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Synthetic and mechanistic studies of silylenium ions in solution

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SYNTHETIC AND MECHANISTIC STUDIES OF SILYLENIUM IONS IN SOLUTION

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Synthetic and mechanistic studies of silylenium ions in solution

by

Yung-Lin Chen

A Dissertation Submitted to the
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For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa

1986

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DEDICATION

To Yu-Ying, Maria

INTRODUCTION

All research hitherto conducted on silylenium cations in solution has concentrated on obtaining evidence for the existence of these elusive species, either experimentally or theoretically. Surprisingly, no investigations regarding the synthetic use of these silylenium cations have been pursued.

This work will explore the synthetic utility of silylenium cations which were generated by hydride abstraction by triphenylmethyl salts in methylene chloride. Decomposition of certain of the silylenium ions which were formed from dimethylsilyl alkyl (aryl) ethers, resulted in the apparent formation of dimethylsilanone transients in high yields under mild conditions. These results provide indirect evidence of silylenium ion formation and also provide a synthetic use of silylenium ions in solution. This work also presents the results of investigations into mechanisms of these silylenium ion fragmentation reactions, using trapping experiments.

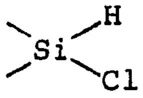
Finally, this dissertation presents different synthetic applications of several silylenium ions as precursors to saturated and unsaturated five- and six-membered cyclic silyl ethers from various dimethylsilyl alkyl (alkenyl and aryl) ethers reacting with triphenylmethyl salts.

A historical section briefly presents the recent developments of several organosilicon reactive intermediates such as silanones, silenes, disilenes and silylenium ions.

NOMENCLATURE

The nomenclature in this dissertation will, with exceptions described below, follow the IUPAC convention. Simple organosilicon compounds will be named as derivatives of silanes (SiH_4), while more complicated linear and cyclic systems will be named as sila-analogs of the corresponding carbon systems. Compounds containing (p-p) π-bonded silicon, will be named as derivatives of silene ($H_2Si=CH_2$), disilene ($H_2Si=SiH_2$) and silanone ($H_2Si=O$). Although the tricoordinate silyl cation, analogous to a carbenium ion, is referred to as silicenium ion by some authors, this dissertation will use the term "silylenium ion". For the sake of simplicity, a methyl substituent on silicon will often be represented as a dash emanating from the silicon.

Examples:



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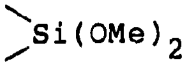

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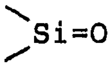

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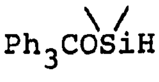
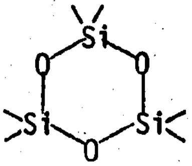
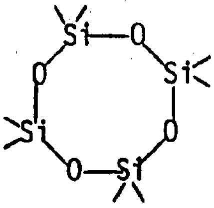


Ph_3COSiH

dimethylsilyl triphenylmethyl ether



hexamethylcyclotrisiloxane, D_3



octamethylcyclotetrasiloxane, D_4

HISTORICAL

The purpose of this historical section is to provide the reader with some basic information about organosilicon chemistry necessary for the understanding of the research to be described herein. The topics reviewed in this dissertation can broadly be classified into three categories: (1) general information about recent achievements in π-bonded silicon, (2) chemistry of silanones and cyclic siloxanes, (3) synthesis and chemistry of silylenium cations. The first part of this review will briefly discuss recent accomplishments in the area of multiple-bonded silicon, such as silenes (Si=C) and disilenes (Si=Si), and provide the most recent references. The second part of the review will discuss basic information about silanones and cyclic siloxanes which relates to this research. A review of silylenium ion chemistry will focus on the basic background, calculations, and detection of silylenium ions.

General

There has been considerable interest in the silicon analogues of organic compounds since the pioneering work of Kipping at the beginning of this century that revealed that replacement of carbon by silicon in an organic molecule could greatly alter the chemical and/or physical properties of the molecule (1).

Several decades of investigation of silicon-centered reactive intermediates such as silenes (Si=C), disilenes (Si=Si), silylenes (Si:), silanones (Si=O), and silylenium ions ($Si^{\oplus}$) have generally failed to prepare such silicon-containing reactive intermediates until recently. The persistent failure to generate these compounds led to the belief that they are inherently unstable because of the weakness of π bonds formed from 3p orbitals on silicon (2, 3).

In the mid 1960s, evidence supporting the possible existence of silicon multiple-bonded species as reactive intermediates began to accumulate from both solution and gas phase studies. At present, many silicon multiply-bonded intermediates have apparently been made as transient species. In the early 1980s, isolation of stable silenes (4, 5) and disilenes (6) at room temperature were reported. Since then, several theoretical treatments of silicon multiple bonds and their relationship to experimental data have been reviewed (7-11). The Si=C double bond has been reviewed by Brook (12, 13) and Wieberg (14). The Si=Si double bond has been reviewed by West (15, 16). The most recent and comprehensive review of experimental results and theoretical calculations of silicon multiple bonded species was published by Raabe and Michl in 1985 (17).

Silanones and Cyclic Siloxanes

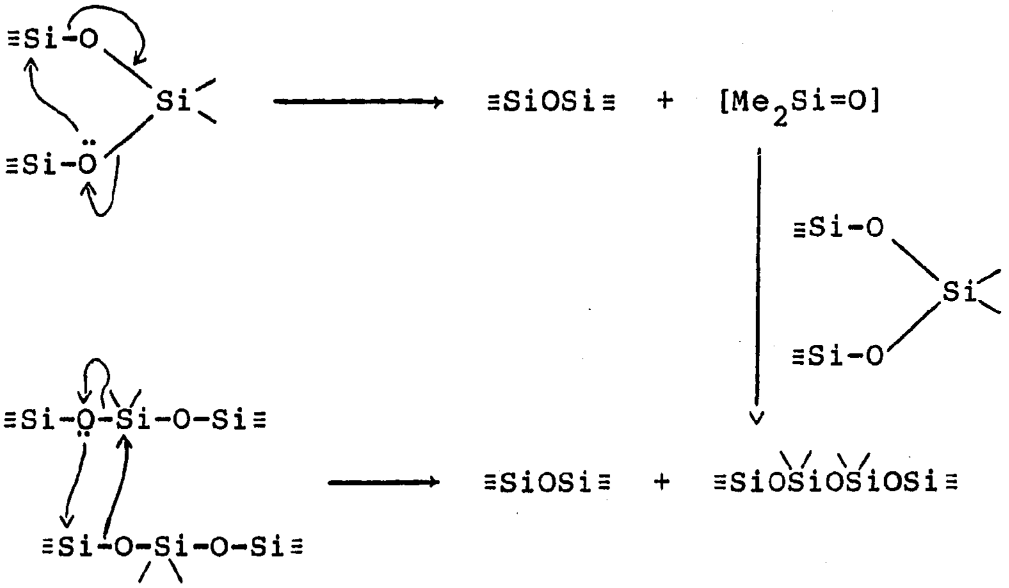
In sharp contrast to the well-studied silenes and disilenes, no stable silanones have been isolated so far even in dilute solutions. The bulk of the present knowledge of silanone properties has been inferred from product analysis and kinetic measurements. Matrix-isolation techniques have been used to spectroscopically observe Me_2SiO (18), H_2SiO (19, 20), F_2SiO (21) and Cl_2SiO (22). Several reviews on the synthesis, calculations and chemistry of silanones have appeared (3, 17, 23-27).

The methods used to generate silanones can broadly be classified into three categories: photochemical generation, gas-phase pyrolytic generation, and silene oxidation. All of these methods have been covered in reviews (3, 17, 23), and will not be discussed in this historical in detail.

Several recent theoretical calculations have focused on silanone and its simple derivatives (11, 24-27). The silanone molecule was calculated to be planar and to contain an extremely polar (4.1 D) (27) silicon-oxygen bond. The Si=O double bond length was calculated to be 1.509 Å (11, 24) and thus is significantly shorter than the Si-O single bond distance of 1.671 Å (27). The C=O in formaldehyde was calculated to be 24.9 kcal/mol stronger than the Si=O bond in silanone (26).

In 1952, Andrianov and Sokolov reported results for the pyrolysis of polydimethylsiloxanes (28). It was discovered that heating polydimethylsiloxanes at 150-200°C led to the formation of new siloxanes that differed from starting siloxanes only by the number of Me_2SiO units. The authors explained these results through the intermediacy of dimethylsilanone. However, Hoekman later provided an alternative mechanism which involved an Me_2SiO unit being transferred via an intermolecular process also leading to the same products (29) (Scheme 1).

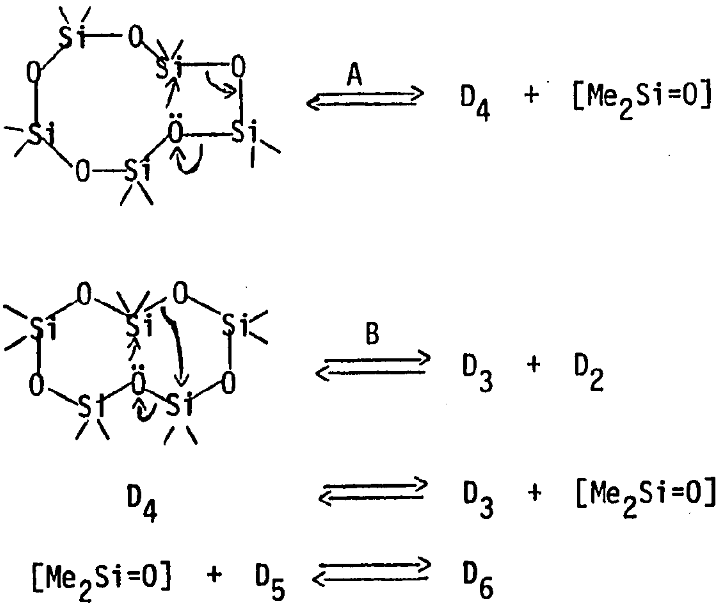
Scheme 1



Gusel'nikov et al. (30) and Nametkin et al. (31) and coworkers studied the pyrolysis reactions of cyclosiloxanes and cyclocarbosiloxanes at 500-700°C. They also found that cyclosiloxanes of formula $(Me_2SiO)_n$ led to the formation of new cyclosiloxanes that differed from the starting materials only in the number of Me_2SiO units. These results were similar to those of Andrianov and Sokolov (28).

Gusel'nikov and coworkers also carried out a kinetic study of the thermal decomposition of decamethylcyclopentasiloxanes (D_5) in the gas phase (30). Their results indicated that the initial decomposition of D_5 followed first-order kinetics. The formation of octamethyltetrasiloxane (D_4) increased initially and then decreased. The formation of hexamethylcyclotrisiloxane (D_3) steadily increased, while the concentration of D_6 remained small but constant. Gusel'nikov and coworkers suggested that the decomposition of D_5 followed two distinct unimolecular pathways (Scheme 2).

Scheme 2



After analysis of the product ratios, these authors suggested that at least 60% of the reaction followed path A with formation of dimethylsilanone. The decomposition of D_4 to D_3 and dimethylsilanone would lead to a steady increase of the concentration of D_3 and decrease of the concentration of D_4 in the final product mixture. The origin of D_6 is presumed to be an addition of dimethylsilanone to D_5.

Davidson and Thompson later performed very similar kinetic studies (32, 33). The gas-phase thermolysis of D_4 was carefully studied and it was concluded that the decomposition of D_4 followed first-order kinetics at least at the beginning of the reaction. Both D_3 and D_5 were formed as products, however, the concentration of D_3 increased while the concentration of D_5 diminished as the reaction progressed (Scheme 3).

Scheme 3

$$D_4 \rightleftharpoons D_3 + [Me_2Si{=}O]$$

$$D_4 + [Me_2Si{=}O] \rightleftharpoons D_5$$

$$D_5 + [Me_2Si{=}O] \rightleftharpoons D_6$$

$$D_6 \longrightarrow 2\ D_3$$

They proposed that during the initial stages of the reaction, D_4 extruded the intermediate dimethylsilanone and formed D_3. The dimethylsilanone would then add to the starting D_4 to form D_5. Another molecule of dimethylsilanone then added to D_5 and formed D_6 which underwent intramolecular decomposition to afford two molecules of D_3. They used this scheme to explain the observation that formation of D_3 was higher than D_5. They also reported that under their gas phase reaction conditions, D_6 decomposed rapidly and formed only D_3. These results were in disagreement with those of Gusel'nikov et al. (30) and Nametkin et al. (31). Nametkin and coworkers pyrolyzed D_6 and also found a mixture of cyclosiloxanes, but the yield of D_5 was almost twice the yield of D_3. In spite of these discrepancies, both groups agreed that free dimethylsilanone was formed in their reactions. Hoekman criticized the free silanone formation as unnecessary in Gusel'nikov et al. (30), Nametkin et al. (31) and Davidson and Thompson (32, 33) reactions. His objections arose mainly from the inconsistencies between these two groups. In particular, both groups pyrolyzed the same D_6 starting material yet derived different product distributions supporting different mechanistic interpretations. Additionally, Davidson and Thompson could not trap dimethylsilanone with ethylene, another strong reason for Hoekman's objections (29).

In the Ph.D. dissertation of G. Hussmann, a few of Hoekman's objections were commented upon (23). Both Nametkin and Davidson agreed D_3 was the final product, although they obtained different product distributions from the pyrolysis of D_6. Both authors also agreed that decomposition of D_5 and D_4 followed first-order kinetics only at the beginning of the reaction, so they proposed that silanone formation occurred only during the initial stages of these decompositions. Pyrolysis at different temperatures and pressures could also account for different product distributions. Davidson and Thompson indicated that they did obtain the trapping products from dimethylsilanone with ethylene which was convincing evidence for the intermediacy of dimethylsilanone (33).

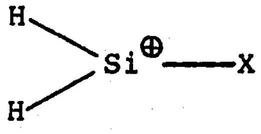
The main evidence supporting silanone intermediacy in the literature was based on the observation of silanone trapped products. Hoekman suggested that these observations were insufficient evidence for silanone formation, since all the trapping products could be explained via a more economical bimolecular silanone-transfer process. Most literature reports which claimed silanone intermediacy did not eliminate the possibility of a bimolecular silanone-transfer process; all of these reports should be carefully reevaluated.

Silylenium Ions

Carbenium ions, $R_3C^{\oplus}$, are readily accessible species in all three phases and possess a well-developed chemistry. In contrast, the silicon analogues, silylenium ions, $R_3Si^{\oplus}$, are far more elusive (34, 35).

Before the early 1980s, a number of chemists had tried to demonstrate the presence of silylenium ions in solution by imitating the structures, reactions, and physiochemical methods which had been used to establish the presence of carbenium ions. Unfortunately, all of the attempts to obtain definitive evidence for these silylenium ionic species failed. These failures have puzzled chemists for years. Since silicon is more electropositive than carbon (1.7 and 2.5 respectively in Pauling's scale (36)), one expects silylenium ions to be formed at least as readily as carbenium ions. Furthermore, silylenium ions are well known to exist in the gas phase as high abundance fragments in the mass spectra (37-46) and ion cyclotron resonance spectra (47-50) of organosilicon compounds.

Murphy and Beauchamp studied the photo-ionization mass spectroscopy of fluoromethylsilanes and their data showed the parent silylenium ion was 30-50 kcal/mol more stable than methyl cation (51). A recent theoretical calculation reported by Apeloig and Schleyer also showed the parent silylenium ion to be 73.5 kcal/mol more stable than methyl cation (52). These calculations were carried out using ab initio SCF-MO Gaussian 70 series programs. Since then, more groups have concentrated on systematic, theoretical studies of the silylenium ion 1.



1

Several groups tried to quantitatively analyze the importance of the various properties of α-substituents (such as σ-inductive effects, lone pair π-donation, and hyperconjugation) in stabilizing $Si^{\oplus}$ centers (52-56). These investigations of α-substituted silylenium ions have been carried out by varying X systematically along the series of first period substituents (52, 53), second period substituents (54), electron-withdrawing substituents (55) and vinyl substituents (56). The results of substitution were compared between carbenium and silylenium ions. All of the above calculations were carried out by using ab initio calculations.

The stability of α-substituted silylenium ions 1 compared with that of the parent $H_3Si^{\oplus}$ cation can be estimated from an isodesmic reaction (eq. 1). The same methods were applied to compare the stabilities of α-substituted methyl cations (eq. 2).

$$SiH_2X^{\oplus} + SiH_4 \longrightarrow SiH_3^{\oplus} + SiH_3X \qquad (1)$$

$$CH_2X^{\oplus} + CH_4 \longrightarrow CH_3^{\oplus} + CH_3X \qquad (2)$$

The results of these calculations clearly showed that all the substituents examined stabilized the silylenium cation center (with the exceptions of electron-withdrawing substituents (55)). However, besides vinyl substituents, all the substituents were more effective in stabilizing carbenium ions than in stabilizing silylenium ions. These differences were most pronounced for the first period substituents which possessed lone electron pairs such as NH_2 and OH. Apeloig and coworkers (52, 54) suspected that the π-donors were less effective in stabilizing silylenium ions due to the different sizes of the interacting orbitals (i.e., $Si^{\oplus}$ (3p) and N (2p)), which would reduce orbital overlap. If this hypothesis is correct, the second period substituents, particularly good π-donors such as R_2P and RS, should provide effective 3p-3p conjugation and might, therefore, be more effective in stabilizing silylenium ions than carbenium ions. Besides π-donor ability, the σ-electron withdrawal ability also should be considered by comparing different elements. The smaller electronegativity of P (2.1 on Pauling scale) versus N (3.0) and of S (2.5) versus O (3.5) would, in addition, cause less inductive destabilization of $Si^{\oplus}$ by the second peroid substituents (P and S). The computational results for

PH_2-$SiH_2^{\oplus}$ were, however, very disappointing. Despite being a stronger π-donor and a weaker σ-withdrawing group relative to NH_2 in NH_2-$Si^{\oplus}H_2$, both ab initio (54) and MNDO calculations (57) predicted PH_2 to be decidedly inferior to NH_2 in stabilizing $Si^{\oplus}$. For example, NH_2 was more stabilizing than PH_2 by 25.2 kcal/mol, MNDO; 24.8 kcal/mol, 3-21G; 17.7 kcal/mol, STO-3G. These calculations suggested that the main reason for poor stabilization by phosphorus was the high barrier from pyramidalization at phosphorus (E inversion on PH_3, 31.5 kcal/mol). The planarization at P required for effective π-donation was so energetically expensive in $PH_2SiH_2^{\oplus}$ that little net stabilization would be provided to the cations. In fact, both ab initio (STO-3G, 3-21G) basis sets predict a pyramidal P in this cation.

In contrast to the case of PH_2 versus NH_2, SH and OH stabilized silylenium ions to a similar extent (STO-3G). Both the $p\pi$-$p\pi$ orbital overlaps and the π-donation to the $H_2Si^{\oplus}$ fragment were similar in the two cations. Only HS, however, was a net electron donor; OH actually withdrew 0.108 electrons from the $H_2Si^{\oplus}$ fragment. The smaller energy difference between the interacting orbitals in $HSSiH_2^{\oplus}$ (3p(S)-3p($Si^{\oplus}$)) compared with $HOSiH_2^{\oplus}$ (2p(O)-3p($Si^{\oplus}$)) also contributed to the stability of $HSSiH_2^{\oplus}$. Both Cl and F were destabilizing relative to hydrogen at the 3-21G level, chlorine being more destabilizing.

Truong et al. also performed ab initio calculations to analyze the ability of vinyl groups to stabilize the $CH_3^{\oplus}$ and $SiH_3^{\oplus}$ groups (56). Their results showed that not only did vinyl groups stabilize the silylenium cation center, but that successive vinylation also increased stabilization of the silylenium ion relative to its carbon analogue.

A direct comparison of the stabilities of substituted silylenium and methyl cations is provided by equation 3:

$$H_2SiX^{\oplus} + H_3CX \longrightarrow H_2CX^{\oplus} + H_3SiX \qquad (3)$$

In this equation, a hydride ion is transferred from carbon to silicon, so this might be used to assess the relative ability of these two atoms to carry a positive charge. Ab initio STO-3G calculations by Apeloig and Schleyer predicted the parent silyl cation to be 73.5 kcal/mol more stable than the methyl cation (52). The parent silylenium ion was more stable than the parent methyl cation by 45.8 kcal/mol at the double-zeta basis level calculation, and the energy difference was decreased to 41.0 kcal/mol by inclusion of polarization functions (55). In agreement with this conclusion, the ion with the positive charge formally located on silicon was the thermodynamically more stable, consistent with the fact that silicon was larger and more electropositive than carbon.

In contrast with the gas phase, the difficulty in obtaining stable $R_3Si^{\oplus}$ species in solution is probably due to the fact that silicon has alternative, energetically very favorable reaction paths available in solution. These pathways, involving pentavalent or hexavalent intermediates, ensure a short life-time for the species or may completely suppress its formation, especially in a nucleophilic solvent (56).

Hydride exchange reactions have been used widely to generate carbenium ions, and this method has also been used recently in studies of reported silylenium ion generation (58, 59). The reaction of silyl hydrides and triphenylmethyl salts in solvents of low nucleophilicity is one possible way to generate silylenium ions (eq. 4).

$$R_3SiH + Ph_3C^{\oplus}X^{\ominus} \longrightarrow Ph_3CH + R_3Si^{\oplus}X^{\ominus} \qquad (4)$$

Generation of a silylenium ion must be attempted in a medium of extremely low nucleophilicity in order to avoid coordination expansion to pentavalent or hexavalent silicon. For this reason, the reactions between several silyl hydrides and three triphenylmethyl salts in methylene chloride were studied (60). Barton and Tully found that these three hydrides (chloromethyldimethylsilane, α-naphthylmethylphenylsilane and di-*t*-butylmethylsilane) reacted with ionic trityl salts (triphenylmethyl perchlorate, triphenylmethyl hexafluoroantimonate and triphenylmethyl tetrafluoroborate) at rates which exhibited anion independence. This work was also supported by polarimetric and kinetic studies of optically pure α-naphthylmethylphenylsilane with same triphenylmethyl salts (61).

Gjerde later also studied the electron demand of silicon in the transition state of silyl hydride abstraction reactions (62). They studied the reactions of various substituted aryldimethylsilanes with ionic triphenylmethyl salts in methylene chloride and obtained a Hammett reaction constant, ρ, of -2.12. This negative ρ-value demonstrated the development of positive charge on silicon in the transition state for silyl hydride abstraction.

Lambert and Schulz reported the first observation of a silylenium ion in (methylene chloride) solution (63). The strategy used was to stabilize the silylenium ion with second row alkylthio substituents. The choice of the alkylthio group was because of its high polarizability, its low electronegativity and the possibility that sulfur could provide better 3p-3p overlap with silicon than 2p-3p overlap of those elements in the first row. Apeloig et al. (54) and Godleski et al. (57) <u>via</u> calculations also suggested that HS would provide net stabilization to the $H_2SiX^{\oplus}$ cation (X = HS). Maximization of stabilization through polarization and 3p-3p overlap suggested that $(RS)_3SiH$ would be an ideal precursor for the generation of a silylenium ion. Further polarization could also possibly be obtained from the use of a reasonably large alkyl group such as isopropyl. Lambert and Schulz chose tris(2-isopropylthio)silane for the silyl hydride exchange reaction with triphenylmethyl perchlorate in methylene chloride at room temperature (eq. 5):

$$(\underline{i}\text{-Pr})_3SiH + Ph_3C^{\oplus}ClO_4^{\ominus} \xrightarrow[\text{r.t.}]{CH_2Cl_2} Ph_3CH + (\underline{i}\text{-Pr})_3Si^{\oplus}ClO_4^{\ominus} \quad (5)$$

The resulting solution had a specific conductance of 110.8 μmho cm^{-1} (4.61×10^{-4} mol for both starting materials), typical of a fully ionized species. This value was comparable to that of a fully ionic species such as trityl perchlorate (5.03×10^{-4} mol), which was 102.0 μmho cm^{-1}. An analogous solution of triphenylsilane (6.86×10^{-4} mol) and triphenylmethyl perchlorate had a specific conductance of only 2.2 μmho cm^{-1}.

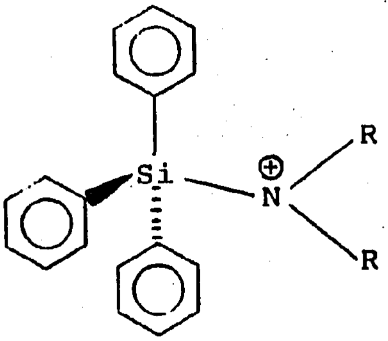
More evidence for this silylenium ion was derived from nuclear magnetic resonance (NMR) spectroscopy. The carbon-13 spectrum showed only a single pair of isopropyl resonances in addition to those of triphenylmethane. The carbon-13 NMR chemical shift studies also eliminated the possibility of sulfonium ion formation ($RS{-}{-}Si^{\oplus}\!<\ \longrightarrow\ RS^{\oplus}{=}Si\!<$). The proton NMR spectrum showed complete loss of the Si-H resonance, along with the emergence of the triphenylmethane methinyl singlet and an aromatic resonance. Reaction of the resulting ionic solution with diisobutylaluminum hydride yielded only the starting silane-tris(2-isopropylthio)silane. From the above observations, the results seemed most in accord with a silylenium ion intermediate. However, silicon-29 NMR, IR, UV and EPR spectra did not provide any additional information to support this study.

