap

In a typical run, equal volumes of a standard solution of 138 (ca. 0.1 g) in ca. 4.5 g o-dichlorobenzene (with ca. 0.05 g of toluene as a NMR standard) were added to a series of NMR tubes. To each NMR tube was also added different amounts (0.0-0.5 g) of silanone trap: diphenyldimethoxysilane or tetramethoxysilane. The volume in each tube was then equalized by the addition of o-dichlorobenzene. Thus, a series of NMR tubes containing equal concentrations of 138 and increasing concentrations of silanone trap were prepared. After freeze-thaw degassing, each tube was sealed under vacuum and all tubes were heated simultaneously at 165°C. At 15-20 min time intervals, the reaction was stopped by immersing the tubes in ice water. The rate of reaction was determined by following the disappearance of the 0.19 ppm $SiCH_3$ absorption of

138 referenced to the toluene standard and calculation of the concentration of **138** remaining. Typical reactions could be followed to 60-75% completion before by-products made integration unreliable. Analysis of each completed run with GC-MS confirmed the presence of **140**, **141**, and the dimethylsilanone trapped products **142** or **143**. The minimum error of these measurements, as estimated from the accuracy of NMR integration, is 5%. In this manner, it was determined that tetramethoxysilane has a rate retardation effect and diphenyldimethoxysilane has either a rate retardation, at concentrations less than 7 molar excess, or a rate acceleration effect, at concentrations greater than 7 molar excess, on the decomposition of **138**.

Relative rate analysis of the thermal decomposition of **138** in *o*-dichlorobenzene, diphenylether and diglyme

All solvents were distilled from CaH_2 under an atmosphere of N_2 prior to their use. To each of 3 NMR tubes were placed *ca.* 0.050 g of **138**, 0.015 g of toluene, and *ca.* 1.0 mL of either *o*-dichlorobenzene, diphenylether, or diglyme. The concentration of **138** in each tube was 0.235 ± 0.01 M. After freeze-thaw degassing, the tubes were sealed under vacuum and heated at 170°C. At 15-20 min intervals, the reaction was stopped by immersion of the tubes in ice water. The concentration of remaining **138** was determined by integration of the 0.19 ppm $\mathrm{SiC\underline{H}_3}$ absorption referenced to the toluene standard. The time at which half of **138** had been consumed ($t_{1/2}$) was noted: *o*-dichlorobenzene 100 ± 10 min, diphenylether 130 ± 10 min, and diglyme 150 ± 10 min. The 10 min error range was estimated by taking the range of $t_{1/2}$ values from 3 runs in o-dichlorobenzene.

Decomposition of 138 in 1,3-dibromopropane

Adduct 138 (0.031 g) and 0.8 mL of freshly distilled 1,3-dibromopropane were charged into a NMR tube, degassed by the freeze-thaw method, and sealed under vacuum. After heating for 20 min at 180°C, no 138 remained as determined by ^1H NMR. GC-MS analysis revealed 140 (95%), D_3 (4%), D_4 (13%), D_5 (10%), and D_6 (7%) which were identified by comparison to authentic samples or to previously reported spectra (132). Also formed and identified by comparative GC-MS were small amounts of 3-bromopropene. Repeating the reaction in identical fashion except for the addition of 0.164 g of D_3 led to similar results. The expected trapping product, D_4, was formed in 4% yield based on insertion of dimethylsilanone into D_3. 1,2-Dihydrophthalic anhydride was formed in 92% yield. The yield of D_4, based on formation from adduct 138 only, was 16%. Thus, no significant trapping of dimethylsilanone was observed.

Vacuum thermolysis of 138

The adduct 138 (0.027 g) was sublimed (1×10^{-4} torr, 60°C) through a horizontal quartz tube packed with quartz chips and heated to 520°C. The pyrolysate (0.019 g) was collected in a liquid N_2 cooled trap. ^1H NMR analysis revealed no 138 remained. The three major products were identified as 140 (59%), D_3 (4.2%), and D_4 (2.6%) by comparison of their GC-MS and retention times to authentic samples. An attempt to trap a long-lived dimethylsilanone by repeating the pyrolysis under identical conditions, except for the addition of diphenyldimethoxysilane to the liquid N_2 cooled trap, met with failure. Analysis of the pyrolysate by GC-MS revealed none of the expected insertion product **142**. Again, the major products were **140**, D_3, and D_4 as determined by GC-MS.

Photolysis of **138** in THF or in diglyme

In a typical reaction, *ca.* 30 mg of **138** and *ca.* 1.0 mL of freshly distilled THF or diglyme were placed in a quartz NMR tube, septum sealed, and degassed with an argon stream. The contents were then irradiated by positioning the tubes adjacent to the quartz cooling jacket surrounding a Hanovia 450 W mercury arc lamp. The progress of the reaction was monitored by ^1H NMR. After 2 h of irradiation in either THF or diglyme, all of **138** had reacted. During the course of irradiation, gas evolution from the reaction mixture was observed. ^1H NMR and GC-MS analysis of the photolysate revealed clean formation of benzene (87% in THF, 72% in diglyme) and D_3 (13% in THF, 10% in diglyme). Also formed in low, but undetermined, yield were D_4 and D_5. Repeating the photolysis of **138** in D_6 benzene afforded little or no decomposition. Irradiation of **138** in an ESR cavity using THF as a solvent yielded no radical signal. A low temperature irradiation of **138**, conducted by immersion of the quartz tube into a dry ice/isopropanol bath in THF, gave results identical to the previously discussed ambient temperature photolysis. No evidence for 1,2-dihydrophthalic anhydride was obtained.

Photolysis of 138 in the presence of dimethyldimethoxysilane or tetramethoxysilane or tetramethoxysilane

To a solution of THF (0.4 mL) and dimethyldimethoxysilane (0.4 mL) or tetramethoxysilane (0.4 mL) contained in a quartz NMR tube was added 0.020 g of 138. After degassing with a stream of argon, the contents of the tube were photolysed for 2 h in the manner described in the previous procedure. Analysis of the yellow photolysate by ^{1}H NMR and GC-MS revealed that benzene (67% in dimethyldimethoxysilane, 89% in tetramethoxysilane) and the dimethylsilanone insertion product 1,3-dimethoxytetramethyldisiloxane 9 (44%) or 1,1-dimethyl(tetramethoxy)disiloxane 143 were cleanly formed. Product 9 was identified by comparison of its ^{1}H NMR and MS to that of an authentic sample: NMR (CCl_4) δ 0.08 (s, 12H), 3.74 (s, 6H); mass spectrum, m/e (% relative intensity) 179 (81), 149 (100), 119 (28), 82 (13), 59 (21). The identity of 143 was established by comparison of its MS to that of a previously prepared sample (see procedure for thermolysis of 138 in tetramethoxysilane).

Photolysis of 144 in D_4

Adduct 144 (50 mg) and 0.60 mL of D_4 were charged into a quartz NMR tube, degassed with argon, and septum sealed. After 1 h of irradiation with a 450 W mercury arc lamp, ^{1}H NMR and GC-MS analysis showed clean formation of *m*-xylene and acetone which were identified by comparison of their spectra to authentic samples. During the course of irradiation, gas evolution was observed.

Relative rate analysis of the photochemical decomposition of 138 with and without added silanone trap

In a typical reaction, equal volumes of a solution of *ca.* 0.1 g of 138 in 1.4 g of freshly distilled diglyme (with *ca.* 0.02 g *t*-butyl methyl ether as an NMR standard) were added to a series of quartz NMR tubes. The volumes in each tube were equalized by the addition of diglyme or trapping reagent ($Me_2Si(OMe)_2$ or $(MeO)_4Si$). The molar excess of trap varied from 0 to 16 in four separate runs. After degassing with argon, the tubes were placed equidistant from the light source and irradiated. At 15-20 min intervals, the progress of the reaction was checked with ^1H NMR, and the amount of benzene formed was determined by integration. In this manner, a standard first-order graph of ln (1-[C_6H_6]/[138] time = 0) verses time was obtained. Figures 3 and 4 illustrate the results from two runs. In no case did the presence of trap influence the rate of benzene formation. To some extent (*ca.* 20% completion), the rate of reaction could be monitored by following the disappearance of 138 with ^1H NMR. Again, no effect from added trap on the rate of reaction was observed. Repeating the reaction in identical fashion, except degassing with O_2, produced little or no effect on yields of products or rates of reaction. GC or GC-MS analysis of all completed photolyses confirmed the presence of cyclosiloxanes, if no trap was added, or 9 or 143, if a silanone trap was added.

Photolysis of 1,2-dihydrophthalic anhydride **140**

1,2-Dihydrophthalic anhydride (10 mg) and 0.30 mL of THF were placed in a quartz NMR tube, degassed with argon, and sealed with a septum. After 10 min of irradiation with a Hanovia 450 W mercury arc lamp, all of **140** had reacted with observable gas evolution. The only product observed, benzene, was formed in quantitative yield by ^1H NMR.

Preparation of 1,1,1,2,3,3,3-heptamethyl-2-chlorotrisilane

1,1,1,2,3,3,3-heptamethyl-2-chlorotrisilane was prepared from tris(trimethylsilyl)methylsilane and PCl_5 according to the precedure of Kumada and coworkers (133).

Preparation of tris(trimethylsilyl)methylsilane

Tris(trimethylsilyl)methylsilane was prepared according to the procedure of Gilman and Harrell except Li wire was substituted for Li sand (125).

Preparation of (Z)-1-(2-heptamethyltrisilanyl)-4-methoxybut-1-yn-3-ene **151**

Compound **151** was prepared in an identical fashion as described for the preparation of **126** except 1,1,1,2,3,3,3-heptamethyl-2-chlorotrisilane was employed in the coupling: 67%; bp 89°C (0.3 torr); NMR ($CDCl_3$ δ 0.06 (s, 18H), 0.12 (s, 3H), 3.65 (s, 3H), 4.34 (d, 1H, J = 8 Hz), 6.05 (d, 1H, J = 8 Hz); IR (neat) 3050, 2975, 2130, 1630, 1245 cm^{-1}; mass spectrum, m/e (% relative intensity) 270 (9), 255 (15), 167 (17), 141 (24), 73 (100); calculated for $C_{12}H_{26}Si_3O$ 270.12916, measured 270.12928.

Preparation of (Z,Z)-4-methoxy-1-(2-heptamethyltrisilanyl)-1,3-butadiene 152

Diene 152 was prepared by DIBAL reduction of 151 in an identical manner with that employed in the synthesis of 127: 48%; bp 73°C (0.1 torr); NMR ($CDCl_3$) δ 0.13 (s, 9H), 0.22 (s, 3H), 3.61 (s, 3H), 5.01 (d of d of d, 1H, J = 12, 6, and <1 Hz), 5.26 (d of t, 1H, J = 13 and 1 Hz), 5.79 (d of t, 1H, J = 6, 1 and <1 Hz), 7.01 (d of d of d, 1H); IR (neat) 3020, 2800, 1640, 1250, 1115 cm^{-1}; mass spectrum, m/e (% relative intensity) 272 (0.9), 257 (2), 169 (16), 131 (25), 89 (30), 73 (100); calculated for $C_{12}H_{28}OSi_3$ 272.14481, measured 272.14570.

Preparation of 1-methyl-1-trimethylsilyl-α-pyran 153

The procedure used was identical with that described for the pyrolysis of 127. Thus, pyrolysis of 152 (650°C, 1 X 10^{-4} torr) afforded two major products, tetramethylsilane (GC-MS identification only) and 153, which was isolated pure by preparative GC (12' 15% OV101). Distillation of the crude pyrolysate and collection of the fraction boiling between 25°C to 55°C at 0.1 torr afford 153 in 60% purity 46% overall yield: NMR (CCl_4) δ 0.09 (s, 9H), 0.30 (s, 3H), 4.89 (d of t, 1H, J = 7, 7, and 1 Hz), 5.32 (d of t, 1H, J = 15, 1, and 1 Hz), 6.50 (m, 2H); IR (neat) 3050, 2960, 1610, 1255 cm^{-1}; mass spectrum, m/e (% relative intensity) 184 (15), 169 (58), 143 (71), 111 (89), 73 (100); calculated for $C_8H_{16}Si_2O$ 184.67698, measured 184.07363.

Reaction of 153 and maleic anhydride

A solution of 153 (0.61 g, 0.0033 mol) and freshly sublimed maleic anhydride (0.30 g, 0.0030 mol) in 15 mL of benzene was stirred at 70°C for 12 h or until maleic anhydride was no longer detected by GC. After removal of the benzene, adduct 154 was isolated and purified by recrystallization from hexane/Et_2O to afford 0.31 g (33%) as a mixture of syn and anti isomers: NMR (C_6D_6) δ [-0.05 (s, SiMe), 0.01 (s, $SiMe_3$), 0.09 (s, SiMe), 0.10 (s, $SiMe_3$), total 12H], 2.65 (m, 3H), 4.82 (m, 1H), 5.90 (m, 2H); IR (KBr) 3040, 2960, 1860, 1780, 1250 cm^{-1}; mass spectrum, m/e (% relative intensity) 237 (19), 179 (100), 149 (82), 122 (65), 73 (72); calculated for $C_7H_{21}O_3Si_3$ (M^+-CH_3) 237.07986, measured 237.08000.

