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Synthetic and mechanistic studies of (p-p) pi-bonded organosilicon and organogermanium reactive intermediates

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SYNTHETIC AND MECHANISTIC STUDIES OF (P-P) PI-BONDED ORGANOSILICON AND ORGANOGERMANIUM REACTIVE INTERMEDIATES

Iowa State University PH.D. 1980

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Synthetic and mechanistic studies of (p-p) π-bonded organosilicon and organogermanium reactive intermediates

by

S. Kent Hoekman

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

Department: Chemistry
Major: Organic Chemistry

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1980

TABLE OF CONTENTS

DEDICATION

To Sheri

INTRODUCTION

Since 1966, the silicon-carbon double bond has been elevated from the position of a nonexistent species to a well-established reactive intermediate. This dissertation will describe the quantitative generation of a silicon-carbon double bond by the photolytic and thermolytic decomposition of an α-silyl diazo compound. In addition to the usual trapping experiments, several new reactions of the silicon-carbon double bond will be discussed. The analogous α-germyl diazo compound was also prepared and was found to be an excellent generator of the germanium-carbon double bond.

The silicon-oxygen double bond has been much less studied than the silicon-carbon double bond. This is due, in part, to the difficulty in preparing a suitable generator of silicon-oxygen double bonds. It will be shown in this dissertation that one such precursor, the 2,3-disila-1,4-dioxane system, is not the convenient, low temperature generator that was desired.

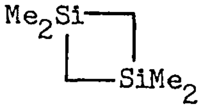
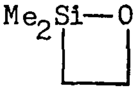
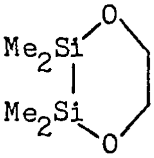
A new method of generation of silicon-oxygen double bonds will be discussed. This method involves the loss of an alkyl radical from a siloxy radical in the same way that a carbon oxy radical forms a carbonyl compound. Pyrolysis of several silyl ethers generated siloxy radicals. Two reactions of siloxy radicals occurred: hydrogen abstraction and S_H^2 attack. No evidence demanding the intermediacy of silicon-oxygen double bonds was obtained.

The chemistry of silyl and bis(silyl)peroxides will also be discussed. Thermally, these peroxides undergo an intramolecular rearrangement rather than homolytic cleavage of the peroxide linkage. While some bis(silyl)peroxides do homolytically cleave photochemically, strong evidence will be presented to show that other bis(silyl)peroxides undergo an intramolecular reaction to form the 2,4-disila-1,3-dioxetane system. Finally, a recent report of the generation of a silicon-oxygen double bond from the thermolysis of a silyl peroxide will be shown to be erroneous and all reports of silicon-oxygen double bonds will be brought into question.

NOMENCLATURE

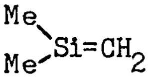
The nomenclature used in this dissertation will, with the exceptions described below, follow the conventions set down by IUPAC. Simple organosilicon compounds will be named as derivatives of silane (SiH_4), while more complicated linear and cyclic systems will be named as sila-analogs of the corresponding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

Examples:

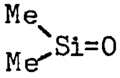
$Me_2Si(OMe)_2$	dimethyldimethoxysilane
Me_3SiOCH_2Ph	benzyloxytrimethylsilane
	1,1,3,3-tetramethyl-1,3-disilacyclobutane
	2,2-dimethyl-2-silaoxetane
	2,2,3,3-tetramethyl-2,3-disila-1,4-dioxane

All compounds containing (p-p) π-bonded silicon will be named as derivatives of silene ($H_2Si=CH_2$) and silanone ($H_2Si=O$).

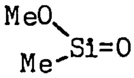
Examples:



1,1-dimethylsilene



dimethylsilanone



methoxymethylsilanone

All germanium compounds will be named as their silicon analogs by substituting "germene" for "silene" and "germa" for "sila."

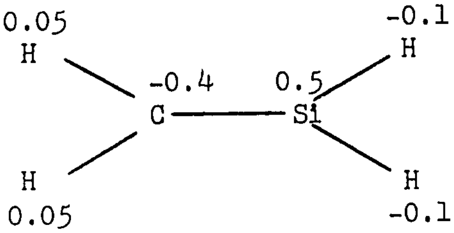
HISTORICAL

Unlike silenes and silanones which have been extensively studied, the analogous (p-p) π-bonded organogermanium intermediates are practically unknown. Germenes and germanones will here be reviewed separately. Also reviewed will be bis(silyl)peroxides which can serve as precursors to siloxy radicals.

Germenes

Since the initial reports suggesting the transient existance of silenes by Nametkin and coworkers in 1966 (1), and by Gusel'nikov and Flowers in 1967 (2), there has been a flurry of activity involving the generation and trapping of these reactive intermediates. The extent of this activity is reflected in the number of reviews which have appeared in recent years (3-7). In sharp contrast with the frequently studied silene stands the little known germene.

Several theoretical studies of silenes have been reported. Walsh (8) used the kinetic data of Gusel'nikov and Flowers (2, 9, 10) and of Davidson and Lambert (11, 12) to estimate the π-bond energy to be in the range of 28-46 kcal/mole. Curtis conducted EHMO and CNDO calculations (13). He concluded that the silene is exceedingly polar in the direction of $^{+}Si=C^{-}$ and should behave like a carbanion-siliconium zwitterion. Damrauer and Williams (14) carried out CNDO/2 calculations on $H_2Si=CH_2$, $F_2Si=CH_2$, $H_2Si=CF_2$, and $F_2Si=CF_2$. Like Curtis, these authors also found the silene to be very polar. The introduction of fluorine substituents in the place of hydrogens affected the charge densities on silicon and carbon in the predicted and expected manner. Ab. initio. calculations of $H_2Si{=}CH_2$ have been carried out by Schlegel, Wolfe, and Mislow (15), Strausz and coworkers (16), and Ahlrichs and Heinzmann (17). The latter authors report that (a) Si-C bond distance is 1.69 Å (.16 Å shorter than a Si-C single bond); (b) $H_2Si{=}CH_2$ has a planar π-bonded singlet ground state about 28 kcal/mole below the lowest triplet which has perpendicular structure; (c) the strength of the Si-C π-bond as determined by the rotational barrier is 46 kcal/mole (about 70% of the C=C bond strength); (d) the Si=C bond is very polar as indicated by the charge distribution shown below; and (e) the cycloaddition reaction of silene is characterized by a small activation energy (14 kcal/mole) and a large reaction energy (76 kcal/mole).



E_{act} = 14 kcal/mole

Δ H = -76 kcal/mole

Gusel'nikov and Nametkin (18) used their kinetic data from the pyrolysis of 1,1-dimethyl-1-silacyclobutane to calculate a Si-C π-bond energy of 28 ± 8 kcal/mole. In the most recent calculation, Pietro and coworkers used ion cyclotron resonance spectroscopy to calculate a Si-C π-bond strength of ca. 34 kcal/mole (19).

The theoretical study of germanium-carbon double bonds has not been nearly as exhaustive. In fact, there are only two reports in the literature concerning the theoretical study of germenes (20, 21). In the first report, Gowenlock and Hunter carried out CNDO/2 calculations on $H_2Ge{=}CH_2$, $H_2Ge{=}CF_2$, $F_2Ge{=}CH_2$, and $F_2Ge{=}CF_2$. Some unusual characteristics of a germanium-carbon double bond are suggested from the data in Table 1.

Table 1. Data from Gowenlock and Hunter (20)

	$H_2Ge{=}CH_2$	$H_2Ge{=}CF_2$	$F_2Ge{=}CH_2$	$F_2Ge{=}CF_2$
dipole moment in the sense $^{-}Ge{=}C^{+}$ (Debye)	1.021	1.222	3.347	3.425
σ-bond order	0.341	0.366	0.366	0.220
π-bond order	1.255	1.007	1.275	1.074

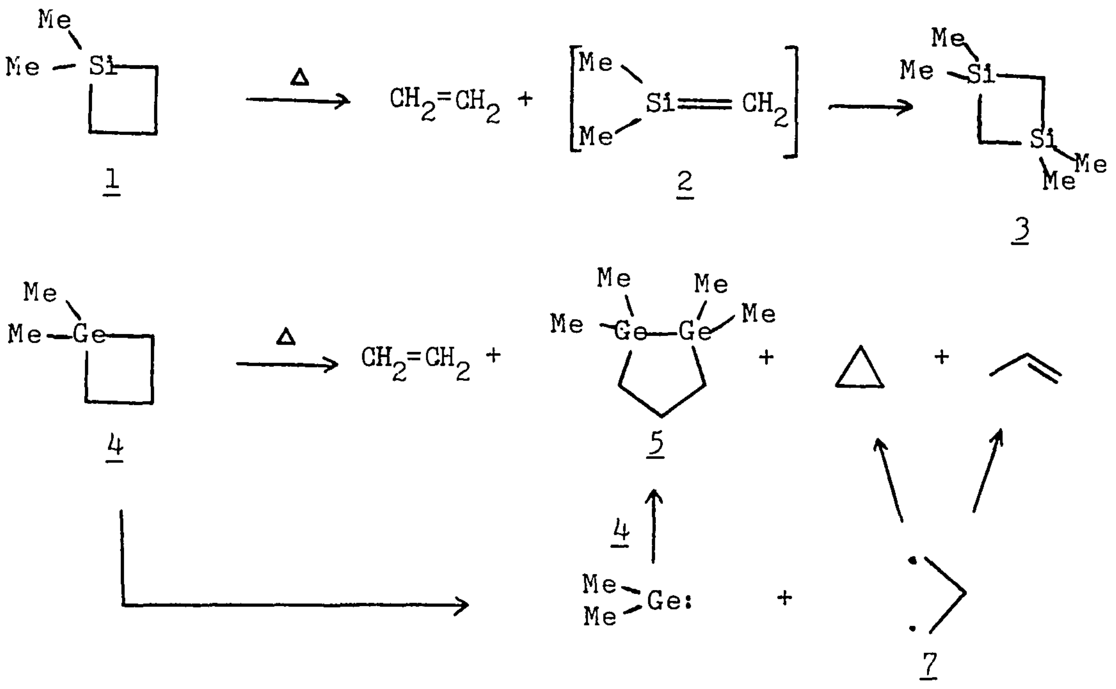
The germene appears to have a relatively weak σ-bond and a much stronger π-bond. Significant use of the germanium d orbitals is attributed to both σ- and π-bonding. The germene also appears to be polarized in a way opposite to that of a silene. This gives some support to the concept of alternation of electronegativity from atom to atom in Group IV (22).

Replacement of hydrogen on carbon by fluorine increases the dipole moment in the unexpected sense. This is opposite of what was observed in the analogous silene systems (14). Gowenlock ana Hunter explain this anomalous result to be a consequence of two opposing trends. On the one hand, introduction of a very electronegative fluorine to the carbon end of the germene should decrease the dipole moment in the sense $^{-}$Ge-C^{+}. On the other hand, introduction of the fluorine to carbon allows for a donation of electrons to the germanium atom via the π-bond. In the germene, this second effect is the stronger one, while in the silene, the first effect is the stronger.

The literature reports only two attempts to prepare a germene (23, 24). Both of these are thermal methods involving high temperature pyrolysis. In the first report, Nametkin and coworkers attempted to mimic the silicon system by pyrolyzing 1,1-dimethyl-1-germacyclobutane (4). Pyrolysis of the silicon analog (1) yields 1,1-dimethylsilene (2) which cyclodimerizes to give 1,1,3,3-tetramethyl-1,3-disilacyclobutane (3) (1, 2).

Pyrolysis of germacyclobutane 4, however, does not result in the formation of any dimer of 1,1-dimethylgermene. The expected cyclodimer, 1,1,3,3-tetramethyl-1,3-digermacyclobutane (6), was independently synthesized and found to be stable to these reaction conditions, thus pyrolysis of 4 does not give 6. The only germanium-containing product isolated from the pyrolysis of 4 was 1,1,2,2-tetramethyl-1,2-digermacyclopentane (5). Scheme 1 shows the mechanism which was proposed to explain the formation of 5 as well as cyclopropane and propene. Extrusion of dimethylgermylene from 4 produces the propyl diradical 7 which leads to propene and cyclopropane. Insertion of the germylene into germacyclobutane 4 leads to product 5. Insertion of the germylene is supported by the observation that carbenes and carbenoids will insert into a Ge-C bond of a germacyclobutane to form the ring expansion

Scheme 1

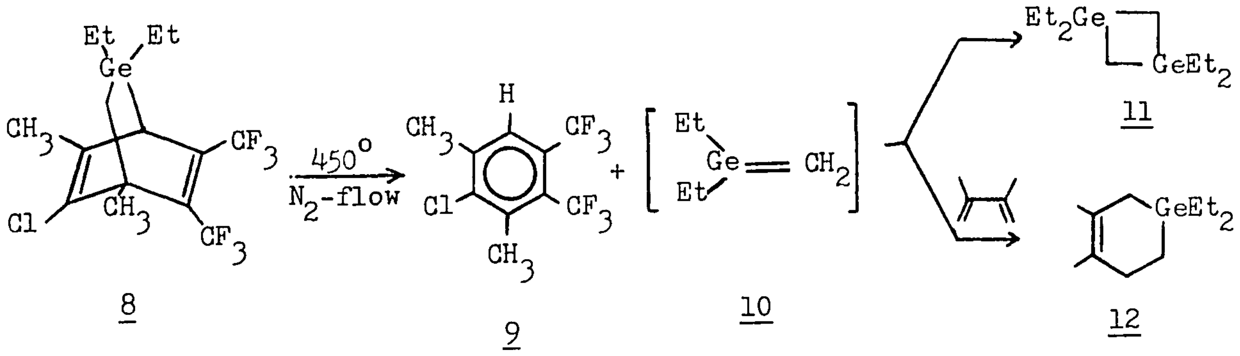


products (25, 26).

Although no germanium-containing products from the pyrolysis of 4 were found which could be attributed to the intervention of a germene, the formation of ethylene leaves open the question whether such a species is involved in at least part of this thermal decomposition.

Barton, Kline, and Garvey (24) reported the flow pyrolysis of the germabicyclo[2.2.2] octadiene compound 8 (Scheme 2). Pyrolysis of 8 produced only two compounds: aromatic compound 9 and 1,1,3,3-tetraethyl-1,3-digermacyclobutane (11). The formation of 11 argues strongly for the intermediacy of 1,1-diethylgermene (10). Formation of 1,3-disilacyclobutanes from thermal precursors is often cited as evidence for the intermediacy of silenes. Indeed, the gas phase pyrolysis of the

Scheme 2

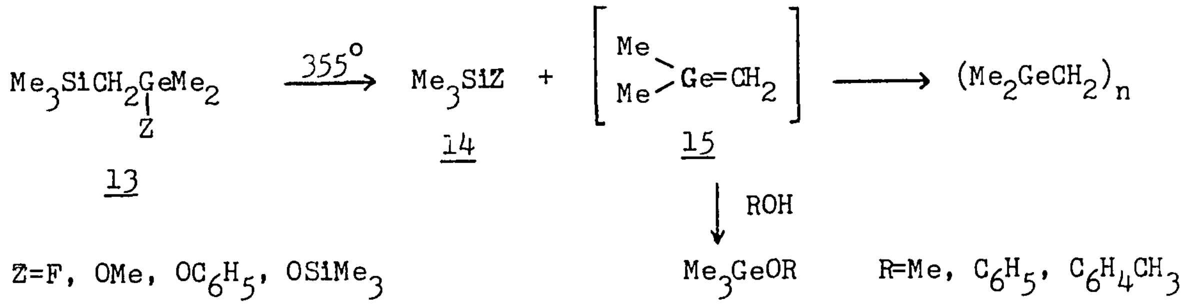


analogous silabicyclo [2.2.2] octadiene system proceeds in a fashion exactly like that shown in Scheme 2 (27).

Trapping of the germene <u>10</u> with anything but itself proved to be quite difficult. The authors were successful, however, in isolating the germacyclohexene compound <u>12</u> where <u>8</u> and 2,3-dimethylbutadiene were heated together at 230° in a sealed tube.

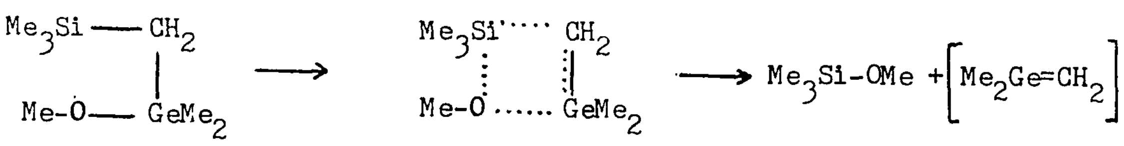
Mazerolles has also prepared a germene and has trapped it with alcohols (28). Pyrolysis of germanium compounds <u>13</u> results

Scheme 3



in beta-elimination of 14 and formation of 1,1-dimethylgermene (15). The thermodynamic driving force for this reaction is the formation of the very strong Si-F or Si-O bond. The proposed mechanism which involves the four-centered transition state 16 is shown in Scheme 4 for the case where Z=OMe.

Scheme 4

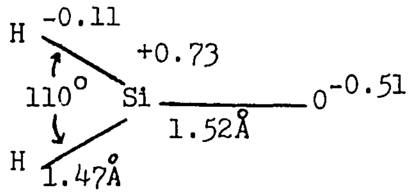


16 15

Silanones

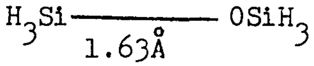
Before a review of the germanone literature is presented, something must be said about silanones. While the silanone literature has been reviewed several times in recent years (5, 7, 29), it has not been done from a critical point of view. When the silanone literature is very carefully analyzed, it becomes apparent that there are almost no instances in which a silanone must be invoked.

There are no reports in the literature of a theoretical calculation of a Si-O double bond. One such study has been carried out, however (30). In this study, Ruedenberg and coworkers have carried out ab. initio, Hartree-Fock-Roothan, SCF calculations on the parent silanone, $H_2Si=O$ (17). Their results are depicted below.



17

ν SiO = 1340 cm^{-1}



$H_3Si \underset{1.63Å}{\text{———}} OSiH_3$

18

ν SiO = 1107 cm^{-1}

The Si-O double bond is calculated to be extremely polar with the charge density on silicon being +0.73 and that on oxygen being -0.51. In addition, the π-electron density was calculated. When the two electrons are localized on silicon and oxygen, the calculations indicate that the π-electron density on silicon is 0.48 and on oxygen is 1.52. The calculated Si-O stretching frequency is 1340 cm^{-1}. These calculations do not allow for an estimate of the strength of the π-bond to be made.

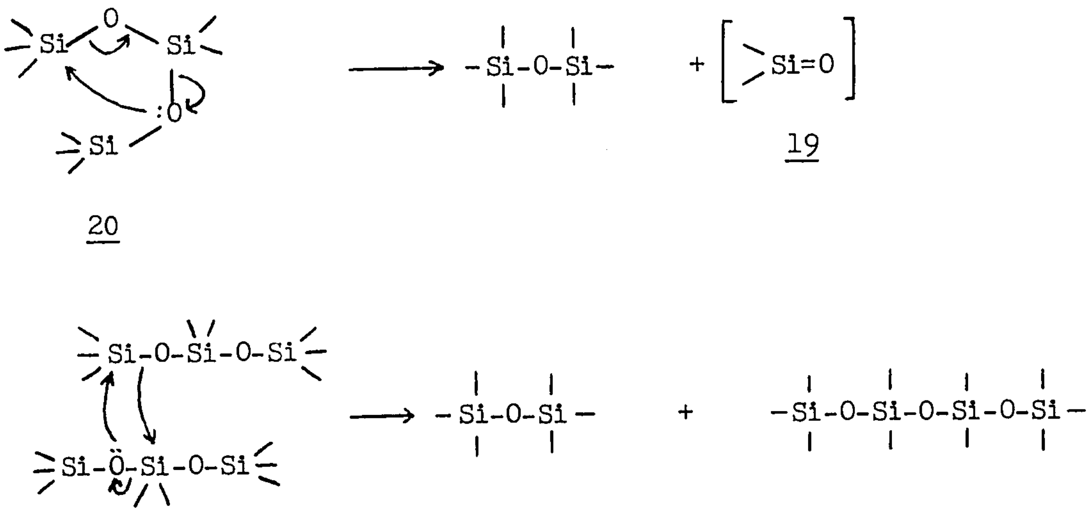
In comparing the calculated Si-O double bond with known Si-O single bonds, several things may be said. The increased strength of a Si-O double bond over a Si-O single bond should be evidenced by an increase of the stretching frequency in the IR spectrum. This is the case, but the magnitude of this frequency change is rather small, being less than 250 cm^{-1}. On the other hand, in going from the C-O single bond in dimethylether to the C-O double bond of formaldehyde, the stretching frequency increases by approximately 600 cm^{-1}. However, this smaller frequency increase in the silicon system versus the carbon system may not be so much an indication of the weakness of the Si-O double bond as it is an indication of the strength of the Si-O single bond. Indeed, the Si-O single bond is an extremely strong bond (D_{Si-O} = 111 kcal/mole) compared with the C-O single bond (D_{C-O} = 85.6 kcal/mole) (31). The generally accepted explanation for the strength of the Si-O single bond is that an overlap of silicon d orbitals with oxygen p orbitals allows for some extent of π-bonding.

Similar arguments can be used when comparing bond lengths of the Si-O double and single bonds. The calculated Si-O bond length in $H_2Si{=}O$ is 1.52 Å, a decrease of only 7% from the Si-O bond in a typical disiloxane. In the carbon system, there is a decrease in C-O bond length of approximately 14% in going from a single to a double bond. Again, this difference may not reflect the weakness of the Si-O double bond so much as it reflects the strength of the Si-O single bond.

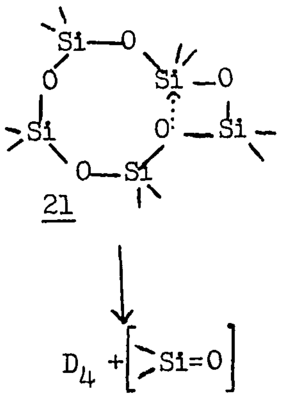
Experimentally, the following three general reactions have been used to prepare silanones: 1) pyrolysis of linear or cyclic polysiloxanes; 2) oxidation of a silylene; and 3) decomposition of a 2-silaoxetane. These three methods of preparation will be reviewed in order.

In 1952, Andrianov and Sokolov reported the pyrolysis of polydimethylsiloxanes (32). They discovered that heating siloxanes of the formula $Me_3SiO(Me_2SiO)_nSiMe_3$ led to the formation of new siloxanes differing from the starting material only by the number of units of Me_2SiO. The authors explained these products by invoking the intermediacy of dimethylsilanone (19). Scheme 5 shows a possible mechanism for the simple case of octamethyltrisiloxane (20). An equally good mechanism to explain these results involves an intermolecular attack. This mechanism, also shown in Scheme 5, does not involve dimethylsilanone.

Scheme 5



A more careful study was carried out by Nametkin, Gusel'nikov, and their coworkers, who pyrolyzed cyclosiloxanes and cyclocarbosiloxanes at 500-700° C (33-35). They found that cyclosiloxanes of formula $(Me_2SiO)_n$ led to the formation of new cyclosiloxanes differing from the starting material only in the number of units of Me_2SiO. In addition, these authors carried out a kinetic study of the thermal decomposition of decamethylcyclopentasiloxane (D_5). Their study indicated that the decomposition of D_5 followed first-order kinetics. Also, the concentration of octamethylcyclotetrasiloxane (D_4) increased initially, passed through a maximum, and then decreased while the concentration of hexamethylcyclotrisiloxane (D_3) increased continuously. These results suggested that the rearrangements occur in a stepwise fashion, i.e., $D_5 \rightarrow D_4 \rightarrow D_3$. Two possible transition states for the thermolysis of D_5 were suggested: 21 would lead to the extrusion of dimethylsilanone to form D_4; 22 would lead to the extrusion of tetramethylcyclodisiloxane (D_2) to form D_3. From studying the product ratios, the authors concluded that 60% of the reaction goes via 21 while 40% goes via 22. Thus, the formation of D_2 plays an important role in these reactions. Nametkin, Gusel'nikov, and coworkers do not comment on what the role of D_2 might be.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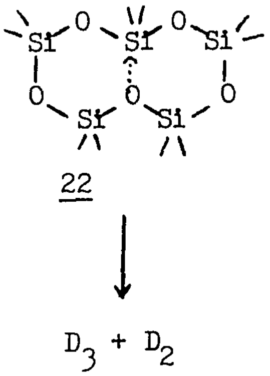

22

A very similar kinetic study of the gas-phase thermolysis of D_4 was reported by Davidson and Thompson (36). They found that the rate of decomposition of D_4, at least initially, was first order and that both D_3 and D_5 were formed. However, D_3 was always formed in higher yields than D_5. This was explained by mechanistic Scheme 6.

According to this mechanism, D_4 extrudes dimethylsilanone to form D_3. The dimethylsilanone then adds to D_4 to form D_5. D_5 then traps another molecule of dimethylsilanone to form D_6 which undergoes an intra-

Scheme 6

$$(Me_2SiO)_4 \leftrightarrows Me_2Si{=}O + (Me_2SiO)_3$$

$$Me_2Si{=}O + (Me_2SiO)_4 \leftrightarrows (Me_2SiO)_5$$

$$Me_2Si{=}O + (Me_2SiO)_5 \leftrightarrows (Me_2SiO)_6$$

$$(Me_2SiO)_6 \rightarrow 2(Me_2SiO)_3$$

molecular reaction to give two molecules of D_3. Davidson and Thompson reported that under their reaction conditions (gas phase), D_6 does rapidly and cleanly afford D_3. However, this is not in agreement with the results of Gusel'nikov and coworkers (34) who reported that thermolysis of D_6 in solution yields a complex mixture of cyclosiloxanes and that the yield of D_5 is always more than twice the yield of D_3.

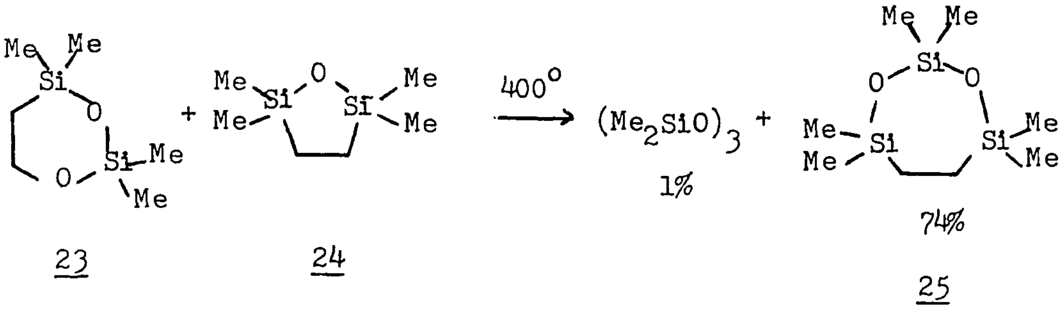
While Davidson and Thompson propose the intramolecular reaction of D_6 to form D_3, they do not consider the identical reaction of D_4 to form D_2. In fact, they do not invoke the intermediacy of D_2 anywhere in their mechanism, while Gusel'nikov and coworkers suggested that D_2 may be involved in as much as 40% of the decomposition of D_5 (34).

Davidson and Thompson also reported that the presence of ethylene, propene, butadiene, or silicone grease inhibited the formation of D_5, but did not affect the formation of D_3. It was suggested that these results indicated the direct formation of D_3 from D_4, but that the formation of D_5 involved a silanone intermediate which could be trapped by these various traps. No trapped products were reported, however. It is understandable that silicone grease could trap a silanone, as nearly any compound containing a Si-O single bond could do; but alkenes and dienes have never been used as successful silanone traps and it is difficult to postulate what kind of trapped products they should give.

From their kinetic data, Davidson and Thompson were able to calculate a minimum value for the strength of the silicon-oxygen π-bond. This value, 37.8 kcal/mole, is the only estimate of the silanone bond strength to appear in the literature.

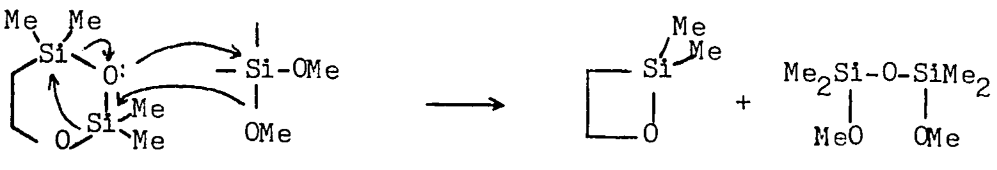
In a more recent study of a cyclosiloxane, Tumey thermolyzed 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxane (23) in the liquid phase at 400° (29).

Scheme 7



When 23 was pyrolyzed with 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (24), the major product isolated was 2,2,4,4,7,7-hexamethyl-1,3-dioxa-2,4,7-trisilacyclopentane (25) (Scheme 7). The explanation given is that compound 23 decomposes to form dimethylsilanone which is trapped by insertion into 24. Compound 24 is a commonly used silanone trap. Similar results were obtained using a different silanone trap, dimethyldimethoxysilane (26), which leads to the formation of sym-dimethoxytetramethyldisiloxane (27). Of course, these trapping experiments could be explained just as easily by intermolecular transfer of silanone units without the formation of a free silanone. This silanone transfer mechanism is shown in Scheme 8. The other product formed by this

Scheme 8

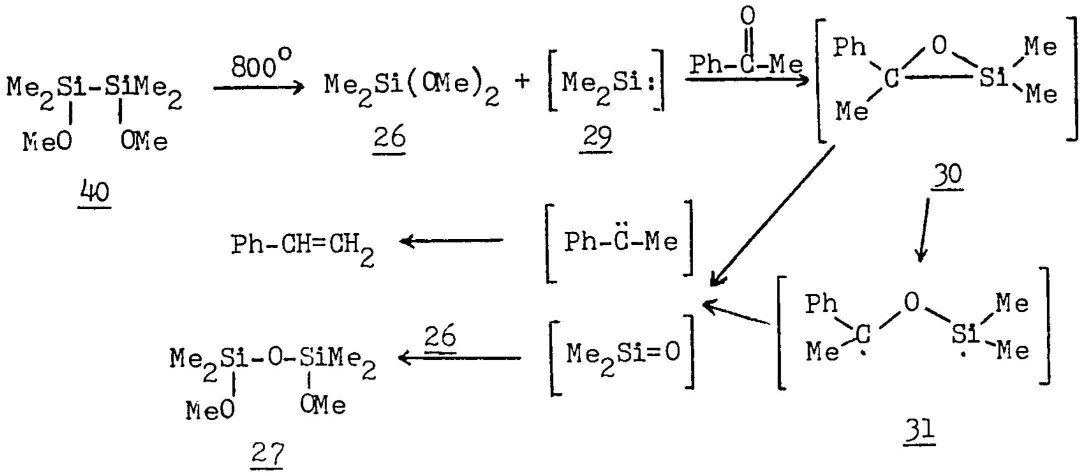


23 26 28 27

mechanism is 2,2-dimethyl-2-siloxetane (28) which could react in an intermolecular fashion with another molecule of 26 to form ethylene and another molecule of 27.

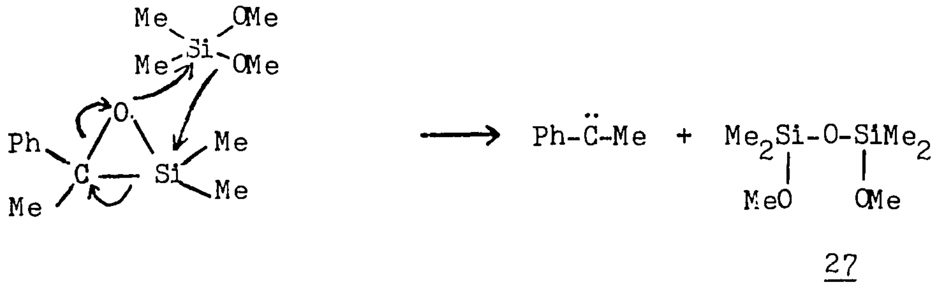
A second general method used for the preparation of silanone intermediates involves oxygen abstraction by a silylene. One such report by Ando and coworkers appeared in 1977 (37). In this work, 1,2-dimethoxy-1,1,2,2-tetramethyldisilane (40) was pyrolyzed to form dimethylsilylene (29) and dimethyldimethoxysilane (26) (38). When the flow pyrolysis was carried out at 800° C with an excess of acetophenone present, the silanone-trapped product 27 was formed in 10% yield along with a 31% yield of styrene. The postulated scheme involving dimethylsilanone is shown in Scheme 9. A key intermediate in this scheme is the silaoxirane 30 which could undergo either direct or stepwise cleavage to give methylphenylcarbene and dimethylsilanone. Carbene rearrangement then yields styrene while insertion of the silanone into 26 yields 27.

Scheme 9



The conclusion of these authors that dimethylsilanone is involved should be viewed with skepticism for three reasons. First, even if intermediate 30 is involved, it could react intermolecularly with 26 and yield 27 and methylphenylcarbene by the silanone-transfer mechanism (Scheme 10). Second, the proposed reaction would appear to be quite general, but in fact, no other ketones were found which gave rise to silanone-derived products. Third, as will be shown later, the pyrolysis

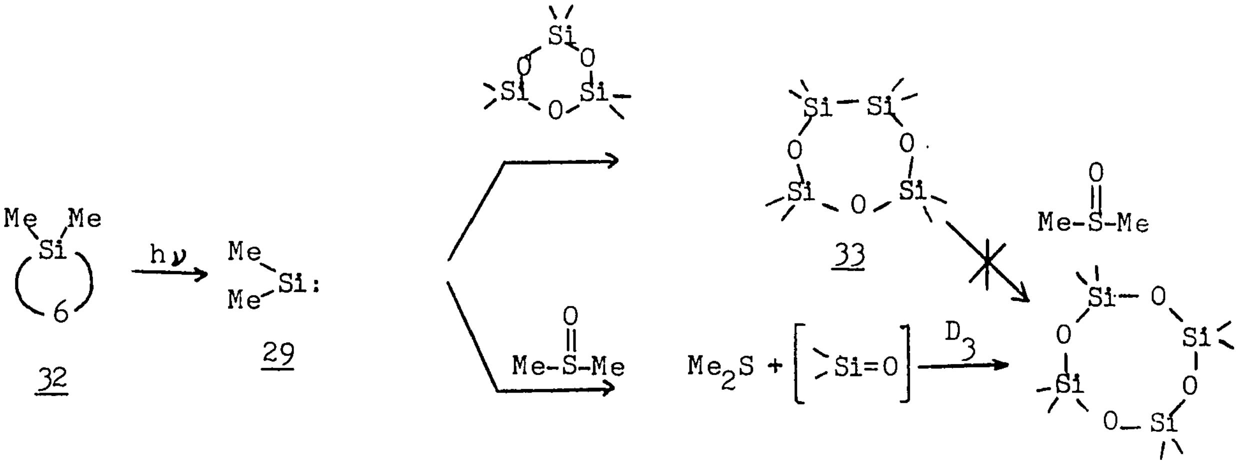
Scheme 10



of compound 26 by itself at 800° yields 27 in a yield higher than 10%. The reaction of 26 to give 27 will be discussed in terms of a radical mechanism.

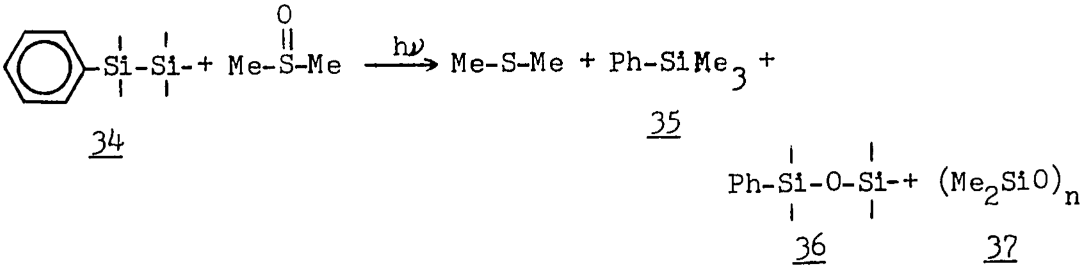
Another report of an oxygen abstraction reaction of a silylene was reported by Soysa and coworkers (39). Photolysis of dodecamethylcyclohexasilane (32) yields dimethylsilylene (29) (40). When 29 was generated in the presence of D_3, it inserted into a Si-O bond to form 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxa-1,2,4,6-tetrasilacycloheptane (33). When dimethylsulfoxide (DMSO) was added, dimethylsulfide was formed along with D_4. In a separate experiment, it was demonstrated that 33 will not react with DMSO to yield D_4. While no mechanism was postulated in the first paper, Soysa claimed the intermediacy of dimethylsilanone.

Scheme 11

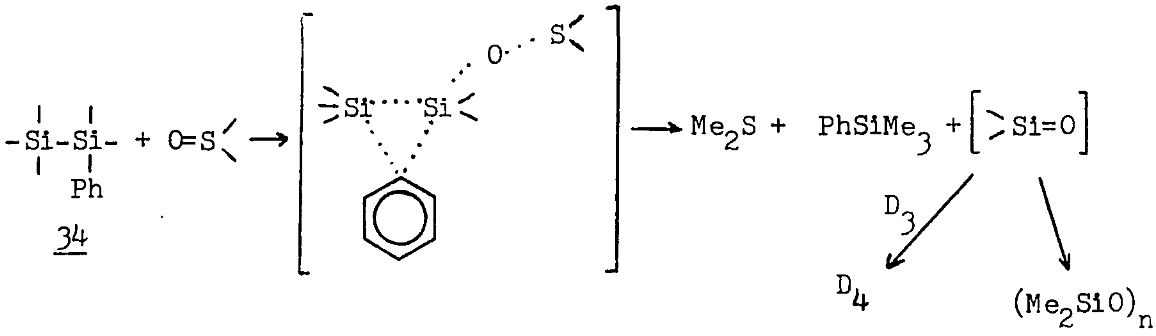


Okinoshima and Weber later reported the photolysis of aryl substituted disilanes in the presence of dimethylsulfoxide (41). Photolysis of pentamethylphenyldisilane (34) in a dioxane solution containing DMSO yielded dimethylsulfide, trimethylphenylsilane (35), pentamethylphenyldisiloxane (36), and dimethylsilicone oligomers (37). Disiloxane 36 is thought to arise via simple oxidation of the disilane linkage. Products 35 and 37 were postulated to arise from a mechanism involving dimethylsilanone as shown in Scheme 13. According to this mechanism,

Scheme 12



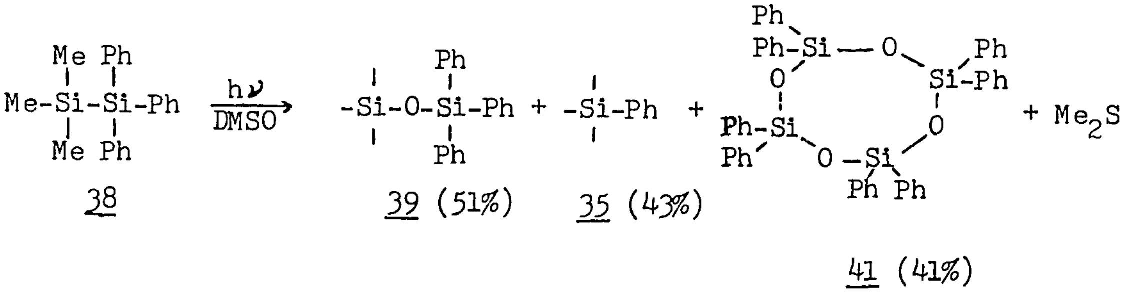
Scheme 13



attack of DMSO on silicon proceeds with simultaneous migration of the aryl group from one silicon to the other one. When D_3 was added, moderate yields of D_4 were formed. Photolysis of aryl substituted tri- and tetrasilanes gave similar results (42). In most cases, the proposed intermediate silanones were trapped in yields less than 20%.

More recently, Swain and Weber reported the photolysis of 1,1,1-trimethyl-2,2,2-triphenyldisilane (38) in the presence of DMSO (43).

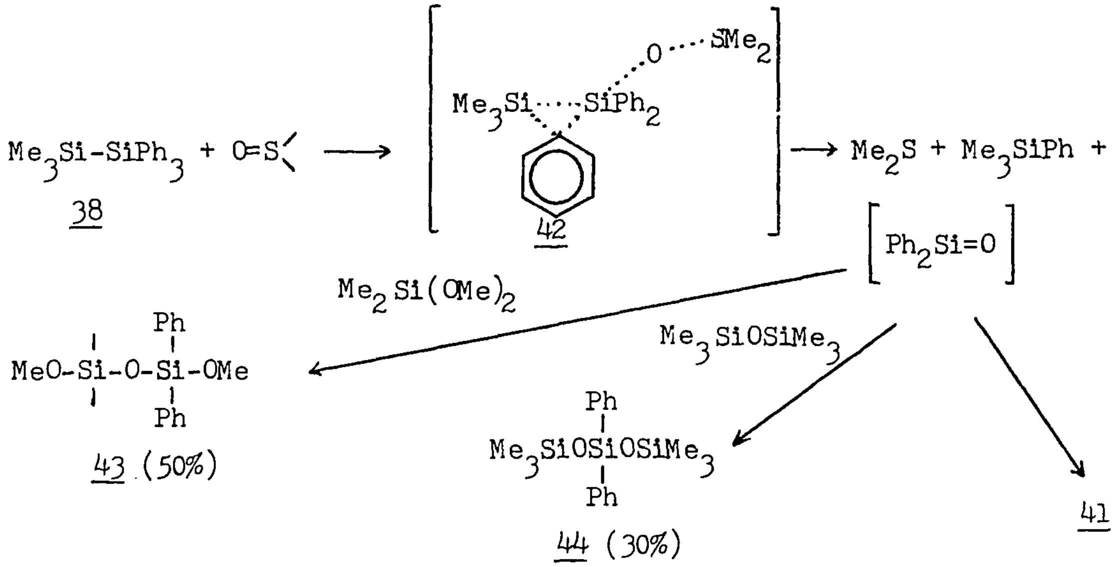
Scheme 14



Photolysis of 38 resulted in the formation of 1,1,1-trimethyl-3,3,3-triphenyldisiloxane (39), trimethylphenylsilane (35), and 1,1,3,3,5,5,7,7-octaphenylcyclotetrasiloxane (41). Again, the disiloxane is explained as arising from oxidation of the disilane linkage. The mechanism postulated to explain the other products is shown in Scheme 15.

The formation of free diphenylsilanone in this reaction is unlikely for two reasons. First, it is inconceivable that the silanone should form only the cyclic tetramer and none of the trimer or pentamer. Second, it is difficult to believe that four silanone molecules should find each other in any fashion, stepwise or not, and form 41 in 41% yield while a silanone trap such as hexamethyldisiloxane only traps the silanone in 30% yield. It is more likely that in this reaction, there is no free silanone formed, but rather the dimer, 1,1,3,3-tetraphenylcyclodisiloxane (45) is directly formed. Dimerization of 45 would then

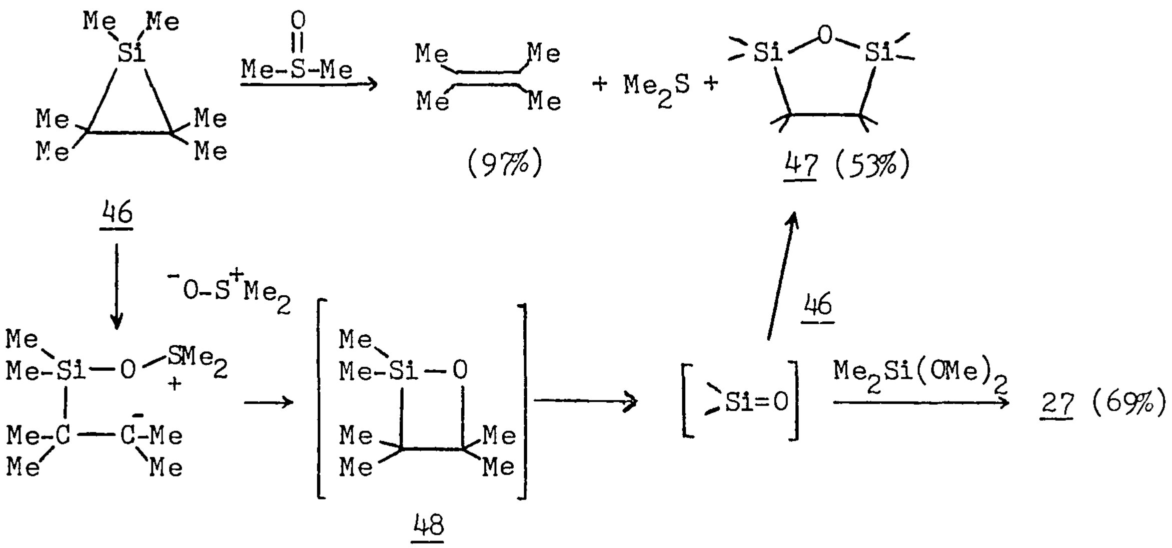
Scheme 15



form 41 and would avoid the formation of the cyclic trimer of diphenylsilanone.

Another reaction with DMSO was reported by Seyferth and coworkers and is shown in Scheme 16 (44). While this reaction appears to be similar to those of Soysa and coworkers, it is actually much different and brings us to the third general method of preparation of silanone intermediates, that involving 2-silaoxetanes. In this case, hexamethylsilacyclopropane (46) with DMSO formed dimethylsulfide, tetramethylethylene, and cyclic siloxane 47. This reaction was carried out at a temperature much lower than that required for dimethylsilylene extrusion from 46 (45, 46). The mechanism proposed by the authors involves attack by DMSO on silarane 46 to yield, by either a concerted or a stepwise process, silaoxetane 48. Compound 48 decomposes to yield tetramethylethylene and dimethylsilanone which is trapped by the

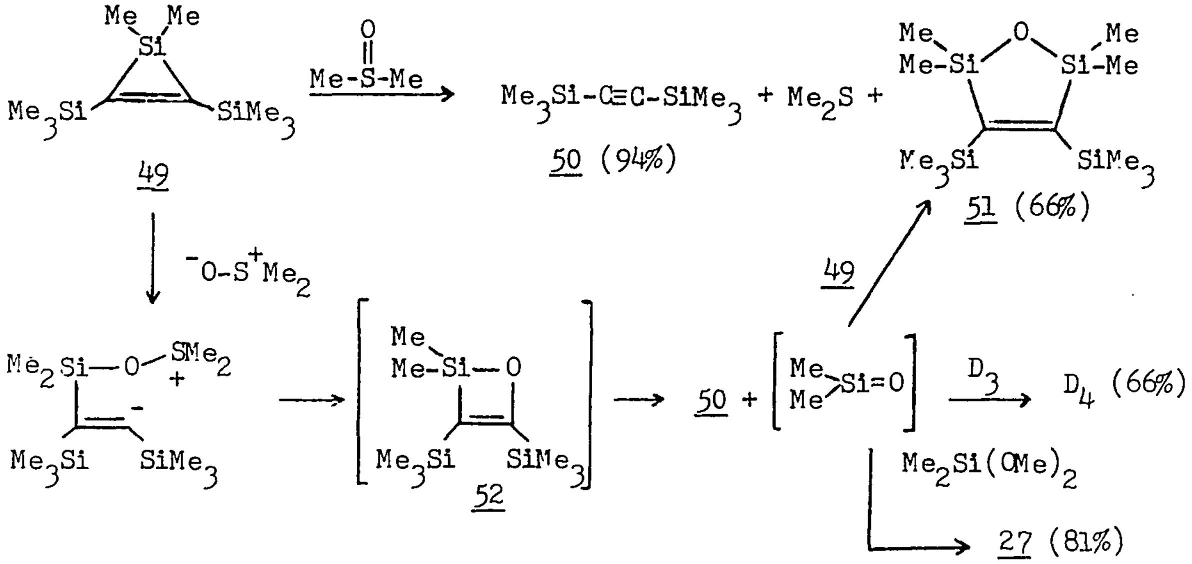
Scheme 16



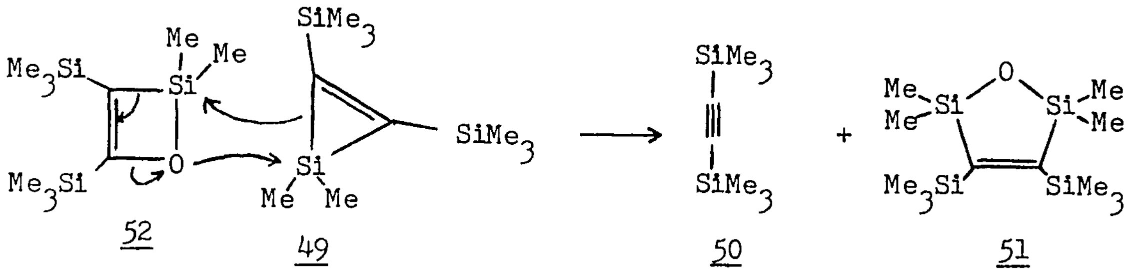
starting silarane to yield cyclic siloxane 47. Analogous results were reported for the reaction of 1,1-dimethyl-2,3,bis(trimethylsilyl)-1-silarene (49) with DMSO (44). Silarenes are not known to be thermal generators of silylenes (47, 48), so again the proposed mechanism involves attack by DMSO on 49 to yield the silaoxetane intermediate 52 (Scheme 17). Decomposition of 52 leads to formation of bis(trimethylsilyl)acetylene (50) and dimethylsilanone, which after insertion into starting silarene, gives cyclic siloxane 51. When other silanone traps were added, the expected trapped products were formed.

An alternative mechanism to explain these results is shown in Scheme 18. This is again a silanone transfer mechanism. In this case, the silaoxetane intermediates transfer the silanone unit to the starting silarane or silarene. Of course, the silaoxetane could equally well transfer a silanone unit to any added silanone trap; thus none of the

Scheme 17



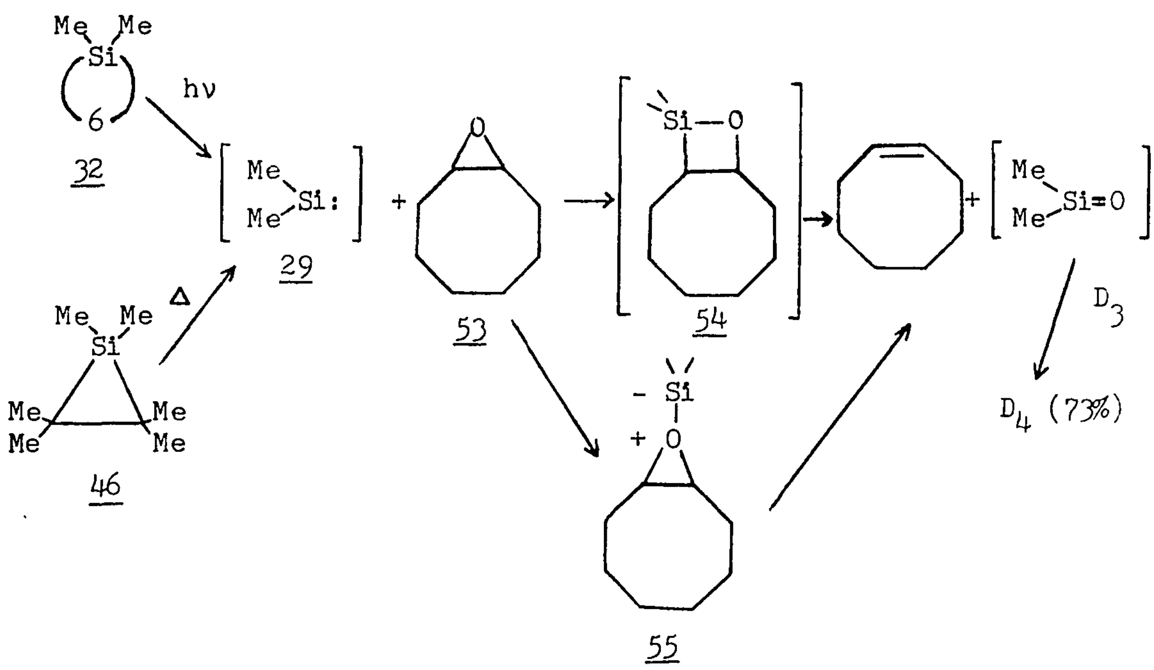
Scheme 18



results of Seyferth and coworkers require the intermediacy of dimethylsilanone.

Another route into a 2-silaoxetane system is reaction of a silylene with an epoxide. The reaction of dimethylsilylene with cyclooctene oxide has recently been studied by Barton and Goure (49). Photolysis of 32 (40) or thermolysis of 46 (50) yields dimethylsilylene (29). It was suggested that 29 and 53 would form the silaoxetane intermediate 54 or

Scheme 19

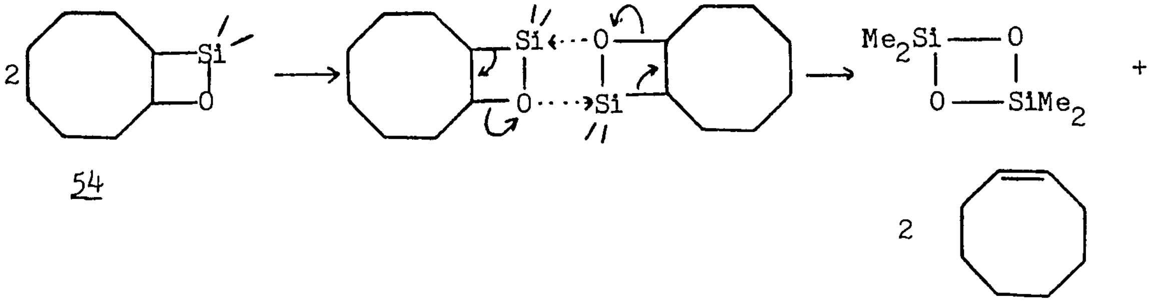


the oxygen ylid 55, either of which would fragment to yield cyclooctene and dimethylsilanone. Trapping of dimethylsilanone with D_3 gives D_4.

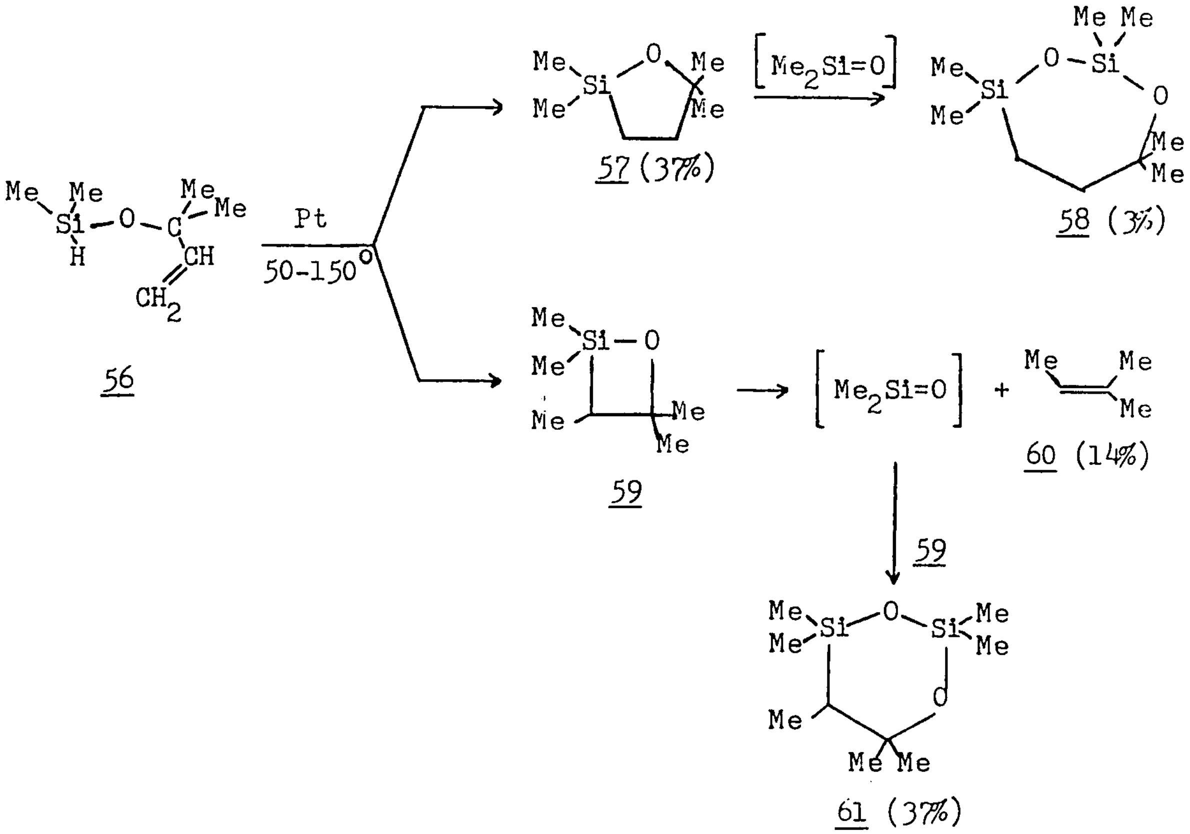
Alternatively, the silanone-transfer mechanism can be used to explain all these results. Intermediate 54 could form cyclooctene by transferring a dimethylsilanone unit to a silanone trap such as D_3, the walls of the glass reaction flask, or another molecule of 54 as shown in Scheme 20. A similar dimerization of ylid 55 could also be written.

The formation of a silaoxetane and its elimination of a silanone were claimed by Lane and Frye who carried out the platinum catalyzed intramolecular hydrosilation of vinyldimethylcarbinoxydimethylsilane (56) (51). This reaction produced 1,1,3,3-tetramethyl-2-oxa-1-silacyclopentane (57), 2,2,4,4,7,7-hexamethyl-1,3-dioxa-2,4-disilacycloheptane (58), trimethylethylene (60), 1,1,3,3,5,5,6-heptamethyl-2,4-

Scheme 20



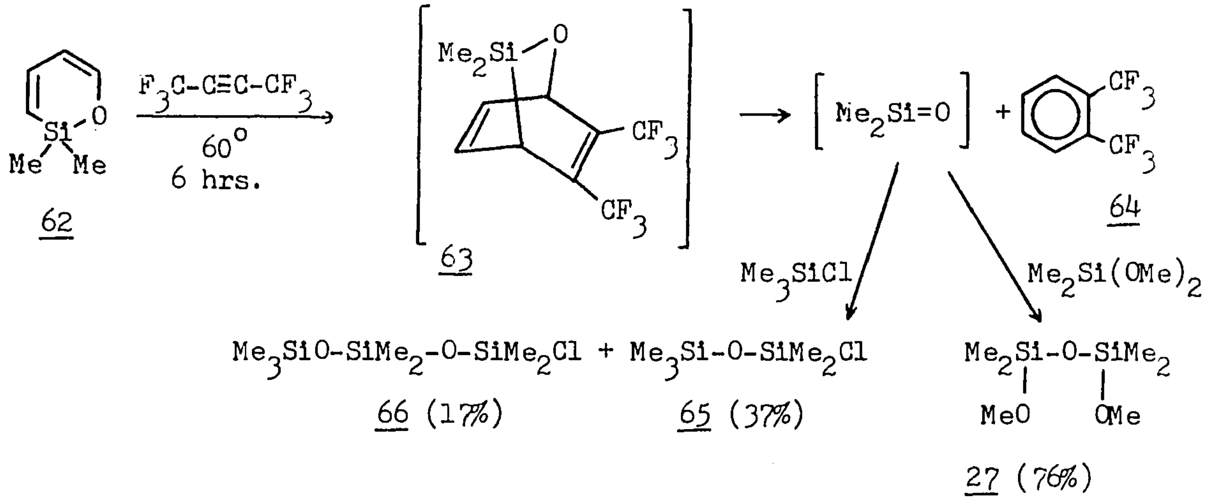
Scheme 21



dioxa-1,3-disilacyclohexane (61), and a small amount of D_3. The authors proposed that the hydrosilation reaction proceeds to yield both the five-membered ring 57 and silaoxetane 59. The silaoxetane then fragments to give 60 and dimethylsilanone which is trapped by another silaoxetane molecule to yield 61. This work marks the first instance in which a silaoxetane is reported to trap a silanone. It is also interesting to note that dimethylsilanone is here proposed to be formed and trapped in the presence of alkene 56, while Davidson and Thompson reported that alkenes trapped dimethylsilanone (36). Of course, there is no evidence in the work of Lane and Frye which demands the intermediacy of dimethylsilanone. The silanone-transfer mechanism explains all the results equally well.

Somewhat related to the silaoxetane method of silanone formation is the reaction recently reported by Barton and Wulff (Scheme 22) (52). In

Scheme 22

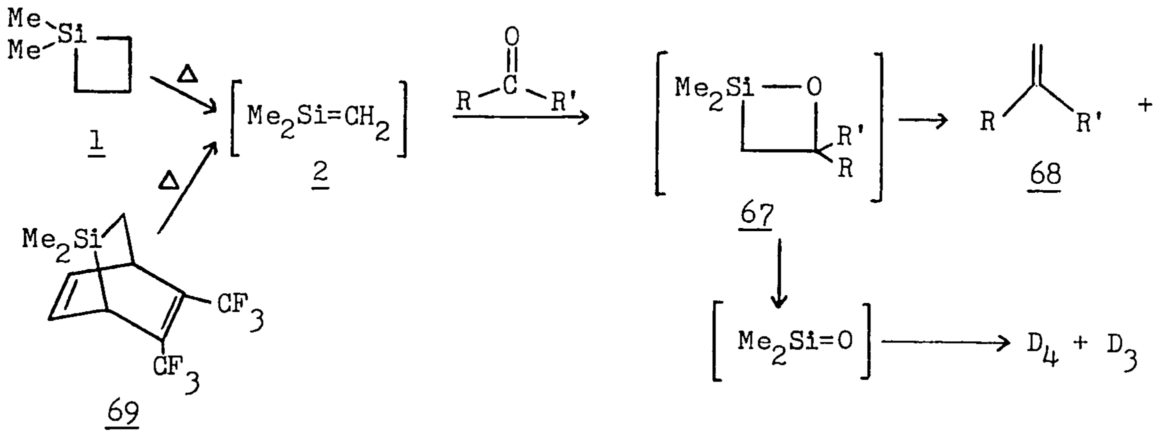


this case, 2,2-dimethyl-1-oxa-2-silacyclohexa-3,5-diene (62) was treated with perfluoro-2-butyne at room temperature for one day to prepare the Diels-Alder adduct 63. None of the adduct 63 was isolated, however, as o-bis(trifluoromethyl)benzene (64) was formed at the same rate as the disappearance of 62. The authors proposed that this reaction represented the room-temperature generation of dimethylsilanone. The silanone was trapped by the usual silanone traps such as dimethyldimethoxysilane and D_3. The example of silanone insertion into a silicon-chlorine bond was also reported. When the Diels-Alder reaction was run in the presence of trimethylchlorosilane, chloropentamethyldisiloxane (65) and 1-chloroheptamethyltrisiloxane (66) were formed. Products 65 and 66 were postulated to arise via insertion of dimethylsilanone into trimethylchlorosilane. These results can all be explained by the silanone-transfer mechanism as well.

In addition, the following reagents were all investigated by Wulff and were found to be unsuccessful in trapping dimethylsilanone: diethyl ether; ethylene oxide; triethylsilane; tetramethylethylene oxide; 1,1,3,3-tetramethyl-1,3-disilacyclobutane; and trans-cinnamyl methyl ether (7).