Most recently, Lambert and coworkers reported the preparation and characterization of triphenyl silylenium cation in acetonitrile and sulfolane solution (64). Numerous earlier attempts had been made to prepare this cation by using different triphenylmethyl salts and a variety of solvents, but all met with failure (34, 63, 65). Lambert's reaction also involved hydride abstraction from triphenylsilane by triphenylmethyl perchlorate in a variety of solvents (eq. 6).

$$Ph_3SiH + Ph_3C^{\oplus}ClO_4^{\ominus} \xrightarrow{\text{solvent}} Ph_3CH + Ph_3Si^{\oplus}ClO_4^{\ominus} \qquad (6)$$

The resulting solutions were examined in a number of solvents with high polarity (to promote ionization) and with low nucleophilicity or donor number (to avoid complexation with solvent). The molar conductance (mho cm^2 mol^{-1}) was only 1.13 in methylene chloride, and 0.28 in 1,2-dichloroethane, but 179.5 in acetonitrile and 12.0 in sulfolane. The low value in sulfolane was caused by high viscosity in comparison with other solvents, as conductivity is inversely proportional to viscosity. By using a log-log plot of molar conductance *versus* concentration it was determined whether the formed species existed either as an ion pair or as free ions. For acetonitrile and sulfolane, the plots were linear and horizontal, as expected for free ions. In contrast, the plots in methylene chloride and 1,2-dichloroethane were linear with a substantial negative slope, as expected for an ion pair. The proton and carbon NMR spectra of equal molar amounts of triphenylsilane and triphenylmethyl perchlorate in CD_2Cl_2 showed the clean production of a single species. The possibility of solvents coordinating with the triphenylsilylenium ion was eliminated by carbon-13 NMR experiments. The data showed that there was little variation of *ipso* and *para* shifts for triphenylsilyl perchlorate in methylene chloride, acetonitrile and sulfolane. The effects of complexation were shown very clearly for the addition of pyridine and other strong nucleophiles (such as dimethylformamide, dimethylsulfoxide etc.) to triphenylsilyl perchlorate in methylene chloride. Addition of acetonitrile or sulfolane to triphenylsilyl perchlorate in methylene chloride had no effect. These results indicated that for the solvents used, coordination did not take place, and that complexes of type <u>2</u> form when stronger nucleophiles were present.

N-15 NMR provided an even more sensitive probe. Since complexation, like protonation, removes the nitrogen lone pair, the ^{15}N shift should move about 100 ppm upfield as the n-π transition is no longer present to cause the larger paramagnetic (downfield) shift of nitriles. The ^{15}N shift of free acetonitrile was found at δ 244.2, and acetonitrile in the presence of triphenylsilyl perchlorate was found at δ 245.7 in methylene chloride. Similar values were obtained in 1,2-dichloroethane. Even if six equivalents of acetonitrile were present, the chemical shift was only δ 244.8. These observations clearly showed no interaction between acetonitrile and triphenylsilylenium ion, so this ionic species was not complexed with solvent in methylene chloride, 1,2-dichloroethane or acetonitrile. The same method was applied to a good nucleophilic solvent, pyridine. One mole of pyridine was placed in the presence of triphenylsilyl



<u>2</u>

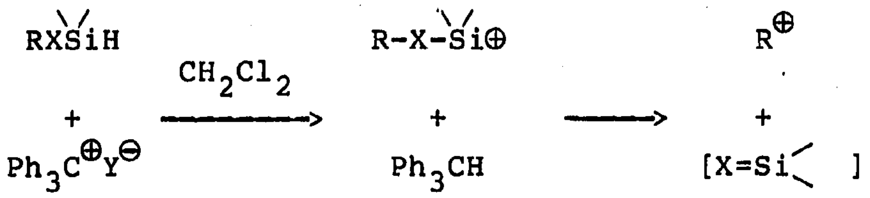
perchlorate in methylene chloride. Whereas free pyridine has an ^{15}N resonance at δ 314.0, pyridine in the presence of triphenylsilyl perchlorate resonated at δ 216.8. This shift of 100 ppm was consistent with complexed pyridine of type <u>2</u>. However, the authors did not provide an explanation as to why triphenylsilylenium ion exists as an ion pair in methylene chloride and 1,2-dichloroethane, and as the free ion in acetonitrile and sulfolane. One possible explanation is that acetonitrile and sulfolane have higher dielectric constants than methylene chloride and 1,2-dichloroethane (66), and would allow better separation of ion pairs leading to the formation of free ions.

Goals of This Research

Previous literature reports in the area of silyl cations have been mainly concerned with the search for evidence to prove the existence of silylenium ions in solution, and it is now known that silylenium ions can be prepared if one can design a suitable reaction system. Despite the work done in this area, one key question remains to be answered. Is it possible for one to investigate the further chemistry of these proposed silylenium ions, for silylenium ions, once generated, would be expected to undergo further reactions such as decompositions or rearrangements. Surprisingly, little work in this area has been done.

This work begins to investigate the chemistry of these proposed silylenium ion intermediates. There are several advantages for the group of Dr. Barton to attack this problem. The group has already established and developed the necessary techniques for the generation of silylenium ions. By using the well-studied silyl hydride abstraction reaction with ionic triphenylmethyl salts in low nucleophilic solvents, it should be straight forward to generate the desired silylenium ions. It should then be possible to design a suitable system to further study reactions of these intermediates.

Combining the above factors, the simple system shown in equation 7 was developed.



$$\mathrm{RX\overset{\diagdown\diagup}{Si}H} + \mathrm{Ph_3C^{\oplus}Y^{\ominus}} \xrightarrow{CH_2Cl_2} \mathrm{R\text{-}X\text{-}\overset{\diagdown\diagup}{Si}^{\oplus}} + \mathrm{Ph_3CH} \longrightarrow \mathrm{R^{\oplus}} + [\mathrm{X{=}Si}\lessdot\ ] \qquad (7)$$

$X = O, CH_2, \overset{\diagdown\diagup}{Si}$

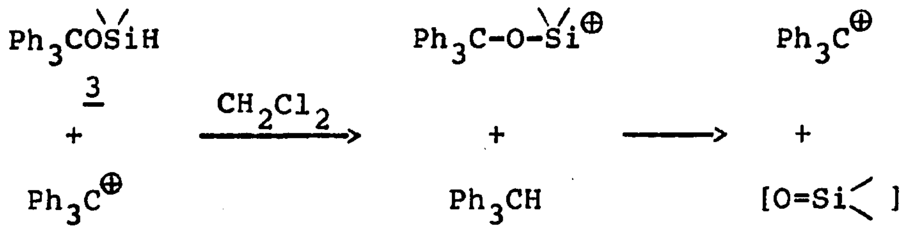
$Y = ClO_4, SbF_6$

R = trityl, t-butyl, benzyl etc.

The first step of this reaction had already been established by numerous groups (58-65). It was suggested that silylenium ions could be generated by abstraction of silyl hydride by ionic triphenylmethyl salts in methylene chloride and other solvents. After silylenium ions have been formed, the leaving group R should play the most important role in subsequent chemistry. One strategy involves finding an alkyl or aryl group which would ultimately form a stable carbenium cation (67-69) as the product of bond heterolysis. Silicon-containing products would be the silicon double bonded species silanones (Si=O), silenes (Si=C) and disilenes (Si=Si) and have been reviewed previously in the historical section. All are known to lead to either oligomers or rearranged products. Compared with known oxonium ions in carbon chemistry (70), we also hope to extend the analogous chemistry to the intramolecular cyclization reaction of silylenium ions to generate cyclic organosilyl ethers.

RESULTS AND DISCUSSION

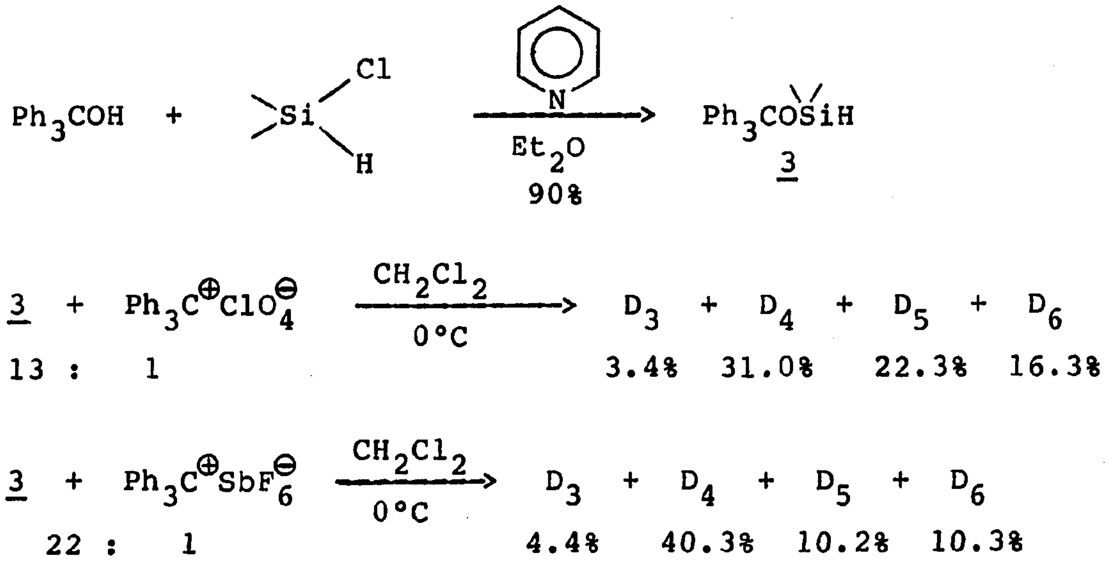
This work began with an examination of the reaction between triphenylmethyl salts and dimethylsilyl triphenylmethyl ether, 3, $Ph_3CO\overset{\backslash /}{Si}H$ in methylene chloride. We were initially interested in this system for several reasons. It was proposed that silyl hydride abstraction by triphenylmethyl salt would form a silylenium ion in solvents of low nucleophilicity (58-65). This system would then offer an excellent opportunity for observing subsequent chemistry of silylenium ions. An intriguing possibility would be loss of the triphenylmethyl cation to form dimethylsilanone (eq. 8).



$$\begin{array}{c} Ph_3CO\overset{\backslash /}{Si}H \\ \underline{3} \\ + \\ Ph_3C^{\oplus} \end{array} \xrightarrow{CH_2Cl_2} \begin{array}{c} Ph_3C\text{-}O\text{-}\overset{\backslash /}{Si}^{\oplus} \\ + \\ Ph_3CH \end{array} \longrightarrow \begin{array}{c} Ph_3C^{\oplus} \\ + \\ [O{=}Si\langle\;] \end{array} \qquad (8)$$

The loss of the stable triphenylmethyl cation would provide part of the necessary driving force for the reaction. Another important feature was that the triphenylmethyl leaving group would be exactly the same as the starting triphenylmethyl abstraction reagent. If this reaction would proceed as expected, then only a catalytic amount of triphenylmethyl salt would be needed to react with compound 3. With these hypotheses in mind, the project was initiated by treating compound 3 with a catalytic amount of triphenylmethyl perchlorate (13:1 mol ratio) in methylene chloride at 0°C. The reaction afforded D_3 (3.3%), D_4 (43.8%), D_5 (22.3%), D_6 (16.3%) and triphenylmethane without any starting material 3 left in the reaction mixture. The reaction was also performed with compound 3 and a catalytic amount of triphenylmethyl hexafluoroantimonate (22:1 mol ratio). The same products were identified with only a slightly different product distribution; D_3 (4.4%), D_4 (40.3%), D_5 (10.2%), D_6 (10.3%) and triphenylmethane with all the starting material 3 consumed. The synthesis of starting material 3 and results of its reactions with triphenylmethyl salts are summarized in Scheme 4.

Scheme 4

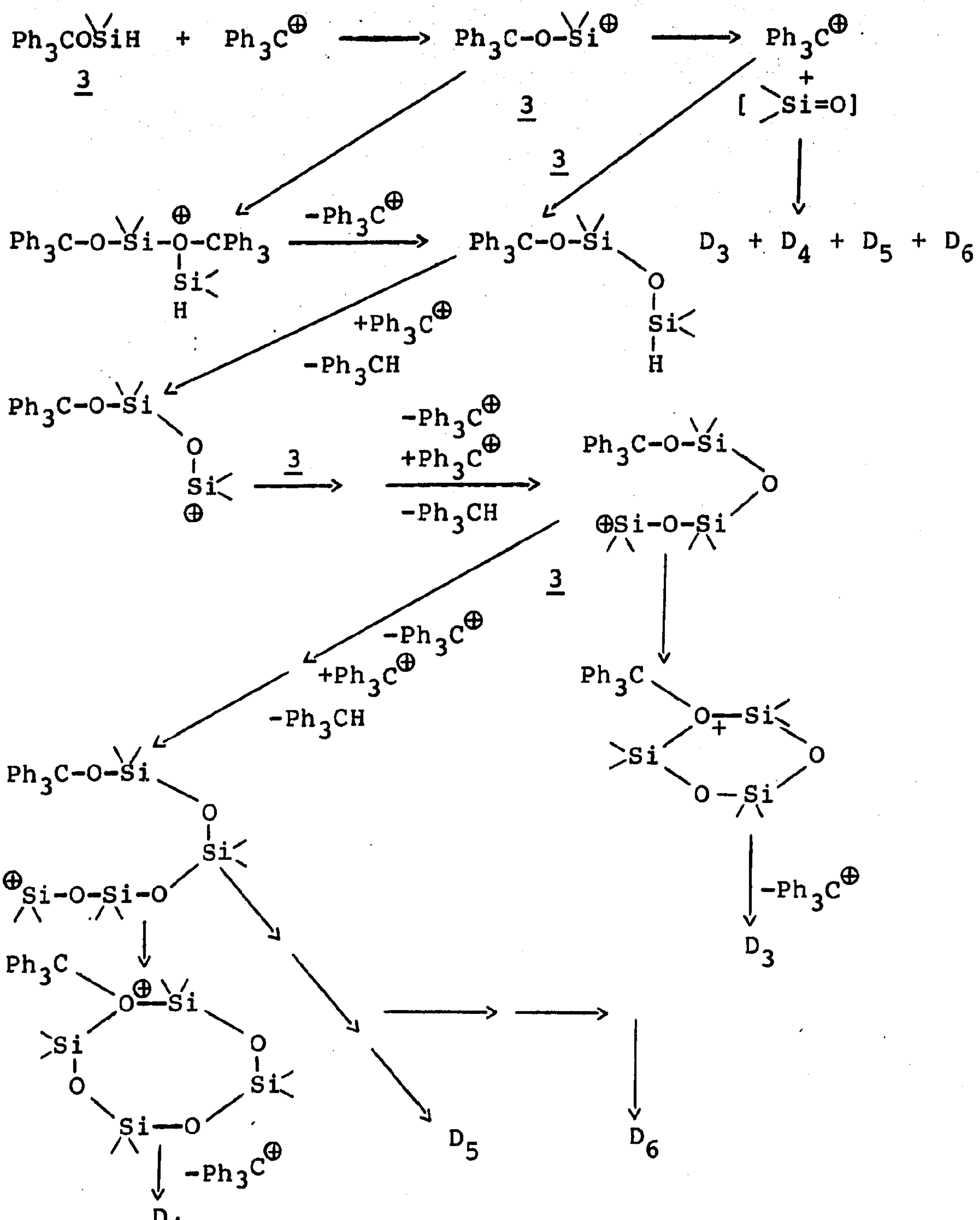


Product analysis could support a unimolecular process via generation of a triphenylmethyl cation and free dimethylsilanone, which is known to form cyclic siloxane oligomers in the absence of a trapping agent (17, 23). However, an intermolecular process via an oxonium type cation must also be considered (Scheme 5).

In the intermolecular process, triphenylmethyl salts abstract a hydride ion from starting material 3 and form a silylenium ion. This silylenium ion reacts with starting material 3 to form the oxonium ion. Loss of triphenylmethyl cation forms a new silicon compound which is exactly the same as the dimethylsilanone insertion into starting material 3. Repeating the same process could form a silylenium ion which contains three silicon units. This silylenium ion could react further by two different pathways. One is to cyclize to an oxonium ion, and lose triphenylmethyl cation to form D_3. The other possible reaction pathway of this silylenium ion is to add another molecule of starting material 3 and repeat the same cyclization process as above. This could lead to higher analogue cyclic siloxane oligomers D_4, D_5, and D_6.

It was surprising to see the small amount of D_3 formed relative to D_4 and D_5, regardless of which pathway the reaction followed. It was known that, in the absence of trapping agent, generation of the dimethylsilanone intermediate via both thermal and photochemical reactions

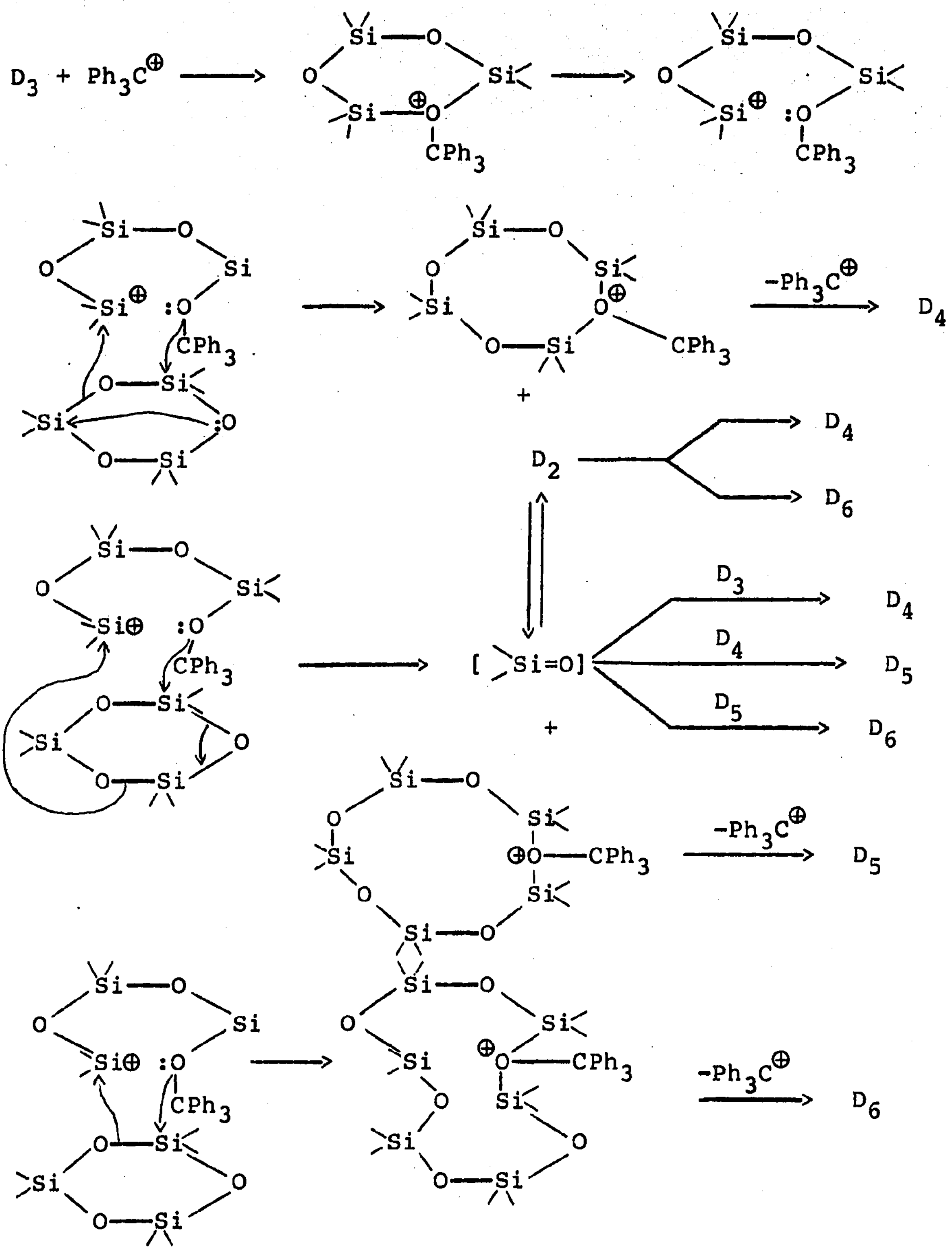
Scheme 5



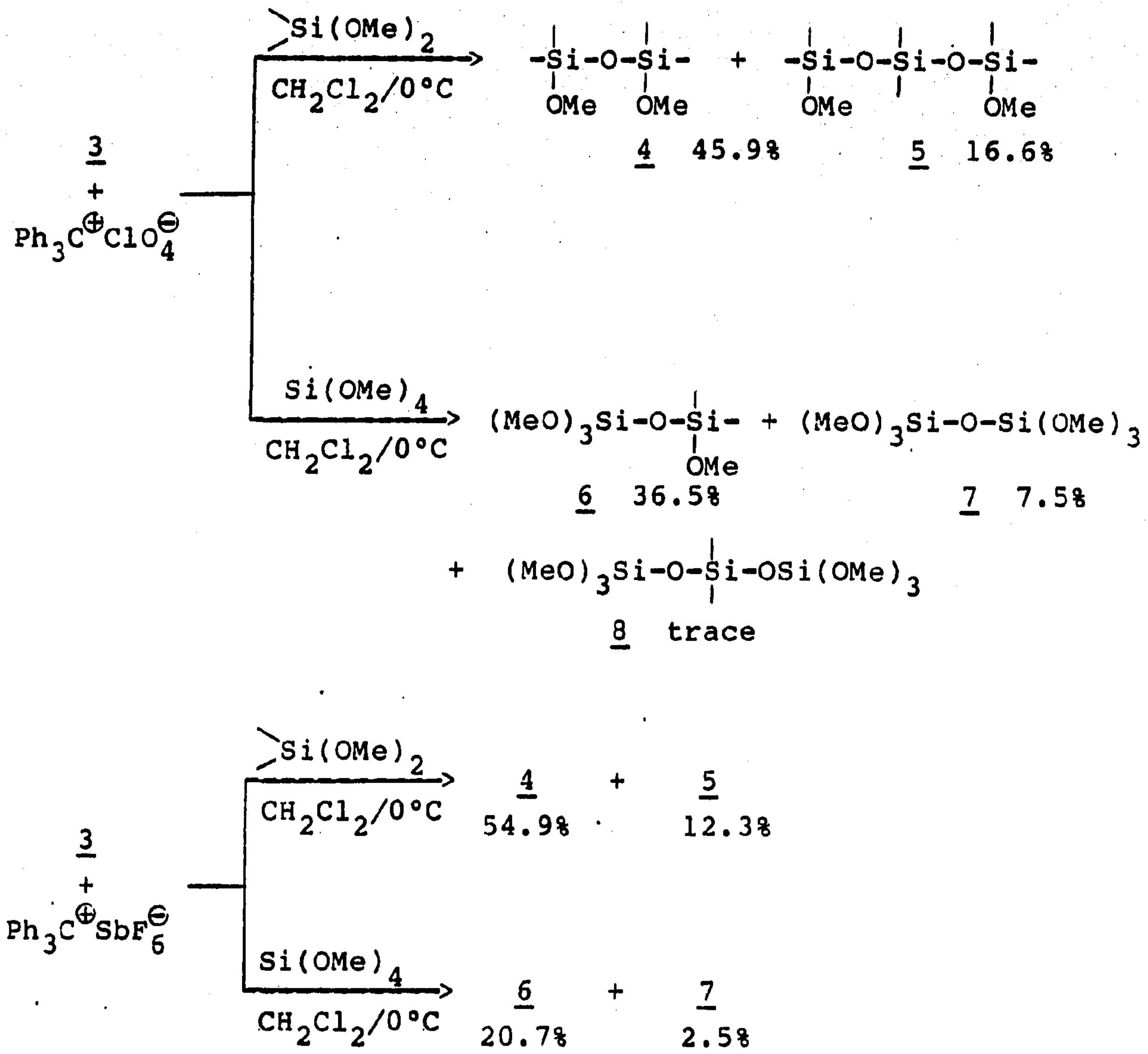
leads to the formation of cyclic siloxane oligomers with D_3 as the major product (17, 23). It was also hard to believe that formation of 8, 10 and 12 membered ring cyclic siloxanes would be more facile than six member ring formation in an intermolecular process. Gusel'nikov et al. (30) and Davidson et al. (33) evaluated the stability of cyclic siloxanes under thermal conditions and their results indicated that D_3 was the more stable cyclic siloxane with respect to other cyclosiloxanes. It was also found that D_5 and D_6 were less stable thermally than D_4. It appears that the chemistry of these cyclic siloxanes in triphenylmethyl salt solution are much different than under thermal conditions. To evaluate the influence of triphenylmethyl salts on the cyclic siloxanes, the decomposition of the reaction mixture of pure D_3, D_4, or D_5 with catalytic amounts of triphenylmethyl salt solutions was studied. Pure D_4 and D_5 under the previous reaction conditions remained unreacted even at long reaction time. However, D_3 under the same reaction conditions, afforded D_4 (11.9%), D_5 (2.9%), and D_6 (34.6%) with very small amounts of D_3 left in the reaction mixture. It appears from these control experiments that D_3, D_4 and small amounts of D_5 might be the primary products from the reaction of compound 3 and triphenylmethyl salts. However, D_3 did not survive under the reaction conditions and isomerized to the higher analogue oligomers. It is not clear and difficult to speculate as to the exact nature of the D_3 isomerization process. The isomerization of D_3 could follow the pathway described in Scheme 6.