Reaction of 153 and perfluoro-2-butyne in the presence of triethylsilane or 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane 2

A solution of 153 (60 mg) and Et_3SiH (1 mL) in a NMR tube was freeze-thaw degassed, and a large excess of perfluoro-2-butyne was distilled into the tube. After sealing under vacuum, the tube was heated at 60-70°C for 10 h until 153 could no longer be detected by NMR. Analysis of the crude reaction mixture by GC-MS revealed that two major products were formed: 155 identified by spectral comparison to authentic sample [NMR (CCl_4) δ 7.86 (m); mass spectrum, m/e (% relative intensity) 214 (73), 195 (69), 164 (28), 145 (100), 75 (23), 69 (26)], and 156 identified by MS only [m/e (% relative intensity) 316 (0.2), 301 (0.9), 243 (3.0), 228 (4.7), 215 (7.4), 147 (9.0), 133 (13), 73 (100)]. No evidence for the product expected from silylene insertion into Et_3SiH, 158, was found. Pyrolysis of 153 in the presence of 2 afforded two major products which were isolated by preparative GC: 155 (57%) and 157 (63%); NMR (CCl_4) δ 0.21 (m, 6H), 0.84 (s, 1H); mass spectrum, m/e (% relative intensity) 292 (5), 277 (8), 219 (58), 191 (18), 73 (100). Compound 157 has been previously prepared (28). When each of the above reactions was repeated by dropping a mixture of 153 in excess Et_3SiH or 2 through a vertical quartz chip packed tube heated at 440-480°C with perfluoro-2-butyne as the carrier gas (40 mL/min), virtually identical results were obtained. With Et_3SiH, 155 and 156 were identified by GC-MS as the major products. With 2, 157 (40%) and 155, in significant but undetermined yield, were formed. In each pyrolysis, 153 (20%) was recovered unchanged.

Copyrolysis of 153 and acetylene

1-Methyl-1-trimethylsilylsila-α-pyran (ca. 0.1 g) in 0.4 mL of C_6D_6 was dropped through a vertical quartz tube packed with quartz chips and heated to 500°C. Acetylene, previously passed through H_2SO_4 and silica gel, was used as the carrier gas (40 mL/min). Analysis of the yellow pyrolysate by GC revealed that at least twenty products, none in significant yield, were formed. A ^1H NMR of the pyrolysate contained numerous ill-defined absorptions from 7.5 ppm to 0.0 ppm. No further analyses were attempted.

Photolysis of 154 in Et_3SiH and in dimethyldimethoxysilane

Adduct 154 (15 mg) was dissolved in *ca.* 200 µL of Et_3SiH, or dimethyldimethoxysilane, contained in a quartz NMR tube. After degassing with argon, the solution was irradiated for 2 h with a 450 W mercury arc lamp. Irradiation in Et_3SiH afforded none of the trapping product 158 as indicated by GC-MS and NMR. The major products were benzene and the D_3 analog 160 identified by spectral comparison to an authentic sample. No yields were determined. Irradiation of 154 in dimethyldimethoxysilane afforded two major products identfied as benzene (54%) and 159 (29%). The trapping product 159 was conclusively identified by spectral comparison to a previously prepared sample: NMR ($CDCl_3$) δ 0.22 (overlapped SiMe, 18H), 3.61 (s, 2 OCH_3, 6H); IR (neat) 2960, 1255, 1060, 1010 cm^{-1}; mass spectrum, m/e (% relative intensity) 237 (19), 179 (100), 149 (82), 133 (65), 73 (72); calculated for $C_7H_{21}O_3Si_3$ (M^+-CH_3) 237.07986, measured 237.08000.

Thermolysis of 154 in Et_3SiH or dimethyldimethoxysilane

To 1.0 mL of Et_3SiH or dimethyldimethoxysilane contained in a NMR tube was added *ca.* 55 mg of 154. After freeze-thaw degassing, the tube was sealed under vacuum. Following 8 h of heating at 150°C, the tube was opened and the contents analyzed. Thermolysis in Et_3SiH afforded two major products, 1,2-dihydrophthalic anhydride and the D_3 analog 160, as determined by matching GC retention times with authentic samples. Thermolysis in dimethyldimethoxysilane yielded three products which were identified by NMR and GC-MS comparison to authentic samples: 1,2-dihydrophthalic anhydride (54%), phthalic anhydride (16%), and 159 (39%). The trapping product 159 was isolated by preparative GC (8' 10% SE-30). Its spectral features are listed in the previous paragraph.

Pyrolysis of 154 at 600°C with butadiene or dimethyldimethoxysilane

Adduct 154 (*ca.* 60 mg) in 1.0 mL of benzene was slowly dropped through a verticl quartz tube packed with quartz chips and heated to 600°C. Butadiene (40 mL/min) was used as the carrier gas. The yellow pyrolysate was collected in a dry ice/isopropanol cooled trap and analyzed by GC-MS. Several (>6) unidentified products were formed, none of which matched the known mass spectrum of the expected trapping product 162. A similar pyrolysis of 154 (45 mg) in 0.5 mL of benzene and 0.5 mL of dimethyldimethoxysilane (600°C, N_2 flow 30 mL/min) afforded none of the expected silanone trapping product 159 as determined by GC-MS. Again, several unidentified products were formed. In either pyrolysis, there was no evidence for the expected by-products of methyl(trimethylsilyl)silanone formation: 1,2-dihydrophthalic anhydride or phthalic anhydride. No further high temperature pyrolyses of 154 were attempted.

Preparation of 1,1-dichlorotetramethyldisilane

1,1-dichlorotetramethyldisilane was prepared from tris(trimethylsilyl)methylsilane and PCl_5 according to the procedure of Kumada and coworkers (133).

Preparation of 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(trimethylsilyl)-cyclotetrasiloxane 161 and 1,3,5-trimethyl-1,3,5-tris(trimethylsilyl)-cyclotrisiloxane 160

To 3.01 g (0.017 mol) of 1,1-dichlorotetramethyldisilane contained in 70 mL of THF was slowly added 3 mL of H_2O. After stirring for 10 h, the solution was extracted with saturated NaCl. The organic layer was separated, dried over $MgSO_4$, and the solvent removed to afford a white semisolid. The D_4 analog 161 was isolated and purified by crystallization from the residue with MeOH: 0.93 g (44%); NMR ($CDCl_3$) δ 0.05 (s, 9H), 0.12 (s, 3H); IR (KBr) 2955, 2895, 1240, 1040 cm^{-1}; mass spectrum, 21 eV, m/e (% relative intensity) 528 (0.01), 513 (2.7), 455 (66), 309 (39), 249 (43), 233 (86), 131 (100), 73 (26); calculated for $C_{15}H_{45}O_4Si_8$ (M^+-CH_3) 513.14723, measured 513.14706; mp 94-95°C. The D_3 analog 160 was isolated from the residue by preparative GC (8' 15% SE-30): NMR ($CDCl_3$) δ 0.21 (s, 3H), 0.12 (s, 9H); mass spectrum, m/e (% relative intensity) 396 (0.7), 381 (1.4), 323 (13), 265 (2.3), 249 (3.7), 205 (4.6), 189 (5.2), 174 (15), 147 (11), 131 (48), 116 (12), 73 (100); calculated for $C_{12}H_{36}O_3Si_6$ 396.12801, measured 396.12946.

Vacuum pyrolysis of 161

The D_4 analog 161 (0.191 g) was sublimed (90°C, 1 X 10^{-4} torr) through a horizontal quartz tube packed with quartz chips and heated to 780°C. The pyrolysate (0.13 g) was collected in a liquid nitrogen cooled trap and analyzed by GC-MS. Three major components were observed:

unreacted 161 (ca. 25%), the D_3 analog 160 (ca. 20%) (both identified by spectral comparison to authentic samples), and an unidentified product whose mass spectrum was consistent with loss of methyl(trimethylsilyl)-silylene from 161 (ca. 30%) [m/e (% relative intensity) 412 (1.4), 397 (3.9), 339 (28), 282 (2.1), 265 (3.8), 252 (2.5), 190 (3.5), 147 (7.9), 116 (100), 73 (12)]. The yield of these products was approximated from relative peak areas. The complexity of the pyrolysate prohibited their isolation. Numerous isomers of 161, 160, and the unidentified product and other unidentified volatile products were also formed.

Pyrolysis of 161 with butadiene or with nitrogen

The D_4 analog 161 (0.219 g) dissolved in 0.8 mL of benzene was slowly dropped through a vertical quartz tube packed with quartz chips and heated to 610°C. Butadiene was used as the carrier gas (40 mL/min). The pyrolysate was collected in a dry ice/isopropanol cooled trap and initially analyzed by GC-MS. The three major components were identified: recovered starting material 161 (67% completion), the D_3 analog 160 (11%), and 162 (72%). Starting material and the D_3 analog were identified by comparison of their mass spectra to those of an authentic sample. Compound 162 was isolated by preparative GC (8' 10% OV101) and identified based on the following spectral data: NMR ($CDCl_3$) δ 0.33 (s, 9H), 0.48 (s, 3H), 1.40 (broad s, 4H), 5.91 (broad s, 2H); mass spectrum, m/e (% relative intensity) 186 (20), 171 (47), 143 (17), 117 (100), 73 (65), 59 (31); calculated for $C_8H_{18}OSi_2$ 186.08963, measured 186.08894. Pyrolysis of 161 in identical fashion, except nitrogen (30 mL/min) was substituted for butadiene as the carrier gas, afforded a complex mixture of at least twenty volatile products. The D_3 analog 160 (21%) was identified as the major product based on comparison of its mass spectrum to that of an authentic sample.

Pyrolysis of 160 with butadiene

The D_3 analog 160 (0.153 g) dissolved in 400 μL of benzene was copyrolyzed with butadiene as the carrier gas (40 mL/min) according to the previously described procedure. Analysis of the pyrolysate by GC-MS revealed that 160 had decomposed to several products, all formed in low yield (91% completion). The silylene trapping product 161 (11%) was identified by comparison of its mass spectrum to that of an authentic sample.

Pyrolysis of 161 with dimethyldimethoxysilane

The D_4 analog 161 (0.192 g) dissolved in 0.8 mL of dimethyldimethoxysilane was dropped through a vertical quartz tube packed with quartz chips and heated to 610°C. Nitrogen was used as the carrier gas (30 mL/min). After collection in a dry ice/isopropanol cooled trap, the pyrolysate was analyzed by GC-MS. No evidence for formation of the expected methyl(trimethylsilyl)silanone insertion product was found. As in previous described pyrolyses of 161 in the absence of butadiene, numerous (>20) unidentified products were formed. The highest yielding product was identified as 1,3-dimethoxytetramethyldisiloxane based on spectral comparison to an authentic sample. Pyrolysis of dimethyldimethoxysilane at comparable temperatures has been reported to afford this product (14).

Preparation of bis-(trimethylsiloxy)trimethylsilylmethylsilane 166

1,1-Dichlorotetramethyldisiloxane (2.81 g, 0.015 mol) and trimethylchlorosilane (4.10 g, 0.038 mol) were added to 100 mL of THF. To this stirring solution was added 6.0 g (0.076 mol) of pyridine followed by the slow addition of 2.5 mL of H_2O. After stirring for 12 h, 100 mL of pentane were added and the resulting solution was extracted with saturated NaCl. Following separation of the organic layer and drying over $MgSO_4$, the solvent was removed. Compound 166 was isolated from the residue by preparative GC (10' 10% OV101): 31%; NMR ($CDCl_3$) δ 0.15 (s, 18H), 0.11 (s, 3H), 0.10 (s, 9H); ^{13}C NMR ($CDCl_3$) δ -2.3, 2.1, 3.4; IR (neat) 2965, 2900, 1260, 1075, 1040, 845 cm^{-1}; mass spectrum, m/e (% relative intensity) 294 (0.3), 279 (1.9), 221 (42), 191 (12), 147 (8.8), 117 (7.9), 73 (100), 59 (5.4); calculated for $C_{10}H_{30}O_2Si_4$ 294.13230, measured 294.13238.

Pyrolysis of 166 with and without butadiene

Compound 166 (0.390 g) was dropped through a vertical quartz tube packed with quartz chips and heated to 620°C. Butadiene was used as the carrier gas (40 mL/min). The pyrolysate (98% completion) was collected in a dry ice/isopropanol cooled trap. The two major silicon containing products were isolated by preparative GC (8' 10% OV101) and identified as hexamethyldisiloxane (70%) and 162 (48%) based on comparison of their

GC-MS and ^{1}H NMR spectra to those of authentic samples. An identical pyrolysis of 166 (0.213 g), except nitrogen was used as the carrier gas (30 mL/min), afforded a yellow pyrolysate (0.181 g, 96% completion) from which hexamethyldisiloxane (73%) was identified by GC-MS as the major product. Several minor products were also formed. The two minor products formed in highest yield were identified as octamethyltrisiloxane (4.0%) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (5.4%) based on comparison of their mass spectra to an authentic sample or to that previously reported (134).