Perhaps the most commonly used method for the preparation of 2-silaoxetanes has been the reaction of a silene with a carbonyl compound. This reaction was first reported by Barton and coworkers (53) who prepared 1,1-dimethylsilene (2) from the pyrolysis of 1,1-dimethyl-1-silacyclobutane (1) or 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo [2.2.2] octa-2,8-diene (69). The authors proposed that dimethylsilene underwent a Wittig-type reaction with carbonyl compounds to form silaoxetanes 67 which, under the pyrolytic conditions, cleaved to form the isolated olefins (68) as well as dimethylsilanone which cyclo-oligomerized to form low yields of D_3 and D_4. Similar investigations

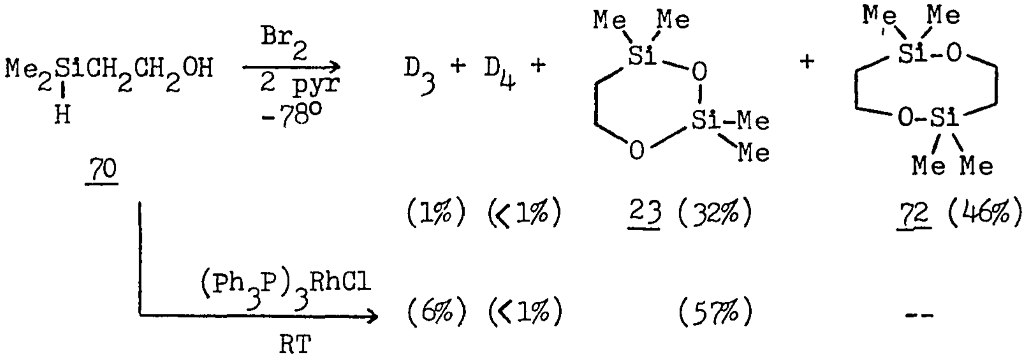
Scheme 23



of the reaction between carbonyl compounds and thermally-generated silenes have been carried out by Roark and Sommer (54) and others (55-57). This well-documented reaction is often used diagnostically for the detection of silene intermediates.

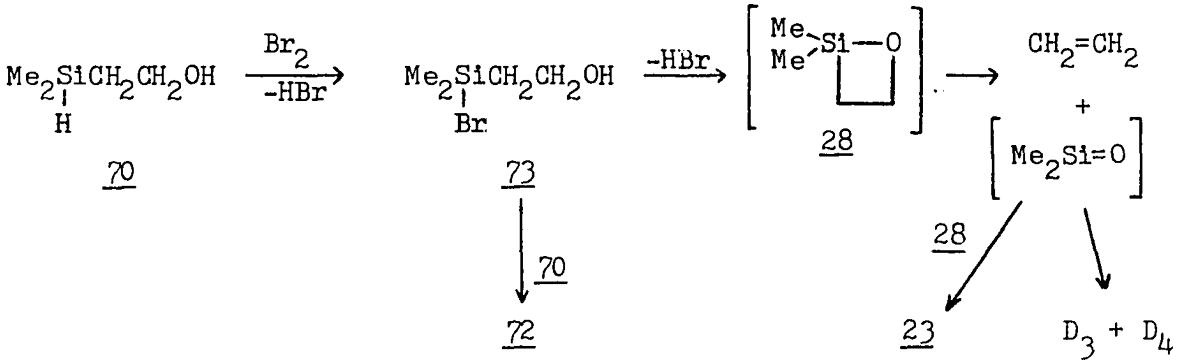
It is understandable that 2-silaoxetanes would cleave under the conditions used to thermally generate silenes. The temperatures used in these gas phase reactions are typically 500-700° C. However, it is not as easy to understand why silaoxetanes should be unstable at lower temperatures. In an effort to study the thermal lability of 2-silaoxetanes, Tumey attempted to prepare 2,2-dimethyl-2-silaoxetane (28) at room temperature or lower (29). Treatment of 2-(dimethylsilyl)ethanol (70) with Br_2 at -78° led to the formation of D_3, D_4, 2,2,4,4-tetra-

Scheme 24



methyl-2,4-disila-1,3-dioxane (23) and 2,2,6,6-tetramethyl-1,5-dioxa-2,6-disilacyclooctane (72). The formation of dioxane 23 is proposed to arise from the insertion of dimethylsilanone into silaoxetane 28 as shown in Scheme 25. This is the same mechanism proposed by Lane and Frye

Scheme 25



to explain the formation of their dioxane (51). The eight-membered dioxane ring 72, while formally a dimer of silaoxetane 28, probably is formed via intermolecular attack by the silyl bromide 73 on 70. This is supported by the observation that 72 is not formed in the rhodium-catalyzed cyclization of 70.

The key intermediate in this work, as well as in other work, is the 2-silaoxetane. A question which must be asked is the following: is it reasonable to expect a silaoxetane to intramolecularly cleave to yield a silanone and an olefin? In answering this question, the following two factors will be addressed: 1) ring strain; and 2) the thermodynamics of the overall bond-breaking and bond-forming processes. At the same time, the similar question regarding the stability of D_2 will be addressed.

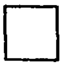
A general trend which is observed for ring strain energies is that replacement of a methylene group with another first row element has little effect on ring strain, while replacing a methylene with a second row element generally decreases the strain energy appreciably. This can be seen from the data in Table 2. Replacing a methylene in either cyclopropane or cyclobutane with an oxygen results in a very small decrease in strain energy, while replacement with a sulfur results in a substantial decrease in strain energy. The strain energy of silacyclobutane 1 is about the same as that of cyclobutane, while disilacyclobutane 3 has considerably lower strain energy. If silacyclobutane 1 can be equated with cyclobutane in terms of ring strain, it is expected that silaoxetane 28 should have less strain, just as oxetane has less strain than cyclobutane. No estimate of the ring strain of 1,3-dioxetane has been reported in the literature, but it is expected to have less strain than cyclobutane. Similarly, D_2 is expected to have less strain than disilacyclobutane 3. Based solely on strain energies, there is no reason to expect either silaoxetane 28 or D_2 to be unstable.

Table 2. Strain energies (kcal/mole)

27.5[a]

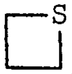
27.2[a]

19.9[a]

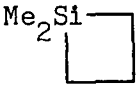


26.7[a]

25.3[a]

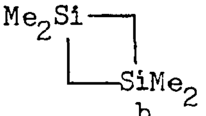


19.7[a]



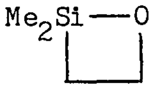
25.9[b]

1

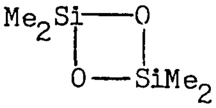


17.7[b]

3



28

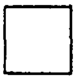
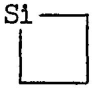
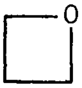
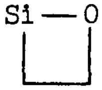
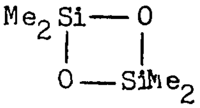


[a]Values taken from reference 58.

[b]Values taken from reference 59.

Table 3 lists the intramolecular cleavage reactions of cyclobutane, silacyclobutane, oxetane, silaoxetane, and D_2. The enthalpies listed are crude figures based only on the energy of the bonds broken and formed. The results shown in Table 3 indicate that of the compounds listed, D_2 is by far the most stable with regards to intramolecular cleavage. The second most stable molecule listed is 2-silaoxetane. Replacement of the two oxygens in D_2 by two sulfurs should increase the likelihood of this decomposition; yet 1,1,3,3-tetramethyl-2,4-dithia-1,3-disilacyclobutane is a stable compound at room temperature (60, 61). Thus, the inability of researchers to isolate D_2 and silaoxetanes appears to be due not to either ring strain or bond energy terms. It appears

Table 3. Intramolecular cleavage reactions of cyclobutane, silacyclobutane, oxetane, silaoxetane, and D_2

			Δ H (kcal/mole)
	$\longrightarrow$	$2\ CH_2{=}CH_2$	40^{a}
	$\longrightarrow$	$H_2Si{=}CH_2 + CH_2{=}CH_2$	$47^{a,\ b}$
	$\longrightarrow$	$H_2C{=}O + CH_2{=}CH_2$	16^{a}
	$\longrightarrow$	$H_2Si{=}O + CH_2{=}CH_2$	$58^{a,\ c}$
	$\longrightarrow$	$2\ Me_2Si{=}O$	$144^{a,\ c}$

[a] C-C, C=C, Si-C, Si-O, C-O, and C=O bond energies taken from reference 31.

[b] Si=C bond energy taken as 46 kcal/mole from reference 18.

[c] Si=O bond energy taken as 38 kcal/mole from reference 36.

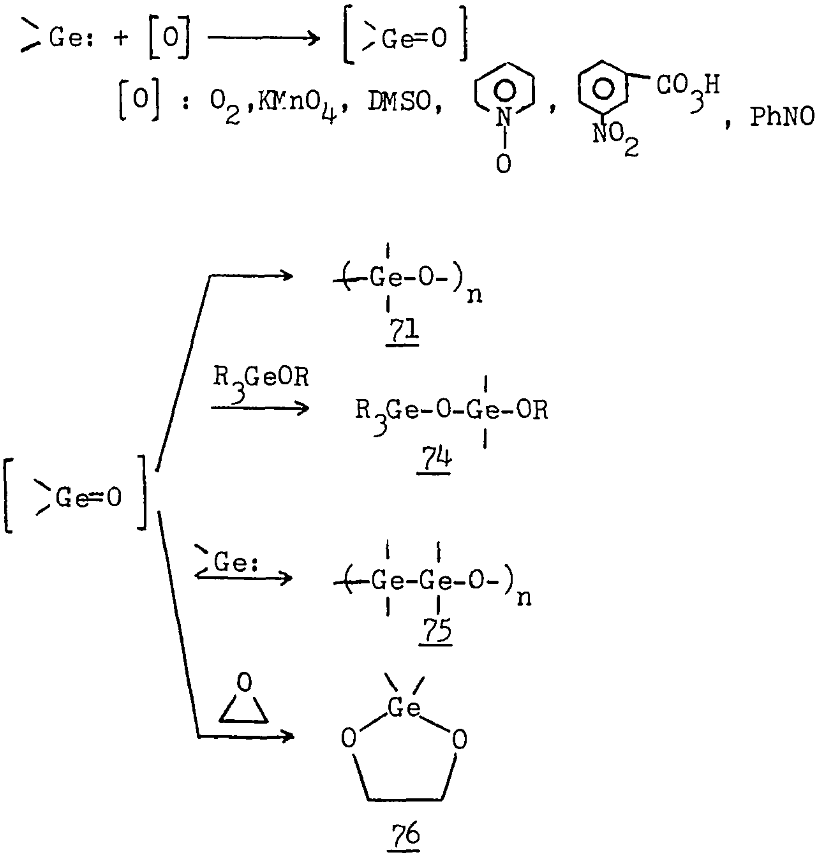
likely that D_2 and silaoxetane are stable with regards to intramolecular cleavage, but are very reactive towards bimolecular reactions. What is necessary to distinguish between unimolecular and bimolecular reactions is a good kinetic study. Other than the work of Nametkin and coworkers (33, 35), and Davidson and Thompson (36), which contain some inconsistencies, no kinetic studies have been carried out.

Germanones

Of the three general methods of silanone generation, only two have been applied to germanones. Pyrolysis of polygermoxanes has not been investigated.

The oxidation of germylenes to germanones has been studied by Satge' and coworkers (62) and others (63). A wide range of oxidizing agents have been used including molecular oxygen, permanganate, DMSO, amine oxides, peroxy acids, and nitrosobenzene (Scheme 26). With no germanone

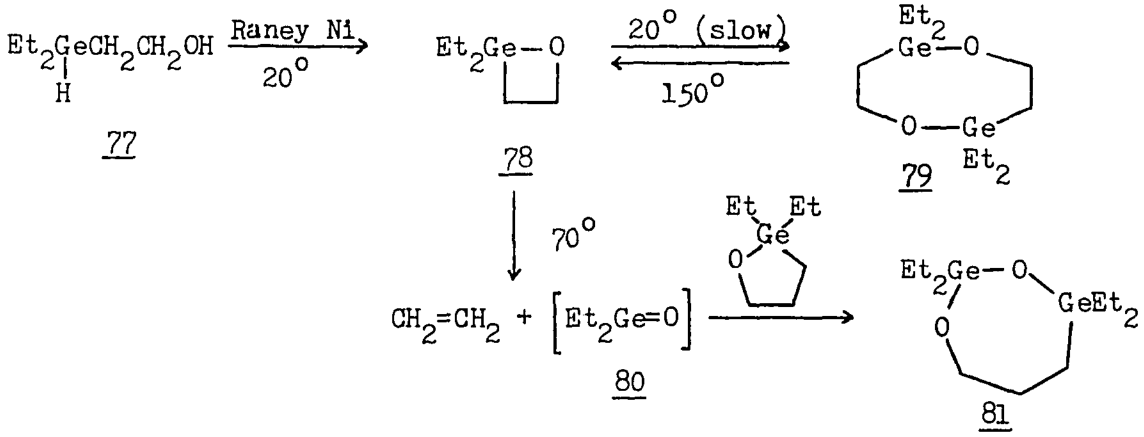
Scheme 26



trap present, the germanone polymerizes to form linear germoxanes (71). The germanone is also trapped with excess germylene to form polymeric germoxanes which contain the digermane linkage (75). The addition of a silylene to a silanone was not reported in the analogous oxidation reactions of silylenes (40-43, 49). The germanones were also reported to be trapped by ethylene oxide to form the dioxagermacyclopentane systems (76). This result is in contrast with the report that dimethylsilanone cannot be trapped by ethylene oxide (7).

The second method of germanone formation is via 2-germaoxetanes (64-67). A striking difference between germaoxetanes and silaoxetanes is that germaoxetanes can be isolated at room temperature. Nickel catalyzed cyclization of 2-(diethylgermyl)ethanol (77) produced 2,2-diethyl-2-germaoxetane (78). Upon standing at room temperature, 78

Scheme 27

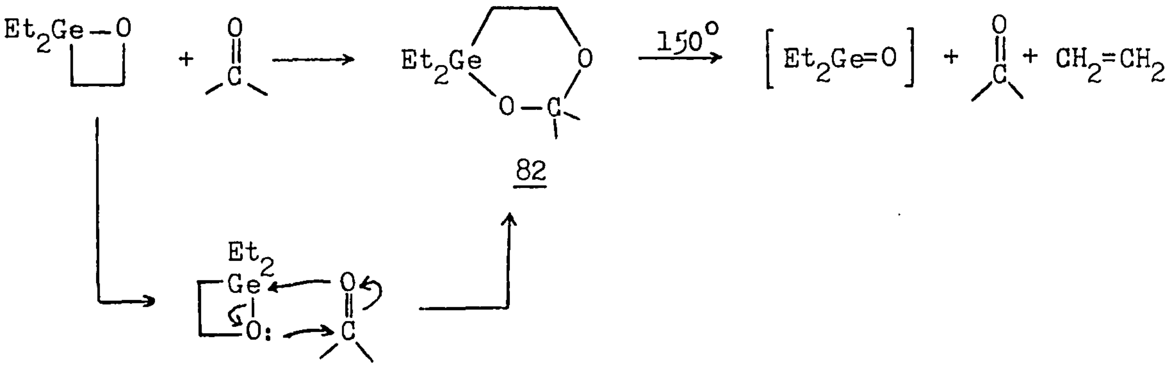


slowly dimerized to give 79. The authors proposed that when 78 was heated, it cleaved to form ethylene and diethylgermanone (80). Product

80 was trapped with itself and with ethylene oxide. In addition, 80 was trapped with 1,1-diethyl-2-oxagermacyclopentane to form 1,1,3,3-tetraethyl-2-oxa-1,3-digermacycloheptane (81) as shown in Scheme 27.

Germaoxetane 73 was also trapped with carbonyl compounds to yield the 2,4-dioxagermacyclohexane ring system (82) (Scheme 28). When thermolyzed, 82 gave rise to ethylene, the carbonyl compound, and diethylgermanone. The mechanism the authors postulated for the formation of 82 very closely resembles the silanone-transfer mechanism. In fact, all of these results can be explained by the analogous germanone transfer mechanism.

Scheme 28



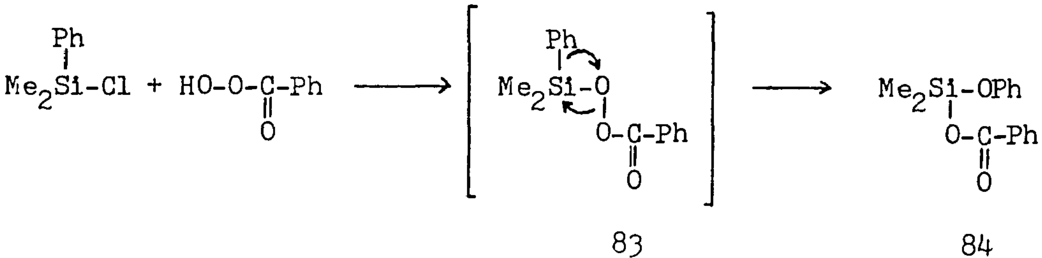
According to bond energies and ring strain, there is no more reason to expect a germaoxetane to cleave than there is to expect a silaoxetane to cleave. The fact that a germaoxetane can be isolated at room temperature and the observation that it slowly dimerizes lend support to the idea that unimolecular decomposition is not the major reaction pathway, but that a bimolecular reaction is. The obvious work which must be done is to carry out a kinetic study on the thermal decomposition of 2-germaoxetanes. The results of such a study should clarify the germanone versus germanone-transfer mechanisms, but would not necessarily comment on the question of free silanone versus silanone-transfer.

Silylperoxides

The silylperoxide literature is quite extensive, so that a complete review is not possible here. Two review articles have appeared in the literature (68, 69). Except for a few recent reports (70-72), both of these review articles adequately cover the preparation of silylperoxides as well as the reactions of these peroxides with acids, nucleophiles, and reducing agents. The reactions of greater interest here, however, are the thermal and photochemical decomposition reactions. The thermal reactions are covered in the early review by Brandes and Blaschette (68), but this report is now outdated. The later paper by Razuvaev and Brilkina (69) does not cover either the thermal or photochemical reactions.

Silylperoxides are known to undergo two types of thermal reactions: 1) homolytic cleavage which forms radicals; and 2) rearrangement which leads to nonperoxide products, isomeric with the starting peroxide. Examples of the rearrangement reaction were given by Buncel and Davies as early as the 1950's (73, 74). These authors attempted to prepare silylperoxide 83 as shown in Scheme 29; but instead, they isolated the rearranged isomer 84. The analogous rearrangement of carbon acyl peroxides had also been observed and on the basis of ^{18}O studies, a concerted mechanism was proposed (75, 76).

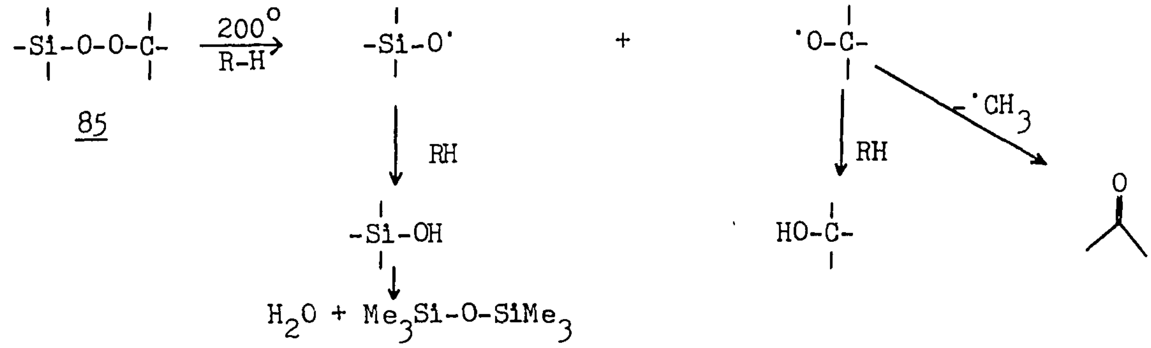
Scheme 29



83 84

This rearrangement is not the exclusive reaction of silylperoxides; homolytic cleavage can also occur. The thermal decomposition of t-butyl trimethylsilylperoxide (85) was reported by Hiatt in 1964 (77). The products of the reaction were acetone, t-butanol, and hexamethyldisiloxane. These come from the trimethylsiloxy and t-butoxy radicals as shown in Scheme 30. Hiatt also studied the kinetics of this reaction and found

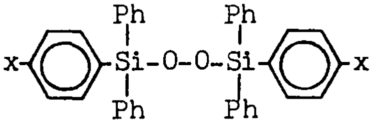
Scheme 30



that the decomposition of 85 was first order in a hydrocarbon solvent. In addition, the decomposition was sensitive to acid and base catalysis. The kinetics of the thermal decomposition of t-butyl trimethylgermyl-peroxide have also been studied and were found to be similar to those of the silicon analog (78).

Dannley and Jalics proposed a similar radical mechanism to explain the thermal decomposition reactions of silyl hydroperoxides (79, 80). They, too, found these reactions to be first order in several solvents. Irradiation with UV light was found to accelerate the reaction while the kinetics remained first order, but addition of an amine base accelerated the reaction while changing the kinetics.

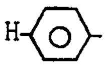
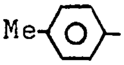
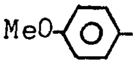
The mechanism of the thermal rearrangement reaction of silylperoxides has been a matter of great debate. The first mechanistic investigation of the rearrangement of bis(silyl)peroxides was carried out by Shubber and Dannley (81). They prepared a series of aryl substituted bis(silyl)peroxides (86-88) and measured the relative migratory aptitudes of the phenyl, p-tolyl, and p-anisyl groups (see illustration below). These low values of relative migratory aptitudes were thought by the authors to be more consistent with a homolytic cleavage reaction than with a heterolytic reaction. They therefore postulated the radical mechanism shown in Scheme 31. The quantitative formation of 89 from 86



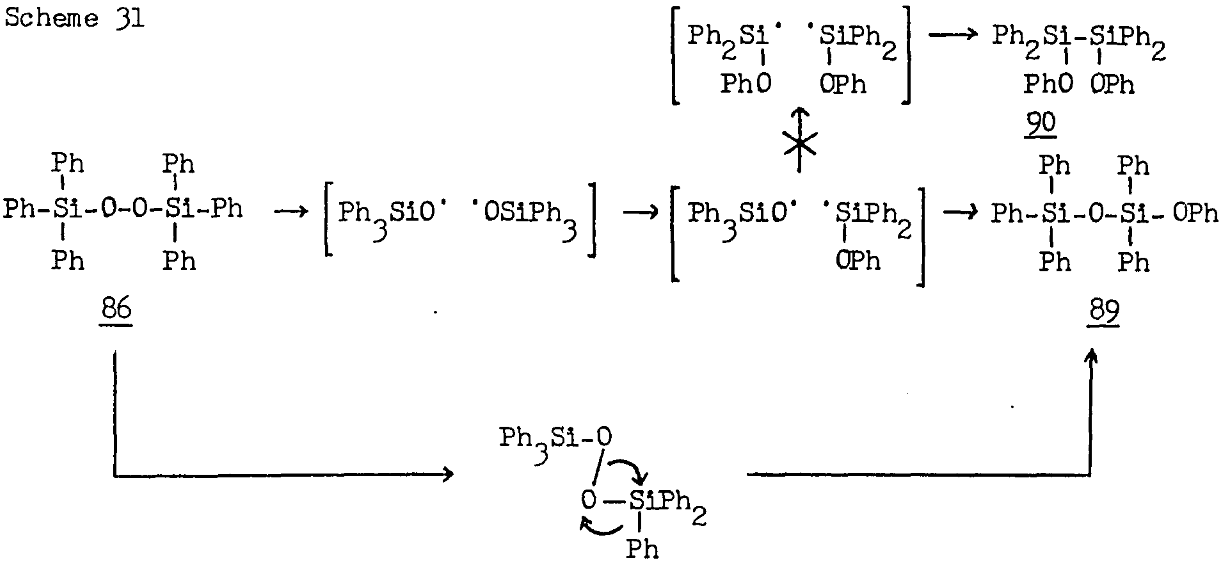
86 x = H

87 x = Me

88 x = OMe

	relative migratory aptitudes
	1.0
	1.1
	6.0

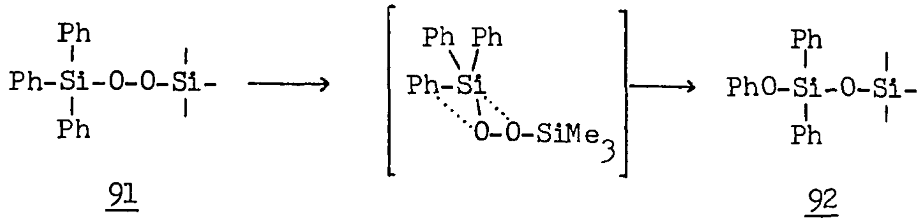
Scheme 31



required Shubber and Dannley to invoke a caged radical pair in which only one radical rearranges before recombining with the other radical to form the product. If a cage were not involved, it would be expected that two rearranged radicals could recombine to form the disilane 90. Dannley and Farrant had earlier proposed a similar mechanism for the thermal rearrangement of the analogous bis(germyl)peroxides (82, 83).

Other work carried out by Yablokov and coworkers indicates that the mechanism of these thermal rearrangements is probably a concerted, intramolecular one (84). Thermal rearrangement of triphenylsilyltrimethylsilyl peroxide (91) quantitatively yields disiloxane 92. This reaction was run in a variety of solvents where a caged radical pair would be unlikely, while Shubber and Dannley (81) had not used any solvent in their reactions. More recently, Yablokov and coworkers have reported the gas phase thermal decomposition of bis(silyl)peroxides (85). The gas phase reactions proceeded the same way as the solution reactions.

Scheme 32



This casts considerable doubt on any caged radical mechanism since in the gas phase there is no reason to expect any cage to exist.

Thermodynamic arguments also lie in favor of a concerted mechanism. The energy of activation for the thermal rearrangement of bis(silyl)-peroxides is approximately 27-29 kcal/mole (84). This is a relatively small barrier which is more consistent with a concerted rearrangement. (Compare this value with the dissociation energy of the O-O bond in $Me_3SiO-OCMe_3$ which is 47 kcal/mole (86)). The activation entropy for the thermal rearrangement of several bis(silyl)peroxides has also been measured (87, 88). In all cases, ΔS has small negative values. A negative entropy value is characteristic of a concerted, intramolecular process.

Another argument in favor of the concerted mechanism comes from studies of the thermal rearrangement reactions under pressure. Increasing the pressure would be expected to increase the rate of reaction if it proceeded by way of the compact cyclic transition state as shown in Scheme 32. For the peroxides studied, the rate of reaction did increase with increasing pressure (89).

To summarize, while a radical mechanism may still be postulated by some to explain the thermal rearrangement of a particular bis(silyl)-peroxide, the generally accepted mechanism is the concerted, intramolecular one.

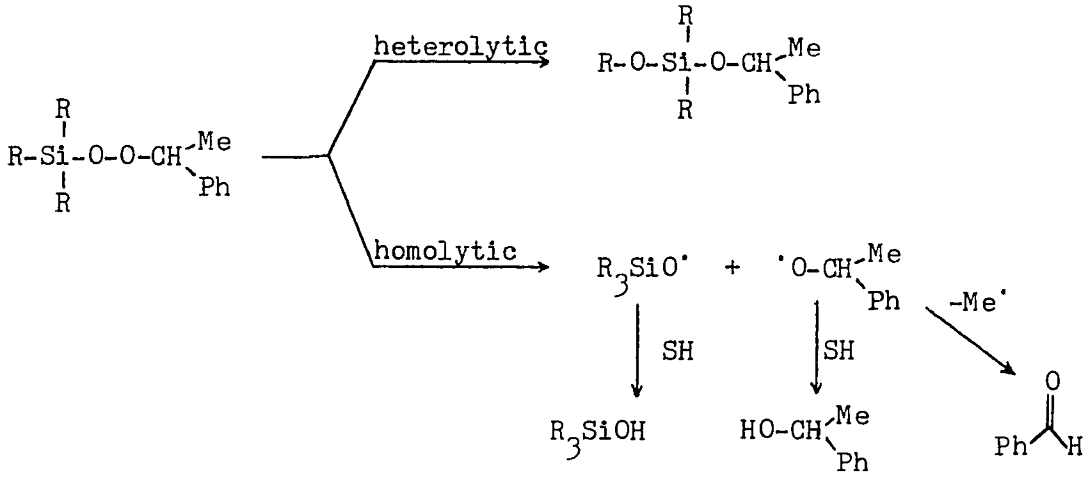
Much of the thermal work with silyl peroxides has been done by the Russian group of Yablokov and coworkers. Some of the more recent work will be reviewed here. This work can be divided into three segments: monosilyl peroxides, silylgermyl peroxides, and bis(silyl)peroxides.

Some of the first monosilyl peroxides studied were the triphenylsilyl and trimethylsilyl peroxides. These were found to react thermally by first order kinetics (90, 91). The rate of reaction depended in part upon the alkyl groups around the central carbon. For the series $Ph_3Si\text{-}O\text{-}O\text{-}CPh_n(Me)_{3-n}$, the relative rates were 1:8:20 for n = 1-3. The rate of reaction also depends on the nature of the alkyl groups around the silicon atom (92). For the series $R_3SiOOCH(Me)(Ph)$, the rates increase in the order $R = Me < Et < Pr$.

The nature of the alkyl groups around silicon also determines the course of the reaction. If these alkyl groups are very poor migrators, such as methyl, then the reaction proceeds entirely via homolytic cleavage of the O-O bond (93). Whether the thermal reaction occurs by homolytic cleavage or concerted rearrangement does not depend upon the nature of the alkyl groups around the central carbon atom.

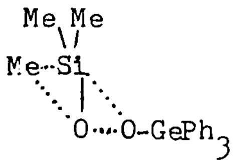
If the alkyl groups around silicon are better migrators than Me, such as Et, Pr, or Ph, then the intramolecular rearrangement process will compete with the homolytic cleavage process (94, 95). An example of such a competition is given in Scheme 33. By analyzing the reaction mixtures for a variety of R groups, it was concluded that the rates of

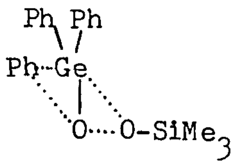
Scheme 33



homolytic decomposition are only weakly dependent upon R, while the rates of intramolecular rearrangements are strongly dependent upon R (96). No monosilyl peroxide has yet been found which reacts exclusively via intramolecular rearrangement, or which reacts by migration of an alkyl group from carbon to oxygen.

Much less work has been done with silylgermyl peroxides than with silyl peroxides. What few reports there are indicate a major difference between the thermal chemistry of silylgermyl peroxides and silyl peroxides. The thermal reaction of a silylgermyl peroxide proceeds only by the concerted rearrangement pathway, with no competing homolytic cleavage (97, 98). In addition, the rearrangement always proceeds by migration of an alkyl group from silicon to oxygen, never from germanium to oxygen. This is true even if silicon has very poor migrating groups attached and germanium has very good migrating groups attached. The explanation given for this is that the d-orbitals of silicon are of a much better size and shape to overlap with the p-orbitals on oxygen than are the d-orbitals of germanium. This makes transition state 93 much more favorable than 94 in the reaction of $Me_3SiO-OGePh_3$.


93


94

For the series of peroxides $R_3SiOOGePh_3$, the relative migratory aptitudes were measured (98) and are listed in Table 4. (k_R/k_{Me}) represents the migratory aptitude of R versus Me.

Table 4. Relative migratory aptitudes

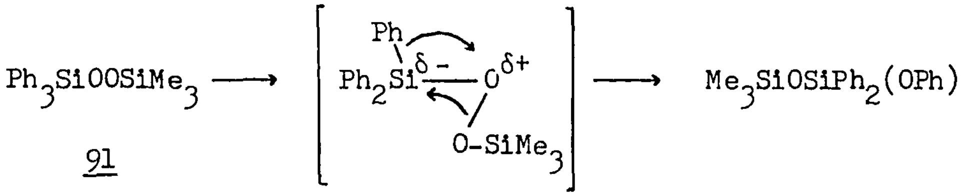
R	(k_R/k_{Me})
Me	1
Et	9
n-Pr	11
n-Bu	16
n-Pentyl	16
Ph	112

Many bis(silyl)peroxides have been made and studied. Thermally, they rearrange quantitatively by way of the concerted intramolecular pathway. The factors which contribute to these rearrangements are many and varied. Some factors oppose others so that in many cases, it is impossible to predict the relative reactivities of bis(silyl)peroxides.

In 1973, Yablokov and coworkers listed the following three factors leading to rearrangement (99):

1. the deficit of electron density on the oxygen atoms;
2. the nucleophilicity of the migrating group; and
3. the ability of peroxides to form a cyclic complex in the activated state.

The cause of the deficit of electron density on the oxygen atoms is attributed to dπ-pπ interaction between silicon and oxygen. This is the same argument which was mentioned earlier to explain the unusual strength of the silicon-oxygen single bond. As a result of this back-bonding, there is a deficit of electron density on the oxygen atoms. Any group on silicon which decreases this deficit should stabilize the peroxide. We would then correctly predict that for triphenylsilyltrimethylsilyl peroxide (<u>91</u>), the phenyl would migrate in preference over the methyl group since the oxygen adjacent to the triphenylsilyl group has the greater electron deficiency. We would also predict that



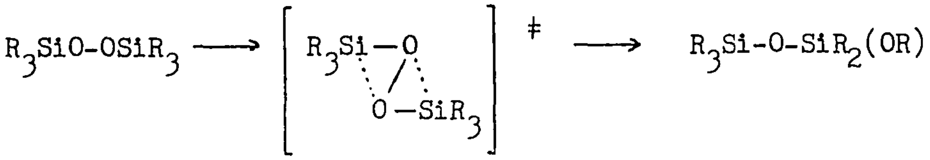
<u>91</u>

$$Ph_3SiOOSiMe_3 \longrightarrow \left[Ph_2Si^{\delta -}(Ph)\cdots O^{\delta +}\text{-}O\text{-}SiMe_3 \right] \longrightarrow Me_3SiOSiPh_2(OPh)$$

successively replacing methyl groups around silicon with phenyl groups would increase the reactivity of the peroxide. This was found to be the case for $Ph_3SiOOSiMe_n(Ph)_{3-n}$ (99, 100).

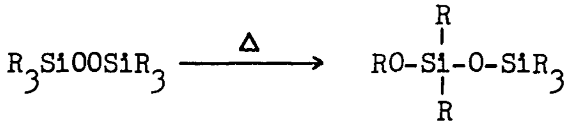
By the same argument, however, it would be predicted that a bis(silyl)peroxide having a p-tolyl group should be less reactive than the same peroxide with only a phenyl group since the tolyl group would decrease the electron deficit on oxygen more than the phenyl group would. Yablokov and coworkers found that just the opposite was true (101). They attributed this result to the greater nucleophilicity of the tolyl group as compared with the phenyl group.

The third factor leading to rearrangement is the ability of peroxides to form a cyclic complex in the activated state. This cyclic complex involves interaction between the p electrons on oxygen with the non-adjacent silicon atom. To form such a complex requires that the central atoms in the peroxide have d-orbitals of the proper size and shape to effectively overlap with the p-orbitals on oxygen. Silicon is better suited for this type of interaction than is germanium; thus silyl peroxides undergo this rearrangement reaction better than germyl peroxides (102).



The three factors leading to rearrangement do not explain the observed trend in reactivity of $R_3SiOOSiR_3$ as shown in Table 5 (103, 104). In going from Me to n-Bu, the nucleophilicity does not change significantly while the inductive effect does increase somewhat. It is expected that with R=n-Bu, the electron deficiency on oxygen should be decreased more than with R=Me. This should result in greater stability of the peroxides as we go from Me to Bu. Instead, just the opposite is

Table 5. Reactivity of $R_3SiOOSiR_3$

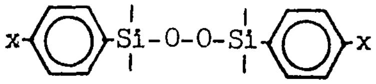


$$R_3SiOOSiR_3 \xrightarrow{\Delta} RO\text{-}\overset{R}{\underset{R}{Si}}\text{-}O\text{-}SiR_3$$

	R	$k \cdot 10^5 (sec^{-1})$
96	Me	13.4
97	Et	19.0
98	*n*-Pr	19.2
99	*n*-Bu	23.2

observed. This is explained by Yablokov and coworkers by the addition of a fourth factor leading to rearrangement (104, 105). This fourth factor is a σ, σ conjugative effect. Such an effect acts in the same direction as the induction effect; they both decrease the electron deficiency on oxygen and thus both are stabilizing effects. However, while the inductive effect is the greatest for *n*-Bu and the least for Me, the conjugative effect is the greatest for Me. Thus, the combination of these two effects accounts for the trend shown in Table 5.

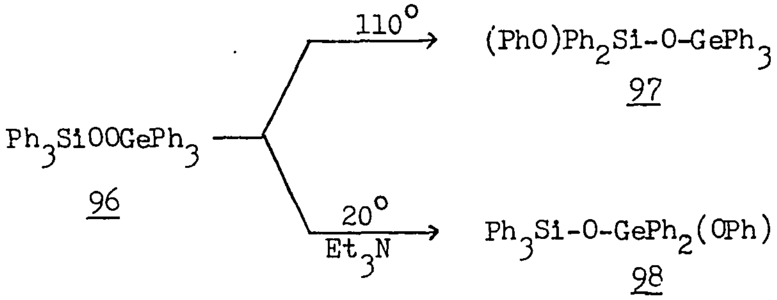
The fact that there are four separate factors used to explain the trends observed in these rearrangement reactions simply reflects the complexity of the influence of the substituents. This complexity is further seen in the inability to corrolate the rate of rearrangement of aryl substituted bis(silyl)peroxides with Hammett or Taft σ constants (105-107). The peroxides studied are shown below.



x = H, Me, OMe, Br

More recently, attempts have been made to understand the rearrangement of peroxides in the presence of catalytic amounts of nucleophiles. The added nucleophiles not only increase the rate of reaction, but in some cases, they result in the formation of different products. The case of triphenylsilyltriphenylgermyl peroxide (<u>96</u>) is shown in Scheme 34 (108, 109). When peroxide <u>96</u> was heated at 110° in an inert solvent,

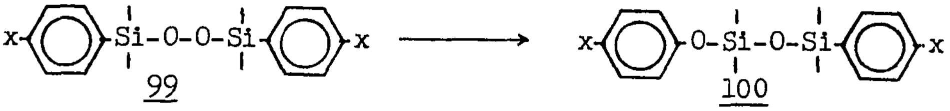
Scheme 34



migration of a phenyl group occurred exclusively from silicon to oxygen to form <u>97</u>. When a catalytic amount of a nucleophile was added, the reaction proceeded at 20° and the migration occurred from germanium to oxygen to form <u>98</u>. The nucleophiles which were used included CN^-, F^-, R_3Sn^-, and Et_3N. The authors proposed that this reaction involved coordination between the nucleophile and the germanium atom. Germanium is known to be more electrophilic than silicon (110, 111). This coordination then weakens the germanium-phenyl bond and promotes the concerted bond redistribution.

Further kinetic work was carried out on the symmetrically substituted bis(silyl)peroxides 99 as shown in Scheme 35 (112). With no

Scheme 35



x = H, Me, Cl, OMe

rate without catalyst: $Cl < H < Me < MeO$

rate with catalyst: $MeO < Me < H < Cl$

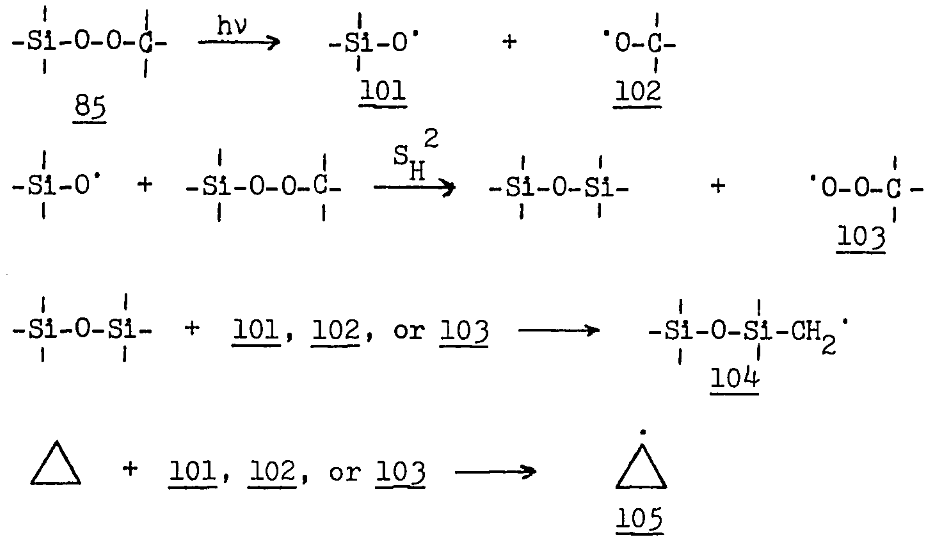
nucleophilic catalyst present, peroxides 99 react from 80-120° to form the rearranged isomer 100. The rate of this rearrangement increases in the order of $Cl < H < Me < MeO$. When a nucleophilic catalyst (Et_3N, F^-, or CN^-) is added, the temperature necessary for the same rates drops by about 60° and the order of the rates reverses to $MeO < Me < H < Cl$. This reversal of rates was proposed by the authors to be a result of a change in mechanism where the rate limiting step is now an S_H^2 attack by the nucleophile on the silicon atom. Such an attack would become more favorable as the substituents around silicon become more electron withdrawing.

Other ways to probe the mechanism and kinetics of these thermal rearrangements have included solvent studies (113-115) and following the reactions by IR (116-119).

Recently, there has been much work on the synthesis and thermal decomposition of molecules containing more than one silyl peroxy group (120-127). For the most part, the chemistry of these species very closely resembles the chemistry of the peroxy compounds that have already been discussed.

While the thermal reactions of silyl peroxides and bis(silyl)peroxides have been studied extensively, the photochemical reactions have not been investigated very thoroughly. In 1973, Edge and Kochi reported the first ESR study of a silyl peroxide (128). They photolyzed trimethylsilyl-t-butyl peroxide (85) in cyclopropane at temperatures from -50° to -150° C. Initially, there appeared in the ESR spectrum an intense singlet whose parameters agreed with those reported for the t-butylperoxy radical in solution (129, 130). Upon continued photolysis, this strong singlet disappeared and was replaced by the spectra of the cyclopropyl radical and the trimethylsiloxydimethylsilylmethyl radical 104. There was no evidence for the formation of trimethylsilyl radicals. The ESR spectrum of the trimethylsiloxy radical, like that of the t-butoxy radical, should be unobservable in solution owing to the orbitally degenerate ground state (131). From all these observations, the authors proposed the processes shown in Scheme 36. Photolysis results in initial homolytic cleavage of the peroxide linkage and formation of radicals 101 and 102, neither of which can be observed by ESR. The trimethylsiloxy radical then attacks the starting peroxide in an S_H2 fashion to form hexamethyldisiloxane and t-butylperoxy radical which is observed by ESR. Observed radicals 104 and 105 are then formed by hydrogen abstraction from hexamethyldisiloxane and cyclopropane. The key step in this scheme

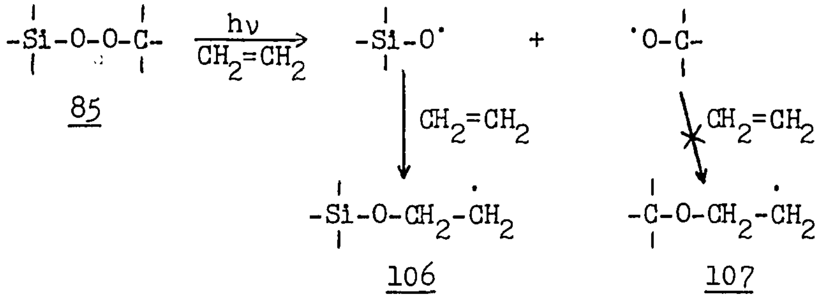
Scheme 36



is the homolytic displacement on silicon. There are few examples of such displacements on silicon, although S_H2 reactions at other nuclei are known (132, 133). Edge and Kochi have no evidence that the t-butoxy radical can also attack the starting peroxide in a S_H2 fashion. Earlier, Hiatt had also demonstrated that peroxide 85 was not attacked by t-butoxy radicals (77).

Edge and Kochi also employed radical-trapping studies in order to further substantiate their proposed mechanism (128). They trapped radicals by running the photolytic reactions in solutions containing the olefins ethylene, propene, isobutylene, and butadiene. The reaction with ethylene is shown in Scheme 37. During the photolysis, an intense ESR spectrum formed. This spectrum, which consisted of a triplet of triplets, was assigned to radical 106. The spectrum was not associated with the similar radical 107 since photolysis of di-t-butyl peroxide

Scheme 37

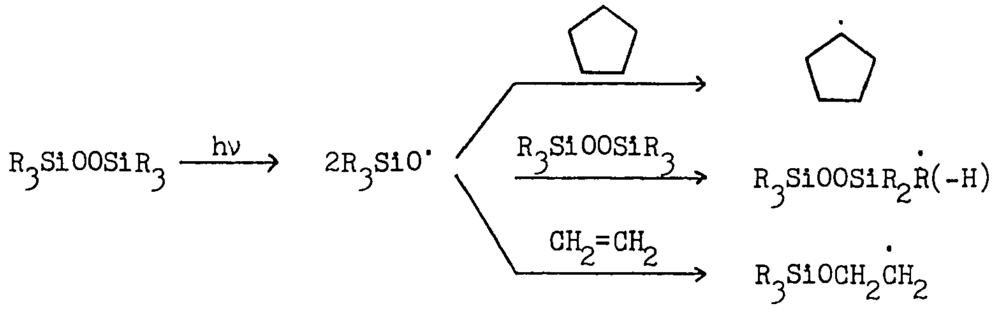


under the same conditions gave no ESR spectrum. Gara and Roberts have also noted this difference in reactivity between t-butoxy and trimethylsiloxy radicals (134). The results of the photolyses with other olefins were all similar. All results were consistent with initial homolytic cleavage of the peroxide linkage followed by S_H2 attack by trimethylsiloxy radical 101 on starting peroxide 85. There was no evidence for the formation of trimethylsilyl radicals.

A report by Cookson and coworkers in 1976 gave quite different results (135). They, too, photolyzed t-butyl trimethylsilyl peroxide (85) and observed the formation of the t-butyl peroxy radical by ESR. The formation of this radical, however, was attributed to the presence of minor amounts of oxygen or t-butyl hydroperoxide. When these two contaminants were scrupulously removed, the ESR signal for t-butylperoxy radical was no longer observed. This result casts considerable doubt on the S_H2 mechanism proposed by Edge and Kochi.

Cookson and coworkers also studied the photolysis of bis(silyl)-peroxides. Some of their results are shown in Scheme 38. When photolyses were carried out in cyclopentane, two radical products were

Scheme 38



observed: the radical formed by hydrogen abstraction from the starting peroxide, and cyclopentyl radical. If an olefin were present, the radical from addition of the trialkylsiloxy radical to the olefin was observed.

When the bis(silyl)peroxide contained alkyl groups other than Me (R = Et, Pr), ESR indicated the formation of the appropriate alkyl radical $R^{\cdot}$. One possible origin of $R^{\cdot}$ is from β-scission of the initially formed trialkylsilyl peroxide (Scheme 39). This is a well-known process

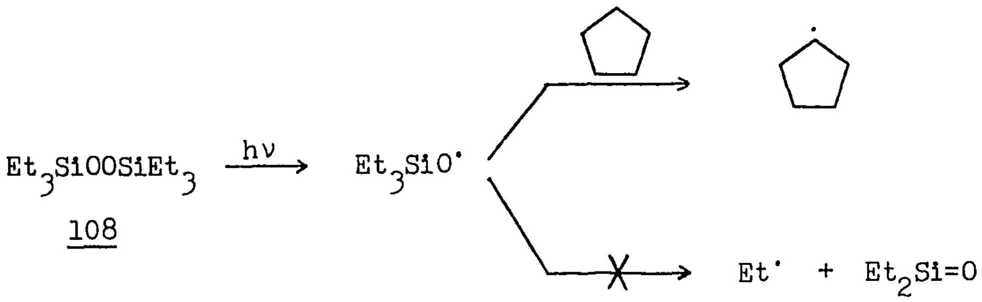
Scheme 39

$$R_3CO^{\cdot} \longrightarrow R^{\cdot} + R_2C{=}O$$

$$R_3SiO^{\cdot} \xrightarrow{?} R^{\cdot} + R_2Si{=}O$$

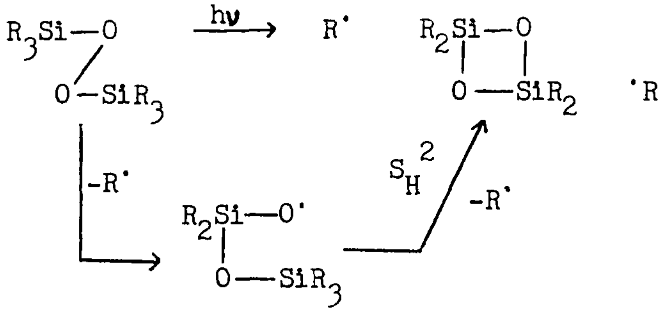
for the corresponding trialkylmethoxy radical (136). Such a process would appear to be unlikely since it involves breaking a strong silicon-carbon σ-bond to form a weak silicon-oxygen π-bond. This is also an unlikely explanation since the alkyl radicals $R^{\cdot}$ were only observed during the photolysis of bis(silyl)peroxides, not during the photolysis of silyl peroxides; yet it is known that photolysis of silyl peroxides also generates trialkylsiloxy radicals. As a further test, the authors photolyzed solutions of bis(triethylsilyl)peroxide (108) in solutions of cyclopropane containing varying amounts of cyclopentane. While the concentration of cyclopentane was varied by a factor of 12, the relative concentrations of R˙ and the cyclopentyl radical did not change. This clearly shows that the two observed radicals are not formed by competing unimolecular and bimolecular reactions of triethylsiloxy radical.

Scheme 40



One other possible origin of R˙ which was briefly mentioned by Cookson and coworkers (135) is depicted in the top of Scheme 41. They

Scheme 41



had no reason to postulate such a reaction in which an analog of D_2 is formed; but as will be shown later, there is now evidence that this overall process is correct. Most likely, a siloxy radical is involved as an intermediate, as shown on the bottom of Scheme 41.

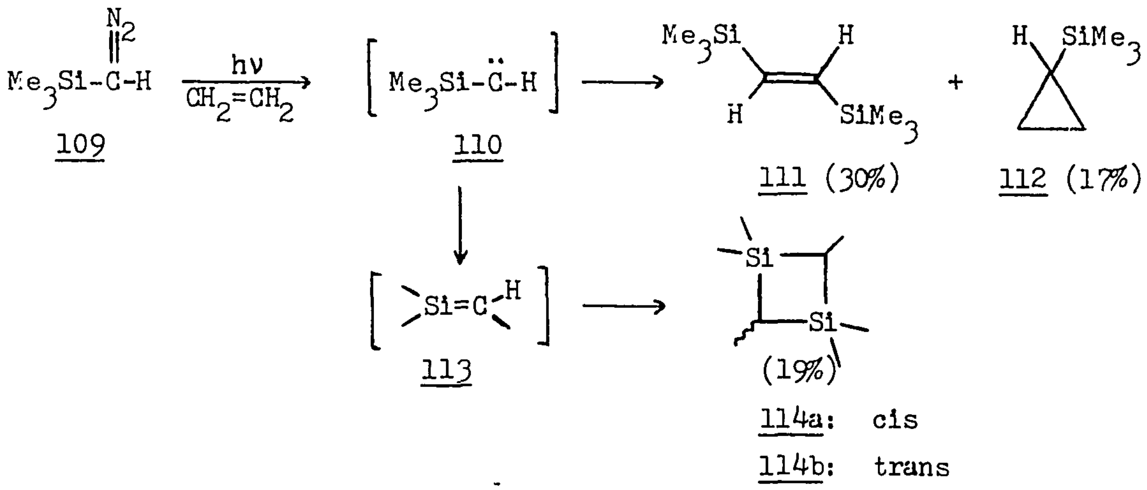
There are only two other reports of photolysis of silyl peroxides in the literature (137, 138). These are both by the Russian group of Aleksandrov and coworkers who photolyzed the peroxides in olefin solutions and observed the two competing reactions of the siloxy radicals, hydrogen abstraction to form silanols and addition to the olefins to form new radicals.

RESULTS AND DISCUSSION

α-Silylcarbenes

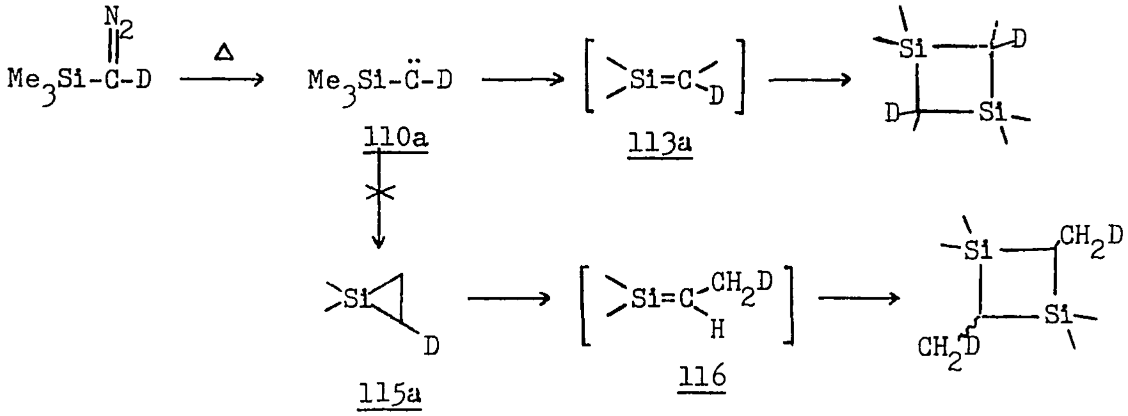
The study of α-silylcarbenes has been greatly enhanced by the recent utilization of α-silyldiazo compounds as precursors for these carbenes. One of the earliest reports was by Haszeldine and coworkers (139) who studied the photolysis of trimethylsilyldiazomethane (109) in alkene solutions. In the presence of excess ethylene, irradiation of 109 led to the formation of the carbene dimer 111 as well as the cyclopropane 112 (Scheme 42). Both of these products indicate that

Scheme 42



trimethylsilylcarbene (110) was formed. The most interesting product, however, was not identified by Haszeldine and coworkers, but was simply called "unidentified carbene dimer." Kreeger and Shechter (140) repeated this work and identified this product to be the two isomeric disilacyclobutanes 114a and 114b. These disilacyclobutanes are easily explained as coming from dimerization of 1,1,2-trimethylsilene (113). It is possible, however, to form 113 from 110 by two different pathways: one involving direct migration of a methyl group; and the other involving the formation of 1,1-dimethyl-1-silacyclopropane (115) which undergoes ring opening and hydrogen migration to form 113 (Scheme 43).

Scheme 43

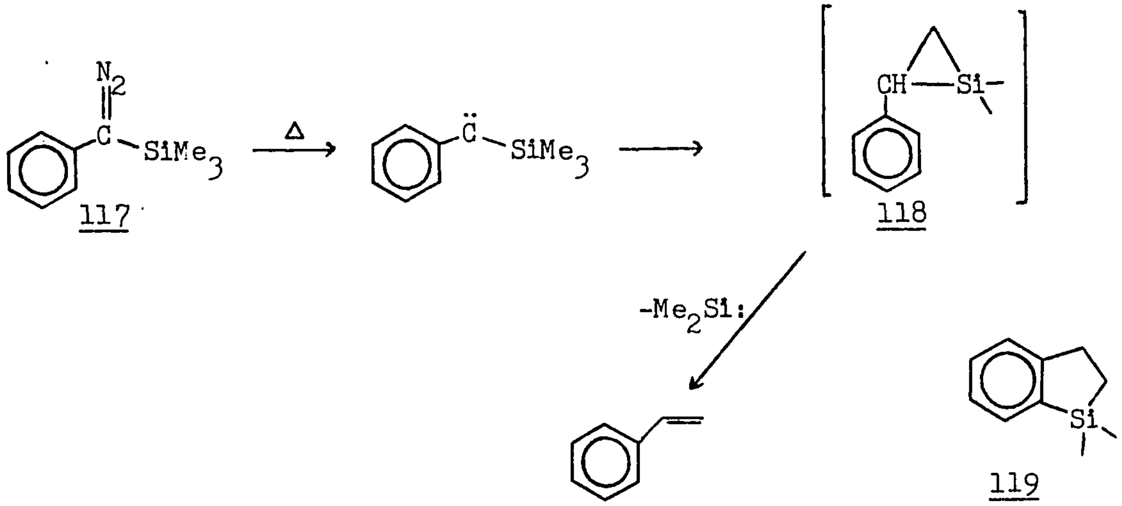


Compound 115 had earlier been proposed as an intermediate in reactions where carbene 110 was formed from α-elimination of chloromethyltrimethylsilane by alkali metals (141), and from the reaction between 1,1-dichloromethyltrimethylsilane and sodium-potassium vapor (142). Kreeger and Shechter (140) eliminated the silacyclopropane possibility by carrying out a labelling experiment. The deuterium-labelled diazo compound should lead to deuterosilacyclopropane 115a (Scheme 43). If 115a rearranges to form a silene, both 113a and 116 should be formed. Analysis of the disilacyclobutane products revealed no deuterated methyl groups, thus eliminating the silacyclopropane pathway.

A more careful study of the photolysis of trimethylsilyldiazomethane led Chedekel and coworkers (143) to postulate that a small amount of silacyclopropane 115 may be formed based on the 2% yield of ethylene observed.

The intermediacy of a silacyclopropane was proposed by Ando and coworkers (145, 146) to explain the formation of the major product from the pyrolysis of phenyltrimethylsilyldiazomethane 117. 1,1-dimethyl-1-silabenzocyclopentene (119) was postulated to arise via an intramolecular rearrangement of silacyclopropane intermediate 118. Later

Scheme 44

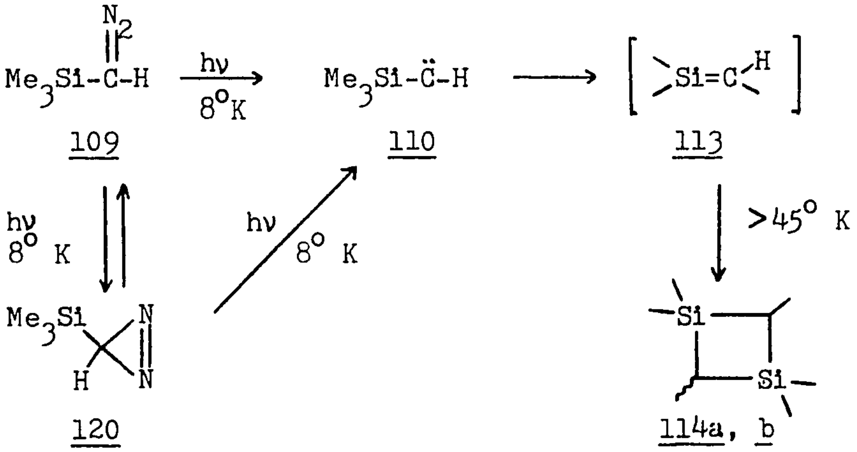


labelling studies clearly showed that 119 did not come from 118 (147). The silacyclopropane was still used, however, to explain the formation of the small yield (<5%) of styrene (148). Very similar reactions were observed when the carbene was formed via α-elimination of an alcohol (149).

The analogous germyldiazo compound has also been studied (150). In this case, styrene was formed in much higher yields (15%). The formation of styrene was attributed to the intermediacy of a germacyclopropane.

Low-temperature photolysis of trimethylsilyldiazomethane in an argon matrix has led to the only spectroscopically observed π-bonded organosilicon species (151). Irradiation of the matrix led initially to the formation of trimethylsilyldiazirene (120) (Scheme 45). Continued irradiation resulted in the disappearance of both 109 and 120 and the formation of silene 113. Warming the matrix to >45° K resulted in the disappearance of 113 and the formation of the cyclic silene dimers.

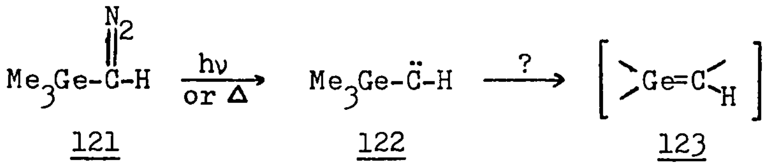
Scheme 45



Trimethylsilyl and Trimethylgermyldiazomethane

It was our initial goal to prepare trimethylgermyldiazomethane (121) and determine whether or not it would mimic its silicon analog and serve as a precursor for a germene (Scheme 46). A literature procedure for the preparation of trimethylsilyldiazomethane had been reported (152, 153), but it required four steps from commercially available

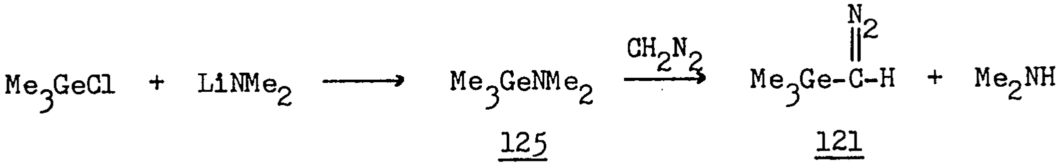
Scheme 46



trimethylchloromethylsilane (<u>124</u>) and had an overall yield of <20%. It was thought that this synthetic procedure could not be easily applied to the germanium analog due to the length of the synthesis (which would be increased to six steps due to the lack of available organogermanium compounds), the low yield, and the high expense of organogermanium compounds.

A literature procedure for the synthesis of trimethylgermyldiazomethane had been reported (154). This procedure involved reaction between dimethylaminotrimethylgermane (<u>125</u>) and diazomethane (Scheme 47). However, this method was not very successful in our hands, and we

Scheme 47

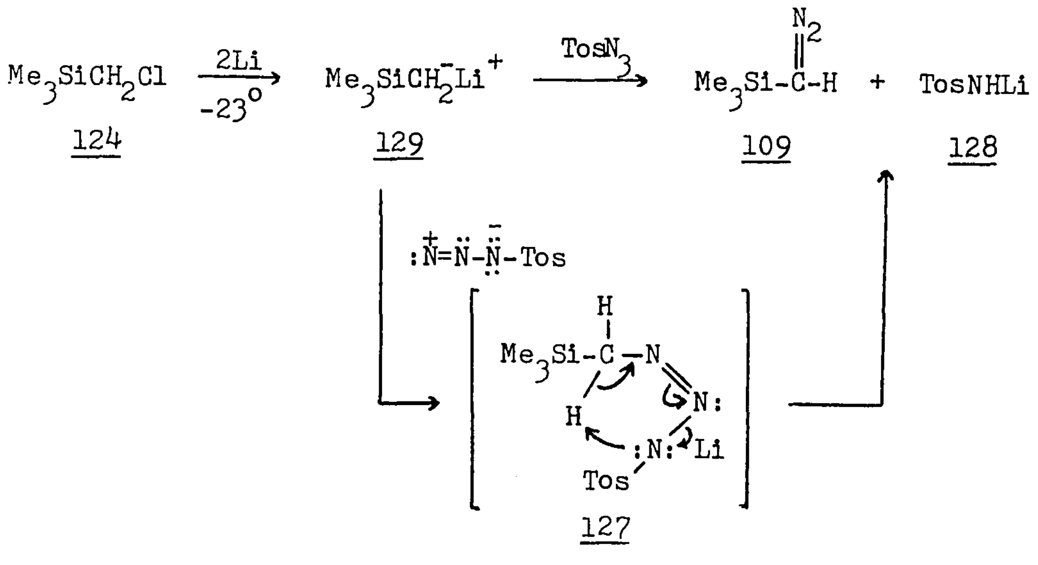


$$Me_3GeCl + LiNMe_2 \longrightarrow \underset{\underline{125}}{Me_3GeNMe_2} \xrightarrow{CH_2N_2} \underset{\underline{121}}{Me_3Ge\text{-}\overset{\overset{N_2}{\|}}{C}\text{-}H} + Me_2NH$$

were never able to isolate pure <u>121</u>. Unchanged germylamine <u>125</u> was always recovered along with hexamethyldigermoxane and some bis(trimethylgermyl)diazomethane (<u>126</u>). A modification of this procedure had been used to prepare bis(trimethylgermyl)diazomethane (155), but we were not able to successfully repeat that work either. In addition, these literature methods suffered from the necessity to use dangerous diazomethane.