Some indirect evidence for the existence of transient dimethylsilanone was obtained by trapping experiments using compounds containing the Si-O moiety, such as dimethoxydimethylsilane (23, 29, 71, 72), tetramethoxysilane (17, 23) and D_3 (17, 71, 73-76) in thermal and photochemical reactions. Mixing compound 3 with catalytic amounts of triphenylmethyl perchlorate or triphenylmethyl hexafluoroantimonate in the presence of excess dimethoxydimethylsilane as trapping agent yielded, in addition to triphenylmethane, the products of apparent trapping by dimethylsilanone, 1,3-dimethoxy-1,1,3,3-tetramethyldisiloxane, 4, as well as 5 which formally corresponds to the insertion of dimethylsilanone into product 4 (Scheme 7). Trapping experiments were also performed employing tetramethoxysilane. The products were identified as the products of apparent trapping by dimethylsilanone, 2,2-dimethyl-1,1,1,3-tetramethoxydisiloxane 6, hexamethoxydisiloxane 7 and 8 which formally corresponds to the insertion of dimethylsilane into product 7 (Scheme 7). Similar trapping experiments were also performed with triphenylmethyl hexafluoroantimonate salt under the same reaction conditions. The same products were identified with only a slightly different product distribution (Scheme 7).

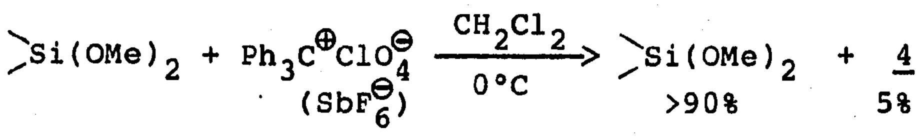
Scheme 6



Scheme 7



Because of the instability of D_3 in the presence of triphenylmethyl salts, it had to be established whether these apparent dimethylsilanone trapped products were not arising from the trapping agents themselves. Thus, dimethoxydimethylsilane was mixed with triphenylmethyl salts under the previously described experimental conditions. The reaction mixture was analyzed by GC. Besides the starting material dimethoxydimethylsilane (>90%), apparent dimethylsilanone trapped product 4 was indeed formed, however in a small amount (5%) (eq. 9).



$$>\!\mathrm{Si(OMe)_2} + \underset{(\mathrm{SbF_6^{\ominus}})}{\mathrm{Ph_3C^{\oplus}ClO_4^{\ominus}}} \xrightarrow[0^\circ\mathrm{C}]{\mathrm{CH_2Cl_2}} \underset{>90\%}{>\!\mathrm{Si(OMe)_2}} + \underset{5\%}{\underline{4}} \qquad (9)$$

The same experiment was also performed with tetramethoxysilane. Again a very small amount (5%) of apparent dimethoxysilanone trapped product 7 was formed. However, the product derived from dimethylsilanone insertion into tetramethoxysilane, 6 was not observed under the reaction conditions (eq. 10).

$$\mathrm{Si(OMe)_4} + \underset{(\mathrm{SbF_6^{\ominus}})}{\mathrm{Ph_3C^{\oplus}ClO_4^{\ominus}}} \xrightarrow{\mathrm{CH_2Cl_2}} \underset{>90\%}{\mathrm{Si(OMe)_4}} + \underset{5\%}{\underline{7}} \qquad (10)$$

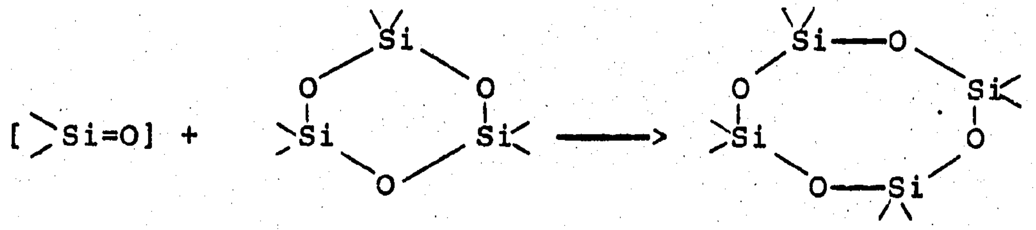
It appears from these control experiments that the apparent dimethylsilanone trapped products with two trapping agents mainly derived from reaction of starting material 3, and not from decomposition of the trapping agents. The reason for the formation of 4 and 7 from trapping agents dimethoxydimethylsilane and tetramethoxysilane are not clear at this point. Compound 7 apparently arose directly from the trapping agent tetramethoxysilane. Formation of trace amounts of 8 from reaction of compound 3, triphenylmethyl salts and tetramethoxysilane suggested dimethylsilanone insertion into compound 7.

The insertion of Me_2SiO into a Si-O bond is a well-known process in both thermal and photochemical reactions. In the previous trapping experiments, both dimethoxydimethylsilane and tetramethoxysilane have Si-O and C-O bonds. Insertion of $Me_2Si{=}O$ into either Si-O or C-O bonds would give identical trapped products. To differentiate between these two possible reactions, a control experiment involving a trapping agent employing only the C-O moiety was performed.

Compound 3, a catalytic amount of triphenylmethyl perchlorate and excess diethyl ether as a trapping agents were mixed under similar reaction conditions. Only cyclic siloxane oligomers D_4, D_5 and D_6 were observed, while no C-O insertion products were observed in the reaction mixture. This finding allowed the conclusion to be made that dimethylsilanone was trapped only by Si-O and not by C-O bonds under these reaction conditions.

The insertion of $Me_2Si{=}O$ into the Si-O bonds of D_3 is a known and effective process under thermal conditions (eq. 11) (17, 71, 73-76).

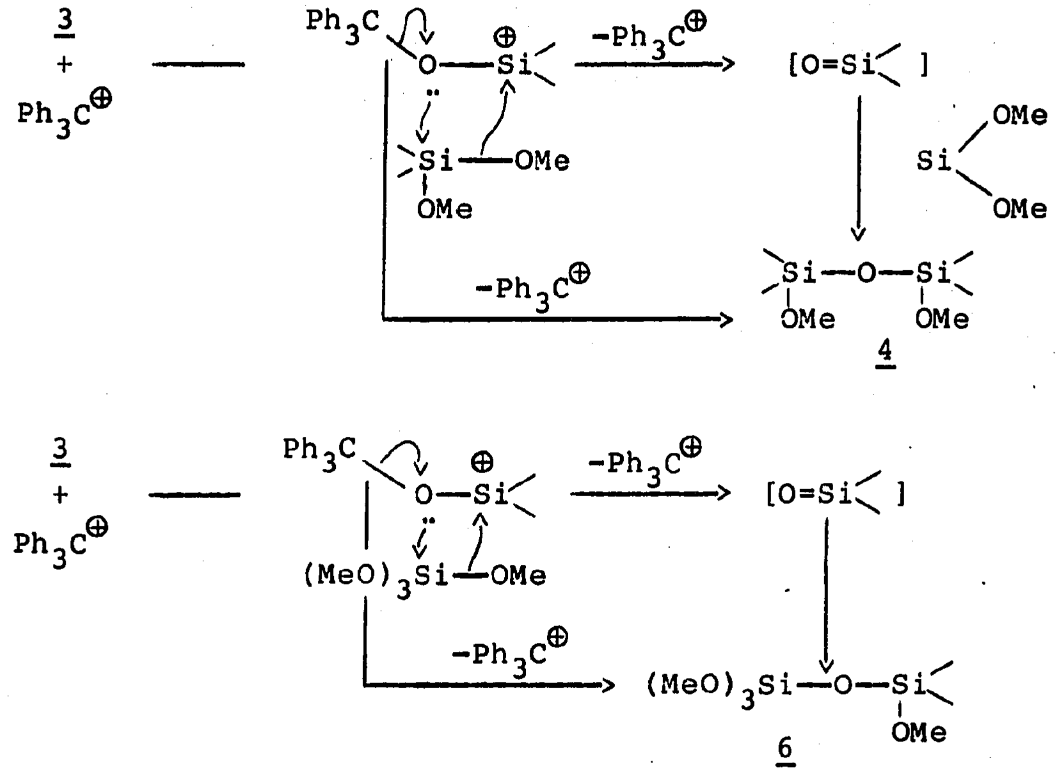
However, under the conditions employed for the triphenylmethyl salts reaction, D_3 isomerizes and thus, is an


(11)

unacceptable trapping agent. However, D_4 and D_5 are stable under the same reaction conditions and also possess Si-O bonds which should be good $Me_2Si=O$ trapping agents. It would thus, be reasonable to employ D_4 and D_5 as trapping agents, and expect to obtain D_5 and D_6 as major trapped products. However, reaction of compound 3 with a catalytic amount of triphenylmethyl perchlorate in the presence of D_4 as the trapping agent, afford D_4 (45.6%), D_5 (23.4%) and D_6 (9.3%) with all of starting material 3 consumed without a substantial increase in the formation of D_5 relative to the reaction of 3 and triphenylmethyl perchlorate alone. These yields were based on the consumption of starting material 3. Under similar reaction conditions, and using D_5 as the trapping agent, again D_4 (35.5%), D_5 (29.7%) and D_6 (11.1%) were observed and with all the starting material 3 consumed, with no substantial increase in the formation of D_6 relative to the reaction between 3 and triphenylmethyl perchlorate alone. It appears from these trapping experiments that D_4 and D_5 do not trap dimethylsilanone in the reaction conditions.

Although in past studies these trapping experiments were sufficient evidence for claiming free silanone formation, it is now recognized that dimethylsilanone trapped products may also be formed in a bimolecular silanone-transfer process which does not necessarily involve a free silanone (23, 29). From previous trapping experiments, the reactions can proceed by free silanone formation as well as by a bimolecular process transferring a $Me_2Si{=}O$ unit to the trapping agents (Scheme 8).

Scheme 8

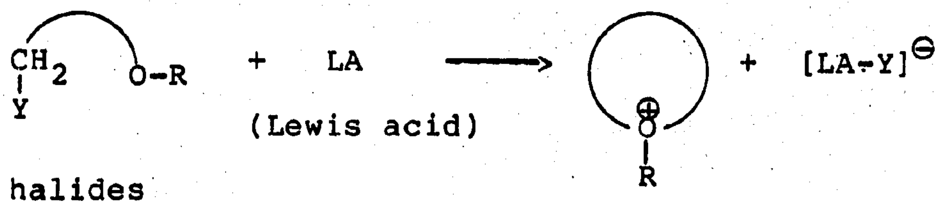


It was surprising that D_4 and D_5 not only would not isomerize under the triphenylmethyl salt solution conditions, but also could not trap dimethylsilanone. The only hypothesis that can be offered was that D_4 and D_5 were stable and unreactive under the triphenylmethyl salt conditions. That was the reason that the reactions between 3 and triphenylmethyl salts gave the identical products in the same yields in the presence or absence of D_4 and D_5 trapping agents.

It was recognized that this work could form the basis of an alternative synthetic route to a dimethylsilanone synthon. The reactions occur under mild conditions in high yields. Problems with the previously mentioned methods of dimethylsilanone generation in the historical section were that these reactions either utilize extremely high temperatures to decompose the dimethylsilanone precursors or employ complicated syntheses from other reactive intermediates, such as silenes or silylenes (17, 18, 28, 29). These conditions and the presence of other reactive intermediates greatly inhibit the ability to form dimethylsilanone.

Acyclic and cyclic oxonium cations are well known in organic chemistry (70). Tertiary cyclic oxonium ions which are formed *via* intramolecular addition of an ethereal oxygen to a carbenium ion are of special interest (Scheme 9). Another synthetic utility of silylenium ions could be applied to the analogous reactions of these oxonium ions. The easiest approach was to use ethereal oxygen attack on the silylenium ion center and subsequent loss of the triphenylmethyl cation to form saturated and unsaturated cyclic silyl ethers.

Scheme 9

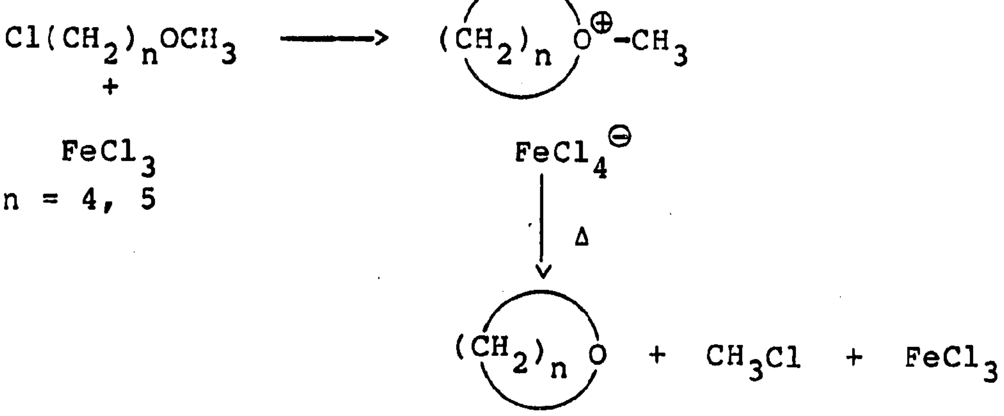


Y = halides
LA = Lewis acid, such as $AlCl_3$, $SbCl_5$, BF_3
R = alkyl, aryl

In the synthesis of oxonium ions by the reaction of alkyl halides on oxygen compounds, the halide ion ($Y^{\ominus}$) should be removed by a suitable acceptor (such as a Lewis acid).

There are numerous methods for preparing oxonium salts (70). The method of Kirrmann and coworkers, however, is especially attractive (77-79). These authors synthesized tetrahydronfuran and tetrahydropyran via intramolecular cyclization of the corresponding methoxybutyl and methoxypentyl halides. Tertiary cyclic tetrahydrofuranium and tetrahydropyranium ions were postulated as reaction intermediates. Upon heating, these oxonium salts decompose to five- and six-membered cyclic ethers in high yields (Scheme 10).

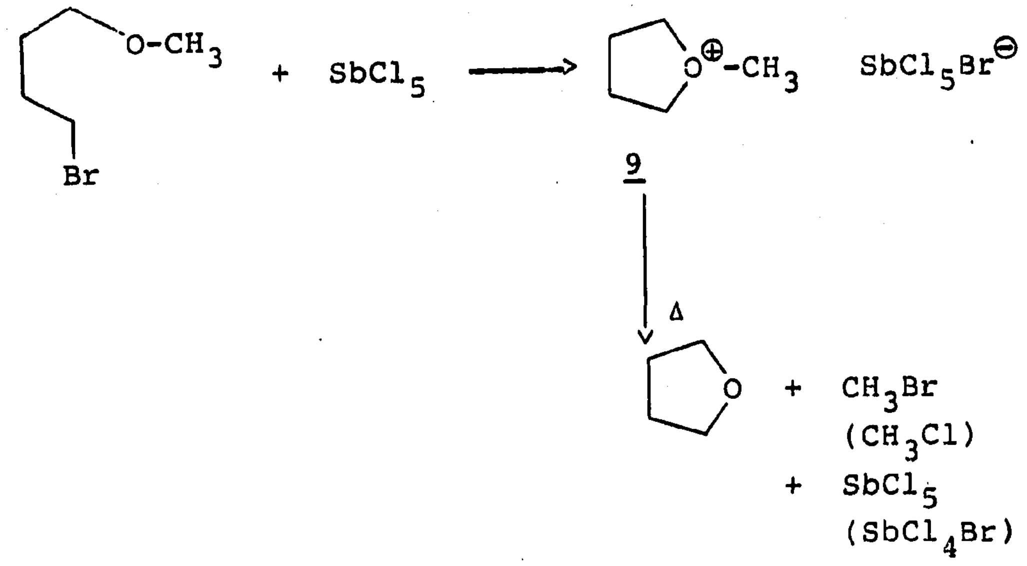
Scheme 10



n = 4, 5

The oxonium salt 9, which has been isolated, also underwent thermal decomposition to tetrahydrofuran and methyl halide (79) (Scheme 11). Kirrmann and Wartski also extended the same method to the syntheses of mono- and di-substituted tetrahydrofuran and tetrahydropyran systems, all in reasonable yields (79).

Scheme 11



By comparison with known oxonium ion chemistry, it was hoped to extend the analogous reaction to the silylenium ion system forming saturated and unsaturated cyclic silyl ethers via intramolecular cyclization of the proposed silylenium ions. Initial interest centered on the formation of five- and six-membered rings of saturated and unsaturated silyl ethers, which are known to be stable under normal reaction conditions. In the unsaturated systems the geometry about the double bond is essential in the ring closure step. The silyl hydride and ether linkage must be located on the same side of the double bond, in order for the oxygen lone pair to be able to reach the silylenium ion. Eisch and coworkers reported the stereospecific cis-addition of aluminum hydride to alkynyl derivatives of group IV elements in the presence of the strong donor solvent N-methylpyrrolidine (80, 81).

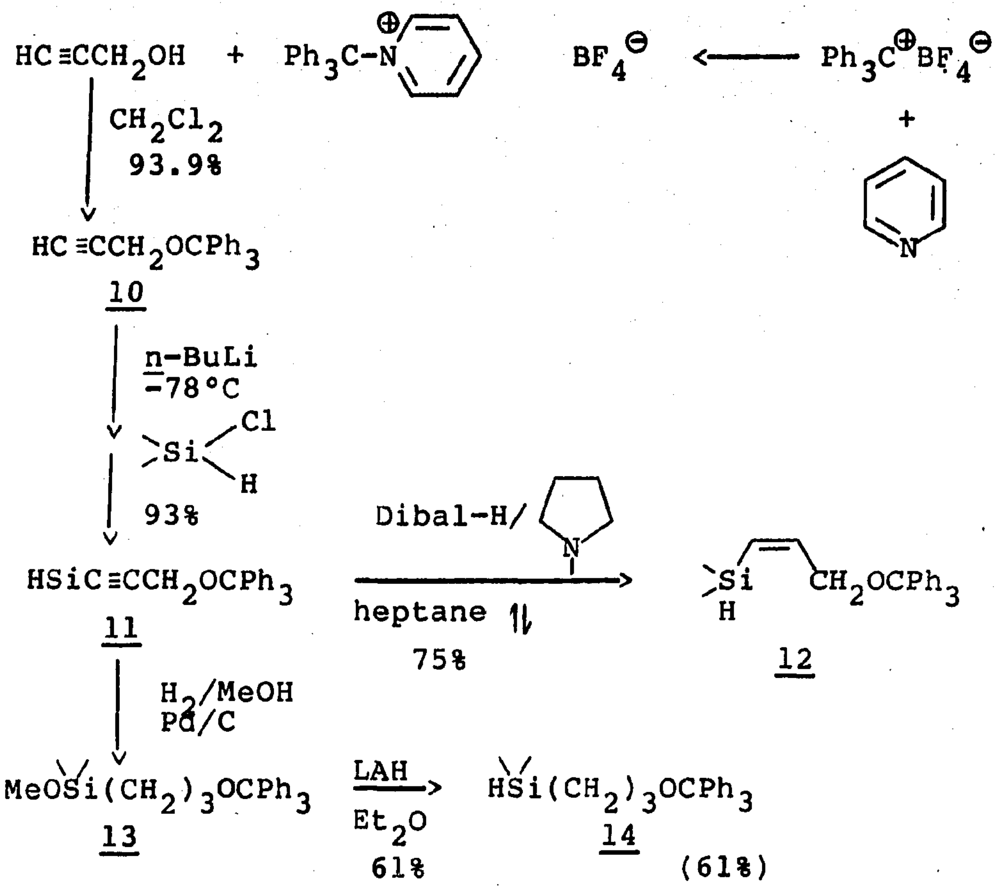
With this available information, a suitable triple-bonded precursor was selected. The bulky triphenylmethyl group has been mainly used to selectively protect the primary hydroxyl group in carbohydrates and nucleosides. Secondary alcohols react, but at a much slower rate (82). It was known that triphenylmethyl ethers could be prepared more readily with triphenylmethyl pyridinium tetrafluoroborate than with triphenylmethyl chloride in pyridine (83). Keiko and coworkers reported the preparation of propargyl triphenylmethyl ether ($HC{\equiv}CCH_2OCPh_3$), 10, by reacting propargyl alcohol and triphenylmethyl alcohol in the presence of $(C_2H_5)_2O{\cdot}BF_3$ (84). However, the yield was extremely disappointing (14.4%) (eq. 12).

$$HC{\equiv}CCH_2OH \;+\; Ph_3C{-}OH \xrightarrow[14.4\%]{(C_2H_5)_2O\cdot BF_3} \underset{\underline{10}}{HC{\equiv}CCH_2OCPh_3} \qquad (12)$$

Replacing the terminal hydrogen in compound 10 with the dimethylsilyl group to afford 3-dimethylsilyl propargyl triphenylmethyl ether $(\mathrm{H\overset{\backslash /}{Si}C{\equiv}CCH_2OCPh_3})$, 11, appears to give a good precursor for the formation of five membered ring saturated and unsaturated cyclic silyl ethers. Keiko's synthesis (84) apparently is not a good synthetic method for the preparation of propargyl triphenylmethyl ether, 10. A more efficient method for the preparation of triphenylmethyl ethers was developed by Hanessian and Staub (83) and allowed preparation of compound 10 in 93.9% yield from the reaction of propargyl alcohol with N-triphenylmethyl pyridinium tetrafluoroborate. Treatment of 10 with *n*-BuLi followed by quenching of the anion with chlorodimethylsilane afforded compound 11 in high yield. Following Eisch's Dibal-H (diisobutylaluminum hydride) reduction procedure (80, 81), the triple bond in 11 was easily reduced to the cis-double bond in 12. Hydrogenation of 11 in MeOH, followed by lithium aluminum hydride reduction afforded the saturated compound 14 (Scheme 12).

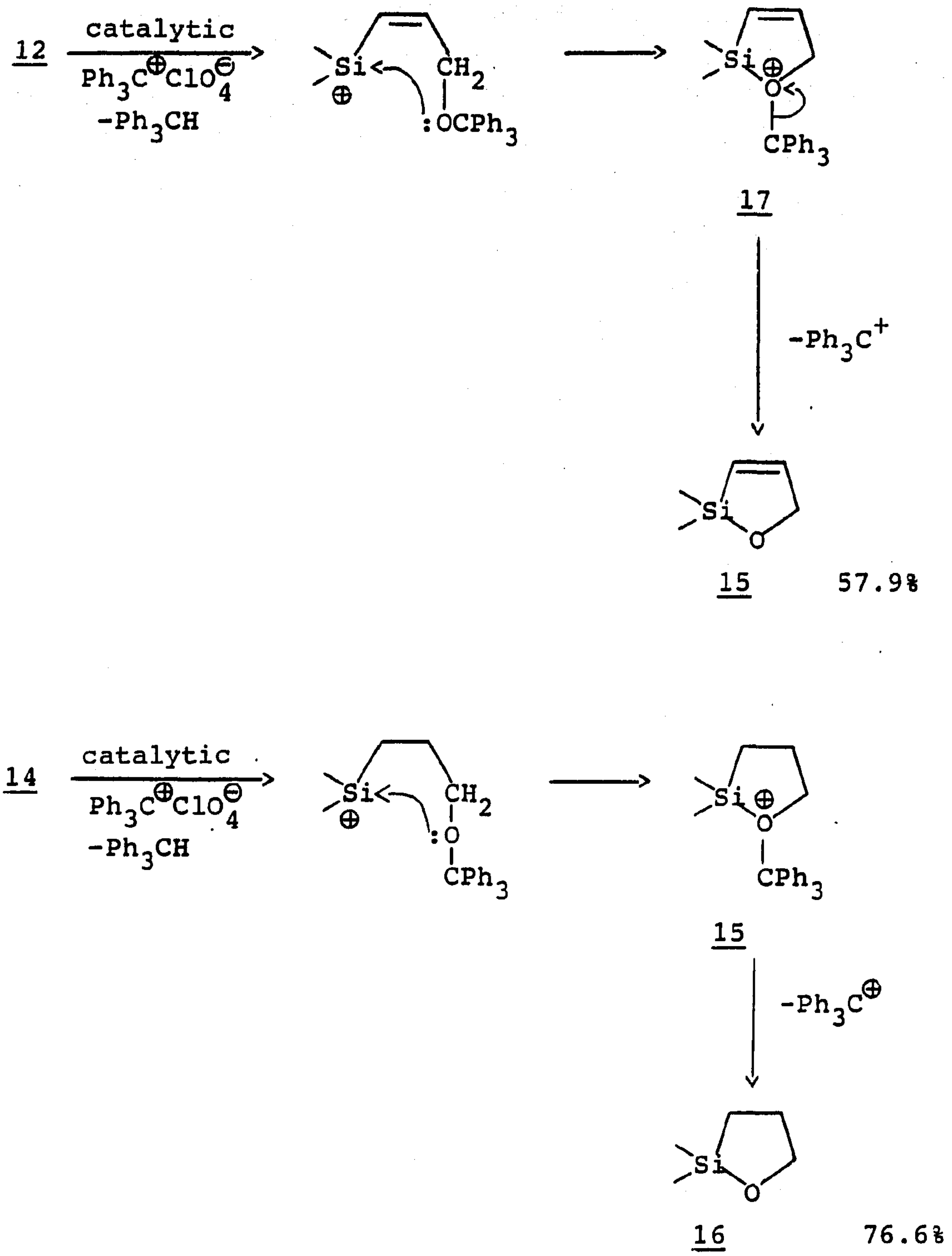
The intramolecular cyclization reaction of the *cis*-olefin 12 followed the same procedure as in the previous reaction. The desired cyclic product 3,3-dimethyl-4-oxa-3-silacyclopentene, 15, was obtained in 57.9% yield. The saturated compound 14 cyclized to 2,2-dimethyl-1-oxa-2-silacyclopentane, 16, in 76.6% yield under the same reaction conditions (Scheme 13).

