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Synthesis, Reactivity and Stereochemistry of Silacyclohexanes and Their Derivatives.

Binh Thanh Nguyen
Louisiana State University and Agricultural & Mechanical College

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SYNTHESIS, REACTIVITY AND STEREOCHEMISTRY OF SILACYCLOHEXANES AND THEIR DERIVATIVES

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SYNTHESIS, REACTIVITY AND STEREOCHEMISTRY OF
SILACYCLOHEXANES AND THEIR DERIVATIVES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agriculture and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Binh Thanh Nguyen
December 1985
To my mother, my family,
and
the memory of my father...
"...he who knows and understands Grignard reactions has a grasp of organic chemistry..." and "...every chemist has carried out the Grignard reaction at least once in his lifetime...".

M. S. Kharasch and T. Urbanski
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ABSTRACT

A number of 1,5-dibromoalkanes have been prepared by using the von Braun degradation method. The ring closure reaction of the diGrignard reagents derived from 1,5-dibromoalkanes and dichlorosilane derivatives were carried out to give C-methylated 1-methyl-1-silasubstituted-1-silacyclohexanes. Since C-methylated 1-chloro-1-substituted-1-silacyclohexanes were available as a mixture in which one isomer predominated greatly, reaction stereochemistry was studied.

The stereochemistries of a number of nucleophilic displacement reactions of C-methylated 1-methyl-1-silasubstituted-1-silacyclohexane have been investigated. Inversion of configuration was observed upon reduction with LiAlH$_4$ in ether, of the chloride, bromide, fluoride and also upon displacement of chloride and fluoride with organometallic reagents such as PhLi and PhMgBr. Methylation of these halosilane derivatives afforded C-methylated 1,1-dimethyl-1-silacyclohexanes. Free radical chlorination and bromination of these methylsilane derivatives gave the corresponding halomethylsilanes with retention of configuration. These stereospecific reactions converted Si-Cl derivatives from a mixture in which one of the two isomers predominated into a mixture in which the other
isomer predominated. Fluorination of chloro- and bromo-
silane; derivatives afforded the corresponding fluoro-
methylsilanes, inversion of stereochemistry was observed.  
The reaction of C-methylated 1-methyl-1-phenyl-1-
silacyclo-hexanes with bromine in carbon tetrachloride  
gave C-methy-lated 1-bromo-1-methyl-1-silacyclohexane with  
inversion of stereochemistry. These bromosilanes  
isomerized to an equilibrium mixture in the presence of an  
excess of bromine.

The conformational energies of C-methylated 1-methyl-
1-silacyclohexane were studied by using MM2 force field  
calculations. The cis/trans isomerization of these  
methylsilane derivatives catalyzed by a small amount of  
nucleophilic reagent such as NH$_4$HF$_2$ and CsF was also  
studied. The experimentally determined equilibrium  
mixture was comparable to that calculated by the force  
field method, and also agreed with the results obtained  
from the direct cyclization.

The ring enlargements of five-membered ring sila-
cyclopentanes containing an exocyclic chloromethyl group  
on silicon to a six-membered ring silacyclohexane in the  
presence of a nucleophilic reagent such as fluoride anion,  
or under thermolysis condition were investigated. The  
carbon center which migrates from silicon to the alpha-
carbon in the ring enlargement is the secondary rather  
than the primary carbon center.

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CHAPTER I: INTRODUCTION
I-1. Review of Preparations of Silacyclohexanes:

The study of organosilicon chemistry began in 1863 when Friedel and Crafts prepared tetraethylsilane from diethylzinc and silicon tetrachloride. A great impetus was provided at the turn of century when Kipping and others applied the newly discovered Grignard reagent to the synthesis of organosilicon compounds.

The present dissertation concerns cyclic organosilicon compounds, examples of which have been known for a long time. A recent review of cyclic organosilanes has appeared, and hence the present introduction will treat mainly recent advances and those most relevant to the current work.

The first report in the chemical literature of cyclic organosilicon compounds appeared as early as 1887, when Hart claimed to have prepared cyclotrimethylenedichlorosilane and "ortho"-diphenylenesilane, by sodium condensations from organic halides and silicon tetrachlorides. These compounds were poorly characterized in
his original paper. Widdowson, who carefully repeated Hart's work, was unable to isolate any traces of these organo-silicon compounds. He concluded that Hart's compositions were mixtures and that compounds 1 and 2 should be stricken from the literature.³

The first cyclic organosilicon compounds, therefore, were 1,1-dichlorosilacyclohexane and its dimethyl and diethyl derivatives, prepared by Bygden in 1915.⁴,⁵ This compound was prepared by the reaction of the diGrignard reagent prepared from 1,5-dibromopentane and silicon tetrachloride:

The 1-alkyl-1-silacyclohexanes have also been prepared directly by Bygden's procedure, using mono- and di-alkyldichlorosilanes⁶ reacting with the diGrignard reagent derived from 1,5-dibromopentane ³. It is interesting to mention that in situ reaction of dimethyl-dichlorosilane, 1,5-dibromopentane and lithium affords 1,1-dimethyl-1-silacyclohexanes, but none of this product is formed from preformed Li(CH₂)₅Li under similar conditions.⁷
Anteunis and his co-workers, 1978, reported the preparation of dimethylsubstituted silacyclohexanes from 1,5-dibromo-3,5-dimethylpentane with silicon tetrachloride and magnesium followed by reduction with lithium aluminum hydride to give 3,5-dimethyl-1-silacyclohexane:°

\[
\text{Me} \quad \text{Me} \quad \text{Me} \quad \text{SiCl}_4 \quad \text{Me} \quad \text{Me} \quad \text{SiSiCl}_2
\]

The main disadvantage in the preparation of silacyclohexanes via the Grignard cyclization route is the limited number of functional groups that can be introduced into the ring or on silicon.

Silicon heterocycles can also be synthesized by intramolecular hydrosilylation reactions. Kobrakov and his co-workers reported that the addition of dimethylsilane to 1,5-hexadiene, in the presence of chloroplatinic acid catalyst, gave 1,1-dimethyl-1-silacycloheptane as major product and 1,1,2-trimethyl-1-silacyclohexane as a minor product:
Other dialkylsilanes were also added to 1,5-hexadiene. Later they found two isomers, 1,1-dimethyl-1-silacyclohexane 5 and 1,1,2-trimethyl-1-silacyclopentane 13, in a 1:9 ratio from ring closure of 5,5-dimethylsilyl-1-pentane 12:

With an appropriately substituted silane, the ring closure reaction results in a silacyclopentane in preference to the expected silacyclohexane.

Fessenden and Kray\(^\text{10}\) reported that the treatment of 5-dimethylsilyl-1-hexene with chloroplatinic acid catalyst in pentane gave a mixture of cis- and trans-
1,1,2,5-tetramethyl-1-silacyclopentane 15 and a trace of 1,1,2-trimethyl-1-silacyclohexane 10:

Swisher and Chen\textsuperscript{11} investigated the overall yield and isomer distributions for the ring closure of \(\omega\)-dimethylsilyl-1-alkenes (\(\text{CH}_2=\text{CH}-(\text{CH}_2)\text{n-SiMe}_2\text{H}\), \(\text{n}=0-6\)) with chloroplatinic acid. They found that when \(\text{n}=3\), the two products 1,1-dimethyl-1-silacyclohexane 5 and 1,1,2-trimethyl-1-silacyclopentane 13 were formed in a 1:9 ratio:
Sakurai and his co-workers also investigated the ring closure of (4-pentenyl)hydrosilanes in the same way with several transition metal salt catalysts, such as $\pi$-C$_5$H$_5$Co(CO)$_5$, [(C$_2$H$_2$)$_2$RhCl]$_2$, (Ph$_3$P)$_4$RhCl.$^{12}$

These ring closure reactions probably follow the mechanism for hydrosilylation as proposed by Chalk and Harrod.$^{13}$ (Scheme 1). Both Si-metal and Si-carbon bonds are involved. The seven-membered intermediate $^{22}$ leading to six-membered ring product $^5$ is apparently less favorable than the six-membered intermediate $^{21}$ leading to five-membered ring product $^{13}$. 

\[ 
\begin{align*}
\text{a- } R_1 &= R_2 = \text{Cl} \\
\text{b- } R_1 &= R_2 = \text{Me} \\
\text{c- } R_1 &= R_2 = \text{Ph} \\
\text{d- } R_1 &= \text{Et}; R_2 = \text{Cl} \\
\text{e- } R_1 &= \text{Ph}; R_2 = \text{Cl}
\end{align*} \]
It should be mentioned that in the hydrosilylation reaction in the presence of $\text{H}_2\text{PtCl}_6$, the silicon is generally added to the terminal carbon of the alkene. Hydrosilylation follows a similar regiochemistry as hydroboration, and cis addition is the usual result. Thus, a deviation from normal regiochemistry is observed when hydrosilylation results in ring closure, presumably because the C-Pt-Si fragment is part of a ring.
Silacyclohexane can also be prepared by cyclization of α-, or γ-silyl carbon radicals. Wilt reported the reduction of (chloromethyl)dimethyl-3-butenylsilane, which was synthesized by the procedure of Connolly and Fryer, and (3-bromopropyl)-dimethylvinylsilane, which was prepared by treatment of vinylmagnesium bromide in ether with one equivalent of (3-bromopropyl)trichlorosilane followed by methylation with two equivalents of methylmagnesium bromide in ether, using tributyltin hydride (TBTH) as the reducing agent and in varying ratio of reactants. Both halides were readily reduced in hexadecane solvent at 25°C at 366 nm using azobis-(isobutyronitrile) (AIBN) as an initiator. The course of the reaction is shown below:
The yield of the silacyclohexane was not very high. The yield of rearrangement product (cyclization) was increased by increasing the concentration of TBTH. Wilt determined the relative rates of cyclization to form five- and six-membered rings in the following sequence:

The cyclization of the alpha silyl carbon radical is unusual in that $k_5 \ll k_6$, a result in strong contrast to the all-carbon system.\(^{16}\) Cyclization was "normal," however, for the isomeric gamma silyl radical. Further studies have now afforded data on the beta silyl analogue and on the kinetic control of these cyclizations. Table 1 shows the data, using the all-carbon system \(1^*\) for reference.
Table 1

<table>
<thead>
<tr>
<th>Radical</th>
<th>% cyclization</th>
<th>$k_5$</th>
<th>$k_6$</th>
<th>$k_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>55</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\alpha$ 1*</td>
<td>5.5</td>
<td>0.03</td>
<td>4.0</td>
<td>7.9</td>
</tr>
<tr>
<td>$\beta$ 1*</td>
<td>2.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma$ 1*</td>
<td>3.0</td>
<td>33</td>
<td>1.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Ingold and his co-workers, 1983, examined the radicals formed during photolysis of di-t-butyl peroxide and a number of alkenyldimethylsilanes by e.s.r. spectroscopy. Only carbon-centered radicals were observed. There were either secondary alkyl radicals formed by the addition of the initially formed silyl radical to a double bond or allyl radicals formed by hydrogen atom abstraction from the alkenyl group. In most cases addition to the double bond was an intermolecular process. However, pent-4-enylsilyl radicals undergo intramolecular addition with endo cyclization to form the six-membered ring:

![Chemical structure](image)
This preference was confirmed by product studies on 3,3-dimethylpent-4-enyldimethylsilane. This result along with the work of Wilt allows an extension of the Baldwin-Beckwith rules for kinetically controlled homolytic cyclization to species in which the radical center is located on a second row element. An explanation will require consideration of the stereoelectronic consequences for the potential (rival) transition states of: i- the increased bond lengths involved; ii- any alteration in the configuration at the radical center; and iii- intramolecular steric factors, conformational factors; and ring strain. An analysis of these factors has not appeared in the literature.

Nametkin and his co-workers reported that 1-chloromethyl-1-methyl-1-silacyclopentane undergoes skeletal rearrangement under the influence of AlCl₃, as a result of which 1-chloro-1-methyl-1-silacyclohexane was formed in more than 90% yield:

He also reported that the reaction for the expansion of silicon-carbon heterocycles of the above indicated type
can also take place under the influence of nucleophilic reagents (sodium methylate; sodium or potassium hydroxide in methyl alcohol). As in the first case with AlCl₃, the reaction is exothermic and proceeds at high speed:

This route suffers from the fact that considerable disiloxane is also formed in the reaction.

The cyclic α-silylketone, 2,2-dimethyl-2-silacyclohexanone, was prepared via 3,3-diphenyl-3-silacyclohexene which has been synthesized from the reaction of trichlorosilane and 5-chloro-1-pentyne in the presence of peroxide. The conditions are known to favor trans addition, hence the formation of the desired cis alkene:
Since the isomer could not be easily separated, the mixture of trichlorosilanes was converted to phenylchlorosilyl derivatives with phenyllithium, and the cis/trans mixture of 1,1-diphenylchlorosilyl-5-chloro-1-pentenes 39 was cyclized using sodium metal in refluxing toluene to give 3,3-diphenyl-3-silacyclohexene 40 in 50% yield. Hydroboration-oxidation of 40 gives predominantly 41 because boron becomes attached to the carbon adjacent to the silicon:
Oxidation of this product 41 with chromium trioxide in acidic medium gives mainly cleavage product 43. However, oxidation with dicyclohexylcarbodiimide (DCC) in DMSO gave 2,2-diphenyl-2-silacyclohexanone 42, the first reported cyclic alpha silylketone, but the yield was not very good (5%).

A more successful route to the 2-silacyclohexanone is the dithiane synthesis, first applied to silylketones by Brook and his co-workers,23 involving the synthesis of intermediate disubstituted spirodithianes and their hydrolysis to give alpha-silylketone derivatives24.

Soderquist and his co-workers reported recently the synthesis of 4,4-dimethyl-4-silacyclohexanone 48 via a boracyclic intermediate.25 The hydroboration of
divinyl(dimethyl)silane 44 using 9-borabicyclo[3.3.1]nonane (9-BBN) gives a single 1,5-diboryl adduct 45. An exchange reaction of this adduct with borane-methyl sulfide complex (BMS) gives, after methanolysis, the corresponding B-methoxy-4-silaborinane product 47 isomerically pure in 80% isolated yield. This product can be converted to 4,4-dimethyl-4-silacyclohexanone 48 in 67% isolated yield by the use of Brown's DCME (α,α-dichloromethyl methyl ether) reaction:26
Reduction of 48 with LiAlH₄ in ether affords the gamma-alcohol 49 in 66% yield, whereas the oxidation of 48 with selenium dioxide in t-butyl alcohol,²⁷ or 2,3-dichloro-5,6-dicyanobenzoquinone (DBQ)²⁸ gave dienone 50 in 60% yield.

Soderquist and Hassner also reported the preparation of 3,5-dimethylated-4,4-dimethyl-4-silacyclohexanone 52 using a cyclic hydroboration.²⁹ The hydroboration of di(α-methylvinyl) dimethylsilane 51 with BMS gave 4-silaborinane, which was reacted with DCME then with H₂O₂/OH to give 3,4,4,5-tetramethyl-4-silacyclohexanone 52 in 40% yield (cis/trans = 55/45). On the other hand, the hydroboration of di(α-methylvinyl)dimethylsilane with the thexylborane³⁰ and cyanoborate process³¹ gave the same product 52 in 38% yield (cis/trans = 59/41):

A one-pot hydroboration/cyanoborate process gave moderate yields of silacyclohexanones, thus providing
another route to several such compounds in addition to those previously reported.  

In the course of the studies on C/Si-bioisosterism a large number of sila-substituted drugs (C/Si-exchange, sila-drugs) has been synthesized and investigated pharmocologically in comparison with their corresponding carbon analogues. Tacke and his co-workers reported the first systematic microbiological transformations of organosilicon compounds. In these studies he has performed the enantioselective microbiological reduction of 2,2-dimethyl-2-silacyclohexanone 53:  

\[
\begin{align*}
\text{Kloeckera} & \quad \text{Corticis} \\
\text{Me} & \quad \text{ATCC 20190} \\
\end{align*}
\]

\[
\begin{align*}
\text{Si} & \quad \text{OH} \\
\text{Me} & \quad \text{H} \\
\end{align*}
\]

Although this research is still in its initial stages, several results have already been obtained showing the high synthetic potential of microbial transformations for organosilicon chemistry. An example is the enantioselective hydrolysis of racemic-55 by pichia pijperi leading to (1R, 2S)-56, which was isolated (separation from the non-reacted acetate (1S, 2R)-55 by chromatography) with an enantiomeric purity of >96% ee. This highly enantioselective hydrolysis is the first example of a
microbial transformation of an organosilicon compound leading to an optically active silane with silicon as asymmetric center.\textsuperscript{34}

\[ \text{Rac-55} \]

Moreover, the biotransformation of racemic 2-methyl-2-phenyl-2-silacyclohexanone \textsuperscript{57} by \textit{Saccharomyces uvarum} is reported, which leads inter alia to the compounds indicated in the following equation:\textsuperscript{35}

\[ \text{57} \rightarrow \text{58} + \text{59} \]
Tacke demonstrated that microbiological transformations may have a high synthetic potential for organosilicon chemistry, especially for the synthetic of optically active organosilicon compounds.

I-2. Stereochemistry and Mechanism at Silicon in Acyclic and Cyclic Systems:

The position of silicon in the upper center of the Periodic Table classifies it as the gentlest of metals. It possesses few of the metallic features of the heavier elements of its group, with only the slightest of tendencies to form stable divalent derivatives and conform with the inert pair effect. While silicon dissolves in aqueous alkali giving orthosilicates, it also generates hydrogen from hydrofluoric acid, thereby indicating distinct amphoteric behavior.

Similar behavior of boron and silicon--their diagonal relationship--stems in the main from the stability of bonds of both elements to oxygen and to fluorine. Both elements have the tendency to form anionic derivatives with electropositive metals, their derivatives readily hydrolyzing in acid to silanes and boranes. Much of the chemistry of silicon has therefore been considered in the light of an element only mildly metallic in character, and the study of organosilicon compounds was the prerogative
of organic chemists until Rochow introduced the inorganic silicate skeleton. The resurgence of organometallic chemistry with the discovery of ferrocene coincided with the commercial production of organochlorosilanes. Silicons were developed to supplement organic polymers, and inorganic chemists played an increasing role in developing the chemistry of substituted organosilicon compounds; e.g., $R_3SiX$ and $R_2SiX_2$ where $X \neq C$. The gamut of these compounds is now being used extensively by organic chemists as synthetic intermediates.