What was needed was a short, high yield synthesis of α-silyl and α-germyldiazomethanes. The diazo transfer reaction had been used as a convenient one step synthesis of many diazo compounds, although it had never been used to form α-silyl or α-germyldiazo compounds. This reaction which was first used synthetically by Doering and DePuy (156) and has been reviewed by Regitz (157), consists of quenching carbanions with tosyl azide to form the corresponding diazo compound. This reaction was successfully used in the synthesis of trimethylsilyldiazomethane as shown in Scheme 48. Trimethylchloromethylsilane (124) was

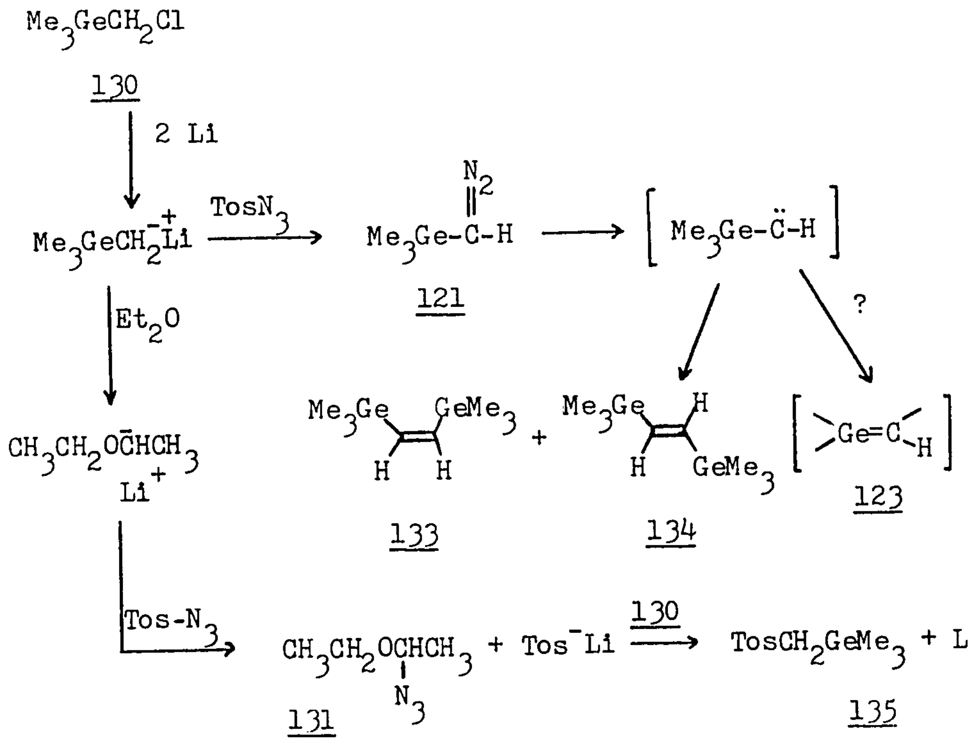
Scheme 48



treated with lithium dispersion in ether at -23° C to form anion 129 which was quenched with tosyl azide to form trimethylsilyldiazomethane in 38% yield as well as lithium tosylamide (128). This reaction most likely proceeds via intermediate 127.

The diazo transfer reaction was then applied to the analogous germanium system in an attempt to prepare trimethylgermyldiazomethane. While lithiation of chloromethyltrimethylgermane (130) (prepared by the method of Seyferth and Rochow (158)) proceeded readily in ether at -23° C, none of the diazo compound was isolated upon quenching the anion with tosyl azide. The major volatile products were 1-azidoethylethylether (131) along with smaller amounts of hexamethyldigermoxane (132) and cis- and trans-1,2-bis(trimethylgermyl)ethylene (133, 134). The major nonvolatile product was trimethylgermyltosylmethane (135). Scheme 49 shows a possible origin

Scheme 49



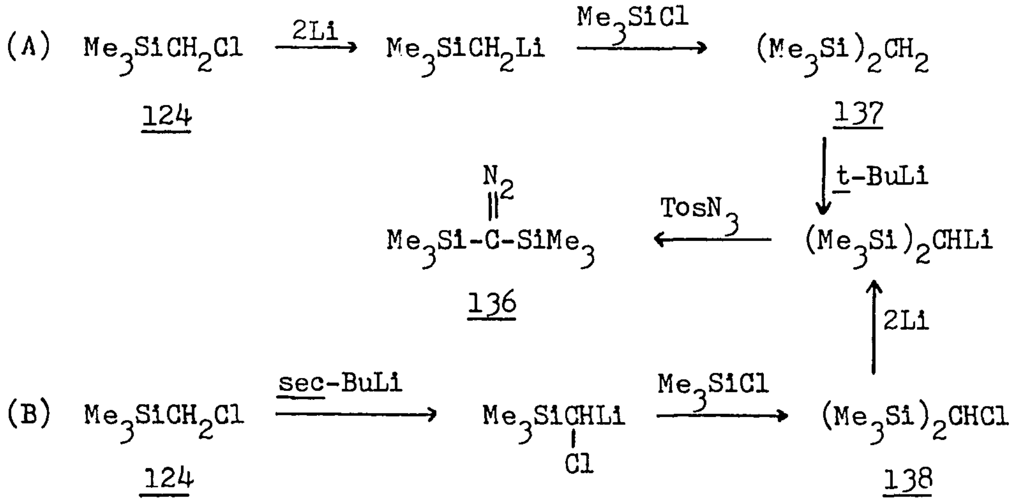
of all these products. While trimethylgermyldiazomethane was not isolated, the presence of 133 and 134 indicates that it may have been formed. Several other minor products were formed but were not identified; so it is not possible to say whether or not germene 123 was formed.

Bis(trimethylsilyl)diazomethane

Our inability to isolate trimethylgermyldiazomethane prompted us to consider bis(trimethylgermyl)diazomethane (126), which we thought would be easier to prepare and just as good a germene generator. We desired to ultimately prepare 126 via the diazo transfer reaction, but decided to first use this reaction to prepare bis(trimethylsilyl)diazomethane (136). A literature route to 136 was available (159), but gave low yields and was very tedious, requiring the synthesis of trimethylsilyldiazomethane as an intermediate.

Scheme 50 shows our synthesis of bis(trimethylsilyl)diazomethane

Scheme 50



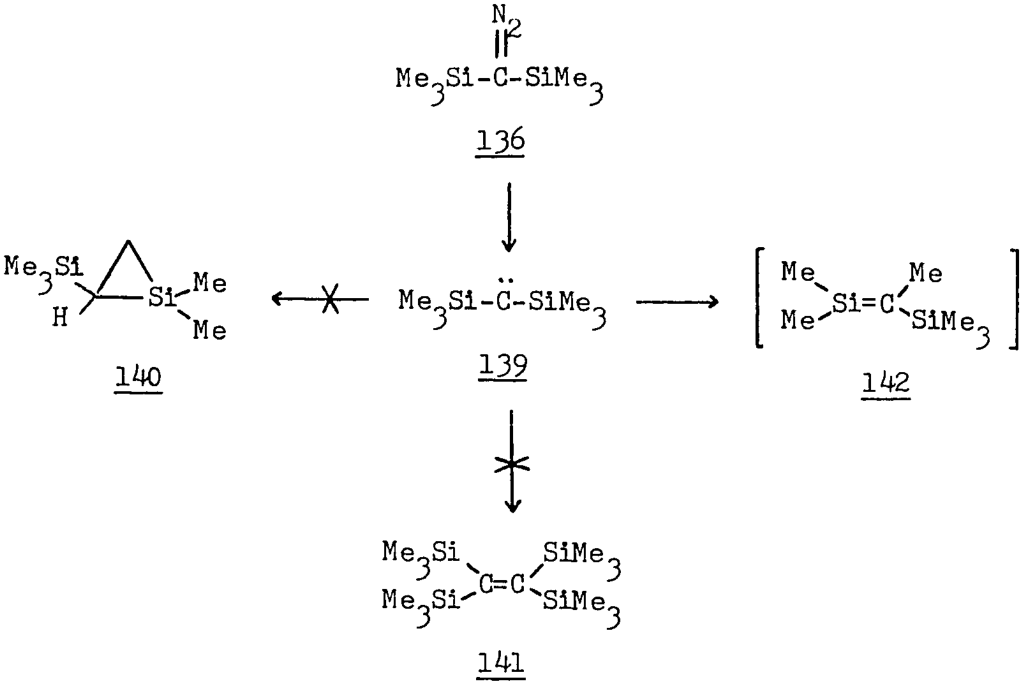
$$\begin{tikzcd}
\text{(A)}\ \underset{\underline{124}}{Me_3SiCH_2Cl} \arrow[r, "2Li"] & Me_3SiCH_2Li \arrow[r, "Me_3SiCl"] & \underset{\underline{137}}{(Me_3Si)_2CH_2} \arrow[d, "t\text{-}BuLi"] \\
& \underset{\underline{136}}{Me_3Si\text{-}\overset{\overset{N_2}{\|}}{C}\text{-}SiMe_3} & (Me_3Si)_2CHLi \arrow[l, "TosN_3"'] \\
\text{(B)}\ \underset{\underline{124}}{Me_3SiCH_2Cl} \arrow[r, "sec\text{-}BuLi"] & Me_3Si\underset{\underset{Cl}{|}}{C}HLi \arrow[r, "Me_3SiCl"] & \underset{\underline{138}}{(Me_3Si)_2CHCl} \arrow[u, "2Li"']
\end{tikzcd}$$

by two different routes, both of which have as the key step the diazo transfer reaction. Route A began by lithiation of readily available chloromethyltrimethylsilane (124) followed by quenching with trimethylchlorosilane to afford bis(trimethylsilyl)methane (137) in 75% yield. Metalation of 137 with t-butyllithium (THF/HMPA, -78 °, 2.5 hr.) followed by addition of tosyl azide produced upon workup a 57% yield of 136. A modification of this synthesis (route B) was carried out by sec-butyllithium induced deprotonation of chloromethyltrimethylsilane, quenching with trimethylchlorosilane to form bis(trimethylsilyl)chloromethane (138) in 70% yield, followed by sequential reaction with lithium and tosyl azide to yield 136 in 37% yield. Of these two methods, route A is far better, not only because of a higher overall yield, but also because bis(trimethylsilyl)methane (137) is now commerically available (160) so that diazo compound 136 can be prepared in a one-pot reaction beginning with an available starting material.

The carbene (139) produced from N_2 extrusion from 136 presents an interesting potential competition between C-H insertion to form a silacyclopropane, and methyl migration to generate a silene (Scheme 51). While on a statistical basis the former process should be favorable (there being 18 C-H bonds available for reaction), and while there is some rather suggestive evidence in the literature for such a process (148), in none of the reactions of 136 was any evidence seen for this insertion reaction. Also, as expected, tetrakis(trimethylsilyl)ethene (141), the formal product of carbene dimerization, has never been observed.

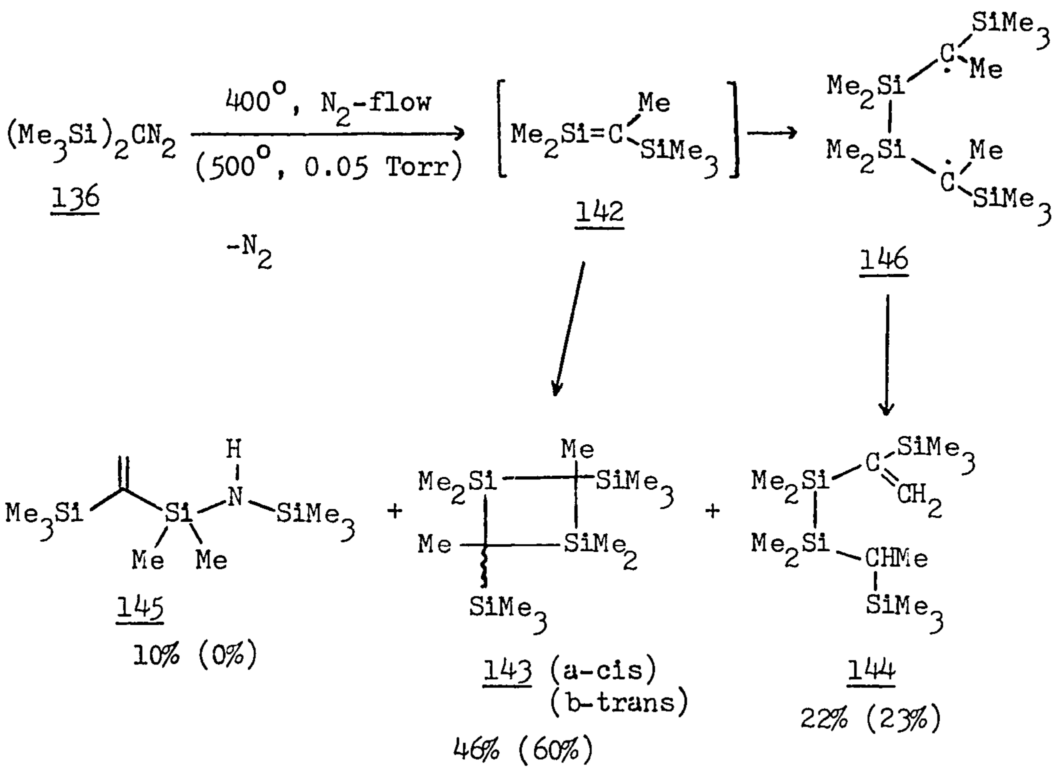
Nitrogen-flow pyrolysis of a 5% solution of 136 in benzene at 400°

Scheme 51



produced as the major products 1,3-disilacyclobutanes 143a and 143b in a combined yield of 46% (Scheme 52). Essentially, equal amounts of the cis and trans isomers were formed in this reaction. Also formed were disilane 144 (22%) and disilazane 145 (10%). The three major products (143a, 143b, and 144) are most economically rationalized as arising from methyl migration in bis(trimethylsilyl)carbene (139) to afford 142. Silene 142 would by precedent (3) be expected to dimerize in a head-to-tail fashion, which here produces 143. However, there are two cases in literature (161-163) where sterically hindered silenes dimerized in a head-to-head manner. Thus, it is not surprising that 142 also dimerizes head-to-head to form diradical 146 which intramolecularly abstracts a hydrogen to form product 144. The formation of disilazane 145 was quite

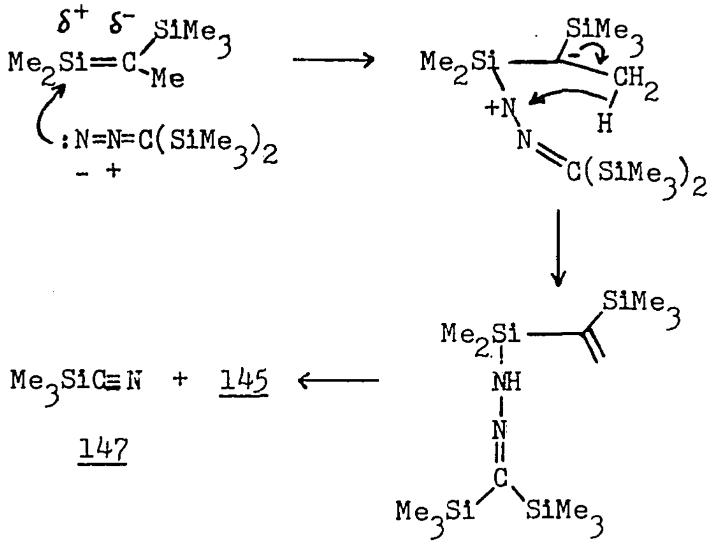
Scheme 52



surprising and is without precedent. A possible route to 145 which we suggest (Scheme 53) involves reaction of 142 and 136. While the details of this mechanism are purely speculative, the general scheme is supported by two observations: first, trimethylsilylnitrile (147) was formed in this pyrolysis; and second, the considerably higher dilution conditions of a vacuum pyrolysis (500°, 0.05 Torr) of 136 produced only 143 (60%) and 144 (23%) with no detectable amounts of 145.

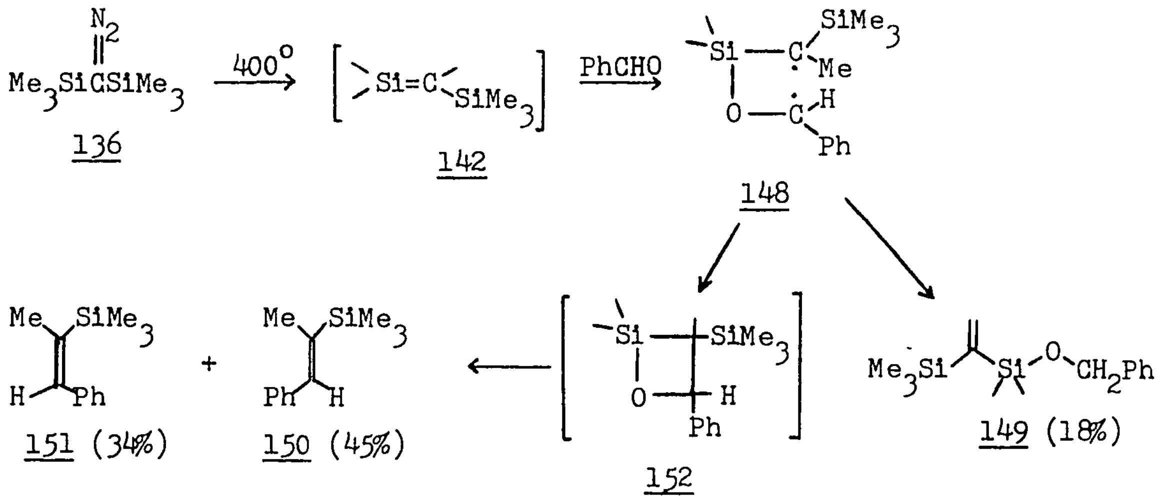
Intermediacy of silene 142 in the thermolysis of 136 was further established through a variety of trapping reactions. Copyrolysis of a 5% solution of 136 in benzaldehyde (400° C, N_2-flow) dramatically affords only three products in a total yield of 97% with a 98% mass

Scheme 53



balance (Scheme 54). Each of these three products clearly arises from the intermediacy of silene 142. Addition of 142 to the carbonyl group

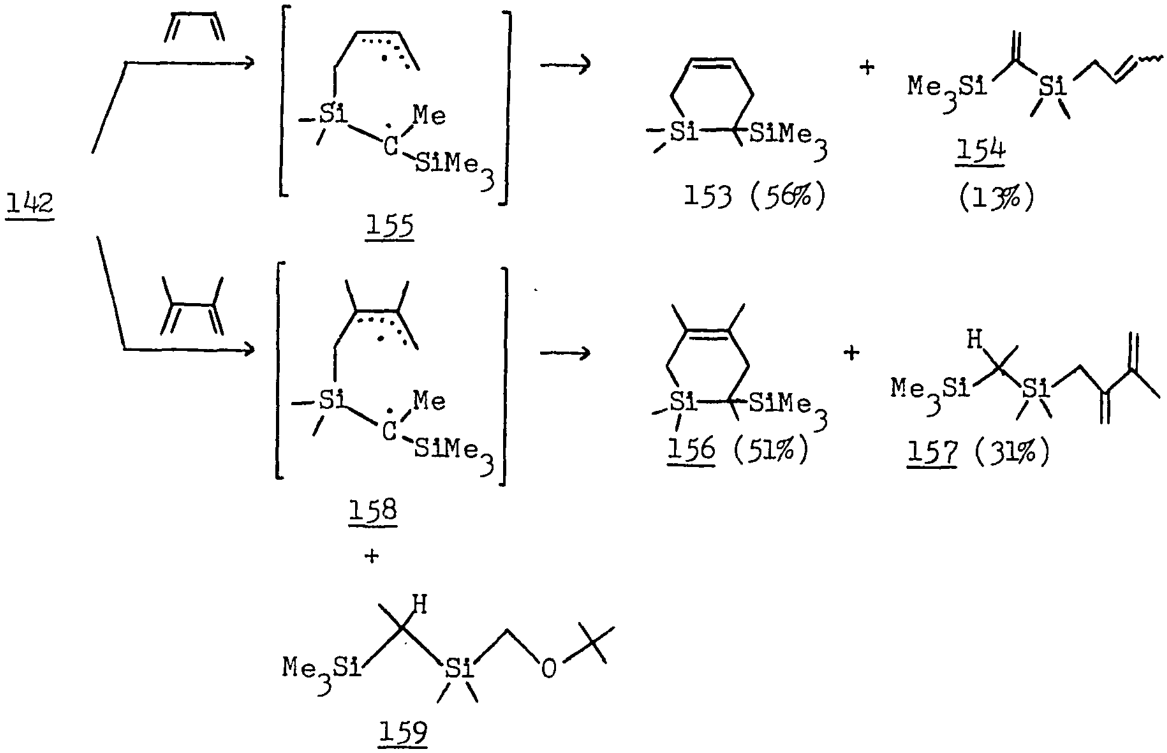
Scheme 54



initially produces diradical 148 which can intramolecularly abstract a hydrogen atom to form the benzyl ether 149, or can close to form silaoxetane 152. The silaoxetane either extrudes or transfers dimethylsilanone to yield olefins 150 and 151.

Flow pyrolysis of 136 at 400° C with 1,3-butadiene as the carrier gas produced the expected, formal Diels-Alder adduct 153 in 56% yield. In addition, a linear adduct, 154, was formed in 13% yield. Both of these products can be rationalized as arising from silene addition to butadiene to produce diradical 155 which either closes to 153 or undergoes hydrogen migration to give 154 (Scheme 55).

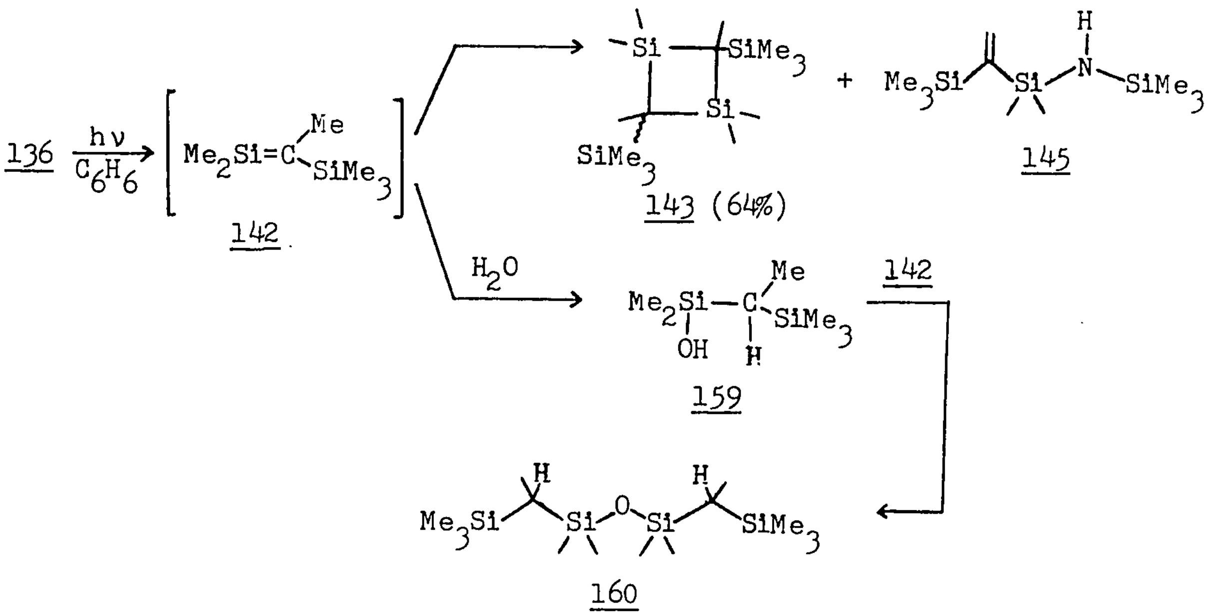
Scheme 55



Similar results were obtained from a flow copyrolysis of 136 and 2,3-dimethyl-1,3-butadiene. This reaction afforded the cyclic adduct 156 in 51% yield and the linear adduct 157 in 31% yield. Both of these products can be rationalized as arising from silene addition to the diene to produce diradical 158 (Scheme 55). In addition to 156 and 157, 159 was formed in variable amounts. While the origin of 159 was never definitely established, we presume it arises from reaction of silene 142 and some unidentified impurity in the commercial diene. Careful fractional distillation and drying of the diene did not eliminate the formation of 159; however, use of a different commercial sample of diene resulted in a significant reduction in the yield of 159 and photolysis of 136 (5% in C_6H_6) in the presence of a 3-fold excess of 2,3-dimethyl-1,3-butadiene resulted in the exclusive formation of 156 and 157, and no 159.

Photolysis of 136 in benzene (2537Å) resulted in rather rapid (<3 hrs.) and complete disappearance of 136 and the formation of equal amounts of 1,3-disilacyclobutanes 143a and 143b in combined yield of 64%, and disilazane 145 in 23% yield (Scheme 56). Trace amounts of disiloxane 160 were sometimes observed. Product 160 arises from either condensation of silanol 159, or from trapping of silene 142 with 159. Obvious in its omission is 144, the head-to-head dimer of silene 142. In no photochemical generation of 142 was head-to-head dimerization observed. It is interesting to note the much higher yield of disilazane 145 in this photochemical reaction than in the thermal reaction of 136. This can be explained on the basis of concentration effects where photochemically the silene is formed in the presence of a high con-

Scheme 56



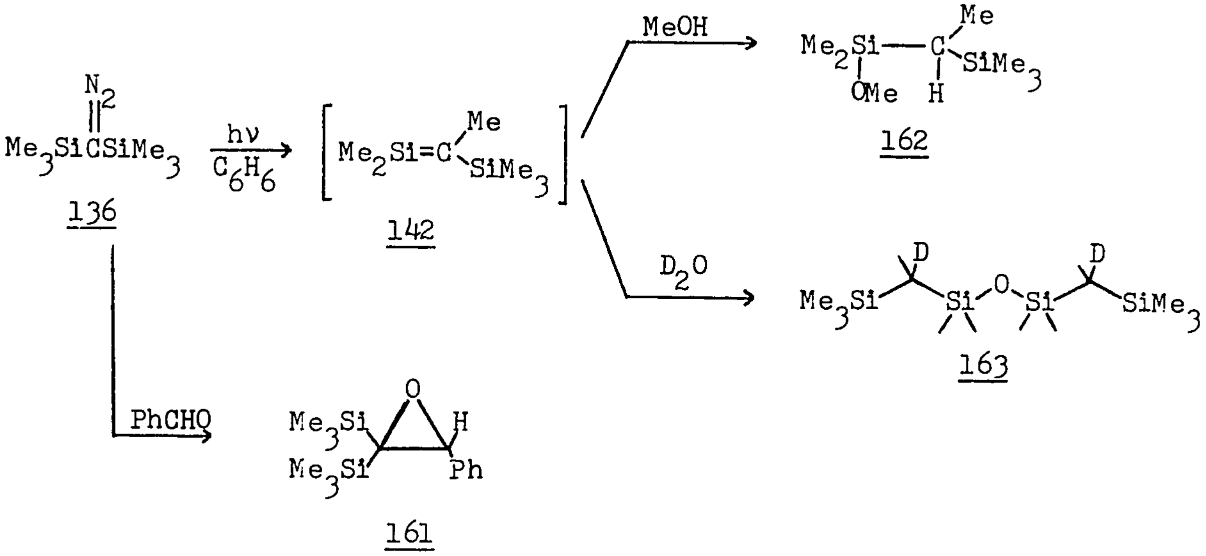
centration of starting diazo compound (see Scheme 53).

In an attempt to trap either bis(trimethylsilyl)carbene (139) or silene 142, solutions of 136 in benzene were photolyzed (2536Å) with the following olefins present in 3-6-fold excesses: cyclohexene, cyclopentene, tetramethylethylene, methylvinylether, and styrene. In all cases, the major products were the disilacyclobutanes 143 and the disilazane 145. In all cases, except the styrene case, the added olefin had no appreciable affect upon either the rate or the products of the reaction. When cyclopentene or cyclohexene was used as the solvent, the reaction proceeded at a much faster rate, but the major products were still 143 and 145. For the styrene case, the reaction proceeded very slowly (ca. 16 hrs. required for the complete disappearance of 136) and was complicated by the dimerization of styrene. No 1:1

adducts of styrene with carbene or silene were observed.

Photolysis of a benzene solution of 136 containing 1.1 equivalents of benzaldehyde resulted in the formation of several products. Only the major product, epoxide 161, was isolated and identified (Scheme 57).

Scheme 57

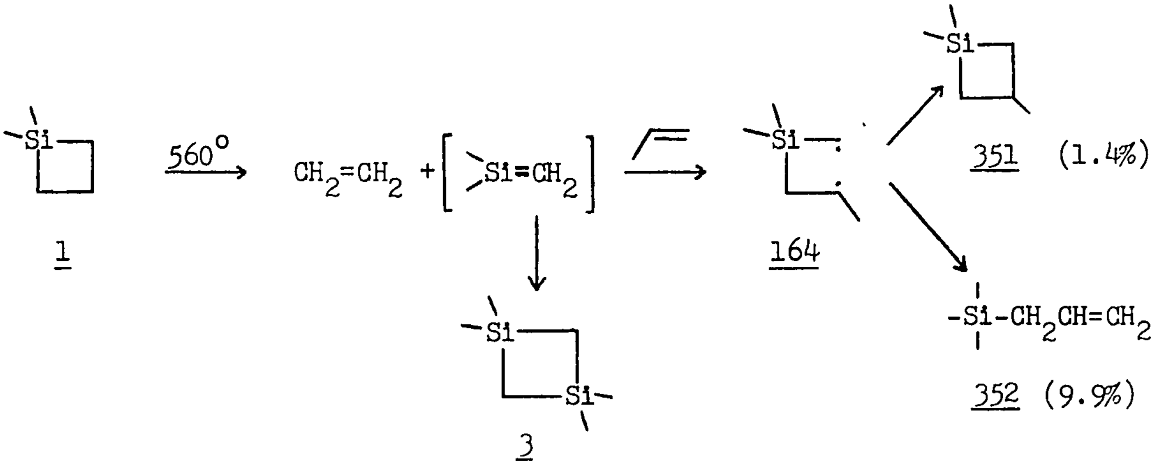


It was observed that as the amount of benzaldehyde was increased, the amount of 161 increased. Silene 142 was probably not formed at all in this photolysis since NMR analysis indicated no formation of a C-Me group.

Photolysis of 136 in benzene containing a 3-fold excess of methanol resulted in the quantitative formation of methoxysilane 162. Likewise, quantitative formation of disiloxane 163 was formed when D_2O was substituted for methanol. These results clearly demonstrate that 136 is a superb photochemical silene generator.

Since we had available the best silene generator known, we decided to investigate one additional trapping experiment, 2+2 cycloaddition with olefins. The trapping of a silene with an olefin has been reported for only one case (164, 165). Nametkin and coworkers pyrolyzed 1,1-dimethyl-1-silacyclobutane (1) in the presence of a 20-fold excess of propene and observed, in addition to ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (3), 1,1,3-trimethyl-1-silacyclobutane (351) and trimethylallylsilane (352). Products 351 and 352 were proposed to arise from trapping of 1,1-dimethylsilene with propene (Scheme 58) to

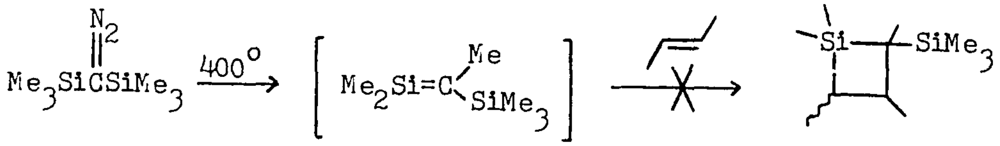
Scheme 58



initially form diradical 164 which can either close to form 351 or undergo hydrogen migration to form 352.

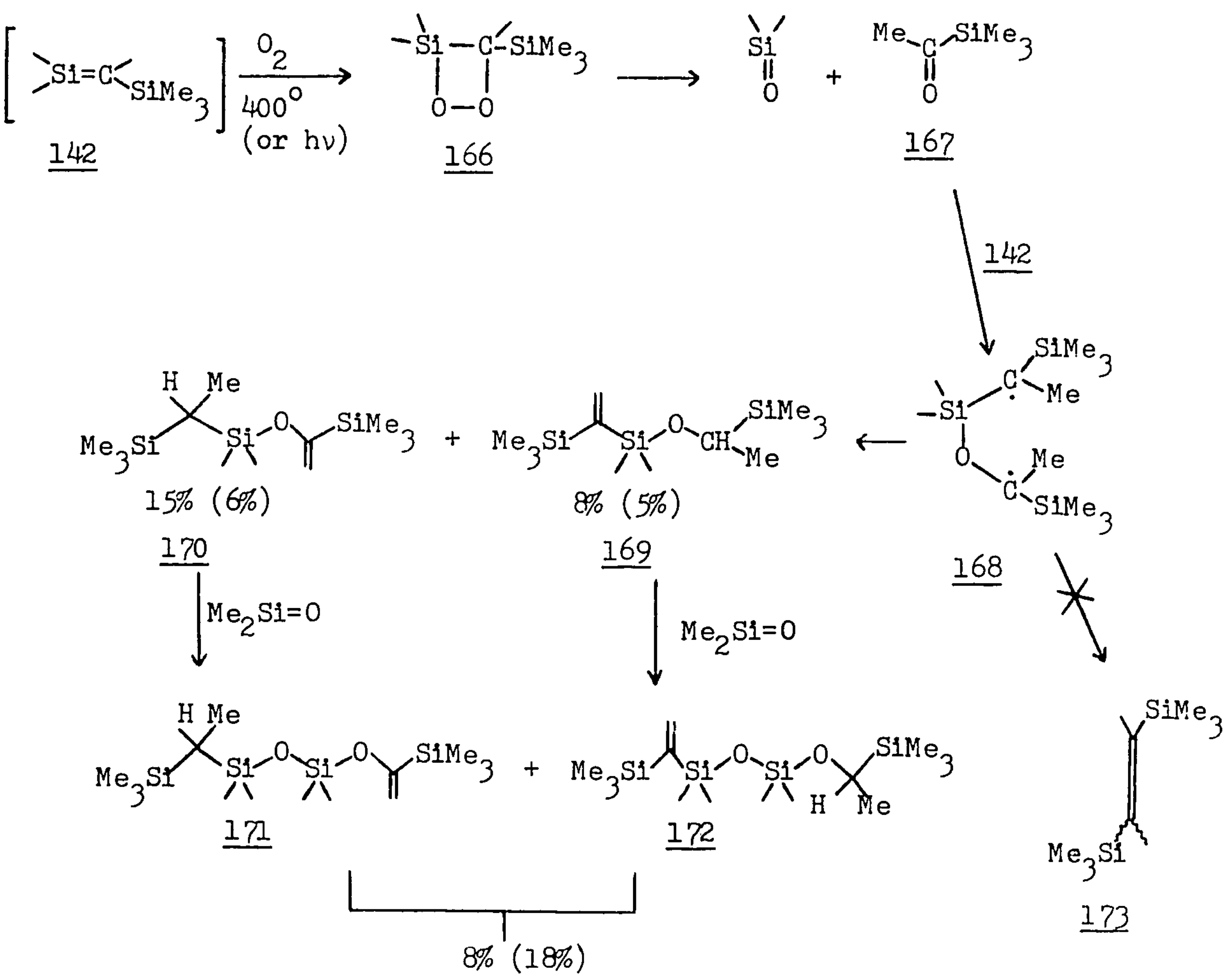
We hoped to not only increase the yield of the olefin-trapped products, but also to learn something of the stereochemistry of the reaction by pyrolyzing a benzene solution of bis(trimethylsilyl)diazomethane (136) in a flow system using cis- or trans-2-butene as the carrier gas. It was previously determined that under the reaction conditions (400° C, 30 mL/min of butene) *trans*-2-butene was stable, but that 20% of the *cis*-2-butene isomerized to the *trans* isomer. It was discovered, however, that in this pyrolysis, no 1:1 adducts of silene and olefin were formed. Instead, a host of products was formed (more than 30 products in all), including the usual silene dimers 143a, 143b, and 144 as well as disilazane 145. Upon closer scrutiny, it was observed that the major products of this reaction all contained oxygen. The origin of the oxygen was very puzzling until it was discovered that the commercial quantities of *cis*- and *trans*-2-butene contained a small amount of O_2 impurity. From the identification of the major products, we propose that O_2 traps silene 142 to form an unprecedented reactive intermediate, siladioxetane 166 (Scheme 60). A siladioxetane might be expected to cleave to yield two carbonyls as a normal dioxetane does (166, 167). Acetyltrimethylsilane (167) which would be formed by siladioxetane decomposition would be expected to trap silene 142 to form diradical 168. Diradical 168 can undergo two different intramolecular hydrogen abstraction reactions to form the major products 169 and 170. Insertion of dimethylsilanone into 169 and 170, perhaps involving a

Scheme 59



165

Scheme 60



transfer mechanism (see Historical section on silanones), leads to the next major products, 171 and 172. Based upon earlier work, it might be expected that diradical 168 would close to form a silaoxetane from which we would observe the olefins E, and Z-2,3-bis(trimethylsilyl)-2-butene (173). These olefins were not observed, perhaps because it is difficult for the bulky ends of the diradical 168 to approach each other.

Addition of O_2 to the reaction system was observed to increase the amount of products 169-172 formed, although many other products were still formed. The same products were formed whether silene 142 was formed thermally or photochemically, although the product ratio changed (see Table 6).

If this reaction scheme is correct, then formation of silene 142 in the presence of an excess of acetyltrimethylsilane (167)should produce a much cleaner product mixture being composed of only products 169 and 170. The data in Table 6 show that this indeed was the case.

Table 6. Trapping of silene 142 with O_2 and 167

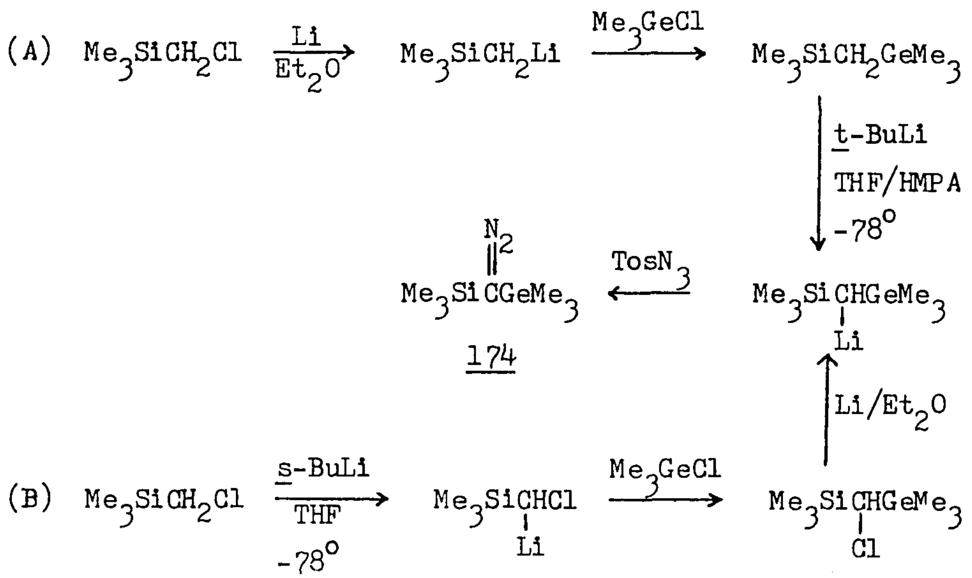
	169 + 170	169/170 ratio	171 + 172
$136 + O_2 \xrightarrow{400^{\circ}}$	23%	1/1.8	8%
$136 + O_2 \xrightarrow{h\nu}$	11%	1/7.0	18%
$136 + 167 \xrightarrow{400^{\circ}}$	84%	1/1.6	0%
$136 + 167 \xrightarrow{h\nu}$	99%	1/7.4	0%

(Acetyltrimethylsilane was found to be inert under the photolytic conditions used, but under the thermolytic conditions, 5-10% rearranged to a more volatile isomer which was probably vinyloxytrimethylsilane (168)). The evidence presented here is all in accord with the formation of the new reactive intermediate siladioxetane. We have sent samples of the precursor bis(trimethylsilyl)diazomethane (142) to other workers (169) in the hope that they will be able to photolyze it in an oxygen matrix and perhaps observe the siladioxetane spectroscopically. If the siladioxetane behaves as a normal dioxetane, chemiluminescence should also be observed.

Trimethylsilyltrimethylgermyldiazomethane

In order to set up a competition between silene and germene formation, we undertook the synthesis of trimethylsilyltrimethylgermyldiazomethane (<u>174</u>). This was accomplished by the two routes outlined in Scheme 61.

Scheme 61



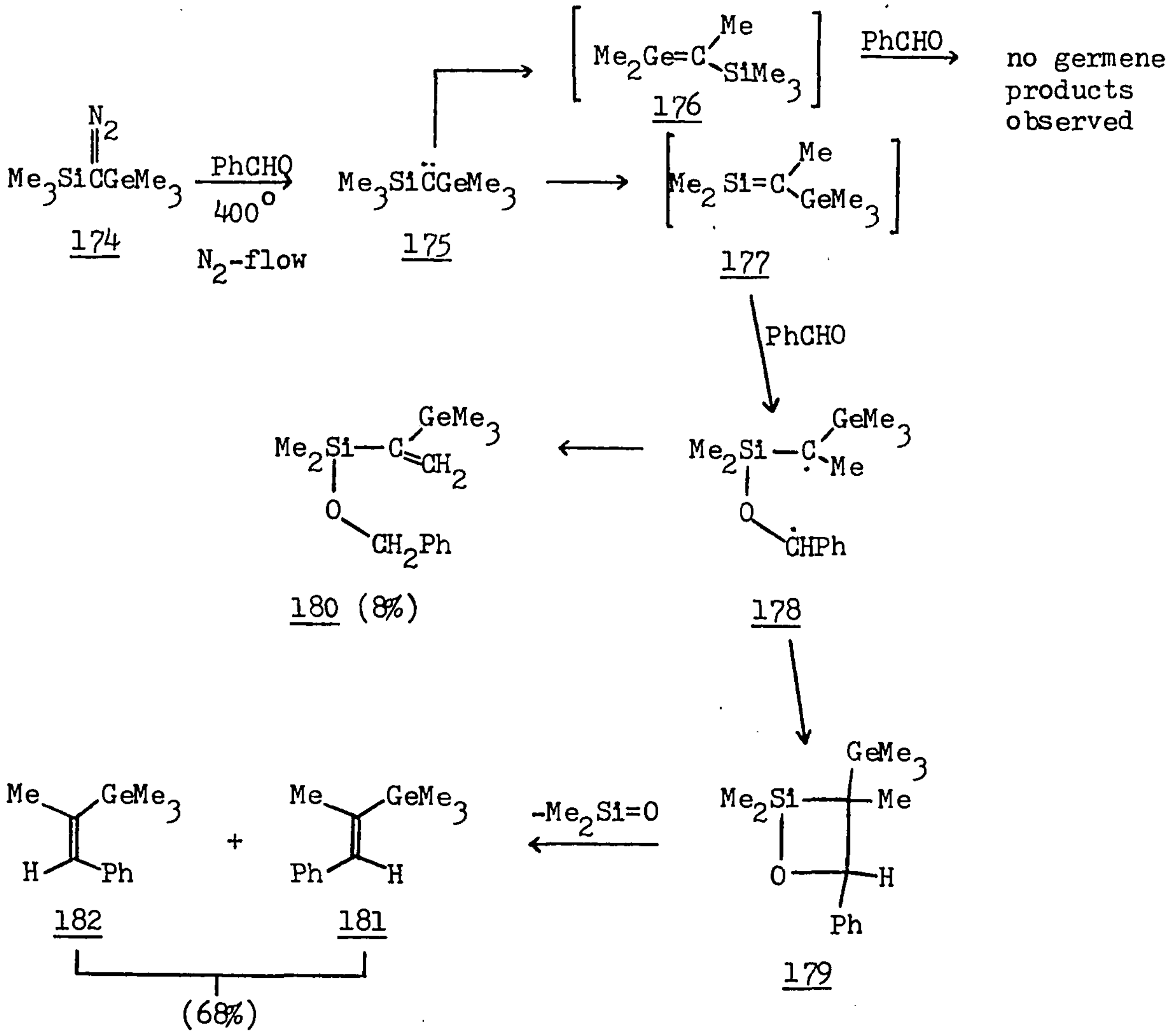
(A) $Me_3SiCH_2Cl \xrightarrow[Et_2O]{Li} Me_3SiCH_2Li \xrightarrow{Me_3GeCl} Me_3SiCH_2GeMe_3 \xrightarrow[\text{THF/HMPA},\ -78^{o}]{\underline{t}\text{-BuLi}} Me_3Si\underset{Li}{CH}GeMe_3 \xrightarrow{TosN_3} Me_3Si\overset{N_2}{\overset{\|}{C}}GeMe_3$ <u>174</u>

(B) $Me_3SiCH_2Cl \xrightarrow[\text{THF},\ -78^{o}]{\underline{s}\text{-BuLi}} Me_3Si\underset{Li}{CHCl} \xrightarrow{Me_3GeCl} Me_3Si\underset{Cl}{CH}GeMe_3 \xrightarrow{Li/Et_2O} Me_3Si\underset{Li}{CH}GeMe_3$

Again, both routes are initiated through metalation of chloromethyltrimethylsilane, and both terminate with a diazo-transfer from tosyl azide. The yield of <u>174</u> in Route A was 48% in the final step, with an overall yield of 35%. The yield of <u>174</u> from Route B was only <u>ca</u>. 10%. The bright green liquid <u>174</u> proved to be quite stable, and was purified by preparative GC.

The carbene <u>175</u> produced from N_2 extrusion from <u>174</u> could either undergo methyl migration from silicon to produce a silene, or from germanium to afford a germene. In order to determine the preferred rearrangement, a copyrolysis of 174 and benzaldehyde was conducted at 400° C in a nitrogen-flow system (Scheme 62). The only products observed were approximately equal amounts of E- and Z-olefins 181 and 182 (combined yield of 68%) and silyl ether 180 (8%). These three products,

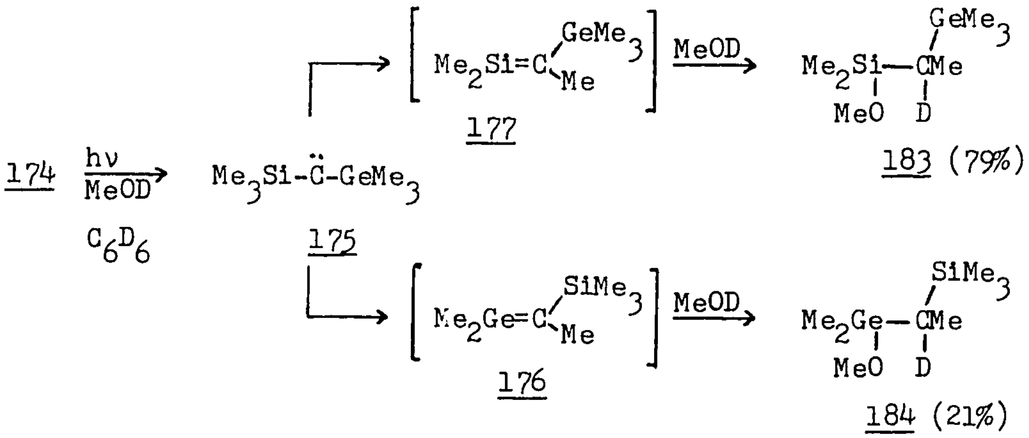
Scheme 62



which together account for 76% of the reaction, can all be explained as coming from silene 177. The silene is trapped by benzaldehyde to form diradical 178 which can close to form silaoxetane 179 that results in the formation of the olefins 181 and 182; or 178 can undergo an intramolecular, hydrogen-abstraction process to form 180. None of the analogous products arising from benzaldehyde trapping of the germene 176 were observed. As 24% of the reaction mixture is unaccounted for, it is still possible that some of the germene is formed. Other workers have noted the inability of carbonyl compounds to trap germenes (170).

A better experiment to determine the preferred rearrangement of carbene 175 involves trapping the (p-p) π-bonded reactive intermediates with methanol. Photochemical generation of carbene 175 was conducted in D_6-benzene with a 6-fold excess of methanol-OD present as a silene/germene trap. The reaction was extremely clean with only ethers 183 and 184 being formed in combined yield of >95% (Scheme 63). Precedent

Scheme 63

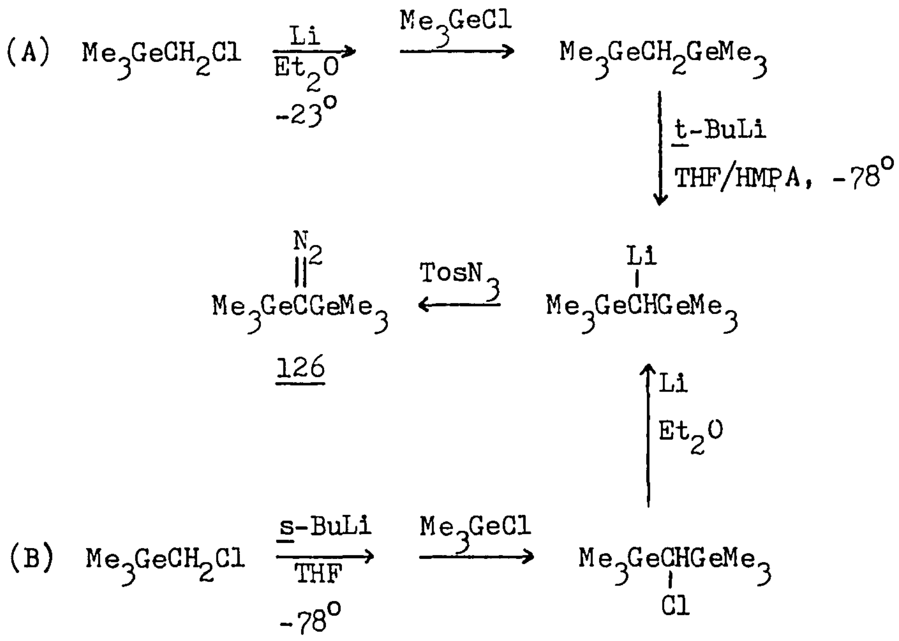


dictates that 183 arises from addition of MeOD across the π-bond of silene 177, and by analogy, 184 is produced by the corresponding reaction with germene 176. Thus, under these photochemical conditions, silene formation is favored over germene formation by a factor of *ca.* four. It is possible that silene formation is favored over germene formation by about the same factor in the thermal reaction where 76% of the reaction occurred via silene, and the remainder, perhaps occurring via germene, was not accounted for.

Bis(trimethylgermyl)diazomethane

Synthesis of 126 was accomplished in the same fashion as for bis(trimethylsilyl)diazomethane (136) and trimethylsilyltrimethylgermyldiazomethane (174), and is outlined in Scheme 64. Of these three diazo

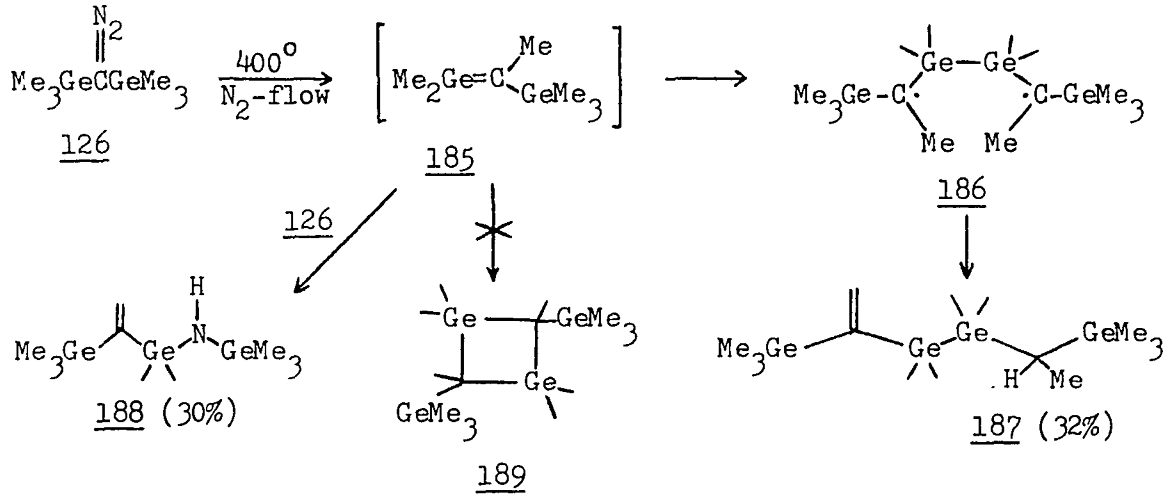
Scheme 64



compounds, the synthesis of 126 was the most difficult. Route A produced 126 in 32% yield, while Route B afforded only a trace amount of 126. Diazo compound 126 proved to be much less stable than either 136 or 174. It was not stable in the reaction mixture and had to be removed immediately. Compound 126 also reacted with CCl_4, thus necessitating the use of D_6-benzene for NMR solutions. However, once purified by preparative GC, 126 can be stored at -10° C for months without decomposition.

Pyrolysis of bis(trimethylgermyl)diazomethane (126) as a 5% solution in benzene in a nitrogen-flow system at 400° C resulted in the formation of two major products (Scheme 65). Head-to-head dimerization

Scheme 65

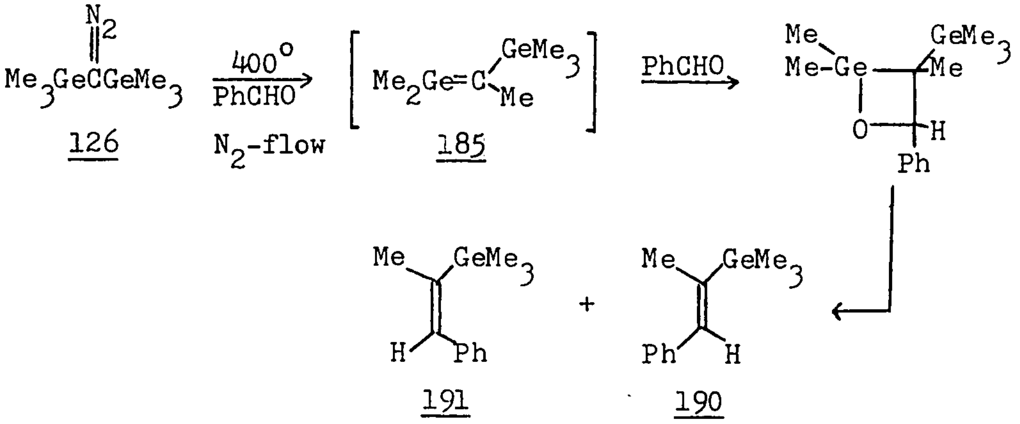


of germene 185 results in the formation of diradical 186 which undergoes intramolecular hydrogen abstraction to yield 187 (32%). Reaction of germene 185 with starting diazo compound forms digermazane 188 (30%).

The major reaction pathway in the pyrolysis of the analogous bis(trimethylsilyl)diazomethane (136) was head-to-tail dimerization of the silene to form the disilacyclobutanes 143. In the reaction of 126, however, no digermacyclobutanes (189) were observed.

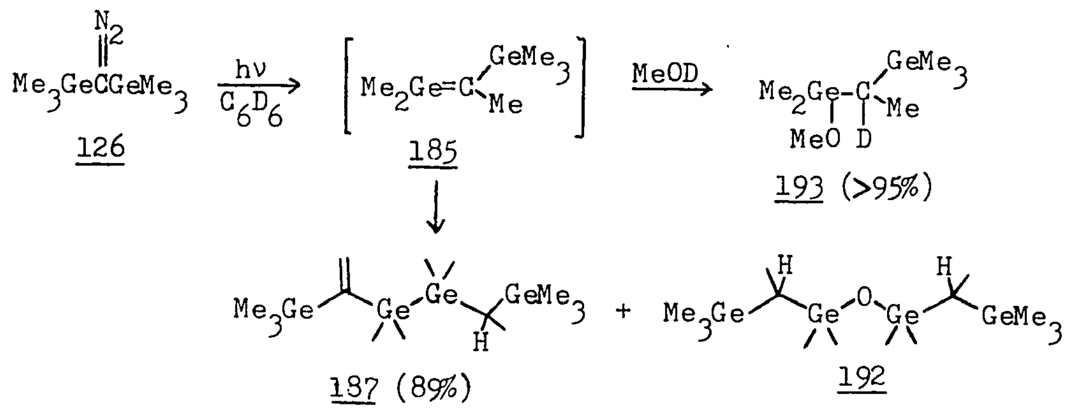
In order to determine whether or not a germene such as 185 could be trapped with a carbonyl compound, we carried out the copyrolysis of 126 in benzaldehyde at 400° C. If the intermediate germene would behave like the analogous silene, the olefins 190 and 191 should be major products of this reaction (Scheme 66). Analysis of the pyrolysate by GC indicated that very many products were present (>20 products). Closer scrutiny with GCMS showed that olefins 190 and 191 were probably both present, but in combined yield of <5%. Thus, it appears that germene 185 cannot be effectively trapped by benzaldehyde in the same way that silenes are trapped.

Scheme 66



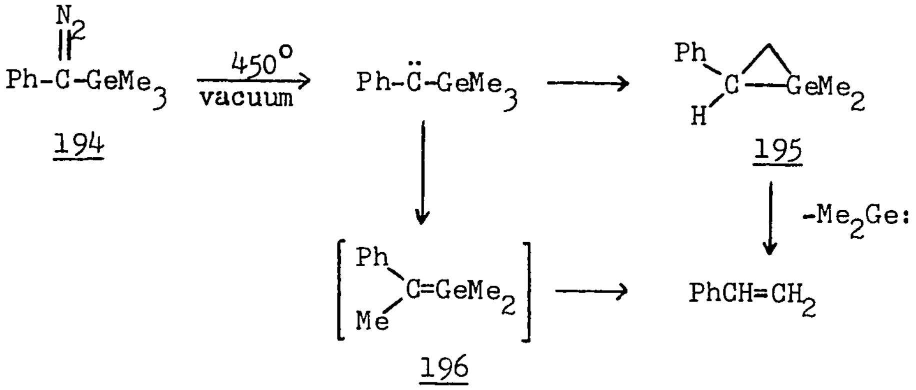
Photochemical generation of germene 185 is even more efficient than thermal generation. Irradiation of 126 (5% in C_6H_6, 2 hrs., 2537Å) produced the linear dimer 187 (89%) along with a small amount of digermoxane 192 (Scheme 67). When the photolysis was carried out in the presence of a 6-fold excess of MeOD, the germene was trapped to form the methoxygermane 193 in near quantitative yield.

Scheme 67



It is of interest to compare our results with those found in the literature for phenyltrimethylgermyldiazomethane (194). Norsoph and coworkers (150) have made the claim that the formation of styrene (15%) in the gas-phase pyrolysis of 194 is evidence for the intermediacy of germacyclopropane 195 (Scheme 68). The analogous carbene insertion into a C-H bond is definitely not taking place in the photochemistry of 126 (or 136 or 174), and there appears to be no reason to suspect this process in the thermolysis of 126, although our mass balances are rather low, and a variety of minor processes could be taking place. In view of our results, we suggest that the origin of styrene is not germacyclopropane 195, but the germene 196. These two paths, however, are in-

Scheme 68

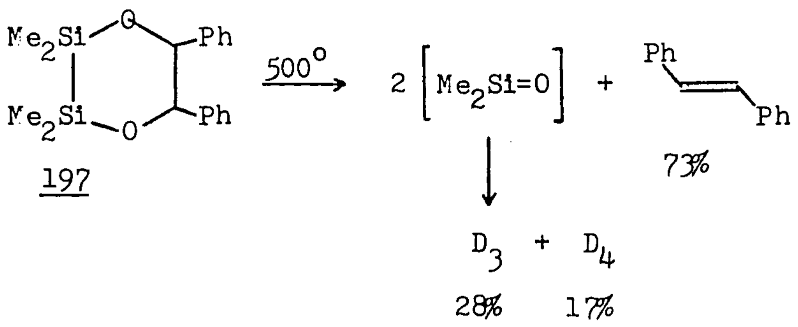


distinguishable without the isolation or trapping of the actual intermediates.

2,3-disila-1,4-dioxanes

One of the greatest problems in studying silanones is the lack of availability of mild silanone generators. Most of the methods used to prepare silanones involved high-temperature thermolytic work (see Historical section on silanones). We thought that the 2,3-disila-1,4-dioxane system (197) could possibly serve as a mild silanone generator.

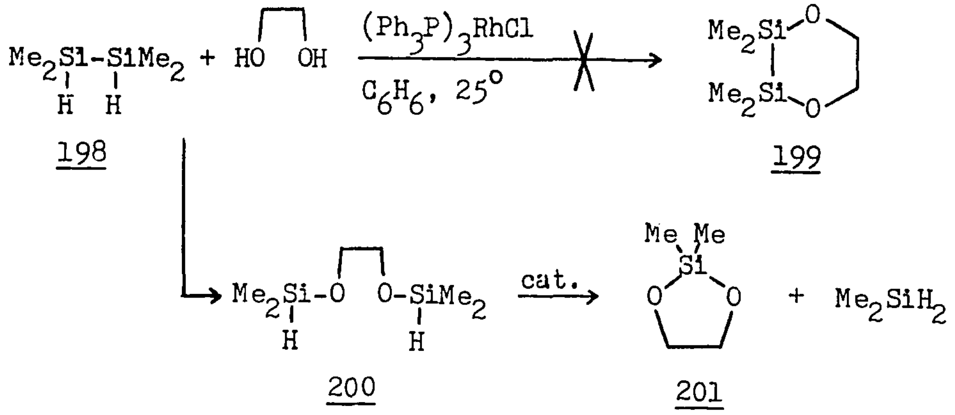
Scheme 69



Thermal decomposition of 197 to form dimethylsilanone would involve cleavage of a relatively weak Si-Si bond (171) while at the same time a molecule of very stable stilbene would be formed. These two factors are both expected to increase the likelihood of 197 being a mild silanone generator. Compound 197 had previously been prepared and pyrolyzed in a N_2-flow system at 500° C (172) (Scheme 69). It was observed that this pyrolysis led to the formation of trans-stilbene (73%) as well as the cyclic oligomers of dimethylsilanone, D_3 (28%), and D_4 (17%).

While 500° C can hardly be called mild conditions, no attempts were made at lower temperature pyrolysis. The 2,3-disila-1,4-dioxane system was not investigated any further at that time, due in part to the difficulty in handling 197 which apparently was very labile. We decided to reinvestigate this ring system and to determine whether or not such compounds could serve as mild silanone generators. Thinking that perhaps the method of preparation contributed to the lability of 197 (treatment of the dichlorodisilane with a diol in the presence of pyridine), we desired to prepare such a ring system by a catalytic reaction which did not involve acid or base. Corriu and Moreau (173) had shown in previous work that Wilkinson's catalyst promoted the dehydrocondensation reaction between alcohols and silylhydrides. While this reaction had never been reported between a silylhydride and a diol, we reacted sym-tetramethyldisilane (198) with ethylene glycol in the hope of preparing 2,2,3,3-tetramethyl-2,3-disila-1,4-dioxane (199) as shown in Scheme 70. However, 199 was not isolated, nor were D_3 and D_4 formed. When the reaction was followed by GC, it was observed that the starting disilane 198 disappeared completely within 24 hours. A new

Scheme 70



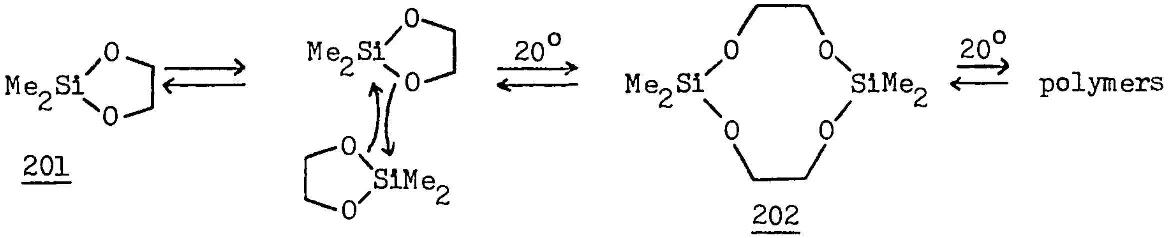
peak which formed within a half hour was maximized after approximately 5 hrs. and was then slowly reduced until it too was completely gone after 24 hours. The only other peak in the GC was a very broad one which gradually increased throughout the course of the reaction.