Scheme 12



The formation of five-membered ring saturated and unsaturated cyclic silyl ethers can be explained *via* a silylenium ion process. In the first step, a silylenium ion was generated by silyl hydride abstraction. The lone pair of electrons in the oxygen ether linkage can then undergo nucleophilic attack on the silylenium ion forming an oxonium ion type intermediate. Loss of triphenylmethyl cation would then give the cyclic silyl ethers.

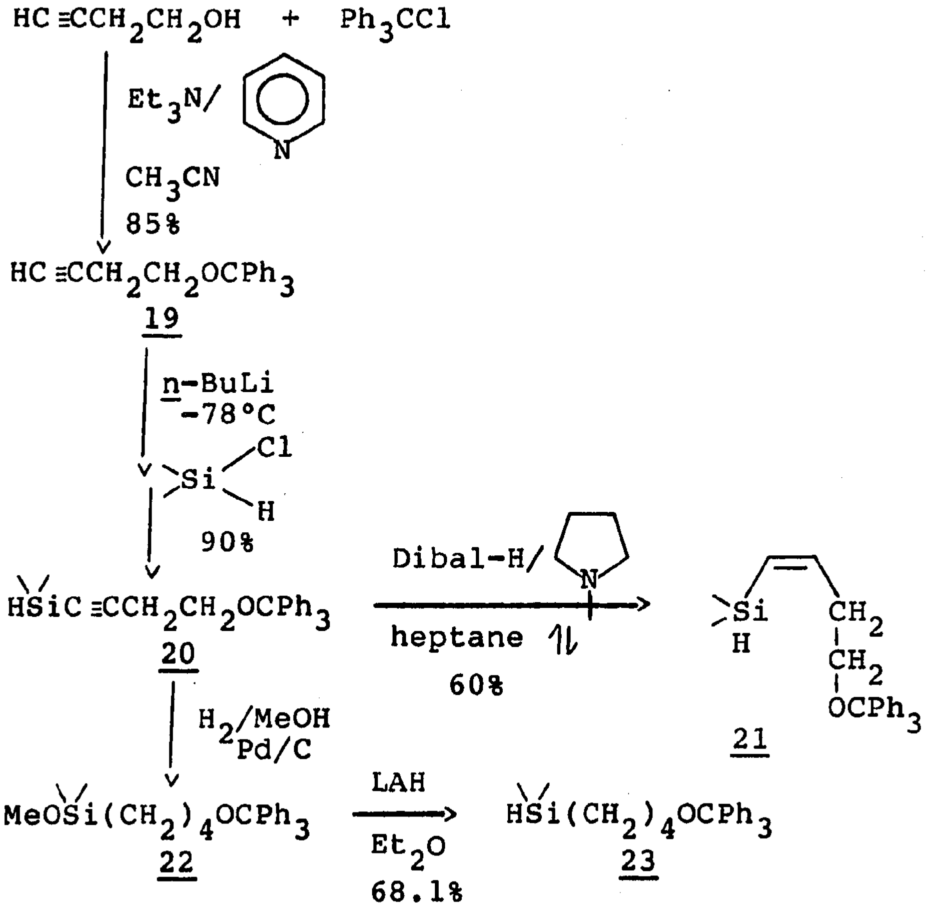
Scheme 13


12
catalytic
$Ph_3C^{\oplus}ClO_4^{\ominus}$
$-Ph_3CH$
Si
CH_2
:$OCPh_3$
Si
O
CPh_3
17
$-Ph_3C^+$
Si
O
15
57.9%
14
catalytic
$Ph_3C^{\oplus}ClO_4^{\ominus}$
$-Ph_3CH$
Si
CH_2
:O
CPh_3
Si
O
CPh_3
15
$-Ph_3C^{\oplus}$
Si
O
16
76.6%

After successfully forming the five-membered cyclic silyl ethers, it was reasonable to extend this work to six-membered ring systems. The synthesis of the required starting materials followed the same routes as in the case of five membered rings (Scheme 14).

The ring closure reaction of the six-membered ring precursor, cis-double bonded compound <u>21</u>, afforded 3,3-dimethyl-

Scheme 14

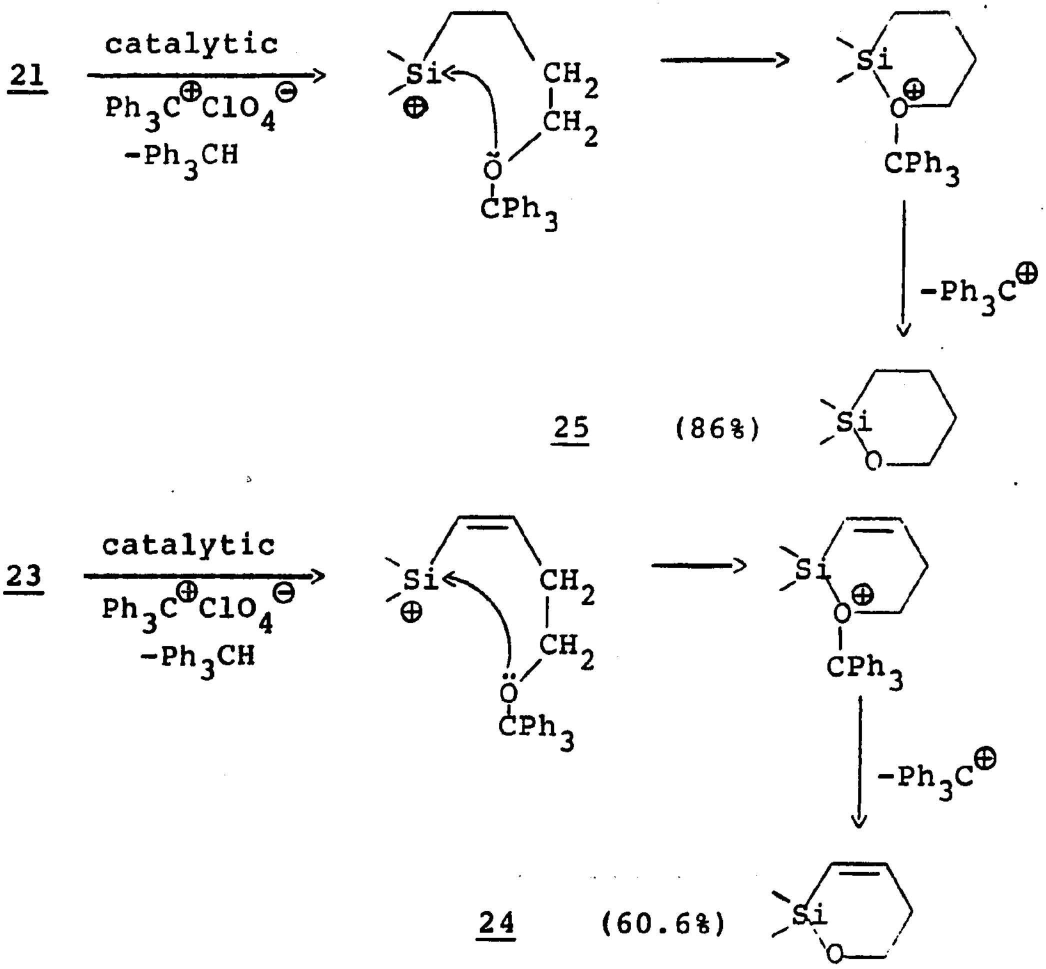


4-oxa-3-silacyclohexene, 24, in 60.6% yield; cyclization of saturated compound 23 afforded 2,2-dimethyl-1-oxa-2-silacyclohexane, 25, in 86% yield (Scheme 15).

These results provided further demonstration of the synthetic use of silylenium ions in solution.

As mentioned earlier, the choice of triphenylmethyl as a leaving group was made for a number of reasons. Not only is it a good leaving group, but it also allows use of triphenyl-

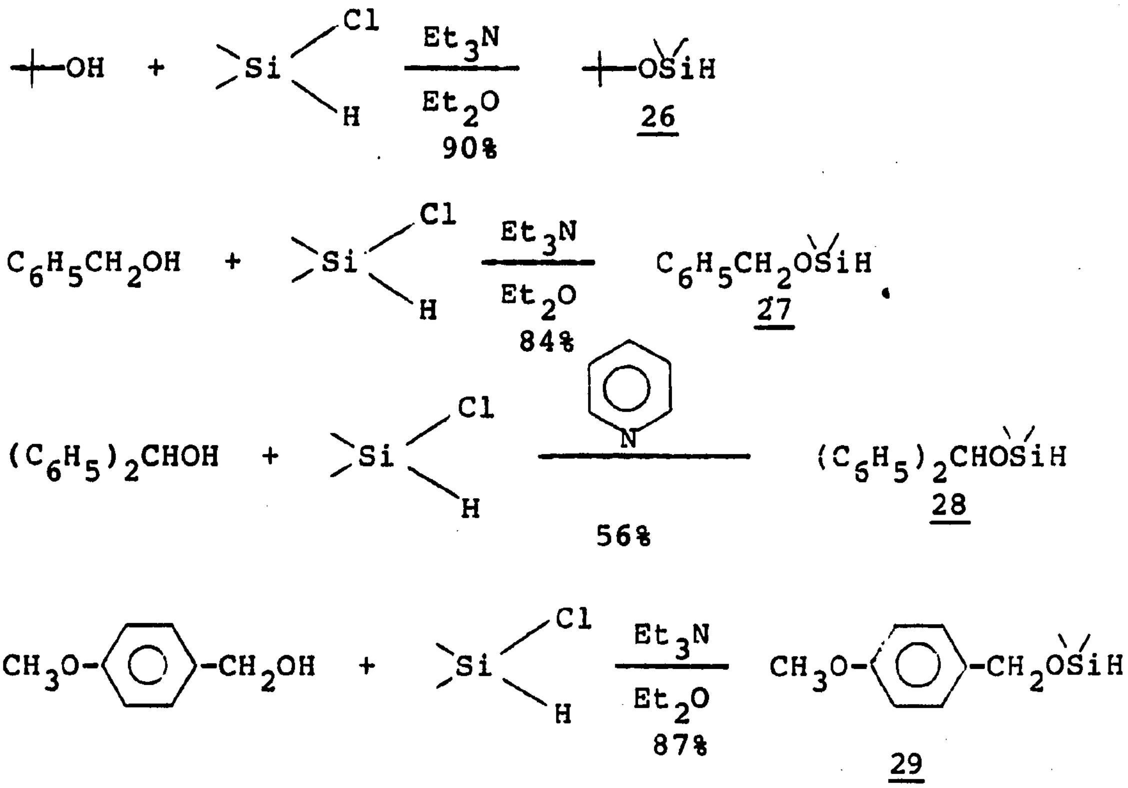
Scheme 15



methyl salts as the catalyst in these reactions. In order to extend this chemistry, other leaving groups were also investigated.

Based on the results of Olah and White (67, 68), Olah et al. (69), several relatively good leaving groups such as t-butyl, benzyl, diphenylmethyl and p-methoxybenzyl carbocations were chosen for the model compounds for the next series of investigations. These reactions were performed by reacting a 1:1 mole ratio of the starting silyl hydrides with triphenylmethyl perchlorate. The syntheses of the required starting materials are summarized in Scheme 16.

Scheme 16



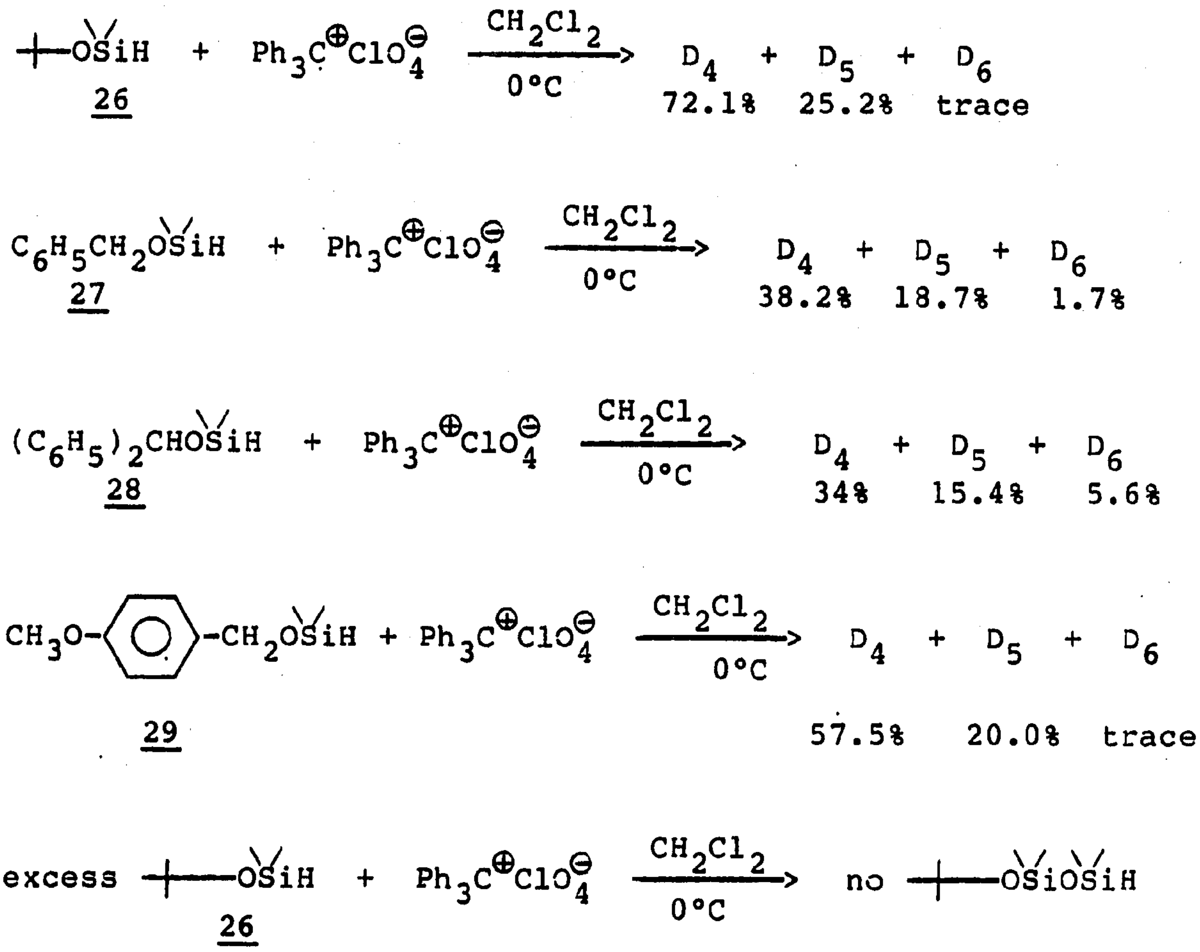
Analyses of the reaction mixtures by GC from treatment of compounds 26-29 with an equivalent of triphenylmethyl perchlorate indicated that only cyclic siloxanes were formed as volatile products (Scheme 17). The results clearly indicated that benzyl, diphenylmethyl, p-methoxybenzyl and *t*-butyl groups were all good leaving groups. In all the reactions, D_4 and D_5 were the major products, which is consistent with the triphenylmethyl case. In order to gain evidence for silanone formation, it was decided to study a reaction in which the silylenium ion precursor also acts as a trapping agent for the dimethylsilanone. The low boiling point of t-butyl dimethylsilyl ether, 26 appeared to make it an attractive candidate for this study.

The reaction was performed by treating a triphenylmethyl perchlorate solution with excess 27. Only cyclic siloxanes were formed and none of the product corresponding to dimethylsilanone-trapped product with compound 26 was found in the reaction mixture. Thus, it appears that either compound 27 is not a good trapping agent for silanone or silanone is not formed (Scheme 17).

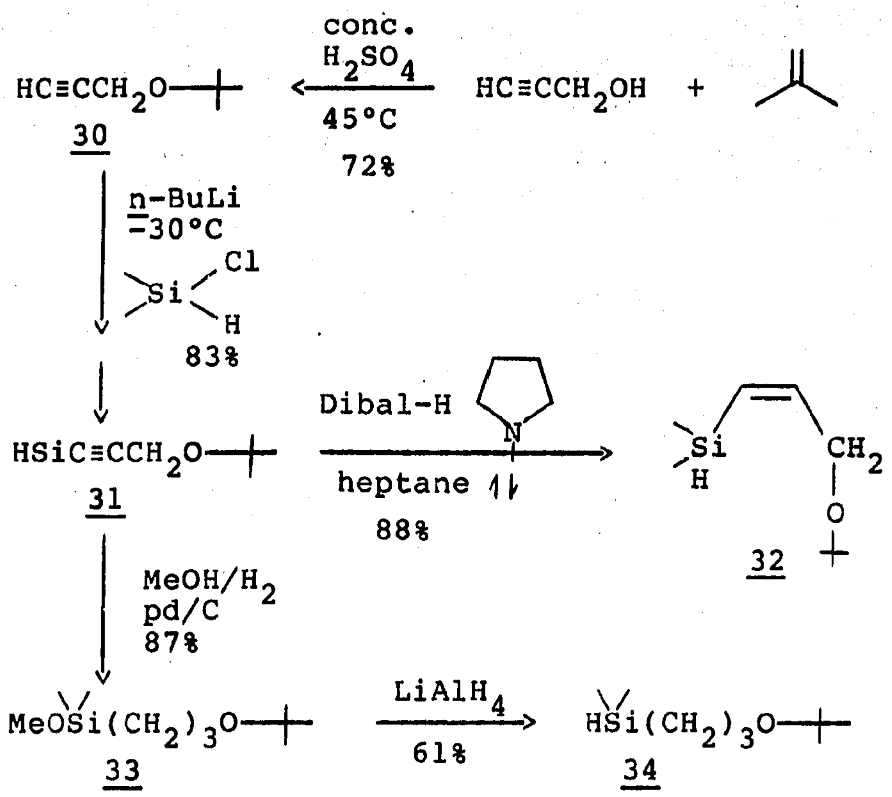
Although it was determined that benzyl, diphenylmethyl, *p*-methoxybenzyl and *t*-butyl were good leaving groups, it was desirable to know how they compared to triphenylmethyl group in the intramolecular cyclization reactions. Benzyl and t-butyl groups were chosen for their different leaving abilities from previous studies.

The syntheses of the required five-membered ring precursors are summarized in Schemes 18 and 19.

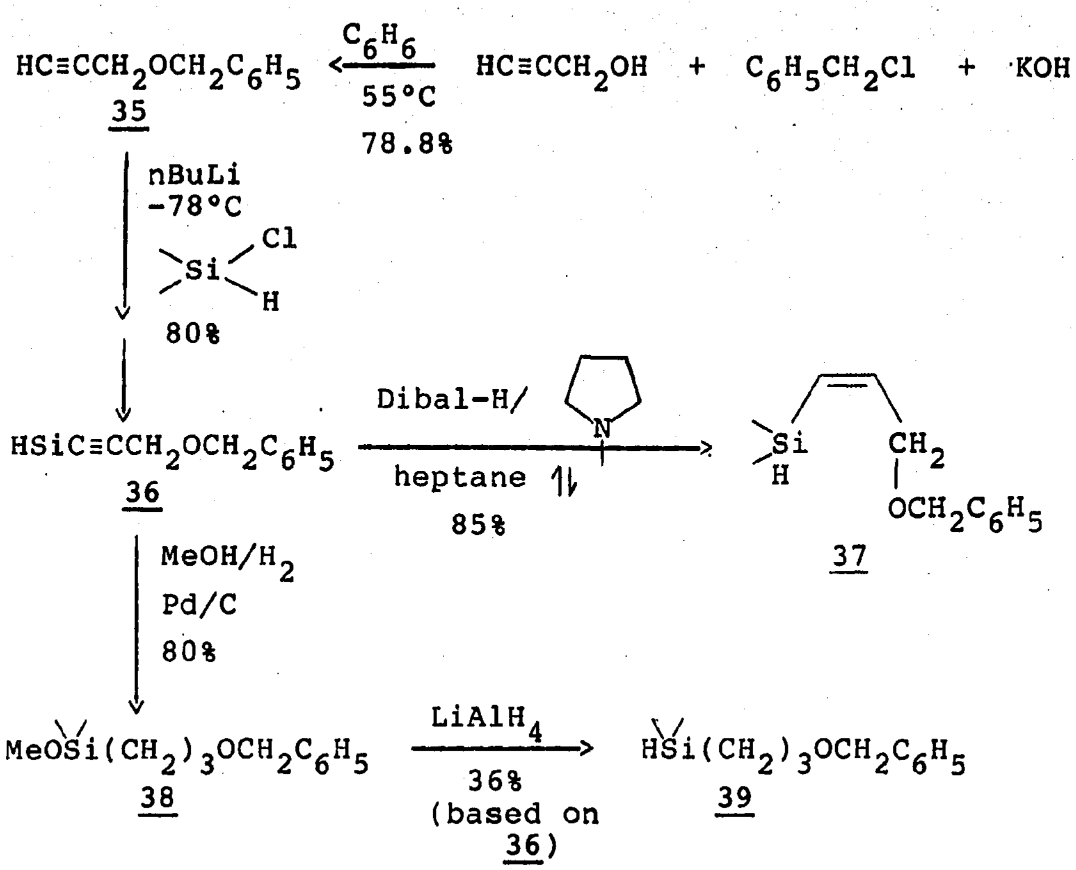
Scheme 17



Scheme 18


HC≡CCH2O—+
30
conc.
H2SO4
45°C
72%
HC≡CCH2OH
+
n-BuLi
-30°C
Si Cl H
83%
HSiC≡CCH2O—+
31
Dibal-H
N
heptane
88%
Si
H
CH2
O
32
MeOH/H2
pd/C
87%
MeOSi(CH2)3O—+
33
LiAlH4
61%
HSi(CH2)3O—+
34

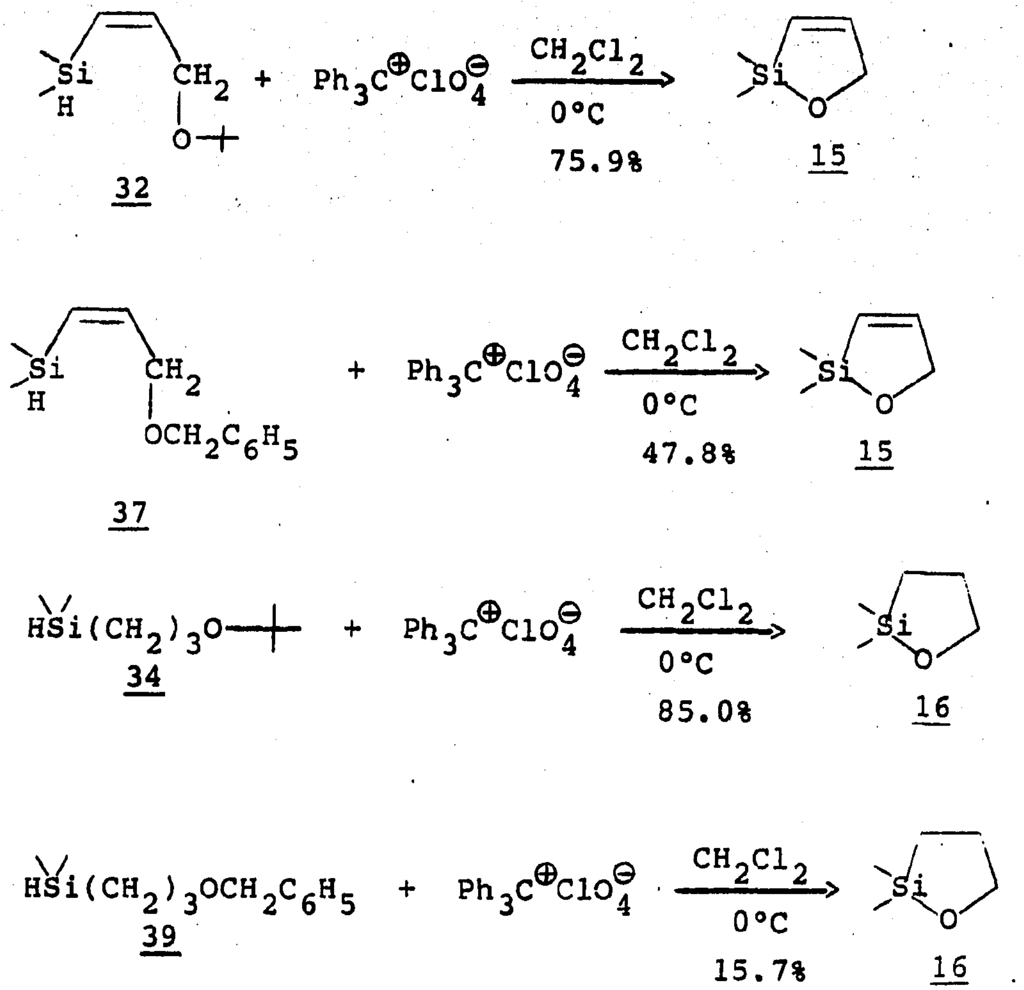
Scheme 19



The cyclization reactions were performed by treating a 1:1 mole ratio of these five-membered ring precursors with triphenylmethyl salt. The results of the cyclization reactions of both cis-double bonded and saturated compounds are summarized in Scheme 20.