Vacuum pyrolysis of 166 with added hexamethyldisiloxane

Hexamethyldisiloxane (1.0 mL) and 166 (0.189 g) were flash distilled (100°C, 1 X 10^{-2} torr) through a horizontal quartz tube packed with quartz chips and heated to 850°C. The pyrolysate was collected in a liquid nitrogen cooled trap. The three major components were isolated by preparative GC (8' 10% OV101) and identified as: starting material (61% completion), 167 (14%) [NMR (CCl_4) δ 0.13 (s, 18H), 0.21 (d, 3H, J = 3 Hz), 4.95 (q, 1H J = 3 Hz); IR (neat) 2965, 2140, 1255, 1055, 840 cm^{-1}; mass spectrum, m/e (% relative intensity) 222 (0.5), 221 (2.8), 207 (66.2), 191 (3.5), 175 (1.1), 133 (11), 96 (20.3), 73 (100)], and 14 (10%) [NMR (CCl_4] δ 0.15 (s, 18H), 0.19 (s, 6H); mass spectrum, m/e (% relative intensity) 221 (52), 205 (4.0), 147 (5.2), 133 (9.5), 103 (15), 73 (100), 59 (12)].

Vacuum pyrolysis of **166** with no added trap

Compound **166** (0.125 g) was slowly distilled (55°C, 1 X 10^{-3} torr) through a horizontal quartz tube packed with quartz chips and heated to 850°C. The pyrolysate (0.091 g) was collected in a liquid nitrogen cooled trap and analyzed by GC-MS. The two major components were identified as hexamethyldisiloxane (in significant, but undetermined, yield) and starting material. Several minor products (<5% yield) were identified by comparison of their mass spectrum to that previously reported: **14**, **167**, **172** (54) [m/e (% relative intensity) 166 (84), 115 (19), 101 (100), 99 (22), 85 (12), 69 (17)]; **168** (135) [m/e (% relative intensity) 130 (53), 129 (7), 115 (100), 99 (6), 73 (31), 59 (14)]; and **173** (136) [m/e (% relative intensity) 144 (24), 129 (100), 101 (12), 73 (13), 59 (25). In addition, two minor products were tentatively identified by their mass spectrum only: **174** [m/e (% relative intensity) 190 (5.4), 189 (8.4), 175 (100), 131 (6.5), 117 (4.9), 115 (5.3), 87 (5.8), 73 (22), 59 (19)] and **175** [m/e (% relative intensity) 204 (2.4), 203 (5.9), 89 (100), 173 (4.7), 131 (6.3), 115 (4.8), 87 (7.4), 73 (26), 59 (22).

Preparation of 2-silyl furans

In a typical preparation, 40 mL (0.060 mol) of *n*-butyllithium in hexane were added to 4.0 g (0.059 mol) of freshly distilled furan in 100 mL of Et_2O at 0°C. After stirring for 30 min and warming to 25°C, 0.060 mol of the appropriate chlorosilane was added and stirring was continued for 10 h. Following extraction of the organic phase with saturated NaCl, drying with Na_2SO_4, and removal of the solvent, the residue was distilled to yield the following 2-silyl furans.

2-Dimethylsilylfuran **185** 2-Dimethylsilylfuran was isolated and purified by distillation: 125°C (47%); NMR (CCl_4) δ 0.35 (d, 6H, J = 6 Hz), 4.45 (h, 1H, J = 6 Hz), 6.30 (d of d, 1H, J = 2 and 3 Hz), 6.59 (d, 1H, J = 3 Hz), 7.55 (d, 1H, J = 2 Hz); IR (neat) 3050, 2960, 2120, 1550, 1455, 1250, 1105, 900 cm^{-1}; mass spectrum, m/e (% relative intensity) 126 (18), 125 (6.4), 111 (100), 85 (33); UV (CH_3CN) λ max 224 nm (10,022).

2-Trimethylsilylfuran **187** 2-Trimethylsilylfuran was obtained in 75% yield by distillation (129°C) and identified by comparison of its spectral data to those previously reported (102): UV (CH_3CN) λ max 222 nm (10,425).

2-Pentamethyldisilylfuran **193** Compound **193** was isolated and purified by vacuum distillation: (105°C, 38 torr); 72%; NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.38 (s, 6H), 6.35 (d of d, 1H, J = 2 and 3 Hz), 6.55 (d, 1H, J = 3 Hz), 7.60 (d, 1H, J = 2 Hz); IR (neat) 3050, 2960, 1550, 1410, 1255, 1090 cm^{-1}; mass spectrum, m/e (% relative intensity) 198 (5.0), 183 (63), 157 (74), 125 (48), 73 (100); UV (CH_3CN) λ max 232 nm (13,324).

2-Phenyl(dimethyl)silylfuran **196** 2-Phenyl(dimethyl)silylfuran was obtained pure by vacuum distillation: (90°C, 0.1 torr); 77%; NMR ($CDCl_3$) δ 0.20 (s, 6H), 6.70 (d of d, 1H, J = 3 and 2 Hz), 7.05 (d, 1H, J = 1 Hz), 7.60 (m, 6H); IR (neat) 3050, 2950, 1540, 1420, 1240, 1105, 995 cm^{-1}; mass spectrum, m/e (% relative intensity) 202 (30), 187 (100), 161 (10), 116 (8), 101 (11); calculated for $C_{12}H_{14}OSi$ 202.08140, measured 202.08124; UV (CH_3CN) λ max 207 nm (10,717).

2-Trimethylsilylbenzofuran 201 To 1.98 g (0.017 mol) of benzofuran in 50 mL of Et_2O were added 0.018 mol of *n*-butyllithium in hexane at 0°C. After stirring for 30 min at 25°C, 2.0 mL (0.018 mol) of trimethylchlorosilane were added. Following additional stirring for 6 h, the crude reaction was extracted with saturated NaCl, the organic phase was dried over Na_2SO_4, and the solvent was removed. Distillation of the residue afforded 2.6 g (86%) of 201: bp 62°C, 0.3 torr; NMR ($CDCl_3$) δ 0.21 (s, 9H), 6.82 (s, 1H), 7.20 (m, 4H); IR (neat) 3180, 2975, 1530, 1445, 1255, 1070 cm^{-1}; mass spectrum, m/e (% relative intensity) 190 (75), 175 (100), 135 (16), 119 (19), 115 (17), 101 (23); calculated for $C_{11}H_{14}OSi$ 190.08140, measured 190.08130.

Preparation of 2,5-disilyl furans

The general procedure was as follows: to 4.0 g (0.059 mol) of furan contained in 100 mL of Et_2O were added 80 mL of 1.5 M *n*-butyllithium in hexane at 0°C. After stirring for 2 h at 25°C, 0.12 mol of the appropriate chlorosilane were added and stirring was continued for 10 h. Following extraction of the crude mixture with saturated NaCl, the organic phase was dried over Na_2SO_4, and the solvent was removed. Distillation of the residue afforded the following 2,5-disilyl furans.

2,5-Bis(trimethylsilyl)furan 190 2,5-Bis(trimethylsilyl)furan was isolated and purified by vacuum distillation: 69%; 92°C, 28 torr.

The spectral properties of 190 were identical to those previously reported (102): UV (CH_3CN) λ max 233 nm (17,588).

2,5-Bis(pentamethyldisilyl)furan 195 Compound 195 was obtained in 48% yield by vacuum distillation: (90°C, 0.5 torr); NMR (CCl_4) δ 0.09 (s, 9H), 0.29 (s, 6H), 6.40 (s, 1H); IR (neat) 3090, 2950, 2890, 1530, 1395, 1240, 1165, 1000 cm^{-1}; mass spectrum, m/e (% relative intensity) 328 (1.5), 255 (5.6), 225 (14), 157 (30), 147 (35), 73 (100); calculated for $C_{14}H_{32}OSi_4$ 328.15304, measured 328.15314.

2,5-Bis(dimethylphenylsilyl)furan 198 Distillation at 150°C and 0.1 torr afforded pure 198 in 71% yield: NMR ($CDCl_3$) δ 0.51 (s, 6H), 6.56 (s, 1H), 7.32 (m, 5H); IR (neat) 3075, 2960, 1530, 1425, 1245, 1110, 920 cm^{-1}; mass spectrum, m/e (% relative intensity) 336 (52), 321 (35), 271 (100), 193 (81), 165 (42), 135 (60); calculated for $C_{20}H_{24}OSi_2$ 336.13658, measured 336.13569.

2,5-Bis(dimethylsilyl)furan 204 Compound 204 was isolated pure by distillation: (79%, 35 torr); 49%; NMR ($CDCl_3$) δ 0.34 (d, 6H, J = 4 Hz), 4.47 (h, 1H, J = 4 Hz), 6.71 (s, 1H): IR (neat) 3100, 2970, 2130, 1540, 1425, 1250, 1175, 1010, 925 cm^{-1}; mass spectrum, m/e (% relative intensity) 184 (20), 169 (33), 143 (100), 119 (75), 73 (48), 59 (55); calculated for $C_8H_{16}OSi_2$ 184.07398, measured 184.07330.

Preparation of 2-trimethylsilyl-5-methylfuran 206

To 11.5 g (0.082 mol) of 2-trimethylsilylfuran contained in 100 mL of Et_2O were added 60 mL (0.086 mol) of *n*-butyllithium in hexane at

0°C. After stirring for 2 h at 25°C, 6.0 mL (0.096 mol) of methyl iodide were added and stirring was continued for 10 h. Following extraction of the residue with saturated NaCl and drying of the organic phase with Na_2SO_4, the solvent was removed. Distillation of the residue (67°C, 35 torr) afforded 5.4 g (43%) of pure **206** whose spectral features were identical to those previously reported (103): UV (CH_3CN) λ max 228 nm (11,627).

Preparation of 2-trimethylsilylthiophene and 2,5-bis(trimethylsilyl)-thiophene

To 1.05 g (0.025 mol) of freshly distilled thiophene in 125 mL of Et_2O were added 0.026 mol of *n*-butyllithium in hexane at 0°C. After stirring for 1 h at 25°C, 3.3 mL (0.026 mol) of trimethylchlorosilane were added and stirring was continued for 8 h. Following extraction of the reaction mixture with saturated NaCl, the organic layer was dried (Na_2SO_4). Removal of the solvent and distillation of the residue (79°C, 35 torr) afforded pure 2-trimethylsilylthiophene (76%) which was identified by NMR and MS comparison to previously reported spectra (137). 2,5-Bis(trimethylsilyl)thiophene was prepared in analogous fashion from 1.02 g (0.025 mol) of thiophene, 0.052 mol of *n*-butyllithium, and 0.052 mol (6.6 mL) of trimethylchlorosilane. Distillation (62°C, 15 torr) afforded 4.3 g (75%) of pure 2,5-bis(trimethylsilyl)-thiophene which was also identified by spectral comparison to those previously reported (137): UV (CH_3CN) λ max 235 nm (9,951).

Preparation of N-methyl-2-trimethylsilylpyrrole 223 and N-methyl-2,5-bis(trimethylsilyl)pyrrole 225

To 5.0 mL (0.056 mol of N-methylpyrrole in 200 mL of Et_2O were added 0.056 mol of *t*-butyllithium. After stirring at 25°C for 12 h, 6.27 g (0.058 mol) of trimethylchlorosilane were added. Following an additional 2 h of stirring, the crude reaction mixture was extracted with saturated NaCl, and the organic phase was separated and dried over Na_2SO_4. Removal of the solvent and distillation (70°C, 13 torr) afforded 4.2 g (48%) of pure 223 which was identified by comparison of its NMR and IR spectra to those previously reported. In similar fashion, 225 was prepared from 1.5 mL (0.017 mol) of N-methylpyrrole, 0.040 mol of *t*-butyllithium, and 4.5 mL (0.040 mol) of trimethylchlorosilane. Distillation (95°C, 12 torr) afforded pure 225 as a solid. Recrystallization from hexane gave 1.7 g (44%) of 225: mp 75-76°C, literature mp 76-77°C (137). Spectral features matched those previously reported: UV (CH_3CN) λ max 235 nm (10,471).

Preparation of N-(trimethylsilyl)pyrrole 292

n-Butyllithium (0.022 mol) was added to 1.5 mL (0.022 mol) of freshly distilled pyrrole contained in 50 mL of Et_2O at 0°C. After stirring at 0°C for 1 h, 2.5 mL (0.022 mol) of trimethylchlorosilane were added followed by an additional 1 h of stirring at 25°C. Addition of pentane (150 mL) and filtration of the precipitated salts gave a clear solution from which the solvent was removed by rotoevaporation.

Distillation of the residue (72°C, 25 torr) afforded **292** in high, but undetermined, yield. The spectral characteristics of **292** matched those previously reported (138).

Preparation of 2,5-di-*t*-butylfuran

2,5-Di-*t*-butylfuran was prepared in five steps, from pinicolone, according to the procedure described by van Tamelen and Whitesides (85).

General procedure for photolysis of silicon-substituted furans, thiophenes, and pyrroles

All solvents were previously distilled from LAH under a nitrogen atmosphere. Irradiations were typically carried out on two scales: NMR and preparative. In a quartz NMR tube sealed with a septum was placed 50 μL of the material being irradiated and 750 μL of pentane. After degassing with a stream of argon, the sample was positioned adjacent to the water cooled, quartz immersion well of a 450 W Hanovia mercury arc lamp and irradiated. The reaction progress was monitored by ^{1}H NMR and IR. Preparative scale reactions were performed using a 200 mL capacity reaction vessel which jacketed the quartz immersion well. Into the reaction vessel was placed 150 mL of pentane and 1.5 mL of the material being photolyzed. After degassing with argon for 20 min, the solution was irradiated. The reaction progress was monitored with ^{1}H NMR and IR. After irradiation was complete, the photolysate was transferred to a 250 mL flask, *via* a double tipped needle, and the pentane removed under vacuum to leave 3-5 mL of residue. Low temperature irradiations were performed by cooling the NMR tube or reaction vessel with a dry ice/isopropanol bath.