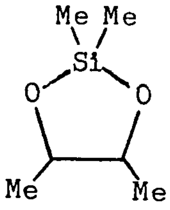
This reaction was repeated but was stopped after 2 hrs. and the intermediate product was isolated by preparative GC and identified to be the bis(dimethylsilyl)ether of ethylene glycol (200). Compound 200 was identified by the usual spectroscopic methods and by comparison with an independently synthesized sample. The formation of 200 from 198 and ethylene glycol is not too surprising in view of the report that Wilkinson's catalyst is very effective for the cleavage of disilanes by alcohols (174).

When an independently synthesized sample of 200 was placed in benzene along with Wilkinson's catalyst, it was observed by GC that the peak due to 200 gradually disappeared while the same broad peak noted before again appeared. The reaction also proceeded with formation of gaseous dimethylsilane (identified by GCMS) as well as some carbon dioxide (the origin of CO_2 remains a mystery). After the reaction was complete, removal of the solvent left behind a white solid which was identified to be 2,2-dimethyl-1,3-dioxa-2-silacyclopentane (201). Compound 201 was identified by the usual spectroscopic methods as well as by comparison with an independently synthesized sample.

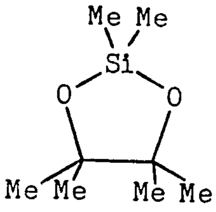
The 5-membered ring 201 is an extremely interesting molecule which has been reported in the literature only twice, and the two reports are somewhat conflicting. Marchand and coworkers (175) reported that at 20° C, 201 forms a dimer and polymers (Scheme 71). Kober and Ruhl (176) reported the synthesis of 201 at 60° C, although a small amount of dimer 202 was also formed. However, the latter authors did not mention that 201 and 202 equilibrate or that any polymers were formed. They did report the boiling point of 201, but neither report mentioned that at room temperature, 201 is a solid (mp ca. 60° C). One other report on methyl substituted 2-sila-1,3-dioxanes 203 and 204 has appeared (177). Apparently the methyl groups stabilize this ring system, possibly by steric hindrance.

Scheme 71





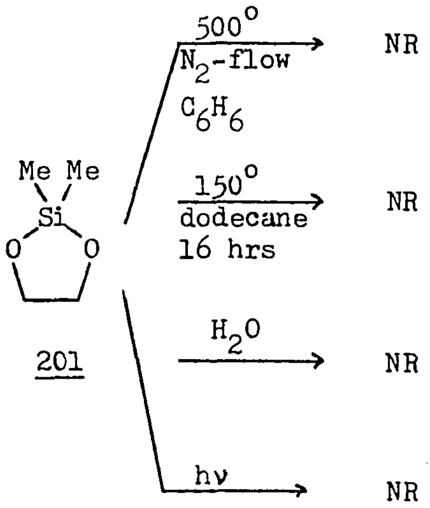
203



204

Since the chemistry of 201 is somewhat obscure, we decided to investigate it further. We found that, in conflict with the literature report (175), 201 was extremely stable thermally and saw no evidence under any conditions of dimerization of 201 to form 202. Pyrolysis of 201 in benzene in a nitrogen-flow system at 500° C resulted in no reaction (Scheme 72). Similarly, no reaction occurred when 201 in

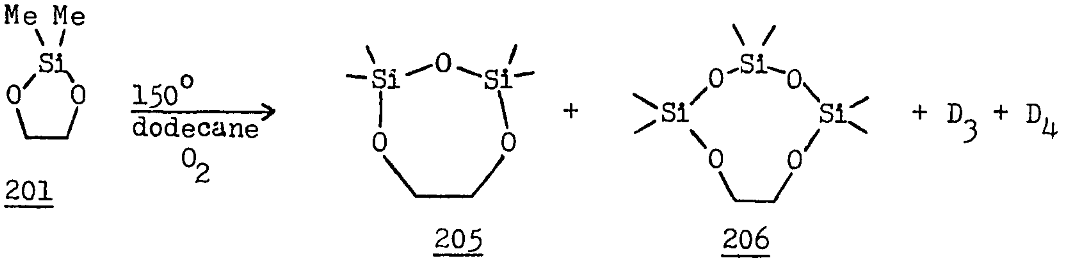
Scheme 72



dodecane was heated in a sealed tube at 110° for two days or at 150° for 16 hrs. Compound 201 also proved to be inert toward neutral H_2O and did not react when photolyzed in cyclohexane with a high pressure Hanovia lamp for 16 hrs.

However, 201 does react, even at room temperature, in the presence of oxygen. When a sample of 201 was left open to the atmosphere for several days, the major product formed was 2,2,4,4-tetramethyl-1,3,5-trioxa-2,4-disilacycloheptane (205). Similarly, a flow pyrolysis of 201 at 500° C in which the carrier gas was composed of 96% N_2 and 4% O_2 formed 205 as the major product. To more closely analyze this reaction, a sample of 201 in dodecane was heated at 150° for 16 hrs. while open to the atmosphere. During this time, the starting material reacted completely. The major products were the 7-membered ring 205 and the 9-membered ring 206 as well as smaller amounts of D_3 and D_4 (Scheme 73).

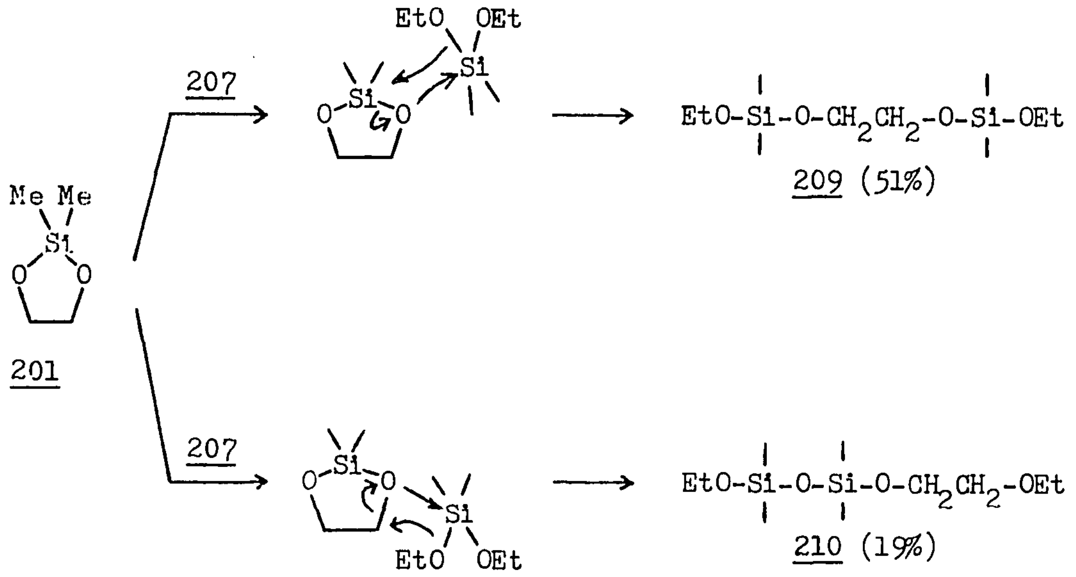
Scheme 73



These products suggest the intermediacy of dimethylsilanone, or perhaps the involvement of a silanone transfer mechanism, although the necessity of oxygen for the reaction to proceed complicates any mechanism one may propose.

In order to further investigate the possibility of silanone involvement, 201 was heated in dimethyldiethoxysilane (207). Compound 207 is a commonly used silanone trap which should lead to the formation of sym-diethoxytetramethyldisiloxane (208) if any dimethylsilanone is involved. Pyrolysis of a 5% solution of 201 in 207 at 130° for 36 hrs. in a sealed tube resulted in the formation of <3% of 208. (It was later found that 207 alone under these conditions produces 208 in an approximately equal amount.) Instead, the major products of the reaction were 209 (51%) and 210 (19%) (Scheme 74). These products must arise via intermolecular

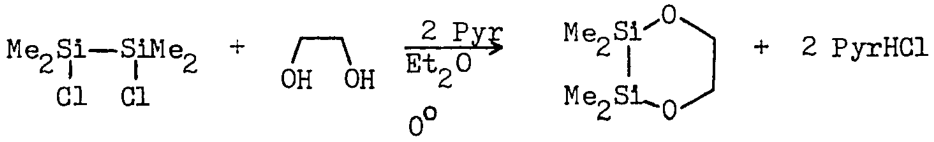
Scheme 74



reaction between 201 and 207; one possibility is shown in Scheme 74. The details of the mechanism are speculative.

Although it is an interesting compound, 2,2-dimethyl-1,3-dioxa-2-silacyclopropane certainly is not a silanone generator, so we again turned our attention to the 2,3-disila-1,4-dioxane ring systems. Compound 199 was easily synthesized by the straightforward approach shown in Scheme 75. The difficulty in handling this dioxane system is

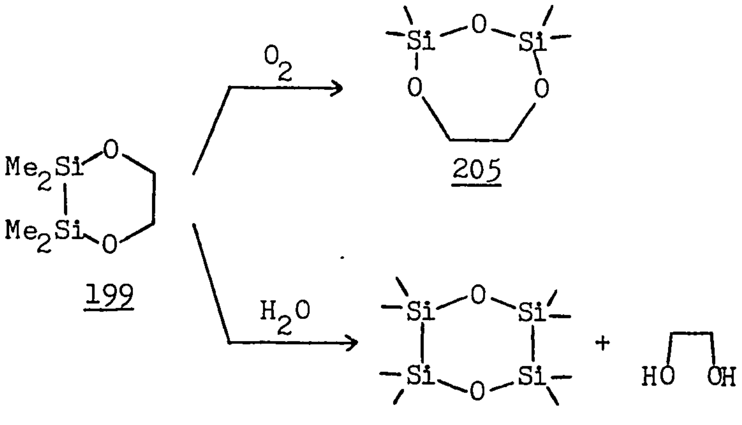
Scheme 75



199 (92%)

clearly not due to the method of preparation. The problem arises when 199 is exposed to the atmosphere. Compound 199 is easily oxidized by air to form the 7-membered ring 205 (Scheme 76). Compound 199 is also

Scheme 76



199

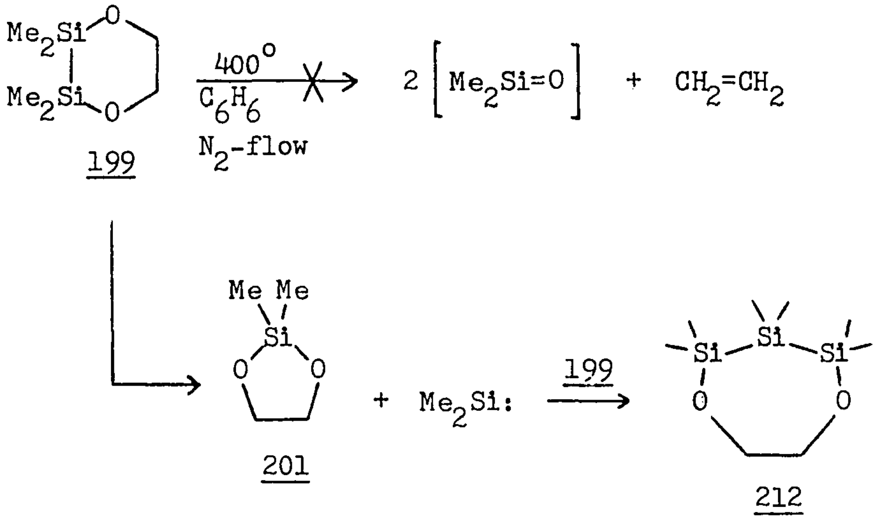
205

211

sensitive to water, leading to the formation of ethylene glycol and 2,2,3,3,5,5,6,6-octamethyl-2,3,5,6-tetrasila-1,4-dioxane (211). Despite these problems, 199 can be prepared quite easily, and when kept in an inert atmosphere, it is very stable.

A 5% solution of 199 in benzene was pyrolyzed in a nitrogen-flow system at 400° C. The starting material reacted completely under these conditions, but there was no evidence that 199 cleaved to give dimethylsilanone. No ethylene formation was observed nor were D_3 and D_4 formed. Instead, the major products were the 5-membered ring 201 and 2,2,3,3,4,4-hexamethyl-1,5-dioxa-2,3,4-trisilacycloheptane (212) (Scheme 77). Under these conditions, 199 appears to extrude dimethylsilylene to form 201. The dimethylsilylene is then trapped by 199 to yield 212. Thermal elimination of dimethylsilylene from a similar disiladioxane has recently been reported by Ando and Ikeno (178).

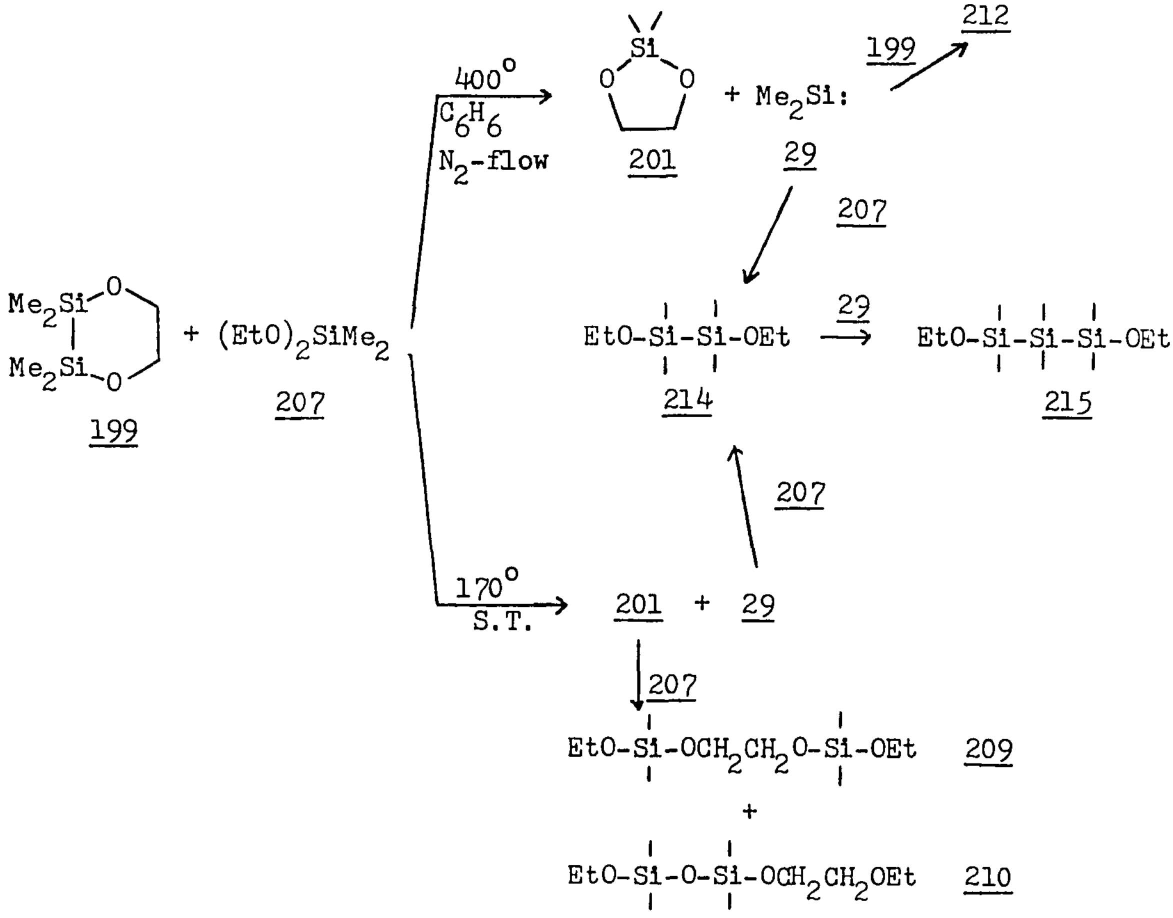
Scheme 77



The reaction of 199 to form 201 and dimethylsilylene is reversible photochemically. When dodecamethylhexasilacyclohexane (32) was photolyzed in a solution of C_6D_6 containing 201, the major initial product was 199.

The absence of silanone involvement in the thermal decomposition of 199 was also demonstrated by carrying out pyrolyses in the presence of silanone traps. Pyrolysis of 199 and a 5-fold excess of D_3 in a nitrogen-flow system produced only a trace amount of D_4. The major products were 201, 212, and the product of dimethylsilylene insertion into D_3 (213). This silylene insertion into D_3 is a well-documented reaction (39). Similarly, nitrogen-flow copyrolysis of 199 and dimethyldiethoxysilane (207) formed as major products 201 and 212 as well as products 214 and 215 which come from insertion of dimethylsilylene into dimethyldiethoxysilane (Scheme 78). The silanone insertion product 208 was formed

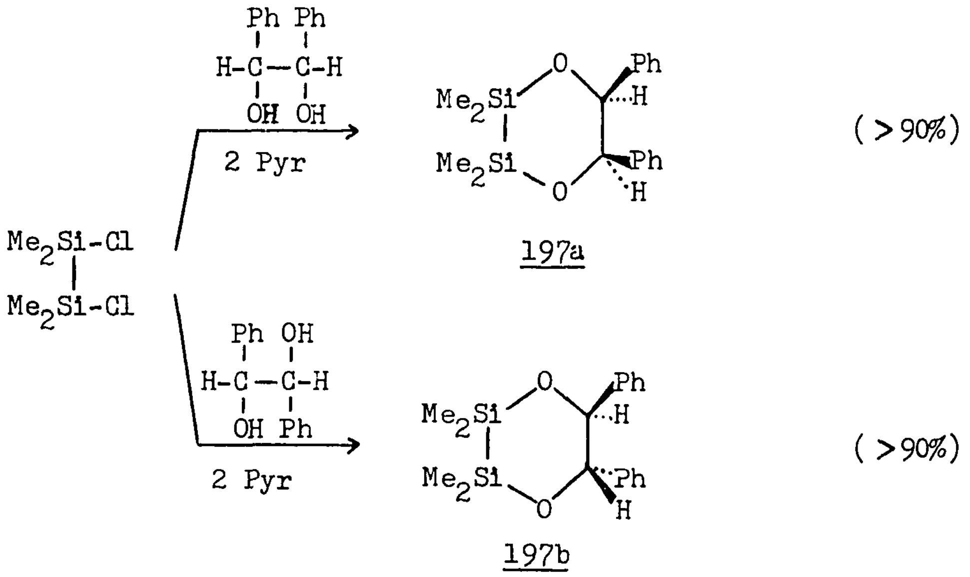
Scheme 78



as a minor product, but as will be shown later, it is also formed from 207 alone under these conditions. In the sealed-tube thermolysis of 199 and 207 (170° C, 12 hrs.), the initially formed 5-membered ring 201 reacts further with 207, as shown previously, to form 209 and 210 as major products.

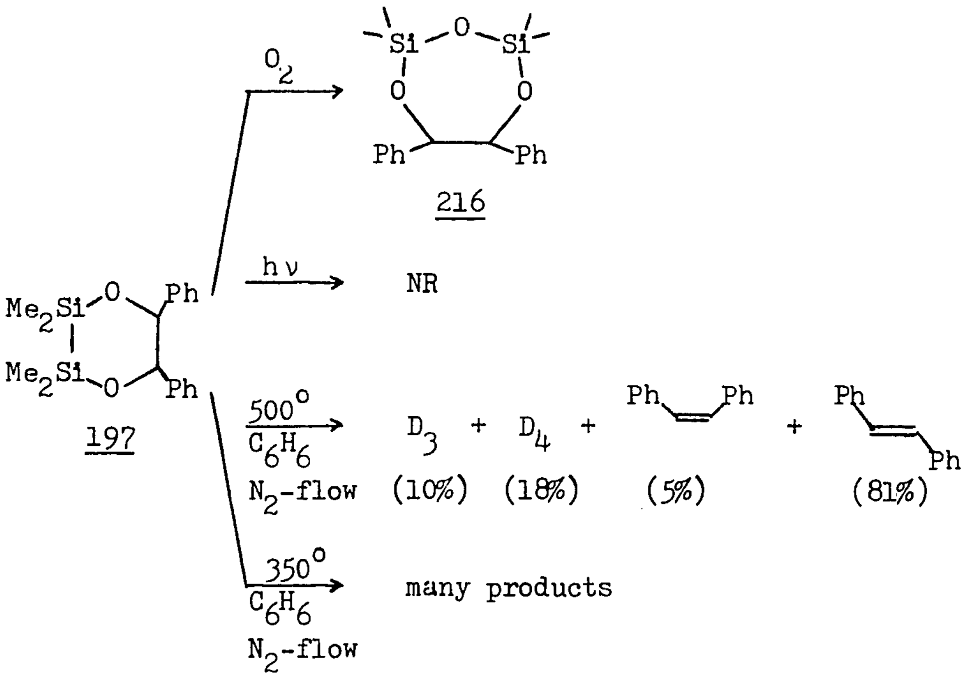
Since the parent compound 199 is clearly not a silanone generator, it was decided to further investigate the phenyl-substituted disiladioxane system. Both the cis (197a) and the trans (197b) systems were prepared in excellent yield by the method outlined in Scheme 79. In all reactions studied, 197a and 197b gave identical results. The expected increase of steric hindrance in 197a did not result in a substantial lowering of the temperature necessary for thermal decomposition.

Scheme 79



Some of the reactions of 197 are shown in Scheme 80. Like the un-

Scheme 80



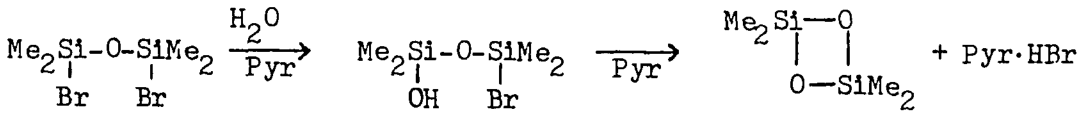
substituted system, 197 is very easily oxidized, with exposure to air being sufficient to form 216. Irradiation of 197 in cyclohexane with a high pressure 450W Hanovia lamp for 2 hrs. resulted in no reaction as observed by NMR and GC, although the solution did become dark-colored. A nitrogen-flow pyrolysis of 197 in deoxygenated benzene at 500° formed as major products D_3 (10%), D_4 (18%), *cis*-stilbene (5%), and *trans*-stilbene (81%). This confirms the literature report of this same reaction (172). The ratio of *cis*-stilbene to *trans*-stilbene is simply the equilibrium ratio at 500° C. This same ratio is obtained when either pure *cis*- or pure *trans*-stilbene in benzene is pyrolyzed under these conditions.

When the temperature of the flow pyrolysis was lowered to 350°, a dramatic change occurred. The disiladioxane 197 still reacted completely, but many more products were formed than at 500° C. D_3, D_4, and the stilbenes were all formed, but in minute amounts. The major products were not identified. Similar results were obtained from sealed tube pyrolyses. When a solution of 197 in dodecane was heated at 300° for 1 hr., all the starting material disappeared, but only trace amounts of the stilbenes were observed. When the solution was heated at 300° C for 4 hrs., the stilbenes had become major products. These results indicate that 197 does not fragment to give dimethylsilanone and stilbene in a synchronous fashion, but that the formation of stilbene must result from some stepwise reaction. It is still possible that dimethylsilanone and the stilbenes are formed synchronously in the high temperature flow pyrolysis. In any case, the 2,3-disila-1,4-dioxane system is not the mild silanone generator as had been hoped.

Attempted Formation of D_2

An interesting approach to the synthesis of D_2 is shown in Scheme 81. Such an approach is attractive not only because of its simplicity,

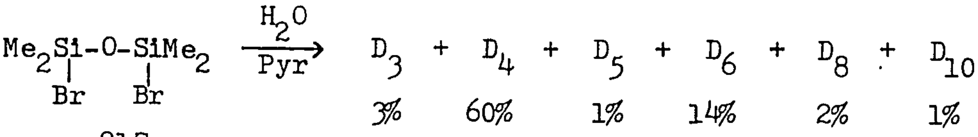
Scheme 81



217

but also because it can be carried out at low temperatures. In a first attempt, a solution of the dibromide and pyridine in CH_2Cl_2 was cooled to -78° C and wet ether was slowly added. The solution was analyzed by GC after it was warmed to room temperature. This reaction dramatically produced the even cyclosiloxanes $D_{4,\ 6,\ 8,\ 10}$ with very small amounts of the odd cyclosiloxanes (Scheme 82). While these results are consistent with the intermediacy of D_2, all the products can also be explained by intermolecular condensations and subsequent cyclizations. Both mechanisms add two "silanone units" at a time, hence the preponderance of the even products.

Scheme 82

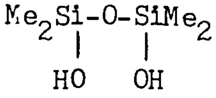


$$\underset{\displaystyle 217}{\underset{Br\quad\ \ Br}{Me_2Si\text{-}O\text{-}SiMe_2}} \xrightarrow[Pyr]{H_2O} \underset{3\%}{D_3} + \underset{60\%}{D_4} + \underset{1\%}{D_5} + \underset{14\%}{D_6} + \underset{2\%}{D_8} + \underset{1\%}{D_{10}}$$

217

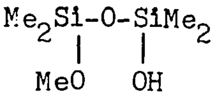
The addition of D_3 (1.5 equivalents) to the reaction mixture before the wet ether was added resulted in no significant changes in the product mixture. The amount of D_4 formed may have increased slightly, but there was no change in the amount of D_5 formed. Similarly, addition of dimethyldimethoxysilane resulted in no significant changes.

In order to minimize intermolecular reactions, it was decided to use inverse addition where a solution of dibromide 217 in CH_2Cl_2 was slowly added to a solution of wet ether and pyridine at -78° C. This resulted in the formation of the cyclosiloxanes in a ratio nearly identical to that obtained before. In addition, one new product, identified by GCMS to be the disiloxanediol 218, was formed. The formation of 218 would be expected from 217 in the presence of an excess of H_2O.



$\underset{HO}{Me_2Si}-O-\underset{OH}{SiMe_2}$

218



$\underset{MeO}{Me_2Si}-O-\underset{OH}{SiMe_2}$

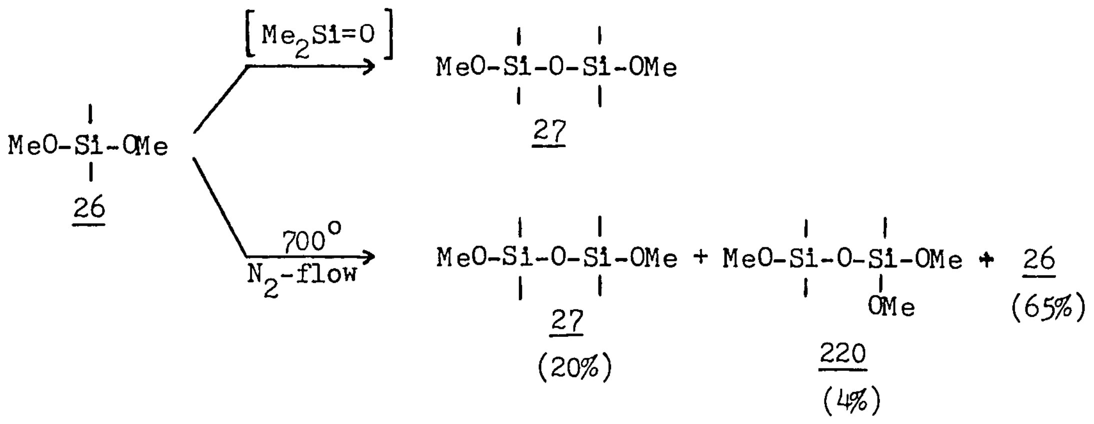
219

The addition of D_3 to the reaction solution resulted in no change, while the addition of dimethyldimethoxysilane did result in the formation of one new product, 219. No yields were determined for any of these inverse addition reactions.

Pyrolysis of Silylethers

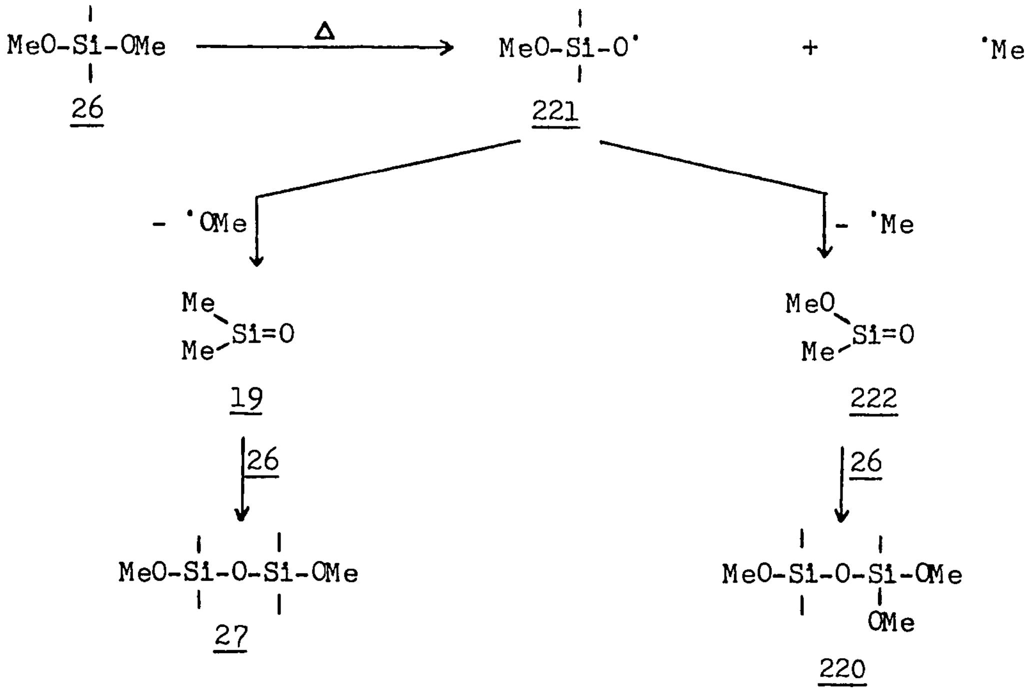
As already noted, silylethers have commonly been used as silanone traps. For example, if dimethylsilanone were generated in the presence of dimethyldimethoxysilane (26), the expected product would be sym-dimethoxytetramethyldisiloxane (27) (Scheme 83). We had observed, however, in some of our high temperature work, that various silylethers used as silanone traps lead to formation of small amounts of the silanone insertion products even when no known silanone generator is present. In order to further investigate these strange observations, dimethyldimethoxysilane was pyrolyzed neat in a nitrogen flow system at 700° C. Even at this very high temperature the pyrolysis was quite clean, giving as major products 27 and 220 as well as unreacted starting material (Scheme 83). A reaction in which a silanone trap leads to

Scheme 83



the formation of a formal silanone insertion product is quite disturbing and certainly deserves some explanation. One possible explanation, shown in Scheme 84, is that dimethyldimethoxysilane actually behaves as a

Scheme 84

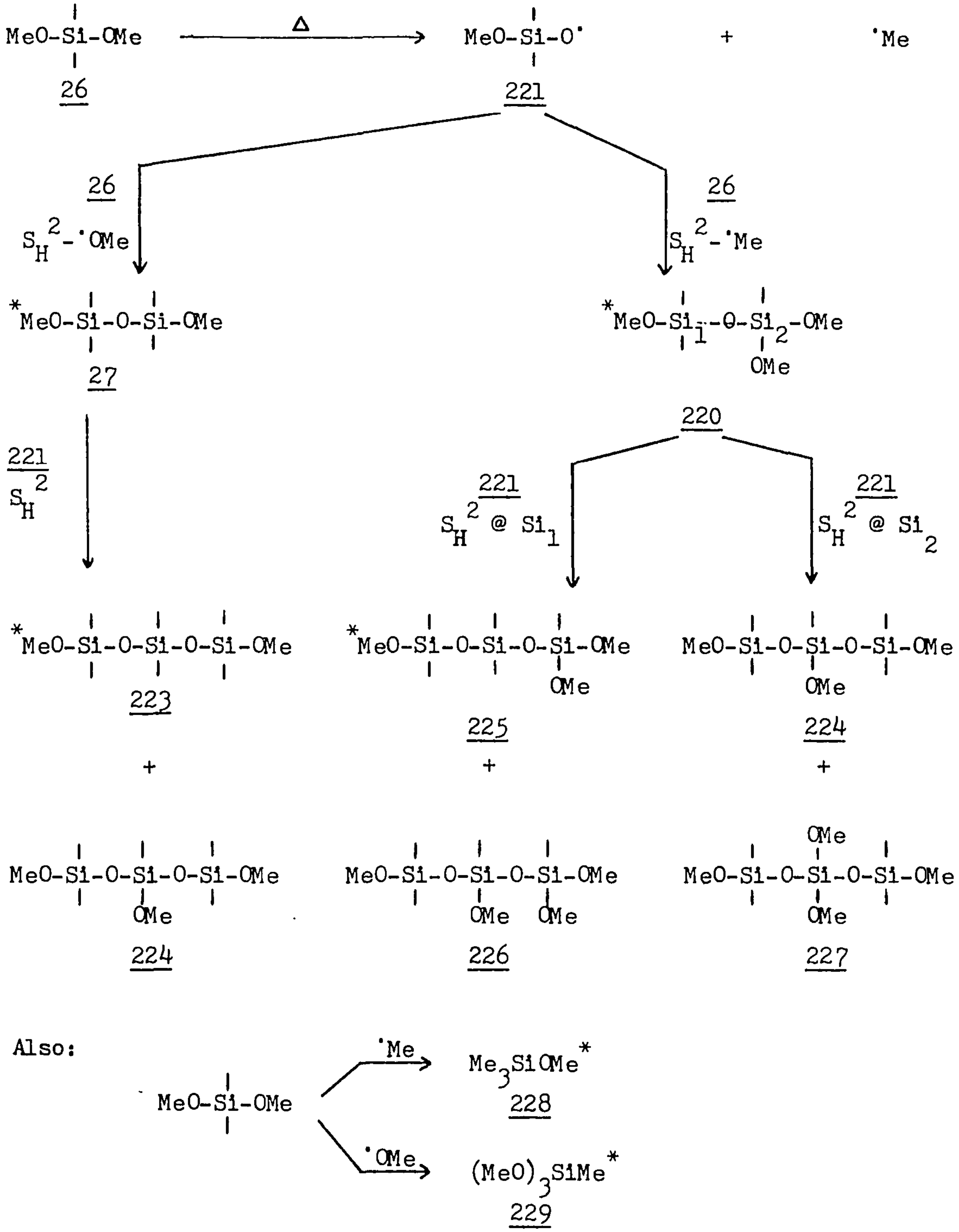


silanone generator. At the high temperatures used, the C-O bond simply cleaves to form siloxy radical 221. Intermediate 221 can then undergo loss of a methoxy radical to form dimethylsilanone (19), or loss of a methyl radical to form methoxymethylsilanone (222). Silanones 19 and 222 would then insert into 26 to form 27 and 220 respectively. If such a mechanism were operative, it would be expected that the silanone intermediates would also insert into the primary products 27 and 220 to form a variety of secondary products.

An alternative explanation which does not involve the intermediacy of silanones is shown in Scheme 85. The first step is the same as in the silanone mechanism, cleavage of the C-O bond to form siloxy radical 221. In this mechanism, however, 221 attacks at the silicon atom in a molecule of starting material. This S_H2 attack can occur with loss of a methoxy radical which leads to 27 or with loss of a methyl radical which leads to 220. These S_H2 processes would be expected to continue with attack by 221 on the primary products to form the secondary products shown in Scheme 85. It is important to note that all these secondary products, with the exception of 227, can also be explained by the addition of the appropriate silanone intermediate into the primary products 27 and 220. (It is not possible to form any product containing an internal silicon bearing two methoxy groups such as 227 by the silanone mechanism.)

Careful analysis of the pyrolysate revealed that in addition to 27 and 220, products 223 and 225 were present in the pyrolysate. The absence of 227 does not allow us to comment on the likelihood of the S_H2 versus the silanone mechanism. However, trimethylmethoxysilane and

Scheme 85



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*Denotes products observed in the pyrolysate.

trimethoxymethylsilane are also formed in this reaction. As shown at the bottom of Scheme 85, these products are most easily explained by S_H2 attack of methyl and methoxy radicals on starting material. If S_H2 attack does occur here, it is expected that S_H2 attack also occurs with siloxy radical <u>221</u>.

In Table 7 are listed the relative mole percentages of the major products isolated in the pyrolysis of dimethyldimethoxysilane at a variety of temperatures. Also reported is the total mass percentage of the pyrolysate composed of these major products.

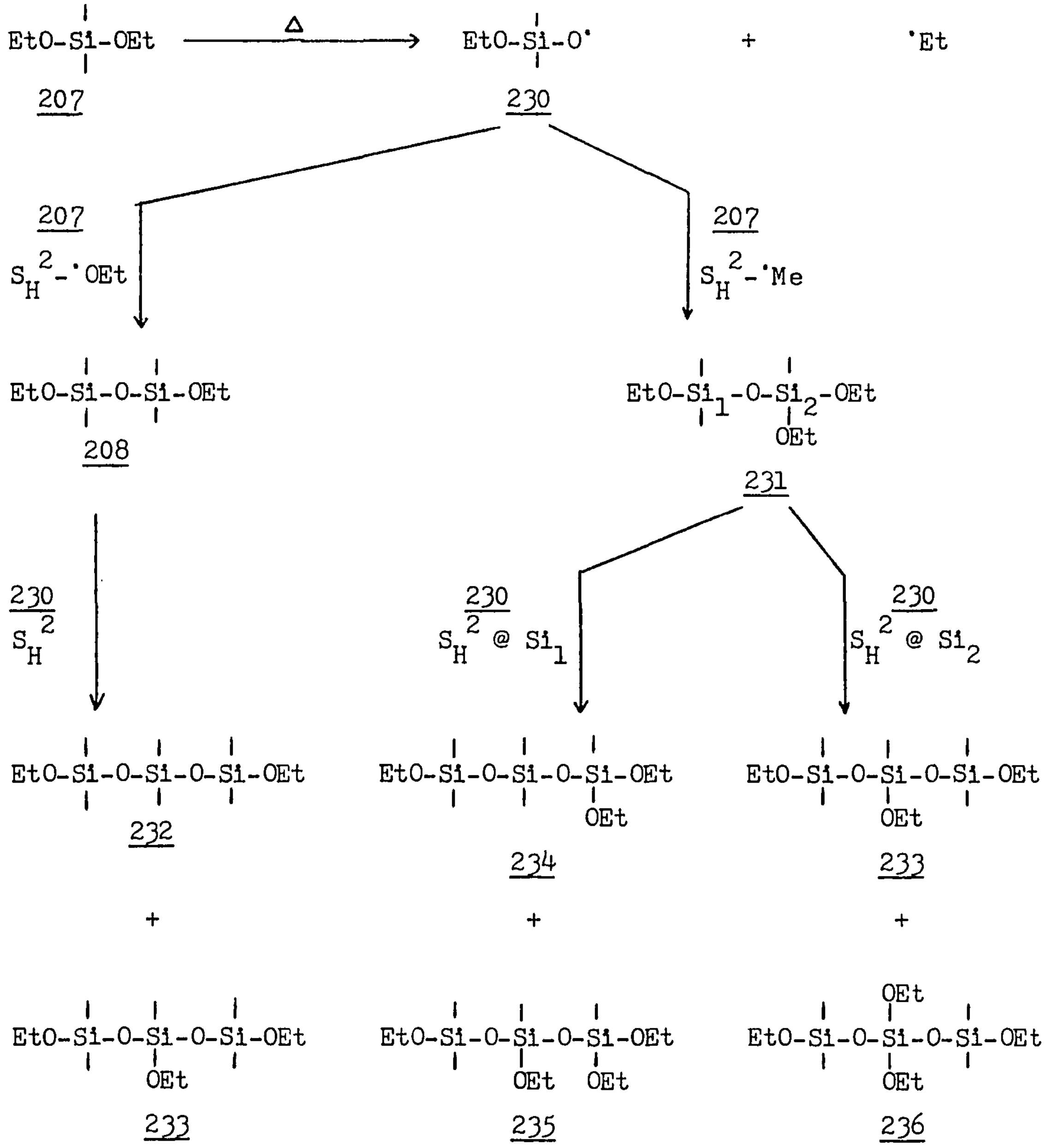
Table 7. Pyrolysis of $(MeO)_2SiMe_2$ (<u>26</u>)

	<u>26</u>	<u>228</u>	<u>229</u>	<u>27</u>	<u>220</u>	<u>223</u>	<u>225</u>	Total mass % identified
600°	95.8	--	--	3.8	0.1	0.3	--	98.1
650°	92.7	0.5	0.1	5.6	0.3	0.8	0.1	97.8
700°	85.0	1.4	1.1	10.0	0.9	1.3	0.2	96.2
750°	65.0	1.9	2.4	20.0	3.8	4.9	2.0	67.9

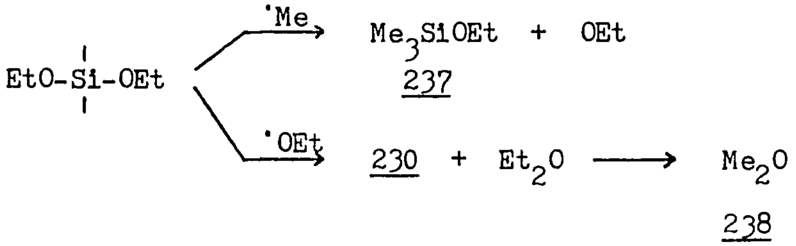
Pyrolysis of dimethyldiethoxysilane (<u>207</u>) produced the analogous products shown in Scheme 86. The temperature required for reaction of <u>207</u> was about 100° lower than for dimethyldimethoxysilane. This lower temperature is attributed to the greater ease of formation of an ethyl radical than a methyl radical.

All the products shown in Scheme 86 were present in the pyrolysate, although <u>232</u>, <u>233</u>, and <u>236</u> all had nearly identical retention times and

Scheme 86



Also:



were therefore not separated, but were identified solely by GCMS. Also formed in this reaction was a small amount of D_3. Diethylether, which might be expected in the pyrolysate, was not observed, but instead, dimethylether (238) was. It was demonstrated in a separate experiment that under the same reaction conditions, diethylether produces dimethylether. Table 8 lists the relative mole percentages of the products of pyrolysis of 207.

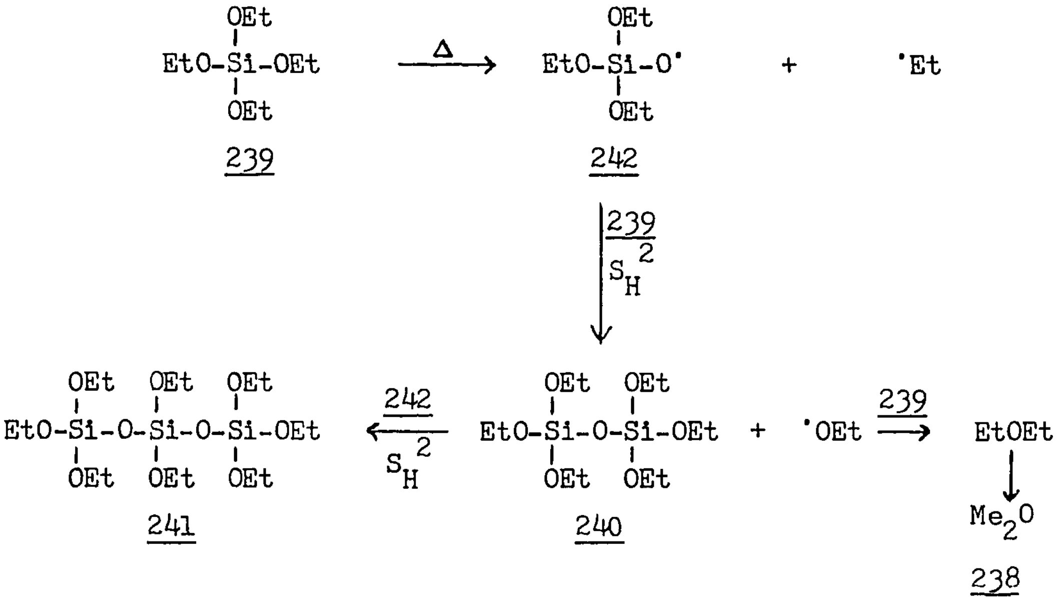
All of the products from the pyrolysis of 207 (except 236) could also be explained by the silanone mechanism. In order to probe for the intermediacy of silanones, a copyrolysis of 207 and D_4 at 600° C was carried out. (It was first established that under identical conditions, D_4 decomposes only slightly to give D_3 (2.4%) and D_5 (1.5%).) If silanones are involved (in this case, dimethylsilanone and methylethoxysilanone), they should be trapped by D_4. Analysis of the pyrolysate, however, indicated that no such trapping had occurred.

In order to simplify the product mixture, it was decided to pyrolyze tetraethoxysilane (239). Since all the groups around silicon are identical, S_H2 attack on 239 should lead to only one primary product, hexaethoxydisiloxane (240) (Scheme 87). Similarly, S_H2 attack on 240 should lead to only one secondary product, octaethoxytrisiloxane (241). Compounds 240 and 241 were found to be the major products along with dimethylether (238) which is again proposed to originate from pyrolysis of diethylether. Table 9 lists the relative mole percentages of the major products. It is noted that the yield of both 240 and 241 reach a maximum value and then decrease as the temperature is raised from 500° to 650° C. At the higher temperatures, these products are

Table 8. Pyrolysis of $(EtO)_2SiMe_2$ (207)

	207	238	237	D_3	208	231	232 + 233 + 236	235	234	Total mass % identified
500°	95.2	0.5	0.5	0.1	2.9	0.2	0.3	0.2	0.1	99.5
550°	88.8	2.9	0.7	0.2	5.1	1.2	0.4	0.6	0.2	96.6
600°	73.3	9.9	1.0	0.8	9.7	2.6	1.0	1.2	0.4	90.3
650°	46.9	33.1	2.2	3.0	8.8	1.8	2.7	1.0	0.4	78.7

Scheme 87



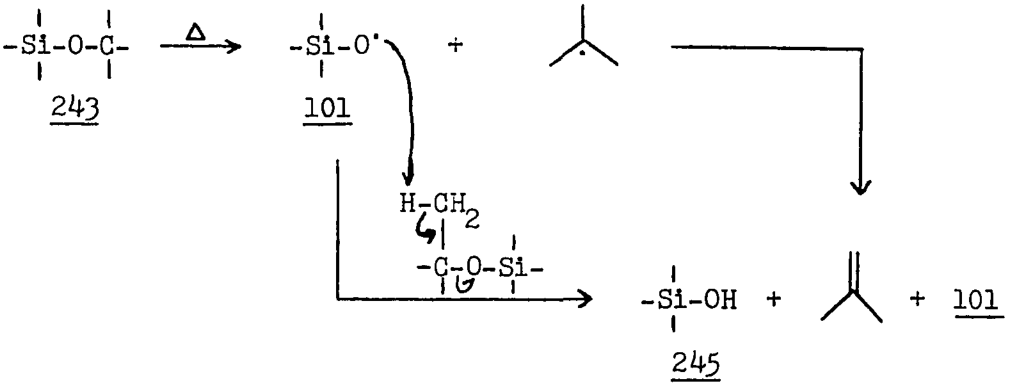
apparently less stable than the starting material 239. The same type of homolytic cleavage of C-O bonds probably occurs with 240 and 241 as with 239.

Table 9. Pyrolysis of $Si(OEt)_4$ (239)

	239	238	240	241	Total mass % identified
500°	92.6	4.1	2.9	0.4	98.1
550°	84.4	11.2	3.8	0.6	97.8
600°	53.7	41.2	4.6	0.4	82.0
650°	16.4	87.7	0.8	0.1	78.1

Since the high temperatures required for the decomposition of silyl ethers resulted in messy reactions, we desired a silyl ether which would decompose at a lower temperature. For this reason, we prepared t-butoxytrimethylsilane (243). Our hope that a lower temperature would be required for decomposition was realized, but the reaction followed an entirely different course (Scheme 88). Decomposition of 243 in a nitrogen-flow system began at ca. 450° C, and at 600°, 243 reacted completely to form trimethylsilanol (245) and isobutylene nearly quantitatively (mass balance of 93%). The t-butyl group did decrease the temperature necessary to form 101, but the siloxy radical now undergoes a precedented (128, 135) and expected reaction, abstraction of a hydrogen atom. It appears that if there are easily-abstractable hydrogens available, the siloxy radical prefers the hydrogen-abstraction reaction over S_H2 attack at silicon. In the case of 101, the siloxy radical can abstract a hydrogen from the t-butyl group of 243, leading eventually to the formation of trimethylsilanol and isobutylene, and

Scheme 88

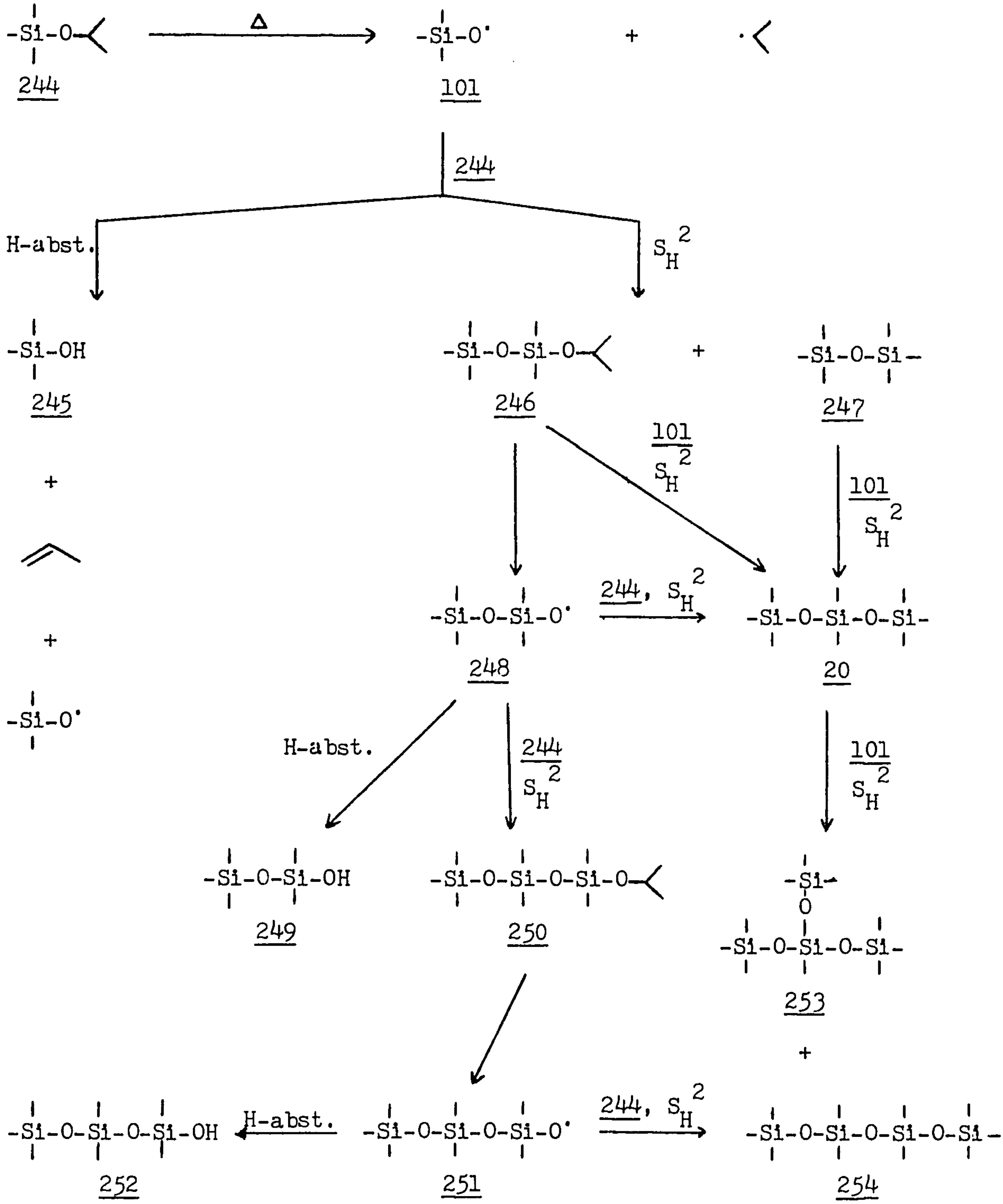


regenerating another siloxy radical.

Pyrolysis of *i*-propoxytrimethylsilane (244) resulted in competition between the hydrogen abstraction and the S_H^2 processes (Scheme 89). Trimethylsiloxy radical (101) underwent H-abstraction to form trimethylsilanol (245), but also underwent S_H^2 attack to form *iso*-propoxypentamethyldisiloxane (246) and hexamethyldisiloxane (247). The initially formed product 246 can undergo S_H^2 by 101, but it can also homolytically cleave to form the new siloxy radical 248. Radical 248 now has all the options available to it that siloxy radical 101 had, so this reaction scheme becomes extremely complicated.

All the products shown in Scheme 89, with the exception of 250, were seen in the pyrolysate. In view of the ease of decomposition of 244 and the very low yield of 246, it is not surprising that 250 was not observed. However, 250 probably was formed since it is the most likely precursor of 252 which was an identified product. In addition to the products shown in Scheme 89, small amounts of D_3, D_4, and D_5 were formed in the pyrolysis of 244. The propene formed in this reaction was not trapped, but was bubbled through a solution of Br_2 in CCl_4 and the 1,2-dibromopropane which resulted was identified. The yield of 1,2-dibromopropane was slightly less than the yield of trimethylsilanol. The observation of product 253 is very important since 253 cannot be rationalized by any silanone mechanism. While this observation does not eliminate the possibility of a silanone mechanism being operative in forming other products, it does add support to the postulate that all products arise via radical mechanisms. Table 10 lists the relative mole percentages for each of the major products.

Scheme 89



-Si-O-
Δ
-Si-O·
+
244
101
H-abst.
S_H 2
-Si-OH
245
-Si-O-Si-O-
246
+
-Si-O-Si-
247
-Si-O·
-Si-O-Si-O·
248
244, S_H 2
-Si-O-Si-O-Si-
20
-Si-O-Si-OH
249
-Si-O-Si-O-Si-O-
250
-Si-
O
-Si-O-Si-O-Si-
253
-Si-O-Si-O-Si-OH
252
-Si-O-Si-O-Si-O·
251
-Si-O-Si-O-Si-O-Si-
254

Table 10. Pyrolysis of $Me_3SiO\underline{i}Pr$ (244)

	244	245	247	249	246	D_3	20	252	D_4	253	254	D_5	Total mass % identified
450°	98.2	0.3	0.8	--	0.7	--	--	--	--	--	--	--	98.6
500°	96.9	0.8	1.2	--	1.1	0.1	--	--	--	--	--	--	98.2
550°	87.5	7.5	2.3	0.7	1.7	0.2	0.1	0.1	--	--	--	--	97.4
600°	51.5	40.1	3.0	2.7	1.0	0.4	0.2	0.5	0.2	0.1	0.2	0.1	89.9
650°	4.5	68.9	7.4	11.7	0.1	0.9	1.6	3.3	0.7	0.3	0.6	0.4	85.6

The pyrolysis of ethoxytrimethylsilane (255) resulted in a product mixture very similar to that obtained from pyrolysis of *i*-propoxytrimethylsilane. In this case also, there was competition between the S_H2 and hydrogen-abstraction processes so that a complicated reaction scheme is again proposed (Scheme 90). In the pyrolysis of 255, D_3 and D_4 are major products. S_H2 attack by siloxy radical 101 on D_3 and D_4 leads to formation of 258 and 259.

All the products shown in Scheme 90, with the exception of 257, were seen in the pyrolysate. Product 257, being the likely precursor to 252, was probably formed, but reacted under the conditions used. The ethylene which was formed was trapped with Br_2 and the 1,2-dibromoethane was identified. Table 11 lists the relative mole percentages for each of the major products.

In order to minimize the H-abstraction reaction, it was desirable to prepare a silyl ether which has no easily abstractable hydrogens. For this reason, we synthesized phenoxytrimethylsilane (260). Nitrogen-flow pyrolysis of 260 required very high temperatures and produced many products (Scheme 91). From product analysis, it appears that the H-abstraction reaction of siloxy radical 101 was eliminated, since no trimethylsilanol was formed; but the H-abstraction reaction of phenyl radical now is important. Apparently, the phenyl radical is a stronger hydrogen abstractor than is trimethylsiloxy radical.

All the products shown in Scheme 91 were observed in the pyrolysis of 260. It is important to note the presence of compound 264 which cannot be derived from a silanone mechanism. Once again, all products are consistent with radical mechanisms. Table 12 lists the relative

Scheme 90

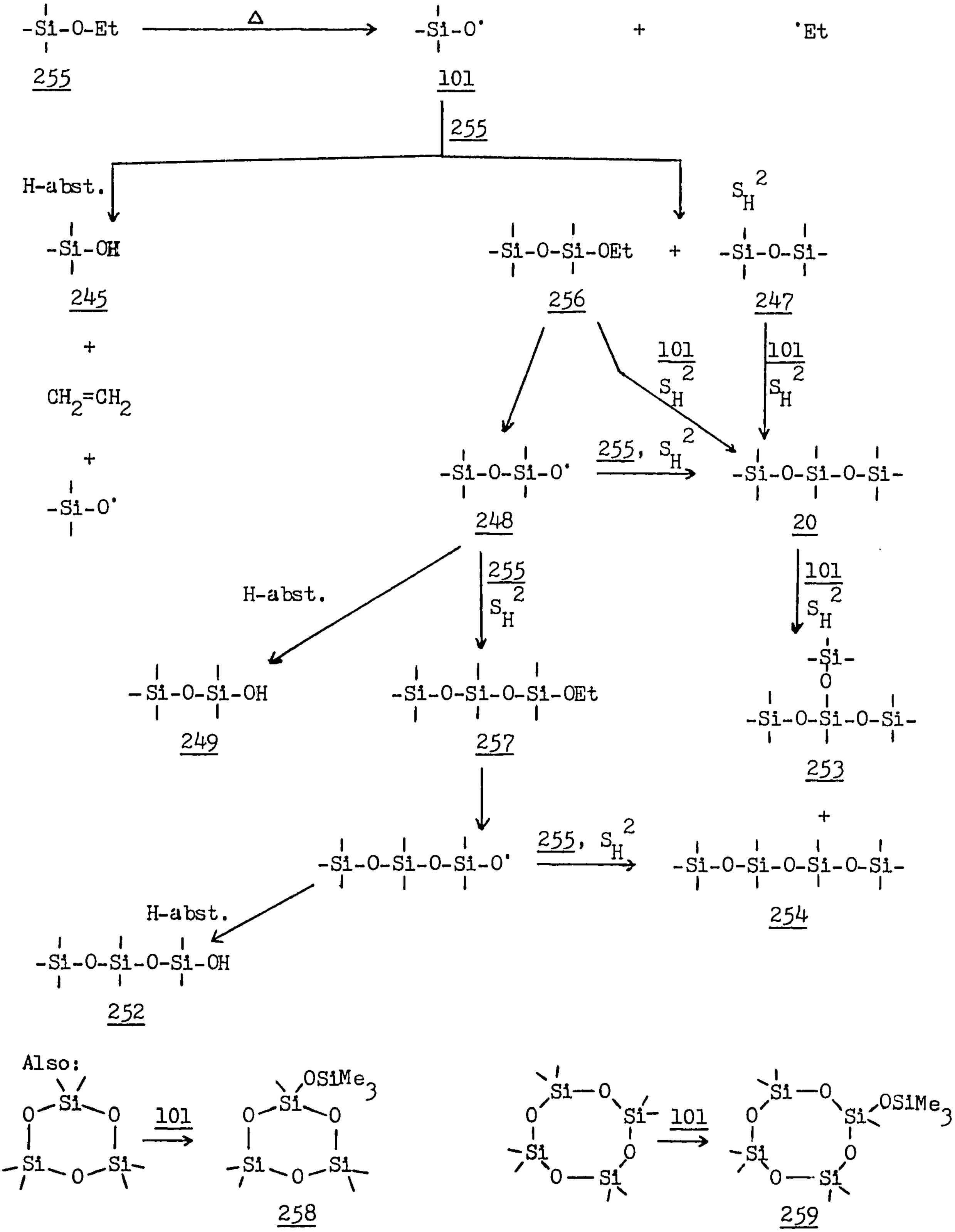
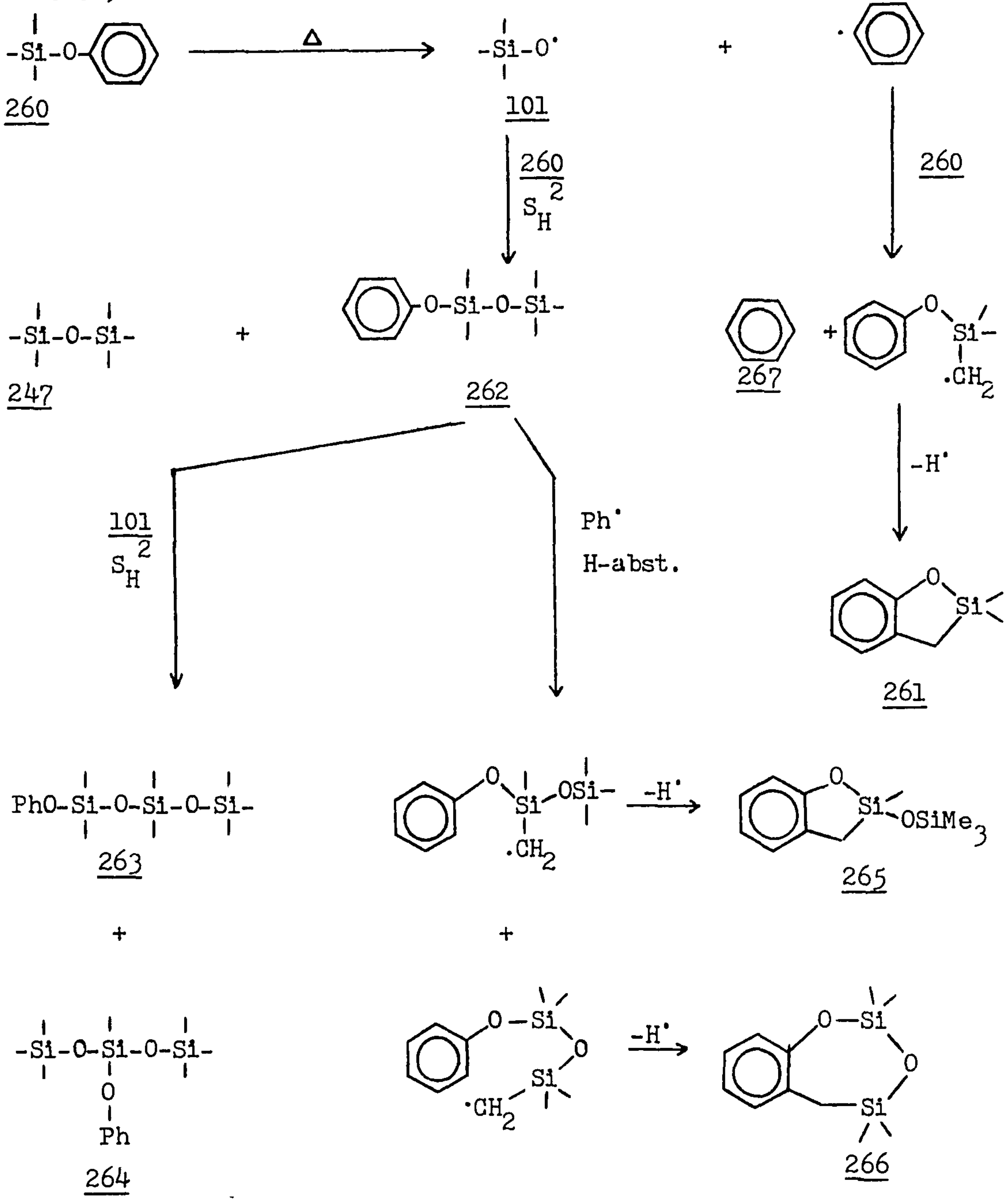

-Si-O-Et
255
Δ
-Si-O˙
101
+
˙Et
255
H-abst.
-Si-OH
245
+
CH$_2$=CH$_2$
+
-Si-O˙
-Si-O-Si-OEt
256
+
S$_H$2
-Si-O-Si-
247
101
S$_H$2
101
S$_H$2
-Si-O-Si-O˙
248
255, S$_H$2
-Si-O-Si-O-Si-
20
H-abst.
255
S$_H$2
101
S$_H$2
-Si-O-Si-OH
249
-Si-O-Si-O-Si-OEt
257
-Si-
O
-Si-O-Si-O-Si-
253
+
-Si-O-Si-O-Si-O˙
255, S$_H$2
-Si-O-Si-O-Si-O-Si-
254
H-abst.
-Si-O-Si-O-Si-OH
252
Also:
101
OSiMe$_3$
258
101
OSiMe$_3$
259

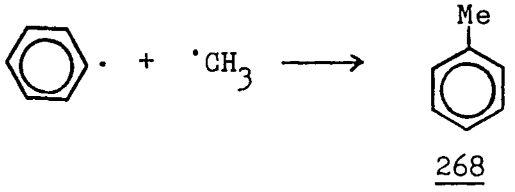
Table 11. Pyrolysis of Me$_3$SiOEt (255)

	255	245	247	249	256	D$_3$	20	252	258	D$_4$	253	254	259	D$_5$	Total mass % identified
500°	96.1	0.8	--	--	2.9	--	0.1	--	--	0.1	--	--	--	--	98.0
550°	93.9	1.4	--	--	4.3	--	0.2	--	0.1	0.1	--	--	--	--	97.4
600°	83.3	4.9	0.2	1.6	--	9.0	0.2	0.1	0.5	0.3	--	--	--	--	95.9
650°	66.8	13.4	0.8	4.7	--	10.7	0.4	0.9	1.4	0.4	0.1	0.1	0.3	0.1	94.3
700°	44.8	23.3	3.0	6.2	--	9.8	1.6	2.7	2.1	3.3	0.3	0.4	1.6	0.9	89.0

Scheme 91



Also:



mole percentages for each of the major products.