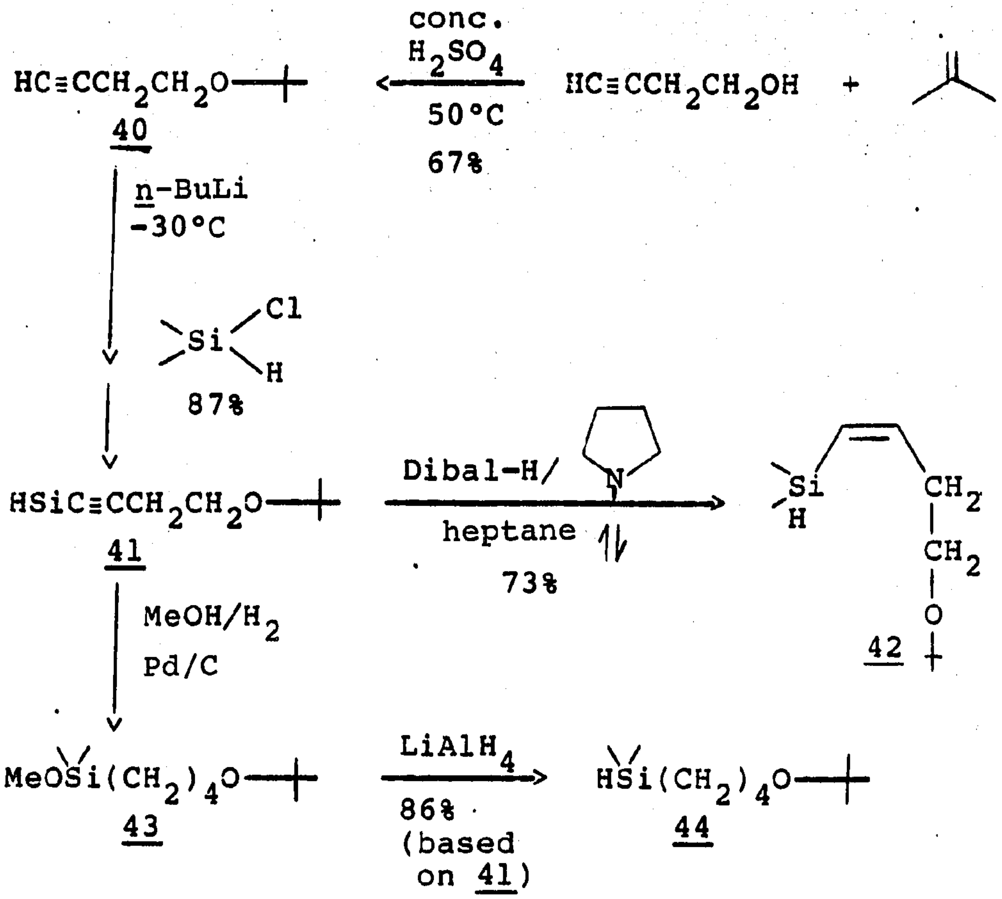
These results again demonstrate that benzyl and *t*-butyl groups provide enough driving force for formation of saturated and unsaturated cyclic silyl ethers.

Scheme 20

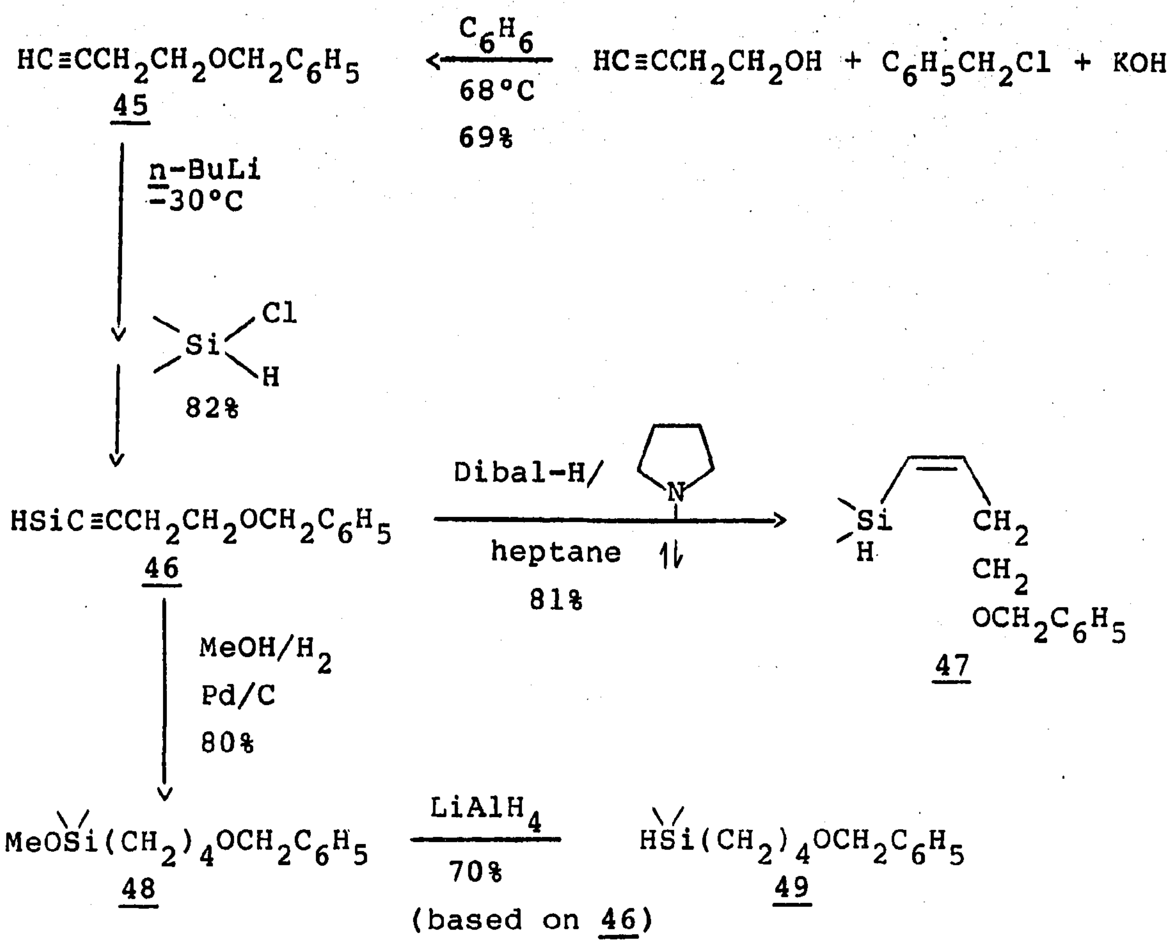


These reactions were also extended to six-membered ring systems. The syntheses of the required precursors are summarized in Schemes 21 and 22.

Scheme 21

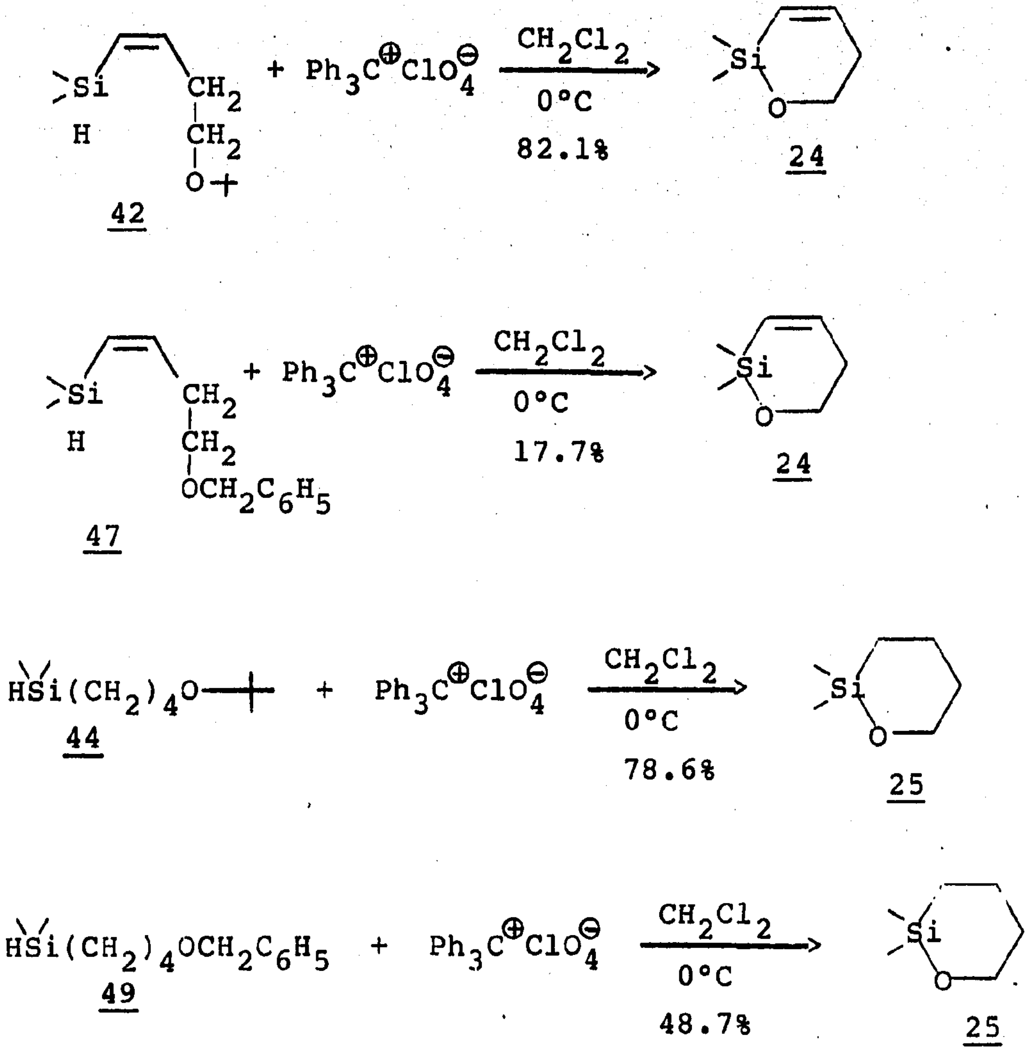

HC≡CCH2CH2O—
40
conc. H2SO4
50°C
67%
HC≡CCH2CH2OH
+
n-BuLi
-30°C
Si
Cl
H
87%
HSiC≡CCH2CH2O—
41
Dibal-H/
N
heptane
73%
Si
H
CH2
CH2
O
42
MeOH/H2
Pd/C
MeOSi(CH2)4O—
43
LiAlH4
86% (based on 41)
HSi(CH2)4O—
44

Scheme 22



The cyclization reactions of cis-double bonded and saturated systems were performed in the same manner as described for the previous five-membered ring closure. The results of these cyclization reactions are summarized in Scheme 23.

Scheme 23



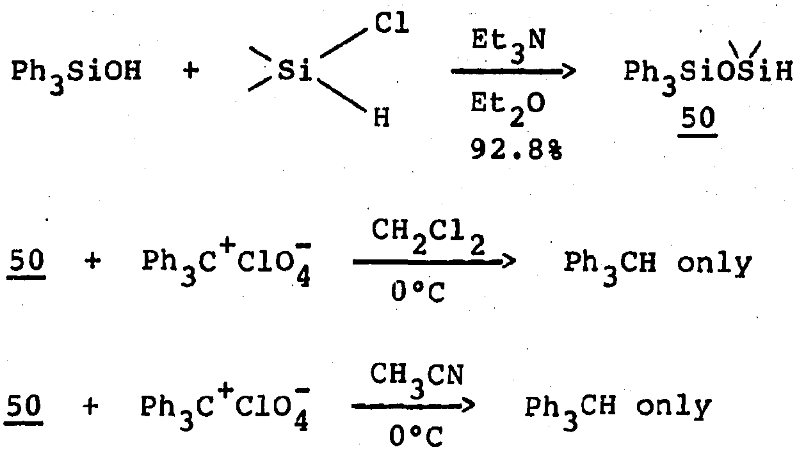
These results again proved saturated and unsaturated cyclic silyl ether formation to be an efficient process.

In a recent report of the generation and spectral observation of the triphenylsilylenium ion, Lambert et al. pointed out that solvent played a very important role for detection of silylenium ions (64). In this thesis work, all of the reactions were studied in methylene chloride. This solvent has been commonly used by many groups in the search for silylenium ions (58-65), and was also used by Lambert and Schulz in the first detection of a silylenium ion in solution (63).

After studying the carbon leaving group effects (eq. 5), it was decided to extend the same study to silicon-analogue leaving groups. From all the calculations on silylenium ions (discussed in the historical section), it appeared that the silylenium ion was a better stabilized cation than a carbenium ion (52-57). It would, thus, be reasonable to suggest that a silylenium ion would have better leaving ability relative to a carbenium ion. Triphenylsilyl dimethylsilyl ether, 50,  $(Ph_3SiO\overset{\backslash /}{Si}H)$ was the model compound for this testing. Unfortunately, after treating one equivalent of triphenylmethyl perchlorate either in methylene chloride or acetonitrile, none of the desired cyclic siloxane oligomers were observed. Not surprisingly, breaking a strong silicon oxygen bond (138 kcal/mol compared with 91 kcal/mol in C-O) and generating two high-energy intermediates was too much to ask (85). The synthesis of compound 50 and its reactions with triphenylmethyl perchlorate are summarized in Scheme 24.

Triphenylmethyl was also used as a leaving group in an attempt to generate a silicon-carbon double bond (a silene) and a silicon-silicon double bond (a disilene) by extrapolation of the method used for silanone generation. Dimethyl-

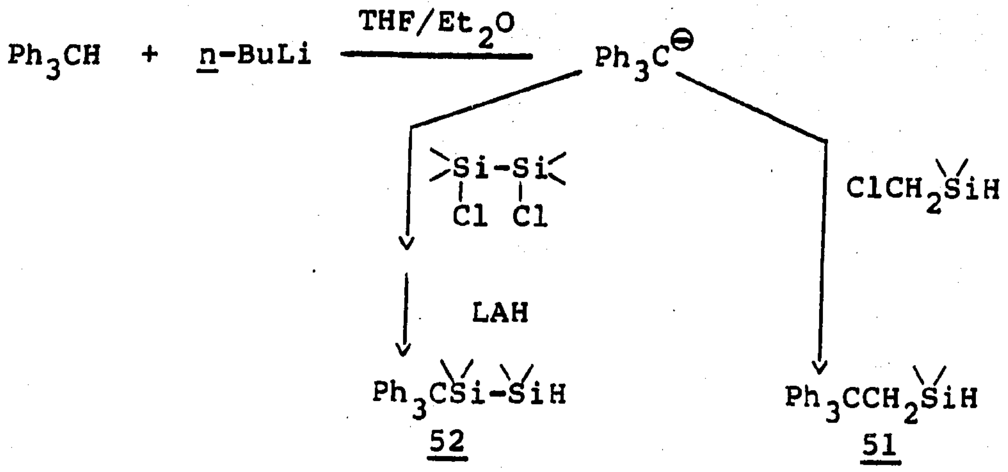
Scheme 24



silyl triphenylmethyl-methane, 51, ($Ph_3CCH_2\overset{\backslash /}{Si}H$) and 1,1,2,2-tetramethyl-2-triphenylmethyldisilane, 52, ($Ph_3CSiSiH$) were chosen for these tests. After treating one equivalent of triphenylmethyl perchlorate with 51 or 52, no silicon-containing products could be detected by GC (Scheme 25).

Gordon and Koob performed calculations on the parent silene and found that the C=Si bond was 30-40 kcal/mol weaker than the C=C bond (86). Several groups also calculated the π-bond strength of the Si=Si bond and estimated it to be about 40 kcal/mol weaker than a C=C bond (87, 88). It seems that intramolecular decomposition of silylenium ions and formation of the weaker C=Si and Si=Si bonds is not a thermodynamically favorable process. With respect to an intermolecular process, it is hard to believe that compounds 51 and 52, which no longer possess any electron pair atoms which can attack the silylenium ion center, would undergo reactions in the same fashion as in the dimethylsilyl triphenylmethyl ether system.

Scheme 25



$$\underline{51} + Ph_3C^{\oplus}ClO_4^{\ominus} \xrightarrow[0°C]{CH_2Cl_2} Ph_3CH$$

$$\underline{52} + Ph_3C^{\oplus}ClO_4^{\ominus} \xrightarrow[0°C]{CH_2Cl_2} Ph_3CH$$

This system which possesses electron pairs on the oxygen atom allows the ethereal oxygen to attack the silylenium ion center and form the oxonium ion in the intermolecular process. The negative results of formation of Si=C and Si=Si in the reaction of compounds 51 and 52 do not reinforce a free silanone mechanism.

CONCLUSION

The synthetic utility of silylenium ions in solution was first studied in this work, and clearly indicated that leaving groups played a very important role in these reactions. The reaction of dimethylsilyl triphenylmethyl ether with a catalytic amount of triphenylmethyl salts afford cyclic siloxane oligomers in high yield. Trapping experiments with dimethoxydimethylsilane and tetramethoxysilane, which give dimethylsilanone trapped products can be explained _via_ an intramolecular free dimethylsilanone formation mechanism; however, an intermolecular dimethylsilanone transfer process cannot be eliminated. Other good carbon leaving groups such as _t_-butyl, benzyl, diphenylmethyl and p-methoxybenzyl in dimethylsilylalkyl (aryl) ethers all led to the formation of cyclic siloxane oligomers upon treatment with one equivalent of triphenylmethyl salt. However, when triphenylsilyl was utilized as a leaving group, either in methylene chloride or acetonitrile, no cyclic siloxane oligomers were observed under the previously described reaction conditions. Presumably, this is because of the large energy required to break the strong Si-O bond. Attempts to synthesize silene and disilene intermediates by using the same methods as employed above, failed. Formation of weak Si=C and Si=Si double bonds _via_ an intramolecular mechanism for the reactions apparently are unfavorable processes. Presumably this is because the silene and disilene precursors cannot form oxonium type intermediates comparable to the previous dimethylsilyl alkyl (aryl) ethers in the intermolecular process.

Alkenes containing an ether linkage and silyl hydride cis to each other, after reacting with triphenylmethyl salts formed unsaturated five- and six-membered ring cyclic silyl ethers. Saturated analogs of the above compounds afforded saturated five- and six-membered ring cyclic silyl ethers after reacting with triphenylmethyl salts. The formation of these cyclic silyl ethers is proposed to proceed through intramolecular cyclization reactions and appear to proceed via oxonium ion type intermediates.

The fragmentation and cyclization reactions of silylenium ions are the first reported examples demonstrating the promising synthetic utility of silylenium ions in solution. This work also provides indirect evidence for silylenium ion formation in solution.

EXPERIMENTAL SECTION

Instrumentation

Routine proton NMR (^1H NMR) spectra were recorded on either a Varian model EM-360A, EM-360L (at 60 MHz) or high resolution Nicolet Model NT-300 spectrometer (at 300 MHz). All chemical shifts are reported as parts-per-million (δ scale) from tetramethylsilane (TMS) using either tetramethylsilane, chloroform or methylene chloride as an internal standard. Carbon NMR (^{13}C NMR) spectra were obtained on either a JEOL FX-90Q (at 22.5 MHz) or NT-300 spectrometer (at 75.5 MHz), and chemical shifts are reported as parts-per-million (δ scale) using solvent chloroform-d (δ 77.06) as internal standard.

Infrared spectra (IR) were recorded on either a Beckmann IR-4250 or an IBM 98 (FT-IR) spectrophotometer.

Gas chromatograph mass spectra (GC-MS) were recorded on either a Finnegan Model 4023 gas chromatograph/mass spectrometer or a Hewlett Packard 5970 mass selective detector attached to a Hewlett Packard 5890 gas chromatograph. Exact mass measurements were obtained on either an AEI-MS-902 or a Kratos MS-50 mass spectrometer. All mass spectra, unless otherwise stated, were recorded at 70 eV.

Analytic gas chromatographic (GC) analyses were performed on either a Hewlett Packard 5890 or 5790 model gas chromatograph using either a 12 m or 30 m RSL-150 column, unless otherwise stated, all GC yields were determined with internal standards and predetermined response factors. Preparative gas chromatography was performed on a Varian model 920, 1700 or Gow-Mac 550P using columns as specified within the experimental section.

Boiling points are reported uncorrected. All melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Mic Anal Organic Microanalysis.

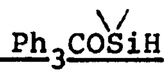
Common Reagents

Solvents and reagents were distilled from appropriate drying agents and stored over molecular sieves (Type 4A). Chlorosilanes were freshly distilled from CaH_2 before use.

The preparations of tritylperchlorate and tritylhexafluoroantimonate were following Dauben's method (89). The solids were dried under vacuum and kept in the dark under vacuum.

Triethylamine was added to terminate reactions involving the triphenylmethyl salt.

Procedures and Results

Synthesis of dimethylsilyl triphenylmethyl ether, 3,  Ph_3COSiH

Triphenylmethanol (10.00 g, 0.039 mol) and 200 mL of Et_2O were added to a 500-mL flask which was purged with N_2. Pyridine (5.00 g, 0.063 mol) was added all at once, then 6.00

g (0.063 mol) of chlorodimethylsilane was added dropwise to the reaction mixture. A white salt formed immediately. The resulting mixture was stirred at reflux for 4 h, then stirred at room temperature overnight.

Skelly B (150 mL) was then added to the reaction mixture, which was filtered through a Celite-padded fritted funnel. The filtrate was extracted once with 50 mL of saturated sodium chloride solution, twice with 50 mL distilled water, and the organic solution was dried over sodium sulfate overnight. After removal of solvent, a white solid was obtained which was recrystallized from Et_2O/Skelly B to afford 3 in 90% yield (11.00 g). Mp=51-53°C; ^1H NMR δ -0.02 (d, 2.8 Hz, 6 H), 4.60 (hep, 2.8 Hz, 1 H), 7.50 (m, 15 H); ^{13}C NMR δ -0.11, 127.87, 128.52, 128.97, 147.38; IR 3090-3020, 2960, 2130, 1595, 1448, 1252, 1090, 1069; calcd for $C_{21}H_{22}OSi$ m/e 318.14400, measured m/e 318.14391; Anal. Calcd for $C_{21}H_{22}OSi$: C, 79.24; H, 6.93. Found: C, 79.22; H, 7.00.

Reaction of triphenylmethyl perchlorate and 3

Compound 3 (125 mg, 0.391 mmol), 15 mg of n-dodecane (internal standard) and 0.5 mL of CH_2Cl_2 were mixed in an NMR tube under N_2. The tube was immersed in an ice bath, and 10 mg (0.029 mmol) of triphenylmethyl perchlorate in 0.5 mL CH_2Cl_2 solution was added slowly to the NMR tube. The mixture was shaken vigorously and then analyzed by GC (10-ft x 1/8-in. 15% OV-3 column temperature programmed from 50-300°C at 15°C per min). The products were identified as D_3 (3.3%), D_4 (31.0%), D_5 (22.3%), D_6 (16.3%) and triphenylmethane with no starting material 3 left. The products were identified by comparison of their GC/MS and ^1H NMR data with those of authentic samples.

Reaction of triphenylmethyl hexafluoroantimonate and 3

The same procedure as described for the previous reaction was followed.

Compound 3 (161 mg, 0.504 mmol) was mixed with 11 mg (0.023 mmol) of triphenylmethyl hexafluoroantimonate in methylene chloride. The products were identified as D_3 (4.4%), D_4 (40.5%), D_5 (10.2%), D_6 (10.3%) and triphenylmethane.

Reaction of triphenylmethyl perchlorate with 3, with D_4 trapping

Compound 3 (159 mg, 0.500 mmol) was mixed with 596 mg (2.010 mmol) of D_4, 72 mg of internal standard and 1 mL of CH_2Cl_2 in an NMR tube under N_2. The tube was immersed in an ice bath and 64 mg (0.186 mmol) of triphenylmethyl perchlorate in 2 mL CH_2Cl_2 solution was added slowly to the NMR tube. The reaction mixture was analyzed by capillary GC; column temperature programmed from 50-250°C at 15°C per min.

The products were identified as D_4 (45.6%), D_5 (23.4%), D_6 (9.3%) and triphenylmethane. The yields were based on the consumption of starting material, compound 3.

Reaction of triphenylmethyl perchlorate with 3, with D_5 trapping

The same procedure as described for the previous D_4 trapping reaction was followed.

The products were identified as D_4 (35.5%), D_5 (29.7%), D_6 (11.1%) and triphenylmethane. The yields were based on the consumption of starting material, 3.

Reaction of triphenylmethyl perchlorate with 3, with dimethoxydimethylsilane trapping

Compound 3 (132 mg, 0.413 mmol) was mixed with 122 mg (1.015 mmol) of dimethoxydimethylsilane, 23 mg of internal standard and 0.5 mL of CH_2Cl_2 in an NMR tube under N_2. The tube was immersed in an ice bath, and 10 mg (0.029 mmol) of triphenylmethyl perchlorate in 0.5 mL CH_2Cl_2 solution was added slowly to the NMR tube. The mixture was shaken vigorously and then analyzed by GC (10 ft x 1/8 in. 15% OV-3 column temperature programmed from 50-300°C at 15°C per min).

The products were identified as 1,3-dimethoxy-1,1,3,3-tetramethyldisiloxane 4 (45.9%), MeO-Si-O-Si-O-Si-OMe, 5 (16.6%) and triphenylmethane with no starting material 3 observed.