Irradiation of 2-dimethylsilylfuran 185

2-Dimethylsilylfuran (50 μL) in 600 μL of pentane was irradiated as described above for 3 h. Polymer formation on the surface of the NMR tube was evident. Analysis of the yellow photolysate by IR and ^{1}H NMR indicated 31% of 185 had reacted, and one major volatile product was formed. Based on its partial spectral data, this product was identified as 186: 53%; NMR (pentane) δ 9.1 (m, 1H, hν at 5.2 collapses to s), 5.2 (m, 2H); IR (pentane) 2120 (SiH), 1930 (C=C=C), 1690 cm^{-1} (C=O). Attempted isolation of 186 by preparative GC (5' 10% OV101) or column chromatography (silica gel/hexane) resulted in its decomposition. Concentration of the pentane solution containing 186, by removal of solvent in a stream of N_2, also resulted in slow decomposition of 186 to numerous unidentified products.

Irradiation of 2-trimethylsilylfuran 187; hydrogenation of 188

2-Trimethylsilylfuran (1.75 g) in 150 mL of pentane was irradiated for 3 h at -78°C according to the general procedure described above. After removal of the solvent, analysis of the residue by ^{1}H NMR and IR indicated 187 had reacted to 87% completion with formation of a single major volatile product tenatively identified as 188: 68%; NMR (pentane/C_6D_6] δ 9.52 (d, 1H, J = 7 Hz), 5.45 (t, 1H, J = 7 Hz), 5.13 (d, 1H, J = 7 Hz); IR (pentane) 1935, 1692 cm^{-1}. Although a concentrated solution of 188 was stable for several hours at 25°C, all attempts to isolate 188 by preparative GC, column chromatography, and distillation met with failure. Conclusive structural identification was achieved by *in situ* catalytic hydrogenation. To the crude photolysate containing 188 was added a catalytic amount of 5% Pd on charcoal. This mixture was stirred over an atmosphere of H_2 for 10 h. After removal of the solvent and filtration of the catalyst, GC analysis of the residue revealed one major product which was isolated by preparative GC (8' 10% OV101) and identified as 189: NMR (CCl_4) δ 0.15 (s, 9H), 0.48 (m, 2H), 1.72 (m, 2H), 2.51 (m, 2H), 9.72 (t, 1H); IR (neat) 2950, 2705, 1730, 1250, 855, 830 cm^{-1}; mass spectrum, m/e (% relative intensity) 144 (0), 129 (4.7), 116 (28), 101 (100), 73 (58), 59 (52); calculated for $C_6H_{13}OSi$ (M^+-CH_3) 129.0736, measured 129.0731. Irradiation of 187 in the presence of excess Et_3SiH or MeOH did not alter the course of the reaction or the yield of 188.

Irradiation of 2,5-bis(trimethylsilyl)furan 190

2,5-Bis(trimethylsilyl)furan (1.5 g) in 150 mL of pentane was irradiated at -78°C for 2 h (65% completion). After removal of the solvent, analysis of the residue by NMR and IR indicated clean formation of two products. Cooling the residue to -78°C afforded isolation of the major product 191 as a crystalline yellow solid which was further purified by repeated crystallization from cold pentane: mp *ca.* 10°C; 84%; NMR (CCl_4) δ 0.21 (s, 9H), 0.22 (s, 9H), 5.32 (d, 1H, J = 7 Hz), 5.59 (d, 1H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ -1.5, -1.0, 87.6, 96.9, 216.8, 234.4; IR (neat) 2960, 2900, 1942, 1595, 1250, 1125, 840 cm^{-1}; mass spectrum, m/e (% relative intensity) 212 (24), 197 (71), 147 (40), 73 (100); calculated for $C_{10}H_{20}Si_2$ 212.10528, measured 212.10594. Analysis of the residue by IR and ^{1}H NMR also revealed the formation of a minor product tentatively identified as 192: 10%; NMR (pentane) δ 5.15 (d, 1H, J = 8 Hz), 9.42 (d, 1H, J = 8 Hz); IR (pentane) 1910, 1675 cm^{-1}. All attempts to isolate 192 met with failure. An identical irradiation of 190 was performed except the solution was degassed with air. Analysis of the resulting photolysate by NMR and IR revealed 191 and 192 were formed in yields similar to the argon degassed photolysis. No other products were observed.

Irradiation of 2-(pentamethyldisilyl)furan 193

Compound 193 (1.5 mL) in 150 mL of pentane was irradiated at -78°C. After 1.5 h (85% completion) considerable polymer formation was evident. Removal of the solvent afforded a yellow residue from which 194 was identified by spectral comparison to 188: 11%; NMR (pentane/C_6D_6) δ 5.10 (d, 1H, J = 6 Hz), 5.46 (d of d, 1H, J = 6 and 7 Hz), 9.50 (d, 1H, J = 7 Hz); IR (pentane) 1920, 1685, 1250 cm^{-1}. Irradiation of 193 was repeated in identical fashion except 10 mL of MeOH were added. Analysis of the residue revealed, in addition to 194, two products identified by GC-MS comparison to authentic samples: 2-dimethylsilylfuran m/e (% relative intensity) 126 (16), 125 (6.6), 111 (100), 85 (35) and 2-dimethylmethoxysilylfuran m/e (% relative intensity)

156 (17), 141 (60), 125 (5), 111 (100), 59 (47). Considerable polymer formation still occurred.

Irradiation of 2,5-Bis(pentamethyldisilyl)furan 195

Irradiation of 1.5 mL of 195 in 150 mL of pentane at -78°C for 1.5 h resulted in disappearance of *ca.* 50% of 195 with formation of large amounts of intractable polymer. After removal of the solvent, analysis of the residue by IR and NMR revealed only trace amounts of an allene. No other volatile products were observed.

Irradiation of 2-(dimethylphenylsilyl)furan 196

Compound 196 (1.52 g) and 150 mL of pentane were photolyzed at -78°C according to the previously described procedure. After 90 min of irradiation, the solution was transferred to a 200 mL flask and the solvent was removed under vacuum. Analysis of the yellow residue by IR and NMR indicated clean formation of one volatile product which was identified as 197 based on comparison of its spectral data to those of 191: 67% completion, 50% yield; NMR (pentane) δ 0.40 (s, 6H), 5.24 (two overlapped d, 2H), 7.21 (m), 9.38 (d, 1H, J = 7 Hz); IR (pentane) 1930, 1705 cm^{-1}. Attempted isolation of 197 by preparative GC, column chromatography, or vacuum distillation was unsuccessful. No material crystallized upon cooling the residue to -78°C.

Irradiation of 2,5-bis(dimethylphenylsilyl)furan 198

Furan 198 (1.33 g) and 150 mL of pentane were irradiated at -78°C. After 90 min, the reaction was stopped, and the solution was transferred to a 200 mL flask. Following removal of the solvent, the yellow residue (4.7 g) was cooled to -78°C. A small amount of solid formed which was isolated and identified as the major product 200: 54% completion, 52% yield; NMR (pentane, C_6D_6) δ 0.20 (s, 6H), 0.28 (s, 6H), 5.30 (d, 1H, J = 6 Hz), 5.72 (d, 1H, J = 6 Hz), 7.3 (m); IR (neat) 3040, 2960, 1930, 1595, 1250, 1110 cm^{-1}; mass spectrum, m/e (% relative intensity) 336 (30), 321 (19), 271 (73), 193 (47), 135 (100), 105 (29); calculated for $C_{20}H_{24}OSi_2$ 336.13658, measured 336.13615. The minor product 199 (6%) was not successfully isolated, and its structure was deduced from partial NMR and IR data only: NMR (pentane) δ 0.38 (s, 12H), 5.19 (d, 1H, J = 8 Hz), 7.3 (m), 9.42 (d, 1H, J = 8 Hz); IR (neat, pentane impurity) 1915, 1675 cm^{-1}.

Irradiation of 2-(trimethylsilyl)benzofuran 201

2-(Trimethylsilyl)benzofuran (1.17 g) in 150 mL of pentane was irradiated at -78°C according to the previously described procedure for 2 h. Formation of a heavy polymer coating onto the surface of the reactor vessel was observed. After removal of the pentane, GC, IR and ^1H NMR analysis of the residue showed only unreacted 201. No evidence for an allene photoproduct was obtained.

Irradiation of 2,4-bis(trimethylsilyl)furan 202

2,4-Bis(trimethylsilyl)furan was obtained pure by injection of 191 onto a GC column (8' 15% SE-30, 150°C) and collection of the major peak. To 750 μL of pentane in a quartz NMR tube were added 50 μL of 202. After degassing with argon, the solution was irradiated at 0°C for 60 min (65% completion). No polymer formation was observed. Analysis of the photolysate by ^1H NMR and IR revealed quantitative conversion to one product which was identified as 203: NMR (pentane) δ 0.21 (broad s, 18H), 5.05 (s, 1H), 9.80 (s, 1H); IR (neat) 2980, 1905, 1670, 1245, 835 cm^{-1}; mass spectrum, m/e (% relative intensity) 212 (27), 197 (90), 171 (15), 147 (29), 73 (100); calculated for $C_{10}H_{20}OSi_2$ 212.10528, measured 212.10581. Pure 203 (>90%) was obtained by continued irradiation (2.5 h) until no 202 remained followed by removal of the solvent under vacuum.

Irradiation of 2,5-bis(dimethylsilyl)furan 204

To 150 mL of pentane were added 0.85 g of 204. After irradiation at -78°C for 2 h, the solvent was removed to afford 3.3 g of a yellow residue. Considerable amounts of polymer were deposited onto the surface of the reactor vessel. Analysis of the residue by NMR and IR indicated formation of one major volatile product which was identified as 205 based on spectral comparison to 191 and 200: 76% completion, 49% yield; NMR (pentane, C_6D_6) δ 0.30 (m, 12H), 4.49 (m, 2H), 5.25 (d of d, 1H, J = 2 and 8 Hz), 5.82 (d of d), 1H, J = 1 and 8 Hz); IR (neat) 2970, 2120, 1925, 1595, 1250, 890 cm^{-1}. Allene 205 could not be isolated pure by either low temperature recrystallization, distillation, or column chromatography; hence, mass spectral data was unavailable. No evidence for formation of any product arising from carbene insertion into a Si-H bond was obtained. Weak absorption at 1705 cm^{-1} and δ 9.4 suggested that the analogous allenyl aldehyde, 2,4-bis(dimethylsilyl)2,3-butadienal, was formed in trace amounts.

Irradiation of 2-trimethylsilyl-5-methylfuran 206

Furan 206 (1.3 g) in 150 mL of pentane was irradiated at -78°C according to the previously described procedure. After 2.5 h, the irradiation was stopped, and the solvent was removed to afford a yellow residue. Examination of the surface of the reactor showed only a small amount of polymer was deposited. Analysis of the residue by ^{1}H NMR revealed clean formation of one volatile product which was isolated (90% purity) by trap to trap distillation (25-40°C, 0.5 torr) and identified as 207: 95% completion, 50% yield; NMR (C_6D_6) δ 0.25 (s, 9H), 2.15 (s, 3H), 5.35 (d, 1H, J = 8 Hz), 5.50 (d, 1H, J = 8 Hz); ^{13}C NMR δ -1.0, 26.3, 87.0, 91.8, 199.1, 214.7; IR (neat) 3100, 2960, 1920, 1680, 1245, 840 cm^{-1}; mass spectrum, m/e (% relative intensity) 154 (11), 139 (55), 125 (31), 75 (83), 73 (100); calculated for $C_8H_{14}OSi$ 154.08140, measured 154.08151.

Irradiation of 1,4-bis(trimethylsilyl)-2,3-butadienone 191

Allenyl ketone 191 was isolated as previously described from the irradiation of 2,5-bis(trimethylsilyl)furan. To 500 µL of freshly distilled pentane contained in a quartz NMR tube were added 25 μL of 191. This solution was degassed with argon and irradiated with a 450 W mercury arc lamp. After 1.5 h ^{1}H NMR analysis revealed none of 191 had reacted. Repeating this irradiation in identical fashion, except C_6D_6 was substituted for pentane or a pyrex NMR tube was substituted for quartz, yielded similar results. In no case was 191 photoreactive.

Irradiation of 2-(trimethylsilyl)thiophene and 2,5-bis(trimethylsilyl)-thiophene

2-(Trimethylsilyl)thiophene (1.5 mL) and 400 mL of pentane were placed in a 500 mL capacity reactor vessel and degassed with argon for 1 h. This solution was then irradiated with a 450 W Hanovia mercury arc lamp for 90 min at -78°C. Extensive formation of an intractable brown polymer was observed. After removal of the solvent under vacuum, analysis of the residue by ^{1}H NMR and IR indicated only the presence of unreacted starting material. Irradiation of 2,5-bis(trimethylsilyl)-thiophene under identical conditions yielded the same results.