Phenoxytrimethylsilane (260) was prepared in order to minimize the H-abstraction reaction of the trimethylsiloxy radical. Instead, the H-abstraction reaction of the phenyl radical became a major process. It was expected that benzyloxytrimethylsilane (269) would be a better system to study since the benzyl radical, being more stable than the phenyl radical, should be less labile. At the same time, it was expected that the temperature required for the pyrolysis of 269 should be less than that of 260.

Pyrolysis of 269 revealed that the temperature required for decomposition was indeed decreased. Analysis of the products, however, indicated that this reaction was very similar to that of phenoxytrimethylsilane; that is, both the H-abstraction reaction of benzyl radical and S_H2 reaction of siloxy radical were important (Scheme 92). In addition, at higher temperatures, the pyrolysis of 269 produced a very complex reaction mixture including those products shown at the bottom of Scheme 92. Table 13 lists the relative mole percentages for each of the major products.

In all the silyl ethers studied thus far, the siloxy radicals which were formed had only methyl and alkoxy groups around the silicon. Yet it is known that in the corresponding carbonoxy radicals, the nature of the groups around the central carbon atom determines the course of the reaction. For example, the *t*-butyldimethylcarboxy radical forms the carbonyl compound more readily than does the *t*-butoxy radical by a factor of 10^3 (Scheme 93) (179). Therefore, we decided to pyrolyze benzyloxydimethyl-*t*-butylsilane (277).

Table 12. Pyrolysis of Me_3SiOPh (260)

	260	benzene	toluene	261	262	265 + 266	264	263	total mass % identified
550°	99.2	0.4	0.2	0.1	0.1	--	--	--	99.4
600°	97.3	0.6	0.6	0.7	0.8	--	--	--	99.0
650°	88.4	1.7	3.6	3.3	2.6	0.2	0.1	0.1	98.7
700°	70.1	3.6	10.2	8.5	6.2	0.8	0.4	0.2	97.7
750°	37.8	9.6	29.9	14.5	5.4	1.6	0.7	0.3	91.2

Scheme 92

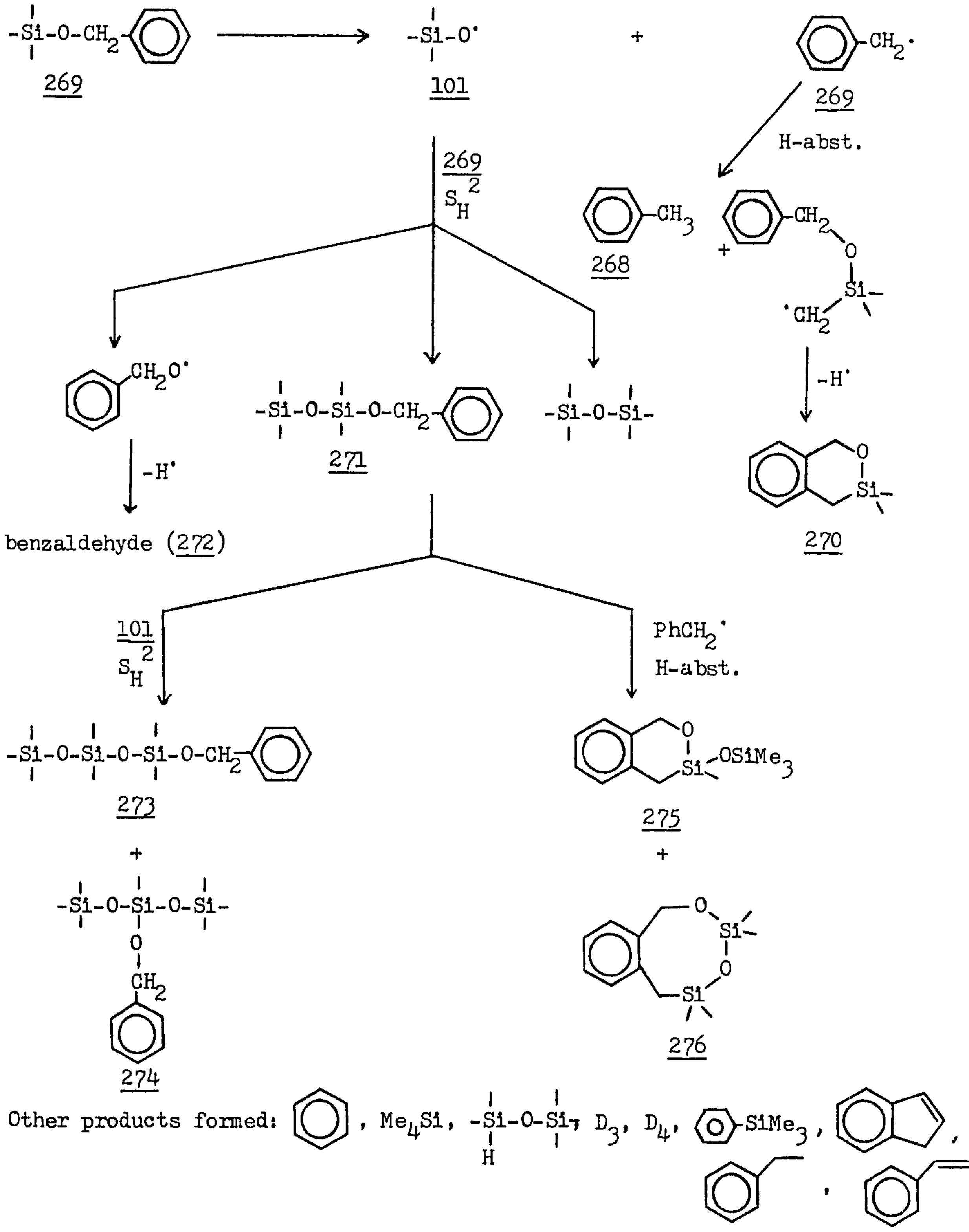
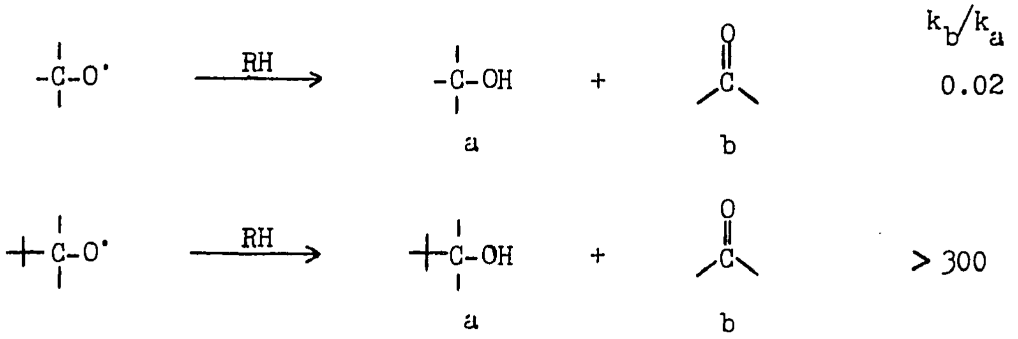

269
101
+
269
H-abst.
269
S_H2
268
+
-H'
270
benzaldehyde (272)
-H'
271
101
S_H2
PhCH$_2$'
H-abst.
273
+
274
275
+
276
Other products formed:
Me$_4$Si
D$_3$
D$_4$
SiMe$_3$

Table 13. Pyrolysis of Me_3SiOCH_2Ph (269)

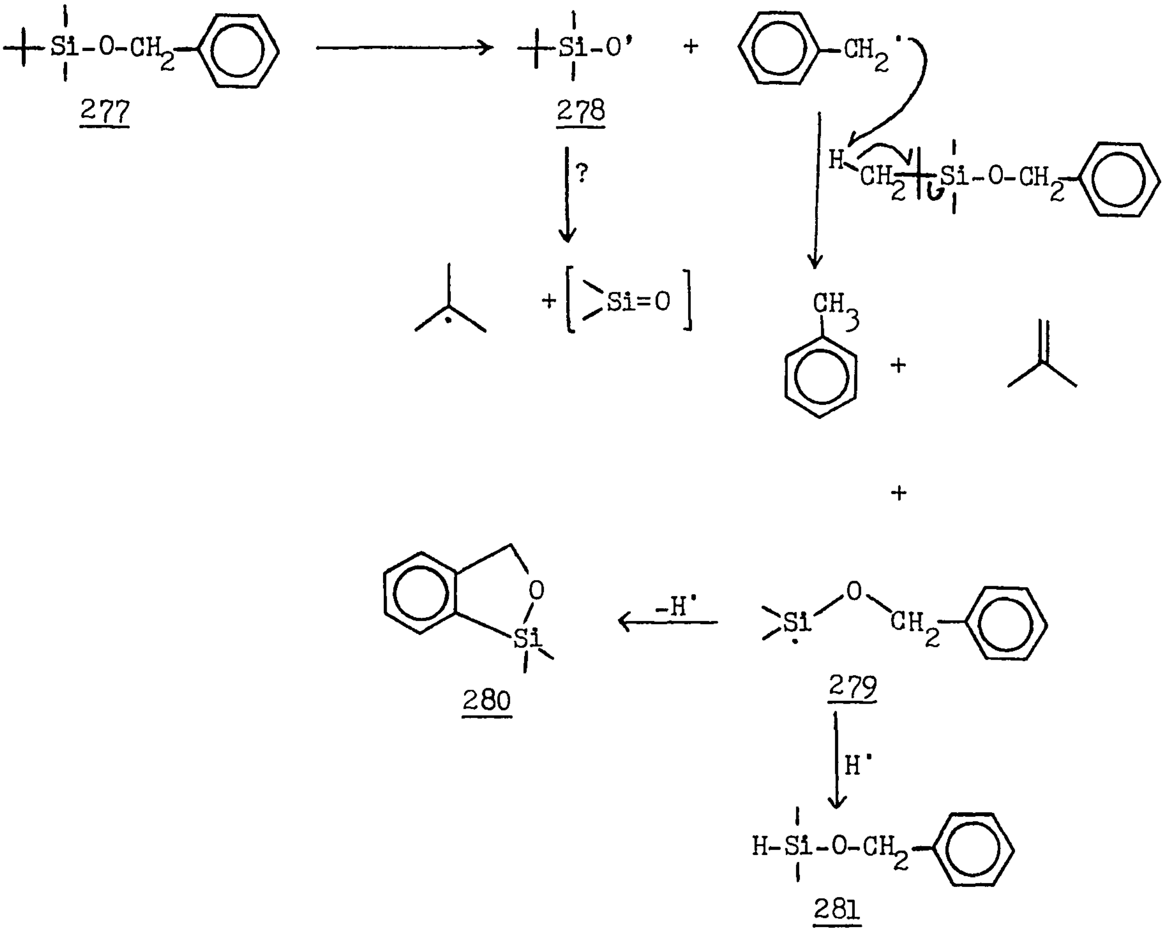
	269	benzene	toluene	272	271	275 + 276	Total mass % identified
500°	100.0	--	--	--	--	--	97.6
550°	99.2	0.3	--	--	0.5	--	95.9
600°	90.2	2.7	1.8	0.6	3.3	1.5	85.6
650°	42.0	16.9	13.7	5.9	11.7	9.7	77.3

Scheme 93



Scheme 94 shows the major reaction pathways. The hydrogen abstraction reaction of the benzyl radical to form toluene is a major process, probably due to the ready availability of easily abstractable hydrogens from the *t*-butyl group on 277. This same reaction also produces isobutylene and the silyl radical 279. Radical 279 has two options: intermolecular abstraction of a hydrogen atom to form silylhydride 281; and intramolecular cyclization with loss of a hydrogen atom to form 280. Analysis of the product ratios indicates that the intramolecular reaction is greatly preferred over the intermolecular one. The fate of the *t*-butyldimethylsiloxy radical (278) is not known. None of the silanol or disiloxane was observed, nor were any products arising from S_H2 attack by 278. However, small amounts of D_3 and D_4 were observed, which at least leaves the possibility of silanone formation open. Other minor products, shown at the bottom of Scheme 94, were also formed. (When a solution of 277 in D_4 was pyrolyzed at 600° C, the amount of D_5 formed was increased about three times over the amount which formed in the pyrolysis of D_4 by itself under these conditions.) Table 14 lists the relative mole percentages for each of the major products.

Scheme 94



Other products formed:

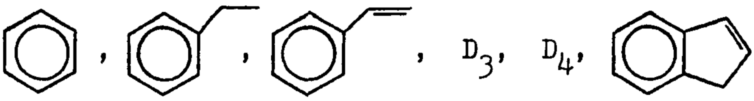


Table 14. Pyrolysis of t-BuSi(Me)$_2$OCH$_2$Ph (277)

	277		benzene	toluene	280	total mass % identified
500°	91.2	2.2	0.9	2.1	3.6	97.8
550°	84.2	3.4	1.3	4.5	6.5	97.3
600°	69.7	6.2	1.9	11.4	10.8	95.5
650°	35.1	14.3	4.2	28.6	17.8	82.9
700°	11.9	12.8	11.3	52.0	12.0	62.9

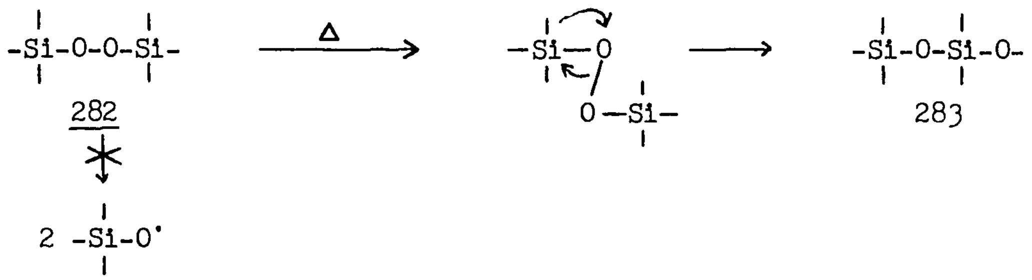
Silylperoxides and Bis(silyl)peroxides

While the pyrolysis of silyl ethers did result in the formation of siloxy radicals, the extreme conditions used were not conducive to the study of these radicals. What really was desired was a much milder method of formation of siloxy radicals. Silylperoxides and bis(silyl)-peroxides were expected to be the mild siloxy radical generators we hoped for.

The simplest bis(silyl)peroxide to prepare is bis(trimethylsilyl)-peroxide (282). This peroxide, like most bis(silyl)peroxides, is prepared by treating two equivalents of the appropriate chlorosilane with one equivalent of hydrogen peroxide. Since chlorosilanes are very sensitive to water, anhydrous hydrogen peroxide must be used. This problem is most easily circumvented by using hydrogen peroxide which is complexed with 1,4-diazabicyclo [2.2.2] octane (DABCO). The DABCO·2H$_2$O$_2$ complex is an easily formed crystalline solid which may be treated as anhydrous H$_2$O$_2$ (180, 181).

According to literature precedence (see Historical section), thermolysis of bis(trimethylsilyl)peroxide (282) would not be expected to form two trimethylsiloxy radicals. We confirmed this expectation by pyrolyzing 282 in the injection port of a GC, in a nitrogen-flow system, and in a sealed tube. In every case, pyrolysis of 282 led to nearly quantitative formation of pentamethylmethoxydisiloxane (283) (Scheme 95).

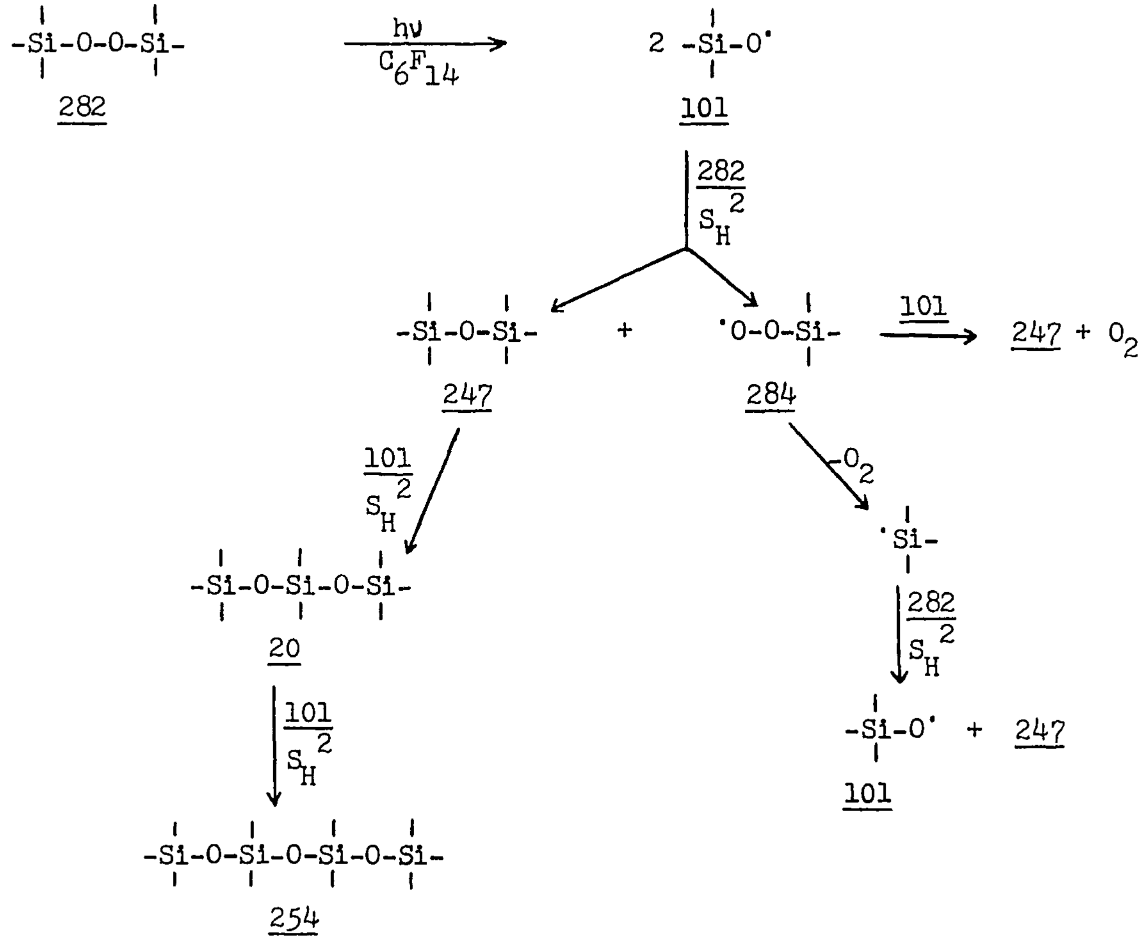
Scheme 95



However, there is evidence that bis(silyl)peroxides do generate siloxy radicals photochemically (see Historical section). Thus, we hoped that 282 would generate two trimethylsiloxy radicals (101). We knew already, from our pyrolyses of silyl ethers, that a very favorable reaction of trimethylsiloxy radical is H-abstraction to form trimethylsilanol (245). We wanted to avoid this reaction and see what 101 would do under conditions in which there were no easily abstractable hydrogens. For this reason, we decided to use a solvent which contained no hydrogens. While hexafluorobenzene had been successfully used as solvent for photolysis of the diazo compounds discussed earlier, for the photolysis of bis(silyl)peroxides it proved to be useless. The UV absorption band of the bis(silyl)peroxides falls in the same region where benzene absorbs, so that the solvent absorbs most of the energy and the peroxide reacts extremely slowly. We therefore chose perfluoro-n-hexane as our solvent.

Photolysis of a 7% solution of 282 in perfluoro-n-hexane for 3 hrs. (2537Å) resulted in the formation of hexamethyldisiloxane (247) (81%), octamethyltrisiloxane (20) (15%), and decamethyltetrasiloxane (254) (2%). Scheme 96 illustrates the S_H2 mechanism used to explain

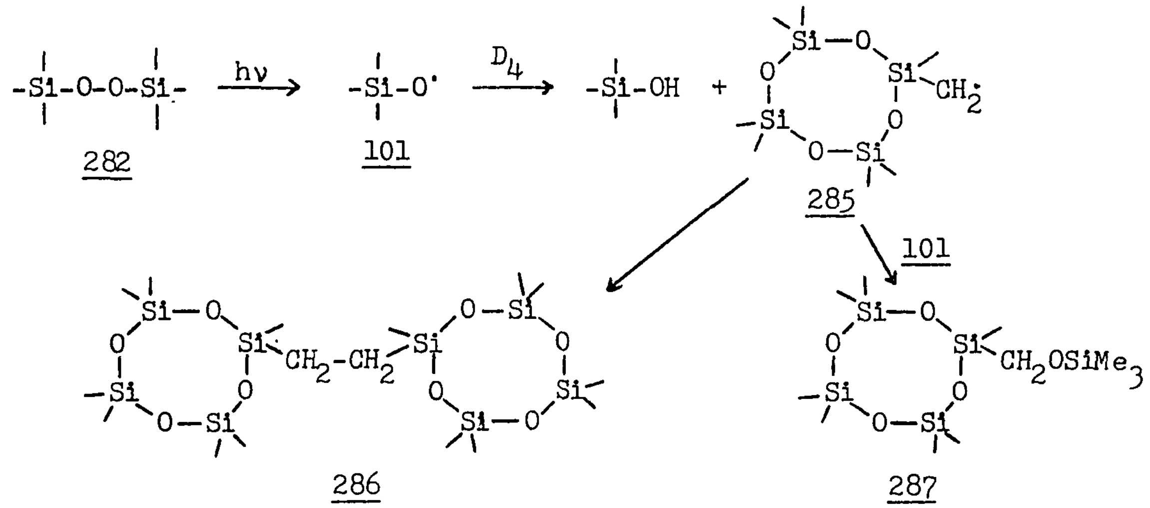
Scheme 96



the near quantitative formation of linear siloxanes. Irradiation of peroxide 282 forms siloxy radical 101 which undergoes S_H^2 attack on 282 to form disiloxane 247 as well as peroxy radical 284. It is expected that 284 would undergo loss of O_2 to form trimethylsilyl radical which after attacking 282 forms 101 and 247. Alternatively, attack by 101 on 284 forms 247 and O_2. S_H^2 attack on the disiloxane leads to the trisiloxane, and attack on trisiloxane leads to tetrasiloxane. There was no silanol observed in this reaction, although as will be shown in later reactions, trimethylsilanol is stable under these conditions; thus disiloxane 247 did not originate from condensation of trimethylsilanol. It was also demonstrated that 247, under these conditions, does not produce 20 or 254. Thus, it appears that the S_H^2 reaction, which was also observed in the thermal reactions of silyl ethers, is the only reaction occurring photochemically. When this reaction was carried out in cyclopentane, the major products were cyclopentene, bicyclopentane, and hexamethyldisiloxane. No trisiloxane 20 was observed, which indicates that the disiloxane probably resulted from condensation of trimethylsilanol. Trimethylsilanol could not be seen by GC since it falls under the cyclopentane peak.

To further demonstrate that the trimethylsiloxy radical does not produce dimethylsilanone, the photolysis of 282 was carried out using D_4 as solvent. This reaction resulted in the formation of no D_5, indicating that there was no silanone formed. Instead, D_4 simply provided hydrogens for the siloxy radical to abstract to form trimethylsilanol and radical 285 (Scheme 97). The radical 285 then dimerized to form the major product 286, or coupled with 101 to form a

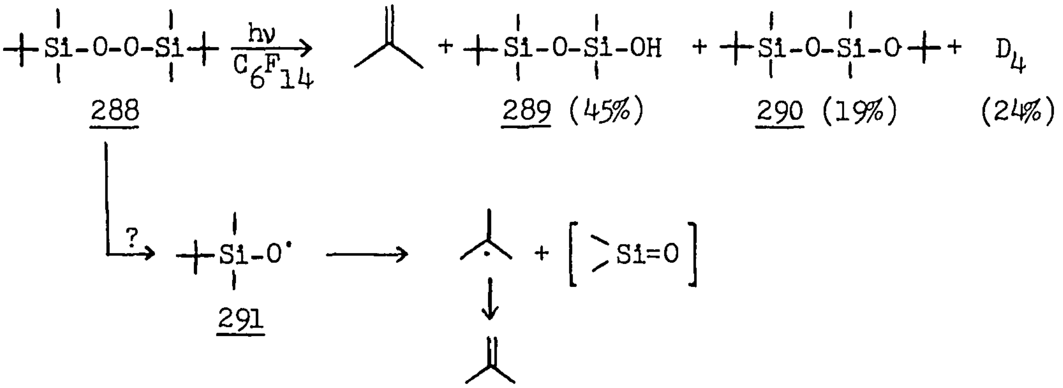
Scheme 97



minor product 287. The second major product was hexamethyldisiloxane 247. While some of 247 could arise from condensation of trimethylsilanol, most of it must have come from the competing S_H2 process shown in Scheme 96 since a substantial amount of the trisiloxane was also formed. The exact yields were not determined in this reaction.

Bis(dimethyl-t-butylsilyl)peroxide (288) was prepared by the reaction between dimethyl-t-butylchlorosilane and DABCO·2H_2O_2. The substitution of a t-butyl group for a methyl resulted in a drastic change in the reaction of the peroxide (Scheme 98). Photolysis of 288 in perfluoro-n-hexane produced silanol 289 (49%), t-butoxydisiloxane 290 (19%), and D_4 (24%), as well as a large but undetermined amount of isobutylene. Product 290 is the expected thermal rearrangement product with the t-butyl being expected to migrate in preference over a methyl group. The presence of isobutylene and D_4 suggest the exciting possibility that photolysis of peroxide 288 produced siloxy radical

Scheme 98

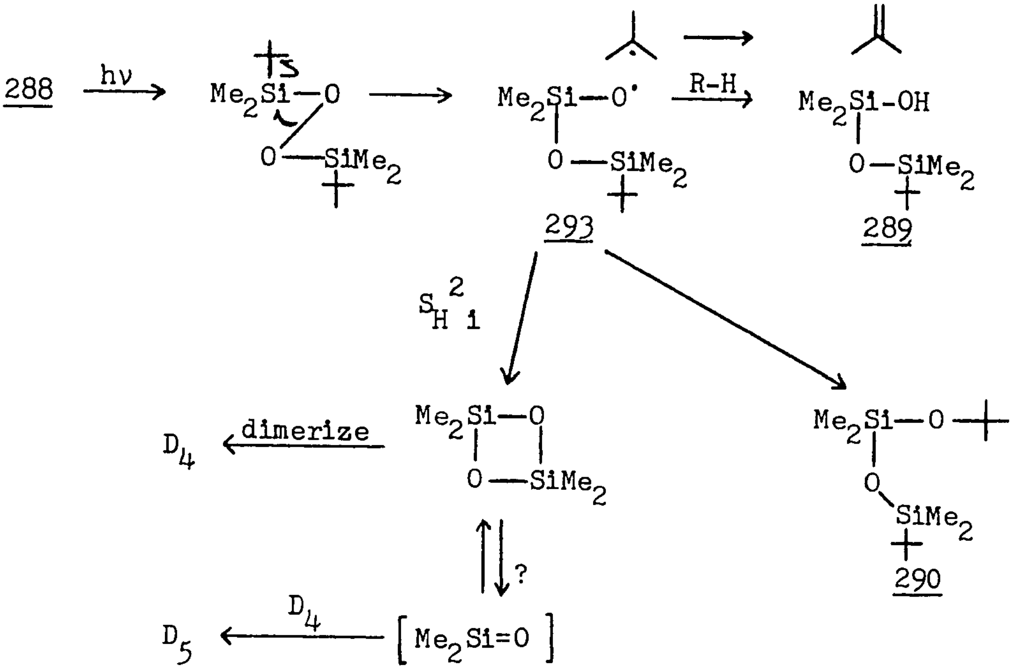


291 which underwent loss of a t-butyl radical to form dimethylsilanone. This silanone scheme suffers at least one serious flaw, that is, it is unreasonable to expect dimethylsilanone to cyclooligomerize to exclusively form D_4 with no D_3. Very careful analysis of the product solution by GCMS does show a trace of D_5 (<1%), but no D_3. This scheme also fails to explain the formation of the major product 289.

Photolysis of 288 in cyclopentane gave results very similar to photolysis in perfluoro-n-hexane. Again the major products were 289, 290, D_4, and isobutylene. In this case, a small amount (<5%) of dimethyl-t-butylsilanol (292) was formed as well as a trace of t-butylcyclopentane. The fact that cyclopentane behaves as an inert solvent indicates that photolysis of 288 does not result in homolytic cleavage to form siloxy radical 291, since 291 should easily abstract a hydrogen from the solvent to yield a silanol.

Trapping experiments also show that photolysis of 288 yields little, if any, silanone. When a solution of 288 in cyclopentane containing a 3-fold excess of dimethyldimethoxysilane was photolyzed, the major products and yields were essentially unchanged, although a small yield (<5%) of the expected silanone insertion products, sym-dimethoxytetramethyldisiloxane was formed. Photolysis of 288 in D_4 resulted in the formation of D_5 in only 2% yield while the major products remained as before. Thus, it is clear that the silanone mechanism is inadequate in describing the reaction of 288. Instead, we postulate the mechanism shown in Scheme 99. The first step in this

Scheme 99



mechanism resembles the thermal rearrangement process of bis(silyl)-peroxides except that instead of migrating to the adjacent oxygen, the t-butyl group is simply lost as a radical, resulting in the formation of the new siloxy radical 293. While unprecedented, this step is not difficult to rationalize since there is a strong, thermodynamic driving force for it to occur, the formation of a new silicon-oxygen bond. Recombination of siloxy radical 293 with t-butyl radical, leads to product 290. It is also possible that at least some of 290 arises via a concerted rearrangement.

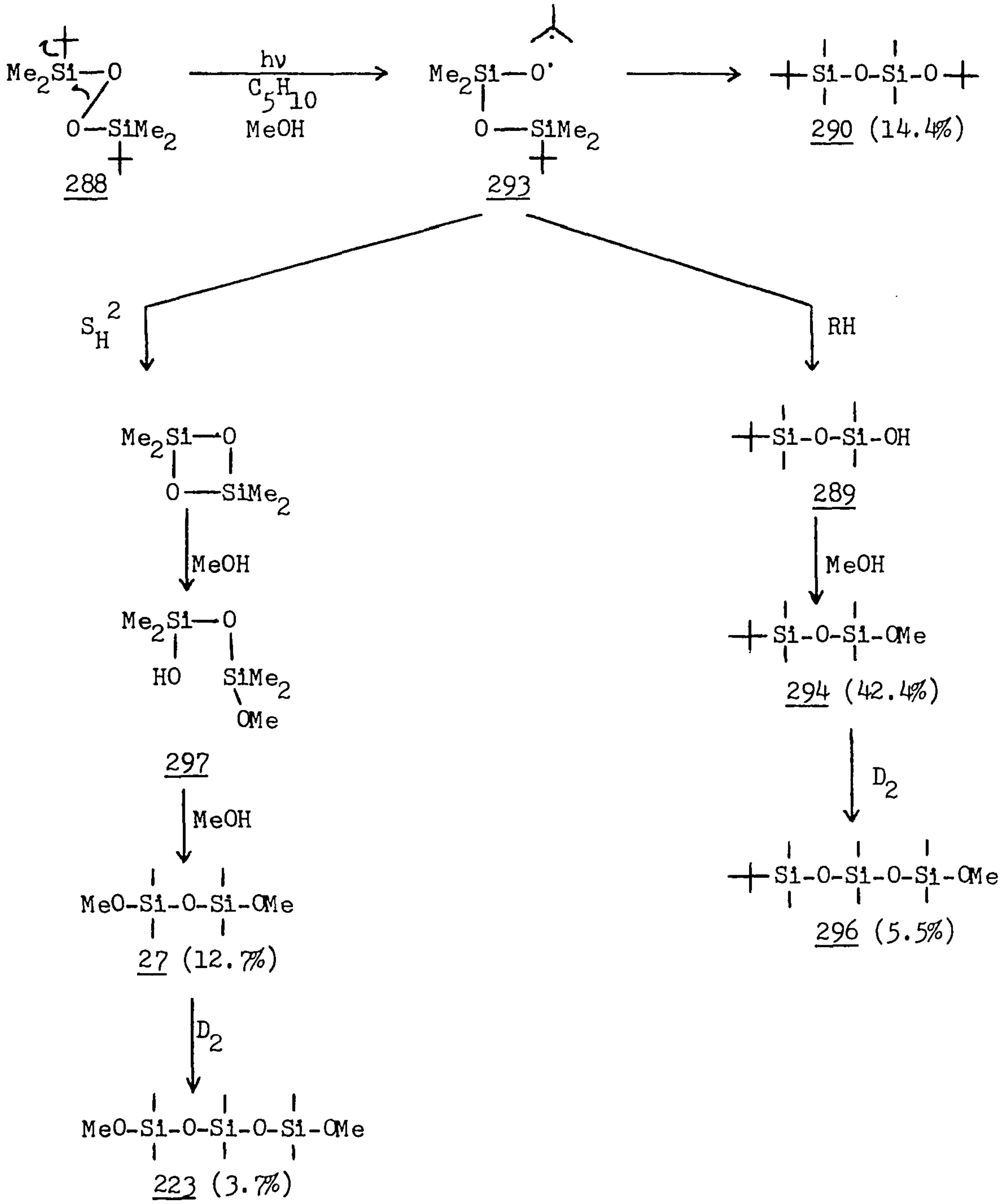
Having learned something about siloxy radicals from the pyrolysis of silyl ethers, we would predict that 293 would undergo two different reactions, H-abstraction and S_H^2 attack. There is a ready availability of hydrogen in this reaction from either solvent or t-butyl groups so that the H-abstraction reaction might be expected to predominate. This reaction leads to formation of silanol 289 which is indeed the major product. (A mechanism could also be written in which 288 forms 289 and isobutylene in a concerted fashion.) Siloxy radical 293 is set up to undergo an S_H^2 displacement of a t-butyl group intramolecularly. Such an attack produces D_2. Being a very reactive species, D_2 simply dimerizes, thus forming D_4 without requiring the formation of any D_3. It is also possible that D_2 serves as a precursor to dimethylsilanone, or at least serves as a silanone transfer agent, thus accounting for the low yields of silanone insertion products observed when silanone traps were present.

In an attempt to trap D_2, peroxide 288 was photolyzed in the presence of methanol. It was hoped that methanol would add across D_2 to form a linear methoxy disiloxane. The major products of this photolysis were isobutylene, 290 (14.4%), sym-dimethoxytetramethyldisiloxane (27, 12.7%), and 1-t-butyl-3-methoxy-1,1,3,3-tetramethyldisiloxane (294, 42.4%). Several minor products were also identified.

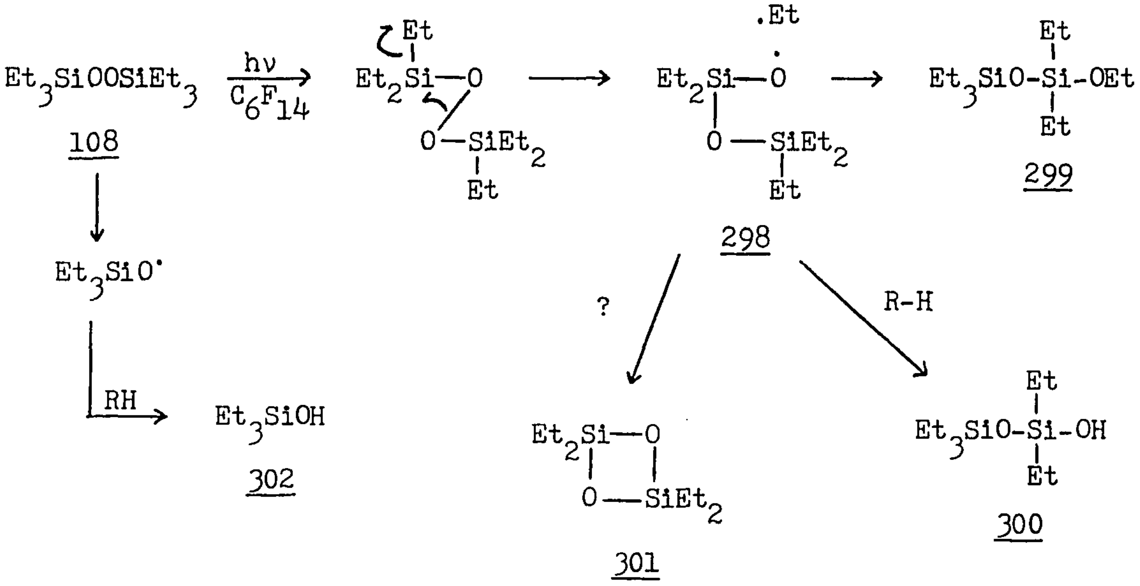
All these products are shown in Scheme 100. Siloxy radical 293 has all the same options available to it: it can recombine with a t-butyl radical to form 290; it can abstract a hydrogen to form silanol 289; and it can undergo internal S_H2 attack to form D_2. Silanol 289 is observed in only trace amounts, but the major product 294 results from condensation of 289 with the excess methanol which was present. Trapping of D_2 with methanol is expected to form silanol 297, which was observed in trace amounts. However, 297 should also condense with methanol to form 27 which was observed in 12.7% yield. Equally important is the observation that the photolysis of 288 in the presence of methanol yielded no D_4. Therefore, whatever was the precursor to D_4 has been effectively trapped with methanol, while at the same time, the reaction with methanol produced a new product, 27. Both of these results are most easily explained by invoking the intermediacy of D_2.

A dramatic change in mechanism has been observed in going from bis(trimethylsilyl)peroxide (282) to bis(t-butyldimethylsilyl)peroxide (288). Photolysis of 282 results in exclusive homolytic cleavage to form two trimethylsiloxy radicals while photolysis of 288 results in essentially no homolytic cleavage to produce t-butyldimethylsiloxy radicals. It might be expected that bis(triethylsilyl)peroxide (108) would react by both pathways. As Scheme 101 indicates, this was found to be the case. Homolytic cleavage to form triethylsiloxy radical is evidenced by the formation of triethylsilanol 302 as well as a low yield of triethylethoxy silane (303). No products were observed to indicate that the triethylsiloxy radical underwent S_H2 attack as did the trimethylsiloxy radical. The intramolecular reaction pathway to form

Scheme 100


hν
C5H10
MeOH
288
293
290 (14.4%)
SH2
RH
289
MeOH
294 (42.4%)
D2
296 (5.5%)
MeOH
297
MeOH
27 (12.7%)
D2
223 (3.7%)

Scheme 101



siloxy radical 298 was also followed as evidenced by the formation of silanol 300. There was no evidence that 298 underwent the internal S_H2 reaction to form the ethyl analog of D_2 (301) since no products arising from 301 were observed. This internal S_H2 attack should be less favorable here than in the case where a *t*-butyl radical is eliminated.

When the photolysis of 108 was carried out in cyclopentane, the major products were the same, but the yields changed, with the biggest change being the increase of triethylsilanol. This result also indicates that both reaction pathways were being followed. Table 15 reports the yield data for photolysis of 108 in both perfluoro-*n*-hexane and cyclopentane.

The dual reaction pathways were also demonstrated when peroxide 108 was photolyzed in D_4. The products and yields for this reaction

Table 15. Photolysis of bis(triethylsilyl)peroxide (108)

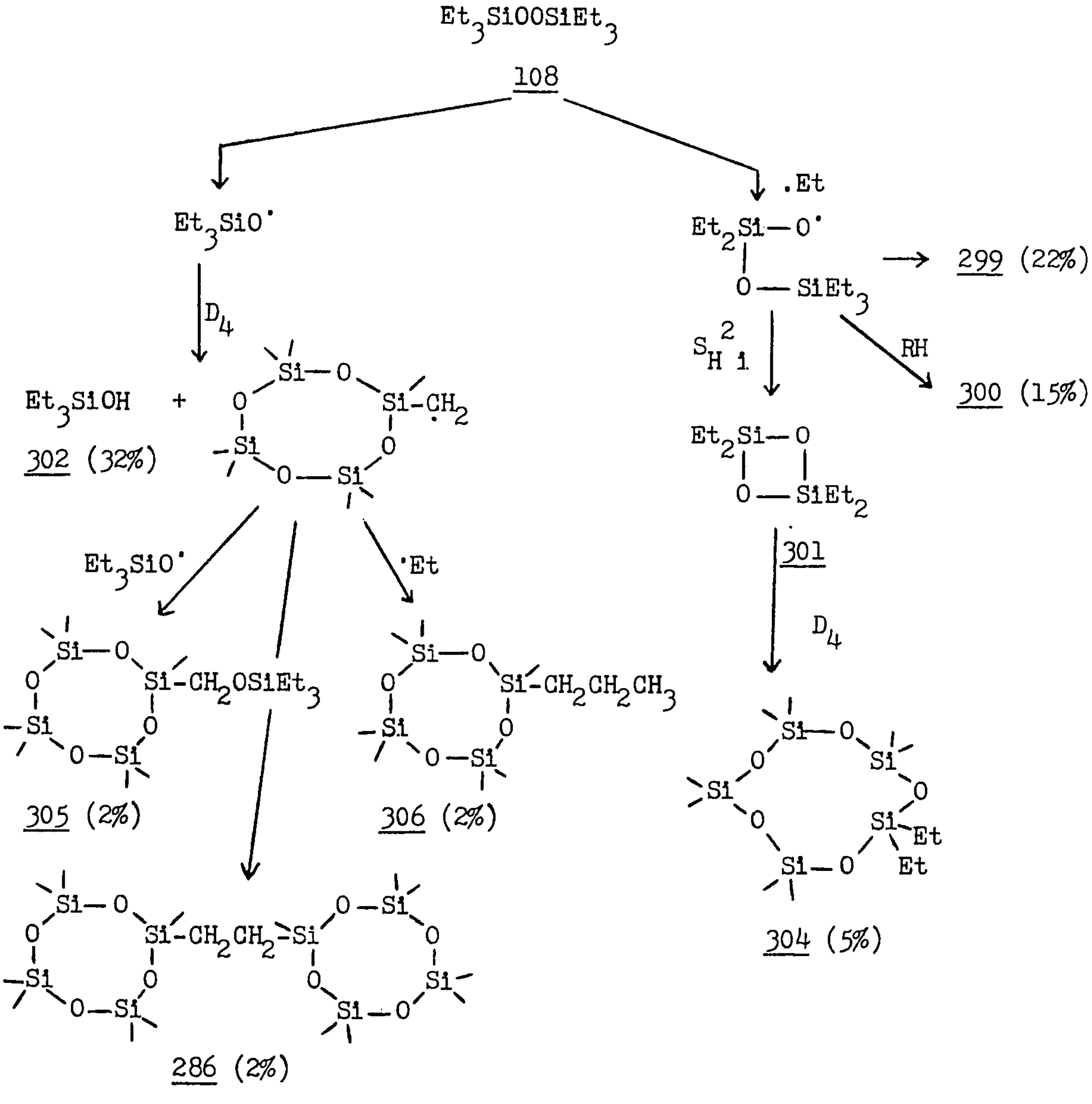
solvent	302	303	300	299	335[a]	total
C_6F_{14}	31.2	0.4	10.7	39.4	--	81.7%
C_5H_{10}	60.2	0.9	12.8	12.9	1.0	87.8%

[a] Product 335 is triethylsiloxycyclopentane.

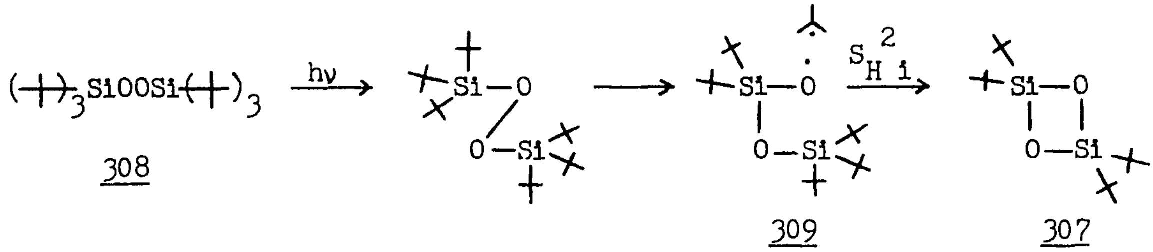
are given in Scheme 102. In this case, there was evidence for the intermediacy of the ethyl analog of D_2 as a low yield of the diethylsilanone insertion product into D_4 was observed by GCMS.

Since D_2 appears to be extremely reactive, although it is probably stable with regards to unimolecular decomposition, it was decided to modify the D_2 system in a way which would decrease its reactivity. The extreme reactivity of D_2 appears to result from intermolecular reactions; therefore it was decided to replace the methyl groups of D_2 with sterically bulky groups which should make intermolecular attack more difficult. The target molecule which we desired is 2,2,4,4-tetra-t-butyl-2,4-disila-1,3-dioxetane (307). In order to form 307 by a route analogous to that used for the generation of D_2 itself, the precursor, bis(tri-t-butylsilyl)peroxide (308) must first be prepared. Scheme 103 shows the proposed route for generation of 307. Even before attempting to carry out this scheme, we were aware that the possibility of failure was great. The problems become evident by observing siloxy radical 309. One reaction of siloxy radicals is hydrogen abstraction to form a silanol. This was, in fact, the major reaction which occurred

Scheme 102


Et3SiOOSiEt3
108
Et3SiO·
D4
Et3SiOH
302 (32%)
+
Si-CH2
.Et
Et2Si—O·
O — SiEt3
299 (22%)
RH
300 (15%)
S_H 2 i
Et2Si—O
O—SiEt2
301
D4
304 (5%)
Et
Et
Et3SiO·
·Et
Si-CH2OSiEt3
305 (2%)
Si-CH2CH2CH3
306 (2%)
Si-CH2CH2-Si
286 (2%)
Si
O

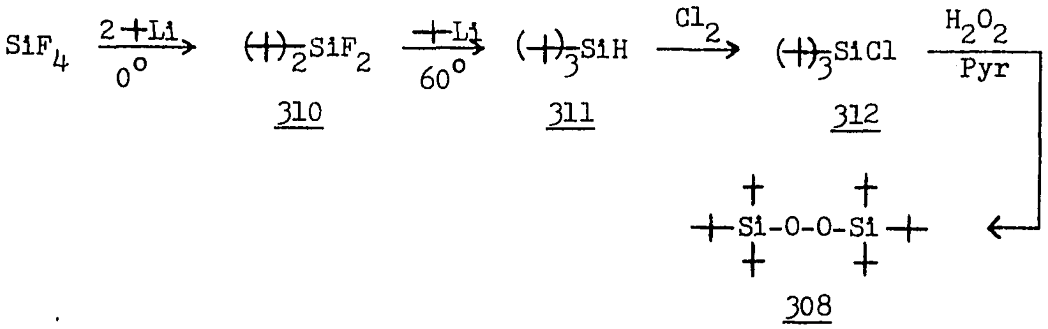
Scheme 103



during photolysis of peroxide 288. In the case of peroxide 308, there are six *t*-butyl groups (as opposed to two in 288) providing a great source of easily abstractable hydrogens so that the H-abstraction reaction of siloxy radical 309 may be the sole reaction. At the same time, the internal S_H^2 attack of 309 would appear to be unlikely since the attack must occur at a silicon atom which bears three extremely bulky *t*-butyl groups. Despite these possible problems, we set out to synthesize peroxide 308.

The first route used to synthesize 308 is shown in Scheme 104.

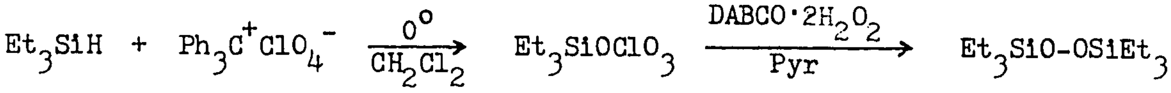
Scheme 104



Tri-*t*-butylsilane (311) was prepared by the method of Dexheimer and Spialter (182, 183). Tri-*t*-butylchlorosilane (312) was prepared by simply bubbling Cl_2 through a solution of 311 in CCl_4 at 0° C. Silyl chloride 312 proved to be an extremely inert compound. It did not react with H_2O or with H_2O_2. (Several forms of H_2O_2 were used, including 30% H_2O_2 in H_2O, 90% H_2O_2, and DABCO·$2H_2O_2$.) In general, silyl iodides are much more reactive than silyl chlorides, so tri-t-butyliodosilane (313) was prepared by treating 311 with I_2 (184). The iodosilane also proved to be inert to both H_2O and H_2O_2.

Realizing that what was needed was a better leaving group than iodide, we turned our attention to the perchlorate. Silyl perchlorates have been demonstrated to be extremely reactive and useful in the preparation of sterically hindered silanes (185, 186). In order to test the unprecedented reaction of a silyl perchlorate with hydrogen peroxide, we first prepared triethylsilyl perchlorate (314). Silyl perchlorate 314 was easily prepared by the exchange reaction of triethylsilane and trityl perchlorate (185). Treatment of an ether solution of triethylsilyl perchlorate with DABCO·$2H_2O_2$ resulted in the formation of bis(triethylsilyl)peroxide (108) in 74% yield (Scheme 105). In the same

Scheme 105

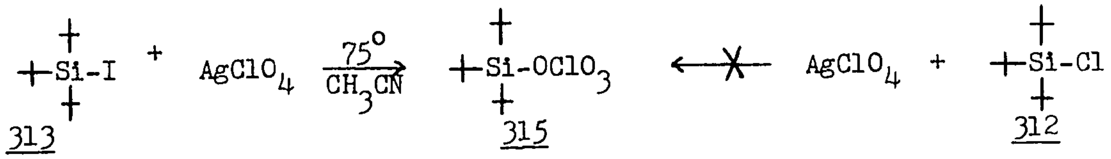


$$Et_3SiH + Ph_3C^+ClO_4^- \xrightarrow[CH_2Cl_2]{0^\circ} \underset{\underline{314}}{Et_3SiOClO_3} \xrightarrow[Pyr]{DABCO\cdot 2H_2O_2} \underset{\underline{108}}{Et_3SiO\text{-}OSiEt_3}$$

reaction, hexaethyldisiloxane was formed in 20% yield. Since the disiloxane was probably formed by hydrolysis of the perchlorate by slightly wet DABCO·$2H_2O_2$ complex, the reaction between triethylsilyl perchlorate and H_2O_2 can be considered to form peroxide 108 nearly quantitatively.

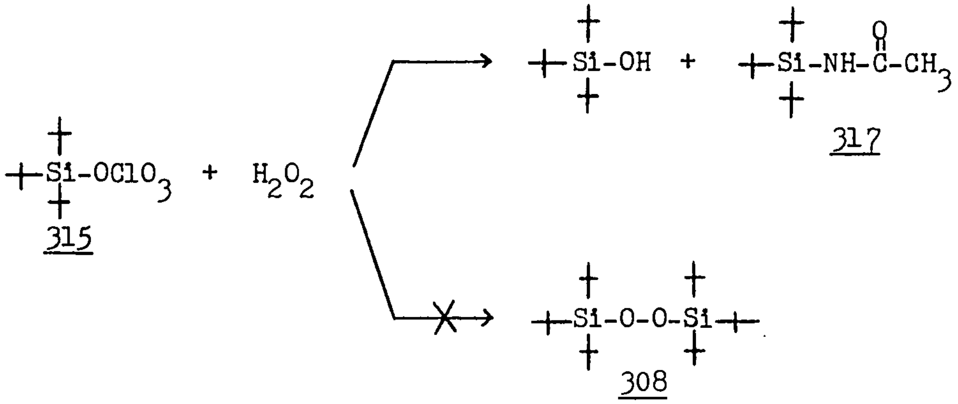
With precedent established for the reaction between silyl perchlorates and H_2O_2, we investigated tri-t-butylsilyl perchlorate (315). Perchlorate 315 was prepared by treatment of tri-t-butylsilyliodide with silver perchlorate (185), as shown in Scheme 106. The analogous reaction

Scheme 106



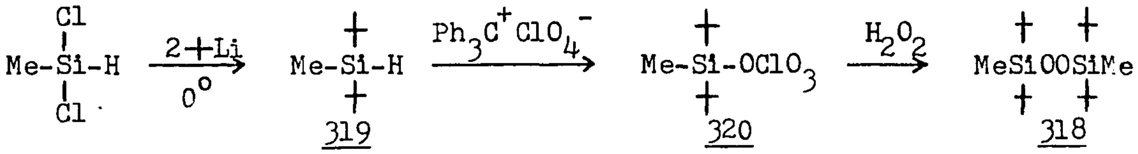
of tri-t-butylchlorosilane with silver perchlorate produced only a small amount of perchlorate 315. The chlorosilane was essentially inert under the reaction conditions used. Since perchlorate 315 was prepared in nearly quantitative yield, it was used without further purification after drying under vacuum for 13 hrs. To an ether solution of tri-t-butylsilyl perchlorate at 0° C was added H_2O_2 (either DABCO·$2H_2O_2$ or 90% H_2O_2). Since perchlorate 315 could be observed by GC, it was possible to follow its rate of disappearance. Addition of one equivalent of H_2O_2 resulted in the formation of two new products while only about half of the starting perchlorate disappeared. This clearly showed that the added H_2O_2 was not reacting with two molecules of perchlorate as is required to form bis(tri-t-butylsilyl)peroxide (308). Addition of a second equivalent of H_2O_2 resulted in the complete disappearance of the starting perchlorate. The two products were identified as tri-t-butylsilanol (316) and silyl amide 317 (Scheme 107). Product 317 probably arises from reaction between acetonitrile and tri-t-butylsilyl perchlorate followed by oxidation with the added H_2O_2. Evidently, perchlorate 315 forms some type of complex with acetonitrile since drying under vacuum for extended periods of time did not remove all the acetonitrile. When tri-t-butylsilyl perchlorate was sublimed (100°, 0.05 Torr), all the acetonitrile was removed. Treatment of sublimed 315 with H_2O_2 resulted in the formation of only tri-t-butylsilanol. Again, only about half of the perchlorate disappeared when one equivalent of H_2O_2 was added.

Scheme 107



It was apparent that the presence of six t-butyl groups provided so much steric bulk that the synthesis of bis(tri-t-butylsilyl)peroxide was impossible, at least by the approaches which were utilized. It was thought that the steric problem could be greatly relieved by replacing one t-butyl group on each silicon by a methyl. The proposed route for synthesis of bis(di-t-butylmethylsilyl)peroxide (318) is shown in Scheme 108. Di-t-butylmethylsilane (319) and di-t-butylmethylsilyl perchlorate (320) were prepared by the methods of Barton and Tully (185).

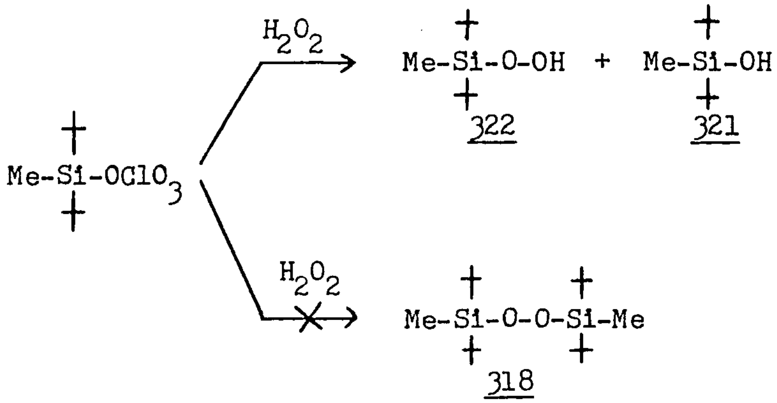
Scheme 108



319 320 318

The reaction of di-t-butylmethylsilyl perchlorate with H_2O_2 was similar to that of tri-t-butylsilyl perchlorate with H_2O_2. In this case, also, one equivalent of H_2O_2 was not sufficient to react with all the starting perchlorate. The major identified product was di-t-butylmethylsilanol (321, Scheme 109). Several minor products were observed by GC, and

Scheme 109

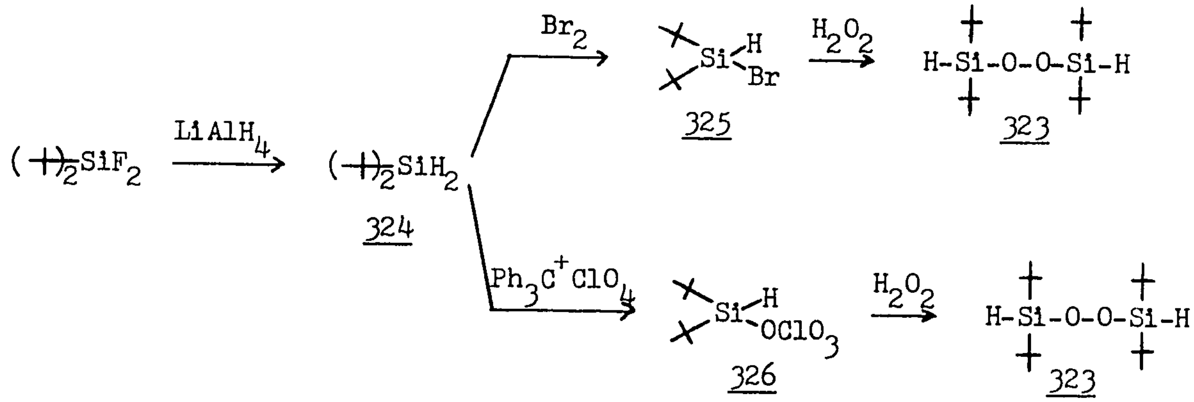


322 321 318

although none of them were positively identified, one appeared to be di-t-butylmethylsilyl hydroperoxide (322). While yields were not determined for this reaction, silanol 321 appeared to account for approximately three-fourths of all the products as determined by GC.

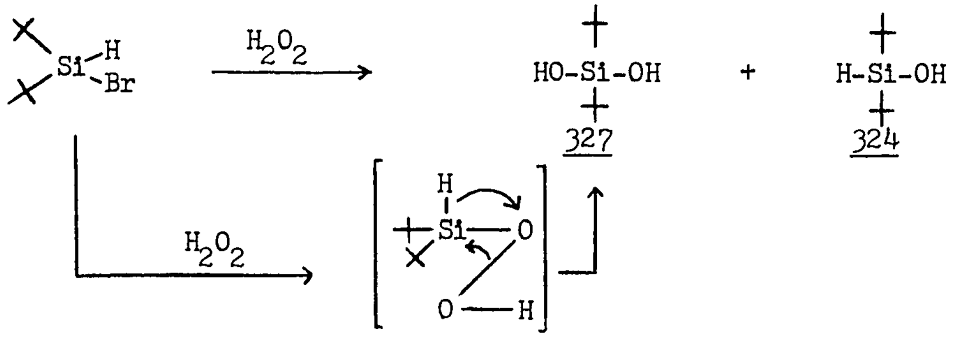
Again, our failure to prepare silyl peroxide 318 was attributed to an excess of steric bulk. It was decided to attempt the synthesis of one more tetra-t-butyl substituted bis(silyl)peroxide. This target molecule, bis(di-t-butylsilyl)peroxide (323) was chosen, in part, due to the ease with which the precursors can be made. Scheme 110 outlines two routes by which we proposed to synthesize 323. Di-t-butylsilane

Scheme 110



(324) was prepared by the $LiAlH_4$ reduction of di-t-butyldifluorosilane (186). Treatment of 324 with one equivalent of bromine resulted in the formation of di-t-butylbromosilane (325) in a distilled yield of 82%. The bromosilane 325 was easily hydrolyzed by H_2O to di-t-butylsilanol (324), so reaction with H_2O_2 to form the bis(silyl)peroxide at least seemed possible. However, when one equivalent of H_2O_2 was added to an ether solution of di-t-butylbromosilane, only about half of the starting material disappeared. The two products which formed were identified to be di-t-butylsilanol (324) and di-t-butylsilanediol (327). The diol probably results from an intramolecular rearrangement of the initially formed hydroperoxide (Scheme 111). This rearrangement must occur with migration of a hydrogen from silicon to oxygen. While the yields were

Scheme 111

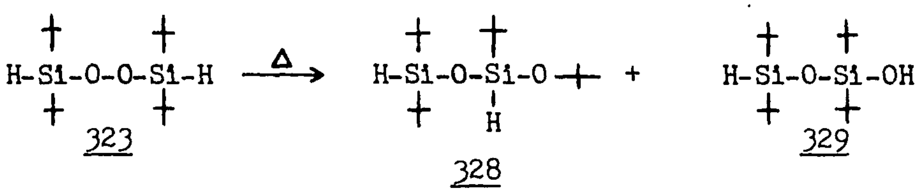


not determined, 327 and 324 were the only products formed. The approximate ratio of 324 to 327 was 1:2.

Although di-t-butylbromosilane did not serve as a precursor to bis(di-t-butylsilyl)peroxide (323), it still appeared likely that 323 could be made from di-t-butylsilyl perchlorate. The reason for this hope was that a large part of the steric problems had been relieved, relative to the tri-t-butyl system, as evidenced by the ease of hydrolysis of di-t-butylbromosilane while the tri-t-butylsilyl halides are inert to H_2O. Thus, treatment of an ether solution of di-t-butylsilyl perchlorate with H_2O_2 resulted in the near quantitative formation of bis(silyl)peroxide 323. A small amount of di-t-butylsilanol was also formed, but this was easily removed by column chromatography. The isolated yield of 323 after chromatography was 87%.

Analysis of bis(silyl)peroxide 323 by GC revealed that upon thermolysis, it rearranged to give two different products (Scheme 112). Both products come from intramolecular rearrangement of 323. When this rearrangement occurs with migration of a t-butyl group, product 328

Scheme 112



results, while if a hydrogen migrates, silanol 329 results. Table 16 lists the relative yields of 328 and 329 for a variety of temperatures.