The products were also isolated by preparative GC (10-ft x 1/4-in. 15% SE-30), compound 4 was also identified by comparison of its GC/MS and ^1H NMR data with those of an authentic sample. 5: ^1H NMR δ 0.10 (s, 18 H), 3.47 (s, 6 H); ^{13}C NMR δ -1.52, 0.93, 49.79; mass spectrum, m/e (% relative intensity) 255 (13), 254 (23), 253 (M-15, 100), 224 (11), 223 (50), 207 (23), 193 (16), 119 (12), 89 (13).

Reaction of triphenylmethyl hexafluoroantimonate with 3, with dimethoxydimethylsilane trapping

The same procedure as described for the previously trapping reaction was followed.

Compound 3 (130 mg, 0.407 mmol) was mixed with 234 mg (1.947 mmol) of dimethoxydimethylsilane and 20 mg (0.042 mmol) of triphenylmethyl hexafluoroantimonate, the products were identified as 4 (54.9%), 5 (12.3%) and triphenylmethane with no starting material 3 observed.

Reaction of triphenylmethyl perchlorate with 3, with tetramethoxysilane trapping

Compound 3 (135 mg, 0.423 mmol) was mixed with 124 mg (0.815 mmol) of tetramethoxysilane, 26 mg of internal standard and 0.5 mL of CH_2Cl_2 in a NMR tube under N_2. The tube was immersed in an ice bath, and 10 mg (0.029 mmol) of triphenylmethyl perchlorate in 0.5 mL CH_2Cl_2 solution was added slowly to the NMR tube and analyzed by GC (10 ft x 1/8 in 15% OV-3 column temperature programmed from 50-300°C at 15°C per min).

The products were identified as 3,3-dimethyl-1,1,1,3-tetramethoxydisiloxane 6 (36.5%), hexamethoxydisiloxane, 7 (7.5%), $(MeO)_3\text{-O-}\overset{\backslash\,/}{\text{Si}}\text{-O-Si(OMe)}_3$, 8 trace amount and triphenylmethane with no starting material 3 remaining. The products were also isolated by preparative GC (10-ft x 1/4-in

15% SE-30) and identified by comparison of their GC/MS and ^1H NMR data with those of authentic samples.

Reaction of triphenylmethyl hexafluoroantimonate with 3, with tetramethoxysilane trapping

The same procedure as described for the previously trapping experiment was followed.

Compound 3 (131 mg, 0.410 mmol) was mixed with 108 mg (0.709 mmol) of tetramethoxysilane and 14 mg (0.029 mmol) of triphenylmethyl hexafluoroantimonate. The products were identified as 6 (20.7%), 7 (2.5%) and triphenylmethane with no starting material 3 remaining.

Reaction of D_3 and triphenylmethyl perchlorate

D_3 (115 mg, 0.518 mmol) was mixed with 77 mg of internal standard and 0.5 mL of CH_2Cl_2 in a NMR tube under N_2. The tube was immersed in an ice bath, and 23.5 mg (0.069 mmol) of triphenylmethyl perchlorate in 0.5 mL of CH_2Cl_2 was added slowly to the NMR tube. The tube was shaken vigorously and analyzed by GC (10 ft x 1/8 in 15% OV-3 column temperature programmed from 50-300°C at 15°C per min).

The products were identified as D_3 (3.0%), D_4 (11.9%), D_5 (2.9%) and D_6 (34.6%).

Reaction of D_3 and triphenylmethyl hexafluoroantimonate

The same procedure as described for the previous triphenylmethyl perchlorate reaction was followed.

D_3 (107 mg, 0.482 mmol) was mixed with 79 mg of internal standard and 22 mg of triphenylmethyl hexafluoroantimonate, the products were identified as D_3 (19.9%), D_4 (7.3%), D_5 (0.8%) and D_6 (26.4%).

Reaction of D_4 and triphenylmethyl perchlorate

D_4 (135 mg, 0.456 mmol) was mixed with 45 mg of internal standard and 1 mL of CH_2Cl_2 in a 5-mL flask under N_2. The flask was immersed in an ice bath, and 25 mg (0.073 mmol) of triphenylmethyl perchlorate in 1 mL CH_2Cl_2 was added slowly to the flask. The mixture stirred at 0°C for 30 min and analyzed by capillary GC. The only product that could be identified was unreacted starting material D_4.

Reaction of D_4 and triphenylmethyl hexafluoroantimonate

The same procedure as described for the previous triphenylmethyl perchlorate reaction was followed.

D_4 (150 mg, 0.507 mmol) was mixed with 55 mg of internal standard and 30 mg (0.063 mmol) of triphenylmethyl hexafluoroantimonate. The mixture stirred at 0°C for 30 min and analyzed by capillary GC. The only product could be identified was unreacted starting material D_4.

Reaction of D_5 and triphenylmethyl perchlorate

D_5 (405 mg, 1.095 mmol) was mixed with 30 mg of internal standard and 0.3 mL of CH_2Cl_2 in a NMR tube under N_2. The tube was immersed in an ice bath, and 30 mg (0.087 mmol) of triphenylmethyl perchlorate in 1 mL CH_2Cl_2 was added slowly to the NMR tube. The tube was shaken vigorously and analyzed by capillary GC. The only product that could be identified was unreacted starting material D_5.

Reaction of D_5 and triphenylmethyl hexafluoroantimonate

The same procedure as described for the previous triphenylmethyl perchlorate reaction was followed.

D_5 (350 mg, 0.946 mmol) was mixed with 50 mg of internal standard and 30 mg (0.063 mmol) of triphenylmethyl hexafluoroantimonate. The only product could be identified was unreacted starting material D_5.

Reaction of dimethoxydimethylsilane and triphenylmethyl perchlorate

Dimethoxydimethylsilane (123 mg, 1.021 mmol) was mixed with 50 mg of internal standard in 0.3 mL CH_2Cl_2 in a NMR tube under N_2. The tube was immersed in an ice bath, and triphenylmethyl perchlorate (30 mg, 0.087 mmol) in 1 mL CH_2Cl_2 was added slowly to the NMR tube. The tube was shaken vigorously and analyzed by capillary GC. The products were identified as dimethoxydimethylsilane (95%) and 1,3-dimethoxy-1,1,3,3-tetramethyldisiloxane, 4 (5%).

Reaction of dimethoxydimethylsilane and triphenylmethyl hexafluoroantimonate

The same procedure as described for the previous triphenylmethyl perchlorate reaction was followed.

Dimethoxydimethylsilane (208 mg, 1.730 mmol) was mixed with triphenylmethyl hexafluoroantimonate (17 mg, 0.035 mmol) in 1 mL CH_2Cl_2 at 0°C. The products were identified as dimethoxydimethylsilane (95%) and 1,3-dimethoxy-1,1,3,3-tetramethyldisiloxane, 4 (5%).

Reaction of tetramethoxysilane and triphenylmethyl perchlorate

Tetramethoxysilane (113 mg, 0.743 mmol) was mixed with (10 mg, 0.029 mmol) of triphenylmethyl perchlorate in 0.5 mL CH_2Cl_2 at 0°C for 1 min. The NMR tube was shaken vigorously and analyzed by GC. The products were identified as tetramethoxysilane (>90%) and hexamethoxydisiloxane, 7 (6.3%).

Reaction of tetramethoxysilane and triphenylmethyl hexafluoroantimonate

The same procedure as described for the previous triphenylmethyl perchlorate reaction was followed.

Tetramethoxysilane (106 mg, 0.697 mmol) was mixed with (14 mg, 0.029 mmol) of triphenylmethyl hexafluoroantimonate in 1 mL CH_2Cl_2 at 0°C for 2 min. The products were identified as tetramethoxysilane (95%) and hexamethoxydisiloxane, 7 (4.1%).

Reaction of triphenylmethyl perchlorate with 3, with diethylether trapping

Compound 3 (1.59 g, 5.00 mmol) was mixed with 1.5 mL Et_2O, 68 mg internal standard in 10-mL round-bottom flask under N_2. The flask was immersed in an ice bath, and 0.515 g (1.50 mmol) of triphenylmethyl perchlorate in 3 mL CH_2Cl_2 was added slowly to the flask. The mixture was stirred at 0°C for 30 min and analyzed by capillary GC.

The products were identified as D_4 (28.7%), D_5 (21.3%), D_6 (9.9%) and triphenylmethyl with no starting material 3 remaining. The products were also identified by comparison of their GC/MS data with those of authentic samples.

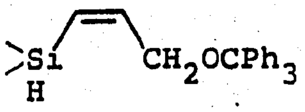
Synthesis of propargyl triphenylmethyl ether, 10, $HC\equiv CCH_2OCPh_3$

To 8.18 g (0.02 mol) of N-tritylpyridinium fluoroborate (83) and 10 mL pyridine in 25 mL of CH_2Cl_2 was added dropwise 1.30 g (0.023 mol) of propargyl alcohol and 10 mL of CH_2Cl_2. After stirring at reflux for 4 h, the mixture was stirred at room temperature overnight. The mixture was concentrated by using a rotary evaporator, filtered and washed with pentane. Filtrate was then concentrated by using a rotary evaporator (above procedure repeated twice), and compound 10 was formed as a white solid. Recrystallization from MeOH, afforded 10 in 93.9% (5.60 g) isolated yield. mp=110-112°C (lit. mp=113-114°C (84)); ^1H NMR δ 2.29 (t, 2.4 Hz, 1 H), 3.67 (d, 2.4 Hz, 2 H), 7.26 (m, 15 H); ^{13}C NMR δ 53.08, 73.34, 80.61, 127.24, 127.96, 128.73, 143.61; IR 3310, 3080-3020, 2140, 1065; calcd for $C_{22}H_{18}O$ m/e 298.13577, measured m/e 298.13509.

Synthesis of 3-dimethylsilyl-2-propynyl triphenylmethyl ether, 11, $H\overset{\diagdown\diagup}{Si}C\equiv CCH_2OCPh_3$

A solution of n-butyllithium in hexane (3.09 mmol, 2.06 M) was added dropwise to a stirring solution of 7 (0.921 g, 3.09 mmol) in 25 mL Et_2O under N_2 at -78°C. The resulting milky white solution was stirred at -78°C for 30 min, then warmed to room temperature (turned to dark brown color) and stirred at room temperature for 2 h. The mixture was then cooled to -78°C, chlorodimethylsilane (1.0 mL, 8.67 mmol) in an equal volume of Et_2O was added dropwise and the reaction mixture was stirred at -78°C for 30 min, warmed to room temperature and stirred for an additional 2 h. The mixture was extracted with saturated $NaHCO_3$, distilled H_2O, and the organic layer was separated and dried over Na_2SO_4. Following removal of solvent, the residue was distilled at 185-190°C, 0.5 torr, to afford 11 in 93% yield. ^1H NMR δ (d, 3.2 Hz, 6 H), 3.80 (s, 2 H), 4.10 (hept, 3.2 Hz, 1 H), 7.40 (m, 15 H); ^{13}C NMR δ -3.00, 53.83, 87.90, 104.22, 127.21, 127.92, 128.81, 143.70; IR 3080-3020, 2180, 2130, 1590, 1358, 1055; calcd for $C_{24}H_{24}OSi$ m/e 356.15965, measured m/e 356.16026; Anal. Calcd for $C_{24}H_{24}OSi$: C, 80.85; H, 6.79. Found: C, 80.89; H, 6.84.

Synthesis of cis-3-dimethylsilyl-2-propenyl triphenylmethyl ether, 12,



To a stirring solution of diisobutylaluminum hydride (Dibal-H) (2.800 mmol, 1.0 M), N-methylpyrrolidine (0.3 mL, 2.800 mmol) and 15 mL of heptane was slowly added 11 (10.982 g, 2.758 mmol) in 25 mL of heptane (80, 81). The mixture stirred at 80°C for 8 h then raised to 100°C and stirred at this temperature for an additonal 8 h. The solution was then cooled to room temperature and poured into a flask containing 50 mL ice-H_2O and 25 mL of hexane and stirred vigorously for 15 min.

The resulting slurry was filtered through a Celite-padded fritted funnel, followed by separation and drying of the organic layer over Na_2SO_4. Following removal of solvent, the residue was distilled at 155-161°C, 0.5 torr, to afford 12 in 75% yield. ^1H NMR δ 0.00 (d, 3.8 Hz, 6 H), 3.72 (dd, 6.2 Hz, 0.9 Hz, 2 H), 4.10 (hep 3.8 Hz, 1 H), 5.63 (dt, 14.2 Hz, 0.9 Hz, 1 H), 6.60 (dt, 14.2 Hz, 6.2 Hz, 1 H), 7.30 (m, 15 H): ^{13}C NMR δ -3.32, 64.79, 126.99, 127.80, 128.85, 129.54, 144.32, 146.03; IR 3090-3020, 2965, 2930, 2150, 1600, 1490, 1450, 1250, 1065; mass spectrum, m/e (% relative intensity) 281 ($M^+-C_6H_5$, 1.2), 244 (43), 243 (30), 167 (25), 166 (15), 165 (39), 114 (20), 99 (100); Anal. Calcd for $C_{24}H_{26}OSi$: C, 80.40; H, 7.31. Found: C, 80.51; H, 7.39.

Synthesis of 3-dimethylsilyl-propanyl triphenylmethyl ether, 14, $H\overset{\backslash /}{Si}(CH_2)_3OCPh_3$

Compound 11 (3.58 g, 10 mmol) and 30 mL of dry MeOH were added to a 50-mL round-bottom flask, a catalytic amount (30 mg) of 10% Pd/charcoal was added to the mixture all at once, the mixture was stirred under a H_2 atmosphere (2.5 atm) and room temperature for 12 h. The solution was filtered and the filtrate was concentrated by using a rotary evaporator. The residue was analyzed by NMR and GC/MS. The products were identified as a mixture of 3-dimethylmethoxysilyl-propanyl triphenylmethyl ether, 13, $MeO\overset{\backslash /}{Si}(CH_2)_3OCPh_3$ (~ 80%) and triphenylmethane (~ 15%).

The resulting residue was then dissolved in 30 mL of Et_2O and was added slowly to lithium aluminum hydride (1.896 g, 20 mmol) in 30 mL of Et_2O. The mixture was stirred at room temperature for 12 h, then distilled H_2O was added slowly to destroy excess lithium aluminum hydride. The reaction mixture was extracted with distilled H_2O, and the organic layer was separated and dried over Na_2SO_4. Organic solvent was removed by using a rotary evaporator, and the residue was distilled at 145-149°C, 0.7 torr to afford 14 in 61% yield (based on starting material 11). 13: ^1H NMR δ 0.20 (s, 6 H), 0.72 (t, 8.5 Hz, 2 H), 1.58 (tt, 8.5 Hz, 7.5 Hz, 2 H), 2.98 (t, 7.5 Hz, 2 H), 3.35 (s, 3 H), 7.35 (m, 15 H); ^{13}C NMR δ -2.55, 12.13, 23.85, 66.35, 86.35, 126.81, 127.69, 128.70, 144.52; mass spectrum, m/e (% relative intensity) 358 (M^+-MeOH, 0.6), 271 (14), 244 (26), 243 (100), 165 (41), 131 (12), 115 (63), 89 (70). 14: ^1H NMR δ 0.30 (d, 3.3 Hz, 6 H), 0.54 (m, 2 H), 1.61 (tt, 7.8 Hz, 6.9 Hz, 2 H), 3.00 (t, 6.9 Hz, 2 H), 3.79 (m, 1 H), 7.25 (m, 15 H); ^{13}C NMR δ -4.39, 10.63, 25.11, 66.35, 126.86, 127.70, 128.85, 144.86; mass spectrum, m/e (% relative intensity) 244 ($M^+-C_5H_{13}OSi$, 16), 243 (18), 167 (40), 165 (44), 115 (4), 105 (32), 77 (19), 59 (100); IR 3080-3020, 2960, 2110, 1595, 1490, 1245, 1070, 1030: Anal. Calcd for $C_{24}H_{28}OSi$: C, 79.95; H, 7.83. Found: C, 80.15, H, 7.84.

Synthesis of 3,3-dimethyl-4-oxa-3-silacyclopentenes, 15,  via intramolecular cyclization of compound 12 and triphenylmethyl perchlorate

Compound 12 (43 mg, 0.143 mmol) was mixed with 15 mg of internal standard and 0.5 mL of CH_2Cl_2 in a NMR tube under N_2. The tube was immersed in an ice bath, and 4 mg (0.014 mmol) of triphenylmethyl perchlorate in 0.5 mL of CH_2Cl_2 was slowly added to the NMR tube. The tube was shaken vigorously and then analyzed by GC (10-ft x 1/8-in 15% OV-101 column, temperature programmed from 50-270°C at 25°C per min).

The products were identified as 15 (57.9%) and triphenylmethane with no starting material 12 remaining. The yield was determined by GC analysis, after preparative GC on a 8-ft x 1/4-in 15% SE-30 Chromosorb W column at 80°C. Pure 15 was obtained. Compound 15 was also identified by comparison of its GC/MS and ^1H NMR with those of an authentic sample (90).

Synthesis of 2,2-dimethyl-1-oxa-2-silacyclopentane, 16,  via intramolecular cyclization of compound 14 and triphenylmethyl perchlorate

The same procedure as described for the previous cyclization reaction was followed.

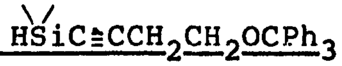
Compound 14 (117 mg, 0.326 mmol) was mixed with 45 mg of internal standard and 10 mg, (0.029 mmol) of triphenylmethyl perchlorate solution at 0°C. The products were identified as 16 (76.6%) and triphenylmethane. The yield was determined by GC analysis. After preparative GC on a 8-ft x 1/4-in 15% SE-30 Chromosorb W column at 90°C, analytically pure 16 was obtained. Compound 16 was also identified by comparison of its GC/MS and ^1H NMR data with those of an authentic sample (91-93).

Synthesis of 3-butynyl triphenylmethyl ether, 19, $HC\equiv CCH_2CH_2OCPh_3$

To 1.402 g (0.020 mol) of 3-butyn-1-ol, 0.015 mol of Et_3N, 0.015 mol of pyridine and 20 mL of CH_3CN was added dropwise a solution containing 5.75 g (0.021 mol) of triphenylmethyl chloride in 30 mL of CH_3CN. After the mixture was stirred at 85°C for 12 h, the solution was cooled to room temperature and extracted with distilled H_2O (2 x 50 mL), and Et_2O (50 mL).

The organic layer was separated and dried over Na_2SO_4. Volatile organic solvent was removed using a rotary evaporator, leaving white solid which was recrystallized from MeOH, to afford 19 in 85% yield. mp=100-102°C; ^1H NMR δ 2.00 (t, 2.6 Hz, 1 H), 2.50 (dt, 7.0 Hz, 2.6 Hz, 2 H), 3.20 (t, 7.0 Hz, 2 H), 7.40 (m, 15 H); ^{13}C NMR δ 20.07, 62.05, 69.26, 86.22, 127.01, 127.82, 128.69, 144.07; IR 3310, 3090-3020, 2120, 1079; calcd for $C_{23}H_{20}O$ m/e 312.15142, measure m/e 312.15145; Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.52, H, 6.40.

Synthesis of 4-dimethylsilyl-3-butynyl triphenylmethyl ether, 20,

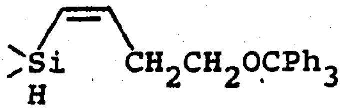


$\overset{\diagdown\diagup}{HSi}C\equiv CCH_2CH_2OCPh_3$

Synthesis of 20 was accomplished following the same procedure as for the preparation of compound 11.

The anion of compound 19 (0.005 mol) was quenched with (0.6 mL, 0.006 mol) chlorodimethylsilane at -78°C. After aqueous work-up and drying, the volatile solvent was removed and the residue was distilled at 155-160°C, 0.05 torr to afford 20 in 90% yield. ^1H NMR δ (d, 3.6 Hz, 6 H), 2.40 (t, 8.0 Hz, 2 H), 3.10 (t, 8.0 Hz, 2 H), 4.00 (hep, 3.6 Hz, 1 H), 7.25 (m, 15 H); ^{13}C NMR δ -2.71, 21.61, 61.95, 86.75, 106.14, 127.02, 127.79, 128.76, 144.13; IR 3080-3020, 2950-2920, 2180, 2135, 1595, 1489, 1445, 1250, 1080; Anal. Calcd for $C_{25}H_{26}OSi$: C, 81.03; H, 7.07. Found: 81.31; H, 7.10; calcd for $C_{25}H_{26}OSi$ m/e 370.17472, measured m/e 370.17498.

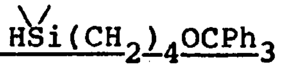
Synthesis of cis-4-dimethylsilyl-3-butenyl triphenylmethyl ether, 21,



Dibal-H reduction of compound 20 followed the same procedure as the preparation of 12.

Compound 20 (7.4 g, 0.02 mole) in 25 ml heptane was added slowly to (0.025 mmol, 1 M) of Dibal-H, (2.15 g, 0.025 mol) of N-methylpyrrolidine solution. After aqueous work-up and drying, removed the volatile solvent, distilled the residue at 158-163°C, 0.5 torr, to afford 21 in 60% yield. ^{1}H NMR δ 0.13 (d, 3.8 Hz, 6 H), 2.49 (ddt, 6.9 Hz, 6.7 Hz, 1.6 Hz, 2 H), 3.08 (t, 6.7 Hz, 2 H), 4.21 (hept, 3.8 Hz, 1 H), 5.53 (dt, 13.9 Hz, 1.6 Hz, 1 H), 6.35 (dt, 13.9 Hz, 6.9 Hz, 1 H), 7.25 (m, 15 H); ^{13}C NMR δ -3.11, 33.99, 63.29, 86.54, 126.98, 127.77, 128.80, 144.40, 146.51; IR 3080-3020, 2950, 2920, 2120, 1600, 1490, 1445, 1250, 1075; Anal. Calcd for $C_{25}H_{28}OSi$: C, 80.59; H, 7.58. Found: C, 80.79; H, 7.62; calcd for $C_{25}H_{28}OSi$ m/e 372.19066, measured m/e 372.19096.

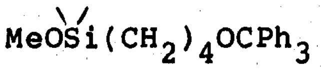
Synthesis of 4-dimethylsilyl butanyl triphenylmethyl ether, 23,



$HSi(CH_2)_4OCPh_3$

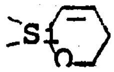
Synthesis of compound 23 followed the same procedure as in the preparation of compound 14.

Hydrogenation of 21 (3.00 g, 8.06 mmol) in 25 mL MeOH, 30 mg of 10% Pd/charcoal and the mixture stirred under a H_2

atmosphere (2.5 atm), afforded 4-dimethyl methoxysilyl butanyl triphenylmethyl ether, 22,  $\mathrm{MeO}\overset{\backslash /}{\mathrm{Si}}(\mathrm{CH_2})_4\mathrm{OCPh_3}$ in 85% yield. Compound 22 was identified by ^{1}H NMR and GC/MS.

The resulting residue was dissolved in 25 mL Et_2O and was added slowly to a lithium aluminum hydride/Et_2O solution. The mixture was stirred at room temperature for 12 h. The work-up procedure was as usual, and the residue was distilled at 160-165°C, 0.4 torr to afford 23 in 68.1% yield (based on starting material 20). 22: ^{1}H NMR δ 0.10 (s, 6 H), 0.55 (m, 2 H), 1.55 (m, 4 H), 3.15 (t, 7.0 Hz, 2 H), 3.48 (s, 3 H), 7.35 (m, 15 H); mass spectrum, m/e (% relative intensity) 372 (M^+-MeOH, 1.6), 244 (19), 243 (71), 165 (34), 145 (30), 129 (76), 105 (37), 89 (100), 59 (30). 23: ^{1}H NMR δ 0.04 (d, 3.7 Hz, 6 H), 0.53 (m, 2 H), 1.42 (m, 2 H), 1.65 (m, 2 H), 3.05 (tt, 6.4 Hz, 2.4 Hz, 2 H), 3.84 (m, 1 H), 7.40 (m, 15 H); ^{13}C NMR -4.35, 11.05, 21.21, 33.49, 63.34, 126.83, 127.69, 128.82, 144.67; IR 3080-3020, 2960, 2920, 2110, 1600, 1490, 1450, 1250, 1080, 1030; mass spectrum, m/e (% relative intensity) 374 (0.1), 244 (65), 243 (100), 167 (129), 165 (38), 104 (24), 77 (11), 59 (47); Anal. Calcd for $C_{25}H_{30}OSi$: C, 80.16; H, 8.07. Found: C, 80.46, H, 8.33; calcd for $C_{25}H_{30}OSi$ m/e 374.20660, measured m/e 374.20686.

Synthesis of 3,3-dimethyl-4-oxa-3-silacyclohexene, 24, via intramolecular cyclization of compound 21 and triphenylmethyl perchlorate



Compound 21 (45 mg, 0120 mmol) was mixed with 31 mg internal standard and 0.5 mL CH_2Cl_2 in a NMR tube under N_2. The tube was immersed in an ice bath, and triphenylmethyl perchlorate (8 mg, 0.024 mmol) in 0.5 mL CH_2Cl_2 was slowly added to the NMR tube. The tube was shaken vigorously and analyzed by GC (10-ft x 1/8-in. 15% OV-101 column, temperature programmed from 50-270°C at 25°C per min).