Irradiation of N-methyl-2-(trimethylsilyl)pyrrole 223

Pyrrole 223 (1.39 g) in 150 mL of pentane was irradiated according to the general procedure described for the irradiation of silyl furans. After 50 min of irradiation, NMR and GC analysis of the yellow photolysate revealed trace amounts of unreacted 223, and clean formation of one product which was isolated by preparative GC (10' 15% SE-30).

Based on its spectral data, this product was identified as 224: 84%; NMR (CCl_4) 0.03 (s, 9H), 3.45 (s, 3H), 6.03 (t, 1H, J = 2 Hz), 6.42 (m, 2H); ^{13}H NMR -0.1, 35.4, 113.4, 122.9, 127.3; IR (neat) 3100, 2960, 1510, 1420, 1245, 1130, 840 cm^{-1}; mass spectrum, m/e (% relative intensity) 153 (22), 138 (100), 94 (6.2), 73 (2.4), 69 (13), 59 (11); calculated for $C_8H_{15}NSi$ 153.09738, measured 153, 09730. Irradiation of 223 (50 μL) in furan (600 μL) also afforded exclusive formation of 224. No evidence of a furan - 5-azabicyclo[2.2.1]pent-2-ene adduct was obtained upon analysis of the crude photolysate with GC-MS or ^1H NMR.

Irradiation of N-methyl-2,5-bis(trimethylsilyl)pyrrole 225

To 600 μL of pentane contained in a quartz NMR tube were added 50 μL of 225. After degassing with a stream of argon, the sample was irradiated with a 450 W mercury arc lamp. The progress of the reaction was monitored by ^1H NMR and GC. After 50 min, 225 was no longer observable, and two products, identified as 226 and 227, were cleanly formed. Continued irradiation resulted in complete disappearance of 226 with a concomitant increase in the amount of 227. A repeat of this reaction on a larger scale (0.50 g of 225, 150 mL of pentane, 35 min of irradiation) allowed isolation of 226 and 227 by preparative GC (10' 20% OV101): 226 39%; NMR (CCl_4) δ 0.22 (s, 9H), 0.35 (s, 9H), 3.70 (s, 3H), 6.05 (d, 1H, J = 3 Hz), 6.58 (d, 1H, J = 3 Hz); IR (neat) 3100, 2960, 1505, 1410, 1250, 1155, 1110, 945 cm^{-1}; mass spectrum, m/e (% relative intensity) 225 (20), 210 (100), 194 (27), 147 (27), 138 (39), 73 (22); calculated for $C_{11}H_{23}NSi_2$ 225.13691, measured 225.13728;

227 41%; NMR (CCl_4) δ 0.21 (s, 18H), 3.71 (s, 3H), 6.58 (s, 2H); IR (neat) 3100, 2960, 1515, 1420, 1245, 1150, 1135, 1095 cm^{-1}; mass spectrum, m/e (% relative intensity) 225 (30), 210 (100), 194 (23), 184 (12), 147 (56), 128 (77), 73 (42); calculated for $C_{11}H_{23}NSi_2$ 225.13691, measured 225.13651. Compound **226** (*ca.* 20 mg) in 400 µL of pentane was placed in a quartz NMR tube, degassed with argon, and irradiated for 1 h. Analysis of the photolysate with ^1H NMR indicated clean conversion (*ca.* 50%) to **227** had occurred. No other products were observed.

Irradiation of N-trimethylsilylpyrrole

Into a quartz NMR tube was placed 50 µL of N-trimethylsilylpyrrole and 750 µL of pentane. After degassing with a stream of argon, the solution was irradiated with a 450 W mercury arc lamp for 1 h. Precipitation of a large amount of a yellow polymer was observed. Analysis of the photolysate by NMR and GC indicated only unreacted starting material. No further photolyses of N-trimethylsilylpyrrole were attempted.

Attempted isolation of **191** by preparative GC

Injection of the crude photolysate (from irradiation of 2,5-bis(trimethylsilyl)furan) containing **191** as the major product onto a GC (10' 15% SE-30, 150°C) afforded one major peak initially attributed to **191**. This peak was collected and identified as 2,4-bis(trimethylsilyl)furan based on the following spectral data: NMR ($CDCl_3$) δ 0.24 (s, 9H), 0.34 (s, 9H), 6.60 (s, 1H), 7.54 (s, 1H); ^{13}C NMR δ -1.4, -0.5, 118.2, 123.3, 151.3, 160.5; IR (neat) 3100, 2970, 1540, 1245, 1100, 970, 835 cm^{-1}; mass spectrum, m/e (% relative intensity) 212 (25), 197 (100), 157 (12), 147 (15), 73 (40); calculated fo $C_{10}H_{20}OSi_2$ 212.10528, measured 212.10461.

Attempted characterization of 191 by hydrogenation

To the crude photolysate containing 191 as the major product (ca. 1.3 g) was added a catalytic amount of 5% Pd on charcoal. After stirring over an atmosphere of H_2 for 12 h, the catalyst was filtered off, and the solvent was removed under vacuum. Analysis of the residue by ^1H NMR revealed quantitative formation of one product which was identified as 202 by comparison of its spectral data to those of an authentic sample. GC-MS analysis of the residue revealed no evidence of a hydrogenated product.

Attempted isolation of 191 by distillation

Distillation of the residue from the photolysis of 190 (1.5 g), containing 191 (1.0 g) as the major product, afforded one fraction (25-40°C, 1.0 torr) (0.5 g). A ^1H NMR of this fraction indicated several compounds were present. The major components were identified as 191, 202, and a compound with absorptions in the silicon methyl region, 4.8 ppm and 6.0 ppm. No further characterization was attempted.

Thermolysis of 191 in a concentrated solution

To 100 μL of CCl_4 contained in a NMR tube were added 250 μL of 191 and 5 μL of benzene as a NMR standard. After degassing with argon and sealing with a septum, the solution was heated at 70°C. The reaction progress was monitored with ^{1}H NMR. After 6 h, quantitative conversion to one product was observed. Based on the following spectral data, this product was tenatively identified as 231: NMR (CCl_4) δ 0.18 (s, 9H), 0.28 (s, 9H), 4.81 (s, 1H), 5.92 (s, 1H, disappears upon addition of D_2O); IR (CCl_4) 3440 (broad) 2960, 2120, 1620, 1255, 1100, 835 cm^{-1}. Attempted isolation of 231 by preparative GC and column chromatography was unsuccessful. A repeat of the reaction in identical fashion with C_6D_6 as the solvent yielded similar results. Upon continued heating (4 h) of the reaction mixture containing 231, its keto form was observable but not isolated: NMR (CCl_4) silicon-methyl region obscured, 3.31 (s, C$\underline{H}_2$); IR (CCl_4) 2160 ($C\equiv C$), 1625 cm^{-1} ($Me_3SiC{=}O$).

Trapping of 231 with trimethylchlorosilane

1,4-Bis(trimethylsilyl)2,3-butadienone 191 (*ca.* 1.0 g) was added to 1.5 mL of CCl_4, and the solution was heated at 70°C until all of 191 had been converted to 231 as determined by NMR (10 h). After cooling to 25°C, 0.4 g of trimethylchlorosilane in 0.6 g of pyridine was added to the solution and the resulting mixture was stirred for 2 h. Following filtration of the salts and solvent removal, analysis of the residue by GC indicated one major product which was isolated by preparative GC (8' 10% OV101) and identified as 232: NMR ($CDCl_3$) δ 0.18 (s, 9H), 0.25 (s, 9H), 0.39 (s, 9H), 5.20 (s, 1H); ^{13}C NMR δ -2.3, 0.1, 1.5, 98.8, 102.0, 102.2, 173.0; IR (neat) 2965, 2150, 1565, 1250, 1145, 1050, 915, 840 cm^{-1}; mass spectrum, m/e (% relative intensity) (20 eV) 284 (64), 269

(5.2), 181 (13), 168 (12), 147 (100), 73 (24); calculated for $C_{13}H_{28}OSi$ 284.1448, measured 284.1445.

Thermolysis of 191 in a dilute solution

To 500 μL of CCl_4 were added 25 μL of 191 and 5 μL of benzene as a NMR standard. After freeze-thaw degassing, the tube was sealed under vacuum, and the contents were heated at 150°C for 30 min. Analysis of the reaction mixture by ^1H NMR revealed quantitative formation of 2,4-bis(trimethylsilyl)furan which was identified by spectral comparison to an authentic sample.

Concentration dependence on the thermolysis of 191

To a series of three NMR tubes (A, B, and C) were added 5 μL each of benzene and 25 μL, 75 μL, and 150 μL of 191, respectively. The total volume in each tube was equalized to 250 μL by the addition of CCl_4. After sealing with a septum, the tubes were heated at 70°C, and the reaction was monitored by ^1H NMR. After 6 h, quantitative conversion of 191 to 202 or 231 had occurred. The ratio of 202 to 231 was calculated: tube A 70/30, tube B 39/61, tube C 12/78.

Attempted isolation of 200 by gas chromatography

Photolysis of 2,5-bis(dimethylphenylsilyl)furan (1.33 g) in pentane afforded crude 200 (*ca.* 0.5 g) after removal of the solvent. Injection of 200 onto a 10' 10% SE-30 gas chromatograph column (injection port 250°C, column 200°C) yielded one major peak which was collected and identified as 2,4-bis(dimethylphenylsilyl)furan based on the following spectral data: NMR (CCl_4) δ 0.53 (s, 6H), 0.58 (s, 6H), 6.55 (s, 1H), 7.31 (m, 11H); IR (neat) 3075, 3060, 2960, 1430, 1255, 1115, 1050 cm^{-1}; mass spectrum, m/e (% relative intensity) 336 (82), 321 (58), 271 (100), 193 (82), 135 (56); calculated for $C_{20}H_{24}OSi_2$ 336.13658, measured 336.13570.

Thermolysis of 200 in a concentrated solution

To 400 μL of CCl_4 contained in a NMR tube were added 500 μL of 200. The tube was septum sealed and heated at 70°C. The reaction progress was monitored by ^1H NMR. After 24 h of heating, all of 200 had reacted with concomitant formation of 234 in high, but undetermined, yield. Enynol 234 was identified by its absorptions at 5.90 ppm (s, 1H, disappears upon addition of D_2O and 4.82 ppm (s, 1H). After cooling to 25°C, 0.20 g of trimethylchlorosilane in 0.22 g of pyridine was added, and the resulting solution was allowed to stand for 4 h with occasional shaking. Following filtration of the salts, GC analysis of the crude reaction mixture indicated one major product which was isolated by preparative GC (6' 10% SE-30) and identified as 238 based on the following spectral data: NMR (CCl_4) δ 0.10 (s, 6H), 0.32 (s, 6H), 0.51 (s, 9H), 5.11 (s, 1H), 7.32 (m, 10H); IR (neat) 3080, 2965, 2140, 1430, 1255, 1115, 920 cm^{-1}; mass spectrum, m/e (% relative intensity) 408 (36), 393 (8), 336 (25), 271 (19), 243 (25), 197 (100), 193 (39), 135 (30), 73 (61); calculated for $C_{23}H_{32}OSi_3$ 408.17611, measured 408.17644.

Attempted isolation of 207 by gas chromatography

The crude photolysate from irradiation of 2-methylsilyl-5-methylfuran, containing 207 as the only volatile product, was injected onto a 10' 20% OV101 gas chromatograph column (injector port 250°C, column 150°C). The only product peak was collected and identified as 2-methyl-4-trimethylsilylfuran based on the following spectral data: NMR ($CDCl_3$) δ 0.20 (s, 9H), 2.24 (s, 3H), 5.87 (s, 1H, broad), 7.05 (s, 1H, broad); ^{13}C NMR ($CDCl_3$) δ -0.6, 13.2, 109.0, 119.7, 145.4, 152.8; IR (neat) 3100, 2965, 1600, 1515, 1255, 1110, 840 cm^{-1}; mass spectrum, m/e (% relative intensity) 154 (23), 139 (100), 100 (10), 66 (13); calculated for $C_8H_{14}OSi$ 154.0814, measured 154.08145.

Thermolysis of 207 in a concentrated and dilute solution

To 100 μL of CCl_4 contained in a NMR tube were added 250 μL of 207. After heating at 70°C for 18 h, no significant reaction had occurred as determined by ^1H NMR. Similar stability was observed upon heating 207 (25 μL) in 500 μL of CCl_4 at 150°C for 10 h.

Thermolysis of 207 in the gas phase

Thermolysis of 207 was carried out by slowly dropping 0.15 g into a vertical quartz tube packed with quartz chips and heated to 350°C. Nitrogen was used as the carrier gas at a flow rate of 30 mL/min. The pyrolysate (0.12 g) was collected in a liquid nitrogen cooled trap. ^1H NMR and IR analysis revealed that all of 207 had reacted with formation of 235 (16%) identified by spectral comparison to an authentic sample as the major product.