In introducing general features of the chemistry of silicon, comparisons can conveniently be drawn with carbon, particularly in the areas of reactivity and multiple bond formation. The multiple bonds to silicon involving $(p-p)\pi$ bonding have long been assumed to be weak, partly because the Si-X bond is much longer than the C-X one, thereby decreasing $\pi$-overlap. The weakness of the silicon-carbon double bond precludes competitive elimination in trimethylchlorosilanes by methoxide in sharp contrast to reactions with t-butyl chloride (Equation 1):

![Equation 1](image-url)
However, an increasing wealth of evidence is being amassed to support the transient existence of intermediates with multiple bonds to silicon from not only second period (carbon, nitrogen, oxygen) but also third period elements (silicon, phosphorus, sulfur). The Si-C bond energy in 1,1-dimethylsilene is estimated to be about 35 kcal/mol, which agrees with the structure recently measured by electron diffraction and by ion cyclotron resonance spectroscopy.\textsuperscript{37,38} Early attempts to synthesize silabenzene were thwarted by the reactivity of the polar silicon-carbon double bond. It has now been isolated in an argon matrix at 10K by the flash pyrolysis of substituted silacyclohexadienes 60 and 61, and the three bands observed in its UV spectrum fit into the series of bathochromic shifts observed with other donor substituted heterobenzenes (Equation 2). The resonance energy of silabenzene has been calculated as two thirds that of benzene.\textsuperscript{39,40}

\begin{equation}
\begin{array}{ccc}
\text{H} & \text{Si} & \text{O} \\
\text{H} & \text{Si} & \text{Me}
\end{array}
\xrightarrow{\Delta} \begin{array}{ccc}
\text{AcOH} & \text{\textbullet} & \text{\textbullet} \\
\text{\textbullet} & \text{\textbullet} & \text{\textbullet}
\end{array}
\xrightarrow{\Delta} \begin{array}{ccc}
\text{H} & \text{Si} & \text{H} \\
\text{H} & \text{C}_3\text{H}_6 & \text{Me}
\end{array}
\end{equation}

\text{Equation 2}
Silenes (carbon-silicon double bonds) have been generated as transient species, and their chemical behavior has been studied. The first stable disilene (silicon-silicon double bonds) produced was tetramesityldisilene, prepared by R. West (Figure 1).

Substitution at silicon is much easier than that at carbon. Attack by protic bases and by organic nucleophiles makes chlorosilanes excellent synthetic intermediates. This stems from the high rate of bimolecular nucleophilic substitution which typifies a third period element and which takes place with much poorer leaving groups than substitution at carbon. Thus the Si-F, Si-OR, Si-C and Si-H bonds can all be cleaved by an appropriate nucleophile. The facility of the above reactions, particularly hydrolysis, is in part due to the strength of bonds silicon forms with electronegative elements. The Si-F bond is one of the strongest encountered, with the
Si-O and Si-Cl bonds significantly stronger than the rest (Si-Br, Si-C, Si-H, Si-I, Si-Si, Si-N, Si-P). The extensive use of silicon compounds as synthetic intermediates in inorganic chemistry is based on the facile cleavage of Si-C, Si-N and Si-S bonds by chlorides of both main group and transition metals. Organic compounds, silylated at carbon or oxygen, can be readily regenerated using fluoride ion.

The extensive studies of Sommer and Eaborn, devoted to elucidating the mechanism of substitution at silicon have now led to close comparisons being made with substitution in phosphorus and organophosphorus derivatives by Corriu. Unlike carbon, optically active organosilicon species are not found in nature and, thus, are not directly available from natural sources. In the early 1900's, F. S. Kipping succeeded in making optically active organosilicon compounds, however, they were tedious to prepare, and the optical rotations were so feeble that stereochemical studies were impossible. The first convenient optically active organosilicon system, 1-naphthylphenylmethylsilanes, was prepared by Sommer and Frye in 1959. Since then several reports have been made on other optically active organosilicon compounds. They are of importance for the study of the stereochemical behavior of reactions at silicon centers.
Nucleophilic substitutions at silicon are found to be very stereoselective, occurring either with retention or inversion of configuration, and have been extensively studied. Sommer explained the characteristics of the reaction in two main ways:

* The $S_N^2$-Si mechanism for inversion.
* The $S_{Ni}$-Si mechanism for retention.

The $S_N^2$-Si mechanism is analogous to the $S_N^2$ reaction for carbon. Initial back-side attack leads to a transition state in which simultaneous bond-breaking and bond-making occur (Figure 2).

The entering group and the leaving group occupy the axial positions in a trigonal bipyramid, and the reaction proceeds with inversion of configuration.

The $S_{Ni}$-Si mechanism involves quasi-cyclic rate-controlling transition states which are generally four-centered, but also may be three-, five-, or six-centered. The entering group provides electrophilic assistance in the rupture of the Si-X bond (Figure 3), and
the reaction proceeds with retention of configuration at silicon:

![Figure 3: S₅ᵣ-Si Transition State (Four-centered mechanism)](image)

Sommer proposed an early rationalization which is sometimes known as the "leaving group" rule: with good leaving groups (the pKa of whose conjugate acid is less than 6) inversion is observed, and with bad leaving groups (the pKa of whose conjugate acid is more than 10) retention is observed. Later studies showed that many factors are important in determining the stereochemistry of substitution. These factors include the nature of organic groups on silicon, the attacking group, the solvent and the bond angle at silicon in addition to the nature of the leaving group.

The presence of extra-coordinate intermediates in reaction at silicon has been proposed innumerable times. Silicon, unlike carbon, possesses comparatively low lying vacant 3d orbitals. These 3d orbitals may stabilize
transition states or pentacoordinate reaction intermediates.\textsuperscript{56-59} These orbitals may thus provide a low energy pathway for nucleophilic displacements in which bond making precedes bond breaking.

One of the best studied examples of octet expansion is the hexafluorosilicate ion, in which X-ray crystallographic analysis\textsuperscript{60} revealed that six fluorine atoms are arranged octahedrally about silicon, implying 3s\textsuperscript{3}p\textsuperscript{2}d\textsuperscript{2} hybrid bonds. Species such as Na\textsubscript{2}Si(CH\textsubscript{3})F\textsubscript{5} probably contain related anions.\textsuperscript{61}

Several types of compounds in which silicon is pentacoordinated are known, including the pioneering work of Klanberg and Muetterties on the pentafluorosilicates, SiF\textsubscript{5}, RSiF\textsubscript{4}, R\textsubscript{2}SiF\textsubscript{3},\textsuperscript{62} and the anion of bis(O-phenylenedioxy)organoaluminumic acid.\textsuperscript{63} Farnham and Harlow reported the spiroaluminumate anions.\textsuperscript{64} McPhail reported a novel five-membered oxygen-, silicon-, and nitrogen-containing heterocycle (O-Si)-chloro-[(N-chlorodimethylsilacetalaminomethyl)methyl]-dimethylsilane.\textsuperscript{65} The intramolecular coordination between Si and N in the triptych-siloxazilidines (known as the biologically potent silatrane)\textsuperscript{66,67} leads to pentacoordination. A new class of organosilicon compound containing a pentacovalent silicon atom, (aryloxymethyl) trifluorosilane was reported by Voronkov.\textsuperscript{68} Recently, two more types of compounds pentacoordinate at silicon were found by Schmidt,\textsuperscript{69} 1,5,5-trimethyl-1-aza-5-silabicyclo
[3.3.0]octane, and 1-aza-5-sila-5-methyltricyclo[3.3.3.0]undecane, and by Pestunovich,\(^7\) \(\beta\)-trifluorosilylorganyl(trifluorosilyl)ethyl sulfoxides.

While there are many known examples of pentacoordinate silicon compounds, it is not clear whether the formation of 5 full bonds to silicon commonly occurs during substitution at silicon. Proposals of 5-coordinates are usually made when the leaving groups attached to silicon are poor.

The role of carbocations, \(R_3C^+\), as reaction intermediate is well documented (\(S_N1\) mechanism).\(^7\) In such reactions that are unquestionably first-order, the carbon atom attached to the leaving group undergoes racemization. Currently \(R_3Si^+\), silyl cations, are not believed to be intermediates in reactions in solution.\(^7\) Increasing the electron donating ability of an aryl substituent on silicon in an attempt to stabilize a silyl cation actually slows down the substitution rather than increasing its rate.\(^7\) There is a special case of a stable silyl cation formed in the reaction of tri(isopropylthio)silane with trityl perchlorate. The tri(isopropylthio)silyl cation in solution was characterized by Lambert and Schult\(^7\) (Equation 3):

\[
(i-PrS)_3SiH + Ph_3C^+ClO_4^- \rightarrow Ph_3CH + (i-PrS)_3Si^+ClO_4^-
\]

Equation 3
Silicon heterocycles have been useful in studying the effects of the organic groups attached to silicon on the stereochemical path of reactions at silicon. The reactivity of sila-substituted rings decreases as the ring size increases so that organometallic nucleophiles react with the chloride, fluoride, and methoxide derivatives 62, 63, 64 with increasing slowness as indicated below:

\[
\begin{align*}
62 & \quad 63 & \quad 64 \\
\end{align*}
\]

The silanes below undergo base-catalyzed hydrolysis increasingly slowly in the order shown.

\[
\begin{align*}
65 & \quad 66 & \quad 67 & \quad 68 \\
\end{align*}
\]

This order of reactivity contrasts sharply with that of the carbon analogs, viz. open chain \( \gg \) cyclopentyl \( \gg \) cyclohexyl \( \gg \) cyclobutyl for \( S_N^2 \) halide exchange.
The bridgehead silanes 71 and 72 are more reactive to base-catalyzed ethanolysis than is triethylsilane. The 1-chloro-1-silabicyclo[2.2.1]heptane 69 is more reactive than the chloro-substituted "adamantyl" silane 73.76,77 Again the small ring is more reactive. Indeed the Cl in 69 is at a bridgehead, and chlorine at the bridgehead of the carbon derivatives is inert:

![Chemical structures](image)

Compound 69 is highly reactive toward both hydrolysis and reduction with lithium aluminum hydride. Comparisons of
the bicycloheptane system with others showed the general trend in reactivity illustrated below:  

\[
\text{Si-Cl} \quad \text{[Me}_3\text{SiCH}_2)_3\text{SiCl} \quad \text{Cl} \quad \text{Me} \quad \text{Si} \quad \text{Me}
\]

The silicon atoms in both the tetrasilaadamantane system and the bicycloheptane system are unable to undergo back-side displacement due to the constraints imposed by the rings. The major difference in these systems lies in the degree of angle strain at silicon.

Our concepts about nucleophilic substitution at silicon have been extensively expanded by recent work, mainly from the laboratories of R. J. P. Corriu. His results show that the stereochemistry is mainly controlled by the following two factors:

(i) When leaving group is replaced by a nucleophile, an increase in the leaving ability leads to a change of the stereochemistry towards inversion, as indicated below: Cl, Br > SR, F > OR >> H predominant stereochemistry: \( \text{IN} \rightarrow \text{RN} \).
(ii) For a given leaving group the stereochemistry is extremely sensitive to the nature of the reagent. Nucleophiles in which the negative charge is highly delocalized lead mainly to inversion, whereas charge-delocalized reagents favor retention.81

Concerning the influence of the structure of the organosilane, the stereochemical patterns reported for optically active 1-naphthylphenylmethyilsilane78 can generally be extended to other acyclic R3Si-X systems illustrated below:

\[
\begin{array}{ccc}
\text{Ph} & \text{Ph} & \text{C6F5} \\
| & | & | \\
\text{1Np-Si-X} & \text{Me-Si-X} & \text{Me-Si-X} \\
| & | & | \\
\text{R} & \text{R} & \text{R} \\
\end{array}
\]

R = Me, Et, i-Pr, R = t-Bu, i-Pr, Et, R = 1Np
Vi82 Ph3Si, Ph3Ge83-84 Ph10,48,79b

Examination of the structures of the above optically active silanes shows that the R groups attached to silicon cover a significant range in their polar and steric effects. The following observations are made:

(i) Concerning possible steric effects on stereochemistry, it seems clear from the results with the above systems that the presence of R groups of moderate to large steric requirements leave stereochemistry unchanged.
(ii) Comparison of 76 and 78 is especially interesting. Steric effects in these systems must be about the same, but the pentafluorophenyl group is known to have a very powerful electron withdrawing effect relative to phenyl. Nevertheless, a thorough study of the stereochemistry of reactions of 78 shows that it does not differ from 76 to any significant degree.

For the silacarbocycles, the structures in which silicon is part of a ring, particularly a strained ring, show stereochemical behavior which is strongly influenced by the geometry of the substrate. The following compounds 79, 80, 87 82, 83, 90 84, 91 and 63, 92 (Figure 4) demonstrated important changes of stereochemistry compared with those for acyclic silanes such as 85.

The most significant observations have the following implications:

(i) Increased angle strain at silicon always leads to a change in the stereochemistry towards retention. This trend is most marked in the case of the most strained systems 79, 80, and 81. Both silacyclobutanes 79 and 80 (angle C2-Si-C4 = 75-80°) react with retention, whatever the nature of the nucleophile. Even coupling reactions between 79 (Si-Cl) and LiAlH4 or Grignard reagents (R=p-MeOC6H4) occur with complete retention of configuration; whereas, the same reactions in the case of 85 (Si-Cl) occur with complete inversion. In a non strained ring
Figure 4
system such as 82, and in the acyclic 85 (Si-Cl), the coupling reactions between Si-Cl and LiAlH₄ or PhLi take place with inversion of configuration. In 81 (angle C₂-Si-C₅ = 92-94.6°)⁹⁴ the Si-Cl bond is also cleaved by LiAlH₄ with inversion of configuration.

(ii) In 81 and 8₂ (angle C₂-Si-C₆ = 106.5°),⁹⁵ and 6₃ (angle C-Si-C = 103.5°),⁹⁶ the coupling reactions of Si-F with LiAlH₄ show a nonstereospecific reaction rather than giving racemic products.

The strained ring of 7₉ (Si-F) leads to a coupling reaction with LiAlH₄ which shows retention of configuration at silicon; whereas, in the non strained acyclic 8₅ (Si-F), the same reaction proceeds with inversion of stereochemistry.

(iii) The cleavage of the Si-OR bond of 7₉, 8₀, 8₂ and 6₃, with LiAlH₄ gave retention of configuration; however, in the case of 6₃ Si-OR was cleaved to give a racemic product.

(iv) Even a small angular strain suffices to cause a stereochemical change. Compound 6₃ shows significant deviations compared to 8₅ (R₃Si-X) (angle C-Si-C = 109°).⁹⁷ Compound 6₃ (with X=Cl) reacts with alkyl-lithiums with complete retention compared with inversion for R₃Si-Cl.

(v) It is necessary to note that the cyclic strain does not change the factors which mainly govern the
stereochemistry at silicon, i.e. the nature of the leaving group and the electronic character of the nucleophile. The stereochemistry changes from inversion to retention on going from Si-Cl to Si-H. The cyclic strain acts as an additional factor favoring displacement of the stereochemistry towards retention.

In general, the nature of substituents attached to silicon must be taken into account; compared with alkyl groups, aryl groups change the nature (i.e. the hybridization) of the Si-X bond, and thus slightly influence the stereochemistry. This influence cannot be easily explained in terms of geometric considerations. In particular the ring strain does not provide an explanation of why inversion is so disfavored in the case of the six-membered ring. Thus, the better explanation is that proposed by Nguyen Trong Anh and Minot, which involves a change of the hybridization of the Si-R bonds around the tetracoordinated silicon atom (Figure 5).

Figure 5
If the R₂SiR₃ angle becomes smaller than the tetrahedral value, the R₁SiX angle becomes larger than 109.28°. The four hybrid atomic orbitals of silicon are no longer equivalent. The two used for making the SiR₂ and SiR₃ bonds have less s character than a sp³ hybrid orbital, while the two remaining atomic orbitals acquire more s character. Nguyen and Minot show from molecular orbital calculations that an increase in the s character implies an easier nucleophilic frontside attack at the σ*-Si-X, and, therefore, a greater proportion of retention. It follows that if the silicon atom is included in a strained ring while X remains exocyclic, the percentage of the retention will increase. Similar reasoning shows that if Si and X are both in the ring, inversion is favored. These conclusions agree well with the experimental data.

The majority of optically active organosilicon compounds so far prepared have at least one bond between an aromatic moiety and silicon. Such a structure is often inconvenient for stereochemical research of certain reactions in which the bond of silicon to aromatic groups cleaves or forms. Cleavage of the bond of silicon to aromatic groups with electrophiles (desilylation) and substitution reactions of silyl radicals on an aromatic nucleus (homolytic aromatic silylation) are examples of such reactions. Moreover, accurate measurement of optical
activity requires a large amount of pure sample. In some cases, separation of optically active products from a reaction mixture is infeasible because of extensive racemization. 101

Silicon heterocycles have played an important role in the development of organosilicon chemistry. In the past ten years, in the Cartledge group, the reactivities and the reaction stereochemistry of silacycloalkanes such as 1,2-dimethyl-1-silacyclobutane and 1,2-dimethyl-1-silacyclopentane and their derivatives have been investigated. The stereochemistry of a number of 1-substituted 1,2-dimethyl-1-silacyclobutanes has been studied. Retention of configuration was observed upon reduction with lithium aluminum hydride in ether, or methoxide, fluoride and chloride derivatives, and upon displacement of chloride with Grignard reagent. In the study of the effect of the ring strain in the reaction at silicon, derivatives of 1,2-dimethyl-1-silasubstituted-1-silacyclopentane were prepared in order to investigate the role of ring strain in determining the stereochemical path of reactions. The silyl chloride, fluoride, and hydride were prepared and their reaction stereochemistry was compared to that observed for the more strained silacyclobutane system. Some nucleophilic displacement reactions studied occurred with inversion of stereochemistry at silicon in the five-membered ring as has previously been observed with acyclic
system. Only retention occurs in the four-membered ring. The silacyclopentane system was also used to study further the mechanism of isomerization at silicon catalyzed by polar aprotic solvent.

With the purpose of continuing to study the sila-heterocycle systems, monomethylated and dimethylated 1-methyl-1-silasubstituted-1-silacyclohexanes and their derivatives have now been prepared. Methylated 1-methyl-1-substituted-1-silacyclohexane derivatives represent unstrained ring systems, and would be useful in determining the stereochemistry of reactions at silicon centers. Comparisons of the reactions of this system with unstrained systems such as those of Corriu, Sommers, and Sakurai and with the strained ring system of silacyclopentanes of Cartledge and Mazerolles and silacyclopentanes of Cartledge should result in a clearer understanding of the effect of strain on the mechanisms of reactions at silicon.

The next section will describe the synthesis of these C-methylated 1-methyl-1-substituted-1-silacyclohexanes. The results of the stereochemical studies of these silacyclohexanes with a number of reagents will be reported in the subsequent sections.
CHAPTER II: RESULTS AND DISCUSSION
II-1. Introduction:

As previously mentioned, stereochemical studies using silacyclohexanes involve geometrical isomers, whereas the 1-naphthylphenylmethylsilyl derivatives\(^{48}\) which have been widely used involve chirality. The methylated 1-methyl-1-substituted-1-silacyclohexanes and their derivatives were chosen in order to study the stereochemical reactions at silicon, conformational preferences, the interrelationship between structure and reactivity, and because they are potentially more advantageous for stereochemical studies. These systems seemed suitable since the relative positions of the methyl groups afford the formation of geometrical isomers. Since the changes in stereochemistry at silicon would result in interconversion of geometrical isomers which differ in spectral properties, methods other than measurement of optical rotation could be used to follow the reaction at silicon. These systems would, therefore, be easier to study than the systems using optical isomers that were investigated by other workers.\(^{48,90,92}\)

II-2. Results and Discussion:

II-2-1. Preparation of Dibromides:

The synthesis of silacarbocycles usually involves the reactions of diorganometallic reagents with an appropriate
dichlorosilane as is shown for the generalizes case in Scheme 2.

The limitations of this approach include potential difficulties in the synthesis of the appropriate organic halide precursors.