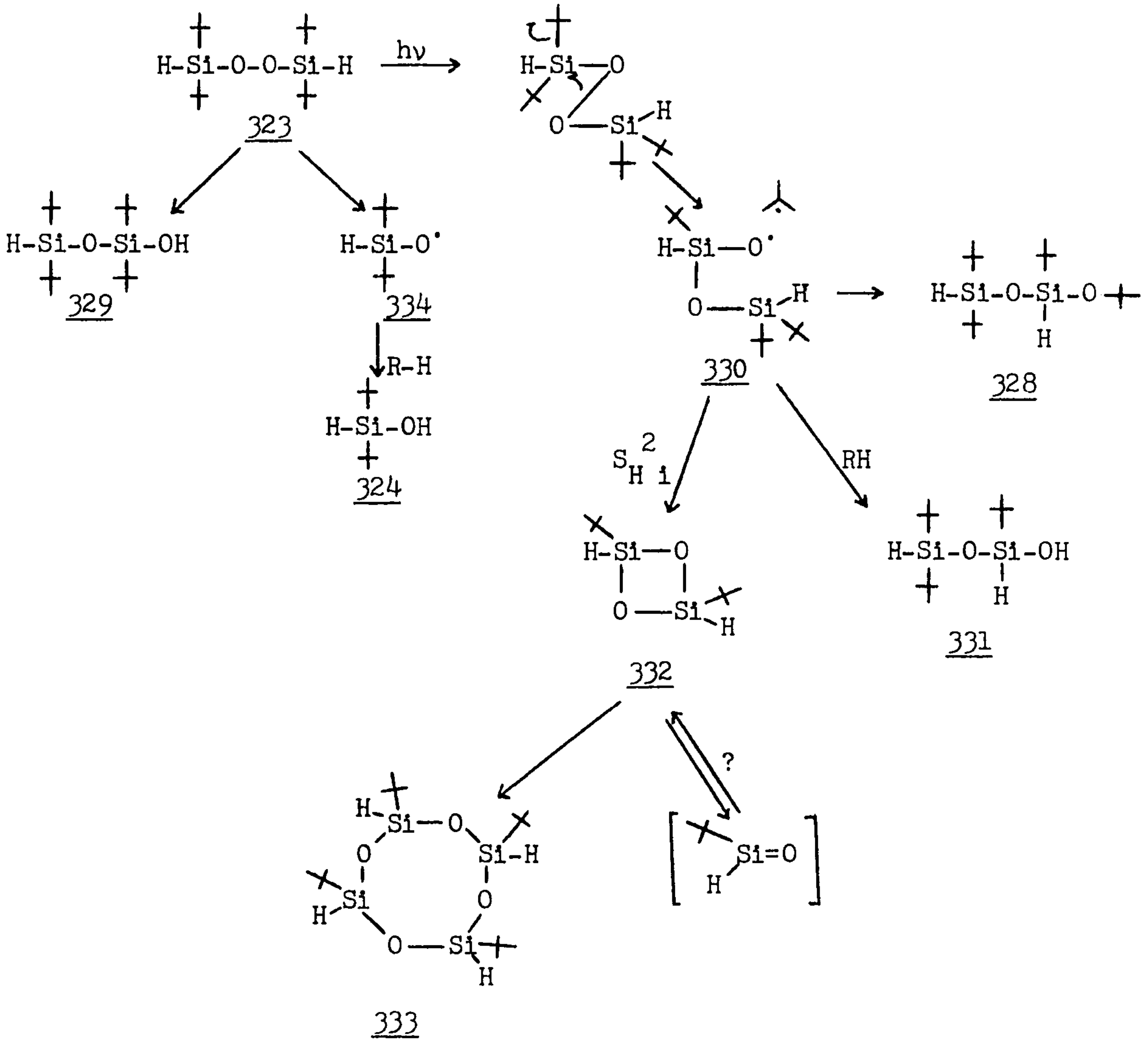
Table 16. Gas phase pyrolysis of 323

temperature	328 : 329
180°	29 : 71
240°	39 : 61
300°	45 : 55

The absolute yields were not determined, but as no other major products were observed, it was assumed that 323 formed 328 and 329 quantitatively. These pyrolyses were carried out in the injection port of a GC. From analysis of these results, it is apparent that 329 is the thermodynamically favored product. This was also found to be the case for the sealed-tube pyrolysis of 323 in heptane at 125° C. This reaction was complete within 3 hrs. and the ratio of 329 to 328 was approximately 8:1. These results show that hydrogen is a better migrating group than is *t*-butyl for the thermal reaction of bis(silyl)peroxides. The relative migratory aptitude of hydrogen in this type of reaction has never been reported in the literature.

The results from photolysis of bis(di-t-butylsilyl)peroxide (323) indicate that a variety of reaction pathways are followed, including the intramolecular S_H^2 process which forms an analog of D_2 (Scheme 113).

Scheme 113



Photolysis of 323 in an inert solvent (C_6F_{14}) results in some homolytic cleavage to form di-*t*-butylsiloxy radical (334) as evidenced by the observation of di-*t*-butylsilanol (324) as a reaction product. The yield of silanol 324 increases slightly from 7.9% to 9.7% upon changing solvents from perfluoro-*n*-hexane to cyclopentane (Table 17).

The concerted intramolecular rearrangement of peroxide 323 which occurred thermally must also occur photochemically as evidenced by the formation of silanol 329. The other rearrangement product, 328, was also formed in this photolytic reaction, but by assuming that hydrogen migration is favored over *t*-butyl migration, as was the case thermally, it is concluded that most of product 328 arises from a reaction pathway other than the concerted intramolecular rearrangement. Using cyclopentane as solvent changes the yield of product 329 very little (Table 15), indicating that the formation of this product does not involve radical intermediates.

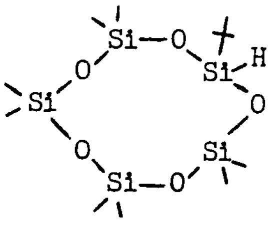
The intramolecular radical reaction to form siloxy radical 330 is used to explain the formation of products 328, 331, and 333. Recombination of siloxy radical 330 with *t*-butyl radical produces 328, while H-abstraction by 330 produces 331. Intramolecular S_H2 attack by 330 produces the D_2 analog 332 which upon dimerization forms the observed product 333. As shown from the data in Table 17, changing the solvent from perfluoro-*n*-hexane to cyclopentane increases the H-abstraction reaction of the siloxy radical at the expense of the other two pathways.

In order to further probe the reaction mechanisms, bis(silyl)-peroxide 323 was photolyzed using D_4 as solvent. The results were

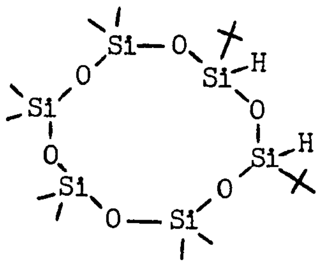
Table 17. Yield data from photolysis of bis(di-*t*-butylsilyl)peroxide (323)

solvent	324	331	328	333	320	336	337	338	Total yield
C_6F_{14}	7.9	15.2	18.4	33.6	6.4	--	--	--	81.5%
C_5H_{10}	9.7	30.5	8.8	25.7	5.5	--	--	--	80.2%
D_4	9.6	31.4	9.1	12.6	5.8	4.9	5.5	--	78.9%
C_5H_{10} + MeOH	12.4	25.6	10.1	--	5.9	--	--	21.4	74.7%

nearly identical to those obtained when cyclopentane was the solvent except that the yield of product 333 was reduced by approximately half. Since 333 results from dimerization of the D_2 analog 332, these results indicate that D_4 acts as a trap for 332, albeit, not a very effective trap as approximately half of the 332 still dimerizes. The two trapped products which were formed, although not positively identified, have masses corresponding to insertion of one and two units of t-butylsilanone and are assigned structures 336 and 337. These two trapped



336

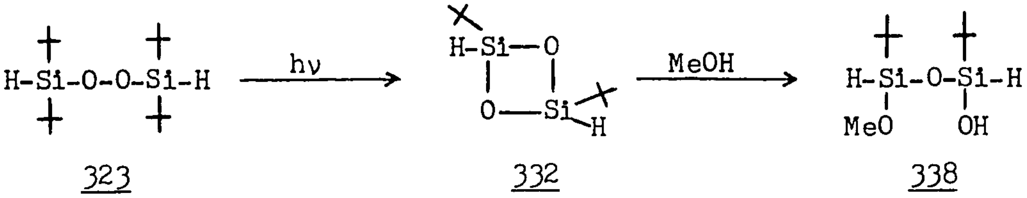


337

products were formed in approximately equal amounts which indicates that not only can the D_2 analog 332 be trapped by D_4, but 332 also acts as a transfer agent of t-butylsilanone or actually forms t-butylsilanone.

Just as was D_2 itself, so the analog 332 was efficiently trapped by methanol. Photolysis of peroxide 323 in a cyclopentane solution containing a 3-fold excess of methanol resulted in complete trapping of 332 so that the analog of D_4, 333, was no longer formed. Instead, the methanol-trapped product, 338, was formed in 21.4% yield (Scheme 114). The presence of a bulky t-butyl group on silicon greatly reduces the condensation reaction of the initially formed silanol with excess methanol. Only a trace of the condensation products of silanols

Scheme 114

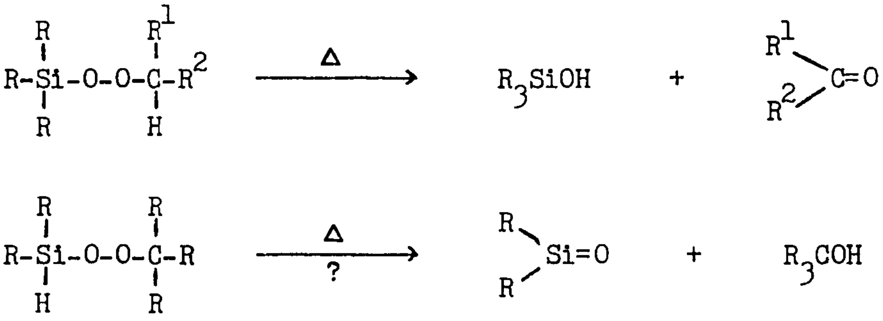


338 and 331 with methanol was observed. The silanols which have two *t*-butyl groups around silicon, 324 and 329, did not undergo any condensation with methanol.

Erroneous Report of Silanone Generation

Very recently, the preparation of a silanone from thermolysis of a silyl peroxide has been reported (187). It is well-known that thermolysis of silyl peroxides of the formula $R_3SiOOC(H)R^1R^2$ proceeds to form considerable amounts of ketones $R^1R^2C{=}O$ (95); thus, Yablokov and coworkers (187) suggested that thermolysis of silyl peroxides of the formula $R_2(H)SiOOOR_3$ might proceed to form silanones $R_2Si{=}O$ (Scheme 115). To

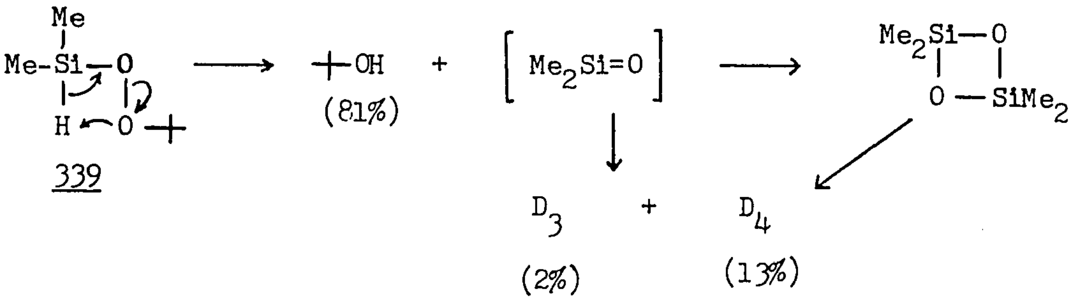
Scheme 115



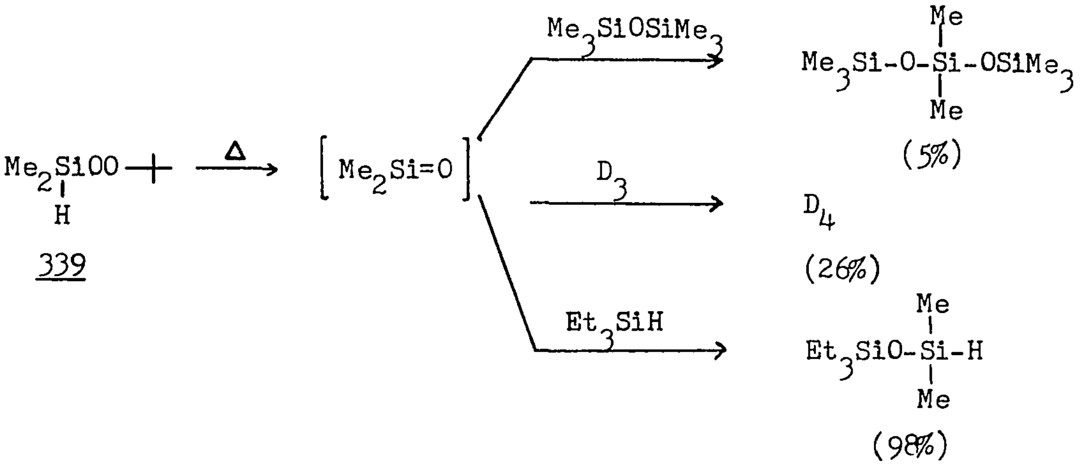
this end, the Russian group prepared a series of silyl peroxides all containing a hydrogen on silicon. All these peroxides behaved similarly, so that only the simplest one, dimethylsilyl-t-butylperoxide (339) will be discussed.

Thermolysis of a 4-5% solution of 339 in nonane at 160° C resulted in the formation of t-butanol (81%), D_3 (2%), and D_4 (13%). Yablokov and coworkers explained these results in terms of a silanone mechanism as shown in Scheme 116. Since the yield of D_4 was much higher than that of D_3, the formation of some D_4 was attributed to the dimerization of D_2. While it is possible to write other mechanisms to account for these products, any bimolecular mechanism is eliminated by the kinetic studies which demonstrated that the rate of disappearance of starting material (339) was first order. Furthermore, Yablokov and coworkers carried out trapping experiments which were consistent with the intermediacy of dimethylsilanone. Hexamethyldisiloxane, D_3, and triethylsilane were used as traps, with the results shown in Scheme 117. The quantitative trapping with triethylsilane is particularly interesting in view of the report by Wulff (7) that dimethylsilanone could not be trapped by tri-

Scheme 116



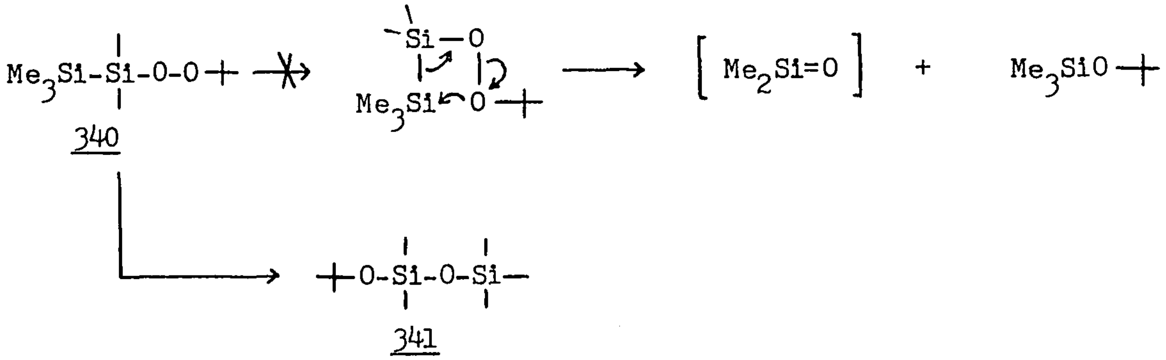
Scheme 117



ethylsilane. If this silyl peroxide of Yablokov and coworkers actually is a precursor to a silanone, structural modifications could be made to enhance silanone formation. One such modification is the replacement of the hydrogen on silicon by a trimethylsilyl group to produce silyl peroxide 340. According to Yablokov and coworkers' mechanism, peroxide 340 would be expected to produce dimethylsilanone much more readily than peroxide 339, since in this case the reaction involves breaking a weaker bond (Si-Si versus Si-H) and forming a stronger bond (Si-O versus H-O) (Scheme 118). However, when peroxide 340 was heated, NMR analysis indicated that clean conversion to the expected thermal rearrangement product had occurred (188).

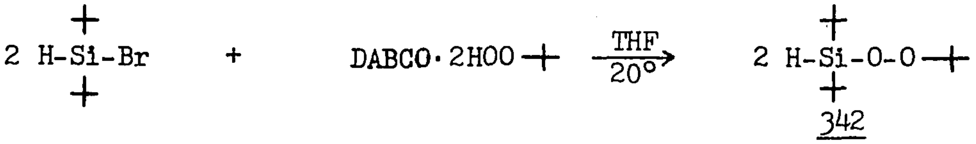
Another structural modification is the replacement of the methyl groups on silicon by t-butyl groups while leaving the silyl hydride. Di-t-butylsilyl-t-butylperoxide (342) was prepared by treating di-t-

Scheme 118



butylbromosilane with DABCO·2HOO—+ (Scheme 119). (The complex between DABCO and *t*-butylhydroperoxide is a convenient form of anhydrous *t*-butylhydroperoxide just as DABCO·2H_2O_2 is a convenient form of anhydrous hydrogen peroxide (189, 190).) If Yablokov and coworkers' mechanism were followed, thermolysis of peroxide 342 would produce di-*t*-butylsilanone. We thought that the bulky *t*-butyl groups might be sufficiently stabilizing to allow for the observation of the tetra-*t*-butyl analog of D_2.

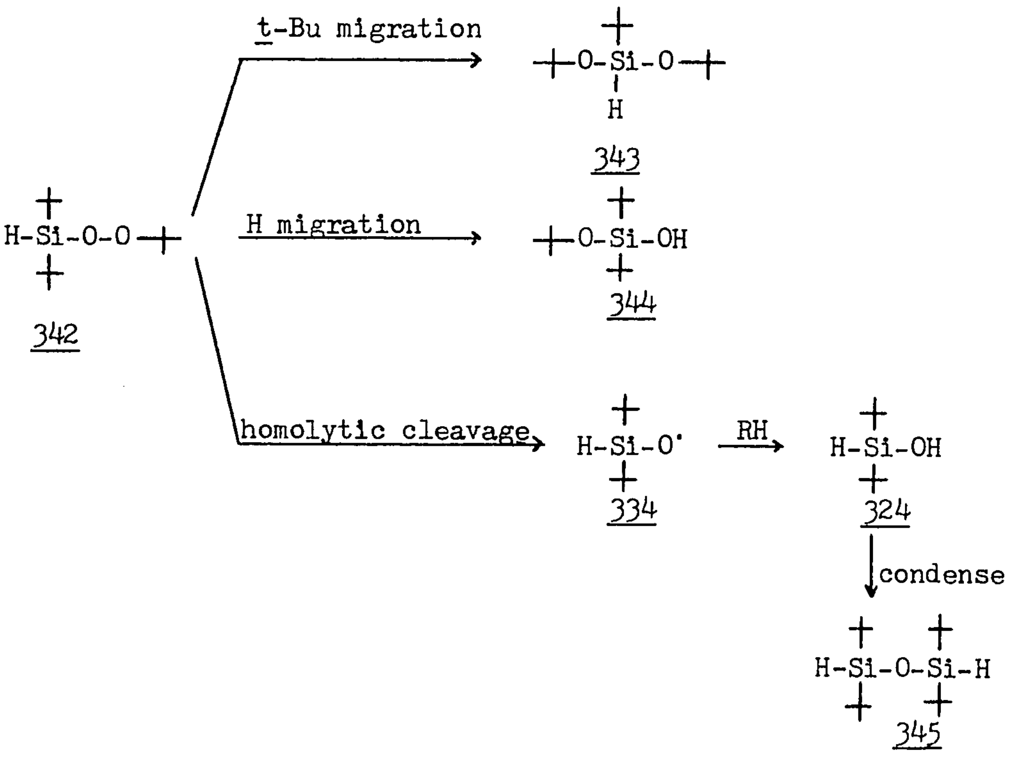
Scheme 119



$$2\ \mathrm{H{-}\underset{+}{\overset{+}{Si}}{-}Br} \quad + \quad \mathrm{DABCO\cdot 2HOO{-}+} \xrightarrow[20^{\circ}]{\mathrm{THF}} 2\ \mathrm{H{-}\underset{+}{\overset{+}{Si}}{-}O{-}O{-}+}$$

Thermolysis of 342 in octane at 150° C resulted primarily in the normal intramolecular rearrangement processes to form products 343 and 344 (Scheme 120). Hydrogen migration results in formation of 344 while *t*-butyl migration forms 343. In addition, some homolytic cleavage to form siloxy radical 334 occurred as evidenced by the observation of

Scheme 120



silanol 324 and disiloxane 345 which were formed. There was no evidence for the formation of di-t-butylsilanone. Triethylamine was found to catalyze this reaction. Thermolysis of 342 with 0.1 equivalents of triethylamine present increased the rate of reaction by approximately 4-fold while changing the yields of the products only slightly (see Table 18). It is seen again from this yield data that hydrogen is an excellent migrating group. If the statistical factor of two t-butyls to one hydrogen is included, the hydrogen is here a better migrator than a t-butyl.

Since neither of our structural modifications of Yablokov and co-

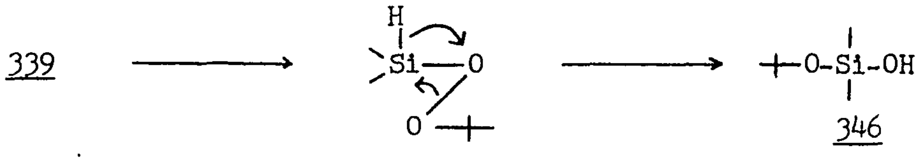
Table 18. Thermolysis of di-t-butylsilyl-t-butylperoxide (342)

	Time	343	344	324	345	Total yield
no Et_3N added	3 hrs.	41.7	30.8	2.5	5.3	80.3%
0.1 eq. Et_3N added	1 hr.	40.7	28.4	11.8	4.3	85.2%

workers' peroxide gave any evidence for the formation of a silanone, we are faced with the problem of explaining the exceptional behavior of peroxide 339. The question is, why does peroxide 339 apparently behave in a manner completely different from the normal, expected, and precedented reactions of silyl peroxides? The most likely answer is that Yablokov and coworkers are mistaken and peroxide 339 does react in the usual manner.

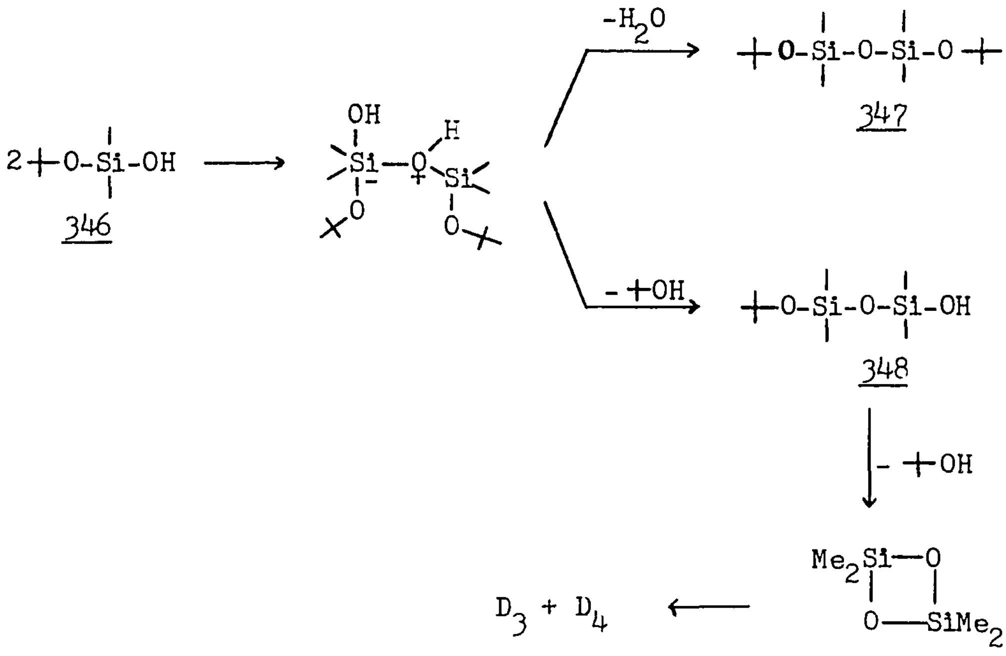
As discussed in the Historical section, silyl peroxides are known to homolytically cleave to form siloxy radicals if there are no good migrating groups on silicon. If there is a good migrating group on silicon, the intramolecular rearrangement reaction will compete with homolytic cleavage. We have presented evidence to show that hydrogen is a very good migrating group, even better than a t-butyl group. Therefore, it would be expected that a major reaction pathway in the thermolysis of 339 would be the intramolecular rearrangement to form dimethyl-t-butoxy silanol (346) (Scheme 121). We thought silanol 346

Scheme 121



could also be the precursor to D_3 and D_4. Silanols are known to readily condense with elimination of water to form disiloxanes. Alkoxy silanols present the possibility of condensation occurring with loss of an alcohol to form disiloxanes. Since this condensation reaction is thought to occur via a pentacoordinate silicon (191), the release of steric strain may favor loss of t-butanol to form silanol 348 over loss of water to form disiloxane 347 (Scheme 122). Silanol 348 can then undergo intramolecular

Scheme 122

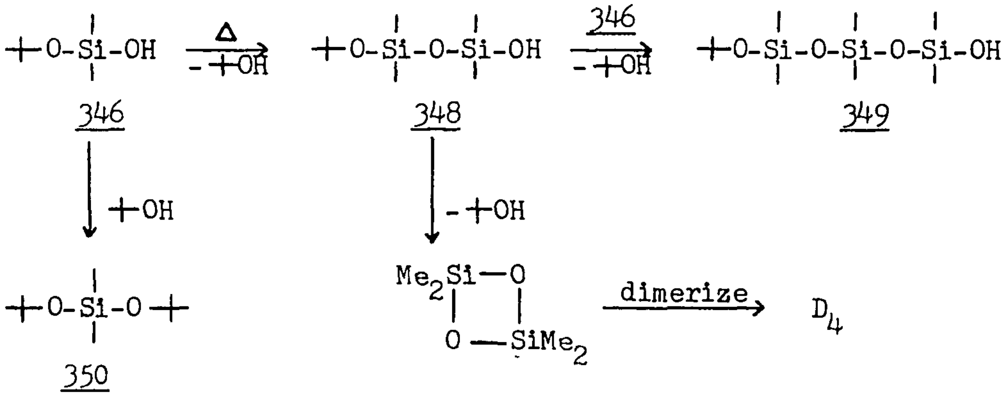


condensation with loss of t-butanol to form D_2. Dimerization of D_2 produces D_4. It is important to note that this scheme is consistent with the kinetic results of Yablokov and coworkers, since in both schemes the reaction of the starting silyl peroxide is unimolecular.

In order to gain evidence in support of this condensation scheme, dimethyl-t-butoxysilanol was independently synthesized and thermolyzed. Silanol 346 was prepared by treating dimethyldichlorosilane with t-butanol, followed by treatment with water. This silanol proved to be quite stable at room temperature, but at temperatures >100°, it reacted rapidly. This made analysis by GC difficult.

Thermolysis in tridecane for 3 hrs. at 150° C resulted in complete disappearance of silanol 346. The products which formed were found to be dependent upon the concentration of the starting silanol. Pyrolysis of dilute solutions (<5% of 346 in tridecane), produced low yields of dimethyldi-t-butoxy silane (350), silanol 348, and D_4 (the exact yields were not determined). Pyrolysis of more concentrated solutions (>30% of 346 in tridecane) produced 350, 348, and 349 as major products, with no detectable amount of D_4 (Scheme 123).

Scheme 123

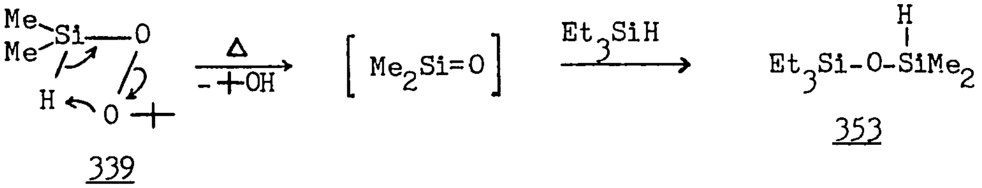


We then decided to repeat the work of Yablokov and coworkers and look for the formation of silanol 348. When solutions of dimethylsilyl-t-butylperoxide (339) in dodecane (from 3-20% solutions) were pyrolyzed

(125-150° C), there was observed by GCMS, silanol 348 in addition to D_4. Silanol 348 was always formed in higher yield than D_4 and only minute traces of D_3 were ever observed. On the GC column used (6 ft. 5% SE30), D_4 and 348 had nearly identical retention times and produced one broad peak. Yablokov and coworkers may have thought this peak was composed entirely of D_4.

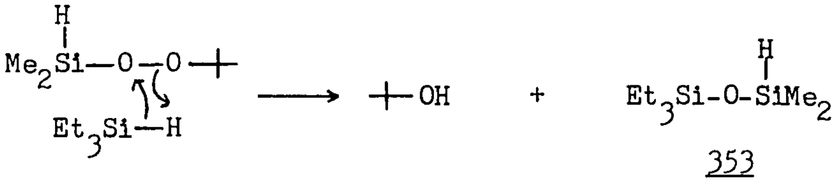
Finally, a word must be said about the thermolysis of peroxide 339 in triethylsilane which produced quantitatively 1,1-dimethyl-3,3,3-triethyldisiloxane (353). Yablokov and coworkers claimed product 353 resulted from insertion of dimethylsilanone into triethylsilane as depicted in Scheme 124. We, however, thought it likely that 353

Scheme 124



resulted from an intermolecular reaction between peroxide 339 and triethylsilane (Scheme 125). An obvious difference between these

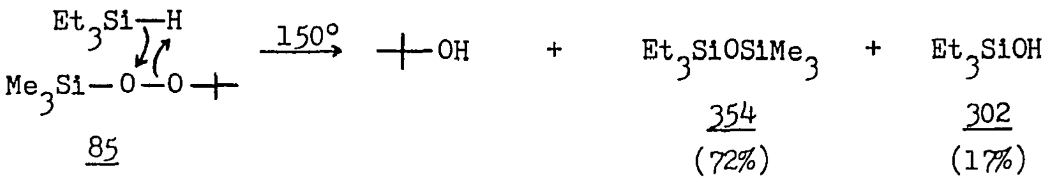
Scheme 125



two schemes is that in the intermolecular mechanism, the silyl hydride remains intact, while in the silanone mechanism, the original silyl hydride is lost and a new silyl hydride forms. An easy way to distinguish between these two schemes is by deuterium labeling. To that end, we prepared deuterated triethylsilane by LAD reduction of triethylchlorosilane. Thermolysis of 339 in an octane solution containing Et_3SiD produced deuterated t-butanol and unchanged 353. The fact that the deuterium label is on the alcohol rather than on the disiloxane demonstrates that the silanone mechanism is incorrect.

To further demonstrate that silyl peroxides do react intermolecularly with silyl hydrides, we treated trimethylsilyl-t-butylperoxide (85) with triethylsilane (Scheme 126). The products of this reaction were 1,1,1-trimethyl-3,3,3-triethyldisiloxane (354, 72%) and triethylsilanol (302, 17%). The triethylsilanol probably resulted from oxidation of triethylsilane by the peroxide. Thus, the reaction between triethylsilane and silyl-t-butyl peroxides appears to be general and does not require the peroxide to have a silyl hydride.

Scheme 126



CONCLUSION

A convenient, one-pot synthesis of trimethylsilyldiazomethane and bis(trimethylsilyl)diazomethane was developed. Pyrolysis and photolysis of α-silyl and α-germyl diazo compounds were used to prepare silenes and germenes. In some cases, these (p-p) π-bonded reactive intermediates were formed quantitatively. Photolysis of trimethylsilyltrimethylgermyldiazomethane revealed that a germene was formed in competition with a silene, while the silene was favored by a factor of <u>ca</u>. 4. Two new trapping reactions of silenes were observed: trapping with O_2; and trapping with the starting α-silyl diazo compound.

Several members of the 2,3-disila-1,4-dioxane ring system were investigated as possible silanone generators. While none of these compounds appeared to be mild silanone generators, at least one is an efficient silylene generator.

In an attempt to observe the intermediacy of a silanone, a variety of silyl ethers were pyrolyzed. The high temperatures required for these pyrolyses (500-700° C) resulted in many complex reaction mixtures. No evidence requiring the intermediacy of a silanone was obtained. All products formed in these pyrolyses are most easily rationalized by two reactions of the initially formed siloxy radical: hydrogen abstraction and S_H2 attack.

Homolytic cleavage of bis(silyl)peroxides by photolysis was investigated as a mild method of siloxy radical generation. The siloxy radicals formed by this method did not undergo loss of an alkyl radical to form a silanone, but underwent the same two reactions which occurred thermally: hydrogen abstraction and S_H2 attack. When the bis(silyl) peroxide contained a good leaving group (t-Bu), photolysis resulted in an intramolecular rearrangement reaction which occurred with loss of this leaving group to form a new siloxy radical. This siloxy radical underwent an internal S_H2 reaction to produce D_2 or an analog of D_2. The D_2 (or analog) which was formed in this way was extremely reactive, with the primary reaction being dimerization to form D_4 (or analog).

The recently reported generation of dimethylsilanone via thermolysis of a silyl peroxide was shown to be erroneous. This report, coupled with all published silanone literature, indicates that there is no good evidence demanding the intermediacy of a silanone. Therefore, at this time, the very existence of silanones remains questionable.

EXPERIMENTAL

General Information

All reactions, unless otherwise noted, were run under a nitrogen atmosphere. Routine proton NMR spectra were recorded on a Varian A60 or HA100 spectrometer. All chemical shifts were reported as parts-per-million (δ scale) from tetramethylsilane. IR spectra were recorded on a Beckman IR 4250 spectrophotometer. UV spectra were recorded on a Cary Model 14 spectrophotometer. Mass spectra were recorded using either a Finnigan Model 4000 or an AEI MS 902, with exact masses obtained on the latter instrument.

Gas chromatographic analyses and separations were performed on Varian Models 3700 and 920, and Aerograph Model A-90-P. GC yields were determined with internal standards after determination of the relevant response factors. High pressure liquid chromatography (HPLC) was performed on a Waters High Pressure Liquid Chromatograph equipped with UV and differential refractometer detectors.

Photolyses were carried out at room temperature in a Rayonet photochemical reactor equipped with 2537Å lamps. Pyrolyses, unless otherwise noted, were carried out in a vertical flow system consisting of a 5/8 in. x 2 ft. quartz tube inside a 1 ft. tube furnace. The tube was packed with quartz chips, and a carrier gas (N_2 unless otherwise stated) was passed through the system at a rate of ca. 30 mL/min. The reaction mixtures were introduced into the tube dropwise via syringe, and the products were collected in traps cooled by liquid nitrogen.

Procedures and Results

Tosyl azide

Tosyl azide was prepared by the procedure of Doering and DePuy (156). It was obtained as a slightly yellow liquid which was stored over molecular sieves in an amber bottle at room temperature. No decomposition was noted over a period of several months. The tosyl azide was used without any further purification.

Trimethylsilyldiazomethane (109)

The apparatus employed consisted of two three-necked flasks connected vertically, with a glass-wool plug and stopcock in between them. The upper flask was equipped with N_2-addition tube, overhead stirrer, a septum inlet, and a surrounding cooling bath. The lower flask was equipped with a septum inlet and magnetic stirrer.

A 30% dispersion of lithium (3.0 g, 143 mmol) in paraffin oil was placed in the top flask and washed three times with 40 mL dry ether under nitrogen. Ether (50 mL) was finally added and the mixture was cooled to -23° (dry ice/CCl_4 bath). Trimethylchloromethylsilane (124) (5.0 mL, 36 mmol) was added via syringe, and the reaction mixture was stirred for 1.5 hrs. Disappearance of 124 was monitored by gas chromatography (GC) using a 6 ft. 5% Dexil 300 column at 60°. To the lower flask was added a solution of tosyl azide (5.3 mL, 36 mmol) in 100 mL of dry ether. After cooling the lower flask to 0°, the anion solution was added dropwise through a glass-wool plug. The temperature was maintained at 0° for 6 hrs. and then 25° for 16 hrs. The precipitated salt (TosNHLi) was filtered to leave a bright yellow-green solution, which was washed with slightly alkaline water and dried over $MgSO_4$. Ether was removed by distillation (atm. pres.) through a 15 cm. vacuum-jacketed column, with the pot temperature never above 45°. After ether removal, the pot temperature was lowered to 0°, and the pressure was slowly decreased to 25 Torr. The flask was then heated to 40° for two hrs. The green distillate was analyzed by GC (5 ft., 5% XF 1150 on Chromasorb P, injector and detector 90°, column 40°) to contain 38% 109 and ether. Preparative GC afforded pure 109 whose spectral characteristics were identical with those reported previously.

Trimethylchloromethylgermane (130)

Trimethylchloromethylgermane was prepared in two steps from germanium tetrachloride by the procedure of Seyferth and Rochow (158). The diazomethane required for this synthesis was prepared from Diazald which is sold by the Aldrich Company.

Attempted synthesis of trimethylgermyldiazomethane (121)

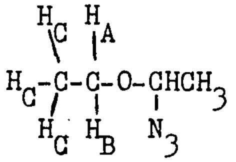
The apparatus employed consisted of two three-necked flasks connected vertically, with a glass-wool plug and stopcock in between them. The upper flask was equipped with a N_2-addition tube, overhead stirrer, a septum inlet, and a surrounding cooling bath. The lower flask was equipped with a septum inlet and magnetic stirrer.

A 30% dispersion of lithium (0.99 g, 42 mmol) in paraffin oil was placed in the top flask and washed three times with 30 mL dry ether.

Ether (40 mL) was finally added and the mixture was cooled to -23° (dry ice/CCl_4 bath). Trimethylchloromethylgermane (130) (1.0 mL, 8.2 mmol) was added via syringe, and the reaction mixture was stirred for 2 hrs. Disappearance of 130 was monitored by GC. To the lower flask was added a solution of tosyl azide (1.2 mL, 8.5 mmol) in 40 mL of ether. After cooling the lower flask to 0°, the anion solution was added dropwise through the glass-wool plug. The temperature was maintained at 0° for 6 hrs. and at room temperature overnight. After filtering, a very pale yellow solution was obtained. This solution was washed with slightly alkaline water and dried over Na_2SO_4. Ether was removed by distillation (atm. pres.) through a 15 cm. vacuum-jacketed column, with the pot temperature never exceeding 50°. After ether removal, the pressure was slowly reduced to full vacuum (*ca*. 0.5 Torr) and all volatiles were collected from room temperature to 60°. Analysis of the distillate by GC showed that several components were present. The components were isolated by preparative GC (12 ft. 15% SE30 on chrom. W) and were identified to be 1-azidoethylethylether (131), hexamethyldigermoxane (132), *cis*-1,2-bis(trimethylgermyl)ethylene (133), and *trans*-1,2-bis(trimethylgermyl)ethylene (134). The undistilled residue contained tosyl azide and trimethylgermyltosylmethane (135). Compound 135 was purified by crystallization from pentane. The yield was not determined for any product. Product 133 was differentiated from 134 only on the basis of the relative amounts formed; it was assumed that more of the trans isomer should be formed. Product 132 was identified by GCMS and NMR comparison with an authentic sample. The spectral properties of products 131, 133, 134, and 135 are summarized below:

1-azidoethylethylether (131):

NMR (CCl_4, 100 MHz) δ 0.52 (t, 3H, J=7.0 Hz), 0.72 (d, 3H, J=5.2 Hz), 3.90 (m, 2H), 4.72 (q, 1H, J=5.2 Hz); irradiation at the doublet at δ 0.72 causes the quartet at δ 4.72 to collapse to a singlet.



$$H_C-\overset{H_C}{\underset{H_C}{C}}-\overset{H_A}{\underset{H_B}{C}}-O-\underset{N_3}{C}HCH_3$$

The multiplet at δ 3.90 is very well resolved so that all the coupling constants can be measured. H_A and H_B are diastereotopic, thus splitting each other leads to two doublets. Irradiation at the triplet at δ 0.52 causes the multiplet to collapse to two doublets, one at δ 3.76 and the other at δ 4.06 (J_{AB}=8.6 Hz). Each of the four peaks composing the two doublets is split into four others by the three H_C's. This results in the formation of 16 peaks, all of which can be seen in the NMR spectrum ($J_{AC}=J_{BC}=$ 6.4 Hz).

IR (film) 2985(s), 2940(m), 2920(m), 2880(m), 2105(s), 1480(w), 1450(m), 1380(s), 1340(m), 1260(sh), 1235(s), 1115(s), 1095(m), 1065(m), 1030(m), 940(m), 850(m), 830(w), 800(m), 715 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 115 (<1, parent ion), 100(1), 86(1), 73(45), 59(2), 45(100)

Exact mass for $C_4H_9O(P-N_3)$ calc. 73.0653; meas. 73.0656

Elemental analysis calc. C 41.73, H 7.87, N 36.50; meas. C 41.71, H 7.67, N 36.79

Cis-1,2-bis(trimethylgermyl)ethylene (133):

NMR (CCl_4) δ 0.22 (s, 18H), 6.56 (s, 2H)

Mass spectrum; m/e (% rel. inten.) 256(3, parent ion for $^{70}Ge_2$), 241(8), 215(2), 115(60), 85(3), the appropriate germanium isotopic patterns were observed (base peak is 119)

Exact mass for $C_8H_{20}Ge_2$ (P + 6 for $^{70}Ge_2$) calc. 262.0001; meas. 262.0025

Trans-1,2-bis(trimethylgermyl)ethylene (134):

NMR (CCl_4) δ 0.08 (s, 18H), 6.60 (s, 2H)

IR (film) 2980(s), 2950(sh), 2910(m), 2800(2), 1410(2), 1235(s), 1160(m), 1000(m), 820(s), 755 cm^{-1}(m).

Mass spectrum; m/e (% rel. inten.) 256(1, parent ion for $^{70}Ge_2$), 241(4), 215(1), 141(2), 125(2), 115(55), 85(9), the appropriate germanium isotopic patterns were observed (base peak is 119)

Trimethylgermyltosylmethane (135)

NMR ($CDCl_3$) δ 0.34 (s, 9H), 2.34 (s, 3H), 2.70 (s, 2H), para disubstituted aromatic pattern centered at 7.52 (4H)

IR (film) 2990(m), 2920(m), 1590(m), 1310(m), 1300(s), 1280(m), 1240(m), 1140(s), 1110(m), 1080(m), 835(m), 810(m), 795(m), 780(s), 750 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 284(<1, parent ion for ^{70}Ge), 269(47), 191(57), 179(30), 115(28), 105(46), 91(43), 85(18)

Chloromethyltrimethylsilane (124)

Chloromethyltrimethylsilane was purchased from Petrarch Systems Inc. and was used without further purification.

Bis(trimethylsilyl)methane (137) (160)

An excess of lithium dispersion in paraffin oil was placed in a three-necked flask equipped with a Hirsch stirrer, and then washed three times with 40 mL of ethyl ether. After a final addition of 60 mL ether, the solution was cooled to -23° C (CO_2/CCl_4 bath). After addition of 5.0 mL (4.4 g, 36 mmol) of chloromethyltrimethylsilane, the mixture was stirred for 2 hrs. followed by addition of one equivalent of trimethylchlorosilane via syringe. After slowly warming the mixture to room temperature, it was extracted three times with H_2O, dried over Na_2SO_4, and distilled to afford 4.3 g of bis(trimethylsilyl)methane (75%).

bp 133-135° C

NMR (CCl_4) δ -0.25 (s, 2H), 0.02 (s, 18H)

lit. (190) δ -0.28, 0.01

IR (film) 2970(s), 2910(m), 2870(w), 1260(s), 1060(s), 845(s, brd.) 790(w), 770(s), 735(s), 690 cm^{-1}(m)

Bis(trimethylsilyl)chloromethane (138)

Chloromethyltrimethylsilane in THF solution was metalated by *sec*-butyllithium in 10 min. at -78°. The general procedure was that of Burford, Cooke, Ehlinger, and Magnus (192), although it was not necessary to employ TMEDA. To the stirred anion solution at -78° was added dropwise one equivalent of neat trimethylchlorosilane. After completion of addition, the temperature was allowed to rise to room temperature. The THF was removed *in vacuo*, and the residue was dissolved in hexane.

The hexane solution was extracted several times with water, dried over Na_2SO_4, and distilled to afford bis(trimethylsilyl)chloromethane in 70% yield.

bp 177-179° C; lit. 178.5° (193)

NMR (CCl_4) δ 0.16 (s, 18H), 2.37 (s, 1H)

IR (film) 2960(s), 2900(m), 1410(m, brd.), 1255(s), 1040(s, brd.), 770 cm^{-1}(m)

Bis(trimethylsilyl)diazomethane (136) from bis(trimethylsilyl)chloromethane

Metallation was by essentially the procedure of Davidson, Harris, and Lappert (194). To an excess of Li dispersion in 60 mL ether was added 3.0 g of bis(trimethylsilyl)chloromethane, and this mixture was refluxed for 20 hrs. The resulting mixture was cooled and filtered through glass-wool, under N_2. To the filtered solution at 0° was added via syringe one equivalent of tosyl azide in ether. The temperature was maintained at 0° for 4 hrs., and then at room temperature overnight. Salts were removed by centrifugation, and the ether was removed by distillation. Distillation of the remainder afforded 136 at 25°/0.1 Torr. The yield of 136 was found by GC technique to be 37%. Purification can be accomplished by preparative GC on either an SE30 or XF1150 column. Both the NMR and IR spectra reported below are in close agreement with those reported in the literature (159).

NMR (CCl_4) δ 0.12(s)

IR (film) 2960(s), 2910(m), 2040(s), 1260(s), 1250(s), 1220(s), 930(s), 840 cm^{-1}(s, brd.)

Mass spectrum; m/e (% rel. inten.) 186(parent ion, 73), 171(41), 144(67), 143(67), 85(80), 83(67), 74(80), 73(100)

Bis(trimethylsilyl)diazomethane (136) from bis(trimethylsilyl)methane

Metallation was by a variation of the procedure of Grobel and Seebach (195). THF (6 mL), HMPA (0.3 mL), and bis(trimethylsilyl)-methane (0.213 g, 1.33 mmol) were cooled to -78° C in a 10 mL flask. To this solution was added, via syringe, one equivalent of *t*-butyllithium in *n*-pentane to immediately produce a bright yellow color. After stirring for 2½ hrs., one equivalent of tosyl azide was added without solvent. The solution immediately darkened, but within 10 sec. lightened to a yellow-orange color. The temperature was maintained at -78° C for 2 hrs., and allowed to rise to room temperature where stirring was continued overnight. The reaction mixture was diluted with 100 mL of hexane, and then extracted several times with slightly alkaline H_2O (pH *ca*. 9). After drying (Na_2SO_4), the solvents were removed to leave 136, which was purified by preparative GC. The GC-determined yield of 136 was 57%.

Nitrogen-flow pyrolysis of bis(trimethylsilyl)diazomethane (136)

A 5% solution of 136 in benzene (0.121 g of 136 in 2.4 g of benzene) was introduced dropwise into a vertical, quartz-packed tube heated at 400° and continuously swept by a nitrogen stream. Products were isolated by preparative GC using a 10 ft., 15% SE30 column. The products identified were silene dimers 143a and 143b (combined yield of 46%), linear dimer 144 (22%), and disilazane 145 (10%). All these products are colorless liquids. Cyclodimers 143a and 143b were formed in *ca*. equal amounts as determined by NMR. They were separated by preparative GC using a 10 ft. 15% poly-m-phenylether column. The spectral properties of the products are summarized below:

143a:

NMR (C_6D_6) δ 0.10 (s, 18H), 0.17 (s, 6H), 0.38 (s, 6H), 1.35 (s, 6H)

IR of 143ab mixture (film) 2960(s), 2910(m), 2870(m), 1465(m), 1410(m), 1265(sh), 1250(s), 1080(m), 1050(w), 995(m), 975(m), 870(sh), 840(s, brd.), 790(w), 760(m), 700(w), 675 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 316(parent ion, 2), 301(3), 242(18), 227(12), 213(6), 201(1), 185(2), 169(3), 159(18), 155(19), 141(8), 131(17), 117(6), 85(34), 73(100), 59(15)

Exact mass for $C_{14}H_{36}Si_4$ (parent ion) calc. 316.1894; meas. 316.1885

143b:

NMR (C_6D_6) δ 0.13 (s, 18H), 0.25 (s, 12H), 1.23 (s, 6H)

Mass spectrum; m/e (% rel. inten.) 316(12), 301(14), 242(1), 227(20), 213(20), 201(3), 185(4), 169(6), 159(5), 155(15), 141(12), 131(14), 85(10), 73(100), 59(18)

144:

NMR (CCl_4) δ 0.00 (s, 9H), 0.06 (s, 3H), 0.10 (s, 12H), 0.18 (s, 3H), 0.20 (s, 3H), 1.02 (d, J=7.5 Hz, 3H), 6.26 (AB q. center, J=4.7 Hz, 2H), the chemical shift of the remaining proton was determined to be ca. δ 0.02 by double irradiation.

IR (film) 3000(w), 2950(s), 2900(m), 2860(m), 2815(w), 1400(m, brd.), 1310(sh), 1300(s), 1140(w), 1100(m), 1000(sh), 990(m), 850(sh), 830(s), 790(s), 780(s), 760(s), 720(w), 680 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 316(parent ion, 2), 301(3), 242(24), 227(13), 213(5), 201(2), 185(3), 169(4), 159(16), 155(16), 131(14), 117(5), 101(3), 85(52), 73(100), 59(16)

Exact mass for $C_{14}H_{36}Si_4$ (parent ion) calc. 316.1894; meas. 316.1899

145:

NMR (CCl_4) δ 0.08 (s, 9H), 0.13 (s, 9H), 6.32 (AB q. center, 2H, J_{AB}= 5 Hz.), NH not observed

IR (CCl_4) 3370(w), 3000(w), 2950(s), 2910(w), 2880(w), 1610(w), 1400(m, brd.), 1250(sh), 1240(s), 1210(s), 1170(s), 1140(m), 1105(w), 1080(w), 960(m), 925(s), 860(sh), 840 cm^{-1}(s, brd.)

Mass spectrum; m/e (% rel. inten.) 245(parent ion, 4), 230(11), 214(3), 172(10), 156(4), 146(100), 142(57), 132(15), 130(26), 116(7), 100(7), 73(51), 59(6), 45(11)

Exact mass for $C_{10}H_{27}NSi_3$ (parent ion) calc. 245.1451; meas. 245.1456

Vacuum-flow pyrolysis of bis(trimethylsilyl)diazomethane (136)

A 0.0914 g sample of neat 136 was slowly distilled through a horizontal, unpacked quartz tube (5/8 in. x 2 ft.) in a 1 ft. tube furnace at 500° C and a vacuum of 0.05 Torr. The sample flask was held at 0° to ensure slow vaporization. Two collection traps were respectively cooled to 0° and -78°. All the products were collected in the 0° trap. Identification of 143a (30%), 143b (30%), and 144 (23%) was made by GCMS comparison. Disilazane 145 was not observed.

Nitrogen-flow copyrolysis of 136 and benzaldehyde

A solution of 136 (.0532 g) in pure PhCHO (1.1 g) was pyrolyzed in the vertical, N_2-flow system at 400° C. The products isolated by preparative GC were 151 (34%), 150 (45%), and 149 (18%), with yields determined by GC. A trace amount of hexamethylcyclotrisiloxane (D_3) was observed by GCMS, and when the percentage of 136 in PhCHO was increased, the amount of D_3 also increased. It is possible that the D_3 arises from trimerization of extruded dimethylsilanone. The spectral properties of the products are summarized below:

151:

NMR (CCl_4) δ -0.08 (s, 9H), 1.95 (d, J=1.5 Hz., 3H), 7.14 (brd. s, 6H)

IR (film) 3030(w, brd.), 3010(w), 2960(s), 2900(m), 2850(w), 1710(s), 1595(s), 1590(sh), 1490(s), 1475(m), 1260(s), 1250(s), 1210(m), 1205(sh), 1125(s), 1080(s, brd.), 1030(s), 985(m), 920(m), 850(sh), 840(s), 790(m, brd.), 745(s), 695 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 190(parent ion, 39), 175(91), 159(19), 135(100), 115(12), 105(7), 73(96), 59(56), 45(24), 43(42)

150:

NMR (CCl_4) δ 0.15 (s, 9H), 1.90 (d, J=1,5 Hz., 3H), 6.66 (q, J=1.5 Hz., 1H), 7.20 (s, 5H)

IR (film) 3080(sh), 3060(w), 3020(w), 2960(s), 2900(m), 2850(w), 1710(s), 1600(m), 1575(w), 1490(m), 1445(m), 1400(w), 1370(w), 1310(w), 1260(sh), 1250(s), 1200(w), 1125(m), 1070(m), 1025(m, brd.), 960(s), 915(m), 850(s), 835(s), 755(s), 745(m), 710(m), 690 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 190(parent ion, 33), 175(70), 159(11), 135(100), 115(10), 105(5), 73(86), 59(49), 45(21), 43(24)

Exact mass for $C_{12}H_{18}Si$ (parent ion) calc. 190.1178; meas. (from mixture of 150 and 151) 190.1175

149:

NMR (CCl_4) δ 0.08 (s, 9H), 0.16 (s, 6H), 4.62 (s, 2H), 6.34 (center of AB q., J_{AB}=5.0 Hz., 2H), 7.20 (brd. s, 5H)

IR (film) 3080(w), 3020(w), 2960(s), 2915(w), 2900(w), 1705(m), 1495(w), 1455(m), 1260(sh), 1255(s), 1210(m), 1150(m), 1125(s), 1090(s), 1070(s), 1030(s), 850(s), 780(m), 730(m), 695 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 249(parent ion-Me, 5), 207(1), 190(1), 165(5), 147(4), 135(7), 91(100), 73(11), 65(5), 59(3)

Copyrolysis of 136 and 1,3-butadiene

Using 1,3-butadiene as the carrier gas (30 mL/min) in the vertical-flow pyrolysis system, a 5% solution of 136 in benzene was pyrolyzed at 400° C. GCMS analysis showed the pyrolysate to contain four isomeric products: 153 (56%); 154 (13%); and two in combined yield of ca. 20% for which separation could not be effected. Products 153 and 154 were isolated by preparative GC, and were colorless liquids. Their spectral properties are summarized below:

153:

NMR (CCl_4) 0.00, 0.04, 0.08 (s, s, s, 15H), 1.04 (s, 3H), 1.15 (m, 2H), 5.50 (m, 2H), 2.12 (center of AB q., J=16 Hz., 2H)

IR (film) 3005(m), 2960(s), 2900(m), 2865(m), 1650(w), 1455(w), 1255(s), 1170(m), 1050(m), 890(m), 860(s), 835(s), 755(m), 715(m), 685 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 212(parent, 4), 197(4), 171(5), 158(7), 143(11), 138(24), 123(12), 109(14), 98(19), 85(8), 83(9), 73(100), 59(33)

154:

NMR (CCl_4) δ 0.08 and 0.12 (brd. s and s, 15H), 1.55 (m, 5H), 5.34 (m, 2H), 6.28 (s, 2H, presumably a tight AB q.)

IR (film) 3010(m), 2960(s), 1650(w), 1400(brd.), 1255(s), 1150(m), 1050(brd., m), 995(m), 965(m), 840(s, brd.), 760(m), 675(m)

Mass spectrum: m/e (% rel. inten.) 212(parent, 2), 197(2), 169(2), 157(25), 141(3), 124(4), 113(3), 97(3), 85(5), 83(8), 73(100), 59(17)

Nitrogen-flow copyrolysis of 136 and 2,3-dimethyl-1,3-butadiene

A 5% solution of 136 (0.0879 g) in 2,3-dimethyl-1,3-butadiene (1.7 g) was pyrolyzed in standard fashion at 400° C in the N_2-flow system. Three products were isolated: 156 (51%); 157 (31%); and 159 (10%). Separation of 159 was accomplished by GC using an SE30 or OV101 column. Separation of 156 from 157 required an XF1150 column. All three products are colorless liquids. The spectral properties of the products are given below:

156:

NMR (CCl_4) δ 0.00 (s, 12H), 0.06 (s, 3H), 0.96 (s, 3H), 1.10 (m, 2H), 1.70 (m, 6H), 2.1 (center of AB q., J=16 Hz., 2H)

IR (film) 2960(s), 2920(m), 2900(m), 2860(s), 1460(w), 1450(m), 1260(sh), 1250(s), 1060(m), 1045(m), 920(m), 905(m), 850(s), 830(s), 790(m), 750(m), 675 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 240(parent, 12), 225(7), 211(1), 198(1), 184(2), 171(16), 166(20), 158(26), 152(15), 143(33), 137(12), 97(23), 85(14), 73(100), 59(43)

Exact mass for $C_{13}H_{28}Si_2$ (parent ion) calc. 240.1730; meas. 240.1728

157:

NMR (CCl_4) δ 0.02 and 0.06 (s, s, 16H), 1.06 (d, J=7.5 Hz., 3H), 1.80 (brd. s, 2H), 1.94 (brd. s, 3H), 4.75 and 4.96 (m, m, 4H)

IR (film) 3100 (w), 2960(s), 2900(m), 2870(m), 1590(m), 1250(s), 1160(m), 990(m), 885(m), 875(m), 855(s), 830(s), 760(m), 675 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 240(parent, 4), 225(7), 166(5), 159(46), 152(4), 143(4), 131(13), 97(6), 85(67), 73(100), 59(26)

159:

NMR (D_6C_6) δ 0.10 (s, 9H), 0.25 (brd. s, 6H), 1.12 (d, J=9 Hz., 3H), 1.18 (s, 9H), 4.04 (d, J=1.5 Hz., 1H), 4.21 (d, J=1.5 Hz., 1H), remaining H hidden under SiMe resonances, with the chemical shift of δ 0.05 determined by double irradiation

IR (film) 3080(w), 2960(s), 2910(s), 1635(m), 1440(s, brd.), 1365(m), 1250(s), 1205(m), 1140(m), 1105(w), 1040(brd. w), 995(m), 885(s), 830(s), 680 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 258(parent, 1), 243(10), 201(76), 185(22), 161(30), 158(28), 147(11), 143(52), 133(10), 129(12), 117(8), 99(7), 85(51), 75(98), 73(100), 59(33), 55(30)

Photolysis of bis(trimethylsilyl)diazomethane (136)

A 5% solution of 136 in benzene (0.0281 g of 136 in 0.560 g of benzene) was placed in a quartz NMR tube, repeatedly degassed by the freeze-thaw method, and sealed under vacuum. After irradiation for 2.5 hrs., the NMR spectrum revealed the complete absence of 136. The products were isolated by preparative GC on a 10 ft., 15% poly-*m*-phenylether column. Silene dimers 143a (cis) and 143b (trans) were formed in *ca*. equal amounts (by NMR) in a combined yield of 64% (GC). Disilazane 145 was formed in 23% (GC), and disiloxane 160 was often observed in $<5\%$ due to trapping of the silene with H_2O. The linear silene dimer, 144, was not observed. The spectral properties of 160 are given below:

160:

NMR (CCl_4) δ -0.04 (s, 18H), 0.04 (brd. s, 12H), 0.97 (d, 6H, J=8 Hz.), the remaining 2H's appeared as a quartet partially obscured by the SiMe resonances and the chemical shift was determined to be δ -0.12 by decoupling the doublet at δ 0.97

Mass spectrum; m/e (% rel. inten.) 334(parent ion, 1), 319(21), 247(10), 233(98), 217(5), 203(5), 189(7), 175(6), 173(6), 159(26), 147(27), 145(23), 133(27), 131(22), 117(12), 85(35), 73(100), 59(17)

Trimethylsilylnitrile (147)

Trimethylsilylnitrile was prepared by the literature method (196). This material was apparently unstable under the GC conditions used for analysis of the thermolysis and photolysis reactions of bis(trimethylsilyl)diazomethane, as no peak corresponding to 147 was observed. The IR spectrum of 147 revealed a C-N stretching frequency of *ca.* 2190 cm^{-1}. This same band was observed by IR analysis of the reaction mixture from photolysis of bis(trimethylsilyl)diazomethane.

Photolysis of bis(trimethylsilyl)diazomethane (136) with olefins added

To a 5% solution of 136 in benzene was added a 3-6 fold molar excess of one of the following olefins: cyclohexene, cyclopentene, tetramethylethylene, methylvinylether, and styrene. The solution was placed in a quartz NMR tube and degassed by the freeze-thaw method. After sealing under vacuum, the tube was placed in a Rayonet equipped with 2537Å lamps. Disappearance of 136 was monitored by NMR. With all olefins, except styrene, the reaction was complete within 3 hrs. and the major products were the silene dimers 143a and 143b and disilazane 145. With styrene present, the reaction proceeded much more slowly (*ca.* 16 hrs. required for complete disappearance of 136) and was complicated by the formation of styrene dimers. In no case was the formation of a 1:1 adduct of silene with olefin observed (by GCMS).

Photolysis of 136 was also carried out using cyclopentene or cyclohexene as solvent rather than benzene. Photolysis was again carried out in sealed, quartz NMR tubes. In these cases, the reaction proceeded at a faster rate, since there was no benzene to absorb the light, but the products 143a, 143b, and 145 were still the only identifiable products. These products were identified by GCMS.

Photolysis of 136 with benzaldehyde added

To a 5% solution of 136 in benzene in a quartz NMR tube was added 1.1 equivalents of benzaldehyde. The solution was degassed by the freeze-thaw method and the tube was sealed under vacuum. Photolysis (2537Å) was carried out for 2½ hrs. NMR indicated that 136 had reacted completely and that no peaks in the C-Me region had grown in. GC analysis revealed that several products had formed. The major product (ca. 60% assuming all products had identical response factors) was isolated by preparative GC (10 ft. 15% SE30 column) and identified by NMR to be epoxide 161.

NMR (CCl_4) δ 0.18 (s, 9H), 0.25 (s, 9H), 4.86 (s, 1H), 7.28 (m, 5H)

Photolysis of 136 with D_2O added

To a 5% solution of 136 in benzene in a quartz NMR tube was added a 3-fold excess of D_2O. The solution was degassed repeatedly and the tube was sealed under vacuum. During irradiation, the tube was shaken vigorously every few minutes to ensure saturation. After 2.5 hrs. of irradiation, the NMR spectrum showed complete conversion of 136 to disiloxane 163. The product, a colorless liquid, was isolated by GC using a 10 ft. 15% SE30 column.

NMR (CCl_4) δ -0.06 (s, 18H), 0.00 (s, 12H), 0.94 (brd. s, 6H)

Mass spectrum; m/e (% rel. inten.) 336(parent ion, <1), 321(10), 247(2), 234(52), 218(3), 204(3), 189(4), 175(3), 160(14), 147(16), 146(13), 133(15), 131(13), 117(8), 86(28), 73(100), 59(16)

Photolysis of bis(trimethylsilyl)diazo methane (136) with MeOH

A degassed 5% solution of 136 in benzene containing a 3-fold molar excess of MeOH was sealed in a quartz NMR tube *in vacuo*. After 2.5 hrs. irradiation, the NMR spectrum revealed total conversion of 136 to 162. The product, a colorless liquid, was isolated by preparative GC using a 10 ft. 15% SE30 column.

NMR (CCl_4) δ 0.00 (s, 9H), 0.06 (s, 6H), 1.00 (d, 3H, J=8 Hz.), 3.34 (s, 3H), the remaining methine H appears as a quartet partially obscured by the SiMe absorption, the chemical shift was determined to be δ -0.08 by decoupling the doublet at δ 1.00

Mass spectrum; m/e (% rel. inten.) 190(parent ion, 2), 175(100), 161(7), 145(10), 133(7), 117(11), 101(6), 89(82), 86(19), 73(35), 59(40), 45(11)

Exact mass for $C_8H_{22}OSi_2$ (parent ion) calc. 190.1209; meas. 190.1218

Nitrogen-flow pyrolysis of bis(trimethylsilyl)diazomethane (136) with oxygen added

The carrier gas which was used for this pyrolysis was composed of *ca*. 98% N_2 and 2% O_2. The total flow rate was 30 mL/min. A 5% solution of 136 in benzene was pyrolyzed at 400°. In addition to the usual silene products, 143a, 143b, 144, and 145, the following were formed: 169 (8%), 170 (15%), 171 and 172 (combined yield of 8%) and 167 (trace amount). Products 169-172 were all assumed to have identical response factors. Acetyltrimethylsilane (167) was identified simply by GCMS comparison with an authentic sample. Products 169, 170, 171, and 172 were isolated by preparative GC (10 ft. 15% SE30). Products 171 and 172 were never separated from each other and were identified only by GCMS. The spectral properties of all the products are summarized below:

169:

NMR (CCl_4) δ 0.01 (s, 9H), 0.12 (s, 12H), 0.18 (s, 3H), 1.20 (d, 3H, J=7.5 Hz.), 3.47 (q, 1H, J=7.5 Hz.), AB q. centered at 6.29 (J_{AB}=5Hz.)