Thermolysis of 188

To a NMR tube containing 150 µL of C_6D_6 were added 100 µL of a solution of 188 (40%) in pentane. The tube was heated at 70°C, and the reaction progress monitored by ^1H NMR. After 24 h, 55% of 188 was quantitatively converted to 237 which was identified by partial NMR and IR only: NMR (C_6D_6, pentane) δ 2.79 (d, 2H, J = 2 Hz), 9.21 (t, 1H, J = 2 Hz); IR (C_6D_6, pentane) 2175 (C≡C), 1740, (C=O), 1250 cm^{-1} ($SiMe_3$). No evidence for the enol form of 237 was observed. Attempts to isomerize 188 to 3-trimethylsilylfuran by injection of a solution (pentane) containing 188 onto a gas chromatograph column (10' 10% OV101) or by heating a dilute solution of 188 in CCl_4 at 150°C met with failure. In each attempt, polymerization appeared to be the major process. In no case was any evidence for formation of 3-trimethylsilylfuran obtained.

Photolysis of 2,5-di-*t*-butylfuran

2,5-Di-*t*-butylfuran (1.55 g) in 150 mL of pentane was photolyzed at -78°C according to the previously described procedure. After 1.5 h of irradiation, the majority of the solvent was removed and the residue analyzed by ^1H NMR. Considerable polymer coating onto the surface of the reactor vessel was evident. Based on spectral comparison to those previously reported, the three major products were identified as 178 (11%), 177 (9.5%), and 176 (2.6%) (85).

Reaction of dimethyldichlorosilane and K_2CO_3

To a stirring solution of K_2CO_3 (0.24 g, 0.0017 mol) and 0.44 g (0.0017 mol) of 18-crown-6 in 100 mL of benzene was added 0.21 g (0.0016 mol) of dimethyldichlorosilane. This solution was stirred at reflux over a nitrogen atmosphere for 48 h. Analysis of the reaction mixture by GC revealed that none of the dimethyldichlorosilane had reacted to afford any volatile products. Repeating the reaction in identical fashion, except with the use of THF or acetonitrile as solvent or with $CaCO_3$ and 15-crown-5 substituted for K_2CO_3 and 18-crown-6, furnished identical results.

Reaction of dimethyldichlorosilane and $NaHCO_3$

To a stirring solution of $NaHCO_3$ (0.51 g, 0.0050 mol, previously dried at 100°C in a vacuum for 24 h) and triethylamine (0.50 g, 0.0050 mol, freshly distilled from CaH_2) in 100 mL of dry THF was slowly added 0.64 g (0.0050 mol) of dimethyldichlorosilane. After 15 h of stirring under an atmosphere of nitrogen, the salts were centrifuged down, and the supernatant was analyzed by GC-MS. During the course of the reaction, gas evolution was observable. The only volatile products were identified as D_3, D_4, and D_5 by comparison of their mass spectra to those of authentic samples. A repeat of the above reaction, except with the addition of 1.0 mL of dimethyldimethoxysilane, and analysis by GC-MS indicated that one major product had been formed. This product was identified as 1,3-dimethoxytetramethyldisiloxane (89%) by comparison of its ^1H NMR and MS to that of an authentic sample.

Reaction of phenylmethyldichlorosilane with $NaHCO_3$ in the presence of dimethyldimethoxysilane

To a stirring solution of $NaHCO_3$ (1.02 g, 0.012 mol), dimethyldimethoxysilane (3.0 g, 0.025 mol), and pyridine (1.04 g, 0.013 mol) in 100 mL of THF was added 1.20 g (0.0064 mol) of phenylmethyldichlorosilane dropwise at 25°C. After stirring for 11 h, the salts were centrifuged down, and the supernatant was concentrated. The four major products were isolated by preparative GC and identified.

1,3-Dimethoxytetramethyldisiloxane **9**: The ^1H NMR and MS matched that of an authentic sample.

1-Phenyl-1,3-dimethoxytrimethyldisiloxane **241**: (18%); NMR ($CDCl_3$) δ 0.21 (s, 6H), 0.29 (s, 3H), 3.50 (s, 3H), 3.52 (s, 3H), 7.30 (m, 5H); mass spectrum, m/e (% relative intensity) 241 (64), 211 (35), 181 (21), 179 (39), 121 (27), 91 (100), 59 (25); calculated for $C_{10}H_{17}O_3Si_2$ (M^+-CH_3) 241.07163, measured 241.07132.

Phenylmethyldimethoxysilane **242**: NMR ($CDCl_3$) δ 0.32 (s, 3H), 3.55 (s, 6H), 7.32 (m, 5H); mass spectrum, m/e (% relative intensity) 182 (10), 167 (100), 151 (3.8), 137 (40), 91 (34), 59 (31).

1,3-Diphenyl-1,3-dimethoxydimethyldisiloxane **243**: (36%); NMR ($CDCl_3$) δ 0.49 (s, 6H), 3.51 (s, 6H), 7.35 (m, 10H); mass spectrum, m/e (% relative intensity) 318 (0.5), 303 (19), 211 (17), 165 (26), 121 (17), 105 (18), 91 (100); calculated for $C_{16}H_{22}O_3Si_2$ 318.11076, measured 318.11172.

Reaction of diphenylsilanediol with phosgene

A standard solution of phosgene (0.190 g) in Et_2O (1.00 g) was prepared by passing phosgene into cold Et_2O and measuring the gain in weight. To 1.8 g of this solution (0.0035 mol $COCl_2$) and 0.71 g (0.0070 mol) of triethylamine in 60 mL of Et_2O were added 0.591 g (0.0027 mol) of diphenylsilanediol. After stirring for 20 h, the salts were filtered, and the solvent removed to afford a clear viscose oil from which a white solid (0.40 g) precipitated. This solid was identified as hexaphenylcyclotrisiloxane by comparison of its ^1H NMR, IR, and MS to those of an authentic sample: (75%); NMR (D_6 acetone) δ 7.45 (m); IR (CCl_4) 3080, 1590, 1435, 1010 cm^{-1}; mass spectrum, m/e (% relative intensity) 594 (10), 516 (11), 439 (100), 362 (22), 220 (37), 219 (90), 181 (76), 154 (53), 78 (24), 77 (40).

Reaction of dilithium diphenyldisilanolate with phosgene

Dilithium diphenyldisilanolate was freshly prepared by the rapid addition of n-butyllithium (2.3 mL, 2.4 M in hexane) to 0.531 g (0.0025 mol) of diphenylsilanediol in 60 mL of Et_2O at 0°C. After stirring for 10 min, 1.8 g of a solution of $COCl_2$ in Et_2O (0.16 g $COCl_2$/g Et_2O), followed by 20 mL of THF, were added and stirring was continued for 10 h. The salts were centrifuged down, and the supernatant was analyzed by TLC and GC. The only observable product was identified as hexaphenylcyclotrisiloxane by comparison of its retention time to that of an authentic sample.

Reaction of dilithium diphenyldisilanolate with phosgene in the presence of dimethyldimethoxysilane

Dilithium diphenyldisilanolate was prepared as described above from 1.51 g (0.0069 mol) of diphenylsilanediol and 6.3 mL (0.014 mol) of *n*-butyllithium (2.2 M in hexane). To the dilithium diphenyldisilanolate in 80 mL of Et_2O was bubbled an excess of $COCl_2$ at 0°C. After stirring the solution at 25°C for 5 h, the salts were centrifuged down, and the supernatant was analyzed by GC-MS. Greater than twenty components were observed. The four major components were identified by comparison of their mass spectra to those previously reported or those of authentic samples.

1,3-Dimethoxytetramethyldisiloxane **9**: The mass spectrum of **9** matched that of an authentic sample.

Diphenyldimethoxysilane: mass spectrum, m/e (% relative intensity) 244 (19), 213 (3.1), 167 (100), 166 (32), 154 (33), 137 (30), 107 (30), 91 (30).

Diphenylchloromethoxysilane: mass spectrum, m/e (% relative intensity) 250 (14), 240 (M^+, 37), 217 (5.4) 171 (71), 170 (45), 154 (100) 141 (50), 91 (98).

1,1-Diphenyl-3,3-dimethyldimethoxydisiloxane **142**: mass spectrum, m/e (% relative intensity) 318 (0.01), 303 (21), 241 (83), 240 (19), 181 (22), 165 (27), 105 (23), 91 (100), 59 (13).

The complexity of the reaction prohibited isolation of these products; hence, absolute yields were not calculated. From peak areas, it was determined that these four products were formed in a 3:4:2:2 ratio, respectively.

Reaction of tetramethyldisiloxane-1,3-diol with phosgene

Tetramethyldisiloxane-1,3-diol was prepared from sym-tetramethyldisiloxane, H_2O, and Pd according the procedure of Barnes and Daughenbaugh (139). To 0.998 g (0.0060 mol) of tetramethyldisiloxane-1,3-diol and 1.27 g (0.013 mol) of triethylamine contained in 80 mL of Et_2O were added 7.6 g of a solution of $COCl_2$ in Et_2O (0.106 g $COCl_2$/g Et_2O). After stirring at 25°C for 6 h, the salts were filtered, and the solvent was removed to afford a clear oil. Analysis of the oil by GC-MS revealed that D_3(3%), D_4 (63%), D_5 (3%), and D_6 (18%) were cleanly formed. These cyclosiloxanes were identified by comparison of their mass spectra to those previously reported (140).

D_3: mass spectrum, m/e (% relative intensity) 207 (100), 191 (12), 177 (5.6), 133 (19), 119 (7.6), 103 (6.1), 96 (58), 73 (5.1).

D_4: mass spectrum, m/e (% relative intensity) 281 (100), 207 (10), 193 (17), 191 (13), 133 (29), 73 (40).

D_5: mass spectrum, m/e (% relative intensity) 355 (6.9), 267 (9.3), 207 (2.6), 73 (100), 59 (9.7).

D_6: mass spectrum, m/e (% relative intensity) 429 (3.8), 341 (11), 325 (3.2), 207 (2.6), 147 (12), 73 (100), 59 (9.6).

Reaction of 251 with trimethylchlorosilane

LDA was prepared by the addition of 10.0 mL (0.022 mol) of *n*-butyllithium (2.2 M in hexane) to a stirring solution of diisopropylamine (2.1 g, 0.021 mol) in 30 mL of THF at -78°C. After warming to 25°C and stirring for an additional 30 min, 0.88 g (0.010 mol) of isobutyric acid was added at 0°C. Following 2 h of stirring at 25°C, 2.6 g (0.024 mol) of trimethylchlorosilane were added and stirring was continued for 1 h. Pentane (100 mL) was added, and the precipitated salts were filtered off. Removal of the solvent afforded a yellow oil from which 252 was isolated by preparative GC (8' 10% OV101): 91%; NMR ($CDCl_3$) δ 0.20 (s, 18H), 1.45 (s, 6H); IR (neat) 2950, 2905, 1690, 1240, 1175, 1155, 990 cm^{-1}; mass spectrum, m/e (% relative intensity) 232 (11), 217 (15), 147 (66), 129 (11), 75 (37), 73 (100), 70 (77), 55 (69); calculated for $C_{10}H_{24}O_2Si_2$ 232.13149, measured 232.13167. The above preparation was repeated, and isolation of 251 was attempted by removal of all volatile components under vacuum. This afforded a white powder which was added to 50 mL of THF. Following the addition of trimethylchlorosilane and stirring for 1 h, GC analysis of the solution revealed that none of the expected ketene acetal 252 had been formed. Attempted preparation of 251 from the slow addition of *n*-butyllithium (10.0 mL, 2.2 M in hexane) to isobutyric acid (0.92 g, 0.10 mol) in THF at -78°C afforded none of the ketene acetal 252 upon addition of trimethylchlorosilane and analysis by GC.

Reaction of **251** and dimethyldichlorosilane

Preparation of **251** was accomplished from 0.029 mol of *n*-butyllithium, 2.8 g (0.028 mol) of diisopropylamine and 1.20 g (0.014 mol) of isobutyric acide in 200 mL of THF according to the previously described procedure. After a slow mechanical addition of dimethyldichlorosilane (1.72 g, 0.013 mol), the reaction mixture was stirred for 6 h at 0°C. Following the addition of 200 mL of pentane, the salts were filtered away. Analysis of the crude mixture by IR revealed that none of the expected dimethylketene was present. In addition, there was no indication that significant quantities of **254** were present as judged from the weak absorptions at *ca.* 1680 cm^{-1} (R_2C=$C(OR)_2$). After removal of the solvent, analysis of the residue by GC-MS revealed that several products had been formed. The cyclosiloxanes, D_3 (38%), D_4 (21%), and D_5 (6%), were identified by comparison of their mass spectra to that of authentic samples. One other product was tentatively identified as **253** (10%, based on its GC response factor being equal to that of D_3) on the basis of its mass spectrum: m/e (% relative intensity) 292 (M^+, 2.3), 277 (M^+-Me, 1.3), 207 (M^+-Me+Me_2CCO, 93), 171 (57), 128 (58), 86 (Me_2CCO_2, 100), 70 (Me_2CCO, 39). In addition, N, N-diisopropylisobutyramide was identified in trace amounts by comparison of its mass spectrum to that of an authentic sample: m/e (% relative intensity) 171 (11), 128 (26), 114 (5.9), 86 (100), 71 (19), 58 (32). This reaction was repeated several times, and in no two experiments were exactly the same results obtained. In every case cyclosiloxanes were formed; however, **253** and

N,N-diisopropylbutyramide were not always observed. The complexity of the reaction mixtures prohibited isolation of any products.