For silacyclohexane and its derivatives 1,5-dibromoalkanes are required, and a number of these dibromo compounds have been prepared in the present work by using the von Braun degradation.\textsuperscript{102} The procedure has been known for many years but has been seldom employed as a route to dibromoalkanes, perhaps because it appears on the surface to be a more involved synthetic route compared with ring opening of cyclic ethers. The von Braun degradation is particularly useful to prepare 1,5-dibromoalkanes because variously substituted piperidines are readily available and ordinarily cheap compared to substituted tetrahydropyrans. Consequently the method is attractive even though
yields are usually lower than in the cyclic ether ring opening with concentrated sulfuric acid or 48% hydrobromic acid. The von Braun reaction involves the treatment of an N-substituted benzamide with phosphorus pentahalides to given an alkyl halide, or alkylene halide, benzonitrile, and phosphoryl halide. This results in a one pot removal of nitrogen from a heterocycle. The von Braun degradation is illustrated below (Equation 4):

![Chemical equation]

Equation 4

The benzamide can be made in essentially quantitative yield. Even with the somewhat crowded 2,6-lutidine, 83% yield of N-benzoyl-2,6-dimethylpiperidine was isolated. A decrease in yield of dibromoalkanes with increasing steric hindrance at the carbon alpha to the nitrogen is observed; for example N-benzoylpiperidine gave 65% yield of 1,5-dibromopentane, whereas N-benzoyl-2,6-dimethylpiperidine gave only 33% yield of 2,6-dibromohexane, and 2,2,6,6-tetramethylpiperidine gave no dibromoalkane product. The
reaction was carried out in two stages; isolating the benzamide in the first stage. The second stage of the von Braun degradation presumably involves nucleophilic attack of bromide on the carbon alpha to nitrogen of the piperidine ring (2-position). The diminution of yield of dibromoalkanes with increasing steric hindrance to approach at the carbon alpha to the nitrogen would be the behavior expected of a bimolecular nucleophilic substitution reaction. The mechanism for the von Braun degradation to give dibromoalkanes was suggested by Leonard and Nonmenson103 and by Fodor104 to be an $S_N2$ type displacement. A simultaneous attack of $PBr_4^+$ and $Br^-$ upon N-benzoylpiperidine leads to 5-bromoamyl-O-tetrabromophosphoryl benzimidoyl bromide and subsequent fragmentation yields benzonitrile, phosphoryl bromide and 1,5-dibromopentane. In the case of a more hindered carbon alpha to the nitrogen of the piperidine ring, the O-tetrabromophosphorylamide (type 87) could be converted to the benzonitrilium salt, which then dissociates into an alkyl cation and benzonitrile (Equation 5). The fate of that cation would then depend on its environment, giving rise to either an olefin or an alkyl bromide. This would account for the low yield of 2,6-dimethylpiperidine and no dibromoalkane from 2,2,6,6-tetramethylpiperidine. Even though yields were slightly lower with 2-methylpiperidine and low in the case of 2,6-lutidine, the route remains an
attractive one. The degradation step involves a vigorous exothermic reaction as bromine is added, and cooling is required, but there is no difficulty in carrying out the process on a large scale. The yields in the preparations of N-benzoylpiperidines and their subsequent degradation to prepare dibromoalkanes (Equation 6) are shown in Tables 2 and 3. For references to earlier preparations of these materials see the experimental section.
Equation 6

Table 2

Yields and boiling points or melting points
of N-benzoylpiperidines

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>b.p. °C/mm</th>
<th>m.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>86</td>
<td>96</td>
<td>181-182/10</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>93</td>
<td>180-181/10</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>94</td>
<td>204-205/10</td>
<td></td>
</tr>
<tr>
<td>97</td>
<td>92</td>
<td>202-203/10</td>
<td></td>
</tr>
<tr>
<td>98</td>
<td>83</td>
<td></td>
<td>110-111°C</td>
</tr>
<tr>
<td>99</td>
<td>88</td>
<td></td>
<td>114-116°C</td>
</tr>
</tbody>
</table>
Table 3

Yields and boiling points of 1,5-dibromoalkanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>b.p. °C/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>88</td>
<td>63</td>
<td>111-112/15</td>
</tr>
<tr>
<td>100</td>
<td>58</td>
<td>119-120/15</td>
</tr>
<tr>
<td>101</td>
<td>61</td>
<td>113-114/15</td>
</tr>
<tr>
<td>102</td>
<td>61</td>
<td>120-121/18</td>
</tr>
<tr>
<td>103</td>
<td>33</td>
<td>110-111/10</td>
</tr>
<tr>
<td>104</td>
<td>44</td>
<td>73-72/2</td>
</tr>
<tr>
<td>105</td>
<td>66</td>
<td>116-116/8</td>
</tr>
</tbody>
</table>

1,5-Dibromo-3,3-dimethylpentane 105, was prepared from 3,3-dimethylglutaric acid 106 following the method of Noller105 and Anteunis.8 Esterification of 106 with absolute methanol and concentrated sulfuric acid afforded dimethyl 3,3-dimethylglutarate 107. Reduction of the diester with LiAlH₄ in dry THF gave 3,3-dimethyl-1,5-pentanediol 108 in 95% yield. The latter compound was converted to the corresponding dibromide 105 in 66% yield by means of phosphorus tribromide (Scheme 3).

II-2-2. **Ring Closure Reactions:**

The ring closure reaction of 1,5-dibromoalkanes with dichlorosilane and magnesium turnings was carried out by using standard procedures at relatively high dilution. Comparable yields were obtained by mixing all of the reactants in one pot or by initial formation of the diGrignard
reagent, followed by addition to the dichlorosilane. Both diethyl ether and THF were used as solvent, and yields were ordinarily several percent higher in ether. Sonication was used, but had little effect on the yield of the product. Since all of the C-methylated 1-methyl-1-silasubstituted-1-silacyclohexanes so far prepared have a methyl group on silicon, and one on carbon, the two methyl groups are referred to as cis and trans, respectively. Throughout this dissertation, suffix $a$ is added to the cis and $b$ to the trans, as illustrated (Figure 6). The isomeric ratios are always reported as cis:trans.
1-Methyl-1-silacyclohexane and the C-methylated 1-silacyclohexanes were prepared from the diGrignard reagent of the corresponding 1,5-dibromoalkane and methyldichlorosilane (Equation 7) in anhydrous diethyl ether. The ring closure reaction resulted in an approximately 55:45
mixture of cis and trans 110; 50:50 for 111; and 52:48 for 112; however, attempts to separate these isomers were not successful. The yields, boiling points, and the cis:trans ratios of these silacyclohexanes as observed in the ring closure steps are listed in Table 4.

Table 4
Yields, boiling points and cis:trans ratios of C-methylated 1-methyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>cis/trans</th>
<th>b.p. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>109</td>
<td>68</td>
<td>117-116/760</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>43</td>
<td>55/45</td>
<td>62-63/65</td>
</tr>
<tr>
<td>111</td>
<td>53</td>
<td>50/50</td>
<td>55-56/71</td>
</tr>
<tr>
<td>112</td>
<td>60</td>
<td>52/48</td>
<td>56-58/71</td>
</tr>
</tbody>
</table>

Yields for the cyclization products were not high, which is not unusual for this type of reaction. The lowest yield was in the case of 110, where a methyl group is attached to the secondary carbon that presumably caused some steric hindrance to the formation of the C-Si bond. The yields of these reactions were decreased when the dilution with solvent was lower. This can be explained in Scheme 4.

1,5-diGrignard reagents 113 react with methyldichlorosilane to give 114 and 115, which can undergo S_N2-Si intramolecular cyclization to form 109, 110, 111 and 112;
Scheme 4

113

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\downarrow & \quad \downarrow \\
\text{Mg} & \quad \text{Mg}
\end{align*}
\]

\[
\text{MeHSiCl}_2
\]

114 + 115

\[
\begin{align*}
\text{R} & \quad \text{R} \\
\downarrow & \quad \downarrow \\
\text{MgBr} & \quad \text{SiCl} \\
\text{SiCl} & \quad \text{MeH}
\end{align*}
\]

\[
\text{MeHSiCl}_2
\]

\[
\begin{align*}
k_1(S_N^2-\text{Si Intra}) & \quad k_2(S_N^2-\text{Si Inter}) \\
\downarrow & \quad \downarrow \\
\text{R} & \quad \text{SiCl} \\
\text{SiCl} & \quad \text{MeH}
\end{align*}
\]

116

\[
\begin{align*}
\text{R} & \quad \text{MgClBr} \\
\downarrow & \\
\text{SiCl} & \quad \text{MeH} \\
\text{MeH} & \quad \text{MeH}
\end{align*}
\]

POLYMER

109 110 111 112
or they also can undergo S_N2-Si intermolecular substitution to form 1,7-disilyl derivative 106 which can polymerize. In high dilution, the rate of \( k_1[S_{N2-Si \text{ intramolecular}}] > k_2[S_{N2-Si \text{ intermolecular}}] \) so the cyclization is favored resulting in the cyclization products being the major ones. However, intermolecular substitution also took place slowly, resulting in the formation of low yields of polymers.

• Cis/Trans Assignment by Proton NMR:

  The cis and trans isomers of the methylsilanes 110, 111 and 112 can be identified even as a mixture by proton NMR, and spectral assignments made on the mixture were confirmed with the pure isomer of 110a. Compound 110a was obtained in almost pure form using the cyclization method already described. However, only one run resulted in nearly pure cis isomer, and several later attempts to repeat the reaction resulted in the cis/trans mixture. The structure of 110a was assigned from its proton NMR spectrum Figure 7 using \(-\text{CH-SiH-CH}_2-\) coupling constants. Irradiation of the Si-Me signal of 110a revealed \( J[\text{SiH(eq)-C}_2\text{H(ax)}] \), \( J[\text{SiH(eq)-C}_6\text{H(eq)}] \), and \( J[\text{SiH(eq)-C}_6\text{H(ax)}] \), to be 1.30, 1.35, and 1.53 Hz, respectively. An approximate Karplus-Conroy relationship between the vicinal coupling constants \( J[(\text{H})\text{Si-C(H)}] \) in a silaethane
Figure 7

$^1$H NMR spectrum of cis 1,2-dimethyl-1-silacyclopentane

SiH signal of 110a and SiH signal when irradiated at the SiMe signal of 110a
fragment and the corresponding torsional angle $\theta$ in silacyclohexanes has been proposed by Anteunis:

$$J(\theta) = 0.84 - 2.59\cos\theta + 5.83\cos^2\theta$$

The calculated dihedral angles derived from the coupling constants using the Anteunis equation are listed in Table 5 along with dihedral angles derived from MM2 force field calculations.

**Table 5**

Coupling constants for SiH-CH of cis 1,2-dimethyl-1-silacyclohexane and its dihedral angle

<table>
<thead>
<tr>
<th></th>
<th>$J$(Hz)</th>
<th>$\theta$(H NMR)</th>
<th>$\theta$(MM2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiHeq-CHeq</td>
<td>1.53</td>
<td>51°</td>
<td>47°</td>
</tr>
<tr>
<td>SiHeq-CHax</td>
<td>1.35</td>
<td>54°</td>
<td>50°</td>
</tr>
<tr>
<td>SiHeq-CHax</td>
<td>1.30</td>
<td>55°</td>
<td>70°</td>
</tr>
</tbody>
</table>

The value of $J[SiHeq-CHax]$ observed in 1,2-dimethyl-1-silacyclohexane is smaller than the $J[CHax-CHeq]$ observed for its carbon analogs, because of the longer Si-C bond (1.87 Å), compared to the C-C bond length of 1.55 Å in cyclohexane. The present analysis of the coupling constants in 110a may not be accurate for this complex system; thus, these coupling constants are not absolute values. However, the relative values are sufficient to assign the stereochemistry. In the trans isomers 110b the
proton on Si and that on C₂ will be diaxial, and MM2 calculations predict a dihedral angle of 172.73°. That angle predicts a coupling constant of 9.15 Hz. It should be noted that the relationship \( J[\text{SiCH}_3\text{ax-Heq}] > J[\text{SiCH}_3\text{eq-Hax}] \) is also true in the case of \( J[\text{C-CH}_3\text{ax-Heq}] \) and \( J[\text{C-CH}_3\text{eq-Hax}] \) in methylcyclohexane.

The Si-Me resonances are of course easily identifiable, as are Si-H resonances. The ring methyl groups generally appear as doublets rising out of the multiplet for the remaining ring protons. Stereochemical assignments have been made on the assumption that we can predict which isomer will have a predominantly equatorial methyl group, and that equatorial Me groups on silicon appear upfield from axial Me. The structures of the most stable conformations of the molecules prepared in this work are shown in Figure 8. The assignments agree with those of Murakami and Sakurai in the cis and trans isomers of 4-t-butyl-1-methyl-1-silacyclohexane and in many methylcyclohexane derivatives. In the spectra of mixtures of cis and trans, double irradiation was used to identify the Si-H signal which corresponded to the proton coupled to the methyl group. In all cases the upfield (predominant equatorial) Si-Me is coupled to the upfield (predominant axial) H on Si. The axial Si-H upfield from equatorial Si-H is also in agreement with the assignment of Murakami and Sakurai, as well as of
Carleer and Anteunis in 3,5-dimethylsilacyclohexane.\textsuperscript{106} In methylcyclohexane vicinal exocyclic $\text{H}_3\text{C}-\text{CH}$ couplings are larger when the ring proton is axial.\textsuperscript{106,107} In the C-methylated 1-methyl-1-silacyclohexane system the vicinal $\text{H}_3\text{C}-\text{SiH}$ couplings are virtually the same in the two isomers. Hence that criterion does not appear to be reasonable on which to base structural assignments. The relationships that are used for the assignment of stereochemical configurations are summarized in Table 6.

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Figure 8}
\end{figure}
\end{center}
Table 6

Chemical shifts and configurations of groups attached to the six-membered ring in chair conformations

<table>
<thead>
<tr>
<th>Group X</th>
<th>Cyclohexane-X&lt;sup&gt;108&lt;/sup&gt;</th>
<th>Methylsilacyclohexane-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Eq. upfield</td>
<td>Eq. upfield</td>
</tr>
<tr>
<td>OMe</td>
<td>Eq. upfield</td>
<td>Eq. upfield</td>
</tr>
<tr>
<td>H</td>
<td>Ax. upfield</td>
<td>Ax. upfield</td>
</tr>
<tr>
<td>JCHax-CHax 8-13 Hz</td>
<td>JSiHax-CHax 6.5 Hz</td>
<td></td>
</tr>
<tr>
<td>JCHax-CHeq 2-6 Hz</td>
<td>JSiHax-CHeq 1.7 Hz</td>
<td></td>
</tr>
<tr>
<td></td>
<td>JSiHeq-CHax 1.0 Hz</td>
<td></td>
</tr>
</tbody>
</table>

The cis and trans structures listed in Table 7 below were assigned assuming the relationships listed in Table 6.

Table 7

<sup>1</sup>H NMR data for 1-methyl-l-silacyclohexane and C-methylated-1-methyl-l-silacyclohexanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si-Me</th>
<th>Si-H</th>
<th>JSi (CH₃) (H) Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>109</td>
<td>0.090</td>
<td>2.900</td>
<td>3.742</td>
</tr>
<tr>
<td>110a</td>
<td>0.150</td>
<td>3.979</td>
<td>3.712</td>
</tr>
<tr>
<td>110b</td>
<td>0.078</td>
<td>3.790</td>
<td>3.653</td>
</tr>
<tr>
<td>111a</td>
<td>0.063</td>
<td>3.979</td>
<td>3.594</td>
</tr>
<tr>
<td>111b</td>
<td>0.106</td>
<td>3.993</td>
<td>3.572</td>
</tr>
<tr>
<td>112a</td>
<td>0.103</td>
<td>3.845</td>
<td>3.510</td>
</tr>
<tr>
<td>112b</td>
<td>0.062</td>
<td>3.774</td>
<td>3.490</td>
</tr>
</tbody>
</table>
The C-methylated 1-chloro-1-methyl-1-silacyclohexanes were prepared by the method described for the preparation of 110, except that methyldichlorosilane was replaced with methyl-trichlorosilane (Equation 8). These reactions were stereoselective and gave one isomer predominating over the other.

\[
\begin{align*}
\text{R}=\text{H} & \quad 88 & \quad 34 & \quad 120 & \quad 36 \\
\text{R}=\text{Me} & \quad 100-1\text{Me} & \quad 117-2\text{Me} & \quad 121-2\text{Me} & \quad 124-2\text{Me} \\
 & \quad 101-2\text{Me} & \quad 118-3\text{Me} & \quad 122-3\text{Me} & \quad 125-3\text{Me} \\
 & \quad 102-3\text{Me} & \quad 119-4\text{Me} & \quad 123-4\text{Me} & \quad 126-4\text{Me}
\end{align*}
\]

Equation 8

The silylchlorides 34, 117, 118 and 119 were the major products. The cis and trans isomers of the silyl chlorides could not be further separated by fractional distillation. The yields, ratios of cis and trans isomers and the boiling points of these silyl chlorides are reported in Table 8.
Yields, cis:trans ratios and boiling points of C-methylated 1-chloro-1-methyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>cis/trans</th>
<th>b.p. °C/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>69</td>
<td></td>
<td>110-111/95</td>
</tr>
<tr>
<td>117</td>
<td>44</td>
<td>30/70</td>
<td>92-93/50</td>
</tr>
<tr>
<td>118</td>
<td>60</td>
<td>70/30</td>
<td>94-95/50</td>
</tr>
<tr>
<td>119</td>
<td>60</td>
<td>30/70</td>
<td>94-95/55</td>
</tr>
</tbody>
</table>

The silyl bromides 120, 121, 122 and 123 were also isolated as minor products in the ring closures forming the silyl chloride. The yields, cis and trans isomer ratios, and boiling points are listed in Table 9.

Yields, cis:trans ratios and boiling points of C-methylated 1-bromo-1-methyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>cis/trans</th>
<th>b.p. °C/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>8-11</td>
<td></td>
<td>60-61/15</td>
</tr>
<tr>
<td>121</td>
<td>15-20</td>
<td>30/70</td>
<td>-</td>
</tr>
<tr>
<td>122</td>
<td>10-15</td>
<td>70/30</td>
<td>68-67/15</td>
</tr>
<tr>
<td>123</td>
<td>10-15</td>
<td>30/70</td>
<td>68-69/15</td>
</tr>
</tbody>
</table>

Furthermore, the reactions yielded small amounts of disiloxane products. In general the silyl bromides and the disiloxanes were not isolated but were identified by
GC/MS. The distribution of the yields of the products from Equation 8 are listed in Table 10.

**Table 10**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si-Cl</th>
<th>Si-Br</th>
<th>Si-O-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Me</td>
<td>69</td>
<td>10-11</td>
<td>10</td>
</tr>
<tr>
<td>1,2-diMe</td>
<td>44</td>
<td>15-20</td>
<td>15-20</td>
</tr>
<tr>
<td>1,3-diMe</td>
<td>60</td>
<td>10-15</td>
<td>10</td>
</tr>
<tr>
<td>1,4-diMe</td>
<td>60</td>
<td>10-15</td>
<td>10</td>
</tr>
</tbody>
</table>

The formation of the side products can be explained as shown in Scheme 5. As mentioned at the beginning, these reactions were carried out in high dilution, and SN2-Si intramolecular cyclization is favored over intermolecular substitution. Thus, 34, 117, 118 and 119 were obtained in good yield, in comparison to the disilyl derivatives 116, which could form polymers. In solution halogen exchange between the already formed silyl chloride derivatives 34, 117, 118 and 119 and MgClBr gave silyl bromides 120, 121, 122 and 123, respectively. It should be noted that the halogen exchange between organosilicon halides and magnesium halides in solution has been observed previously but such exchange products have usually been ignored in the literature. Since the silyl
Scheme 5

\[ \text{R} \quad \text{MgBr} \quad \text{MgBr} \]

\[ \text{MeSiCl}_3 \]

\[ \text{R} \quad \text{MgBr} \quad \text{SiCl}_2 \]

\[ \text{Me} \quad \text{Me} \]

\[ k_1(S_{N^2-Si}) \]

\[ \text{R} \quad \text{SiCl}_2 \]

\[ \text{Me} \quad \text{Me} \]

\[ k_2(S_{N^2-Si}) \]

\[ \text{Me} \quad \text{Me} \]

\[ \text{POLYMER} \]
halides are sensitive to moisture, disiloxanes could also be observed. The bromides and disiloxanes were not isolated in pure form but were identified by their mass spectral fragmentation patterns.