IR (CCl_4) 2960(s), 2920(w), 2895(w), 1365(w), 1245(s), 1210(m), 1145(w), 1095(w), 1045(m), 980(w), 960(w), 940(w), 855(s), 840(s), 685 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 259(parent ion-CH_3, 3), 231(3), 201(2), 185(2), 171(9), 157(11), 147(100), 143(11), 133(9), 117(9), 103(10), 73(89), 59(8)

170:

NMR (CCl_4) δ -0.03 (s, 9H), 0.02 (s, 9H), 0.11 (brd. s, 6H), 0.99 (d, 3H, J=8.0 Hz.), 4.38 (d, 1H, J=1.0 Hz.), 4.66 (d, 1H, J=1.0 Hz.), the remaining H is hidden under the Si-Me region, but its chemical shift was determined by a double irradiation experiment to be ca. δ -0.05

IR (CCl_4) 3050(w), 2970(s), 2920(m), 2880(w), 1725(brd., m), 1650(m), 1255(s), 1110(m), 1050(brd., m), 995(m), 840 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 259(parent ion-CH_3, 5), 233(11), 201(14), 187(14), 171(7), 159(9), 147(68), 133(18), 131(15), 117(8), 99(6), 85(36), 73(100), 59(13)

171 and 172:

These products were only identified by GCMS. The mass spectra of these two compounds are nearly identical. The spectrum of a mixture of 171 and 172 is presented here.

Mass spectrum; m/e (% rel. inten.) 333(parent ion-CH_3, 2), 307(3), 293(4), 275(4), 261(2), 247(4), 235(8), 221(49), 205(18), 191(9), 175(5), 159(7), 147(19), 133(14), 117(6), 99(8), 85(10), 73(100), 59(11)

Photolysis of bis(trimethylsilyl)diazomethane (136) with oxygen added

A 5% solution of 136 in benzene was placed in a quartz tube. The total volume of solution was ca. 1.0 mL. The tube was sealed with a rubber septum. A slow stream of O_2 was bubbled through the solution via a needle through the septum. A second needle through the septum allowed the O_2 to escape. Photolysis (2537Å) was carried out for 2½ hrs. The product solution was analyzed by GC and was found to contain 169 (2%), 170 (12%), 171 and 172 (combined yield of 18%).

Acetyltrimethylsilane (167)

Acetyltrimethylsilane was prepared by the dithiane method as described in the literature (197, 198).

NMR (CCl_4) δ 0.05 (s, 9H), 2.06 (s, 3H)

lit. (198) 0.18, 2.18

IR (film) 3270(w), 2960(s), 2900(m), 1640(s), 1405(m), 1335(s), 1245(s), 1130(s), 950(w), 835(s), 740(s), 690 cm^{-1}(m)

Pyrolysis of acetyltrimethylsilane (167)

Approximately 25 mg of 167 in $\frac{1}{2}$ mL of benzene was pyrolyzed in the N_2-flow system at 400°. Approximately 80-90% of the starting material was recovered. The remaining 10-20% had rearranged to a more volatile isomer which was identified by GCMS to be the expected product, vinyloxytrimethylsilane (168).

Pyrolysis of bis(trimethylsilyl)diazomethane (136) with acetyltrimethylsilane (167) added

To a 5% solution of 136 in benzene was added a 3-fold molar excess of 167. This solution was then pyrolyzed in the N_2-flow system at 400°. Analysis of the pyrolysate by GC indicated that the major products were 169 (32%) and 170 (52%). Products 171 and 172 were not observed.

Photolysis of acetyltrimethylsilane (167)

Approximately 25 mg of 167 and $\frac{1}{2}$ mL of benzene were placed in a quartz NMR tube. After repeated degassing by the freeze-thaw method, the tube was sealed under vacuum. Photolysis was carried out in a Rayonet with 2537Å lamps. After 16 hrs. of photolysis, NMR indicated that no reaction had occurred. The tube was then opened and the solution was analyzed by GC. This also indicated complete recovery of 167.

Photolysis of bis(trimethylsilyl)diazomethane (136) with 167 added

To a 5% solution of 136 in benzene was added a 3-fold molar excess of 167. This solution was placed in a quartz NMR tube where it was repeatedly degassed by the freeze-thaw method. After sealing under vacuum, the tube was placed in a Rayonet where photolysis was carried out for 2½ hrs. The reaction mixture was analyzed by GC and found to contain only 169 (12%) and 170 (87%).

Trimethylsilyltrimethylgermylmethane

A suspension of 80 mmol Li in 60 mL Et_2O was cooled to -23° C (CO_2/CCl_4 bath). After addition of 5.0 mL of chloromethyltrimethylsilane (36 mmol), vigorous stirring (Hirsch) was continued for 2½ hrs., and then 28.3 mmol of trimethylchlorogermane was added by syringe. The reaction mixture was allowed to warm to room temperature, drained through a stopcock on the bottom of the flask (leaving behind the excess Li), diluted with 150 mL Et_2O, washed with saturated NH_4Cl, dried over Na_2SO_4, and the solvent evaporated. Trimethylsilyltrimethylgermylmethane was isolated in 72% after distillation.

bp 140-142°C; lit. (199, 200) 139°C

NMR (CCl_4) δ -0.15 (s, 2H), 0.03 (s, 9H), 0.18 (s, 9H)

IR matches the spectra reported in references 199 and 200

Trimethylsilyltrimethylgermylchloromethane

To a solution of 3.0 mL (2.66 g, 22 mmol) chloromethyltrimethylsilane in 50 mL THF at -78° C was added one equivalent of *sec*-butyllithium in cyclohexane by syringe. After stirring for 30 min, one equivalent of neat trimethylchlorogermane was added, and the temperature was allowed to slowly rise to room temperature. The solvent volume was reduced by evaporation to *ca*. 10 mL, diluted with 100 mL *n*-hexane, and extracted several times with H_2O. After drying (Na_2SO_4) and removal of solvent *in vacuo*, 3.66 g of colorless liquid trimethylsilyltrimethylgermylchloromethane remained, 70% yield. GC analysis showed the purity to be $>95\%$; thus, it was used without further purification.

NMR (CCl_4) δ 0.13 (s, 9H), 0.28 (s, 9H), 2.55 (s, 1H)

IR (film) 2970(s), 2910(m), 1410(brd. m), 1260(m), 1245(s), 1230(m), 1030(s), 860(s), 830(s), 815(s), 760(m), 690 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 236(parent ion for ^{70}Ge, <1), 221(1), 159(39), 115(53), 103(26), 85(64), 73(100), 59(12), the appropriate isotopic patterns were present

Trimethylsilyltrimethylgermyldiazomethane (174) from trimethylsilyltrimethylgermylmethane

A solution of trimethylsilyltrimethylgermylmethane (0.229 g), THF (6.0 mL) and HMPA (0.5 mL) was cooled to -78° C. One equivalent of *t*-BuLi in pentane was added to immediately produce a bright yellow color. After stirring for 45 min at -78°, one equivalent of tosyl azide was added, and the mixture was kept at -78° for an additional hour before allowing it to warm to room temperature for 2 hrs. The reaction mixture was diluted with *n*-hexane (100 mL), extracted several times with slightly alkaline H_2O (pH *ca.* 9), dried over Na_2SO_4, and the solvent largely removed by distillation. GC analysis revealed a 48% yield of 174 accompanied by 24% starting material. Purification of bright green liquid 174 was by preparative GC on a glass SE30 column.

NMR (C_6D_6) δ 0.18 (s, 9H), 0.30 (s, 9H)

IR (film) 2970(s), 2920(m), 2880(sh), 2040(s), 1410(brd. m), 1250(s), 1230(s), 925(m), 900(m), 835(s, brd.), 820(sh), 760 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 288(parent ion for ^{70}Ge isomer, 2), 213(1), 185(2), 143(7), 115(42), 99(14), 89(22), 85(51), 73(100), 59(32), the appropriate isotopic patterns were observed

Trimethylsilyltrimethylgermyldiazomethane (174) from trimethylsilyltrimethylgermylchloromethane

Metallation of the chloride was accomplished by vigorously stirring for 7 hrs. a refluxing solution of 0.50 mL trimethylsilyltrimethylgermylchloromethane and 1.5 excess of Li dispersion in 50 mL Et_2O. The resulting mixture was filtered through a glass-wool plug in the bottom directly into a second N_2-filled flask. After sitting overnight at 0°, the anion solution was added by syringe to a solution containing a slight excess of tosyl azide in 20 mL Et_2O at 0° C. After two hrs. at 0° and overnight a room temperature, the mixture was filtered and the majority of the Et_2O was evaporated. GC analysis showed that 174 was present in *ca*. 10% along with many other products.

Nitrogen-flow copyrolysis of trimethylsilyltrimethylgermyldiazomethane (174) and benzaldehyde

A 5% solution of 174 (0.0242 g) in benzaldehyde (0.52 g) was pyrolyzed at 400° C in the N_2-flow system. The only major products observed were 181, 182 (equal amounts by NMR and GC, combined yield 68%), and 180 (8%). Neither NMR nor GCMS analysis showed any evidence of products derived from a germene. Products 181 and 182 were isolated by preparative GC as colorless liquids. Ether 180 was formed in insufficient quantity to isolate, and was identified solely from its GCMS spectrum and subtraction of 181 and 182 from the NMR spectrum of the product mixture. The spectral characteristics of the three products are summarized below:

182 (Z isomer):

NMR (CCl_4) δ 0.13 (s, 9H), 2.06 (d, J=1.6 Hz., 3H), 7.18 (center of mult., 6H)

Mass spectrum; m/e (% rel. inten.) 232(parent ion for ^{70}Ge, 10), 217(97), 201(10), 177(31), 147(22), 131(41), 115(93), 101(96), 87(100), 73(25), 65(27), 51(28), appropriate isotopic patterns for one Ge were present

181 (E isomer):

NMR (CCl_4) δ 0.35 (s, 9H), 2.07 (d, J=1.6 Hz., 3H), 6.64 (q, J=1.6 Hz., 1H), 7.27 (s, 5H)

Mass spectrum; the mass spectra of 181 and 182 are virtually identical

180:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 291(parent ion-CH_3 for ^{70}Ge, 15), 215(1), 199(2), 189(13), 159(4), 145(4), 115(33), 90(100), 77(6), 73(58), 65(44), 59(16)

Photolysis of trimethylsilyltrimethylgermyldiazomethane (174) with MeOD added

In a quartz NMR tube was placed 400 µL of a 5% solution of 174 in C_6D_6, and a 6-fold molar excess of MeOD was added. The solution was repeatedly degassed, and then sealed under vacuum. After 2.5 hrs. irradiation, the NMR spectrum showed complete conversion to methoxy silane 183 and methoxy germane 184. Based on the NMR spectrum, 183 predominated by a factor of four. Assuming identical response factors, the GC ratio of 183:184 was 79:21. The spectral properties of 183 and 184 are given below:

183:

NMR (CCl_4) δ 0.07 (s, 6H), 0.15 (s, 9H), 1.07 (brd. s, 3H), 3.37 (s, 3H)

Mass spectrum; m/e (% rel. inten.) (parent ion not observed), 218(P-Me for ^{70}Ge, 38), 188(5), 159(5), 128(6), 115(24), 89(100), 73(25), 59(62)

184:

NMR (CCl_4) δ 0.03 (s, 9H), 0.31 (slightly brd. s, 6H), 1.11 (brd. s, 3H), 3.38 (s, 3H)

Mass spectrum; m/e (% rel. inten.) (parent ion not observed), 218(P-Me for ^{70}Ge, 29), 188(4), 159(6), 143(2), 131(22), 128(7), 115(8), 105(33), 101(21), 89(100), 86(41), 73(55), 59(39)

Trimethylchloromethylgermane

Trimethylchloromethylgermane was prepared from germanium tetrachloride according to the literature procedures (201, 202). The diazomethane used in this synthesis was obtained from Diazald which is sold by the Aldrich Company.

Bis(trimethylgermyl)methane

To a cooled (-23° C, CO_2/CCl_4 bath) suspension of 85 mmol Li dispersion in 60 mL Et_2O was added 4.70 g (28 mmol) Me_3GeCH_2Cl by syringe. The mixture was vigorously stirred for 2 hrs. after which time 28 mmol of neat Me_3GeCl was added. After separating the solution from the excess Li, it was diluted with 150 mL Et_2O, extracted several times with saturated aq. NH_4Cl, then with H_2O, and finally dried over Na_2SO_4. Evaporation of the Et_2O left a colorless liquid, which was shown by GC to be $>$95% pure (isolated yield, 69%) bis(trimethylgermyl)methane.

bp 152-155° C; lit. (203) 156-157° C

NMR (CCl_4) δ 0.21 (s, 18H), 0.00 (s, 2H)

IR (film) 2980(s), 2915(s), 2895(m), 1410(brd. m), 1240(s), 1045(s), 820(s), 780(m), 770(sh), 685 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) (parent ion not observed), 235(P-Me for most intense peak in that ensemble in which all of the required isotope peaks for a fragment ion with Ge_2 are observed, 32), 119(100), 105(11), 89(27)

Bis(trimethylgermyl)chloromethane

A solution of Me_3GeCH_2Cl (0.50 g) in 10 mL THF was cooled to -78° C before addition of one equivalent of <u>sec</u>-butyllithium in hexane. After stirring the solution for 30 min, one equivalent of Me_3GeCl was added by syringe. The temperature was allowed to rise to room temperature, and the solution was poured into 100 mL hexane. After extracting several times with H_2O, drying over Na_2SO_4, and evaporation of solvents, colorless liquid bis(trimethylgermyl)chloromethane was isolated in 60% with >95% GC determined purity. This material was used without further purification.

NMR (CCl_4) δ 0.27 (s, 18H), 2.72 (s, 1H)

IR (film) 2980(s), 2910(s), 2810(w), 1415(w, brd.), 1245(s), 1035(m), 820(s, brd.), 760(m), 695 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 284(P + 6 for $^{70}Ge_2$, 1), 269(2), 152(6), 131(13), 119(100), 105(17), 89(21)

Exact mass for $C_7H_{19}ClGe_2$ (parent ion for $^{70}Ge_2$) calc. 277.9660; meas. 277.9661

Bis(trimethylgermyl)diazomethane (126) from bis(trimethylgermyl)methane

To a solution containing $(Me_3Ge)_2CH_2$ (0.240 g), THF (5 mL), and HMPA (0.25 mL) at -78° C was slowly added one equivalent of t-butyllithium. After stirring for 30 min, one equivalent of neat tosyl azide was added to almost immediately change the solution from bright yellow to dark brown to a light yellow-orange color. The temperature was allowed to rise to 0° C, at which point the reaction mixture was poured into 100 mL n-hexane, and then extracted several times with slightly alkaline H_2O (pH ca. 9). The organic solution was dried (Na_2SO_4) and then evaporated to leave a mixture containing 126 (32%), $Me_3GeCH_2GeMe_2$t-Bu (8%), $(Me_3Ge)_2CH_2$, Me_3Ge-t-Bu, $(Me_3Ge)_2O$, and several unidentified minor components. It was discovered that 126 is not stable in the reaction mixture, and must be removed as quickly as possible. Purification of

126 was by preparative GC on a 6 ft. 15% SE30 glass column with a column temperature of 120° C. After purification, 126 is a bright green liquid which can be stored at -10° C for months without decomposition. When the synthesis of 126 is performed on a larger scale, better results are obtained with an inverse addition, that is, anion solution to tosyl azide. The spectral characteristics of the major products are summarized below:

126:

NMR (C_6D_6, 126 is not stable in CCl_4) δ 0.28 (s) (lit. δ 0.15 (155) and 0.22 (154))

IR (film) 2950(s), 2920(m), 2890(sh), 2850(w), 2040(s) (lit. 2050 for CN_2 (155)), 1250(s), 1220(s), 925(s), 830(s, brd.), 750(m), 680 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 276(most intense peak for P-Me fragment ion cluster, 9), 261(5), 233(10), 191(26), 175(8), 145(20), 131(18), 119(100), 89(63)

Trimethylgermyl-t-butyldimethylgermylmethane

NMR (CCl_4) δ -0.08 (s, 2H), 0.10 (s, 6H), 0.20 (s, 9H), 0.97 (s, 9H)

IR (film) 2980(s), 2960(s), 2930(s), 2910(sh), 2890(s), 2860(s), 1470(m), 1460(m), 1415(w), 1365(m), 1240(s), 1040(s), 1015(w), 825(s), 790(s), 750(m), 685 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 277(most intense peak for P-Me fragment ion cluster, 5), 235(41), 221(9), 205(4), 191(4), 159(6), 119(100), 89(25)

Bis(trimethylgermyl)diazomethane (126) from bis(trimethylgermyl)-chloromethane

Metallation was accomplished by refluxing for 5 hrs. a mixture of $(Me_3Ge)_2CHCl$ (0.6 mL), 1.5-fold excess of Li dispersion, and 60 mL of Et_2O. The mixture was filtered through a glass-wool plug at the bottom of the flask into a second flask, and then added via syringe to a solution of one equivalent of tosyl azide in 20 mL Et_2O at 0° C. After stirring at 0° C for 4 hrs., the mixture was filtered, the solvent evaporated, and GCMS analysis showed only ca. 1% yield of 126.

Nitrogen-flow pyrolysis of bis(trimethylgermyl)diazomethane (126)

A 5% solution of 126 (0.0206 g) in benzene (0.40 g) was pyrolyzed in the N_2-flow system at 400° C. The two major products were isolated by preparative GC and identified to be 187 (32%) and 188 (ca. 30%). Only a minute amount of digermazane 188 was isolated; it was identified by comparison of its NMR and mass spectra with those of the analogous disilazane (145). The spectral characteristics of 187 and 188 are given below:

187:

NMR (CCl_4) δ 0.12 (s, 9H), 0.22 (s, 12H), 0.23 (s, 3H), 0.33 (s, 3H), 0.34 (s, 3H), 1.16 (d, J=7.5 Hz., 3H), 6.12 (center of AB q., J=3.5 Hz., 2H), methine quartet was not observed due to low concentration.

IR (film) 2980(s), 2945(s), 2910(s), 2870(m), 2810(w), 1680(w), 1460(w), 1420(m, brd.), 1260(m), 1245(s), 1130(m), 1100(m, brd.), 1010(m, brd.), 950(m), 830(s), 785(s), 670(s), 600 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 494(P^++10 for $^{70}Ge_4$,<1), 479(<1), 377(3), 347(2), 319(3), 247(13), 207(10), 191(5), 175(2), 159(2), 145(4), 131(18), 119(100), 105(14), 89(18)

<u>188</u>:

NMR (CCl_4) δ 0.14 (brd. s, 24H), 6.12 (brd. s, 2H), the amine hydrogen was not seen due to very low concentration

Mass spectrum; m/e (% rel. inten.) (parent ion not observed), 262(P-Me_3Ge + 6 for $^{70}Ge_2$, 3), 247(14), 221(6), 191(2), 145(6), 129(4), 119(100), 89(21)

Copyrolysis of bis(trimethylgermyl)diazomethane (126) and benzaldehyde

A 5% solution of <u>126</u> in benzaldehyde was pyrolyzed in the N_2-flow system at 400° C. The pyrolysate was analyzed by GC. None of the many products (*ca*. 20 products) were isolated or positively identified. By GCMS, two products, which were present in approximately equal amounts (< 5% combined yield), and which had identical mass spectra, were identified as olefins <u>190</u> and <u>191</u>.

Mass spectra; m/e (% rel. inten.) 236(parent ion + 6 for ^{70}Ge, 5), 221(49), 205(4), 181(17), 139(10), 115(42), 105(100), 89(31), 77(51), 65(8), 51(27)

Photolysis of bis(trimethylgermyl)diazomethane (126)

A solution of <u>126</u> (0.0270 g) in benzene (0.50 g) was repeatedly degassed in a quartz NMR tube, and the tube was then sealed *in vacuo*.

Photolysis was carried out for 2 hrs. after which time GC analysis revealed an 89% yield of 187 and ca. 1% of digermoxane 192. Product 192 was produced by the trapping of germene 185 by water. This product was eliminated by preparative GC of the diazo compound just prior to photolysis. Compound 192 was identified by the spectra shown below.

192:

NMR (CCl_4) δ 0.20 (s, 18H), 0.32 (s, 6H), 0.33 (s, 6H), 1.22 (d, J=8.0 Hz., 6H), the remaining 2H q was not observed due to low concentration

Mass spectrum; m/e (% rel. inten.) 497(parent-Me + 10 for $^{70}Ge_4$, 8), 367(9), 249(13), 235(8), 221(7), 207(10), 191(3), 175(2), 161(2), 145(3), 131(28), 119(100), 105(21, 89(13), 73(3)

Photolysis of bis(trimethylgermyl)diazomethane (126) with MeOD added

To 0.50 mL of a 5% solution of 126 in C_6D_6 was added a 6-fold excess of MeOD. This solution was repeatedly degassed, and the NMR tube was then sealed in vacuo. After 2 hrs. irradiation, both NMR and GC analysis showed complete conversion of 126 to 193.

NMR (CCl_4) δ 0.15 (s, 9H), 0.31 (s, 3H), 0.32 (s, 3H), 1.17 (brd. s, 3H), 3.36 (s, 3H)

Mass spectrum; m/e (% rel. inten.) 266(parent -Me + 6 for $^{70}Ge_2$, 66), 236(42), 207(43), 191(18), 149(10), 132(69), 119(100), 105(97), 89(58), the appropriate isotopic clusters were present.

Attempted catalytic preparation of 2,2,3,3-tetramethyl-2,3-disiladioxane (199)

In a 100 mL round-bottomed flask was placed 50 mL of deoxygenated benzene (deoxygenated by bubbling N_2 through for several minutes). To the flask was added a small amount ($<$ .05 g) of tris(triphenylphosphine)-rhodium chloride. The catalyst all dissolved within 1-2 minutes. Ethylene glycol (0.25 mL, 4.47 mmol) was added via syringe. The ethylene glycol did not all dissolve even after stirring for 1 hr. 1,1,2,2-tetramethyldisilane (198) (0.75 mL, 4.50 mmol) was added via syringe. After stirring for 2 hrs., all the ethylene glycol had disappeared and the GC showed one major peak. The benzene was distilled at room temperature and reduced pressure (ca. 30 Torr) and the residue was then distilled at full vacuum. The major product was isolated from the distillate by preparative GC (10 ft. 15% SE30 column) and was identified as the bis(dimethylsilyl)ether of ethylene glycol (200).

When the reaction between ethylene glycol and 198 in the presence of Wilkinson's catalyst was allowed to proceed for 24 hrs., the initial major product 200, nearly completely disappeared. Removal of the benzene by rotary evaporator left a dirty solid which was sublimed (60-70° C at atmospheric pressure) to produce fine plate-like, colorless crystals (mp 59-61° C). The product was identified as 2,2-dimethyl-2-sila-1,3-dioxacyclopentane (201).

Both products 200 and 201 were identified by comparison with independently synthesized samples. The spectral characteristics of these products are summarized as follows:

<u>200</u>:

NMR (CCl_4) δ 0.18 (d, J=2.7 Hz., 12H), 3.65 (s, 4H), 4.90 (heptet, J= 2.7 Hz., 2H)

IR (film) 2960(m), 2930(m), 2900(sh), 2865(m), 2105(s), 1455(s), 1420(w), 1385(w), 1370(s), 1285(s), 1245(s), 1140(s), 1090(s), 945(s), 925(s), 885(s), 825(m), 770(sh), 755(m), 715 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) 177(parent ion -H, 5), 163(21), 149(10), 135(64), 133(77), 119(93), 103(21), 89(98), 73(42), 59(100), 45(33)

Exact mass for $C_3H_{15}O_2Si_2$ (parent ion $-CH_3$) calc. 163.0611; meas. 163.0609

<u>201</u>:

NMR (CCl_4) δ 0.10 (s, 6H), 3.73 (s, 4H)

IR (CCl_4) 2980(m), 2945(m), 2920(m), 2880(m), 2740(w), 1460(w), 1395(w), 1375(s), 1295(m), 1260(s), 1155(s), 1125(s), 1105(s), 960(s), 935(s), 840 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 118(parent ion, 11), 103(100), 101(11), 88(30), 77(7), 75(6), 73(2), 61(17), 58(42), 47(2), 45(14)

Exact mass for $C_4H_{10}O_2Si$ (parent ion) calc. 118.0450; meas. 118.0445

<u>Independent synthesis of 200</u>

To a 250 mL round-bottomed flask equipped with a mechanical stirrer were added 150 mL of Et_2O and 10.0 mL of ethylene glycol (0.179 mole). The ethylene glycol did not all dissolve until 29.0 mL of pyridine (0.358 mole) was added. The Et_2O solution was cooled to 0° C and 40.0 mL of dimethylchlorosilane (0.359 mole) was added dropwise via addition funnel. After all the dimethylchlorosilane was added, the temperature was allowed to rise to room temperature where stirring was continued for 1 hr. The mixture was then added to 200 mL of hexane, was extracted with saturated $NaHCO_3$ and with water, and was dried over Na_2SO_4. The solvents were evaporated with a rotory evaporatory to leave a colorless liquid which was distilled (bp 144-147° C) to produce 25.0 g of 200 (78%).

Independent synthesis of 201

To a 250 mL three-necked flask equipped with a mechanical stirrer and an addition funnel were placed 200 mL of THF, 4.0 mL of ethylene glycol (0.0715 mole), and 22 mL of Et_3N (0.158 mole). This solution was cooled to -78° C and 8.4 mL of dimethyldichlorosilane (0.0693 mole) was slowly added. After the addition was complete, the temperature was slowly raised to room temperature. Most of the THF was removed by rotary evaporator. Skelly A (300 mL) was added, and this mixture was extracted several times with H_2O. After drying ($NaSO_4$), all solvents were removed by rotary evaporator to leave 7.771 g of a pale yellow solid, which was nearly pure 201 (95%). This solid contained a small amount (<5%) of the seven-membered ring 205. Separation of 201 from 205 was attempted by GC, column chromatography, sublimation, and HPLC; none of these methods proved successful.

Treatment of 200 with Wilkinson's catalyst

In a 5 mL round-bottomed flask were placed 3 mL of benzene, a small amount (ca. .01 g) of Wilkinson's catalyst, and 0.221 g of 200 (1.239 mmol). After stirring at room temperature for 24 hrs., the GC indicated that 201 had been formed in 95% yield. Also formed were dimethylsilane and a small amount of CO_2. Both of these gaseous products were identified by GCMS. In a separate experiment, the amount of CO_2 was measured by the usual method of trapping with ascarite (204). It was found that *ca.* 0.074 mole of CO_2 was formed per mole of 200 which was used.

Nitrogen-flow pyrolysis of 2,2-dimethyl-2-sila-1,3-dioxacyclopentane (201)

A 5% solution of 201 in pesticidal quality hexane was prepared. Samples of this solution were pyrolyzed in the N_2-flow system (flow rate was approximately 30 mL/min) at temperatures from 320° to 580° C. Compound 201 was recovered unreacted in every case. At temperatures >500° C, the hexane solvent did react to some extent.

Sealed-tube pyrolysis of neat 201

In a small sealing tube, 0.285 g of 201 (2.42 mmol) was placed. After degassing, the tube was sealed under vacuum. After heating for 48 hrs. at 110°, the tube was opened. The starting material had changed from a white solid to a slightly dark viscous liquid. To dissolve this liquid, 1.0 mL of benzene was added. GC analysis showed this material to be essentially pure 201. Water (*ca.* .025 g) was added to the benzene solution. After stirring for two days, the water had not all dissolved, and the GC showed that no reaction had occurred.

Sealed-tube pyrolysis of 201 in dodecane

In a sealing tube, 0.0549 g of 201 and ca. 1.0 mL of dodecane were placed. The solution was degassed by the freeze-thaw method and the tube was sealed under vacuum. After heating at 150° for 16 hrs., the tube was opened. GC analysis showed that no reaction had occurred.

Photolysis of 201

Approximately 30 mg of 201 and 0.5 mL of cyclohexane were placed in a quartz NMR tube. After degassing by the freeze-thaw method, the tube was sealed under vacuum. The solution was photolyzed with a high pressure 450W Hanovia lamp. After 16 hrs. of photolysis, the solution had become a yellow color, but NMR indicated that no reaction had occurred. The tube was then opened and GC analysis also showed that no reaction had occurred.

Pyrolysis of 201 in tetradecane while open to the atmosphere

To a 10 mL flask equipped with a condenser and a sidearm were placed 0.124 g of 201 and 2 mL of tetradecane. The system was open to the atmosphere through a drying tube on top of the condenser. The flask was placed in an oil bath at 140° C. The progress of the reaction was monitored by GC. After 6 hrs., almost all the starting material had disappeared, and the major product was the 7-membered ring 205, while D_3, D_4, and 206 were minor products. After heating for 22 hrs., 205 had become a minor product with D_3, D_4, and 206 now being the major products. D_3 and D_4 were simply identified by comparison with authentic samples. Product 206 was identified solely by GCMS, while 205 was compared with an independently synthesized sample (205). The spectral characteristics of 205 and 206 are summarized as follows:

205:

NMR (CCl_4) δ 0.13 (s, 12H), 3.81 (s, 4H)

IR (CCl_4) 2965(m), 2940(m), 2870(m), 1460(w), 1295(m), 1260(s), 1135(s), 1110(s), 1100(sh), 1000(s), 925(s), 840 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 177(P^+ $-CH_3$, 68), 159(4), 151(4), 147(23), 133(100), 119(4), 103(9), 89(5), 73(13), 59(8)

Exact mass for $C_5H_{13}O_3Si_2$ (parent ion $-CH_3$) calc. 177.0403; meas. 177.0405

Exact mass for $C_3H_9O_2Si_2$ (D_2 $-CH_3$) calc. 133.0141; meas. 133.0146

206:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 251(P^+ $-CH_3$, 16), 236(1), 221(12), 207(100), 193(15), 191(16), 177(4), 163(2), 147(3), 133(9), 119(4), 103(6), 96(11), 89(8), 73(9), 57(10)

Nitrogen-flow pyrolysis of 201 with O_2 added

The carrier gas was composed of 96% N_2 and 4% O_2, with a total flow rate of ca. 30 mL/min. A 5% solution of 201 in benzene was pyrolyzed from 400° to 600° C. Approximately 50% of 201 reacted at 400°; all of it reacted at 600°. Many products were formed including D_3, D_4, 205, and 206.

Pyrolysis of 201 in dimethyldiethoxysilane (207)

In a sealing tube, 0.0930 g of 201 (0.786 mmol) and 2 mL of dimethyldiethoxysilane were placed. After degassing, the tube was sealed under vacuum. Pyrolysis was carried out at 130° C for 36 hrs. Only a trace of the dimethylsilanone-trapped product, sym-diethoxytetramethyldisiloxane was formed. The major products were 209 (51%) and 210 (19%). These products were isolated by preparative GC. Their spectral characteristics are summarized as follows:

209:

NMR ($CDCl_3$) δ 0.15 (s, 12H), 1.23 (t, J=8 Hz., 6H), 3.75 (q, J=8 Hz., 4H), 3.76 (s, 4H)

IR (film) 2970(s), 2930(m), 2910(sh), 2875(m), 1395(w), 1295(w), 1260(s), 1165(sh), 1150(s), 1110(s), 1080(s), 955(s), 840(s), 795(s), 730(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 251(P^+ -CH_3, 6), 221(4), 207(23), 179(18), 177(42), 163(41), 151(22), 149(9), 133(74), 119(11), 103(100), 89(57), 75(41), 59(22), 45(14)

Exact mass for $C_9H_{23}O_4Si_2$ (parent ion -Me) calc. 251.1135; meas. 251.1135

Exact mass for $C_7H_{19}O_3Si_2$ (P^+ -Me-CH_3CHO) calc. 207.0873; meas. 207.0871

Exact mass for $C_4H_{11}OSi$ ($EtO\overset{\cdot+}{Si}Me_2$) calc. 103.0579; meas. 103.0574

210:

NMR ($CDCl_3$) δ 0.13 (s, 6H), 0.14 (s, 6H), 1.21 (brd. t, 6H), 3.73 (brd. q, 4H), 3.74 (brd. s, 4H)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 251(P^+ -CH_3, 7), 221(68), 207(12), 193(6), 177(81), 163(10), 149(32), 133(59), 119(7), 103(100), 89(24), 75(30), 59(21), 45(14)

2,2,3,3-tetramethyl-2,3-disila-1,4-dioxane (199)

In a 50 mL three-necked flask equipped with an overhead stirrer and an addition funnel were placed Et_2O (25 mL), ethylene glycol (0.333 g, 5.36 mmol), and pyridine (0.888 g, 11.23 mmol). This solution was cooled to 0° C and 1,2-dichlorotetramethyldisilane (1.000 g, 5.34 mmol) in 5 mL of ether was slowly added. After the addition was complete, the temperature was allowed to rise to room temperature where stirring was continued for one more hour. GC analysis indicated that 199 was formed in 92% yield. After filtering, the Et_2O was evaporated under a stream of N_2 to leave a colorless liquid which was nearly pure 199. A sample was purified by preparative GC.

NMR (CCl_4) δ 0.10 (s, 12H), 3.67 (s, 4H)

IR (CCl_4) 2965(m), 2945(m), 2930(sh), 2875(m), 1460(w), 1290(m), 1260(sh), 1250(s), 1120(s), 1095(m), 930(w), 910(sh), 900(s), 630 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 176(parent ion, <1), 161(3), 149(4), 133(100), 131(7), 117(18), 115(11), 103(7), 89(3), 75(7), 73(31), 59(16), 45(14)

Exact mass for $C_5H_{13}O_2Si_2$ (parent ion $-CH_3$) calc. 161.0454; meas. 161.0468

Hydrolysis of 199

A fresh sample of 199 (*ca*. 30 mg), which had been isolated by preparative GC, was placed in an NMR tube along with CCl_4. Approximately 10 mg of H_2O was added and the tube was shaken for several minutes. NMR showed only a single Si-Me peak, the CH_2 peak had completely disappeared. A single product was isolated by preparative GC and was identified to be 2,2,3,3,5,5,6,6-octamethyl-2,3,5,6-tetrasiladioxane (211).

mp 40-45° C; lit. 45-46° (206)

NMR (CCl_4) δ 0.08 (s)

IR (CCl_4) 2970(s), 2890(m), 1400(w), 1245(s), 1015(s), 845(m), 665(m), 545 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 264(parent ion, 8), 249(18), 233(1), 221(3), 205(53), 191(34), 175(11), 161(4), 147(23), 133(3), 131(10), 117(21), 103(2), 101(2), 84(14), 73(100), 59(9), 49(18)

Nitrogen-flow pyrolysis of 199

A 5% solution of 199 in deoxygenated benzene was pyrolyzed in the N_2-flow system at 400° C. All of 199 reacted. The pyrolysate contained no ethylene, D_3, or D_4. The products which were observed and identified only on the basis of GCMS were the 5-membered ring 201 and the 7-membered ring 2,2,3,3,4,4-hexamethyl-2,3,4-trisila-1,5-dioxacycloheptane (212). No yields were determined.

Mass spectrum; m/e (% rel. inten.) 234(parent ion, 3), 219(4), 205(2), 191(35), 175(8), 159(2), 147(19), 133(15), 131(18), 116(100), 103(8), 101(27), 85(5), 73(92), 59(22), 43(20)

Nitrogen-flow copyrolysis of 199 and D_3

To a 5% solution of 199 in benzene was added a large excess of D_3 (ca. 8-fold excess). This solution was pyrolyzed in the nitrogen-flow system at 400° C. No noticeable increase in the amount of D_4 was observed. (The D_3 which was used was contaminated with a small amount of D_4.) In addition to products 201 and 212 was formed a new product which was identified on the basis of GCMS to be 1,1,2,2,4,4,6,6-octamethyl-1,2,4,6-tetrasilatrioxacycloheptane (213), which arises via dimethylsilylene insertion into D_3. The mass spectrum reported below is identical to that given by an authentic sample of 213.

Mass spectrum; m/e (% rel. inten.) 280(parent ion, 7), 265(62), 249(4), 235(2), 221(2), 207(37), 191(12), 189(6), 177(13), 163(3), 147(5), 133(8), 125(6), 117(5), 103(5), 73(100), 59(7), 45(11)

Nitrogen-flow copyrolysis of 199 and dimethyldiethoxysilane (207)

To a 5% solution of 199 in benzene was added a large excess of dimethyldiethoxysilane (ca. 8-fold excess). This solution was pyrolyzed in the N_2-flow system at 350° C. In addition to products 201 and 212 were formed two new products which were identified by GCMS to be 1,2-diethoxytetramethyldisilane (214) and 1,3-diethoxyhexamethyltrisilane (215). The mass spectra of these products are reported below:

214:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 191(P^+ -Me, 6), 177(23), 161(7), 149(166), 147(14), 133(100), 119(18), 117(25), 103(51), 87(5), 75(69), 73(55), 59(35), 45(32)

215:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 249(P^+ -Me, 6), 235(17), 219(4), 207(8), 191(39), 175(13), 161(12), 147(14), 133(22), 117(92), 116(100), 103(47), 75(50), 73(96), 59(32), 45(24)

Meso- and dl-dihydrobenzoin

Meso-dihydrobenzoin was prepared by the $NaBH_4$ reduction of benzoin (207). Epimerization of meso- to dl-dihydrobenzoin was accomplished by heating with KOH under vacuum (208).

Cis- and trans-5,6-diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (197a and 197b)

The same procedure was used to prepare both 197a and 197b. In a 50 mL three-necked flask equipped with an overhead stirrer and an addition funnel were placed Et_2O (25 mL), pyridine (0.28 mL, 3.48 mmol), and the appropriate dihydrobenzoin (0.364 g, 1.70 mmol). This solution was cooled to 0° C. 1,2-dichlorotetramethyldisilane (0.32 mL, 1.72 mmol) in 5 mL of Et_2O was slowly added. After all the disilane was added, the temperature was allowed to slowly rise to room temperature where stirring was continued for one more hour. The solution was filtered under N_2 and the Et_2O was evaporated under a stream of N_2 to leave behind a white, viscous liquid which was shown by NMR to be nearly pure dioxane 197. Both 197a and 197b are oxidized by air to form cis- and trans-6,7-diphenyl-2,2,4,4-tetramethyl-2,4-disilatrioxacycloheptane 216. The spectral characteristics of 197a, 197b, and 216 are summarized as follows:

197a:

NMR (CCl_4) δ 0.36 (s, 12H), 5.15 (s, 2H), 7.02 (m, 10H)

IR (CCl_4) 3090(w), 3060(m), 3030(m), 2955(s), 2895(s), 2885(sh), 1600(w), 1495(m), 1450(s), 1370(s), 1315(w), 1245(s), 1195(m), 1110(s), 1095(s), 1065(s), 1025(m), 955(m), 915(m), 880(s), 855(s), 690(s), 640 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 328(parent ion, <1), 313(<1), 270(4), 237(1), 207(19), 193(2), 180(100), 179(87), 165(48), 149(22), 133(30), 131(35), 116(14), 105(22), 89(9), 77(18), 73(54), 59(14), 45(11)

197b:

NMR (cyclohexane) δ 0.35 (s, 12H), 4.70 (s, 2H), 6.98 (m, 10H)

Mass spectrum; identical to that of 197a

216:

Mass spectrum; m/e (% rel. inten.) 344(parent ion, 5), 329(1), 270(10), 238(44), 223(24), 195(4), 180(17), 179(23), 167(46), 149(39), 133(26), 117(13), 106(38), 105(100), 91(28), 77(72), 51(35)

Photolysis of 197b

Approximately 30 mg of 197b and 0.5 mL of cyclohexane were placed in a quartz NMR tube. This solution was degassed and the tube was sealed under vacuum. Photolysis was carried out for 2 hrs. with a 450W high pressure Hanovia lamp. The solution became yellow-colored, but both

NMR and GC indicated that no noticeable reaction had occurred.

Nitrogen-flow pyrolysis of 197

A 5% solution of 197 in deoxygenated benzene was pyrolyzed in the N_2-flow system at 500°. The only products formed were D_3 (9.7%), D_4 (18.1%), cis-stilbene (4.9%), and trans-stilbene (80.7%). All products were identified by comparison with authentic samples. The observed cis: trans ratio is simply the thermodynamic equilibrium ratio at 500° as was demonstrated by pyrolysis of pure cis- and pure trans-stilbene under identical conditions.

When the N_2-flow pyrolysis of 197 was conducted at 350°, D_3, D_4, cis- and trans-stilbene were all formed along with many other unidentified products. Compound 197 completely reacted at 350°.

1,3-dibromotetramethyldisiloxane (217)

Compound 217 was prepared by bromination of 1,1,3,3-tetramethyldisiloxane according to the literature procedure (209).

Attempted synthesis of D_2 by hydrolysis of 217

In a 100 mL three-necked flask equipped with an overhead stirrer and an addition funnel were placed 217 (0.70 g, 2.4 mmol), pyridine (0.50 mL, 6.2 mmol), and CH_2Cl_2 (20 mL). This solution was cooled to -78° and wet Et_2O (10 mL containing ca. 5 mmol H_2O) was added dropwise. After all the ether solution was added, stirring at -78° was continued for a half hour. The solution was then filtered under N_2 and the filtrate was warmed to room temperature. GC analysis revealed the formation of D_3 (3%), D_4 (66%), D_5 (1%), D_6 (14%), D_8 (2%), and D_{10} (1%). All the cyclosiloxanes were identified by GCMS.

The addition of D_3 or dimethyldimethoxysilane to the CH_2Cl_2 solution of 217 before the addition of H_2O resulted in no change in the reaction. The cyclosiloxanes were still formed in approximately the same ratio.

Inverse addition of 217 to H_2O in Et_2O

In a 100 mL three-necked flask equipped with an overhead stirrer and an addition funnel were placed wet Et_2O (25 mL) and pyridine (0.30 mL, 3.7 mmol). This solution was cooled to -78° C and 10 mL of .12 M solution of 217 in CH_2Cl_2 (1.2 mmol) was added dropwise. After all the dibromide was added, the solution was filtered under N_2. The filtrate was warmed to room temperature and was analyzed by GC. D_4 was still the major product, but D_6 and D_8 were present in only trace amounts, while D_{10} was not seen at all (exact yields were not determined). The second major product was identified by GCMS to be tetramethyldisiloxane-1,2-diol (218).

The addition of D_3 to the wet ether solution before the addition of 217 resulted in no change in the reaction. The addition of dimethyldimethoxysilane to the wet ether solution before the addition of 217 resulted in the formation of one new product. This product, identified by GCMS to be 3-methoxy-1,1,3,3-tetramethyldisiloxane-4-ol (219), was formed in about the same yield as product 218 (the exact yields were not determined).

Pyrolysis of silyl ethers

All silyl ethers were purified before pyrolysis by preparative GC. Dimethyldimethoxysilane (26), dimethyldiethoxysilane (207), and tetraethoxysilane (239) were purchased from Petrarch Systems Inc. All trimethylsilyl ethers were prepared from the appropriate alcohol in hexamethyldisilazane at temperatures from 25-90° C. No solvents were used. In some cases, a trace of trimethylchlorosilane was added to start the reaction.

All yields were calculated using a CSI Supergrator 3. The response factors for all products in each pyrolysis were assumed to be the same. The relative mass percentage given by the integrator for each product was converted to relative mole percentage. For each pyrolysate, the total of the relative mole percentage of all identified products was defined to be 100%. Also reported in each case was the total mass percentage of the pyrolysate which was composed of the identified products. Each silyl ether was pyrolyzed at several temperatures. The yield data for pyrolysis at each temperature were presented in the Results and Discussion section of this dissertation.

Pyrolysis of dimethyldimethoxysilane (26)

Samples of neat dimethyldimethoxysilane (26) were pyrolyzed in the N_2-flow system at temperatures from 600° to 750° C. The pyrolysate was found to contain, in addition to 26, trimethylmethoxysilane (228), trimethoxymethylsilane (229), *sym*-dimethoxytetramethyldisiloxane (27), 1,1,3-trimethoxytrimethyldisiloxane (220), 1,5-dimethoxyhexamethyltrisiloxane (223), and 1,1,5-trimethoxypentamethyltrisiloxane (225).

Product 228 was identified only by GCMS, while 229, 27, 220, 223, and 225 were all isolated by preparative GC (10 ft. 15% SE30 column), and were identified by a variety of spectroscopic techniques. The spectral characteristics of all these products are summarized below:

228:

Mass spectrum; m/e (rel. inten.) 104(parent ion, 1), 89(100), 75(4), 73(4), 59(86), 45(18), 43(21)

- the GCMS gave a satisfactory match with the library spectrum

229:

NMR (CCl_4) δ 0.00 (s, 3H), 3.45 (s, 9H)

IR (film) 2970(sh), 2950(s), 2920(sh), 2840(s), 1460(w), 1265(s), 1190(s), 1085(s), 835(s), 785(s), 730 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) 136(parent ion, $<$1), 121(100), 105(14), 91(57), 75(20), 59(17), 45(9)

27:

NMR (CCl_4) δ 0.02 (s, 12H), 3.42 (s, 6H)

IR (film) 2980(s), 2960(sh), 2920(m), 2850(s), 1260(s), 1195(m), 1100(s), 1060(s), 850(s), 800(s), 730 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 179(P^+ -Me, 100), 163(6), 149(91), 133(27), 119(59), 105(15), 103(15), 89(22), 83(2), 75(21), 73(17), 67(12), 59(43)

Exact mass for $C_5H_{15}O_3Si_2$ (parent ion $-CH_3$) calc. 179.0560; meas. 179.0553

Exact mass for $C_4H_{13}O_2Si_2$ (parent ion $-CH_3-CH_2O$) calc. 149.0454; meas. 149.0446

220:

NMR (CCl_4) δ 0.04 (s, 3H), 0.08 (s, 6H), 3.42 (s, 3H), 3.45 (s, 6H)

IR (film) 2965(s), 2940(m), 2910(sh), 2840(s), 1260(sh), 1255(s), 1185(m), 1085(s), 1055(s), 1015(m), 840(s), 805(s), 790(sh), 770(m), 725 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 195(P^+ -Me, 82), 179(8), 165(100), 149(26), 135(70), 121(7), 119(30), 105(29), 103(11), 89(11), 82(11), 75(31), 73(6), 67(6), 59(24)

Exact mass for $C_5H_{15}O_4Si_2$ (parent ion $-CH_3$) calc. 195.0509; meas. 195.0504

Exact mass for $C_4H_{13}O_3Si_2$ (parent ion $-CH_3-CH_2O$) calc. 165.0403; meas. 165.0389

223:

NMR (CCl_4, 100 MHz) δ 0.05 (s, 12H), 0.08 (s, 6H), 3.41 (s, 6H)

IR (film) 2960(s), 2940(sh), 2900(m), 2830(s), 1255(s), 1180(m), 1090(s), 1040(s), 845(s), 790(s), 725 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 253(P^+ -Me, 100), 237(3), 223(69), 207(35), 193(29), 177(15), 163(7), 149(8), 133(25), 119(35), 104(31), 97(3), 89(49), 75(15), 73(50), 59(41)

Exact mass for $C_7H_{21}O_4Si_3$ (parent ion $-CH_3$) calc. 253.0748; meas. 253.0752

Exact mass for $C_6H_{19}O_3Si_3$ (parent ion $-CH_3-CH_2O$) calc. 223.0642; meas. 223.0647

225:

NMR (CCl_4, 100 MHz) 3 peaks from δ 0.06 to 0.10 (3 singlets, 15H), 3.42 (s, 6H), 3.44 (s, 3H)

IR (film) 2960(s), 2940(sh), 2910(m), 2840(s), 1260(s), 1190(m), 1090(s, brd.), 1050(s), 845(s), 815(sh), 795(s), 725 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 269(P^+ -Me, 100), 253(4), 239(46), 223(24), 209(29), 207(9), 193(66), 179(30), 177(11), 165(12), 163(13), 149(12), 133(17), 127(9), 119(28), 112(29), 105(19), 97(11), 89(40), 75(20), 73(26), 59(40)

Exact mass for $C_7H_{21}O_5Si_3$ (parent ion $-CH_3$) calc. 269.0697; meas. 269.0689

Exact mass for $C_6H_{19}O_4Si_3$ (parent tion $-CH_3-CH_2O$) calc. 239.0591; meas. 239.0581

Pyrolysis of dimethyldiethoxysilane (207)

Samples of neat dimethyldiethoxysilane (207) were pyrolyzed in the N_2-flow system at temperatures from 500° to 650° C. The pyrolysate was found to contain, in addition to 207, dimethylether, D_3, trimethylethoxysilane (237), sym-diethoxytetramethyldisiloxane (208), 1,1,3-triethoxytrimethyldisiloxane (231), 1,5-diethoxyhexamethyltrisiloxane (232), 1,3,5-triethoxypentamethyltrisiloxane (233), 1,3,3,5-tetraethoxytetramethyltrisiloxane (236), 1,1,3,5-tetraethoxytetramethyltrisiloxane (235), and 1,1,5-triethoxypentamethyltrisiloxane (234). Dimethylether, D_3, and 237 were not isolated, but were identified by GCMS. All other products were isolated by preparative GC (10 ft. 15% SE30 column). Products 234 and 235 were collected together, but were separated from each other by further preparative GC (5 ft. 15% XF1150 column). Products 232, 233, and 236 were collected together. Due to the small amount of these three products, no further separation was attempted, thus only GCMS data are available. The spectroscopic properties of all the products are summarized below:

237:

Mass spectrum; m/e (% rel. inten.) 118(parent ion,<1), 103(11), 73(45), 61(4), 45(100)

208:

NMR (CCl_4) δ 0.05 (s, 12H), 1.16 (t, 6H, J=7 Hz.), 3.68 (q, 4H, J=7 Hz.)

IR (film) 2970(s), 2915(m), 2900(m), 2880(m), 1440(w), 1390(m), 1260(s), 1165(m), 1110(s), 1075(sh), 1060(s), 1020(s), 950(s), 840(s), 800(s), 720 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen) , 207(P^+ -Me, 35), 177(30), 163(60), 151(53), 149(18), 135(100), 133(51), 119(46), 105(13), 103(24), 89(10), 75(42), 73(28), 66(25), 59(16)

Exact mass for $C_7H_{19}O_3Si_2$ (parent ion $-CH_3$) calc. 207.0873; meas. 207.0872

231:

NMR (CCl_4, 100 MHz) δ 0.05 (s, 3H), 0.09 (s, 6H), 1.19 (overlapping t, 9H, J=7 Hz.), 3.70 (q, 2H, J=7 Hz.), 3.72 (q, 4H, J=7 Hz.)

IR (film) 2970(s), 2930(m), 2900(sh), 2880(m), 1635(w), 1480(w), 1445(w), 1390(m), 1295(w), 1265(s), 1170(s), 1110(s), 1080(s, brd.), 955(s), 840(s), 825(m), 800(2), 770(2), 725 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 237(P^+ -Me, 84), 207(65), 193(99), 181(8), 165(48), 163(53), 153(61), 149(36), 135(100), 119(84), 105(25), 103(24), 96(19), 89(13), 75(40), 73(9), 61(14), 59(10)

Exact mass for $C_8H_{21}O_4Si_2$ (parent ion $-CH_3$) calc. 237.0978; meas. 237.0979

Exact mass for $C_6H_{17}O_3Si_2$ (parent ion $-CH_3-CH_3CHO$) calc. 193.0716; meas. 193.0709

232:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 281(P^+ -Me, 7), 251(4), 237(18), 225(5), 207(100), 193(31), 177(5), 163(3), 149(2), 133(15), 119(8), 103(8), 96(9), 89(6), 75(7), 73(10), 59(6)

233:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 311(P^+ -Me, 11), 281(10), 267(100), 251(14), 223(6), 193(45), 179(9), 164(7), 149(6), 133(29), 125(11), 119(9), 103(9), 75(10), 61(4), 45(8)

236:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 341(P^+ -Me, 39), 325(13), 295(4), 283(2), 263(1), 163(36), 155(28), 147(4), 141(3), 85(2), 73(100), 59(8)

235:

NMR (CCl_4, 100 MHz) δ 0.07 - 0.12 (3 singlets, 12H), 1.18 (overlapping triplets, 12H, J=7 Hz.), 3.69 (q, 2H, J=7 Hz.), 3.71 (q, 4H, J=7 Hz.), 3.74 (q, 2H, J=7 Hz.)

IR (CCl_4) 2970(s), 2920(w), 2880(w), 1440(w), 1390(w), 1265(s), 1260(sh), 1165(m), 1115(s), 1070(s, brd.), 950(s), 850 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 341(P^+ -Me, 9), 311(7), 297(3), 285(8), 269(60), 267(100), 253(19), 251(19), 237(8), 223(6), 207(5), 193(23), 179(7), 163(3), 148(3), 133(9), 126(17), 119(8), 73(7), 59(3)

234:

NMR (CCl_4, 100 MHz) δ 0.07 - 0.09 (overlapping singlets, 15H), 1.17 (overlapping triplets, 9H, J=7 Hz.), 3.69 (q, 4H, J=7 Hz.), 3.71 (q, 2H, J=7 Hz.)

IR (CCl_4) 2970(s), 2920(w), 2880(w), 1440(w), 1390(w), 1255(s), 1065(m), 1110(s), 1070(s), 1050(sh), 950(s), 835 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 311(P^+ -Me, 5), 283(6), 281(4), 267(11), 255(4), 237(56), 227(11), 223(10), 209(52), 207(37), 193(100), 179(26), 165(6), 149(3), 133(12), 119(6), 96(4), 75(8), 73(7), 59(4)

Exact mass for $C_{10}H_{27}O_5Si_3$ (parent ion $-CH_3$) calc. 311.1166; meas. 311.1155

Pyrolysis of tetraethoxysilane (239)

Samples of neat tetraethoxysilane (239) were pyrolyzed in the N_2-flow system at temperatures from 500° to 650° C. The pyrolysate was found to contain, in addition to 239, dimethylether, hexaethoxydisiloxane (240), and octaethoxytrisiloxane (241). The dimethylether was identified only by GCMS. Products 240 and 241 were isolated by preparative GC. The spectral characteristics of these products are summarized below:

240:

NMR (CCl_4) δ 1.20 (t, 18H, J=Hz.), 3.80 (q, 12H, J=7 Hz.)

IR (film) 2980(s), 2930(s), 2895(s), 1485(w), 1445(m), 1390(m), 1365(w), 1295(m), 1170(s), 1100(s), 1080(s), 965(s), 805(sh), 790(s), 680 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 342(parent ion, 1), 297(100), 283(3), 269(34), 253(60), 241(14), 225(38), 213(15), 197(29), 185(20), 169(21), 157(93), 141(85), 139(74), 123(66), 107(10), 79(8), 55(12)

Exact mass for $C_{12}H_{30}O_7Si_2$ (parent ion) calc. 342.1530; meas. 342.1541

Exact mass for $C_{10}H_{25}O_6Si_2$ (parent ion -OEt) calc. 297.1190; meas. 297.1181

241:

NMR (CCl_4, 100 MHz) δ 1.21 (overlapping triplets, 24H, J=7 Hz.), 3.80 (q, 12H, J=7 Hz.), 3.82 (q, 4H, J=7 Hz.)

IR (film) 2980(s), 2925(s), 2890(s), 1480(w), 1440(m), 1390(m), 1365(w), 1295(m), 1165(s), 1100(s), 1075(s), 965(s), 790(s), 690 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 431(P^+ -OEt, 12), 401(40), 387(4), 373(20), 357(49), 347(11), 329(35), 313(19), 301(21), 285(18), 274(16), 273(26), 257(18), 235(100), 217(77), 201(60), 199(54), 185(37), 183(40), 167(15), 149(6), 123(2), 91(7), 71(12), 55(29)

Exact mass for $C_{14}H_{35}O_9Si_3$ (parent ion -OEt) calc. 431.1589; meas. 431.1584

Pyrolysis of *t*-butoxytrimethylsilane (243)

Samples of neat *t*-butoxytrimethylsilane (243) were pyrolyzed in the N_2-flow system at temperatures from 400° to 600° C. At 600°, the pyrolysis resulted in complete disappearance of 243 and nearly quantitative formation of isobutylene and trimethylsilanol (245) (mass balance of 93%). Upon standing, the trimethylsilanol slowly condensed to form hexamethyldisiloxane and water. Isobutylene was not isolated, but was identified by comparison of the GCMS and NMR with those of an authentic sample. Trimethylsilanol (245) was isolated by preparative GC and its spectra are given below:

245:

NMR (CCl_4) δ 0.10 (s, 9H), 3.50 (brd. s, 1H)

Mass spectrum; m/e (% rel. inten.) 90(parent ion, 1), 75(100), 73(2), 59(4), 47(20), 45(27)

Exact mass for $C_3H_{10}OSi$ (parent ion) calc. 90.0501; meas. 90.0501

Exact mass for C_2H_7OSi (parent ion $-CH_3$) calc. 75.0266; meas. 75.0263

Pyrolysis of i-propoxytrimethylsilane (244)

Samples of neat i-propoxytrimethylsilane (244) were pyrolyzed in the N_2-flow system at temperatures from 450° to 650° C. The pyrolysate was found to contain, in addition to unreacted 244, propene, trimethylsilanol (245), hexamethyldisiloxane (247), pentamethyldisiloxane-1-ol (249), i-propoxypentamethyldisiloxane (246), D_3, octamethyltrisiloxane (20), heptamethyltrisiloxane-1-ol (252), D_4, 3-trimethylsiloxyheptamethyltrisiloxane (253), decamethyltetrasiloxane (254), and D_5. Products 245, 247, D_3, D_4, and D_5 were all identified by comparison of their GCMS with those of authentic samples. The propene which formed was not isolated, but was trapped by bubbling through a solution of Br_2 in CCl_4. The resulting 1,2-dibromopropane was identified by NMR and GCMS. Products 253 and 254 were not formed in sufficient quantities to isolate, so they were identified solely by GCMS. Products 249, 246, 20, and 252 were isolated by preparative GC (16 ft. 5% OV101 column).

The spectral properties of the products are summarized below:

249:

NMR (CCl_4) δ 0.07 (s, 6H), 0.10 (s, 9H), 3.45 (brd. s, 1H)

IR (CCl_4) 3700(s), 2960(s), 2900(m), 1415(m), 1260(s), 1255(sh), 1060(s, brd.), 910(s), 840 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 149(P^+ -Me, 100), 133(99), 119(8), 115(16), 105(5), 103(7), 89(9), 75(40), 73(12), 68(6), 61(17)

Exact mass for $C_4H_{13}O_2Si_2$ (parent ion $-CH_3$) calc. 149.0454; meas. 149.0446

246:

NMR (CCl_4, 100 MHz) δ 0.04 (s, 6H), 0.09 (s, 9H), 1.14 (d, 6H, J=6 Hz.), 4.04 (heptet, 1H, J=6 Hz.)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 191(P^+ -Me, 15), 149(100), 147(37), 133(34), 131(4), 119(4), 117(6), 115(4), 103(3), 88(11), 75(14), 73(24), 66(23), 59(13)

20:

NMR (CCl_4) δ 0.04 (s, 6H), 0.11 (s, 18H)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 221(P^+ -Me, 88), 205(8), 189(7), 175(1), 159(1), 147(9), 132(12), 131(6), 119(3), 117(4), 115(4), 103(20), 95(5), 87(4), 73(100), 66(2), 61(2)

- a library search by the Finnegan GCMS gave a satisfactory match for octamethyltrisiloxane

252:

NMR (CCl_4) δ 0.06 - 0.11 (3 singlets, 21 H), 2.74 (s, 1H)

IR (CCl_4) 3700(s), 2960(s), 2900(m), 1410(m), 1260(s), 1250(sh), 1070(sh), 1050(s), 910(s), 840 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 223(P^+ -Me, 19), 207(100), 191(16), 163(2), 149(2), 133(18), 119(5), 115(4), 104(9), 96(9), 87(4), 75(14), 73(13), 61(4)

Exact mass for $C_6H_{19}O_3Si_2$ (parent ion $-CH_3$), calc. 223.0642; meas. 223.0641

253 and 254 (nearly identical mass spectra):

Mass spectra; m/e (% rel. inten.) (parent ion not seen), 295(P^+ -Me, 4), 279(1), 265(1), 247(1), 207(49), 191(5), 177(2), 163(1), 147(2), 140(1), 131(2), 119(2), 117(1), 103(1), 87(1), 85(2), 73(100)

Pyrolysis of trimethylethoxysilane (255)

Samples of neat trimethylethoxysilane (255) were pyrolyzed in the N_2-flow system at temperatures from 500° to 700° C. The pyrolysate was found to contain, in addition to unreacted 255, ethylene, trimethylsilanol (245), hexamethyldisiloxane (247), pentamethyldisiloxane-1-ol (249), ethoxypentamethyldisiloxane (256), D_3, octamethyltrisiloxane (20), heptamethyltrisiloxane-1-ol (252), trimethylsiloxypentamethylcyclotrisiloxane (258), D_4, 3-trimethylsiloxyheptamethyltrisiloxane (253), decamethyltetrasiloxane (254), trimethylsiloxyheptamethylcyclotetrasiloxane (259), and D_5. In addition, when the pyrolysis was carried out at low temperature (<550° C), a trace of 1-ethoxyheptamethyltrisiloxane (257), identified only by GCMS, was observed. Products 245, 247, 249,

D_3, 20, 252, D_4, 253, 254, and D_5 were all identified by comparison of their GCMS with those of authentic samples. The ethylene which formed was not isolated, but was trapped by bubbling through a solution of Br_2 in CCl_4. The resulting 1,2-dibromoethane was identified by NMR and GCMS. Products 256, 258, and 259 were formed in insufficient amounts to isolate, so they were identified only by GCMS. The mass spectra of 256, 257, 258, and 259 are reported below:

256:

m/e (% rel. inten.) (parent ion not seen), 177(P^+ -Me, 67), 149(67), 147(19), 133(100), 131(3), 119(8), 103(8), 89(3), 81(8), 73(23), 66(24), 61(6), 45(11)

257:

m/e (% rel. inten.) (parent ion not seen), 251(P^+ -Me, 21), 223(15), 221(7), 207(100), 191(18), 177(4), 161(3), 133(18), 119(5), 103(16), 96(7), 87(4), 75(5), 43(21)

258:

m/e (% rel. inten.) (parent ion not seen), 281(P^+ -Me, 100), 265(10), 249(6), 235(1), 205(4), 193(13), 191(11), 177(5), 163(3), 133(27), 119(3), 103(2), 97(2), 73(16)

259:

m/e (% rel. inten.) (parent ion not seen), 355(P^+ -Me, 7), 339(1), 325(1), 281(2), 267(13), 251(2), 249(1), 237(1), 207(2), 193(2), 179(1), 163(1), 147(1), 133(1), 103(1), 87(1), 73(100)

Pyrolysis of trimethylphenoxysilane (260)

Samples of neat trimethylphenoxysilane (260) were pyrolyzed in the N_2-flow system at temperatures from 550° to 750° C. The pyrolysate was found to contain, in addition to unreacted 260, benzene, toluene, 2,2-dimethyl-2-sila-1-oxabenzocyclopentane (261), phenoxypentamethyldisiloxane (262), 2-trimethylsiloxy-2-methyl-2-sila-1-oxabenzocyclopentane (265), 2,2,4,4-tetramethyl-2,4-disila-1,3-dioxabenzocycloheptane (266), 3-phenoxyheptamethyltrisiloxane (264), and 1-phenoxyheptamethyltrisiloxane (263). The benzene and toluene which were formed were identified by comparison of their GCMS with those of authentic materials as well as by retention time. All the other products were isolated by preparative GC (16 ft. 5% OV101 column). Products 265 and 266 had nearly identical retention times and were therefore collected together. NMR showed that approximately equal amounts of 265 and 266 were formed. The spectral characteristics of products 261, 262, 265, 266, 263, and 264 are summarized below:

261:

NMR (CCl_4) δ 0.38 (s, 6H), 1.98 (s, 2H), 6.48 - 7.20 (m, 4H)

IR (film) 3070(w), 3040(w), 3020(w), 2960(m), 2900(w), 1600(m), 1575(m), 1470(s), 1455(s), 1390(m), 1290(w), 1270(m), 1250(s), 1225(s), 1120(s), 1080(w), 1015(m), 920(m), 865(s), 840(s), 820(s), 770(w), 745 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 164(parent ion, 61), 149(100), 147(18), 135(8), 133(12), 121(12), 105(17), 103(12), 89(38), 77(30), 73(5), 67(28), 63(20), 51(21)

Exact mass for $C_9H_{12}OSi$ (parent ion) calc. 164.0658; meas. 164.0654

Exact mass for C_8H_9OSi (parent ion - CH_3) calc. 149.0423; meas. 149.0417

<u>262</u>:

NMR (CCl_4) δ 0.08 (s, 9H), 0.18 (s, 6H), 6.67 - 7.32 (m, 5H)

IR (film) 3095(w), 3060(w), 3035(w), 3020(sh), 2950(s), 2895(w), 1590(s), 1580(sh), 1485(s), 1260(sh), 1250(s), 1150(m), 1055(s), 1015(sh), 990(m), 915(s), 865(m), 830(s), 800(s), 785(s), 740(s), 700(w), 675 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 240(parent ion, 27), 225(100), 209(69), 207(5), 195(7), 191(1), 181(13), 151(15), 147(19), 137(8), 133(45), 131(11), 119(5), 115(10), 112(44), 105(18), 103(10), 95(8), 91(68), 89(6), 77(47), 73(65), 65(13), 59(25), 51(23), 45(30)

Exact mass for $C_{11}H_{20}O_2Si_2$ (parent ion) calc. 240.1002; meas. 240.1013

<u>265</u> and <u>266</u>:

NMR of <u>265</u> (CCl_4) δ 0.07 (s, 9H), 0.38 (s, 3H), 1.85 (brd. s, 2H), 6.58 - 7.20 (m, 4H)

NMR of <u>266</u> (CCl_4) δ 0.07 (s, 6H), 0.18 (s, 6H), 2.07 (s, 2H), 6.58 - 7.20 (m, 4H)

IR of <u>265</u> and <u>266</u> mixture (film) 3080(w), 3045(w), 3015(w), 2965(m), 2900(w), 1600(m), 1580(m), 1490(s), 1475(s), 1460(m), 1450(m), 1260(s), 1240(s), 1230(s), 1185(w), 1155(m), 1125(m), 1050(brd. s), 1015(s), 930(sh), 920(s), 880(m), 860(s), 840(s), 805(s), 790(m), 750 cm^{-1}(s)

Mass spectra of <u>265</u> and <u>266</u> (nearly identical spectra); m/e (% rel. inten.)