Reaction of 251 with 1,3-dichlorotetramethyldisiloxane

The dioxyanion 251 was prepared from 2.16 g (0.021 mol) of diisopropylamine, 9.8 mL of n-butyllithium (2.2 M in hexane), and 0.90 g (0.010 mol) of isobutyric acid according to the previously described procedure. After a slow addition of 2.3 g (0.011 mol) of 1,3-dichlorotetramethyldisiloxane, the solution was stirred at -78°C for 1 h. Pentane (100 mL) was added, and the salts were filtered away. Following removal of the solvent, the residue was analyzed by GC-MS. None of the expected product 255 was observed. The three major products were tentatively identified by their mass spectra.

253: The mass spectrum of 253 matched that previously observed (see preceding paragraph).

256: m/e (% relative intensity) 366 (M^+, 3.3), 351 (M^+-Me, 0.4), 281 (M^+-Me+Me_2CCO), 218 (9.1), 144 (9.5), 70 (100), 55 (25).

257: m/e (% relative intensity) 436 (M^+, 0.04), 281 (13), 219 (100), 203 (9.1), 133 (15), 70 (48), 69 (71), 55 (27).

Among the numerous minor products, D_3 and D_4 were identified by comparison of their mass spectra to those of authentic samples. These results proved difficult to consistently reproduce.

General procedure for preparation of o-silylphenols

Preparation of the o-silylphenols was accomplished by modification of the procedure of Mironov and coworkers (116, 117). To a stirring solution of o-bromophenol (1.5 g, 0.0087 mol) and triethylamine (0.91 g, 0.0090 mol) in 75 mL of Et_2O was added the appropriate chlorosilane (0.0090 mol). After stirring for 24 h, 100 mL of pentane were added and the precipitated salts were removed by filtration. Following removal of the solvent, the residue was distilled to afford the following o-bromophenoxysilanes.

o-Bromophenoxy(dimethyl)silane: 63%; bp 53°C (1.0 torr). The ^1H NMR and MS of o-bromophenoxy(dimethyl)silane matched those previously reported (117).

o-Bromophenoxy(t-butylmethyl)silane: 92%; bp 57°C (0.03 torr); NMR (CCl_4) δ 0.28 (d, 3H, J = 4 Hz), 1.05 (s, 9H), 4.67 (q, 1H), J = 4 Hz), 6.85 (m, 4H); IR (neat) 3080, 2950, 2115, 1485, 1290, 1250, 1045, 1030, 935 cm^{-1}; mass spectrum, m/e (% relative intensity) 274 (4.1), 272 (M^+, 4.1), 257 (8.9), 215 (100), 135 (57); calculated for $C_{11}H_{17}OSiBr$ 272.02320, measured 272.02326.

o-Bromophenoxy(di-t-butyl)silane: It was found necessary to reflux the reactants in benzene for 24 h in order to obtain complete reaction: 53%; bp 92°C (0.1 torr); NMR (CCl_4) δ 1.10 (s, 18H), 4.51 (s, 1H), 6.95 (m, 4H); IR (neat) 3060, 2930, 2860, 2100, 1475, 1285, 1045, 1025, 920 cm $^{-1}$; mass spectrum, m/e (% relative intensity) 316 (0.20), 314 (M^+, 0.21), 259 (44), 257 (46), 230 (31), 229 (32), 149 (49), 137

(61), 135 (67), 77 (100); calculated for $C_{14}H_{23}OSiBr$ 314.07016, measured 314.07032.

2-(o-Bromophenoxy)heptamethyltrisilane: 46%; bp 90°C (0.1 torr); NMR ($CDCl_3$) δ 0.16 (s, 18H), 0.57 (s, 3H), 6.89 (m, 4H); IR (neat) 3065, 2960, 1420, 1275, 1240, 900, 840 cm^{-1}; mass spectrum, m/e (% relative intensity) 347 (6), 345 (M^+, 7) 289 (52), 287 (54), 193 (49), 172 (34), 117 (30), 73 (100); calculated for $C_{12}H_{22}BrOSi_3$ (M^+-CH_3) 345.01618, measured 345.01499.

The appropriate o-bromophenoxysilane (0.0070 mol) was slowly added to a stirring solution of 0.25 g (0.010 mol) of magnesium powder in 10 mL of dry THF. After the exothermic reaction had ceased, the solution was refluxed for 3.5 h over a nitrogen atmosphere. The temperature was slowly raised to 170°C, and the THF was allowed to escape. After 3.5 h at 170°C, the reaction mixture was cooled to 25°C. The glassy residue was dissolved in a THF/H_2O mixture. Following the addition of 50 mL of Et_2O, the solution was extracted with saturated NH_4Cl. The organic phase was then dried over $MgSO_4$. After removal of the solvent, the residue was distilled to afford the following o-silylphenols.

o-Dimethylsilylphenol 262: 55%; bp 75°C (2 torr). The ^1H NMR and MS of o-dimethylsilylphenol matched those previously reported (116).

o-Methyl-t-butylsilylphenol 272: 78%; bp 63°C (0.07 torr); NMR (CCl_4) δ 0.35 (d, 6H, J = 4 Hz), 1.10 (s, 9H), 4.41 (q, 1H, J = 4 Hz), 4.72 (s, 1H, broad), 6.8 (m, 4H); IR (neat) 3540 (broad), 2940, 2100, 1595, 1440, 1280, 835 cm^{-1}; mass spectrum, m/e (% relative intensity) 194 (5.5), 179 (0.3), 137 (100), 119 (9.0), 91 (18); calculated for $C_{11}C_{18}OSi$ 194.11270, measured 194.11213.

o-Di-*t*-butylsilylphenol 273: 72%; bp 95°C (0.3 torr); NMR (CCl_4) δ 1.06 (s, 18H), 3.99 (s, 1H), 5.24 (s, 1H, broad), 6.90 (m, 4H); IR (neat) 3540 (broad), 2935, 2850, 2095, 1590, 1475, 1280, 1185, 1065, 815 cm^{-1}; mass spectrum, m/e (% relative intensity) 236 (0.4), 179 (19), 151 (6.6), 137 (100), 123 (21), 91 (13), 75 (28); calculated for $C_{14}H_{24}OSi$ 236.15965, measured 236.15937.

o-[Bis(trimethylsilyl)methylsilyl]phenol 276: 56%; bp 95°C (0.1 torr); NMR (CCl_4) δ 0.09 (s, 18H), 0.34 (s, 3H), 4.42 (s, 1H, broad), 6.95 (m, 4H); IR (neat) 3540, 3075, 2960, 1440, 1245, 835 cm^{-1}; mass spectrum, m/e (% relative intensity) 282 (0.1), 267 (0.2), 209 (35), 193 (100), 179 (10), 135 (11), 73 (99); calculated for $C_{13}H_{26}OSi_3$ 282.12916, measured 282.12795; 276 was further purified by preparative GC (8' 10% OV101).

Reaction of *o*-dimethylsilylphenol with Pd

To a solution of 5% Pd on charcoal (0.0010 g) in 500 mL of dry THF was slowly added 0.0469 g (0.0031 mol) of *o*-dimethylsilylphenol. Gas evolution was observable. After stirring for 2 h at 25°C, the catalyst was filtered off, and the excess solvent removed under vacuum. Analysis of the crude residue by ^1H NMR and GC-MS revealed that one product, identified as 263, was cleanly formed: 93% yield; NMR ($CDCl_3$) δ 0.66 (s, 6H), 7.21 (m, 4H); mass spectrum, m/e (% relative intensity) 300 (22), 285 (100), 226 (45), 211 (46), 165 (28), 133 (34), 91 (74); calculated for $C_{16}H_{20}O_2Si_2$ 300.10019, measured 300.10078. Compound **263** was isolated pure by preparative GC.

The above reaction was repeated in the presence of dimethyldimethoxysilane by a slow addition of 0.048 g (0.00031 mol) of *o*-dimethylsilylphenol to a stirring solution of 5% Pd on charcoal in 25 mL of dimethyldimethoxysilane. After filtration of the catalyst, the excess solvent was removed. Analysis of the residue by GC-MS revealed the formation of seven major products. The complexity of the reaction mixture prohibited the isolation of these products, and their structural assignment was based solely on MS:

1,3-Dimethoxytetramethyldisiloxane **9**: The MS of this product matched that of an authentic sample.

263: 17%; the MS of **263** matched that of an authentic sample.

266: 10%; m/e (% relative intensity) 270 (M^+, 9.2), 255 (M^+-CH_3, 58), 225 (24), 209 (23), 195 (49), 193 (38), 119 (24), 105 (54), 91 (95), 59 (100).

267: 8%; m/e (% relative intensity) 244 (M^+, 8.6), 229 (M^+-CH_3, 3.0), 211 (34), 150 (100), 135 (23), 94 (35).

268: 32%; m/e (% relative intensity) 182 (M^+, 13), 167 (M^+-CH_3, 5.3) 150 (90), 137 (100), 135 (26), 91 (46), 61 (21), 59 (24).

269: 3%; m/e (% relative intensity) 224 (M^+, 21), 209 (M^+-CH_3, 100), 181 (15), 133 (12), 105 (28), 91 (57).

270: 4%; m/e (% relative intensity) 224 (M^+, 22), 209 (M^+-CH_3, 100), 181 (15), 133 (13), 105 (21), 97 (13), 91 (62).

Reaction of o-(t-butylmethylsilyl)phenol and o-(di-t-butylsilyl)phenol with Pd

To a stirring solution of 5% Pd on charcoal (0.0010 g) in 400 mL of THF was added 0.216 g (0.0011 mol) of o-(t-butylmethylsilyl)phenol. After stirring at reflux for 20 h, the catalyst was filtered off, and the solution was concentrated. Analysis of the residue by GC-MS revealed that greater than 75% of the starting material had not reacted. The only volatile component observed by GC-MS was tentatively identified as 271: <1%; mass spectrum, m/e (% relative intensity) 369 (M^+-CH_3, 0.3), 327 (M^+-t-butyl, 68), 285 (95), 271 (100), 211 (85), 209 (40), 195 (41), 165 (35), 133 (29), 91 (70), 57 (55). A repeat of the above reaction, except with o-(di-t-butylsilyl)phenol (0.063 g, 2.6 X 10^{-4} mol) in 5 mL of THF, afforded only unreacted starting material after 24 h of reflux as determined by GC and ^1H NMR analysis.

Reaction of o-(di-t-butylsilyl)phenol with bromine

To a solution of bromine (0.15 g, 9.3 X 10^{-4} mol) and pyridine (0.15 g, 0.0019 mol) in 5 mL of CCl_4 was added 0.21 g (9.3 X 10^{-4} mol of o-(di-t-butylsilyl)phenol. After stirring at 65°C for 4 h, the solution was cooled to 25°C, and the salts were centrifuged down. Analysis of the supernatant by GC-MS revealed three components which were isolated by preparative GC (4' 20% OV101) and identified as starting material (73%), 274 [(7%); NMR (CCl_4) δ 1.12 (s, 9H), 3.99 (s, 1H), 5.85 (s, 1H), 6.82 (t, 1H, J = 8 Hz), 7.48 (m, 2H); IR (neat) 3515, 2940, 2865, 2095, 1420, 1230, 1075, 815 cm^{-1}; mass spectrum, m/e (% relative intensity) 316 (18), 314 (M^+, 19), 301 (9), 299 (10), 259 (26), 257 (28), 217 (54), 215 (58), 149 (45), 91 (100), 75 (64)] and 275 [(8%); NMR (CCl_4) δ 1.10 (s, 9H), 3.85 (s, 1H), 5.20 (s, 1H), 7.25 (m, 3H); IR (neat) 3520, 2960, 2865, 2095, 1475, 1295, 820 cm^{-1}; mass spectrum, m/e (% relative intensity) 316 (2.4), 314 (2.1), 259 (26), 257 (27), 217 (77), 215 (82), 91 (66), 77 (44), 75 (89), 61 (85), 57 (100)].

Photolysis of o-(dimethylsilyl)phenol in CCl_4

To CCl_4 (1.0 mL) contained in a pyrex NMR tube was added 75 mg (8.9×10^{-4} mol) of D_5 pyridine and 37 mg (2.4×10^{-4} mol) of o-(dimethylsilyl)phenol. This solution was photolyzed with a 275 W sunlamp, and the reaction progress was monitored by ^1H NMR and GC. After 24 h of irradiation, the formation of a considerable amount of solid was observed. One volatile product had cleanly formed and was identified as 263 (65%, based on reacted starting material) from comparison of its ^1H NMR and GC retention time to that of an authentic sample. Photolysis of o-(dimethylsilyl)phenol (25 mg) in 500 µL of pentane contained in a quartz NMR tube with a 450 W mercury arc lamp did not afford any detectable reaction after 8 h.

Pyrolysis of *o*-(dimethylsilyl)phenol

o-(Dimethylsilyl)phenol (0.312 g) was distilled (45°C, 1 X 10^{-3} torr) through a horizontal quartz tube packed with quartz chips and heated to 750°C. The pyrolysate either sublimed immediately out of the hot zone (0.206 g) or was collected in a liquid nitrogen cooled trap (0.048 g). Analysis of the solid pyrolysate by ^{1}H NMR showed only a broad singlet at 0.6 ppm and a broad multiplet at 7.2 ppm. This material would not pass through a GC. Analysis of the volatile pyrolysate by ^{1}H NMR and GC indicated the formation of **263** which was identified by spectral comparison to an authentic sample.