The structures of silyl chlorides 117, 118 and 119 (Figure 9) were assigned from their chemical shifts in a manner analogous to that used for silyl hydrides 110, 111 and 112. The axial Si-Me gave a resonance downfield from the equatorial Si-Me. The chemical shifts of C-methylated 1-chloro-1-methyl-1-silacyclohexanes are listed in Table 11.

![Figure 9](image_url)
### Table 11

Chemical shifts of Si-Me signals of C-methylated 1-chloro-1-methyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Si-Me (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>0.421</td>
</tr>
<tr>
<td>117b</td>
<td>0.392</td>
</tr>
<tr>
<td>117a</td>
<td>0.427</td>
</tr>
<tr>
<td>118a</td>
<td>0.412</td>
</tr>
<tr>
<td>118b</td>
<td>0.443</td>
</tr>
<tr>
<td>119b</td>
<td>0.408</td>
</tr>
<tr>
<td>119a</td>
<td>0.443</td>
</tr>
</tbody>
</table>

C-methylated 1,1-dimethyl-1-silacyclohexanes were prepared by the same reaction of diGrignard reagents derived from 1,5-dibromoalkanes and dichlorodimethylsilane (equation 9). The yields, boiling points and cis:trans isomer ratios (where appropriate) are listed in Table 12.
\[
\begin{align*}
&\text{R}_1=\text{R}=\text{H} & 99 \quad & 5 \\
&\text{R}_1=\text{H}; \text{R}=\text{Me} & 100-1\text{Me} \quad & 10-2\text{Me} \\
& & 101-2\text{Me} \quad & 127-3\text{Me} \\
& & 102-3\text{Me} \quad & 128-4\text{Me} \\
&\text{R}_1=\text{R}=\text{Me} & 103-1,5-\text{diMe} \quad & 129-2,6-\text{diMe} \\
& & 104-2,4-\text{diMe} \quad & 130-3,5-\text{diMe} \\
& & 105-3,3-\text{diMe} \quad & 131-3,3-\text{diMe}
\end{align*}
\]

Equation 9

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>b.p. °C/mm</th>
<th>cis/trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>61</td>
<td>60-61/58</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>43</td>
<td>64-65/40</td>
<td></td>
</tr>
<tr>
<td>127</td>
<td>50</td>
<td>62-63/40</td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>55</td>
<td>65-66/40</td>
<td></td>
</tr>
<tr>
<td>129</td>
<td>32</td>
<td>97-98/70</td>
<td>50/50</td>
</tr>
<tr>
<td>130</td>
<td>40</td>
<td>80-81/65</td>
<td>50/50</td>
</tr>
<tr>
<td>131</td>
<td>66</td>
<td>91-92/90</td>
<td></td>
</tr>
</tbody>
</table>

Table 12
Yields, cis:trans ratios and boiling points of C-methylated 1,1-dimethyl-1-silacyclohexanes
With 129 and 130 the ratios of cis and trans isomers were 50:50, but they isomerized to a 54:46 and 48:52 mixture, respectively, of cis and trans isomers after several weeks.

C-methylated 1-methyl-1-phenyl-1-silacyclohexanes were prepared in the same way as the previous examples, using dichloromethylphenylsilane (Equation 10). The yields, cis/trans isomer ratios and boiling points are listed in Table 13.

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>R</th>
<th>Yield</th>
<th>cis/trans</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>88</td>
<td>50/50</td>
<td>132</td>
</tr>
<tr>
<td>Me</td>
<td>100-1Me</td>
<td>100/0</td>
<td>133-2Me</td>
</tr>
<tr>
<td></td>
<td>101-2Me</td>
<td></td>
<td>134-3Me</td>
</tr>
<tr>
<td></td>
<td>102-3Me</td>
<td></td>
<td>135-4Me</td>
</tr>
</tbody>
</table>

Equation 10
Table 13

Yields, cis:trans ratios and the boiling points of 1-methyl-1-phenyl and C-methylated 1-methyl-1-phenyl-1-silacyclohexane

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>cis/trans</th>
<th>b.p.°C/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>132</td>
<td>73</td>
<td></td>
<td>125-126/5</td>
</tr>
<tr>
<td>133</td>
<td>50</td>
<td>58/42</td>
<td>126-127/5</td>
</tr>
<tr>
<td>134</td>
<td>64</td>
<td>42/58</td>
<td>128-129/6</td>
</tr>
<tr>
<td>135</td>
<td>60</td>
<td>58/42</td>
<td>100-101/1</td>
</tr>
</tbody>
</table>

From all the results above, it is obviously indicated that in all cases, when the methyl group was at the 2 position the yield was lowest. That might be due to a steric effect on the ring cyclization reaction or to the fact that secondary Grignard reagents tend to give more side products than primary Grignards.

II-2-3. Reactions of Methylated Silacyclohexanes and Their Derivatives:

II-2-3-A. Stereospecific Reactions:

As mentioned earlier, since the mixtures of C-methylated 1-chloro-1-methyl-1-silacyclohexanes were obtained with one isomer greatly predominating over the other, reaction stereochemistry could be studied. Of particular interest were the reactions of 1-chloro-, 1-fluoro-, and 1-bromo- derivatives with lithium aluminum
hydride, with organometallic reagents such as MeLi, MeMgBr, PhLi and PhMgBr, free radical chlorination and bromination of silyl hydride derivatives and bromodesilylation of phenylsilane derivatives.

The reduction reaction of silyl chlorides with LiAlH₄ most often proceeds with inversion of configuration regardless of the solvent; however, in ring strained¹⁸⁶,¹⁸⁷ or bicyclic systems,⁷⁷ or bridgehead chlorosilanes, the reaction occurs by retention of configuration.⁹⁰ LiAlH₄ reduction has usually been considered to be a direct displacement of the Sₐ₂-Si type;⁴⁸ however, recently evidence in the related displacement of chloride by Grignard reagents has been interpreted in terms of formation of a pentacoordinated intermediate¹¹⁰ (Figure 10).

Either inversion mechanism would require the silacyclohexane ring to span two equatorial positions in a trigonal bipyramidal intermediate (or transition state), thus placing considerable strain on the ring system. The silacyclobutane (angle C₂-Si-C₄ = 75-80°)⁹³ ring system
can not easily span two equatorial positions and therefore reacts by a retention mechanism in which the intermediate is presumably a trigonal bipyramid with the ring spanning one equatorial and one axial position.\textsuperscript{107} Since silacyclopentane (angle C\textsubscript{2}-Si-C\textsubscript{5} = 92-96°)\textsuperscript{112} is less strained than the silacyclobutane ring system but has more strain than an acyclic system (angle C\textsubscript{1}-Si-C\textsubscript{2} = 109°),\textsuperscript{97} it could presumably react by either retention or inversion of configuration. The reaction stereochemistry in the LiAlH\textsubscript{4} reduction of silacyclopentane derivatives should help in determining the amount of strain that is required to produce retention of configuration at a silicon center. In the C-methylated 1-methyl-1-silacyclohexane system, the angles C\textsubscript{2}-Si-C\textsubscript{6} were found from MM\textsubscript{2} force field calculations to be comparable to those of acyclic systems (Table 14). Thus it is reasonable that silacyclohexane can span two equatorial positions in a trigonal bipyramidal transition state as in the S\textsubscript{N}2-Si mechanism proposed by Sommer or via a pentacoordinated silicon center as proposed by Corriu.\textsuperscript{53,100}

\textbf{Table 14}

C\textsubscript{2}-Si-C\textsubscript{6} angles (from MM2 calculation)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C\textsubscript{2}-Si-C\textsubscript{6}</th>
</tr>
</thead>
<tbody>
<tr>
<td>109</td>
<td>104.7-104.8°</td>
</tr>
<tr>
<td>110</td>
<td>105-104.6°</td>
</tr>
<tr>
<td>111</td>
<td>104.5-104.7°</td>
</tr>
<tr>
<td>112</td>
<td>104.5-104.2°</td>
</tr>
</tbody>
</table>
The cis and trans isomers of C-methylated 1-chloro-1-methyl-1-silacyclohexanes were prepared by the free radical chlorination of the silyl hydride isomers as previously described. These silyl chloride derivatives were then reduced back to the silyl hydrides with LiAlH₄ in ether to give the reaction stereochemistries noted in Equation 11.

\[
\begin{align*}
R=\text{H} & \quad 109 \\
R=\text{Me} & \quad 110\text{-}2\text{Me} \quad 117\text{-}2\text{Me} \\
& \quad 111\text{-}3\text{Me} \quad 118\text{-}3\text{Me} \\
& \quad 112\text{-}4\text{Me} \quad 119\text{-}4\text{Me}
\end{align*}
\]

Equation 11

The free radical chlorination of 109, 110, 111 and 112 with carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide gave silyl chlorides 34, 117, 118 and 119 in quantitative yield with retention of configuration. Since free radical chlorination of Si-H compounds has been shown to proceed with retention of
configuration, the silyl chlorides \(117, 118\) and \(119\) should have the same configuration as the corresponding silyl hydrides. One of these free radical chlorination mechanisms is illustrated in Figure 11.

![Figure 11](image)

The isomerization of the silyl radical is slow compared to rate of abstraction of Cl. For silyl radicals, the experimental evidence is consistent with a considerable barrier to inversion and/or an inversion process that is slow relative to the abstraction process. As can be seen the overall reaction (Equation 11) sequence occurs with inversion of configuration. Since as noted earlier, the free radical chlorination occurs with retention of configuration, the LiAlH\(_4\) reduction must take place with inversion of configuration at the silicon center. The
observed reaction stereochemistry provide a strong indication that the stereochemical assignments based on proton NMR are valid.

These observations allow one to conclude that the silacycloclohexane ring system is capable of spanning two equatorial positions in a trigonal bipyramidal transition state (Figure 10); however, it is impossible to conclude whether or not a stable intermediate is formed in this reaction. The results of individual reduction with LiAlH₄ in ether are listed in Table 15, and the free radical chlorinations are in Table 16.

Table 15
Yields, cis:trans ratios and stereochemistry the reduction of 1-chloro-1-methyl-1- and C-methylated 1-chloro-1-methyl-1-silacyclohexanes with LiAlH₄ in ether

<table>
<thead>
<tr>
<th>Si-Cl</th>
<th>Si-H</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>cis/trans</td>
<td>Yield</td>
</tr>
<tr>
<td>34</td>
<td>45/55</td>
<td>95</td>
</tr>
<tr>
<td>117</td>
<td>55/45</td>
<td>95</td>
</tr>
<tr>
<td>118</td>
<td>66/34</td>
<td>93</td>
</tr>
<tr>
<td>116</td>
<td>35/65</td>
<td>94</td>
</tr>
<tr>
<td>119</td>
<td>35/65</td>
<td>94</td>
</tr>
<tr>
<td>119</td>
<td>65/35</td>
<td>94</td>
</tr>
</tbody>
</table>
Table 16
Yields, cis/trans ratios and stereochemistry of the free radical chlorination of 1-methyl-1- and methylated 1-methyl-1-silacyclohexanes with CCl₄ and BPO

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si-H</th>
<th>Si-Cl</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis/trans</td>
<td>Yield</td>
<td>cis/trans</td>
</tr>
<tr>
<td>109</td>
<td>55/45</td>
<td>63</td>
<td>55/45</td>
</tr>
<tr>
<td>110</td>
<td>45/55</td>
<td>65</td>
<td>46/54</td>
</tr>
<tr>
<td>111</td>
<td>35/65</td>
<td>63</td>
<td>35/65</td>
</tr>
<tr>
<td>112</td>
<td>66/34</td>
<td>65</td>
<td>67/33</td>
</tr>
<tr>
<td>112</td>
<td>34/66</td>
<td>66</td>
<td>35/65</td>
</tr>
</tbody>
</table>

The results in Tables 15 and 16 indicate that these reactions are highly stereospecific with the degree of stereospecificity independent of the position of the methyl group on the ring. The reactions are easily carried out and given essentially quantitative yields.

C-methylated 1-fluoro-1-methyl-1-silacyclohexanes can not be prepared directly by cyclization reaction; however, halogen exchange reactions between fluoride anions and silyl chlorides can be used to prepare these silyl fluoride compounds in good yields (Equation 12). No solvent was used, except in the case of NaBF₄/acetone. The
substitution occurred very rapidly (all were complete within 5 min.). The reactions were carried out with many sources of fluoride anions, including NH$_4$HF$_2$, ZnF$_2$, KF, CsF, and NaBF$_4$ in acetone. The results of the fluorination of silyl chlorides are listed in Table 17. The reactions are stereospecific with inversion of stereochemistry at the silicon center. When the reaction was followed by $^1$H NMR the silyl chloride did not isomerize after several days, while the substitution of chloride by fluoride has already taken place within 5-10 min. In addition, in the presence of a catalytic amount of fluoride, the silyl fluorides did not isomerize after 4

<table>
<thead>
<tr>
<th>R</th>
<th>34</th>
<th>136</th>
<th>109</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>117-2Me</td>
<td>137-2Me</td>
<td>110-2Me</td>
</tr>
<tr>
<td></td>
<td>118-3Me</td>
<td>138-3Me</td>
<td>111-3Me</td>
</tr>
<tr>
<td></td>
<td>119-4Me</td>
<td>139-4Me</td>
<td>112-4Me</td>
</tr>
</tbody>
</table>

Equation 12
Table 17
Yields, cis:trans ratios and stereochemistry of the fluorination reactions of silyl chlorides 34, 117, 118 and 119 with fluoride anion

<table>
<thead>
<tr>
<th>Fluoride</th>
<th>Compound</th>
<th>cis/trans Si-Cl</th>
<th>cis/trans Si-F</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$HF$_2$</td>
<td>34</td>
<td>55/45</td>
<td>45/55</td>
<td>91</td>
</tr>
<tr>
<td>ZnF$_2$</td>
<td>34</td>
<td>55/45</td>
<td>46/54</td>
<td>90</td>
</tr>
<tr>
<td>NH$_4$HF$_2$</td>
<td>117</td>
<td>45/55</td>
<td>54/66</td>
<td>93</td>
</tr>
<tr>
<td>ZnF$_2$</td>
<td>117</td>
<td>45/55</td>
<td>55/45</td>
<td>91</td>
</tr>
<tr>
<td>NH$_4$HF$_2$</td>
<td>118</td>
<td>67/33</td>
<td>35/65</td>
<td>92</td>
</tr>
<tr>
<td>ZnF$_2$</td>
<td>118</td>
<td>67/33</td>
<td>35/65</td>
<td>91</td>
</tr>
<tr>
<td>CsF</td>
<td>118</td>
<td>67/33</td>
<td>36/64</td>
<td>90</td>
</tr>
<tr>
<td>KF</td>
<td>118</td>
<td>67/33</td>
<td>34/66</td>
<td>94</td>
</tr>
<tr>
<td>NaBF$_4$</td>
<td>118</td>
<td>67/33</td>
<td>36/64</td>
<td>78</td>
</tr>
<tr>
<td>NH$_4$HF$_2$</td>
<td>118</td>
<td>36/64</td>
<td>65/35</td>
<td>95</td>
</tr>
<tr>
<td>ZnF$_2$</td>
<td>118</td>
<td>36/64</td>
<td>65/35</td>
<td>90</td>
</tr>
<tr>
<td>CsF</td>
<td>118</td>
<td>38/62</td>
<td>62/38</td>
<td>84</td>
</tr>
<tr>
<td>KF</td>
<td>118</td>
<td>36/64</td>
<td>66/34</td>
<td>84</td>
</tr>
<tr>
<td>NaBF$_4$</td>
<td>118</td>
<td>35/65</td>
<td>61/39</td>
<td>76</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Compound</td>
<td>Si-Cl cis/trans</td>
<td>Si-F cis/trans</td>
<td>Yield</td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
<td>----------------</td>
<td>----------------</td>
<td>-------</td>
</tr>
<tr>
<td>NH$_4$HF$_2$</td>
<td>119</td>
<td>35/65</td>
<td>65/35</td>
<td>98</td>
</tr>
<tr>
<td>ZnF$_2$</td>
<td>119</td>
<td>35/65</td>
<td>65/35</td>
<td>81</td>
</tr>
<tr>
<td>CsF</td>
<td>119</td>
<td>35/65</td>
<td>64/36</td>
<td>86</td>
</tr>
<tr>
<td>KF</td>
<td>119</td>
<td>35/65</td>
<td>63/37</td>
<td>89</td>
</tr>
<tr>
<td>NaBF$_4$</td>
<td>119</td>
<td>35/65</td>
<td>61/39</td>
<td>85</td>
</tr>
<tr>
<td>NH$_4$HF$_2$</td>
<td>119</td>
<td>64/36</td>
<td>35/65</td>
<td>98</td>
</tr>
<tr>
<td>ZnF$_2$</td>
<td>119</td>
<td>64/36</td>
<td>35/65</td>
<td>86</td>
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<tr>
<td>CsF</td>
<td>119</td>
<td>64/36</td>
<td>38/62</td>
<td>89</td>
</tr>
<tr>
<td>KF</td>
<td>119</td>
<td>64/36</td>
<td>39/61</td>
<td>88</td>
</tr>
<tr>
<td>NaBF$_4$</td>
<td>119</td>
<td>64/36</td>
<td>39/61</td>
<td>83</td>
</tr>
</tbody>
</table>
weeks. Thus, the stereochemistry being observed is that of the exchange reaction itself, uncomplicated by isomerization processes. The lack of isomerization of methylated 1-fluoro-1-methyl-1-silacyclohexanes is in contrast to results in other systems. Racemic products were obtained in the case of 4-t-butyl-1-fluoro-1-methyl-1-silacyclohexane, and 1,2-dimethyl-1-fluoro-1-silacyclopentane gave isomerization rather than a stereospecific reaction. The fluoride/chloride exchange took place with inversion of stereochemistry at the silicon center of methylated silacyclohexane derivatives, which can be explained by the $S_N^2$-Si mechanism of Sommer. The structures of these silyl fluoride derivatives are shown in Figure 12, in which axial Si-Me resonates at downfield relative to equatorial Si-Me.

Figure 12
The coupling constant $J[\text{Si-Me(ax)-F(eq)}]$ is larger than $J[\text{Si-Me(eq)-F(ax)}]$ by a very small amount. The chemical shifts of Si-Me and the coupling constants $J[\text{SiMe-F}]$ of these C-methylated 1-fluoro-1-methyl-1-silacyclohexanes are listed in Table 18.

The reduction of a mixture of cis and trans silyl fluoride derivatives with LiAlH$_4$ in ether showed stereospecific inversion of configuration at the silicon center.