The products were identified as 24 (60.6%) and triphenylmethane with no starting material 21 left. The yield was determined by GC analysis. After preparative GC on a 8-ft x 1/4-in. 15% SE-30 Chromosorb W column at 100°C. Pure 24 was obtained. 24: ^1H NMR δ 0.17 (s, 6 H), 2.25 (tdd, 5.3 Hz, 4.0 Hz, 2.0 Hz, 2 H), 3.95 (t, 5.3 Hz, 2 H), 5.74 (dt, 14.2 Hz, 2.0 Hz, 1 H), 6.82 (dt, 14.2 Hz, 4.0 Hz, 1 H); ^{13}C NMR δ -0.62, 31.12, 61.73, 127.23, 147.76; IR 2974, 2931, 1585, 1261, 1087, 1050; calcd for $C_6H_{12}OSi$ m/e 128.06575, measured m/e 128.06600; Anal. calcd for $C_6H_{12}OSi$: C, 56.19; H, 9.43; Found: 56.50; H, 9.36.

Synthesis of 2,2-dimethyl-1-oxa-2-silacyclohexane, 25,  via intramolecular cyclization of compound 23 and triphenylmethyl perchlorate

The same procedure as described for the intramolecular cyclization reaction of 21 was followed.

Compound 23 (121 mg, 0.325 mmole), 61 mg of internal standard and 10 mg of triphenylmethyl perchlorate solution were mixed together at 0°C. The products were identified as 25 (86%) and triphenylmethane with no starting material 23 left. The yield was determined by GC analysis. After preparative GC on a 8-ft x 1/4-in. 15% SE-30 on Chromosorb W at 100°C. Pure 25 was obtained. Compound 25 was also identified by comparison of its GC/MS and ^1H NMR data with those of an authentic sample (91-93).

Synthesis of t-butyl dimethylsilyl ether, 26  $\mathrm{+\!\!-\!-O\overset{\backslash /}{Si}H}$ (94)

t-Butanol (3.70 g, 0.05 mol) and 200 mL Et_2O were added to a 500-mL round-bottom flask under N_2. Triethylamine (5.10 g, 0.05 mol) was added to the flask all at once. Chlorodimethylsilane (4.73 g, 0.05 mol) in an equal volume of Et_2O was added dropwise to the reaction mixture. A white solid formed immediately. The resulting solution was stirred at room temperature for 12 h.

The mixture was filtered through a Celite-padded fritted funnel, filtrate was extracted with saturated NaCl solution, then distilled H_2O, and the organic layer was dried over

Na_2SO_4. The product was distilled at 88-90°C (lit. b.p. = 89°C (94)) to afford 26 in 90% yield. ^1H NMR δ 0.16 (d, 3.0 Hz, 6 H), 1.26 (s, 9 H); 4.73 (hep, 3.0 Hz, 1 H); ^{13}C NMR δ 0.84, 32.55, 72.55; IR 2980, 2120, 1370, 1260, 1100, 1050; mass spectrum, m/e (% relative intensity) 132 (0.3), 117 (60), 101 (6), 75 (100), 61 (75); calcd for $C_6H_{16}OSi$ m/e (M^+-H) 131.08920, measured m/e 131.08900.

Synthesis of benzyl dimethylsilyl ether, 27, $C_6H_5CH_2O\overset{\backslash /}{Si}H$

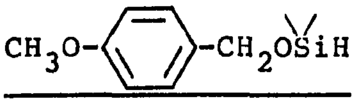
The procedure followed was the same as for the preparation of compound 26. Benzyl alcohol (10.80 g, 0.10 mol), 10.10 g (0.10 mol) of triethylamine and 9.45 g (0.10 mol) of chlorodimethylsilane and 300 mL of Et_2O were mixed together. After aqueous work-up and drying, the volatile solvent was removed by using a rotary evaporator, the residue was distilled at 89-91°C, 20 torr, afforded 27 in 84% yield. ^1H NMR δ 0.24 (d, 2.9 Hz, 6 H), 4.73 (m, 3 H), 7.33 (m, 5 H); ^{13}C NMR δ 1,52, 65.82, 126.98, 127.62, 128.53, 140.89; IR 3060, 3040, 2970, 2120, 1500, 1460, 1380, 1260, 1100, 1075; mass spectrum, m/e (% relative intensity) 166 (0.1), 151 (7.7), 149 (2.6), 121 (8), 91 (85), 75 (100), 65 (23); Anal. Calcd for $C_9H_{14}OSi$: C, 65.00; H, 8.49; Found: C, 65.33; H, 8.55; calcd for $C_9H_{14}OSi$ m/e (M^+-H) 165.0736, measured m/e 165.0738.

Synthesis of diphenylmethyl dimethylsilyl ether, 28,

$Ph_2CHOSi(CH_3)_2H$

The preparation of 28 followed the same method as described in the literature (95), with the exception that chlorodimethylsilane was substituted for chlorotrimethylsilane. Diphenylmethyl alcohol (9.20 g, 0.05 mol), 7.90 g (0.10 mol) of pyridine, 4.73 g (0.05 mol) of chlorodimethylsilane and 100 mL of xylene were mixed together. The solution was heated to reflux for 1/2 hr. After aqueous work-up and drying, the volatile solvent was removed by using a rotary evaporator, the residue was distilled at 113-116°C, 1.5 torr, afforded 28 in 56% yield. ^{1}H NMR δ 0.18 (d, 3.0 Hz, 6 H), 4.70 (hep, 3.0 Hz, 1 H), 5.80 (s, 1 H), 7.40 (m, 10 H); ^{13}C NMR δ -1.03, 78.08, 126.58, 127.22, 128.26, 144.22; IR 3070, 3030, 2960, 2120, 1590, 1490, 1450, 1250, 1080, 1055; Anal. Calcd for $C_{15}H_{18}OSi$: C, 74.38; H, 7.49; Found: C, 74.10, H, 7.31; calcd for $C_{15}H_{18}OSi$ m/e (M^+-H) 241.10487, measured m/e 241.10455.

Synthesis of p-methoxybenzyl dimethylsilyl ether, 29,



The preparation of 29 followed the same route as the preparation of compound 26. *p*-Methoxybenzyl alcohol (6.90 g, 0.050 mol), 5.10 g (0.050 mol) of triethylamine, 4.73 g (0.050 mol) of chlorodimethylsilane and 250 mL Et_2O were mixed together. After aqueous work-up and drying, the volatile solvent was removed by using a rotary evaporator, the residue was distilled at 98-100°C, 2.0 torr, afforded 29 in 87% yield. ^{1}H NMR δ 0.55 (d, 2.7 Hz, 6 H), 4.11 (s, 3 H), 4.98 (s, 2 H), 5.10 (hept, 2.7 Hz, 1 H), 7.19 (d, 9.0 Hz, 2 H), 7.57 (d, 9.0 Hz, 2 H); ^{13}C NMR δ -1.44, 55.23, 65.95, 113.79, 128.36, 132.59, 159.03; IR 3050, 3020, 2960-2930, 2125, 1615, 1515, 1465, 1380, 1250, 1080; mass spectrum, m/e (% relative intensity) 196 (13), 181 (33), 151 (6), 135 (5), 121 (100), 91 (15), 77 (18); Anal. Calcd for $C_{10}H_{16}O_2Si$: C, 61.18; H, 8.22; Found: C, 61.44; H, 8.27; calcd for $C_{10}H_{16}O_2Si$ m/e 196.09196, measured m/e 196.09180.

Reaction of triphenylmethyl perchlorate and 26

Compound 26 (53.5 mg, 0.405 mmol), 33 mg of internal standard and 0.5 mL of CH_2Cl_2 were mixed in a NMR tube under N_2. The tube was immersed in an ice bath, and 140 mg (0.405 mmol) of triphenylmethyl perchlorate in 1 mL CH_2Cl_2 was added slowly to the NMR tube. The mixture was shaken vigorously and analyzed by GC (10-ft x 1/8-in. 10% OV-101, column temperature programmed from 50-270°C at 25°C per min).

The products were identified as D_4 (72%), D_5 (25%), D_6 (trace) and triphenylmethane with no starting material 26 left. The yields were determined by GC analysis. The products were also identified by comparison of their GC/MS with those of authentic samples.

Reaction of triphenylmethyl perchlorate and 27

The same procedure as described for the previous reaction was followed.

Compound 27 (166 mg, 1.00 mmol), 25 mg of internal standard and 1 mL of CH_2Cl_2 was added slowly to a 10-mL round-bottom flask containing 344 mg (1.00 mmol) of triphenylmethyl perchlorate in 3 mL of CH_2Cl_2 at 0°C under N_2. The mixture was stirred at 0°C for 20 min. The mixture was then analyzed by GC (using a capillary column, temperature programmed from 50-250°C at 15°C per min).

The products were identified as D_4 (38.2%), D_5 (18.7%), D_6 (1.7%), and triphenylmethane with no starting material 27 left. The yields were determined by GC analysis. The products were also identified by comparison of their GC/MS with those of authentic samples.

Reaction of triphenylmethyl perchlorate and 28

The reaction followed the same procedure as described in the previous reaction.

Compound 28 (53 mg, 0.219 mmol), 33 mg of internal standard and 0.5 mL CH_2Cl_2 were mixed together. Triphenylmethyl perchlorate (76 mg, 0.220 mmol) in 0.5 mL CH_2Cl_2 was added slowly to the mixture at 0°C.

The products were identified as D_4 (34%), D_5 (15.4%), D_6 (5.6%), diphenylmethane (72%) and triphenylmethane with no starting material 28 remaining. Diphenylmethane was isolated by preparative GC (10-ft x 1/4-in. 10% SE-30 on Chromosorb W at 200°C) and identified by comparison of its GC/MS and ^{1}H NMR data with those of an authentic sample. The yields were determined by GC analysis. Cyclic siloxanes were also identified by comparison of their GC/MS with those of authentic samples.

Reaction of triphenylmethyl perchlorate and 29

The same procedure as described for the previous reaction was followed.

Compound 29 (70 mg, 0.357 mmol), 33 mg of internal standard and 0.5 mL CH_2Cl_2 were mixed together. Triphenylmethyl perchlorate (123 mg, 0.357 mmol) in 2 mL CH_2Cl_2 was added slowly to the mixture at 0°C. Analysis of the mixture was by GC (10-ft x 1/8-in. 10% OV-101, column temperature programmed from 50-270°C at 25°C per min).

The products were identified as D_4 (57.5%), D_5 (20.0%), D_6 (trace) and triphenylmethane with no starting material 29 left. The yields were determined by GC analysis. The products were also identified by comparison of their GC/MS with those of authentic samples.

Reaction of triphenylmethyl perchlorate and excess 26

Compound 26 (1.32 g, 10 mmol), and 26 mg of internal standard in 5 mL CH_2Cl_2 were slowly added to 1.92 g (5.6 mmol) of triphenylmethyl perchlorate in 10 mL CH_2Cl_2 at 0°C. The mixture was stirred at 0°C for 15 min. The mixture was analyzed by GC (15-m capillary column, column temperature programmed from 50-250°C at 15°C per min).

The products were identified as unreacted starting material 26 (11%), D_4 (58.3%), D_5 (24.1%), D_6 (4.3%) and triphenylmethane. The yields were determined by GC analysis. The products were also identified by comparison of their GC/MS with those of authentic samples.

Synthesis of t-butyl propargyl ether, 30, +—$OCH_2C\equiv CH$

The preparation of 30 followed the method described by Mantione (96). Propargyl alcohol (5.6 g, 0.1 mol) and three drops of conc. H_2SO_4 were added to a 25-mL 3-neck flask equipped with mechanical stirrer and condenser. The mixture was heated to 45°C. Isobutene was introduced and the mixture was stirred at 45°C for 2.5 h.

The mixture was neutralized with 10 mL, 10% NaOH, then washed with saturated NaCl followed by distilled water. The organic layer was dried over $CaCl_2$ for 3 h. The product 30 was distilled at 116-117°C (lit. b.p. = 116-117°C (96)) in 72% yield. ^1H NMR δ 1.28 (s, 9 H), 2.88 (t, 2.4 Hz, 2 H), 4.07 (d, 2.4 Hz, 1 H); ^{13}C NMR δ 27.40, 50.24, 72.81, 74.35, 81.65; mass spectrum, m/e (% relative intensity) 111 (M^+-H, 1), 98 (60), 97 (M^+-CH_3, 24), 79 (31), 69 (46), 67 (24), 57 (100), 55 (71).

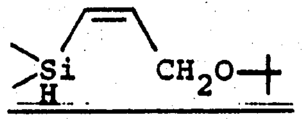
Synthesis of 3-dimethylsilyl-2-propynyl t-butyl ether, 31,

$H\overset{\vee}{Si}C\equiv CCH_2O\!-\!\!\!+$

A solution of n-butyllithium in hexane (50 mmol, 2.32 M) was added dropwise to a stirring solution of compound 30 (5.6 g, 50 mmol) in 25 mL THF at -30°C under N_2. The resulting solution was stirred at -30°C for 2 h (turned brown color). Chlorodimethylsilane (5.20 g, 55 mmol) in 10 mL of THF was added dropwise to the solution at -30°C and the reaction mixture was stirred at this temperature for 2 h, then slowly warmed up to room temperature and stirred for an additional 8 h.

The mixture was extracted with saturated NaCl solution followed by distilled water, and the organic layer was separated and dried over Na_2SO_4. Following removal of the volatile solvent, the residue was distilled at 100-103°C, 45 torr, to afford 31 in 83% yield. ^1H NMR δ 0.22 (d, 3.0 Hz, 6 H), 1.23 (s, 9 H), 4.08 (s, 2 H), 4.12 (hep, 3.0 Hz, 1 H); ^{13}C NMR δ -3.12, 27.50, 51.11, 74.47, 86.58, 105.08; IR 2980-2960, 2180, 2130, 1470, 1390, 1370, 1255, 1200, 1070, 1050; mass spectrum, m/e (% relative intensity) 155 (M^+-CH_3, 84), 113 (9), 97 (75), 75 (68), 67 (30), 57 (100); Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65; Found: C, 63.19; H, 10.60; calcd for $C_9H_{18}OSi$ m/e (M^+-CH_3) 155.08920, measured 155.08930.

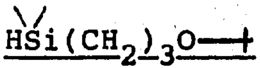
Synthesis of Cis-3-dimethylsilyl-2-propenyl t-butyl ether, 32,



To a stirring solution of Dibal-H (20 mmol, 1.0 m) in heptane, N-methylpyrrolidine (1.70 g, 20 mmol) and 10 mL of heptane was slowly added a solution of compound 31 (3.40 g, 20 mmol) in 10 mL heptane. The mixture was stirred at 60°C for 6 h. The temperature was raised to 100°C and the mixture was stirred at this temperature for an additional 12 h. The solution was then cooled to room temperature and poured into a flask containing 100 mL of ice/H_2O and 25 mL of hexane. The mixture was vigorously stirred for 15 min.

The resulting slurry was filtered through a Celite-padded fritted funnel. The filtrate was extracted with saturated NaCl solution and followed by distilled water, and the organic layer was separated and dried over Na_2SO_4. Following removal of the volatile solvent using a rotary evaporator, the residue was distilled at 82-85°C, 35 torr, to afford 32 in 88% yield. ^1H NMR δ 0.15 (d, 3.2 Hz, 6 H), 1.21 (s, 9 H), 4.00 (dd, 5.6 Hz, 1.1 Hz, 2 H), 4.24 (hep, 3.2 Hz, 1 H), 5.62 (dt, 13.2 Hz, 1.1 Hz, 1 H), 6.51 (dt, 13.2 Hz, 5.6 Hz, 1 H); ^{13}C NMR δ -2.93, 27.69, 62.26, 73.36, 127.88, 146.99; IR 2980-2950, 2120, 1610, 1460, 1385, 1360, 1245, 1190, 1070; mass spectrum, m/e (% relative intensity) 157 (M^+-CH_3, 1), 155 (39), 113 (4), 97 (100), 75 (41), 57 (64); Anal. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70; Found: C, 62.65; H, 12.00; calcd for $C_9H_{20}OSi$ m/e (M^+-CH_3) 157.10487, measured 157.10453.

Synthesis of 3-dimethylsilyl propanyl t-butyl ether, 34,



$H\overset{\backslash /}{S}i(CH_2)_3O{-}\!\!+$

Compound 31, (3.40 g, 20 mmol) and 30 mL of dry MeOH was added to a 50-mL round-bottom flask under N_2, and 30 mg of 10% Pd/charcoal was added to the mixture all at once. The resulting mixture was stirred at room temperature under 1 atm of H_2 for 12 h. The catalyst was filtered out, and the filtrate was concentrated using a rotary evaporator. The residue was distilled at 70-73°C, 5 torr, afforded 3-dimethylmethoxysilylpropanyl t-butyl ether, 33, in 87% yield.

Compound 33 was then mixed in 30 mL Et_2O and was added dropwise to lithium aluminum hydride (0.38 g, 10 mmol) in 30 mL of Et_2O at room temperature. The resulting solution was stirred at room temperature for 12 h. Distilled water (25 mL) was slowly added at 0°C to destroy any excess lithium aluminum hydride. The resulting slurry was filtered through a Celite-padded fritted funnel. The filtrate was extracted with saturated NaCl solution followed by distilled water, and the organic layer was separated and dried over Na_2SO_4. Volatile solvent was removed using a rotary evaporator, and the residue was distilled at 83-86°C, 5 torr, to afford 34 in 61% yield.

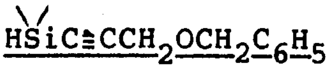
33: ^1H NMR δ 0.11 (s, 6 H), 0.60 (m, 2 H), 1.19 (s, 9 H), 1.60 (m, 2 H), 3.30 (t, 7.0 Hz, 2 H), 3.43 (s, 3 H); ^{13}C NMR δ

-2.63, 12.10, 24.52, 27.68, 50.33, 64.46, 72.50; IR 2980-2950, 1460, 1380, 1355, 1245, 1190, 1080; mass spectrum, m/e (% relative intensity) 189 (M^+-CH_3, 3), 163 (6), 147 (6), 115 (48), 101 (9), 91 (37), 89 (100), 57 (61); calcd for $C_{10}H_{24}O_2Si$ m/e (M^+-CH_3) 189.13136, measured 189.13108. 34: ^1H NMR δ 0.06 (d, 3.2 Hz, 6 H), 0.56 (m, 2 H), 1.17 (s, 9 H), 1.55 (m, 2 H), 3.29 (tt, 7.0 Hz, 3.0 Hz, 2 H), 3.85 (m, 1 H); ^{13}C NMR δ -4.37, 10.42, 25.65, 27.68, 64.34, 72.53; IR 2980-2950, 2120, 1460, 1390, 1360, 1250, 1195, 1085; mass spectrum, m/e (% relative intensity) 159 (M^+-CH_3, 3), 117 (17), 103 (12), 101 (8), 87 (8), 75 (63), 59 (75), 57 (100); Anal. Calcd for $C_9H_{22}OSi$: C, 62.00; H, 12.72; Found: C, 62.06; H, 12.90; calcd for $C_9H_{22}OSi$ m/e (M^+-CH_3) 159.12052, measured 159.12051.

Synthesis of benzyl propargyl ether, 35, $HC{\equiv}CCH_2OCH_2C_6H_5$

Benzyl propargyl ether was prepared according to the procedure of Marszak and coworkers (97). Propargyl alcohol (5.60 g, 0.10 mol), 5.60 g (0.10 mol) of KOH and 50 mL of benzene were added to 250-mL round-bottom flask and freshly distilled benzyl chloride (12.65 g, 0.10 mol) in 50 mL of benzene was added dropwise to the reaction mixture, which was stirred at 55°C for 12 h. Following extraction, and drying, the residue was distilled at 86-90°C, 10 torr, (lit. b.p. = 100-101°C., 18 torr (97)) to afford 35 in 78.8% yield. ^1H NMR δ 2.53 (t, 2.4 Hz, 1 H), 4.22 (d, 2.4 Hz, 2 H), 4.66 (s, 2 H), 7.41 (m, 5 H); ^{13}C NMR δ 57.07, 71.53, 74.62, 79.66, 127.88, 128.09, 128.42, 137.29; IR 3300, 3060-3020, 2980-2950, 2130, 1100; mass spectrum, m/e (% relative intensity) 146 (8), 145 (29), 131 (3), 117 (60), 116 (45), 115 (86), 107 (80), 89 (38), 79 (100), 77 (29); calcd for $C_{10}H_{10}O$ m/e (M^+-H) 145.0653, measured 145.0652.

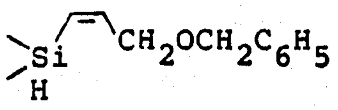
Synthesis of 3-dimethylsilyl-2-propynyl benzyl ether, 36,



$HSiC{\equiv}CCH_2OCH_2C_6H_5$

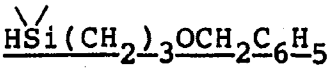
Compound 36 was prepared in an identical fashion as described for the preparation of 3-dimethylsilyl-2-propynyl t-butyl ether, 31, except compound 35 was employed in the anion generation. Following extraction and drying, the residue was distilled at 82-84°C, 0.6 torr, to afford 36 in 80% yield. ^{1}H NMR δ 0.26 (d, 3.4 Hz, 6 H), 4.17 (m, 3 H), 4.60 (s, 2 H), 7.34 (m, 5 H); ^{13}C δ NMR -3.04, 57.91, 71.68, 88.74, 102.98, 127.09, 128.44, 137.40; IR 3080, 3040, 2980, 2920, 2160, 2140, 1620, 1520, 1440, 1370, 1270, 1100, 1040, 1010; mass spectrum, m/e (% relative intensity) 204 (1), 203 (2), 189 (10), 145 (29), 135 (8), 107 (1), 98 (12), 91 (100), 83 (51), 77 (24), 59 (38); Anal. Calcd for $C_{12}H_{16}OSi$: C, 70.53; H, 7.89; Found: C, 70.61; H, 8.06; calcd for $C_{12}H_{16}OSi$ m/e (M^+-H) 203.0892, measured 203.0894.

Synthesis of cis-3-dimethylsilyl-2-propenyl benzyl ether, 37,



Compound 37 was prepared in an identical Dibal-H reduction as described for the preparation of cis-3-dimethylsilyl-2-propenyl t-butyl ether, 32, except compound 36 was employed for the Dibal-H reduction. Following extraction and drying, the residue was distilled at 70-72°C, 0.3 torr, to afford 37 in 85% yield. ^{1}H NMR δ 0.14 (d, 3.7 Hz, 6 H), 4.14 (dd, 6.1 Hz, 1.3 Hz, 2 H), 4.20 (hept, 3.7 Hz, 1 H), 4.53 (s, 2 H), 5.75 (dt, 14.2 Hz, 1.3 Hz, 1 H), 6.52 (dt, 14.2 Hz, 6.1 Hz, 1 H), 7.30 (m, 5 H); ^{13}C NMR δ -3.10, 70.12, 72.40, 127.63, 127.85, 128.38, 129.77, 138.27, 145.47: IR 3060, 3020, 2950, 2120, 1620, 1480, 1450, 1360, 1250, 1090; mass spectrum m/e (% relative intensity) 191 (M^+-CH_3, 0.5), 165 (6), 135 (19), 115 (12), 99 (48), 91 (100), 77 (15), 65 (46), 59 (80); Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.85; H, 8.79; Found: C, 70.04; H, 8.82; calcd for $C_{12}H_{18}OSi$ m/e (M^+-CH_3) 191.08922, measured 191.08912.

Synthesis of 3-dimethylsilyl propanyl benzyl ether, 39,



$HSi(CH_2)_3OCH_2C_6H_5$

Compound 39 was prepared in an identical fashion as described for the preparation of 3-dimethylsilyl propanyl t-butyl ether, 34.

Hydrogenation of 36 in MeOH at room temperature afforded 3-dimethylmethoxysilyl propanyl benzyl ether, 38, in 80% yield. Lithium aluminum hydride of compound 39 in Et_2O at room temperature afforded 39 in 36% yield (based on starting material 36). B.p. 115-120°C, 3.0 torr; 38: ^1H NMR δ 0.05 (s, 6 H), 0.60 (m, 2 H), 1.60 (m, 2 H), 3.40 (tt, 6.8 Hz, 3.0 Hz, 2 H), 4.45 (s, 3 H), 4.62 (s, 2 H), 7.30 (m, 5 H); ^{13}C NMR δ 0.35, 14.42, 23.60, 72.83, 73.24, 126.96, 127.62, 128.32, 138.40; mass spectrum m/e (% relative intensity) 223 (M^+-CH_3, 1), 206 (20), 205 (7), 165 (4), 115 (20), 104 (19), 92 (18), 91 (28), 89 (100), 59 (48). 39: ^1H NMR δ 0.07 (d, 3.6 Hz, 6 H), 0.61 (m, 2 H), 1.66 (tt, 6.8 Hz, 6.8 Hz, 2 H), 3.45 (tt, 6.8 Hz, 3.1 Hz, 2 H), 3.82 (m, 1 H), 4.46 (s, 2 H), 7.30 (m, 5 H); ^{13}C NMR δ -4.44, 10.38, 24.66, 72.86, 72.95, 127.46, 127.63, 128.33, 138.69; IR 3070, 3030, 2960-2930, 2120, 1600, 1490, 1450, 1360, 1250, 1100; mass spectrum, m/e (% relative intensity) 208 (0.3), 193 (1), 117 (28), 115 (25), 104 (26), 101 (83), 93 (25), 92 (62), 89 (42), 65 (100), 59 (55); Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67; Found: C, 69.44; H, 10.05; calcd for $C_{12}H_{20}OSi$ m/e (M^+-CH_3) 193.10487, measured 193.10500.