Photolysis of **276**

To 700 µL of pentane contained in a quartz NMR tube were added 50 µL of **276**. After degassing with a stream of argon, the solution was irradiated for 60 min with a 450 W mercury arc lamp. Analysis of the photolysate by ^{1}H NMR, GC-MS, and GC-IR revealed that **276** had completely reacted with formation of one major volatile product in considerable, but undetermined, yield. This product was identified as hexamethyldisilane based on comparison of its spectra to those of an authentic sample. Several minor products (>11) were also formed; however, it was determined that none of these minor products corresponded to **278** or its dimer or contained a Si-H bond. No further analysis was attempted. In a similar fashion, **276** was photolyzed in dimethyldimethoxysilane or through a vycor filter. Identical results were obtained. Photolysis of **276** through a pyrex filter, in an otherwise identical fashion, did not result in any detectable reaction (^{1}H NMR) after 3 h of irradiation.

Photolysis of 276 with butadiene

Compound 276 (0.192 g) was added to 50 mL of pentane contained in a 30 cm X 2 cm quartz tube. After degassing with argon, the tube was septem sealed and cooled to -78°C. Butadiene was passed into the tube until the total volume of solution had increased by *ca.* 1 mL. This solution was then irradiated at -78°C with a 450 W mercury arc lamp. After 1 h, the tube was opened, and the resulting yellow photolysate analyzed by GC-MS. The two major products were isolated by preparative GC and identified as hexamethyldisilane (59%) based on spectral comparison to an authentic sample and 279 (16%): NMR (CCl_4) δ 0.48 (s, 3H), 1.57 (s, 4H, broad), 4.90 (s, 1H, broad), 5.96 (s, 2H, broad), 6.90 (m, 4H); IR (neat) 3500 (broad), 3010, 2895, 1595, 1435, 1270, 1090, 835 cm^{-1}; mass spectrum, m/e (% relative intensity) 190 (10), 175 (31), 162 (100), 148 (53), 147 (31), 135 (50), 92 (55), 92 (41), 77 (29); calculated for $C_{11}H_{14}OSi$ 190.08140, measured 190.08114.

Preparation of 2-phenyl-2-vinylhexamethyltrisilane

Phenyllithium was prepared by addition of 5.0 mL of *n*-butyllithium (2.2 M in hexane) to a stirring solution of bromobenzene (1.73 g, 0.011 mol) in Et_2O at -78°C. After stirring for 30 min at 25°C, this solution was added to 2.41 g (0.0098 mol) of 2,2-dichloroheptamethyltrisilane in 150 mL of Et_2O. Stirring was continued for an additional 2 h. To this reaction mixture was then added 4.8 mL of vinyllithium (2.1 M in THF, Organometallics, Inc.). After stirring for 10 h, the reaction mixture was extracted with saturated NaCl, and the organic phase was separated and dried over $MgSO_4$. Following removal of the solvent, distillation of the residue afforded pure 2-phenyl-2-vinylheptamethyltrisilane (87%): bp 84°C (0.7 torr); NMR ($CDCl_3$) δ 0.19 (s, 18H), 5.51-6.63 (m, 3H), 7.30 (m, 5H); IR (neat) 3070, 2985, 1635, 1435, 1250, 840 cm^{-1}; mass spectrum, m/e (% relative intensity) 278 (0.8), 262 (8.4), 204 (18), 178 (23), 163 (37), 145 (18), 135 (74), 121 (49), 116 (28), 113 (21), 105 (19), 73 (100); calculated for 278.13424, measured 278.13409.

Preparation of 2-phenyl-2-(β-ethanol)hexamethyltrisilane 280

To 0.15 g (5.4×10^{-4} mol) of 2-phenyl-2-vinylhexamethyltrisilane in 10 mL of Et_2O was added 1.5 mL of 1.0 M $BH_3 \cdot THF$. After standing for 10 h, 2 mL of H_2O were added followed by simultaneous addition of 1 mL of 3N NaOH and 1.5 mL of 30% H_2O_2. Following 30 min of agitation, the mixture was extracted with 50 mL of hexane and 100 mL of saturated NaCl. The organic layer was separated and dried over $MgSO_4$. Following removal of the solvent, the residue was chromatographed (silica gel, hexane/ EtOAC 10:1) to afford pure 280 (31%): R_f = 1.8; NMR ($CDCl_3$) δ 0.21 (s, 18H), 1.28 (s, 1H, broad, O<u>H</u>), 1.51 (t, 2H, complex) 3.82 (t, 2H, complex), 7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 135.8, 134.9, 128.1, 128.0, 61.5, 16.2, -0.41; IR (neat) 3300 (broad), 3065, 2950, 1425, 1240, 830 cm^{-1}; mass spectrum, m/e (% relative intensity) 279 (M^+-OH, 0.1), 267 (M^+-C_2H_5, 0.5), 223 (2.8), 206 (9.3), 195 ($Me_3SiSi(Ph)OH$, 100), 178 (52), 118 (14), 117 (14), 73 (4.5); calculated for $(Me_3Si)_2Si(Ph)O^{\dot{+}}$ 267.10568, measured 267.10562.

Photolysis of 280

Pentane (400 μL) and 0.085 g of 280 were charged into a quartz NMR tube, degassed with argon, and sealed with a septum. After 30 min of irradiation with a 450 W mercury arc lamp, the photolysate was analyzed by GC-MS and TLC. One major product was formed which was identified as hexamethyldisilane (69%) by comparison of its mass spectrum to that of an authentic sample. The two remaining volatile components were identified as starting material (2%) and trimethylphenylsilane (12%). The mass spectrum of trimethylphenylsilane matched that previously reported (141): m/e (% relative intensity) 150 (12), 135 (100), 121 (1.8), 119 (3.3), 105 (9.1), 93 (3.4), 91 (3.7). TLC analysis of the photolysate showed the presence of high molecular weight material. Photolysis of 280 in identical fashion, except for the addition of $Me_2Si(OMe)_2$ (250 μL) or Et_3SiH (250 μL), afforded similar results. Analysis of each photolysate by GC-MS revealed that hexamethyldisilane had been formed in considerable amounts. No evidence for trapping of phenylsilanone by $Me_2Si(OMe)_2$ or silylene 281 by Et_3SiH was obtained. Except for hexamethyldisilane, only trace amounts of other volatile products were formed.

Preparation of 1-chloro-1-(2-chloroethoxy)silacyclo-2,4-hexadiene 286

1,1-Dichloro-1-silacyclo-2,4-hexadiene was prepared from a copyrolysis of hexachlorodisilane and cyclopentadiene according to previously published procedure (142). To 16.4 g (0.102 mol) of 1,1-dichloro-1-silacyclo-2,4-hexadiene contained in a solution of pyridine (7.91 g, 0.100 mol) and Et_2O (750 mL) were added 5.78 g (0.072 mol) of β-chloroethanol at 0°C. After stirring for 1.5 h, 750 mL of pentane were added, and the precipitated salts were filtered under a nitrogen atmosphere. Following removal of the solvent, the residue was distilled to afford 3.1 g (21%) of 286: bp 81°C (2.0 torr); NMR (CCl_4) δ 1.90 (d of d, 2H, J = 4 and 1 Hz), 3.57 (t, 2H, J = 6 Hz), 3.99 (t, 2H, J = 6 Hz), 6.03 (m, 3H), 6.95 (m, 1H); IR (CCl_4) 3010, 2940, 1615, 1110 cm^{-1}; mass spectrum, m/e (% relative intensity) 210 (2.9), 208 (M^+, 4.0), 195 (0.9), 193 (1.2), 166 (4.5), 164 (5.1), 129 (11), 117 (4.1), 115 (7.0), 79 (31), 66 (100), 62 (43).

Reaction of 286 with Rieke Mg

Rieke Mg was prepared from 0.54 g (0.0057 mol) of anhydrous $MgCl_2$, 0.51 g (0.013 mol) of K, and 0.43 g (0.0026 mol) of KI contained in 50 mL of dry THF according to previously published procedure (121). To this solution was added 0.54 g (0.0026 mol) of 286 at 0°C over a period of 1.5 h. After stirring for 2.5 h, the salts were centrifuged down, and the supernatant was concentrated by distillation. Analysis of the residue by GC-MS revealed that at least eleven volatile products were formed, none in significant yield. No evidence for a dimer of the expected silene 285 or a trimer of the expected silanone 284 was obtained. Further identification of the volatile products was not attempted. The above reaction was repeated in similar fashion except for the addition of 2.1 g (0.018 mol) of dimethyldimethoxysilane to the Rieke Mg/THF solution prior to the addition of 286. Following an identical workup procedure, analysis of the residue by GC-MS revealed that greater than fifteen volatile products had been formed. The major product was identified as 1,3-dimethoxytetramethyldisiloxane by comparison of its mass spectrum to that of an authentic sample. The only other product identified was tentatively assigned the structure 287 based on its mass spectrum: m/e (% relative intensity) 230 (M^+, 0.9), 215 (M^+-CH_3, 13), 207 (4.8), 198 (100), 149 (42), 119 (33), 105 (31), 59 (42). The yield of 297 was estimated, based on relative peak areas, to be no greater than 10%. The complexity of the reaction mixture prohibited isolation of 287. No starting material remained unreacted. If the above coupling reaction was repeated with the use of Mg powder (0.5 g, 0.62 g of 286 in 15 mL of THF) instead of Rieke Mg, no detectable reaction ensued. After 24 h of reflux, only unreacted starting material was detected by GC.

Photolysis of 1,1-dimethylsila-α-pyran

To 35 mL of pentane contained in a 25 cm X 2 cm quartz tube were added 0.25 g (0.0020 mol) of freshly purified 1,1-dimethylsila-α-pyran. After degassing with argon, this solution was irradiated for 45 min with a 450 W mercury arc lamp. A GC-MS taken of the photolysate revealed that 5% of the starting material remained, and one major volatile product had been formed. This product was isolated by preparative GC (8' 15% SE-30) and tentatively identified as 289 based on the following data: 27%; NMR ($CDCl_3$) δ 0.19 (s, 3H), 0.31 (s, 3H), 5.3-7.0 (m, 4H); ^{13}C NMR δ 143.3, 140.8, 139.2, 131.1, 127.4, 119.7, 115.4, -1.4, -3.1; IR (neat) 3035, 2980, 1640, 1260, 1180, 1125, 1035, 840 cm^{-1}; mass spectrum, m/e (% relative intensity) 252 (1.7), 237 (0.4), 209 (3.0), 193 (3.2), 163 (3.3), 159 (6.9), 149 (6.8), 142 (67), 133 (83), 129 (52), 111 (100), 104 (72), 103 (22), 95 (31), 78 (29), 59 (33); calculated for $C_{12}H_{20}O_2Si_2$ 252.10010, measured 252.10027; UV (CH_3CH) λ max 238 nm. A 300 MHz ^1H NMR of the vinyl region revealed the following absorptions: ($CDCl_3$) δ 6.95 (d of d of d, H_A, J_{AE} = 0.9 Hz, J_{AF} = 19 Hz, J_{AH} = 9 Hz), 6.74 (d of d, H_B, J_{BC} = 11 Hz, J_{BG} = 13 Hz), 6.59 (d of d of d, H_C, J_{CD} = 12 Hz, J_{GC} = 0.9 Hz), 6.36 (d, H_D), 6.19 (d of d of d, H_E, J_{EF} = 1 Hz, J_{EH} = 6 Hz), 5.86 (d, broad, H_F, J_{FH} = 1 Hz), 5.41 (d, broad, H_G), 5.38 (d of d of d, H_H). Three minor products, formed in trace amount, were identified as isomers of 289 based on their mass spectra showing a M^+ peak of m/e 252. A repeat of this photolysis in identical fashion, except for the addition of 1.0 mL of dimethyldimethoxysilane, afforded the same results. Analysis of the photolysate by GC-MS revealed that 289 was the major product and that an adduct of 288 and dimethyldimethoxysilane was not formed. The photolysis of 120 was also repeated in the presence of 1.0 mL of MeOH in otherwise identical fashion. Analysis of the photolysate by GC-MS revealed that 289 had still formed, albeit in lower yield. In addition, four products consistent with the addition of MeOH to 288 were observed: m/e (% relative intensity), A 158 (M^+, 16), 143

(9.5), 89 (100), 59 (61); **B** 158 (M^+, 11) 157 (9.2), 143 (30), 127 (42), 111 (39), 89 (100), 84 (61), 69 (51), 59 (53); **C** 158 (31), 157 (18), 143 (42), 127 (60), 111 (51), 101 (36), 89 (100), 75 (42), 59 (84); **D** 158 (1.7), 143 (7.1), 111 (17), 89 (100), 59 (92). These isomers could not be separated by preparative GC (12' 20% OV101).

Reaction of **289** and maleic anhydride

To 30 mg of freshly sublimed maleic anhydride and 1 mL of $CDCl_3$ contained in an NMR tube were added *ca.* 50 mg of **289**. This solution was heated at 60°C for 10 h. GC-MS analysis of the crude reaction mixture revealed that **289** had decomposed or isomerized to at least eight unidentified products. At least six maleic anhydride adducts of a compound with a molecular weight of 252 were also formed as judged from the M^+ peak of m/e 350. Because of the complexity of the reaction mixture, no further product identification was attempted.

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