The reduction of 38:62 and 65:35 mixtures of $^{139}$ with LiAlH$_4$ in ether gave the mixtures 63:37 and 35:65, respectively, of silyl hydride $^{112}$. It is evident that the reduction of silyl fluoride is stereospecific, since the equilibrium ratio of cis and trans $^{112}$ is known to be 55:45 (see the discussion at the end of this section). Furthermore, in order to test whether the silicon hydride was being isomerized immediately upon formation, an extra amount of silyl hydride that was predominantly one isomer was added to the reaction mixture. This excess hydride does not isomerize. If the reaction was nonstereospecific, the equilibrium ratio of $^{112}$ would probably have been formed. The results revealed that the racemization observed by Corriu in the reduction of the six-membered cyclic fluorosilane 1-naphthyl-2-sila-2-tetrahydro-1,2,3,4-naphthalene$^{92}$ (angle C-Si-C = 103°)$^{96}$ is not characteristic of all silacyclohexanes.
### Table 18

Chemical shifts of Si-Me and the coupling constants $J[\text{SiMe-F}](\text{Hz})$ of C-methylated 1-fluoro-methyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>Cpd</th>
<th>Si-Me(eq)</th>
<th>$J[\text{SiMe(eq)-F(ax)}]$</th>
<th>Si-Me(ax)</th>
<th>$J[\text{SiMe(ax)-F(eq)}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>137</td>
<td>0.193</td>
<td>7.310</td>
<td>0.261</td>
<td>7.511</td>
</tr>
<tr>
<td>138</td>
<td>0.199</td>
<td>7.340</td>
<td>0.247</td>
<td>7.520</td>
</tr>
<tr>
<td>139</td>
<td>0.197</td>
<td>7.349</td>
<td>0.254</td>
<td>7.585</td>
</tr>
</tbody>
</table>
As can be seen the overall reaction sequence occurs with retention of configuration starting from silyl chloride 119 to silyl fluoride 139 via halogen exchange and finally to silyl hydride 112 by reduction with LiAlH₄ in ether (Scheme 6). The reduction of the same cis/trans ratio of silyl chloride 119 with LiAlH₄ in ether gave the same silyl hydride 112 with inversion of stereochemistry at the silicon center. The agreement in both these schemes among the expected stereochemical outcomes and the NMR structural assignments adds confidence to these conclusions.

Scheme 6
As was mentioned earlier in the introduction, the reduction of 1,2-dimethyl-1-fluoro-1-silacyclobutane \(79^{86}\) and of 1-fluoro-7-methyl-7-silabenz[d,e]anthracene \(84^{90}\) with LiAlH\(_4\) gave the silyl hydrides with retention of configuration at the silicon center; but the same reaction with 1-fluoro-1,2-dimethyl-1-silacyclopentane \(81,88\) 1-fluoro-1-naphthyl-2-sila-2-tetrahydro-1,2,3,4-naphthalene \(63^{92}\) and 4-t-butyl-1-fluoro-1-methyl-1-silacyclohexane \(82,89\) gave isomerized or racemic products. With acyclic compounds such as 1-NpMePhSiF \(85,78\) the reduction reaction gave the product with inversion of configuration.

The fluoride is a borderline leaving group; that is, the stereochemistry of fluoride displacement can be either retention or inversion, depending on other factors.

In C-methylated 1-fluoro-1-methyl-1-silacyclohexanes, hydride replaced F\(^-\) with inversion of stereochemistry as explained by an \(S_N2\)-Si mechanism (Figure 13).
The results of the reduction of silyl fluoride derivatives 136, 137, 138 and 139 are listed in Table 19.

**Table 19**

Yields, cis/trans ratios and stereochemistry of the reduction of 1-fluoro-l-methyl-1- and C-methylated 1-fluoro-l-methyl-1-silacyclohexanes with LiAlH₄ in ether

<table>
<thead>
<tr>
<th>Compound</th>
<th>cis/trans</th>
<th>Yield</th>
<th>Si-H cis/trans</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>136</td>
<td></td>
<td>96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>137</td>
<td>55/45</td>
<td>94</td>
<td>44/56</td>
<td>INV.</td>
</tr>
<tr>
<td>137</td>
<td>45/55</td>
<td>92</td>
<td>55/45</td>
<td>INV.</td>
</tr>
<tr>
<td>138</td>
<td>66/34</td>
<td>97</td>
<td>34/66</td>
<td>INV.</td>
</tr>
<tr>
<td>138</td>
<td>35/65</td>
<td>96</td>
<td>65/35</td>
<td>INV.</td>
</tr>
<tr>
<td>139</td>
<td>65/35</td>
<td>98</td>
<td>35/65</td>
<td>INV.</td>
</tr>
<tr>
<td>139</td>
<td>35/65</td>
<td>94</td>
<td>65/35</td>
<td>INV.</td>
</tr>
</tbody>
</table>

The studies of reaction stereochemistries of chloride, fluoride and hydride derivatives of the C-methylated silacyclohexanes showed the stereochemical course to be in good agreement with the results obtained by using optically active silicon compounds. At the beginning of this chapter it was mentioned that angle strain at a silicon center can lead to a remarkable cross-over from retention to inversion. However, we can now conclude
that the relatively stainfree silicon center in six-membered rings behaves stereochemically like acyclic organosilicon compounds with few exceptions.

It was decided to continue these investigations with the preparation of the silyl bromides which were the same as those isolated in small amounts as minor products from the ring closures. Free radical bromination of silyl hydride $109$, $111$ and $112$ with bromoform in the presence of a catalytic amount of benzoyl peroxide afforded the silyl bromides in good yields (Equation 13).

![Chemical Structure](image)

Equation 13

Retention of configuration was observed at the silicon center, as in the free radical chlorination. The silyl bromides were shown to be identical to the ones obtained
as minor products from direct cyclization. The results are listed in Table 20.

Table 20
Yields, cis/trans ratios and stereochemistry of free radical bromination 1-methyl-1- and C-methylated 1-methyl-1-silacyclohexanes with CHBr₃/BPO

<table>
<thead>
<tr>
<th>Si-H</th>
<th>Si-Br</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>cis/trans</td>
<td>Yield</td>
</tr>
<tr>
<td>109</td>
<td>67/33</td>
<td>91</td>
</tr>
<tr>
<td>111</td>
<td>35/65</td>
<td>95</td>
</tr>
<tr>
<td>112</td>
<td>66/34</td>
<td>92</td>
</tr>
<tr>
<td>112</td>
<td>35/65</td>
<td>94</td>
</tr>
</tbody>
</table>

The structure of the cis and trans isomers and the chemical shifts of the Si-Me in the silyl bromides 122 and 123 are shown in Figure 14.

![Figure 14](image_url)
The silyl bromides 122 and 123 were also prepared stereospecifically with retention of configuration by the reaction of silyl hydride derivatives 111 and 112 with bromine in carbon tetrachloride. The results are listed in Table 21.

Table 21

Yields, cis/trans ratios and the stereochemistry of the bromination of 1-methyl-1- and C-methylated 1-methyl-1-silacyclohexanes with \( \text{Br}_2/\text{CCl}_4 \)

<table>
<thead>
<tr>
<th>Compound</th>
<th>cis/trans</th>
<th>Yield</th>
<th>cis/trans</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>109</td>
<td>66/34</td>
<td>95</td>
<td>65/35</td>
<td>RET.</td>
</tr>
<tr>
<td>111</td>
<td>35/65</td>
<td>91</td>
<td>35/65</td>
<td>RET.</td>
</tr>
<tr>
<td>112</td>
<td>66/34</td>
<td>94</td>
<td>65/35</td>
<td>RET.</td>
</tr>
<tr>
<td>112</td>
<td>35/65</td>
<td>95</td>
<td>35/65</td>
<td>RET.</td>
</tr>
</tbody>
</table>

Sommer investigated this type of reaction in the 1-NpPhMeSi series, and retention of configuration at the silicon center was observed. Sommer proposed that the result was due to the formation of an intermediate bromonium ion (Figure 15).48
The observation of retention of configuration for the methylated 1-methyl-1-silacyclohexane system confirms Sommer's observation.

The silyl bromides were reduced to silyl hydride derivatives with LiAlH₄ in ether. The reaction was stereospecific, and inversion of configuration at the silicon center was obtained (Equation 13). The results are listed on Table 22.

**Table 22**

Yields, cis/trans ratios and stereochemistry of reduction of 1-bromo-1-methyl and C-methylated 1-bromo-1-methyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si-Br</th>
<th>Si-H</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>122</td>
<td>65/35</td>
<td>95</td>
<td>34/66 INV.</td>
</tr>
<tr>
<td>122</td>
<td>34/66</td>
<td>94</td>
<td>65/35 INV.</td>
</tr>
<tr>
<td>123</td>
<td>35/65</td>
<td>95</td>
<td>65/35 INV.</td>
</tr>
<tr>
<td>123</td>
<td>65/35</td>
<td>94</td>
<td>34/66 INV.</td>
</tr>
</tbody>
</table>
Again the overall reaction sequence (Equation 13) occurred with inversion of configuration, since free radical bromination took place with retention and was followed by inversion in the reduction reaction. Nucleophilic displacement of bromide with inversion is expected because bromide ion is a better leaving group than chloride. Presumably the SN2-Si mechanism operates here (Figure 16).

![Figure 16](image)

Thus, the stereochemical course of these reactions again was in agreement with the results obtained by using optically active silicon compounds.48

A silyl bromide-forming reaction proceeding with inversion stereochemistry would be expected to require displacement of a good leaving group.116 Such a leaving group was found in bromodesilylation reactions which proceed through a Wheland intermediate (Scheme 7).117 The mechanism for this reaction is different from the previous
reaction of silyl hydride with Br₂. Cleavage can be accomplished with most of the reagents that give electrophilic aromatic substitution, and as expected, the

\[
\begin{align*}
X^- + \text{SiR}_3^- & \rightarrow \text{SiR}_3^+ + Y^- \\
YSiR_3 & + \\
\end{align*}
\]

Scheme 7

reaction occurs with inversion of configuration in the case of halogen.\(^{118}\) Inversion of configuration was reported for the reaction of 1-anisyl-1,2-dimethyl-1-silacyclobutane\(^ {119}\) and 1-anisyl-1,2-dimethyl-1-silacyclopentane\(^ {120}\) with Br₂/CCl₄, due to the fact that bromoanisole is a good leaving group. Bromobenzene is also a good leaving group, and it was found that bromination of C-methylated 1-methyl-1-phenyl-1-silacyclohexanes with Br₂/CCl₄ gave the corresponding silyl bromides with inversion of configuration at the silicon center (Equation 14).
The yields, cis/trans ratios and the stereochemistry of the bromodesilylation reaction above are listed in Table 23.

Table 23
Yields, cis:trans ratios and the stereochemistry of the bromination of C-methylated 1-methyl-1-phenyl-1-silacyclohexanes with Br$_2$/CCl$_4$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si-Ph</th>
<th>Si-Br</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>132</td>
<td></td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>134</td>
<td>59/41</td>
<td>93</td>
<td>40/60</td>
</tr>
<tr>
<td>134</td>
<td>42/58</td>
<td>92</td>
<td>59/41</td>
</tr>
<tr>
<td>135</td>
<td>40/60</td>
<td>95</td>
<td>61/39</td>
</tr>
<tr>
<td>135</td>
<td>58/42</td>
<td>93</td>
<td>40/60</td>
</tr>
</tbody>
</table>
The stereospecific bromination of the methylphenyl-silanes 134 and 135 with inversion of configuration can be explained by the $S_N2$-Si mechanism with back side attack by bromide anion leading preferentially to inversion. The cleavage of the anisyl group was the first reaction that was noted to proceed with inversion of configuration in the silacyclobutane system. The mechanism for the bromination of C-methylated 1-methyl-1-silacyclohexane with bromine in carbon tetrachloride is illustrated in Scheme 8.
It should be noted that in the preparation of silyl bromide derivatives 122 and 123 from 111, 112, 134 and 135 with Br$_2$/CCl$_4$, the molar ratio to silyl hydride (Table 22) or to phenylsilane derivative (Equation 14) must be 1:1 or less. An excess of Br$_2$ causes the silyl bromides to isomerize to an equilibrium mixture in which the cis:trans ratio is 72:28 and 28:72 of 122 and 123, respectively. In order to confirm these results, the free radical bromination of a mixture of cis and trans 111 or 112, in which one isomer was predominant over the other, was carried out with bromoform in the presence of benzoyl peroxide. The reactions gave the silyl bromides 122 and 123 with retention of configuration, and isomerization was not observed. The bromination was also carried out while keeping the ratio of Br$_2$:silyl hydride less than unity (0.8), and the silyl bromide was obtained with retention of configuration, and no isomerization was seen. If one starts with silyl bromide 122 having cis:trans ratios of 35:65 and 66:34, and adds small amounts of Br$_2$/CCl$_4$ and follows the reaction by $^1$H NMR, the isomerization starts to take place and continues until it reaches the equilibrium position in which the ratio of these isomers is 72:28. With silyl bromide 123 having cis:trans ratio 35:65 and 65:35, under the same conditions, at the equilibrium position the cis:trans ratio was 28:72.
C-methylated 1-methyl-1-phenyl-1-silacyclohexane derivatives \[132, 134\] and \[135\] were also prepared from the corresponding silyl chloride and silyl fluoride derivatives by reaction with PhLi or PhMgBr in ether (Equation 15). The phenylation reaction was easy to carry out, and the yield was moderate (60%). Yields were a little higher when PhLi was used in comparison with PhMgBr.

\[
\begin{align*}
\text{PhLi or PhMgBr} & \quad \rightarrow \\
\text{Me Ph} & \\
\end{align*}
\]

\[
\begin{array}{ccc}
R=H; & X=Cl, F: & 34, 136 \\
R=Me; & X=Cl, F: & 118, 138 \\
& X=F, Cl: & 119, 139 \\
\end{array}
\]

Equation 15

The phenylations gave the product with stereospecific inversion of configuration at silicon. The results are listed in Table 24.

The observation of inversion of configuration for the silacyclohexane system agrees with Sommer's results with acyclic silanes, and also with the work of Sakurai and Murakami\(^89\) and of Citron.\(^90\)
Table 24

Yields and cis:trans ratios and stereochemistry in the phenylation reaction of C-methylated 1-methyl-1-halogenated silacyclohexanes

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>Si-X cis/trans</th>
<th>Si-Ph PhLi</th>
<th>Si-Ph Yield</th>
<th>PhMgBr</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>34/66</td>
<td>67</td>
<td>39/61</td>
<td>53</td>
<td>40/60</td>
</tr>
<tr>
<td>118</td>
<td>66/34</td>
<td>67</td>
<td>60/40</td>
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<td>35/65</td>
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<td>68</td>
<td>61/39</td>
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<td>40/60</td>
</tr>
<tr>
<td>119</td>
<td>65/35</td>
<td>65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X=F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>179</td>
<td>63</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>138</td>
<td>36/64</td>
<td>54</td>
<td>61/39</td>
<td>68</td>
<td>60/40</td>
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<tr>
<td>138</td>
<td>62/38</td>
<td>58</td>
<td>40/60</td>
<td>57</td>
<td>41/59</td>
</tr>
<tr>
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<td>65/35</td>
<td>57</td>
<td>38/62</td>
<td>71</td>
<td>38/62</td>
</tr>
<tr>
<td>139</td>
<td>35/65</td>
<td>60</td>
<td>61/39</td>
<td>68</td>
<td>63/37</td>
</tr>
</tbody>
</table>
Compounds \textbf{5}, \textbf{10}, \textbf{127} and \textbf{128} were also prepared by the methylation of C-methylated 1-methyl-1-halo-1-silacyclohexane with organometallic reagents such as MeLi and MeMgBr in ether (Equation 16). The yields were moderate. The results of the methylation reactions are listed in Table 25. The methylation was slower in the case where MeMgBr was used and a little faster with MeLi. The reactivity of the silyl halide derivatives decreased in the order Si-Br > Si-Cl > Si-F.

\begin{equation}
\begin{array}{c}
\text{MeLi or MeMgBr} \\
\end{array}
\end{equation}

\begin{align*}
R=\text{H; } & X=\text{Cl,F,Br}: \text{34,136,120} & \text{5} \\
R=\text{Me; } & X=\text{Cl,F,Br}: \text{117,137} & \text{10-2Me} \\
& & \text{118,138,122} & \text{127-3Me} \\
& & \text{119,139,123} & \text{128-4Me}
\end{align*}

Equation 16
Table 25
Yields and the reaction time for the methylation of C-methylated 1-halo-1-methyl-1-silacyclohexanes with MeLi and MeMgBr in ether

<table>
<thead>
<tr>
<th>Compound</th>
<th>MeLi</th>
<th></th>
<th>MeMgBr</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield</td>
<td>Time (h)</td>
<td>Yield</td>
<td>Time (h)</td>
</tr>
<tr>
<td>34</td>
<td>91</td>
<td>4</td>
<td>80</td>
<td>6</td>
</tr>
<tr>
<td>120</td>
<td>90</td>
<td>4</td>
<td>86</td>
<td>6</td>
</tr>
<tr>
<td>136</td>
<td>91</td>
<td>8</td>
<td>88</td>
<td>8</td>
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<tr>
<td>117</td>
<td>61</td>
<td>4</td>
<td>58</td>
<td>6</td>
</tr>
<tr>
<td>118</td>
<td>83</td>
<td>4</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>119</td>
<td>86</td>
<td>4</td>
<td>82</td>
<td>6</td>
</tr>
<tr>
<td>137</td>
<td>60</td>
<td>10</td>
<td>59</td>
<td>10</td>
</tr>
<tr>
<td>139</td>
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<td>10</td>
</tr>
<tr>
<td>138</td>
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<td>8</td>
<td>83</td>
<td>10</td>
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<tr>
<td>122</td>
<td>84</td>
<td>4</td>
<td>83</td>
<td>6</td>
</tr>
<tr>
<td>123</td>
<td>86</td>
<td>4</td>
<td>81</td>
<td>6</td>
</tr>
</tbody>
</table>

A kinetic study has been made of the reaction of methylmagnesium halides with Me$_3$Si-X and some related halides. The results are best interpreted in terms of initial coordination by magnesium at the halogen on silicon (which is reasonable in view of the polarity of the Si-X bonds) followed by a concerted cyclic process with a transition state as shown in Figure 17. This mechanism is consistent: (i) with the smallness of the...
rate increase caused by replacing one methyl group on silicon by the relatively electron withdrawing ClCH\textsubscript{2} group, (ii) with the small range of activation free energy within the range of hydrosilanes and Grignard reagents, and (iii) with the absence of detectable effects from changes in the polarity or ionic strength of the medium. The mechanism above would also account for the very marked sensitivity of the reaction to the presence of large groups on the silicon atom\textsuperscript{122} for since "flank" attack on the silicon is involved there would be crowding of these groups in the transition state (e.g. PhLi or PhMgBr).