238(parent ion, 32), 233(100), 207(2), 195(31), 181(4), 179(3), 161(2), 149(8), 133(23), 119(10), 112(16), 105(35), 97(3), 91(12), 89(9), 73(13), 59(5), 51(2), 45(7)

Exact mass for $C_{11}H_{18}O_2Si_2$ (parent ion) calc. 238.0845; meas. 238.0856

263:

NMR (CCl_4, 100 MHz) δ 0.04 (s, 6H), 0.08 (s, 9H), 0.21 (s, 6H), 6.72 - 7.24 (m, 5H)

Mass spectrum; m/e (% rel. inten.) 314(parent ion, 10), 299(83), 283(2), 267(26), 253(4), 239(3), 221(24), 207(29), 191(17), 181(4), 163(3), 151(14), 133(17), 119(5), 105(8), 91(30), 77(27), 73(100), 59(10), 51(6), 45(13)

Exact mass for $C_{13}H_{26}O_3Si_3$ (parent ion) calc. 314.1240; meas. 314.1232

264:

NMR (CCl_4, 100 MHz) δ 0.10 (s, 18H), 0.16 (s, 3H), 6.72 - 7.24 (m, 5H)

Mass spectrum; m/e (% rel. inten.) 314(parent ion, 13), 299(96), 283(3), 267(30), 253(6), 239(2), 223(10), 221(2), 207(29), 191(17), 181(4), 163(3), 151(17), 133(17), 119(5), 105(8), 91(35), 77(29), 73(100), 59(10), 51(6), 45(15)

Exact mass for $C_{13}H_{26}O_3Si_3$ (parent ion) calc. 314.1240; meas. 314.1193

Exact mass for $C_{12}H_{23}O_3Si_3$ (parent ion $-CH_3$) calc. 299.0955; meas. 299.0956

Pyrolysis of benzyloxytrimethylsilane (269)

Samples of neat benzyloxytrimethylsilane (269) were pyrolyzed in the N_2-flow system at temperatures from 500° to 650° C. The major components of the pyrolysate were found to be, in addition to unreacted 269, benzene, toluene, benzaldehyde, benzyloxypentamethyldisiloxane (271), 3-trimethylsiloxy-3-methyl-3-sila-2-oxabenzocyclohexane (275), and 3,3,5,5-tetramethyl-3,5-disila-2,4-dioxabenzocyclooctane (276). Several minor products were also formed including tetramethylsilane, pentamethyldisiloxane, D_3, D_4, phenyltrimethylsilane, indene, ethylbenzene, styrene, 1-benzyloxyheptamethyltrisiloxane (273), and 3-benzyloxyheptamethyltrisiloxane (274). Due to the complexity of the pyrolysate, no products were isolated, but all products were identified by GCMS. The mass spectra of the new silicon-containing products are given below:

271:

m/e (% rel. inten.) 254(parent ion, 12), 239(8), 209(2), 193(2), 181(1), 165(5), 147(20), 133(22), 120(14), 115(8), 105(7), 91(100), 73(31), 65(35)

273 and/or 274:

m/e (% rel. inten.) 328(parent ion, 3), 313(2), 221(2), 205(1), 191(3), 163(1), 156(1), 91(100), 73(8), 65(7)

275 and 276 (nearly identical spectra):

m/e (% rel. inten.) 252(parent ion, 8), 237(15), 220(6), 207(14), 191(3), 179(5), 163(2), 147(5), 133(8), 119(7), 104(51), 91(100), 73(10), 59(9), 45(5)

Dimethyl-*t*-butylbenzyloxysilane (277)

In a 25 mL flask were placed dimethyl-*t*-butylchlorosilane (2.596 g, 17.2 mmol, available from Petrarch), pyridine (1.5 mL, 19 mmol), benzyl alcohol (1.8 mL, 17.5 mmol), and THF (20 mL). This solution was refluxed for 8 hrs. After filtering through a glass-wool plug, most of the THF was removed by a rotary evaporator. To the residue was added 100 mL of pentane, and the solution was extracted several times with water. After drying (Na_2SO_4), the solvent was evaporated to leave nearly pure 277 in ca. 90% yield.

NMR (CCl_4) δ 0.07 (s, 6H), 0.97 (s, 9H), 4.69 (s, 2H), 7.22 (brd. s, 5H)

IR (film) 3090(w), 3065(w), 3030(w), 2960(s), 2930(s), 2900(sh), 2880(m), 2855(s), 1500(w), 1475(m), 1465(m), 1455(m), 1380(m), 1365(w), 1255(s), 1210(m), 1110(s), 1095(s), 1070(s), 1025(m), 1005(w), 935(w), 850(sh), 840(s), 775(s), 725(m), 690 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 222(parent ion,$<$1), 207(1), 165(89), 149(5), 135(71), 121(1), 105(2), 91(100), 89(4), 75(12), 73(11), 65(21), 59(7)

Exact mass for $C_{12}H_{19}OSi$ (parent ion $-CH_3$) calc. 207.1205; meas. 207.1223

Exact mass for $C_9H_{13}OSi$ (parent ion -t-Bu) calc. 165.0735; meas. 165.0725

Pyrolysis of dimethyl-t-butylbenzyloxysilane (277)

Samples of neat dimethyl-t-butylbenzyloxysilane (277) were pyrolyzed in the N_2-flow system at temperatures from 500° to 700° C. The major components of the pyrolysate, in addition to unreacted 277, were found to be isobutylene, benzene, toluene, and 1,1-dimethyl-1-sila-2-oxa-benzocyclopentane 280. Several minor products were also formed including ethylbenzene, styrene, D_3, D_4, indene, and dimethylbenzyloxysilane (281). Only the major silicon-containing product, 280, was isolated by preparative GC (10 ft. 15% SE30 column). All other products were identified by GCMS. The spectral characteristics of 280 and 281 are summarized below:

280:

NMR (CCl_4) δ 0.35 (s, 6H), 5.03 (s, 2H), 7.03 - 7.55 (m, 4H)

IR (film) 3060(m), 3005(m), 2960(m), 2900(m), 2860(m), 1595(2), 1445(m), 1350(m), 1265(m), 1250(s), 1195(m), 1130(m), 1065(s), 1050(s), 1020(s), 855(s), 825(s), 805(m), 785(s), 740(s), 690 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 164(parent ion, 53), 149(100), 133(9), 131(7), 119(5), 105(23), 103(8), 89(15), 77(14), 63(11), 53(11), 45(18), 43(24)

Exact mass for $C_9H_{12}OSi$ (parent ion) calc. 164.0657; meas. 164.0646

281:

Mass spectrum; m/e (% rel. inten.) 166(parent ion, 8), 151(100), 132(33), 121(65), 117(49), 105(14), 91(44), 77(12), 65(10), 59(31), 51(15), 43(26)

Bis(trimethylsilyl)peroxide (282)

Bis(trimethylsilyl)peroxide (282) was prepared by the method of Cookson, Davies, and Fazal (181). The peroxide was purified by preparative GC (6 ft. 5% SE30 column, injector temperature 180° C).

NMR (CCl_4) δ 0.19 (s)

IR (film) 2960(s), 2900(m), 1300(w), 1250(s), 1050(brd. m), 935(w), 840(brd. s), 760(m), 745(m), 730(s), 685 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) 178(parent ion, 1), 163(3), 147(2), 133(100), 115(3), 103(3), 89(2), 75(26), 73(15), 59(14), 45(16)

Exact mass for $C_6H_{18}O_2Si_2$ (parent ion) calc. 178.0845; meas. 178.0838

Exact mass for $C_3H_9O_2Si_2$ (D_2-CH_3) calc. 133.0141; meas. 133.0140

UV (hexane) broad band from 3200Å to 2100Å where the solvent absorbed -- no maximum was observed

Pyrolysis of bis(trimethylsilyl)peroxide 282

A 10% solution of bis(trimethylsilyl)peroxide (282) in benzene was pyrolyzed in the N_2-flow system. At temperatures $>300°$ C, the peroxide quantitatively rearranged to form methoxypentamethyldisiloxane (283). Injection of 282 into a GC also resulted in quantitative formation of 283 when the injector temperature was $>300°$.

NMR (CCl_4) δ 0.04 (s, 6H), 0.12 (s, 9H), 3.42 (s, 3H)

IR (film) 2960(s), 2940(sh), 2900(w), 2835(m), 1260(s), 1190(w), 1095(s), 1060(s), 845(s), 815(s), 795(s), 750(m), 730 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 163(83), 147(5), 133(100), 117(9), 103(6), 89(7), 73(25), 59(28), 45(8)

Photolysis of bis(trimethylsilyl)peroxide (282) in C_6F_{14}

In a quartz NMR tube were placed 50 μL of bis(trimethylsilyl)peroxide (282) and 500 μL of perfluoro-n-hexane. (Compound 282 is not very soluble in perfluoro-n-hexane, so that this was the most concentrated solution which could be prepared). The solution was degassed by the freeze-thaw method and the tube was sealed under vacuum. Photolysis was carried out in a Rayonet photochemical reactor equipped with 2537Å lamps. Disappearance of 282 was monitored by NMR. After 2½ hrs., all of 282 had reacted and a small layer of liquid had formed on top of the perfluoro-*n*-hexane. (The products of this reaction are much less soluble in perfluoro-*n*-hexane than is 282.) The tube was opened and the solution was analyzed by IR, GC, and GCMS. No silanol products were formed as evidenced by the IR spectrum. The products formed were hexamethyldisiloxane (247, 81%), octamethyltrisiloxane (20, 15%), and decamethyltetrasiloxane (254, 2%).

Photolysis of bis(trimethylsilyl)peroxide (282) in D_4

A 7% solution of bis(trimethylsilyl)peroxide (282) in D_4 was placed in a quartz NMR tube. The solution was repeatedly degassed by the freeze-thaw method and the tube was sealed under vacuum. Photolysis (2537Å) was carried out for 3 hrs. The tube was opened and the solution was analyzed by IR, GC, and GCMS. Two major products were formed in approximately equal amounts. They were isolated by preparative GC and identified as hexamethyldisiloxane (247) and 1,2-bis(1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane)ethane (286). Several minor products including trimethylsilanol, octamethyltrisiloxane (20), and 1-trimethylsiloxymethyl-1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (287) were identified by GCMS. The spectral characteristics of the new products are summarized below:

286 (a white solid):

NMR (CCl_4) δ 0.12 (s, 42H), 0.46 (s, 4H)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 575(P^+ -Me, 2), 487(1), 471(1), 457(1), 427(1), 415(1), 385(1), 353(2), 327(1), 293(1), 281(100), 265(6), 251(7), 235(1), 219(2), 207(7), 191(4), 177(1), 163(1), 147(8), 133(3), 117(2), 103(1), 85(6), 73(84), 59(8), 45(4)

Exact mass for $C_{15}H_{43}O_8Si_8$ (parent ion $-CH_3$) calc. 575.1112; meas. 575.1108

Exact mass for $C_7H_{21}O_4Si_4$ (D_4-CH_3) calc. 281.0517; meas. 281.0506

287:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 369(P^+ -Me, 2), 353(1), 325(1), 281(49), 267(6), 265(5), 253(4), 237(1), 223(1), 207(3), 193(2), 191(3), 179(1), 177(1), 163(1), 147(1), 133(1), 87(23), 73(100), 59(31), 45(11)

Bis(dimethyl-t-butylsilyl)peroxide (288)

In a 100 mL flask were placed Et_2O (50 mL) DABCO·$2H_2O_2$ (0.441 g, 2.45 mmol), and Et_3N (0.70 mL, 5.0 mmol). This solution was cooled to 0° C and dimethyl-t-butylchlorosilane (1.45 g, 9.62 mmol) in 8 mL of Et_2O was added dropwise via addition funnel. Once all the chlorosilane was added, the temperature was allowed to rise to room temperature where stirring was continued for 4 hrs. The solution was filtered through a glass-wool plug and most of the Et_2O was removed with a rotary evaporator. Pentane (150 mL) was added to the residue and the solution was again filtered. Removal of all solvents with a rotary evaporator left a slightly yellow liquid which was primarily the desired peroxide <u>288</u>. The major impurity, dimethyl-<u>t</u>-butylsilanol, was completely removed from <u>288</u> by column chromatography using a 3 in. silica gel column with hexane as eluent. After evaporation of the hexane, pure <u>288</u> was obtained (<u>ca</u>. 60% isolated yield). Peroxide <u>288</u> will pass through the GC unchanged if all temperatures are $< 170^\circ$; but with the injector at 300°, <u>288</u> rearranges quantitatively to form 1-<u>t</u>-butyl-3-<u>t</u>-butoxytetramethyldisiloxane (<u>290</u>). The spectral characteristics of <u>288</u> and <u>290</u> are summarized below:

<u>288</u>:

NMR (CCl_4) δ 0.10 (s, 12H), 0.92 (s, 18H)

IR (film) 2960(s), 2935(s), 2900(m), 2890(m), 2860(s), 1475(m), 1465(m), 1390(w), 1365(m), 1260(s), 1250(sh), 1010(w), 1005(w), 935(w), 835(s), 820(s), 805(s), 780(s), 750(m), 710(w), 660 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 247(P^+ -Me, 2), 205(4), 191(1), 173(2), 163(12), 149(100), 147(28), 133(99), 119(7), 115(8), 103(4), 89(4), 75(47), 73(22), 57(71), 45(16), 41(47)

Exact mass for $C_{11}H_{27}O_2Si_2$ (parent ion $-CH_3$) calc. 247.1550; meas. 247.1549

Exact mass for $C_3H_9O_2Si_2$ (D_2-CH_3) calc. 133.0141; meas. 133.0130

UV (hexane) broad band from 3100Å to 2100Å where the solvent absorbed -- no maximum was observed, but there was a shoulder at approximately 2500Å

<u>290</u>:

NMR (CCl_4, 100 MHz) δ 0.05 (s, 6H), 0.07 (s, 6H), 0.89 (s, 9H), 1.25 (s, 9H)

IR (film) 2980(sh), 2970(s), 2960(m), 2905(w), 2895(w), 2865(m), 1475(m), 1390(w), 1365(m), 1260(s), 1205(m), 1060(s, brd.), 1005(w), 940(w), 850(sh), 840(m), 790 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 247(P^+ -Me, 5), 205(1), 191(4), 189(2), 175(1), 149(100), 133(26), 117(6), 103(2), 95(5), 75(6), 73(15), 66(4), 57(27), 45(3), 41(12)

Exact mass for $C_{11}H_{27}O_2Si_2$ (parent ion $-CH_3$) calc. 247.1549; meas. 247.1547

Hydrolysis of dimethyl-t-butylchlorosilane

In a 10 mL flask were placed dimethyl-t-butylchlorosilane (ca. 0.5 g) and THF (ca. 7 mL). To this solution was added H_2O (ca. 0.25 mL). The chlorosilane immediately hydrolyzed to dimethyl-t-butylsilanol. This silanol very slowly condensed to give sym-di-t-butyltetramethyldisiloxane. After 2 weeks at reflux, ca. 25% of the silanol remained uncondensed. The products were isolated by preparative GC (10 ft. 15% SE30 column). Their spectral characteristics are summarized below:

Dimethyl-t-butylsilanol:

NMR (CCl_4) δ 0.05 (s, 6H), 0.92 (s, 9H), 3.95 (brd. s, 1H)

IR (film) 3600-3000(brd. s), 2960(s), 2930(s), 2895(sh), 2885(m), 2860(s), 1475(m), 1465(m), 1390(w), 1360(m), 1260(s), 1005(m), 935(w), 850(s, brd.), 830(s), 770(s), 660 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 132(parent ion, 3), 117(1), 101(<1), 99(<1), 75(100), 61(4), 45(14)

Exact mass for $C_6H_{16}OSi$ (parent ion) calc. 132.0971; meas. 132.0976

Sym-di-t-butyltetramethyldisiloxane

NMR (CCl_4) δ 0.03 (s, 12H), 0.88 (s, 18H)

IR (film) 2960(s), 2930(s), 2895(sh), 2885(m), 2860(s), 1470(m), 1460(m), 1390(w), 1360(m), 1255(s), 1070(s), 1050(s), 1005(m), 935(w), 835(s), 785(sh), 775(s), 690(w), 665 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 246(parent ion, 1), 231(1), 189(23), 147(100), 133(10), 131(7), 117(11), 103(2), 73(38), 66(4), 59(9), 57(7), 45(6)

Exact mass for $C_{12}H_{30}OSi_2$ (parent ion) calc. 246.1835; meas. 246.1821

Exact mass for $C_5H_{15}OSi_2$ ($Me_3SiO\overset{+\cdot}{Si}Me_2$) calc. 147.0661; meas. 147.0656

Photolysis of bis(dimethyl-t-butylsilyl)peroxide (288) in C_6F_{14}

In a quartz NMR tube were placed 288 (0.0254 g, 0.0967 mmol) and C_6F_{14} (ca. 0.7 mL). The solution was degassed by the freeze-thaw method and the tube was sealed under vacuum. Photolysis (2537Å) was carried out for 2 hrs. after which time all the starting material had reacted. Analysis by NMR, GC, and GCMS indicated that the following four major products were present: 3-t-butyltetramethyldisiloxane-1-ol (289, 45%), 1-t-butoxy-3-t-butyltetramethyldisiloxane (290, 19%), D_4 (24%), and isobutylene (undetermined yield). In addition, GCMS indicated that trace amounts of several other products were formed. These include 2,2,3,3-tetramethylbutane, t-butyldimethylsilanol, D_5, 5-t-butylhexamethyltrisiloxane-1-ol, and 1-t-butoxy-5-t-butylhexamethyltrisiloxane. The latter three compounds can be thought of as coming from formal addition of dimethylsilanone to D_4, 289, and 290 respectively. The major products, 289, 290, and D_4, were isolated by preparative GC (16 ft. 5% OV101 column). Products 289 and D_4 were collected together, but were separated by preparative GC using a 10 ft. 15% poly-m-phenylether column. The spectral characteristics of the new products are summarized below:

289:

NMR (CCl_4) δ 0.08 (s, 6H), 0.12 (s, 6H), 0.93 (s, 9H), 2.17 (s, 1H)

IR (film) 3550-3050(brd. s), 2960(s), 2930(s), 2890(m), 2860(s), 1470(m), 1460(w), 1390(w), 1360(m), 1260(s), 1070(brd. s), 1000(m), 885(s), 845(sh), 830(s), 790(s), 775 cm^{-1}(sh)

Mass spectrum; m/e (% rel. inten.) 206(parent ion, 1), 191(1), 173(1), 149(100), 133(38), 119(7), 115(4), 103(2), 89(2), 75(14), 73(5), 67(4), 61(4), 57(3), 45(4), 41(5)

Exact mass for $C_7H_{19}O_2Si_2$ (parent ion $-CH_3$) calc. 191.0924; meas. 191.0924

Exact mass for $C_4H_{13}O_2Si_2$ (parent ion -t-Bu) calc. 149.0454; meas. 149.0447

5-t-butylhexamethyltrisiloxane-1-ol:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 265(P^+ -Me, 5), 223(31), 207(100), 191(12), 177(6), 161(1), 115(3), 96(7), 87(2), 75(10), 47(3)

1-t-butoxy-5-t-butylhexamethyltrisiloxane:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 321(P^+ -Me, 1), 265(5), 247(1), 223(8), 207(8), 191(6), 177(2), 163(1), 131(1), 103(6), 95(2), 57(100)

Photolysis of bis(dimethyl-t-butylsilyl)peroxide (288) in cyclopentane

The photolysis of 288 in cyclopentane was carried out in exactly the same way as photolysis of 288 in perfluoro-n-hexane. All the products which formed in C_6F_{14} also formed in C_6H_{10} in approximately the same yield. The biggest change was that t-butyldimethylsilanol, which was formed in a trace amount in C_6F_{14}, was formed in ca. 5% in cyclopentane.

Photolysis of bis(dimethyl-t-butylsilyl)peroxide (288) in D_4

In a quartz NMR tube were placed 288 (0.0280 g, 0.1067 mmol) and D_4 (ca. 0.6 mL). The solution was degassed by the freeze-thaw method and the tube was sealed under vacuum. Photolysis (2537Å) was carried out for 2 hrs. The tube was opened and found to contain t-butyldimethylsilanol (3.2%), 290 (15.2%), and D_5 (2.0%). Due to the large excess of D_4 which was present, it was not possible to determine the yield of either D_4 or 289.

Photolysis of bis(dimethyl-t-butylsilyl)peroxide (288) with MeOH added

In a quartz NMR tube were placed 288 (0.0232 g, 0.0884 mmol), MeOH (0.041 g, 1.281 mmol), and cyclopentane (ca. 0.6 mL). The solution was degassed and the tube was sealed under vacuum. After photolysis (2537Å, 2 hrs.), the tube was opened and the solution was analyzed by GC. All products were identified solely by GCMS. The solution was found to contain t-butyldimethylmethoxysilane (3.1%), sym-dimethoxytetramethyldisiloxane (27, 12.7%), 1-methoxy-3-t-butyltetramethyldisiloxane

(294, 42.4%), 1,5-dimethoxyhexamethyltrisiloxane (223, 3.7%), 290 (14.4%), and 1-methoxy-5-t-butylhexamethyltrisiloxane (296, 5.5%). The mass spectra of the new compounds are given below:

294:

m/e (% rel. inten.) (parent ion not seen), 205(P^+ -Me, 4), 189(1), 173(1), 163(100), 147(5), 133(56), 119(6), 117(7), 103(4), 89(7), 73(14), 59(12), 45(5), 41(6)

296:

m/e (% rel. inten.) (parent ion not seen), 279(P^+ -Me, 2), 265(1), 247(3), 237(12), 223(3), 207(10), 205(11), 191(7), 173(5), 163(25), 149(100), 133(82), 119(9), 115(7), 103(5), 89(7), 75(43), 73(25), 57(62), 41(40)

Bis(triethylsilyl)peroxide (108)

Bis(triethylsilyl)peroxide (108) was prepared by the method of Cookson, Davies, and Fazal (181). The peroxide was contaminated with triethylsilanol (302) and hexaethyldisiloxane. The silanol was easily removed by passing the crude reaction mixture through a 3 in. column of silica gel with hexane as eluent. Separation of the disiloxane from the peroxide was more difficult, but was successfully achieved using HPLC (2 ft. μ-porasil column, hexane eluent). The spectral characteristics of peroxide 108 are given below:

NMR (CCl_4) δ 0.50 - 1.30 (complex multiplet)

IR (film) 2980(s), 2940(m), 2915(m), 2880(s), 1460(m), 1410(m), 1235(m), 1015(m), 1000(m), 780(s), 730 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) 262(parent ion, <1), 233(40), 217(1), 205(10), 189(23), 177(24), 175(18), 161(73), 149(49), 147(79), 133(95), 121(50), 119(68), 105(57), 103(36), 93(38), 91(62), 87(14), 75(85), 59(38), 47(100), 45(75)

Exact mass for $C_{10}H_{25}O_2Si_2$ (parent ion -Et) calc. 233.1393; meas. 233.1400

UV (hexane) broad band from 3200Å to 2100Å where the solvent absorbed -- no maximum was observed

Pyrolysis of bis(triethylsilyl)peroxide (108)

Peroxide 108 was quantitatively rearranged to ethoxypentaethyldisiloxane (299) in the injection port of a GC (injector temperature >300°)

NMR (CCl_4) δ 0.40 - 1.30 (complex multiplet, 28H), 3.70 (q, 2H, J=7 Hz.)

IR (film) 2960(s), 2940(sh), 2910(m), 2880(s), 1460(m), 1415(w), 1240(m), 1165(w), 1110(m), 1070(s), 1015(sh), 1005(m), 770(w), 740 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 233(P^+ -Et, 100), 217(4), 205(16), 189(26), 177(10), 175(6), 161(36), 147(13), 133(17), 119(14), 105(19), 103(12), 91(12), 75(11), 66(6), 59(10), 47(5)

Photolysis of bis(triethylsilyl)peroxide (108) in C_6F_{14} or C_5H_{10}

A 3 % solution of bis(triethylsilyl)peroxide (108) in the appropriate solvent was placed in a quartz NMR tube (108 is only slightly soluble in C_6F_{14}). The solution was repeatedly degassed by the freeze-thaw method before the tube was sealed under vacuum. Photolysis (2537Å) was carried out for 3 hrs. The solution was analyzed by GCMS and found to contain triethylsilanol (302), triethylethoxysilane (303), ethoxypentaethyldisiloxane (299), and pentaethyldisiloxane-1-ol (300). The yields varied with solvent as shown in the Results and Discussion section. In addition, when cyclopentane was used as solvent, low yields of ethylcyclopentane, bicyclopentane, and triethylsiloxycyclopentane were observed. Products 299, 300, and 302 were isolated by preparative GC (16 ft. 5% OV101 column). Products 299 and 300 were collected together, but were separated by preparative GC using a 10 ft. 15% poly-m-phenylether column. The spectroscopic properties of products 300 and 302 are summarized below:

300:

NMR (CCl_4) δ 0.40 - 1.20 (complex multiplet, 25H), 1.90 (s, 1H)

IR (CCl_4) 3700(s), 2960(s), 2940(sh), 2915(s), 2880(s), 1460(m), 1415(m), 1380(w), 1245(s), 1240(sh), 1215(m), 1070(brd. s), 1015(sh), 1005(s), 970(m), 945(m), 860(s), 720(s), 690 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 205(P^+ -Et, 100), 177(46), 175(9), 161(1), 149(39), 147(17), 133(1), 121(20), 119(17), 103(9), 93(19), 91(13), 88(11), 75(22), 61(4), 47(11)

Exact mass for $C_8H_{21}O_2Si_2$ (parent ion -Et) calc. 205.1080; meas. 205.1072

302:

NMR (CCl_4) δ 0.30 - 1.30 (complex multiplet, 15H), 3.85 (s, 1H)

IR (film) 3600-3000(s), 2960(s), 2945(sh), 2920(s), 2880(s), 1460(m), 1415(m), 1375(w), 1240(m), 1010(s), 1000(sh), 835(s), 820(s), 735(s), 725(sh), 670 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) 132(parent ion, 2), 103(84), 75(100), 61(4), 47(33), 45(26)

Photolysis of bis(triethylsilyl)peroxide (108) in D_4

A 5% solution of bis(triethylsilyl)peroxide (108) in D_4 was placed in a quartz NMR tube. After the solution was degassed, the tube was sealed under vacuum. Photolysis (2537Å) was carried out for 4 hrs. The solution was found to contain triethylsilanol (302, 32%), triethylethoxysilane (303, 1%), pentaethyldisiloxane-1-ol (300, 15%), ethoxypentaethyldisiloxane (299, 22%), 1,1-diethyloctamethylcyclopentasiloxane (304, 5%), n-propylheptamethylcyclotetrasiloxane (306, 2%), and triethylsiloxymethylheptamethylcyclotetrasiloxane (305, 2%). The mass spectra of the new compounds are presented below:

303:

m/e (% rel. inten.) (parent ion not seen), 131(P^+ -Et, 100), 115(2), 103(90), 101(2), 87(20), 75(56), 73(12), 67(1), 61(2), 59(30), 47(29), 45(37)

304:

m/e (% rel. inten.) (parent ion not seen), 383(P^+ -Et, 9), 353(1), 341(1), 325(1), 309(1), 295(2), 281(9), 267(8), 253(5), 237(2), 233(4), 207(1), 193(3), 177(2), 163(1), 156(1), 147(2), 133(2), 125(1), 101(12), 87(64), 73(100), 59(45), 45(7)

306:

m/e (% rel. inten.) (parent ion not seen), 309(P^+ -Me, 22), 281(P^+ -Pr, 100), 267(53), 251(9), 249(11), 235(2), 207(14), 193(22), 191(15), 177(5), 163(2), 147(3), 133(32), 126(30), 119(6), 111(2), 103(4), 73(32), 59(8), 45(6)

305:

m/e (% rel. inten.) (parent ion not seen), 411(P^+ -Me, 1), 397(P^+ -Et, 1), 383(1), 305(6), 281(59), 277(42), 267(5), 249(38), 233(5), 221(32), 207(5), 193(20), 191(12), 177(6), 165(18), 149(8), 137(14), 115(18), 101(21), 87(77), 73(100), 59(83), 45(12)

Tri-*t*-butyliodosilane (313)

Tri-*t*-butylsilane (311) was prepared by the method of Dexheimer and Spialter (182). Iodination of 311 by the method of Weiderbruch and Peter (184) produced tri-*t*-butyliodosilane (313). Product 313 was purified before use by recrystallization from acetonitrile.

Tri-*t*-butylchlorosilane (312)

Tri-*t*-butylsilane (*ca*. 8.0 g) and CCl_4 (60 mL) were placed in a 100 mL flask equipped with a magnetic stirrer. After cooling to 0° C, a slow stream of Cl_2 was bubbled through the solution for 1 hr. N_2 was then bubbled through the solution to remove the excess Cl_2. The CCl_4 was removed with a rotary evaporator to leave behind a slightly yellow, viscous liquid. GC showed this liquid to be ca. 80% 312. The product was purified by column chromatography (4 in. silica gel column, hexane eluent) to yield a colorless, viscous liquid. This liquid was essentially pure 312 (recovered yield of approximately 70%). A small sample of 312 was further purified by recrystallization from MeOH to yield a sticky, white solid (mp 121-124°).

NMR (CCl_4) δ 1.18 (s)

IR (film) 3000(m), 2980(sh), 2960(s), 2950(s), 2900(m), 2870(s), 1485(s), 1475(s), 1390(m), 1370(m), 1015(w), 935(w), 820(s), 620 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) 234(parent ion, 1), 179(4), 177(12), 137(14), 135(41), 121(2), 105(4), 95(43), 93(100), 79(6), 73(4), 63(6), 57(30)

Treatment of tri-t-butylchlorosilane (312) with H_2O_2

In a 50 mL flask were placed Et_2O (40 mL), and tri-t-butylchlorosilane (1.041 g, 4.43 mmol) and Et_3N (4.60 mmol). This solution was cooled to 0° C before 90% H_2O_2 (60 µL, ca. 2.2 mmol) was added via syringe. No visible reaction occurred as no amine hydrochloride was formed. The solution was stirred at room temperature for 2 days after which time no reaction had occurred. GCMS confirmed that chlorosilane 312 had not reacted. Similarly, 312 was found to be inert to H_2O and $DABCO \cdot 2H_2O_2$.

Treatment of triethylsilylperchlorate (314) with H_2O_2

Triethylsilylperchlorate (314) was prepared from triethylsilane by the method of Barton and Tully (185). In a 25 mL flask were placed DABCO·$2H_2O_2$ (0.092 g, 0.51 mmol), Et_2O (10 mL), and pyridine (0.20 mL, 2.5 mmol). This solution was cooled to 0° C and triethylsilylperchlorate (0.411 g, 1.91 mmol) was added via syringe. After ½ hr., the ice bath was removed and stirring was continued for another ½ hr. The solution was analyzed by GC and GCMS and found to contain bis(triethylsilyl)-peroxide (74%) and hexaethyldisiloxane (20%).

Treatment of tri-t-butylsilylperchlorate (315) with H_2O_2

Tri-t-butylsilylperhclorate (315) was prepared from tri-t-butyliodosilane and silver perchlorate in acetonitrile by the method of Barton and Tully (185). It was used without purification by sublimation. In a 25 mL flask were placed crude 315 (ca. 0.33 g, 1.1 mmol), Et_2O (15 mL), and pyridine (0.24 mL, 3.0 mmol). To this solution was added DABCO·$2H_2O_2$ (0.05 g, 0.24 mmol). White amine hydrochloride began to precipitate nearly immediately. The progress of the reaction was followed by GC which showed that two new products had formed in approximately equal amounts, but that after 3 hrs., only half of 315 had disappeared. Addition of another equivalent of DABCO·$2H_2O_2$ resulted in the complete disappearance of 315 after 2 hrs. Very similar results were obtained when 90% H_2O_2 was used instead of DABCO·$2H_2O_2$. The two products were isolated by preparative GC (10 ft. 15% SE30 column) and identified as tri-t-butylsilanol (316) and N-(tri-t-butylsilyl)acetamide (317). When a sublimed sample of 315 was used (100°, 0.05 Torr), only product 316 was formed. The spectral characteristics of 316 and 317 are summarized below:

316:

IR (CCl_4) 3700(m), 2995(sh), 2975(s), 2940(s), 2890(s), 2860(s), 1475(s), 1465(sh), 1385(m), 1365 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 159(P^+ -t-Bu, 8), 117(15), 102(1), 87(3), 75(100), 61(5), 57(9)

317:

NMR (CCl_4) δ 1.15 (s, 27H), 2.00 (s, 3H), the remaining amide hydrogen is not observed

IR (CCl_4) 3420(m), 2980(s), 2940(s), 2890(s), 2860(s), 1700(s), 1685(sh), 1475(s), 1440(s), 1410(s), 1385(s), 1355(m), 1235(m), 990(w), 920 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 200(P^+ -t-Bu, 72), 158(14), 142(2), 125(1), 116(39), 99(27), 87(21), 86(20), 75(100), 73(32), 57(32), 47(9)

Exact mass for $C_{10}H_{22}ONSi$ (parent ion -t-Bu) calc. 200.1457; meas. 200.1470

Treatment of di-t-butylmethylsilylperchlorate (320) with H_2O_2

Di-t-butylmethylsilylperhclorate (320) was prepared from di-t-butylmethylsilane and trityl perchlorate by the method of Barton and Tully (185). In a 25 mL flask were placed DABCO·$2H_2O_2$ (0.145 g, 0.80 mmol), Et_2O (15 mL), and pyridine (0.18 mL, 2.2 mmol). This solution was cooled to 0° C and 320 (ca. 0.82 g, 3.2 mmol) was added via syringe. After stirring at room temperature overnight, the solution was analyzed by GCMS. No products having the mass of bis(di-t-butylmethylsilyl)-peroxide were observed. The major product was identified as di-t-butylmethylsilanol.

m/e (% rel. inten.) 174(parent ion, 1), 159(1), 147(1), 117(27), 101(1), 87(1), 75(100), 61(15), 57(16), 60(19), 47(12)

Di-t-butylbromosilane (325)

In a 100 mL flask equipped with a magnetic stirrer were placed CH_2Cl_2 (60 mL), pyridine (4.4 mL, 54.3 mmol), and di-t-butylsilane (7.724 g, 53.5 mmol, prepared by the method of Barton and Tully (186)). This solution was cooled to -23° C (CO_2/CCl_4 bath) and 27 mL of a 2.00 M solution of Br_2 in CH_2Cl_2 was slowly added via addition funnel. The temperature was allowed to slowly rise to room temperature at which point the solution was poured into 150 mL of pentane. After filtering, the solvents were removed with a rotary evaporator to leave an orange-colored residue. Distillation under reduced pressure (bp ca. 90°, 40 Torr) yielded 9.792 g of colorless 325 (82% distilled yield).

NMR (CCl_4) δ 1.13 (s, 18H), 4.20 (s, 1H)

IR (CCl_4) 2970(s), 2935(s), 2895(s), 2860(s), 2125(s), 1470(s), 1440(w), 1390(m), 1365(s), 1005(m), 930(m), 620(w), 580(w)

Mass spectrum; m/e (% rel. inten.) 222(parent ion, 3), 165(P^+ -t-Bu, 7), 164(8), 149(4), 137(15), 123(11), 107(8), 85(3), 73(4), 57(100), the appropriate isotopic pattern for one Br atom was observed

Exact mass for $C_8H_{19}BrSi$ (parent ion) calc. 222.0439; meas. 222.0441

Treatment of di-t-butylbromosilane (325) with H_2O_2

In a 25 mL flask were placed Et_2O (15 mL), 325 (0.430 g, 1.93 mmol), and pyridine (0.16 mL, 1.98 mmol). The solution was cooled to 0° C and 25 μL of 90% H_2O_2 was added (ca. 0.91 mmol of H_2O_2 and 0.22 mmol of H_2O). Immediately a large amount of pyridinium hydrobromide formed. GC showed that two new products had formed, but only two-thirds of 325 had disappeared. The rest of 325 did not disappear until more H_2O_2 was added (15 μL). The two products were isolated by preparative GC (10 ft. 15% SE30 column) and identified to be di-t-butylsilanol (324) and di-t-butylsilanediol (327). The ratio of 324 to 327 was approximately 1:2. No yields were determined, but 324 and 327 were the only products observed by GC. The physical and spectral characteristics of 324 and 327 are summarized below:

324:

soft solid, mp 53-56°

NMR (CCl_4) δ 0.99 (s, 18H), 2.38 (s, 1H), 4.00 (s, 1H)

IR (CCl_4) 3700(s), 2960(s), 2935(s), 2895(m), 2860(s), 2100(s), 1470(s), 1440(w), 1390(w), 1365(m), 935 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) 160(parent ion, 3), 103(11), 102(10), 87(4), 75(100), 61(60), 57(33), 45(30), 41(48)

Exact mass for $C_8H_{20}OSi$ (parent ion) calc. 160.1284; meas. 160.1283

327:

colorless solid, mp 149-153°

NMR (CCl_4) δ 1.01 (s, 18H), 3.70 (brd. s, 2H)

IR (CCl_4) 3700(s), 2965(s), 2935(s), 2895(m), 2860(s), 1475(s), 1390(w), 1365(w), 935(w), 890 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 176(parent ion, 1), 119(8), 103(1), 89(1), 77(100), 63(8), 57(9), 56(17), 44(10), 40(67)

Exact mass for $C_8H_{20}O_2Si$ (parent ion) calc. 176.1233; meas. 176.1229

Bis(di-t-butylsilyl)peroxide (323) from di-t-butylsilylperchlorate (326)

Silyl perchlorate 326 was prepared from di-t-butylsilane and trityl perchlorate by the method of Barton and Tully (186). In a 100 mL flask equipped with a magnetic stirrer were placed DABCO·$2H_2O_2$ (1.140 g, 6.31 mmol), Et_2O (70 mL), and pyridine (1.4 mL, 17.4 mmol). This slurry was cooled to -23° (CO_2/CCl_4 bath). Di-t-butylsilylperchlorate (326) was then added via syringe (5.6 mL, 24.4 mmol). The temperature was allowed to slowly warm to room temperature where stirring was continued overnight. The solution was then poured into 150 mL of pentane and was filtered. All solvents were removed with a rotary evaporator to leave a colorless liquid which was nearly pure 323 along with a small amount of di-t-butylsilanol (324). After column chromatography (4 in. silica gel column, hexane eluent), pure 323 was isolated (3.385 g, 87% yield).

NMR (CCl_4) δ 1.07 (s, 36 H), 4.15 (s, 1H)

IR (film) 2965(s), 2935(s), 2890(m), 2860(s), 2110(s), 1470(s), 1460(sh), 1385(w), 1360(m), 1005(m), 930(w), 820(s), 770(s)

Mass spectrum m/e (% rel. inten.) (parent ion not seen), 303(P^+ -Me, <1), 261(49), 219(38), 205(21), 177(100), 161(17), 149(48), 135(73), 121(33), 119(30), 105(21), 89(8), 75(50), 57(57)

Exact mass for $C_{15}H_{35}O_2Si_2$ (parent ion $-CH_3$) calc. 303.2176; meas. 303.2175

Exact mass for $C_{12}H_{29}O_2Si_2$ (parent ion -t-Bu) calc. 261.1706; meas. 261.1691

UV (hexane) broad band from 3000Å to 2100Å where the solvent absorbs -- no maximum was observed

Pyrolysis of bis(di-t-butylsilyl)peroxide (323)

Samples of 5% 323 in heptane were injected into a GC while varying the injector temperature from 180° to 300° C. Silylperoxide 323 quantitatively rearranged to form 1-t-butoxy-1,3,3-tri-t-butyldisiloxane (328) and 1,1,3,3-tetra-t-butyldisiloxane-1-ol (329). The ratio of 328:329 varied with injector temperature as reported in the Results and Discussion section. When this same solution was sealed in a capillary tube and heated at 125° C for 3 hrs., 323 quantitatively rearranged to yield 328 and 329 in a ratio of approximately 1:8. These two products were isolated by preparative GC (10 ft. 15% SE30 column); their spectral characteristics are summarized below:

328:

NMR (CCl_4) δ 0.88 (s, 9H), 1.00 (s, 18H), 1.30 (s, 9H), 4.12 (s, 1H), 4.53 (s, 1H)

IR (film) 2970(s), 2940(s), 2900(m), 2865(s), 2120(m), 2100(m), 1475(m), 1465(sh), 1390(w), 1370(m), 1240(w), 1200(m), 1055(brd. s), 1025(w), 1010(m), 940(w), 880(w), 855(m), 825 cm^{-1}(s)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 303(P$^+$ -Me, 1), 261(1), 219(1), 205(44), 189(1), 177(11), 163(34), 149(9), 147(7), 135(31), 121(36), 119(19), 105(19), 91(9), 75(6), 57(100)

Exact mass for $C_{15}H_{35}O_2Si_2$ (parent ion -CH_3) calc. 303.2176; meas. 303.2173

Exact mass for $C_{12}H_{29}O_2Si_2$ (parent ion -t-Bu) calc. 261.1706; meas. 261.1702

329:

NMR (CCl_4) δ 1.03 (brd. s, 36H), 1.73 (s, 1H), 4.22 (s, 1H)

IR (CCl_4) 3700(s), 2965(s), 2930(s), 2890(s), 2860(s), 2090(s), 1470(s), 1445(w), 1385(m), 1360(m), 1180(w), 1060(brd. s), 1000(m), 930(m), 635(m), 570 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 303(P$^+$ -Me, 1), 261(16), 219(19), 203(2), 191(2), 177(100), 161(6), 149(77), 135(99), 133(37), 119(64), 105(34), 89(10), 75(31), 57(77)

Exact mass for $C_{15}H_{35}O_2Si_2$ (parent ion -CH_3) calc. 303.2176; meas. 303.2176

Photolysis of bis(di-t-butylsilyl)peroxide (323) in C_6F_{14} or C_5H_{10}

In a quartz NMR tube were placed 30 μL of bis(di-t-butylsilyl)peroxide (323) and 500 μL of cyclopentane. After degassing repeatedly by the freeze-thaw method, the tube was sealed under vacuum. Photolysis (2537Å) was complete after 1 hr. The solution was found to contain isobutylene, di-t-butylsilanol (324), 1,3,3-tri-t-butyldisiloxane-1-ol (331), 1-t-butoxy-1,3,3-tri-t-butyldisiloxane (328), 1,3,5,7-tetra-t-butylcyclotetrasiloxane (333), and 1,1,3,3-tetra-t-butyldisiloxane-1-ol (329). The yields of these products varied with solvent as shown in the Results and Discussion section. Products 324, 328, and 329 were identified by comparison with authentic samples, while products 331 and 333 were isolated by preparative GC (10 ft. 15% SE30 column). The spectral characteristics of 331 and 333 are summarized below:

331:

NMR (CCl_4) δ 0.93 (s, 9H), 1.00 (s, 18H), 2.35 (brd. s, 1H), 4.07 (s, 1H), 4.45 (s, 1H)

IR (film) 3700(m), 2960(s), 2935(s), 2895(m), 2860(s), 2120(m), 2095(m), 1470(s), 1445(w), 1390(w), 1365(m), 1080(brd. s), 1000(m), 935(w), 900(m), 860(m), 630 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 205(P^+ -t-Bu, 62), 187(1), 177(27), 163(67), 149(36), 145(4), 135(100), 133(15), 121(61), 119(34), 105(37), 91(30), 89(10), 75(21), 61(22), 57(30), 47(6)

Exact mass for $C_8H_{21}O_2Si_2$ (parent ion -t-Bu) calc. 205.1080; meas. 205.1077

333: (more than one isomer was formed as the GC peak was very broad, however, GCMS was identical throughout the entire peak)

NMR (CCl_4) δ 0.92 (brd. s, 36H), 4.45 (brd. s, 4H)

IR (CCl_4) 2960(s), 2935(s), 2895(m), 2860(s), 2140(s), 1470(m), 1460(m), 1440(w), 1390(w), 1360(w), 1215(w), 1085(brd. s), 1000(w), 935(w), 870 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 393(P^+ -Me, 1), 351(P^+ -t-Bu, 100), 323(4), 309(86), 295(5), 293(5), 281(23), 267(90), 253(26), 239(67), 237(32), 225(60), 209(36), 195(26), 179(39), 165(38), 151(21), 135(7), 119(7), 112(6), 105(5), 73(10), 57(97)

Exact mass for $C_{15}H_{37}O_4Si_4$ (parent ion $-CH_3$) calc. 393.1769; meas. 393.1768

Exact mass for $C_{12}H_{31}O_4Si_4$ (parent ion -t-Bu) calc. 351.1299; meas. 351.1293

Photolysis of bis(di-t-butylsilyl)peroxide (323) in D_4

In a quartz NMR tube were placed 0.0397 g of 323 and 0.50 mL of D_4. The solution was degassed and the tube was sealed under vacuum. Photolysis (2537Å) was complete after 1½ hrs. The solution contained all the products which were formed in cyclopentane and perfluoro-n-hexane, although in slightly different yields (see Table 17 in Results and Discussion section). In addition, two other products were formed in ca. 5% yield each. These products had masses corresponding to the addition of one and two units of t-butylsilanone. They were identified solely by GCMS to be 1-t-butyl-3,3,5,5,7,7,9,9-octamethylcyclopentasiloxane (336) and 1,3-di-t-butyl-5,5,7,7,9,9,11,11-octamethylcyclohexasiloxane (337). The mass spectra of 336 and 337 are summarized below:

336:

m/e (% rel. inten.) (parent ion not seen), 383(P^+ -Me, 11), 341(P^+ -t-Bu, 25), 325(2), 311(2), 295(1), 281(1), 267(28), 253(9), 237(2), 223(1), 205(3), 193(4), 177(2), 163(4), 155(1), 149(2), 135(4), 121(2), 115(1), 101(3), 85(1), 73(100), 59(16)

337:

m/e (% rel. inten.) (parent ion not seen), 485(P^+ -Me, 8), 443(P^+ -*t*-Bu, 7), 383(1), 369(5), 355(1), 341(14), 327(19), 313(5), 297(3), 283(4), 267(2), 253(2), 239(2), 221(3), 207(4), 193(5), 179(9), 165(5), 147(5), 133(8), 115(3), 103(4), 85(2), 73(100), 59(23)

Photolysis of bis(di-*t*-butylsilyl)peroxide (323) with MeOH added

In a quartz NMR tube were placed 323 (0.0410 g, 0.129 mmol), MeOH (20 µL, 0.494 mmol) and cyclopentane (0.50 mL). The solution was degassed and the tube was sealed under vacuum. Photolysis (2537Å) was complete after 1½ hrs. Products 324 (12.4%), 331 (25.6%), 328 (10.1%), and 329 (4.9%) were all identified by comparison with authentic samples. Cyclotetrasiloxane (333) was not formed, but there was one additional product identified solely by GCMS to be 1,3-di-*t*-butyl-3-methoxydisiloxane-1-ol (338, 21.4%).

m/e (% rel. int.) 236(parent ion, <1), 221(P^+ -Me, <1), 203(2), 179(P^+ -*t*-Bu, 100), 161(3), 151(93), 137(59), 121(63), 107(32), 105(18), 91(23), 77(15), 61(9), 57(22), 47(6)

DABCO·2HOO-+

The DABCO·2HOO-+ complex was prepared by a modification of the procedure of Fan and Shaw (190). In a 250 mL flask equipped with a mechanical stirrer were placed DABCO (13.9 g, 0.123 mole) and Et_2O (200 mL).

This slurry was cooled to 0° C and t-butylhydroperoxide (25 mL, ca. 0.25 mole) was slowly added. After stirring at 0° for $\frac{1}{2}$ hr., the solution was poured into 400 mL of pentane, at which time the DABCO·2HOO+ precipitated out. After cooling in a freezer (-20° C) for 2 hrs., the solution was filtered and the crystals were washed with pentane. The complex was dried overnight on a vacuum line to yield glistening white crystals (approximate yield of 70%).

Di-t-butylsilyl-t-butylperoxide (342)

In a 100 mL flask equipped with a magnetic stirrer were placed di-t-butylbromosilane (7.958 g, 35.6 mmol). THF (80 mL) and DABCO·2HOO+ (5.71 g, 195 mmol). This solution was stirred at room temperature for 24 hrs. before pouring into 150 mL of pentane. After cooling to 0°, the solution was filtered. The solvents were removed with a rotary evaporator to leave behind a pale yellow liquid. This material was chromatographed (4 in. silica gel column, hexane eluent) to yield pure 342 (6.209 g, 75% yield).

NMR (CCl_4) δ 1.05 (s, 18H), 1.23 (s, 9H), 4.12 (s, 1H)

IR (film) 2960(s), 2930(s), 2890(s), 2855(s), 2120(s), 1470(s), 1460(sh), 1390(m), 1365(s), 1260(w), 1240(w), 1195(m), 1060(w), 1010(m), 935(w), 900(m), 850(s), 825(s), 795(s), 750 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 217(P^{+} -Me, <1), 175(P^{+} -t-Bu, 1), 161(1), 145(1), 119(2), 103(4), 87(1), 77(36), 75(25), 63(100), 57(82), 47(5)

Exact mass for $C_{11}H_{25}O_2Si$ (parent ion $-CH_3$) calc. 217.1624; meas.

217.1621

Exact mass for $C_8H_{19}O_2Si$ (parent ion -t-Bu) calc. 175.1154; meas. 175.1152

Thermolysis of di-t-butylsilyl-t-butylperoxide (342)

A solution containing 342 (0.0432 g) and n-octane (0.50 mL) was placed in several capillary mp tubes. These tubes were sealed and placed in an oven at 150° C. A tube was removed every half hour and the progress of the reaction was analyzed by GC. The reaction was complete after 3 hrs. The products formed were di-t-butylsilanol (324, 2.5%), di-t-butoxy-t-butylsilane (343, 41.7%), di-t-butyl-t-butoxysilane (344, 30.8%), and sym-tetra-t-butyldisiloxane (345, 5.3%).

The reaction was repeated with 0.1 equivalents of Et_3N added. Under the same conditions, this reaction was complete in 1 hr. The same products were formed, but in slightly different yields (see Table 16 in Results and Discussion section). Product 324 was identified by comparison with an authentic sample. Product 345 was identified only by GCMS. Products 343 and 344 were isolated by preparative GC (10 ft. 15% SE30 column). The spectral characteristics of 343, 344, and 345 are summarized below:

343

NMR (CCl_4) δ 0.85 (s, 9H), 1.28 (s, 18H), 4.48 (s, 1H)

IR (film) 2970(s), 2925(s), 2890(m), 2855(s), 2110(m), 1470(m), 1460(m), 1385(m), 1360(s), 1235(m), 1200(m), 1185(m), 1050(brd. s), 1020(m), 1000(w), 935(w), 865(m), 835(s), 795 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) 232(parent ion, 1), 217(P^+ -Me, 9), 207(1), 175(P^+ -t-Bu, 14), 161(11), 133(1), 119(69), 103(22), 89(3), 77(100), 63(72), 57(60)

Exact mass for $C_{12}H_{28}O_2Si$ (parent ion) calc. 232.1859; meas. 232.1849

Exact mass for $C_{11}H_{25}O_2Si$ (parent ion $-CH_3$) calc. 217.1623; meas. 217.1624

Exact mass for $C_8H_{19}O_2Si$ (parent ion -t-Bu) calc. 175.1154; meas. 175.1152

344:

NMR (CCl_4) δ 0.98 (s, 18H), 1.32 (s, 9H), the remaining H was not observed

IR (film) 3700(w), 3600-3200(brd. w), 2970(s), 2930(s), 2890(m), 2855(s), 1470(m), 1460(sh), 1385(m), 1360(s), 1235(w), 1195(s), 1065(brd. s), 1010(w), 935(w), 820(s), 785(m), 635 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) 232(parent ion, 1), 217(P^+ -Me, 6), 175(P^+ -t-Bu, 13), 159(1), 145(1), 133(2), 119(45), 103(9), 89(2), 77(100), 75(83), 63(13), 57(14), 56(13)

Exact mass for $C_{12}H_{28}O_2Si$ (parent ion) calc. 232.1859; meas. 232.1852

Exact mass for $C_{11}H_{25}O_2Si$ (parent ion $-CH_3$) calc. 217.1623; meas. 217.1626

Exact mass for $C_8H_{19}O_2Si$ (parent ion -t-Bu) calc. 175.1154; meas. 175.1150

345:

Mass spectrum; m/e (% rel. inten.) 302(parent ion, 1), 245(P^+ -t-Bu, 1), 203(10), 189(1), 165(1), 149(1), 141(4), 125(1), 109(4), 57(100)

Dimethyl-t-butoxychlorosilane

In a 1000 mL three-necked flask equipped with an overhead stirrer were placed dimethyldichlorosilane (60.18 g, 0.466 mole), Et_2O (500 mL), and pyridine (38 mL, 0.471 mole). The solution was cooled to 0° C and t-butanol (34.6 g, 0.467 mole) in 50 mL of Et_2O was slowly added via addition funnel. After all the alcohol was added, stirring was continued overnight at room temperature. After filtering the solution, the Et_2O was removed by distillation. Fractionation of the residue with a 12 in. vigreux column yielded 53.9 g of pure dimethyl-t-butoxychlorosilane (bp 119^o-122^o, 69% distilled yield).

NMR (CCl_4) δ 0.42 (s, 6H), 1.33 (s, 9H)

Dimethyl-t-butoxysilanol (346)

In a 100 mL Morton flask equipped with a magnetic stirrer were placed Et_2O (75 mL), dimethyl-t-butoxychlorosilane (2.193 g, 13.16 mmol), and pyridine (1.08 mL, 14.4 mmol). The solution was cooled to 0^o C and H_2O (0.26 mL, 14.4 mmol) was slowly added via syringe. The solution was stirred for 2 hrs. while the temperature was allowed to slowly rise to room temperature. After pouring into 100 mL of pentane and drying over Na_2SO_4, the solution was filtered. Removal of the solvents with a rotary evaporator left behind a colorless, viscous liquid which was nearly pure 346 (yield ca. 90%). Product 346 was used without purification.

NMR (CCl_4) δ 0.08 (s, 6H), 1.28 (s, 9H), 2.60 (s, 1H)

IR (film) 3600-3000 (brd. s), 2970(s), 2915(m), 2900(m), 2870(w), 1590(w), 1470(w), 1460(w), 1440(m), 1385(m), 1360(s), 1255(s), 1240(m), 1200(s), 1050(brd. s), 1020(w), 1000(sh), 875(s), 840(s), 780(s), 695(w), 675 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) 148(parent ion, 1), 133(P^+ -Me, 61), 117(2), 115(1), 103(1), 77(86), 75(100), 59(16), 47(16)

Thermolysis of dimethyl-t-butylsilanol (346)

Solutions of 346 in tridecane were prepared (5%, 10%, 20%, and 40% solutions). Samples of each solution were placed in capillary tubes which were sealed. The tubes were then placed in an oven at 150° C. Progress of the reaction was monitored by periodically removing sample tubes and analyzing the solutions by GC. The time required for complete reaction of 346 varied with concentration; the 5% solution required 1 hr. while the 40% solution required 2½ hrs. The major products of the 5% solution were found to be 3-t-butoxytetramethyldisiloxane-1-ol (348), dimethyldi-t-butoxysilane (350), and D_4. The major products of the concentrated solutions (20% and 40%) were found to be 348, 350, and 5-t-butoxyhexamethyltrisiloxane-1-ol (349). No D_4 was observed in these concentrated solutions.

Products 350 and D_4 were identified by GCMS, while 348 and 349 were isolated by preparative GC (10 ft. 15% SE30 column). The spectral characteristics of these products are summarized below:

348:

NMR (CCl_4) δ 0.00, 0.01 (s, s, 12H), 1.18 (s, 9H), 2.78 (s, 1H)

IR (CCl_4) 3700(m), 2980(s), 2930(w), 2905(w), 2870(w), 1460(w), 1390(w), 1365(m), 1255(s), 1210(sh), 1195(s), 1050(brd. s), 910(m), 665(w), 630 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen) 207(P^+ -Me, 12), 191(1), 167(1), 151(100), 149(84), 135(12), 133(48), 119(8), 105(3), 103(3), 96(7), 89(4), 75(27), 57(56), 47(6)

349:

NMR (CCl_4) δ 0.06 (brd. s, 18H), 1.22 (s, 9H), 2.66 (s, 1H)

IR (CCl_4) 3700(m), 2970(s), 2930(w), 2905(w), 2870(w), 1390(w), 1360(m), 1255(s), 1200(m), 1040(brd. s), 905(m), 660 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 281(P^+ -Me, 1), 267(1), 251(1), 225(10), 223(12), 207(32), 193(8), 191(7), 177(2), 165(1), 149(2), 133(9), 125(3), 119(2), 103(3), 96(4), 75(12), 73(8), 57(100), 47(2)

350:

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 189(P^+ -Me, 17), 133(36), 117(1), 115(2), 101(1), 87(5), 77(67), 75(100), 57(24), 47(5)

Dimethylsilyl-*t*-butylperoxide (339)

In a 100 mL flask were placed DABCO·2HOO┼ (6.862 g, 23.5 mmol) and Et_2O (60 mL). This solution was cooled to 0^o C and dimethylchlorosilane was added neat via syringe (5.0 mL, 44.9 mmol). A large amount of white precipitate formed immediately. Sitrring was continued for 2 hrs. while the temperature was gradually increased to room temperature. The solution was then poured into 150 mL of pentane and was extracted. Removal of the solvents with a rotary evaporator left *ca*. 4.0 g of a colorless liquid which was nearly pure 339. The recovered yield (ca. 60%) was quite low due to the high volatility of peroxide 339. The peroxide was used without further purification. Attempted purification by column chromatography was unsuccessful as 339 decomposed on silica gel. The spectral properties of 339 are reported below:

NMR (CCl_4) δ 0.18 (d, 2H, J=2.5 Hz.), 1.17 (s, 9H), 4.58 (heptet, 1H, J=2.5 Hz.)

IR (film) 2980(s), 2935(w), 2870(w), 2140(s), 1460(w), 1385(m), 1365(s), 1255(s), 1195(s), 905(brd. s), 880(s), 845(s), 805(w), 760(m), 725 cm^{-1}(m)

Mass spectrum; m/e (% rel. inten.) (parent ion not seen), 133(P^+ -Me, 76), 119(100), 117(6), 103(12), 87(4), 73(47), 66(5), 59(45), 47(3)

Thermolysis of dimethylsilyl-t-butylperoxide (339)

A 5% solution of 339 in dodecane was prepared and placed in several capillary tubes. After sealing, these tubes were placed in an oven at 150° C. The starting peroxide completely disappeared within a half hour. The major products, as observed by GCMS, were D_4 and silanol 348. As the initial concentration of 339 in dodecane was increased, the yield of 348 increased.

Reaction of dimethylsilyl-t-butylperoxide (339) with Et_3SiD

Deuterotriethylsilane was prepared by treatment of triethylchlorosilane with lithium aluminum deuteride in Et_2O. The Et_3SiD was purified by preparative GC (10 ft. 15% SE30 column) just prior to use.

To a 5% solution of 339 in octane was added a 3-fold molar excess of Et_3SiD. This solution was placed in several capillary tubes. After sealing, the tubes were placed in an oven at 135°. The reaction was complete within a half hour. The major products were *t*-butanol-OD and 1,1-dimethyl-3,3,3-triethyldisiloxane (353). The deuterated alcohol was only identified by GCMS while 353 was isolated by preparative GC (6 ft. 30% SE column).

NMR (CCl_4, 100 MHz) δ 0.16 (d, 6H, J=2.5 Hz.), 0.35 - 1.10 (complex multiplet, 15H), 4.68 (heptet, 1H, J=2.5 Hz.); irradiation at δ 4.68 causes the doublet at δ 0.16 to collapse to a singlet

IR (CCl_4) 2965(s), 2940(sh), 2920(m), 2880(s), 2120(s), 1465(m), 1420(m), 1380(w), 1250(brd. s), 1065(brd. s), 1000(s), 910 cm^{-1}(s); the region of Si-D absorption (1520 cm^{-1} for Et_3SiD) is clear

Mass spectrum; m/e (% rel. inten.) 190(parent ion, 1), 175(P^+ -Me, 3), 161(P^+ -Et, 100), 147(4), 133(82), 119(5), 105(67), 87(7), 73(13), 66(13), 59(41)

Reaction of trimethylsilyl-*t*-butylperoxide (85) with Et_3SiH

A solution containing peroxide 85 (0.0728 g, 0.448 mmol), Et_3SiH (0.188 g, 1.62 mmol), dodecane (0.514 g), and undecane (0.0344 g, GC standard) was prepared. Samples of this solution were placed in capillary tubes which were sealed and placed in an oven at 150° C. The reaction was complete after 1½ hrs. The major products formed were triethylsilanol (302, 17%) and 1,1,1-trimethyltriethyldisiloxane (354, 72%). Silanol 302 was identified by comparison with an authentic sample while 354 was isolated by preparative GC (6 ft. 30% SE30 column). The spectral properties of 354 are summarized below:

NMR (CCl_4) δ 0.08 (s, 9H), 0.40 - 1.20 (complex multiplet, 15H)

IR (film) 2980(s), 2920(s), 2885(s), 1460(m), 1415(m), 1250(s), 1240(sh), 1065(brd. s), 1010(s), 860(s), 840(s), 750(s), 735(s), 720(s), 640 cm^{-1}(w)

Mass spectrum; m/e (% rel. inten.) 204(parent ion, 1), 189(P^+ -Me, 6), 175(P^+ -Et, 100), 161(9), 147(80), 133(12), 119(75), 117(13), 105(15), 103(12), 87(11), 80(9), 73(39), 66(28), 59(36)

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