Intramolecular cyclization of 32 by triphenylmethyl perchlorate

The reaction was performed in an identical fashion as described for the previous intramolecular cyclization reaction of 21.

Compound 32 (42 mg, 0.244 mmol), 38 mg of internal standard and 0.5 mL CH_2Cl_2 were mixed together. Triphenylmethyl perchlorate (84 mg, 0.245 mmol) in 1 mL CH_2Cl_2 was added slowly to the mixture at 0°C. The products were analyzed by GC (10-ft x 1/8-in. 15% OV-101 column, temperature programmed from 50-270°C at 25°C per min).

The products were identified as 3,3-dimethyl-4-oxa-3-silacyclopentene 15 (75.9%) and triphenylmethane with no starting material 32 left. The yield was determined by GC analysis. After preparative GC on a 10-ft x 1/4-in. 10% SE-30 Chromosorb W column at 90°C, pure 15 was obtained. Compound 15 was also identified by comparison of its GC/MS and ^1H data with those of an authentic sample (90).

Intramolecular cyclization of 37 by triphenylmethyl perchlorate

The reaction was performed in an identical fashion as described in a previous reaction.

Compound 37 (117 mg, 0.571 mmol), 28 mg of internal standard and 0.5 mL CH_2Cl_2 were mixed in a 5-mL round-bottom flask. Triphenylmethyl perchlorate (197 mg, 0.574 mmol) in 2 mL of CH_2Cl_2 was added slowly to the mixture at 0°C. The products were analyzed by capillary GC (column temperature programmed from 50-250°C at 15°C per min).

The products were identified as 3,3-dimethyl-4-oxa-3-silacyclopentene, 15, (47.8%) and triphenylmethane. The yield was determined by GC analysis. Compound 15 was identified by comparison of its GC/MS with that of an authentic sample (90).

Intramolecular cyclization of 34 by triphenylmethyl perchlorate

The reaction was performed in an identical fashion as described in a previous reaction.

Compound 34 (124 mg, 0.713 mmol), 47 mg of internal standard and 0.5 mL CH_2Cl_2 were mixed in a 5-mL round-bottom flask. Triphenylmethyl perchlorate (245 mg, 0.714 mmol) in 2 mL of CH_2Cl_2 was added slowly to the mixture at 0°C. The products were analyzed by GC (10-ft x 1/8-in. 15% OV-101 column, temperature programmed from 50-270°C at 25°C per min).

The products were identified as 2,2-dimethyl-1-oxa-2-silacyclopentane, 16 (85.0%) and triphenylmethane with no starting material 34 left. The yield was determined by GC analysis. After preparative GC on a 10 ft x 1/4 in. 10% SE-30 chromosorb W column at 90°C, pure 16 was obtained. Compound 16 was identified by comparison of its GC/MS and ^1H NMR data with those of an authentic sample (91-93).

Intramolecular cyclization of 39 by triphenylmethyl perchlorate

The reaction was performed in an identical fashion as described in a previous reaction.

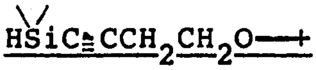
Compound 39 (75 mg, 0.361 mmol), 48 mg of internal standard and 0.5 mL of CH_2Cl_2 were mixed in a 5-mL round-bottom flask. Triphenylmethyl perchlorate (125 mg, 0.363 mmol) in 3 mL of CH_2Cl_2 was added slowly to the mixture at 0°C. The products were analyzed by GC (10-ft x 1/8-in. 15% OV-101, column temperature programmed from 50-270°C at 25°C per min).

The products were identified as 16 (15.7%) and triphenylmethane with no starting material 39 left. The yield was determined by GC analysis. Compound 16 was identified by comparison of its GC/MS data with that of an authentic sample (91-93).

Synthesis of 3-butynyl t-butyl ether, 40, $HC\equiv CCH_2CH_2O$—+

Compound 41 was prepared in an identical fashion as described for the preparation of compound 30, except the starting material was 3-butyn-1-ol. The mixture was stirred at 50°C for 4 h. Following extraction and drying, the residue was distilled at 126-129°C and afforded 40 in 67% yield. ^1H NMR δ 1.19 (s, 9 H), 2.38 (td, 7.0 Hz, 2.7 Hz, 2 H), 3.46 (t, 7.0 Hz, 2 H), 3.72 (t, 2.7 Hz, 1 H); ^{13}C NMR δ 20.86, 27.53, 60.33, 68.99, 73.21, 81.76; IR 3300, 2980-2950, 2120, 1470, 1390, 1360, 1180, 1080; mass spectrum, m/e (% relative intensity) 111 (M^+-CH_3, 3), 87 (18), 81 (24), 59 (46), 57 (100), 53 (50); calcd for $C_8H_{14}O$ m/e (M^+-CH_3) 111.08099, measured 111.08100.

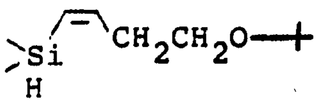
Synthesis of 4-dimethylsilyl-3-butynyl t-butyl ether, 41,



$\overset{\diagdown\!\diagup}{HSi}C{\equiv}CCH_2CH_2O{-\!\!-\!\!+}$

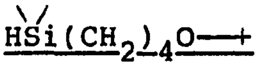
Compound 41 was prepared in an identical fashion as described for the preparation of compound 31 except compound 40 was employed in the anion generation. Following extraction and drying, the residue was distilled at 101-104°C, 35 torr, afforded 41 in 87% yield. ^1H NMR δ 0.20 (d, 3.8 Hz, 6 H), 1.18 (s, 9 H), 2.44 (t, 7.4 Hz, 2 H), 3.64 (t, 7.4 Hz, 2 H), 4.10 (hep, 3.8 Hz, 1 H); ^{13}C NMR δ -2.72, 22.39, 27.59, 60.41, 73.28, 77.35, 105.95; IR 2980-2950, 2180, 2130, 1470, 1390, 1365, 1250, 1195, 1090; mass spectrum, m/e (% relative intensity) 169 (M^+-CH_3, 4), 128 (25), 96 (62), 87 (52), 85 (51), 59 (76), 57 (100); Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94; Found: C, 65.42; H, 10.90; calcd for $C_{10}H_{20}OSi$ m/e (M^+-CH_3) 169.10487, measured 169.10501.

Synthesis of cis-4-dimethylsilyl-3-butenyl t-butyl ether, 42,



Compound 43 was prepared in an identical fashion as described for the Dibal-H reduction of compound 31 except compound 41 was employed for the Dibal-H reduction. Following extraction and drying, the residue was distilled at 98-101°C, 40 torr, to afford 42 in 73% yield. ^1H NMR δ 0.15 (d, 3.8 Hz, 6 H), 1.18 (s, 9 H), 2.40 (td, 7.1 Hz, 1.1 Hz, 2 H), 3.36 (t, 7.2 Hz, 2 H), 4.21 (hep, 3.8 Hz, 1 H), 5.57 (dt, 13.9 Hz, 1.1 Hz, 1 H), 6.40 (dt, 13.9 Hz, 7.0 Hz, 1 H); ^{13}C NMR δ -3.09, 27.61, 34.72, 61.30, 72.76, 128.05, 146.46; IR 2980-2950, 2120, 1605, 1470, 1385, 1355, 1245, 1190, 1080; mass spectrum, m/e (% relative intensity) 129 ($M^+-C_4H_9$, 3), 115 (24), 98 (25), 87 (29), 85 (28), 75 (45), 59 (87), 57 (100); Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90; Found: C, 64.72; H, 12.15; calcd for $C_{10}H_{22}OSi$ m/e ($M^+-C_4H_9$) 129.07357, measured 129.07346.

Synthesis of 4-dimethylsilyl butanyl t-butyl ether, 44,



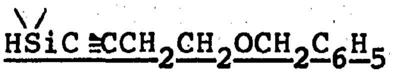
$HSi(CH_2)_4O-\!\!+$

Compound 44 was prepared in an identical fashion as described for the preparation of compound 34. Hydrogenation of 41 in MeOH at room temperature afforded 4-dimethylmethoxysilyl butanyl t-butyl ether, 43, in 90% yield. Lithium aluminum hydride reduction of 43 in Et_2O at room temperature. Following extraction and drying, the residue was distilled at 104-105°C, 40 torr, to afford 44 in 86% yield (based on starting material 41). 43: ^1H NMR δ 0.12 (s, 6 H), 0.62 (m, 2 H), 1.19 (s, 9 H), 1.40-1.62 (m, 4 H), 2.02 (s, 3 H), 3.36 (t, 6.6 Hz, 2 H); ^{13}C NMR δ -0.14, 17.50, 20.07, 27.59, 33.70, 61.37, 72.69; IR 2980-2950, 1470, 1390, 1360, 1250, 1195, 1080; mass spectrum, m/e (% relative intensity) 161 ($M^+-C_4H_9$, 0.5), 129 (12), 107 (13), 91 (21), 89 (100), 59 (38), 57 (50). 44: ^1H NMR 0.05 (d, 3.8 Hz, 6 H), 0.58 (m, 2 H), 1.34-1.57 (m, 4 H), 1.59 (s, 9 H), 3.32 (t, 6.5 Hz, 2 H), 3.83 (m, 1 H); ^{13}C NMR δ -4.37, 14.10, 21.12, 27.66, 34.16, 61.28, 72.47; IR 2980-2950, 2110, 1470, 1390, 1360, 1245, 1195, 1080; mass spectrum, m/e (% relative intensity) 133 (82), 131 ($M^+-C_4H_9$, 41), 130 (56), 115 (66), 105 (34), 87 (41), 75 (76), 61 (59), 57 (100), 55 (98); Anal. Calcd for $C_{10}H_{24}OSi$: C, 63.76; H, 12.84; Found: C, 64.00; H, 13.02; calcd for $C_{10}H_{24}OSi$ m/e ($M^+-C_4H_9$) 131.0892, measured 131.0891.

Synthesis of 3-butynyl benzyl ether, 45, $HC{\equiv}CCH_2CH_2OCH_2C_6H_5$

Compound 45 was prepared in an identical fashion as described for the preparation of compound 35 except the starting material was 3-butyn-1-ol. Following extraction and drying, the residue was distilled at 101-104°C, 10 torr, to afford 45 in 69% yield. ^1H NMR δ 1.99 (t, 2.6 Hz, 1 H), 2.49 (td, 7.0 Hz, 2.6 Hz, 2 H), 3.59 (t, 7.0 Hz, 2 H), 4.56 (s, 2 H), 7.43 (m, 5 H); ^{13}C NMR δ 19.93, 53.74, 68.19, 71.47, 73.00, 127.68, 128.03, 128.39, 138.01; IR 3300, 3080-3030, 2980-2940, 1600, 1490, 1450, 1355, 1080; mass spectrum, m/e (% relative intensity) 160 (1.5), 159 (10), 105 (17), 98 (8), 91 (100), 77 (7), 65 (18), 51 (10); calcd for $C_{11}H_{12}O$ m/e (M^+-H) 159.0810, measured 159.0812.

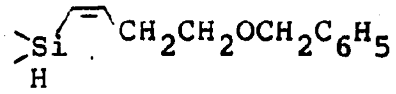
Synthesis of 4-dimethylsilyl-3-butynyl benzyl ether, 46,



$\mathrm{HSi(CH_3)_2C{\equiv}CCH_2CH_2OCH_2C_6H_5}$

Compound 46 was prepared in an identical fashion as described for the preparation of compound 36 except compound 45 was employed in the anion generation. Following extraction and drying, the residue was distilled at 106-109°C, 1.5 torr, to afford 46 in 82% yield. ^{1}H NMR δ 0.16 (d, 3.7 Hz, 6 H), 2.50 (t, 7.0 Hz, 2 H), 3.54 (t, 7.0 Hz, 2 H), 4.05 (hep, 3.7 Hz, 1 H), 4.50 (s, 2 H), 7.28 (m, 5 H); ^{13}C NMR δ -2.80, 21.42, 68.21, 72.96, 83.22, 105.36, 127.69, 128.04, 128.40, 138.10; mass spectrum, m/e (% relative intensity) 218 (1), 203 (5), 189 (44), 159 (100), 97 (37), 92 (37), 92 (46), 91 (20), 77 (23), 65 (81); IR 3080-3020, 2980-2950, 2160, 2120, 1600, 1495, 1455, 1380, 1355, 1255, 1080; Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31; Found: C, 71.37; H, 8.20; calcd for $C_{13}H_{18}OSi$ m/e (M^+-CH_3) 203.08922, measured 203.08920.

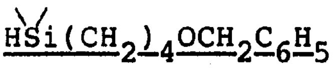
Synthesis of cis-4-dimethylsilyl-3-butenyl benzyl ether, 47,



$\mathrm{HSi(CH_3)_2CH{=}CHCH_2CH_2OCH_2C_6H_5}$

Compound 47 was prepared in an identical fashion as described for the Dibal-H reduction of compound 36 except compound 46 was employed for the Dibal-H reduction. Following extraction and drying, the residue was distilled at 96-99°C, 4.0 torr, to afford 47 in 81% yield. ^{1}H NMR δ 0.15 (d, 3.6 Hz, 6 H), 2.50 (tdd, 7.0 Hz, 7.0 Hz, 1.2 Hz, 2 H), 3.51 (t, 7.0 Hz, 2 H), 4.25 (hep, 3.6 Hz, 1 H), 4.51 (s, 2 H), 5.61 (dt, 13.8 Hz, 1.2 Hz, 1 H), 6.39 (dt, 13.8 Hz, 7.0 Hz, 1 H), 7.35 (m, 5 H); ^{13}C NMR δ 3.62, 33.64, 57.72, 71.43, 75.12, 127.69, 127.98, 128.33, 137.65, 145.88; IR 3040-3020, 2980-2950, 2120, 1605, 1490, 1450, 1355, 1245, 1185, 1070; mass spectrum, m/e (% relative intensity) 220 (0.1), 205 (0.3), 159 (6), 129 (8), 113 (16), 101 (21), 92 (37), 91 (100), 77 (16), 75 (22), 59 (40); Anal. Calcd for $C_{13}H_{20}OSi$: C, 69.85; H, 8.79; Found: C, 69.94; H, 8.82; calcd for $C_{13}H_{20}OSi$ m/e (M^+-CH_3) 205.10487, measured 205.10490.

Synthesis of 4-dimethylsilyl butanyl benzyl ether, 49,



$HSi(CH_2)_4OCH_2C_6H_5$

Compound 49 was prepared in an identical fashion as described in the preparation of compound 39. Hydrogenation of 46 in MeOH afforded a 4-dimethyl-methoxysilyl butanyl benzyl ether, 48 in 80% yield. Lithium aluminum hydride reduction of 48 in Et_2O at room temperature. Following extraction and drying, the residue was distilled at 100-102°C, 1.5 torr, to afford 49 in 70% yield (based on starting material 46). 48: ^{1}H NMR δ 0.10 (s, 6 H), 0.60 (m, 2 H), 1.43-1.64 (m, 4 H), 3.42 (s, 3 H), 3.47 (t, 6.6 Hz, 2 H), 4.50 (s, 2 H), 7.35 (m, 5 H); ^{13}C NMR δ -2.71, 15.68, 19.79, 33.28, 50.16, 69.97, 72.81, 127.36, 127.50, 128.22, 138.63; mass spectrum, m/e (% relative intensity) 220 (M^+-MeOH, 74), 165 (25), 129 (63), 117 (41), 104 (29), 101 (27), 92 (95), 91 (20), 77 (35), 65 (86), 59 (100). 49: ^1H NMR δ 0.06 (d, 3.6 Hz, 6 H), 0.59 (ttt, 7.5 Hz, 3.2 Hz, 2 H), 1.44-1.66 (m, 4 H), 3.47 (tt, 6.5 Hz, 3.2 Hz, 2 H), 3.84 (hept, 3.6 Hz, 1 H), 4.50 (S, 2 H), 7.70 (m, 5 H); ^{13}C NMR δ -4.41, 14.04, 21.10, 33.19, 70.13, 72.89, 127.45, 127.61, 128.33, 138.75; IR 3060-3020, 2980-2940, 2110, 1490, 1450, 1360, 1245, 1080; mass spectrum, m/e (% relative intensity) 207 (M^+-CH_3, 0.1), 135 (5), 131 (9), 115 (77), 92 (53), 89 (35), 87 (58), 77 (14), 75 (88), 65 (88), 55 (100); Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97; Found: C, 70.59; H, 10.19; calcd for $C_{13}H_{22}OSi$ m/e (M^+-CH_3) 207.12052, measured 207.11988.

Intramolecular cyclization of 42 by triphenylmethyl perchlorate

The reaction was performed in an identical fashion as described for the previous intramolecular cyclization reaction of 21.

Compound 42 (52 mg, 0.279 mmol), 28 mg of internal standard and 0.5 mL of CH_2Cl_2 were mixed in a 5-mL round-bottom flask under N_2. Triphenylmethyl perchlorate (100 mg, 0.291 mmol) in 2 mL CH_2Cl_2 was added slowly to the flask at 0°C. The products were analyzed by GC (10-ft x 1/8-in. 15% OV-101 column temperature programmed from 50-270°C at 25°C per min).

The products were identified as 3,3-dimethyl-4-oxa-3-silacyclohexene, 24 (82.1%) and triphenylmethane with no starting material 42 left. The yield was determined by GC analysis. After preparative GC on a 10 ft x 1/4 in. 10% SE-30 chromosorb W at 120°C, pure 24 was obtained. Compound 24 was identified by comparison of its GC/MS and ^1H NMR data with those of an authentic sample.

Intramolecular cyclization of 47 by triphenylmethyl perchlorate

The reaction was performed in an identical fashion as described for the previous reaction.

Compound 47 (115 mg, 0.523 mmol), 59 mg of internal standard and 0.5 mL CH_2Cl_2 were mixed in a 5 mL round-bottom flask under N_2. Triphenylmethyl perchlorate (181 mg, 0.528 mmol) in 2 mL CH_2Cl_2 was added slowly to the flask at 0°C. The products were analyzed by capillary GC (column temperature programmed from 50-250°C at 15°C per min).

The products were identified as 3,3-dimethyl-4-oxa-3-silacyclohexene, 24 (17.7%) and triphenylmethane with no starting material 47 left. The yield was determined by GC analysis. Product 24 was identified by comparison of its GC/MS with that of an authentic sample.

Intramolecular cyclization of 44 by triphenylmethyl perchlorate

The reaction was performed in an identical fashion as described for the previous reaction.

Compound 44 (110 mg, 0.585 mmol), 48 mg of internal standard and 0.5 mL CH_2Cl_2 were mixed in a 5-mL round-bottom flask under N_2. Tritylperchlorate (205 mg, 0.586 mmol) in 3 mL of CH_2Cl_2 was added slowly to the flask at 0°C. The products were analyzed by GC (10-ft x 1/8-in. 15% OV-101 column temperature programmed from 50-270°C at 25°C per min). The products were identified as 2,2-dimethyl-1-oxa-2-silacyclohexane, 25 (78.6%) and triphenylmethane with no starting material 44 left. The yield was determined by GC analysis. After preparative GC on a 10-ft x 1/4-in. 10% SE-30 Chromosorb W column at 110°C, pure 25 was obtained. Compound 25 was identified by comparison of its GC/MS and ^1H NMR data with those of an authentic sample (91-93).

Intramolecular cyclization of compound 49 by triphenylmethyl perchlorate

The reaction was performed in an identical fashion as described for the previous reaction.

Compound 49 (104 mg, 0.468 mmol), 38 mg of internal standard and 0.5 mL of CH_2Cl_2 were mixed in a 5-mL round-bottom flask under N_2. Triphenylmethyl perchlorate (162 mg, 0.472 mmol) in 2 mL CH_2Cl_2 was added slowly to the flask at 0°C. The products were analyzed by capillary GC (column temperature programmed from 50-270°C at 15°C per min). The products were identified as 25 (48.7%) and triphenylmethane with no starting material 49 left. The yield was determined by GC analysis. Compound 25 was identified by comparison of its GC/MS with that of an authentic sample (91-93).

Synthesis of dimethylsilyl triphenylsilyl ether, 50, $Ph_3SiO\overset{\backslash /}{Si}H$

The preparation of compound 50 followed the same procedure as for the preparation of compound 3.

Triphenylsilanol (2.76 g, 0.10 mol), 1.88 g (0.20 mol) of chlorodimethylsilane, and 1.58 g (0.20 mol) of pyridine were mixed in 100 mL of Et_2O. Following extraction and drying, the volatile solvent was removed using a rotary evaporator, and a white solid was obtained which was recrystallized from Et_2O/Skelly B at 0°C to afford 50 in 92.8% yield (based on the consumption of triphenylsilanol). M.p. = 31-33°C; ^1H NMR δ 0.14 (d, 2.8 Hz, 6 H), 4.85 (hep, 2.8 Hz, 1 H), 7.50 (m, 15 H); ^{13}C NMR δ 0.96, 127.81, 129.87, 134.99, 135.85; IR 3070-3040, 2960, 2110, 1430, 1252, 1120, 1070; Anal. Calcd for $C_{20}H_{22}OSi_2$: C, 71.80; H, 6.63; Found: C, 71.99; H, 6.71; calcd for $C_{20}H_{22}OSi_2$ m/e 334.12093, measured 334.12118.

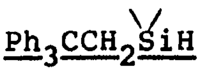
Reaction of triphenylmethyl perchlorate and compound 50 in CH_2Cl_2

Compound 50 (145 mg, 0.434 mmol), 40 mg of internal standard and 2 mL ofCH_2Cl_2 in 10-mL round-bottom flask. Triphenylmethyl perchlorate (148 mg, 0.431 mmol) in 5 mL of CH_2Cl_2 was added slowly to the flask at 0°C. GC analysis indicated starting material 50 was consumed with formation of triphenylmethane. No cyclic silanone oligomer was found in the reaction mixture.

Reaction of triphenylmethyl perchlorate and 50 in CH_3CN

Compound 50 (0.98 g, 29.3 mmol) and 2 mL of CH_3CN were mixed in a 25-mL round-bottom flask. Triphenylmethyl perchlorate (1.02 g, 29.7 mmol) in 10 mL of CH_3CN was added slowly to the flask at 0°C. GC analysis indicated the formation of triphenylmethane with loss of starting material 50, no cyclic silanone oligomer was found in the reaction mixture.

Synthesis of dimethylsilyl triphenylmethylmethane, 51,



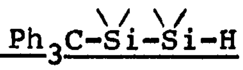
$Ph_3CCH_2\overset{\diagdown\diagup}{Si}H$

Triphenylmethyl anion was generated by reacting 4.89 g (0.020 mol) triphenylmethane and 0.0180 mol of *n*-butyllithium in Et_2O/THF (20 mL:50 mL) at room temperature (98). This anion was quenched by chloromethyldimethylsilane (1.956 g, 0.018 mol) (99). The reaction mixture was extracted with saturated NaCl solution, and distilled H_2O, and the organic layer was separated and dried over Na_2SO_4. Following removal of solvent, to afford a mixture of 51 and triphenylmethane (75:25 ratio) in 84% yield. 51: ^1H NMR δ 0.14 (d, 3.7 Hz, 6 H), 2.45 (d, 2.6 Hz, 2 H), 4.02 (m, 1 H), 7.65 (m, 15 H); ^{13}C NMR δ -3.02, 15.33, 125.79, 127.71, 129.03, 148.78. IR 3060, 3040, 2960, 2920, 2140, 1600, 1500, 1455, 1255.

Reaction of triphenylmethyl perchlorate and 51 in CH_2Cl_2

Compound 51 (49 mg, 0.155 mmol), 51 mg of internal standard and 0.5 mL CH_2Cl_2 were mixed in a NMR tube. Triphenylmethyl perchlorate (40 mg, 0.117 mmol) in 1 mL CH_2Cl_2 was added slowly to the NMR tube at 0°C. GC analysis only showed the formation of triphenylmethane and some unreacted starting material 51.

Synthesis of 1,1,2,2-tetramethyl-2-triphenylmethyl-disilane, 52,



$Ph_3C\text{-}\overset{\backslash /}{Si}\text{-}\overset{\backslash /}{Si}\text{-}H$

Triphenylmethyl anion was generated by mixing (5.0 g, 0.205 mol) of triphenylmethane and 0.0246 mol of *n*-butyllithium in Et_2O/THF at room temperature (98). This anion was quenched by 1,2-dichloro-1,1,2,2-tetramethyldisilane (4.0 g, 0.0214 mol). Subsequent lithium aluminum hydride reduction afforded a mixture of 52 and triphenylmethane (50:50 ratio) in 55% yield. 52: ^1H NMR δ 0.31 (d, 4.3 Hz, 6 H), 0.53 (s, 9 H), 3.90 (hep, 4.3 Hz, 1 H), 7.40 (m, 15 H); ^{13}C NMR δ -6.47, -3.33, 128.31, 128.99, 129.51, 133.88. IR 3065, 3030, 2960, 2900, 1600, 1495, 1450, 1395, 1250.

Reaction of triphenylmethyl perchlorate and 52 in CH_2Cl_2

Compound 52 (240 mg, 0.666 mmol), 230 mg of internal standard and 1 mL of CH_2Cl_2 were mixed in a 5-mL round-bottom flask. Triphenylmethyl perchlorate (80 mg, 0.233 mmol) in 2 mL of CH_2Cl_2 was added slowly to the flask at 0°C. GC analysis only showed the formation of triphenylmethane and some unreacted starting material <u>52</u>.

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