The halogen exchange between silyl chloride and fluoride anion is known in the acyclic system, but there are no known examples of reaction between silyl bromides and fluoride anion in silacarbocycles, especially in silacyclohexanes. The reactions of fluoride anion with silyl chlorides in a silacyclohexane system have been reported by Sakurai,\textsuperscript{89} and by Corriu.\textsuperscript{92} The reactions were not
stereospecific but led to a 50:50 mixture of cis and trans isomers. However, the results in the methylated silacyclohexane system were different. The fluorination of silyl chlorides $\text{117, 118}$ and $\text{119}$ was stereospecific with inversion of configuration at silicon, as was the fluorination of silyl bromides $\text{122}$ and $\text{123}$ with $\text{NH}_4\text{HF}_2$ and $\text{CsF}$ (Equation 17). The reaction was easy to carry out, and the products were formed in quantitative yield. The results are listed in Table 26.

\[
\begin{align*}
\text{R=H} & \quad 120 & \quad 136 \\
\text{R=Me} & \quad 122-3\text{Me} & \quad 138-3\text{Me} \\
 & \quad 123-4\text{Me} & \quad 139-4\text{Me}
\end{align*}
\]

Equation 17

Since the fluoride is a good nucleophile and bromide is a good leaving group, an inversion of stereochemistry would be expected. During the course of the reaction, the silyl bromides did not isomerize prior to substitution.
### Table 26

Yields, cis:trans ratios and stereochemistry of fluorination of C-methylated 1-bromo-1-methyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>F⁻</th>
<th>Compound</th>
<th>cis/trans</th>
<th>Yield</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄HF₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td></td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>ZnF₂</td>
<td></td>
<td></td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>CsF</td>
<td></td>
<td></td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td></td>
<td>120</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>NaBF₄</td>
<td>120</td>
<td></td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>NH₄HF₂</td>
<td></td>
<td>122</td>
<td>60/40</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>122</td>
<td></td>
<td>85</td>
<td>64/36</td>
</tr>
<tr>
<td>NH₄HF₂</td>
<td></td>
<td>123</td>
<td>40/60</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>123</td>
<td>62/38</td>
<td>90</td>
<td>39/61</td>
</tr>
<tr>
<td>CsF</td>
<td>122</td>
<td></td>
<td>88</td>
<td>40/60</td>
</tr>
<tr>
<td>CsF</td>
<td>122</td>
<td></td>
<td>85</td>
<td>65/35</td>
</tr>
<tr>
<td>CsF</td>
<td>123</td>
<td>40/60</td>
<td>87</td>
<td>60/40</td>
</tr>
<tr>
<td>CsF</td>
<td>123</td>
<td>62/38</td>
<td>88</td>
<td>38/62</td>
</tr>
</tbody>
</table>
In conclusion, the results of the stereochemical studies in the reactions above were in good agreement with the results obtained by using optically active silicon compounds. Since C-methylated 1-methyl-1-substituted-1-silacyclohexane is a simple molecule, a saturated silacyclohexane system, in contrast to a majority of the optically active systems previously developed which contain at least one double bond within the silacyclohexane ring or have at least one double bond between an aromatic moiety and silicon. Such structures are often inconvenient because of common reactions in which the bond of silicon to an aromatic group leaves, for example desilylation. The absence of the phenyl or naphthyl group in the present system makes some reactions, such as free radical chlorination or bromination possible without complications from side reactions. The stereochemical course can be monitored readily by proton NMR and GC/MS, hence each reaction requires only a small amount of reactant.

II-2-3-B. Isomerization Reactions of Methylated 1-Methyl-1-Silacyclohexanes

The studies of the isomerization of cyclic silanes 110, 111 and 112 could aid in understanding conformational preferences in silacyclohexanes.

The composition of the equilibrium mixture of silyl hydrides 110, 111 and 112 was determined using isomerization in the presence of a catalytic amount of a fluoride
source such as \( \text{NH}_4\text{HF}_2 \) or CsF. The isomerization of silyl hydride derivatives in the presence of CsF was a little faster than in the case of \( \text{NH}_4\text{HF}_2 \), but the results were almost the same. The experiment was followed by \(^1\text{H} \) NMR at 200 MHz. The \(^1\text{H} \) NMR of the silyl hydride was taken before \( \text{F}^-/\text{CCl}_4 \) was added, and the cis and trans ratio was measured by recording the intensities of the Si-Me signals. The proton NMR spectrum was recorded periodically until a stable equilibrium composition was obtained. The ratio of cis and trans isomers in the equilibrium mixture found by the isomerization experiments using fluoride anion, by MM2 force field calculation, and the ratio obtained from direct cyclization (from Equation 7) are listed in Table 27.

The pathways by which silyl hydrides could reach an equilibrium position under the influence of fluoride are suggested in Scheme 9. In mechanism 1, fluoride attacks silicon to replace H giving II with inversion of configuration. Silyl fluoride II can than isomerize to III. Hydride then substitutes for fluoride with inversion of configuration to afford IV. The total process II↔IV occurs with inversion of stereochemistry. However, the experimental data showed that the isomerization of II↔III took place very slowly (several weeks), whereas silyl hydride isomerized in a few hours. This mechanism is therefore ruled out. A reasonable explanation is the
Table 27

Equilibrium mixture of cis and trans of methylated 1-methyl-1-silacyclohexanes catalyzed by fluoride anion, by MM2 calculation and by direct cyclization method

<table>
<thead>
<tr>
<th>Cpds</th>
<th>Start</th>
<th>F/CCl4</th>
<th>Final</th>
<th>MM2</th>
<th>Direct</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-H</td>
<td>cis/trans</td>
<td>cis/trans</td>
<td>cis/trans</td>
<td>cis/trans</td>
<td>cis/trans</td>
</tr>
<tr>
<td>110</td>
<td>45/55</td>
<td>NH4HF2</td>
<td>55/45</td>
<td>54/46</td>
<td>55/45</td>
</tr>
<tr>
<td>110</td>
<td>55/45</td>
<td>NH4HF2</td>
<td>54/46</td>
<td>54/46</td>
<td>55/45</td>
</tr>
<tr>
<td>110</td>
<td>45/55</td>
<td>CsF</td>
<td>55/45</td>
<td>54/46</td>
<td>55/45</td>
</tr>
<tr>
<td>110</td>
<td>55/45</td>
<td>CsF</td>
<td>56/44</td>
<td>54/46</td>
<td>55/45</td>
</tr>
<tr>
<td>111</td>
<td>66/34</td>
<td>NH4HF2</td>
<td>45/55</td>
<td>45/55</td>
<td>50/50</td>
</tr>
<tr>
<td>111</td>
<td>34/66</td>
<td>NH4HF2</td>
<td>46/54</td>
<td>45/55</td>
<td>50/50</td>
</tr>
<tr>
<td>111</td>
<td>66/34</td>
<td>CsF</td>
<td>45/55</td>
<td>45/55</td>
<td>50/50</td>
</tr>
<tr>
<td>111</td>
<td>34/66</td>
<td>CsF</td>
<td>45/55</td>
<td>45/55</td>
<td>50/50</td>
</tr>
<tr>
<td>112</td>
<td>65/35</td>
<td>NH4HF2</td>
<td>55/45</td>
<td>56/44</td>
<td>52/48</td>
</tr>
<tr>
<td>112</td>
<td>35/65</td>
<td>NH4HF2</td>
<td>55/45</td>
<td>56/44</td>
<td>52/48</td>
</tr>
<tr>
<td>112</td>
<td>65/35</td>
<td>CsF</td>
<td>56/44</td>
<td>56/44</td>
<td>52/48</td>
</tr>
<tr>
<td>112</td>
<td>35/65</td>
<td>CsF</td>
<td>55/45</td>
<td>56/44</td>
<td>52/48</td>
</tr>
</tbody>
</table>

Second mechanism which proposes that in the first step fluoride attacks silicon to form a pentacoordinate intermediate A, which undergoes pseudorotation at silicon to give intermediate B. This is followed by loss of fluoride to afford IV with inversion of stereochemistry.
Scheme 9

- **Mechanism 1:**

\[
\begin{align*}
F^- + & \quad \text{structure I} \quad \rightarrow \quad \text{structure II} \\
F^- + & \quad \text{structure IV} \quad \rightarrow \quad \text{structure III}
\end{align*}
\]

- **Mechanism 2:**

\[
\begin{align*}
F^- + & \quad \text{structure I} \quad \leftrightarrow \quad \text{structure A} \\
F^- + & \quad \text{structure IV} \quad \leftrightarrow \quad \text{structure B}
\end{align*}
\]
II-2-3-C. MM2 Calculation of Conformational Energies of Silacyclohexanes

The structure and the steric energies of silacyclohexane and the various methyl-l-silacyclohexanes have been calculated using a force field method\textsuperscript{123} by Ouellette. Silacyclohexane is predicted to exist in a modified chair conformation in which the ring is more flattened than cyclohexane in the region of silicon and is more puckered in the region of C\textsubscript{4}. The 2-, 3- and 4-methyl-l-silacyclohexanes are calculated to be 1.27, 1.66, 1.87 kcal/mole, respectively, more stable in the equatorial conformation. However, 1-methyl-l-silacyclohexane is predicted to be more stable in the axial conformation by 0.20 kcal/mol. The preference of the 1-methyl group for the axial position is due to a larger negative nonbonded energy term for the axial conformation. The conformational energies of 1-methyl-l-silacyclohexanes listed in Table 28 below are those reported by Ouellette.

Allinger\textsuperscript{124} predicts the same order of stability of 1-methyl-l-silacyclohexane but the energy difference is -0.06 kcal/mol. For each of the three pairs of compounds (2-, 3-, 4-methyl-), slight increase in Er (bond stretching energy) and E\textphi (torsional energy) occurs in the axial conformation over the equatorial conformation. However, the most significant change is a decrease in the overall attractive character of Enb (nonbonding) and a large
Table 28

Conformational energies of methylated silacyclohexanes

<table>
<thead>
<tr>
<th>Position</th>
<th>$E_r$</th>
<th>$E_{nb}$</th>
<th>$E_{\theta}$</th>
<th>$E_{\phi}$</th>
<th>Steric Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1e</td>
<td>0.61</td>
<td>-2.33</td>
<td>1.73</td>
<td>0.53</td>
<td>0.54</td>
</tr>
<tr>
<td>1a</td>
<td>0.60</td>
<td>-2.61</td>
<td>1.73</td>
<td>0.62</td>
<td>0.34</td>
</tr>
<tr>
<td>2e</td>
<td>0.77</td>
<td>-0.96</td>
<td>2.06</td>
<td>0.48</td>
<td>2.35</td>
</tr>
<tr>
<td>2a</td>
<td>0.90</td>
<td>-0.60</td>
<td>2.66</td>
<td>0.57</td>
<td>3.62</td>
</tr>
<tr>
<td>3e</td>
<td>0.79</td>
<td>-1.77</td>
<td>1.84</td>
<td>0.55</td>
<td>1.40</td>
</tr>
<tr>
<td>3a</td>
<td>0.93</td>
<td>-1.43</td>
<td>2.85</td>
<td>0.71</td>
<td>3.06</td>
</tr>
<tr>
<td>4e</td>
<td>0.82</td>
<td>-1.73</td>
<td>1.98</td>
<td>0.53</td>
<td>1.61</td>
</tr>
<tr>
<td>4a</td>
<td>0.96</td>
<td>-1.11</td>
<td>2.86</td>
<td>0.77</td>
<td>3.48</td>
</tr>
</tbody>
</table>

An increase in $E_{\theta}$ (bond angle deformation) for the axial conformation. For 1-(axial) methyl-1-silacyclohexane the $E_r$ and $E_{\theta}$ terms change less than for the other isomers. In addition $E_{\theta}$ does not change at all and $E_{nb}$ indicates increased attractive character. Thus, while the axial conformers of the 2-, 3- and 4-methyl isomers involve structural distortions to move the axial methyl groups away from the other axial hydrogens, the 1-methyl-1-silacyclohexane group finds a favorable total attractive position in the axial conformation (Figure 18).
The conformational energies of \( 109, 110, 111 \) and \( 112 \) were calculated by using a force field method. The force field used here is the MM2 program of Allinger with updated parameters. The MM2 program apportions the total energies into classical compression, bending, stretch-bend, van der Waals and torsional energies. The form of these equations can be found in the reference above. The results for the conformational energies of \( 109, 110, 111 \) and \( 112 \) were in agreement with the results from Ouellette and Allinger. The chair form is favored for the silacyclohexane. The Si-Me prefers an axial over an equatorial position, whereas the C-Me prefers an equatorial position. The results of the calculations of conformational energies are listed in Table 29 below.
Table 29
Conformational energies of 1-methyl-1-silacyclohexane and C-methylated 1-methyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Position</th>
<th>Total Steric Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>109</td>
<td>lax (Si-Me)</td>
<td>3.66</td>
</tr>
<tr>
<td>109</td>
<td>leq (Si-Me)</td>
<td>3.78</td>
</tr>
<tr>
<td>110</td>
<td>lax, 2eq</td>
<td>4.49</td>
</tr>
<tr>
<td>110</td>
<td>leq, 2eq</td>
<td>4.59</td>
</tr>
<tr>
<td>111</td>
<td>lax, 3eq</td>
<td>4.28</td>
</tr>
<tr>
<td>111</td>
<td>leq, 3eq</td>
<td>4.42</td>
</tr>
<tr>
<td>112</td>
<td>lax, 4eq</td>
<td>4.39</td>
</tr>
<tr>
<td>112</td>
<td>leq, 4eq</td>
<td>4.54</td>
</tr>
</tbody>
</table>

These results indicate that the axial orientation of a methyl group on silicon is favored by a little over 0.1 kcal/mol regardless of whether there are other methyl groups in the ring.

The MM2 force field calculation was also used to determine the conformational energies of the 1,1,2,6- and 1,1,3,5-tetramethyl-1-silacyclohexanes, \( \text{129} \) and \( \text{130} \) respectively. The results indicated that the most stable conformations are those in which the Me groups are in equatorial positions. These results agree with the experimental observations. The results of these conformational energy calculations on \( \text{129} \) and \( \text{130} \) are listed in Table 30.
Table 30
The conformational energies 1,1,2,6- and 1,1,3,5-
tetramethyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Total Steric Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>129 2eq, 6eq</td>
<td>3.41</td>
</tr>
<tr>
<td>129 2eq, 6ax</td>
<td>4.49</td>
</tr>
<tr>
<td>129 2ax, 6ax</td>
<td>6.14</td>
</tr>
<tr>
<td>130 3eq, 5eq</td>
<td>3.18</td>
</tr>
<tr>
<td>130 3eq, 5ax</td>
<td>5.53</td>
</tr>
<tr>
<td>130 3ax, 5ax</td>
<td>9.48</td>
</tr>
</tbody>
</table>

Conformational Equilibria of Methylated and
Dimethylated 1-methyl-1-silacyclohexanes

It is well known that conformational equilibrium in a
substituted cyclohexane favors the equatorial position of
the substituents. The "conformational free energy" (also
called an A-value) is the standard free energy difference
between equatorial and axial conformations.

\[
\Delta G (\text{kcal/mol}) = -RT\ln K \quad \text{where} \quad K = e/a
\]
The conformational equilibria of C-methylated dimethylated 1-methyl-1-silacyclohexanes were determined by assuming that the difference in conformational energy is equal to the steric energy ($\Delta G = \Delta E$) and by applying the equation:

$$\Delta E = \Delta G = -RT\ln K \text{ (in kcal/mol)}$$

The results giving the total steric energies, $E_t$, the conformational energy differences $\Delta E$ (or $A$ values) and the equilibrium positions for the C-methylated 1-methyl-1-silacyclohexanes are listed in Tables 31-36.

The results from Tables 31-33 indicate that the conformational equilibria of methylated 1-methyl-1-silacyclohexanes favor, as expected, the isomers with SiMe axial and CMe equatorial. The $\Delta E$'s are all expressed as $E_{axSiMe} - E_{eqSiMe}$. In the geometrical isomers in which SiMe can be axial and CMe equatorial simultaneously, $\Delta E$ values are -1.08, -1.51 and -1.65 kcal/mol, respectively, for the 1,2-, 1,3- and 1,4-dimethyl-1-silacyclohexanes. The $\Delta E$ values are slightly larger in the 1,3- and 1,4-dimethyl conformers, because of the 1,3-diaxial interaction between CMe(ax) and the axial hydrogens. This interaction moves the methyl group away from these hydrogens resulting in structural distortion so that the bending and torsional energies increase. The $\Delta E$ values
for the equilibria in which the SiMe(eq)-CMe(eq) isomers are favored 0.92, 2.11 and 1.43 kcal/mol, respectively. ΔE is large (2.11 kcal/mol) when 1,3-dimethyl groups are axial resulting in a large steric effect between 1,3-diaxial methyls and the axial hydrogen again resulting in distortion and increased bending and torsional energies. ΔE values for 1,2,6-trimethyl-1-silacyclohexane are -2.65, -0.04 and 2.51 kcal/mol (Table 35), and those for 1,3,5-trimethyl-1-silacyclohexane are -4.78, 5.98 and 0.72 kcal/mol (Table 34). The expected large ΔEs are due to the 1,3-axial interactions between the methyl group(s) and hydrogen(s).
Table 31
Conformational equilibrium of 1,2-dimethyl-1-silacyclohexane

![Diagram of conformers of 1,2-dimethyl-1-silacyclohexane]

<table>
<thead>
<tr>
<th>Conformer</th>
<th>$E_t$</th>
<th>$\Delta F$</th>
<th>$K^*$ and ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.30</td>
<td>-1.08</td>
<td>6.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[1:2 = 86:14]</td>
</tr>
<tr>
<td>2.</td>
<td>5.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>4.40</td>
<td>0.92</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[4:3 = 17:83]</td>
</tr>
<tr>
<td>4.</td>
<td>5.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*K is the ratio of $\text{SiMe(ax)}/\text{SiMe(eq)}$ of two conformers (e.g. 1/2)
### Table 32
Conformational equilibrium of 1,3-dimethyl-1-silacyclohexane

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Et</th>
<th>$\Delta E$</th>
<th>$K^*$ and ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.11</td>
<td>-1.51</td>
<td>12.93 [1:2 = 93:7]</td>
</tr>
<tr>
<td>2.</td>
<td>5.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>4.23</td>
<td>2.12</td>
<td>0.03 [4:3 = 3:97]</td>
</tr>
<tr>
<td>4.</td>
<td>6.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*K is the ratio of SiMe(ax)/SiMe(eq) of two conformers (e.g. 1/2)*
### Table 33

Conformational equilibrium of 1,4-dimethyl-1-silacyclohexane

![Conformational Structures]

<table>
<thead>
<tr>
<th>Conformer</th>
<th>$\Delta F$</th>
<th>$K^*$ and ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.22</td>
<td>-1.64, 16.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[1:2 = 94:6]</td>
</tr>
<tr>
<td>2.</td>
<td>5.86</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>4.35</td>
<td>1.43, 0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[4:3 = 8:92]</td>
</tr>
<tr>
<td>4.</td>
<td>5.78</td>
<td></td>
</tr>
</tbody>
</table>

*K is the ratio of SiMe(ax)/SiMe(eq) of two conformers (e.g. 1/2)*
Table 34
Conformational equilibrium of 1,3,5-trimethyl-1-silacyclohexane

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Et</th>
<th>$\Delta E$</th>
<th>$K^*$ and ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.55</td>
<td>-4.78</td>
<td>$3.3 \times 10^3$</td>
</tr>
<tr>
<td>2.</td>
<td>9.33</td>
<td></td>
<td>[1:2 = 100:0]</td>
</tr>
<tr>
<td>3.</td>
<td>4.67</td>
<td>5.99</td>
<td>$3.93 \times 10^{-5}$</td>
</tr>
<tr>
<td>4.</td>
<td>10.66</td>
<td></td>
<td>[4:3 = 0:100]</td>
</tr>
<tr>
<td>5.</td>
<td>6.09</td>
<td>0.73</td>
<td>0.29</td>
</tr>
<tr>
<td>6.</td>
<td>6.82</td>
<td></td>
<td>[6:5 = 23:77]</td>
</tr>
</tbody>
</table>

*K is the ratio of SiMe(ax)/SiMe(eq) of two conformers (e.g. 1/2)
Table 35
Conformational equilibrium of 1,2,6-trimethyl-1-silacyclohexane

<table>
<thead>
<tr>
<th>Conformer</th>
<th>$E_t$</th>
<th>$\Delta E$</th>
<th>$k^*$ and ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.95</td>
<td>-2.65</td>
<td>89.38</td>
</tr>
<tr>
<td>2.</td>
<td>7.60</td>
<td></td>
<td>[1:2 = 99:1]</td>
</tr>
<tr>
<td>3.</td>
<td>5.95</td>
<td>-0.04</td>
<td>1.07</td>
</tr>
<tr>
<td>4.</td>
<td>5.99</td>
<td></td>
<td>[3:4 = 52:48]</td>
</tr>
<tr>
<td>5.</td>
<td>7.54</td>
<td>2.52</td>
<td>0.01</td>
</tr>
<tr>
<td>6.</td>
<td>5.02</td>
<td></td>
<td>[5:6 = 1:99]</td>
</tr>
</tbody>
</table>

*K is the ratio of SiMe(ax)/SiMe(eq) of two conformers (e.g. 1/2)
Table 36
Conformational equilibrium of 1,4,4-trimethyl- and 1-methyl-1-silacyclohexanes

Conformer | $E_t$ | $\Delta E$ | $K^*$ and ratio
--- | --- | --- | ---
1. | 3.66 | -0.12 | 1.22
   | | | [1:2 = 55:45]
2. | 3.78 | | |
3. | 6.57 | -0.11 | 1.19
   | | | [3:4 = 55:45]
4. | 6.68 | | |

*K is the ratio of SiMe(ax)/SiMe(eq) of two conformers (e.g. 1/2)
Cis:Trans Isomerization Equilibria: Calculated Values Compared to Fluoride Results

The previous data referred to conformational equilibria which are rapidly established at room temperature by ring flipping motions. Those motions do not interconvert geometric isomers. However, as discussed earlier, the fluoride does catalyze cis/trans isomerization, and an equilibrium position can be determined experimentally. That position has been compared to the equilibrium position calculated from MM2 steric energy differences. The results are listed in Tables 37-39, expressed as $E_{\text{cis}} - E_{\text{trans}}$. The $\Delta E$s of cis/trans isomers are relatively small compared to $\Delta E$ in the conformational equilibria. The $\Delta E$s of interest are those between the lower steric energy conformers of the cis and trans isomers. Those values are -0.11, 0.12 and -0.13 kcal/mol for 1,2-, 1,3-, and 1,4-dimethyl-1-silacyclohexanes, respectively. The results afford the cis/trans isomers ratios: 54/46; 45/55 and 56/44 which agree with the experimental results of the isomerization (Table 27).

The results indicate that for the stable conformation, no matter where the C-Me(eq) group is, the C-methylated 1-methyl-1-silacyclohexanes are more stable when Si-Me is in an axial position, and the conformational preference is about 0.10 kcal/mol. That preference was also observed in the calculations for the 1-methyl and 1,4,4-trimethyl-1-silacyclohexanes (Table 36).
Table 37
Cis:trans isomers equilibrium, and results from fluoride isomerization reaction of 1,2-dimethyl-1-silacyclohexane

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Et</th>
<th>ΔE</th>
<th>Kc** and ratio</th>
<th>Kexpt.***</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.30</td>
<td>-0.10</td>
<td>1.20</td>
<td>[1:2 = 54:46] [1:2 = 55:45]</td>
</tr>
<tr>
<td>2.</td>
<td>4.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>5.32</td>
<td>0.06</td>
<td>0.91</td>
<td>[4:3 = 47:53]</td>
</tr>
<tr>
<td>4.</td>
<td>5.38</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** Kc is the ratio: cis/trans.

*** Kexpt. is the experimental ratio: cis/trans.
Table 38

Cis:trans isomers equilibrium, and results from fluoride isomerization reaction of 1,3-dimethyl-1-silacyclohexane

![Chemical structures showing cis and trans isomers of 1,3-dimethyl-1-silacyclohexane]

<table>
<thead>
<tr>
<th>Conformer</th>
<th>$\Delta E$</th>
<th>$K_c^{**}$ and ratio</th>
<th>$K_{expt.}^{***}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.11</td>
<td>0.12 0.81</td>
<td>[2:1=45:55] [2:1=45:55]</td>
</tr>
<tr>
<td>2.</td>
<td>4.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>6.35</td>
<td>0.73 0.29</td>
<td>[3:4=23:77]</td>
</tr>
<tr>
<td>4.</td>
<td>5.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** $K_c$ is the ratio: cis/trans.**

*** $K_{expt.}$ is the experimental ratio: cis/trans.***
Table 39
Cis:trans isomers equilibrium, and results from fluoride isomerization reaction of 1,4-dimethyl-1-silacyclohexane

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Et</th>
<th>$\Delta E$</th>
<th>$K_c$<strong>and ratio</strong></th>
<th>$K_{expt.}$***</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td></td>
<td>4.22</td>
<td>-0.13</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[1:2=56:44]</td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td>4.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>5.78</td>
<td>0.08</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[3:4=49:51]</td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td>5.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** $K_c$ is the ratio: cis/trans.
*** $K_{expt.}$ is the experimental ratio: cis/trans.
II-2-4. Discussion of the Mass Spectra of
C-methylated 1-methyl-1-substituted-1-
silacyclohexanes

While the mass spectrometry of organic compounds has
been extensively studied, the mass spectrometry of organo-
metallic compounds, and in particular organosilicon com­
ounds, is a much less explored field. The silyl center
has a profound and usually dominant effect on the mass
spectral behavior of organosilicon compounds with silyl
cation fragments being formed in great abundance. Mass
spectrometry provides insights into the nature and
behavior of silyl cations, species which are often diffi­
cult to study in solution.

The mass spectra of trimethylalkylsilanes are domi­
nated by silyl cations formed by fragmentation of an alkyl
group from the quartenary silyl center.126-128 The parent
ion is frequently not observed since fragmentation at the
silyl center is such a highly favored process. Cleavage
at a branched center to form a tertiary carbocation is a
known process from the mass spectra of organic compounds.
On the basis of Pauling's electronegativity scale, silyl
cations are expected to be more stable than carbocations,
since silicon is more electronegative than carbon. The
mass spectra of tetraalkylsilanes support the conclusion
that silyl cations are not inherently unstable, although
they are seldom observed in solution.
In the silacyclohexane system, the mass spectral fragmentation patterns are very typical for cyclic silanes; indeed, for silanes in general. The fact that the present set of derivatives has methyl groups in so many different positions, however, allows one to reach some conclusions about the nature of the fragmentation pathways. The molecular ions are present in low abundances, with the exception of cases in which there are one or more methyl groups on C₂. Then the molecular ion is more prominent (>42%). Fragmentation patterns, as with methylsilanes in general, are dominated by peaks containing Si and which arise by loss of Me radicals or olefins (C₂H₄, C₃H₆, C₄H₈, etc.). For instance, Scheme 10 below accounts for the prominent fragments from 1,1,2-trimethyl-1-silacyclohexane.

Assuming that the masses 114 and 100 are the molecular ions of the silacyclobutanes, then the fragments expected from these species should be observed and are. The (M-43) peak is generally prominent, and is the base peak in the spectra of all SiMe₂ series having one C-Me. It is written in Scheme 12 as arising via loss of Me then C₂H₄, since it is much more prominent than would be expected if it arose via the 1,1,2-tetramethyl-1-silacyclobutane molecular ion.

However, the situation is not so simple as Scheme 10 implies. If the olefins being eliminated are being formed
in all cases by cleavage of a single Si–C and C–C bond, then loss of C\textsubscript{3}H\textsubscript{6} should not be prominent in 131 (but it is). Indeed, loss of C\textsubscript{2}H\textsubscript{4} is a prominent peak in the spectrum of 130, which has no contiguous CH\textsubscript{2} groups. Clearly, either what is being eliminated is not CH\textsubscript{2}=CH\textsubscript{2}, or some deep-seated rearrangement has taken place prior to fragmentation. Indeed, ring expansion reactions of silacycloalkane molecular ions involving the C–Me group have
been proposed by Gussel'nikov and co-workers on the basis of deuterium labeling studies.\(^\text{122}\)

Loss of Me radical from \(\text{Me}^+\) leads to a prominent peak in all the spectra, but is only occasionally the base peak. There is no obvious pattern of ring Me placement that makes \((\text{Me}-\text{Me})^+\) more abundant. Among the hydrides, only the parent \(109\) shows \((\text{Me}-\text{H})^+\) as a significant peak, however, \((\text{Me}-\text{C}_2\text{H}_4)^+\); \((\text{Me}-29)^+\), is prominent in all of the hydrides, but in none of the SiMe\(_2\) derivatives. Loss of CH\(_2\) from \(\text{Me}^+\) is occasionally seen.

The \((\text{M}-41)^+\) peak, seen as a metastable transition by Chernyak\(^{123,124}\) in the spectrum of \(109\), and leading to m/e=73, is not at all prominent generally in the derivatives here. However, m/e=73, presumably Me\(_3\)Si\(^+\), is generally prominent particularly when there is a C-Me in the ring, again indicating the possibility for substantial rearrangement.

While it is not obvious that ring methyl placement can be readily diagnosed from the mass spectral fragmentation patterns (except with respect to the presence or absence of Si-H) there are nevertheless obvious differences among the isomers, and indeed some differences between cis and trans isomers.

It is also interesting to take a general look at the mass spectral fragmentation of the fluoro and chloro
derivatives of C-methylated 1-methyl-1-substituted-1-silacyclohexanes. In the fragmentation of methylfluoro-
silane derivatives, the molecular ions are present in relatively low abundance for 137, and 138 (14%), however, in 139 the molecular ion is more prominent (40%). Similar to the case of the methylsilane derivatives, the fragmentation of the fluoromethylsilanes is dominated by the peaks containing Si and which arise by the loss of Me radical, ethylene, C_3H_6 and C_4H_8. Table 40 shows a part of the mass spectrum of C-methylated 1-fluoro-1-methyl-1-
silacyclohexanes (masses less than m/e 85 are not listed in this table). Scheme 11 below, demonstrates the typical fragmentation of 1-fluoro-1,3-dimethyl-1-silacyclohexane.

Assuming that the masses 118 and 104 are the molecular ions of fluorosilacyclobutanes, then the fragmentation expected from these species should be observed. In general the peak [M-Me]^+ is prominent in all these fluoro compounds. This peak is more significant in 137 and 138 (>85%) than in 139 (60%). In 138a the peak [M-Me]^+ shows maximum intensity (100%). The loss of C_2H_4 gives the peak [M-C_2H_4]^+, which is the base peak in 139, but shows very low abundance in 137 and 138 (2%). The peak [M-C_4H_8]^+ is also significant in 139 (>87%), but in 137 and 138 this peak is present in low intensity (5%). However, the situation is different for the peak [M-CH_3-C_2H_4]^+. It is the base peak in 137, 138b and 138a (85%), but less prominent
in 139 (38%). The peak \([M-C_3H_6]^+\) is more prominent in 137 and 138 (40%) but shows low abundance in 139 (3%). The peak \([M-CH_3-C_3H_6]^+\) and \([M-C_3H_6-C_2H_4]^+\) are significant in all these C-methylated 1-fluoro-1-methyl-1-silacyclohexanes. The mass m/e 77 (intensity varies from 20-65%), presumably \(Me_2SiF^+\), is present in all of the methylfluoro-silane derivatives, indicating there is some type of rearrangement involved in the fragmentation of the C-methylated 1-fluoro-1-methyl-1-silacyclohexanes. It seems
Table 40
Mass spectra of C-methylated 1-fluoro-1-methyl-1-silacyclohexane

<table>
<thead>
<tr>
<th>Ion type</th>
<th>m/e</th>
<th>137a</th>
<th>137b</th>
<th>138a</th>
<th>138b</th>
<th>139a</th>
<th>139b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. M$^+$</td>
<td>146</td>
<td>15</td>
<td>7</td>
<td>14</td>
<td>19</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>2. [M-CH$_3$]$^+$</td>
<td>131</td>
<td>86</td>
<td>98</td>
<td>100</td>
<td>86</td>
<td>63</td>
<td>60</td>
</tr>
<tr>
<td>3. [M-C$_2$H$_4$]$^+$</td>
<td>118</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>4. [M-C$_3$H$_6$]$^+$</td>
<td>104</td>
<td>44</td>
<td>32</td>
<td>28</td>
<td>49</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>5. [M-CH$_3$-C$_2$H$_4$]$^+$</td>
<td>103</td>
<td>100</td>
<td>100</td>
<td>85</td>
<td>100</td>
<td>38</td>
<td>39</td>
</tr>
<tr>
<td>6. [M-C$_4$H$_8$]$^+$</td>
<td>90</td>
<td>8</td>
<td>7</td>
<td>5</td>
<td>5</td>
<td>87</td>
<td>90</td>
</tr>
<tr>
<td>7. [M-CH$_3$-C$_3$H$_6$]$^+$</td>
<td>89</td>
<td>32</td>
<td>30</td>
<td>23</td>
<td>35</td>
<td>36</td>
<td>33</td>
</tr>
<tr>
<td>8. [M-C$_3$H$_6$-C$_2$H$_4$]$^+$</td>
<td>86</td>
<td>64</td>
<td>62</td>
<td>38</td>
<td>65</td>
<td>41</td>
<td>43</td>
</tr>
</tbody>
</table>

that if there is a methyl group at C$_4$ in the ring, the loss of C$_2$H$_4$ is prominent; however, if the methyl group is at C$_2$ and C$_3$ the situation is different, and the loss of Me radical giving [M-Me]$^+$ and [M-CH$_3$-C$_2$H$_4$]$^+$ dominates the fragmentation.

The fragmentation of chloromethylsilane derivatives is similar to the other cases. Table 41 shows a part of the mass spectra of C-methylated 1-chloro-1-methyl-1-silacyclohexanes (masses less than m/e 105 are not listed in this table). Scheme 12 below demonstrates the typical fragmentation of 1-chloro-1,3-dimethyl-1-silacyclohexane.
The peak arising from the loss of Me radical [M-Me]$^+$ is the base peak in 118; however, it appears at low intensity in 117 and 119 (18%). The peak [M-C$_2$H$_4$]$^+$ is prominent in 117 (56% for cis and 67% for trans) and 119 (90% for cis and 32% for trans), but it is not significant in 118 (2%). The peak [M-C$_3$H$_6$]$^+$ is significant in 118 (31% for cis and 56% for trans) but has less intensity in 117 and 119.
Table 41
Mass spectra of C-methylated 1-chloro-1-methyl-1-silacyclohexanes

<table>
<thead>
<tr>
<th>Ion type</th>
<th>m/e</th>
<th>117a</th>
<th>117b</th>
<th>118a</th>
<th>118b</th>
<th>119a</th>
<th>119b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. M⁺</td>
<td>162</td>
<td>34</td>
<td>31</td>
<td>7</td>
<td>14</td>
<td>26</td>
<td>32</td>
</tr>
<tr>
<td>2. [M-CH₃]⁺</td>
<td>147</td>
<td>19</td>
<td>18</td>
<td>100</td>
<td>100</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>3. [M-C₂H₄]⁺</td>
<td>134</td>
<td>56</td>
<td>67</td>
<td>2</td>
<td>4</td>
<td>90</td>
<td>32</td>
</tr>
<tr>
<td>4. [M-C₃H₆]⁺</td>
<td>120</td>
<td>12</td>
<td>9</td>
<td>31</td>
<td>56</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>5. [M-CH₃-C₂H₄]⁺</td>
<td>119</td>
<td>49</td>
<td>55</td>
<td>72</td>
<td>96</td>
<td>46</td>
<td>47</td>
</tr>
<tr>
<td>6. [M-C₄H₈]⁺</td>
<td>106</td>
<td>100</td>
<td>100</td>
<td>5</td>
<td>9</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>7. [M-C₃H₆-CH₃]⁺</td>
<td>105</td>
<td>49</td>
<td>45</td>
<td>26</td>
<td>35</td>
<td>31</td>
<td>26</td>
</tr>
</tbody>
</table>

(<10%). The peaks [M-CH₃-C₂H₄]⁺ and [M-C₃H₆-CH₃]⁺ are prominent in all these chloromethylsilane derivatives; however, the peak [M-C₄H₈]⁺ shows maximum intensity in 117 and 119 but very low abundance in 118 (5% for cis and 9% for trans). The presence of m/e 94 and 92 (intensity varies from 20-98%), presumably Me₂SiCl⁺, indicates that some form of rearrangement was involved in the fragmentation of C-methylated 1-chloro-1-methyl-1-silacyclohexanes. In general, it seems that when there is a methyl group at C₂ or C₄, the fragmentation of C-methylated 1-chloro-1-methyl-1-silacyclohexanes is dominated by the loss of C₂H₄ and C₄H₈ from the molecular ion to give the peaks at [M-C₂H₄]⁺ and [M-C₄H₈]⁺. But if there is a methyl group at
C₃, the fragmentation is dominated by the peak arising from the loss of Me radical (M-Me)⁺ from the molecular ion.

II-2-5. Ring Expansion Reaction of Methylated Silacyclopentanes

The reaction for expansion of silaheterocycles containing a silicon atom bearing a chloromethyl group has been previously reported.²⁰ The rearrangement with ring enlargement occurs on treatment of the chloromethyl derivatives with AlCl₃ (Equation 18). 1-(Chloromethyl)-1-methyl-1-silacyclopentane ³³ and 1-(chloromethyl)-1-substituted-1-silacyclohexane ¹⁴⁰ undergo ring expansion to afford 1-chloro-1-methyl-1-silacyclohexane ³⁴ and

Equation 18
1-chloro-1-substituted-1-silacycloheptane 141, respectively. 131 This rearrangement can also take place under the influence of a nucleophilic reagent such as sodium methoxide; or sodium or potassium hydroxide in absolute methyl alcohol (Equation 19). 21

Corey reported the ring enlargement of the six-membered ring of tricyclic silicon heterocycles, dibenzo[b,f]silepins 142, which contain an exocyclic chloromethyl group on silicon. The reactions occur in the presence of Lewis acids such as AlCl₃ or AlBr₃ in refluxing benzene to afford seven-membered ring dibenzo[b,f]silocins 143 (Equation 20). 132
Replacement of a methylene group of 142 by a heteroatom with a lone pair results in the formation of an addition complex of AlCl$_3$ and no ring enlargement. Corey found that this disadvantage could be eliminated, since the above transformation could be initiated by an anion such as fluoride. Fluoride induced ring expansion of the six-membered ring of 144 in refluxing acetonitrile gave seven-membered ring dibenzoheterosilepins 145 (Equation 21).

\[
\text{Corey also reported that the reaction of fluoride with the seven-membered ring dibenzo[b,e][1,4]oxasilepin 146 generates two isomers of dibenzo[b,f]oxasilocin 147 and 148 (Equation 22). No reaction was observed between 146 and KF.HF in refluxing acetonitrile after 20 h, and with addition of 18-crown-6 only minor reaction occurred after 22 h. With KF (tech), reaction was also slow, but}
\]
when 18-crown-6 was added, no starting material was observed after 24 h. These experiments demonstrate that an eight-membered ring may be generated by anion-induced rearrangement of halomethyl-substituted silepins although not as smoothly nor in as high yields as has been demonstrated for six-membered ring conversions. The fluoride rearrangement with prior attack at silicon has been suggested as an explanation for conversion of $\text{Me}_3\text{SiCH}_2\text{I}$ to $\text{Me}_2\text{EtSiF}$ with KF/DMF. A thermal rearrangement of $\text{Ph}_3\text{SiCHFPh}$ to $\text{Ph}_2\text{SiFCHPh}_2$ has also been reported.

This type of ring enlargement reaction is interesting to us because it affords a method to prepare methylated 1-methyl-1-silacyclohexanes by a route different from ring cyclization, and because of our desire to obtain new
information about the rearrangement. The 1-methyl-1-sila-
cyclohexane derivatives could be prepared from 1-chloro-
methyl-1-silacyclopentane derivatives in the presence of nucleophilic or electrophilic reagents. In 33 a ring bond migrates from silicon in preference to a methyl group. However, there is no indication in the literature regarding the effects of ring substituents which make the ring unsymmetrical, thus requiring a choice of different ring bonds as migrating center.

We have studied 1-chloromethyl-1-silacyclopentane derivatives and have found that 1-chloromethyl-1,2-
dimethyl-1-silacyclopentane 150 is a suitable compound for rearrangement. The molecule contains two chiral centers, one at silicon and another at the carbon alpha to silicon. Compound 150 was prepared from the reaction of the diGrignard reagent of 1,4-dibromopentane 149 with chloromethyldichlorosilane in ether (Equation 23).

Fortunately, this cyclization afforded a 61/39 mixture of cis and trans isomers of the desired product 150. Because
one isomer was predominant over the other, the stereochemistry of the rearrangement to form a six-membered ring could be investigated.

The ring-expansion of a 61/39 mixture of 150 occurs under the influence of the nucleophilic reagent $\text{NH}_4\text{HF}_2$ in refluxing acetonitrile over 3 days (Equation 24). The yield was not high but the result was very interesting.

![Equation 24](attachment:image.png)

The product is 1-fluoro-1,3-dimethyl-1-silacyclohexane 138 which had been previously prepared as mentioned earlier in this dissertation. The proton NMR spectrum of the product indicated that it was a 45:55 mixture of cis and trans isomers. This rearrangement reaction thus gives predominant inversion of configuration at either the silicon atom or the carbon (which becomes C₃ in 138), but not at both. The migrating center is undergoing a 1,2-sigmatropic shift, and on the grounds of arguments based on orbital symmetry and also steric factors probably migrates with
retention. Hence inversion is probably occurring at silicon. Since we do not have a mixture of 150 isomers in which the trans isomer predominates, we have only observed the reaction going from predominantly cis reactant to predominantly trans product. It is possible, but we think less likely, that the reaction is stereoselective and involves isomerization to an equilibrium mixture of product isomers.

The same type of ring expansion was also observed under thermal conditions (Equation 25). A 61/39 mixture of cis and trans isomers of 150 was placed in a thick walled NMR tube, sealed and immersed in an oil bath at 200°C. The reaction was followed by proton NMR, which indicated that the rearrangement took place over 4-5 h to give a 43/57 mixture of cis and trans isomers of 1-chloro-1,3-dimethyl-1-silacyclohexane 118. Thus, predominant inversion occurred in this reaction as well.
The results are surprising because the carbon center C₂ (a secondary carbon) migrates rather than the primary carbon center C₅. Steward¹³⁷ and Damrauer¹³⁸ studied the migratory aptitudes of various organanic organic groups in the fluoride- and AlCl₃-induced rearrangements of (chloromethyl)triorganosilanes:

Their results showed that migration was faster in the order Et > Me > 1-propyl. The mechanism for AlCl₃ catalyzed rearrangement has been proposed and discussed by Eaborn et al.,¹³⁹ who suggested an intermediate like Figure 19. The migration of the organic group from silicon to the alpha carbon is facilitated by electron-release as shown by the relative rates of migration of substituted phenyl groups, but is inhibited, relative to methyl, by branching at the alpha carbon. The mechanism
for the fluoride induced rearrangement was proposed by Damrauer\textsuperscript{138} to involve a pentacoordinated adduct at the silicon center. Since electron withdrawing groups stabilize the anion, they accelerate migration.

The thermal rearrangement of alpha halosilanes $R_3SiCHXR'$ was proposed by Brook\textsuperscript{136} to have a mechanism involving initial migration of X to silicon, to form an "inverse ylide":

$$R_3SiX \rightarrow^{+} \text{CHR}'$$

Brook found that the ease of migration of R from silicon to the alpha carbon decreased in the order Ph $>$ Me, Et, but there is no comparison of the migrating rates of various alkyl groups, e.g. methyl, ethyl, isopropyl.

At the moment discrepancies still remain about the migratory aptitudes of various groups in these rearrangements, and the mechanistic proposals must be considered as tentative. Our work demonstrates a highly regiospecific reaction, but it remains unclear why an anion-induced rearrangement would lead to migration of a secondary carbon in preference to a primary carbon. Structural and mechanistic studies of these compounds and their rearrangement reactions are continuing.
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CHAPTER III: EXPERIMENTAL
III-1. General Comment

Since most of the synthesis of monomethylated 1-methyl-1-silasubstituted-1-silacyclohexanes and their chemical reactions were carried out in the same manner, a typical sequence of reactions of one series, such as 1,4-dimethyl-1-silasubstituted-1-silacyclohexanes will be described in this section. The preparation of 1,1,2,6- and 1,1,4,4-tetramethyl-1-silacyclohexanes are also reported. Spectroscopic data of the other compounds are listed in the next section.

General for All Experiments

Unless otherwise stated, all Grignard reagents were prepared in a three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, an addition funnel and nitrogen inlet system. All glassware was oven dried, assembled hot, and flushed with nitrogen prior to conducting the reaction under an atmosphere of nitrogen. All products were distilled through a 195 mm Vigreaux column. Ether and THF were removed with a 250 mm variable reflux distillation head unless otherwise stated.

In general infrared spectra were recorded on either a Perkin Elmer IR-137 or IR-621 grating spectrometer as neat liquid films or in CCl₄ for the solid N-benzoylpiperidine and are reported in cm⁻¹. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker
WP-200 FT spectrometer with a probe temperature of 297°K. The spectra were recorded in CDCl₃ solution and chemical shifts are reported in parts per million (§) downfield from tetramethylsilane as internal standard.

Mass spectra were obtained on a Hewlett Packard 5985 GC/MS, operating at 70 eV using a 30mmx0.25mmIDx0.2 film OV-1-B.P., fused silica capillary column and are reported as m/e (relative abundance). The precise mass measurements were obtained on a Kratos MS 80 RFK high resolution mass spectrometer, operating at 70 eV by using a heliflex capillary column 13683 (30mx0.25mm -150 max.temp.330°C).

The cis/trans isomer ratios formed in ring cyclization reactions were measured from ¹H NMR and GC peak areas. For bromination, chlorination, fluorination, and reduction reactions, the reported cis/trans ratios were measured by ¹H NMR.

Piperidine and its derivatives were distilled from sodium or potassium pellets before use. The dichlorosilane derivatives were used as purchased without further purification. Commercial anhydrous ether was used as supplied. The reaction for preparation of the dibromoalkanes were carried out in an efficient hood.
III-2. Experimental

1. Preparation N-Nenzoyl-4-methylpiperidine.

Sodium hydroxide pellets (52.5 g, 1.3 mol) and 400 mL of distilled water were placed in a three-necked round-bottomed flask equipped with magnetic stirrer, an addition funnel and nitrogen inlet system. The sodium hydroxide solution was maintained at room temperature by using an ice cold water bath. 4-Methylpiperidine (99.18 g, 1.0 mol) was poured into the flask and stirred. From an addition funnel, benzoyl chloride (140.5 g, 1.0 mol) was dropped slowly into the piperidine/sodium hydroxide solution and the temperature was kept around room temperature throughout the reaction. When the addition was completed, ca. 3 h, the reaction mixture was stirred at room temperature for an additional hour. After transfer to a separatory funnel, the yellow oily liquid (the top layer) was collected. The product was distilled under reduced pressure at 203°C/10 mm, giving 186.0 g (92%) of product as a very thick colorless oily liquid. It solidified very quickly at room temperature.

\(^1\)H NMR: \(\delta\) 0.85 (d:J=6.100 Hz, 3H, C-Me), 1.00-1.80 (m, 5H, -CH\(_2\)-CH\(_2\)-); 2.60-3.10 (m, 2H, -CH\(_2\)-N); 3.70-4.30 (m, 2H, -CH\(_2\)-N); 7.30 (s, 5H, Ar-H).

IR: 3000, 2950, 2920, 2860, 2240, 1635, 1615, 1600, 1590, 1580, 1480, 1460, 1440, 1430, 1370, 1310, 1270, 1250, 1210, 1160, 1090, 970, 910, 800.
MS: 203(30), 202(88), 188(2), 105(100), 77(37), 51(5).

Anal. Calcd. for C_{13}H_{17}ON: C, 76.84; H, 8.37; N, 6.90; O, 7.88. Found: C, 76.95; H, 8.42; N, 6.89.

2. **Preparation of 1,5-Dibromo-3-methylpentane.**

N-benzoyl-4-methylpiperidine (95.2 g, 0.42 mol) in 300 mL of carbon tetrachloride was placed in a one liter three-necked round-bottomed flask, equipped with an addition funnel, thermometer, reflux condenser, nitrogen inlet system, a magnetic stirrer and an ice cold water bath, and stirred. Phosphorus tribromide (115.0 g, 0.42 mol) was added dropwise to the piperidine solution while stirring. The addition took about 3 h to complete, an ice water cooling bath was used to maintain the reaction temperature between 24-34°C. Bromine (31.8 mL, 0.42 mol) was added dropwise over 5 h to the reaction mixture. This is an exothermic reaction, so the temperature was carefully controlled by using an ice cold water bath. The reaction mixture became a dark yellow thick oil liquid, which was heated slowly to remove some fumes. Carbon tetrachloride was removed by simple distillation and the residue then co-distilled at 110-120°C/5 mm. The residue was a dark brown polymeric product. The distillate which contained phosphoryl bromide, phenyl cyanide, and 1,5-dibromo-3-methylpentane was poured into a beaker which contained 300 g of crushed ice and the mixture allowed to
stand for 2 h. The liquid was decanted, then extracted with (2x300 mL) of ligroine. The ligroine was washed carefully with concentrated sulfuric acid (10x15 mL) in order to convert phenyl cyanide to benzoic acid. The organic layer was washed with dilute sodium hydroxide solution (2x100 mL) and with 200 mL of distilled water, dried over anhydrous calcium chloride, and the ligroine removed by fraction distillation. The residue was vacuum distilled at 120-121°C/18 mm, and yielded 62.5 g (61%) of product as a colorless oily liquid.

\[ \text{H NMR: } 0.94 (d; J = 6.019 Hz, 3H, C-CH}_3, 1.50-2.22 (m, 5H, -C-CH}_2), 3.25-3.68 (m, 4H, CH}_2-Br). \text{ MS: } 246(0.6), 244(1.5), 242(0.8), 165(10), 163(12), 83(100), 69(9), 55(59). \]

IR: 3010, 2960, 2930, 2870, 2830, 1470, 1450, 1535, 1390, 1285, 1270, 1240, 860, 770. \[ \text{13C NMR (CDCl}_3): 17.89 (s, 1C, C-CH}_3), 30.25 (s, 1C, C}_3), 30.92 (s, 2C, C}_2 and C}_4), 39.01 (s, 2C, C}_3 and C}_5). \]

Anal. Calcd. for C\text{6}H\text{12}Br\text{2}: C, 29.51; H, 4.92; Br, 65.57.
Found: C, 29.66; H, 5.05.

3. Preparation of 1,1,4-trimethyl-1-silacyclohexane.

The magnesium turnings (2.3 g, 0.1 mol) in 100 mL of anhydrous ether were activated with 1.0 mL of 1,2-dibromoethane for 3 h. A solution of 1,5-dibromo-3-methylpentane (10.0 g, 0.04 mol) in 250 mL of anhydrous
ether was added very slowly to the activated magnesium turnings. After the addition the mixture was refluxed for an additional 8 h, then cooled to room temperature. Dimethyldichlorosilane (4.6 mL, 0.04 mol) in 100 mL of anhydrous ether was added very slowly to the diGrignard solution. After the addition was completed, the reaction mixture was refluxed for 16 h and cooled to room temperature. Saturated ammonium chloride was added until two layers clearly formed (an ice cooling bath was used to maintain the reaction temperature around 25°C), then an additional 50 mL of ice cold water was added. The ethereal layer was separated, washed with (2x100 mL) of distilled water and dried over anhydrous magnesium sulfate for 3 h. Ether was removed by fractional distillation and the product was distilled under reduced pressure by using a short-path still to give a colorless oily liquid boiling at 65-66°C/40 mm yielded 3.2 g (55%). $^1$H NMR:

$\delta$  -0.03 (s, 3H, Si-Me equatorial),
0.01 (s, 3H, Si-Me axial), 0.86 (d:J=6.174 Hz, 3H, C-Me),
0.20-0.81 (m, 4H, -CH$_2$-Si-CH$_2$-),
0.94-2.15 (m, 5H, -CH$_2$-CH-CH$_2$-).

$^{13}$C NMR (CDCl$_3$): -2.05 (s, 1C, Si-Me),
-1.61 (s, 1C, Si-Me), 13.43 (s, 2C, C$_2$ and C$_6$),
23.19 (s, 1C, C-CH$_3$), 32.87 (s, 1C, C$_4$),
35.63 (s, 2C, C$_3$ and C$_5$).

IR: 2950, 2910, 2890, 2840, 1460, 1450, 1410, 1380, 1260,
1190, 1170, 1100, 930, 920, 860, 840, 790, 730. MS: 142(3), 129(4), 128(10), 127(96), 115(4), 114(25), 111(2), 101(4), 100(10), 99(100), 97(12), 87(6), 86(22), 85(41), 83(5), 81(2), 73(13), 72(26), 71(11), 59(25), 58(8), 55(5), 43(7), 41(3). Exact Mass Calcd. for C₈H₁₈Si: 142.1177; found: 142.1161.

4. Preparation of 1,4-Dimethyl-1-silacyclohexane.

Magnesium turnings (3.0 g, 0.13 mol) and 200 mL of anhydrous ether were activated with 1.5 mL of 1,2-dibromoethane for 3 h. A solution of 1,5-dibromo-3-methylpentane (12.7 g, 0.052 mol) in 300 mL of anhydrous ether was added dropwise (two phased formed), then the reaction mixture was refluxed for 8 h. After cooling to room temperature, methyldichlorosilane (6.01 g, 0.052 mol in 200 mL of anhydrous ether) was added dropwise to the diGrignard reagent solution. After the addition was complete, the reaction mixture was refluxed for 16 h, and cooled to room temperature. Saturated ammonium chloride was added to the reaction mixture, with an ice cold water bath being used to control the reaction temperature around 25°C, until two layers were formed clearly. The mixture was transferred to a separatory funnel, the organic layer was separated and washed with (2x100 mL) of distilled water, and dried over anhydrous magnesium sulfate for 3 h. Ether was removed by distillation, and the product was
distilled under reduced pressure to give a colorless liquid at 57-58°C/71 mm 3.85 g (60%). A 52/48 mixture of cis and trans isomers of 1,4-dimethyl-1-silacy-clohexane was indicated by GC analysis.

$^1$H NMR:

δ 0.06 (d: J=3.490 Hz, 3H, Si-Me equatorial),
0.10 (d: J=3.510 Hz, 3H, Si-Me axial),
0.86 (d: J=6.200 Hz, 6H, C-CH$_3$),
0.25-0.80 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.90-2.15 (m, 10H, -CH$_2$-CH-CH$_2$);
3.77 (m, 1H, Si-H axial), 3.84 (m, 1H, Si-H equatorial).

IR: 2940, 2910, 2890, 2840, 2125, 1460, 1410, 1380, 1300, 1260, 1185, 1105, 1070, 1030, 1005, 940, 920, 890, 780, 720, 690, 610. MS: cis isomer: 128(16), 127(8), 126(36), 113(4), 112(1), 111(6), 101(6), 100(62), 99(11), 98(6), 97(5), 86(9), 85(52), 83(6), 74(5), 73(16), 72(100), 71(19), 59(14), 58(20), 55(6), 45(7), 43(7). Trans isomer: 128(25), 127(7), 126(6), 113(4), 101(9), 100(58), 99(13), 97(5), 86(10), 85(44), 83(5), 74(4), 73(13), 72(100), 71(19), 59(15), 58(16), 55(6), 45(7), 43(6).

5. **Preparation of 1-Chloro-1,4-dimethyl-1-silacyclohexane.**

Magnesium turnings (9.84 g, 0.41 mol) and 300 mL of anhydrous ether were activated with 2 mL of 1,2-dibromoethane for 3 h. A solution of 1,5-dibromo-3-methylpentane (40 g, 0.16 mol) in 400 mL of anhydrous ether was added slowly to the activated magnesium turnings. After the addition was complete, the reaction mixture was refluxed for 8 h, then cooled to room temperature. Methyltrichlorosilane (23.84 g, 0.16 mol) in 500 mL of anhydrous ether was added dropwise to the diGrignard solution. After the addition was complete, the reaction mixture was refluxed for three days, cooled to room temperature, and the precipitated salt filtered off under nitrogen. The ether was removed by distillation, and the residue was distilled under reduced pressure to give a colorless oily liquid boiling at 94-95°C/55 mm 15.5 g (60%). A 32/68 mixture of cis and trans isomers was indicated by GC analysis.

$^1$H NMR: δ 0.41 (s, 3H, Si-CH$_3$ equatorial),
0.44 (s, 3H, Si-CH$_3$ axial),
0.21-0.80 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.92-2.20 (m, 10H, -CH$_2$-CH-CH$_2$-),
0.91 (d:J=6.220 Hz, 6H, C-CH$_3$). IR: 2950, 2920, 2900, 2870, 2850, 1460, 1405, 1400, 1380, 1260, 1185, 1070, 1030, 1010, 930, 910, 850, 830, 800, 770, 760, 630. MS:
trans isomer (major): 164(10), 162(32), 162(32), 149(6), 147(18), 137(4), 136(32), 135(11), 134(92), 121(16), 120(5), 119(47), 111(9), 109(7), 108(33), 107(26), 106(100), 105(26), 97(8), 95(26), 94(25), 93(63), 92(46), 91(6), 83(5), 81(17), 80(10), 79(46), 78(22), 67(4), 66(4), 65(11), 63(22). Cis isomer (minor): 164(11), 162(26), 149(7), 147(18), 136(32), 135(9), 134(90), 121(15), 119(46), 111(11), 109(8), 108(32), 107(32), 106(100), 105(31), 97(8), 95(23), 94(26), 93(61), 92(51), 91(6), 83(5), 81(17), 80(10), 79(46), 78(22), 67(4), 65(12), 63(22), 55(4), 41(2). Anal. Calcd. for C_{7}H_{15}SiCl: C, 51.69; H, 9.23; Si, 17.23; Cl, 21.85. Found: C, 51.51; H, 9.26.

6. Preparation of 1,4-Dimethyl-l-phenyl-l-silacycloclohexane.

Magnesium turnings (3.9 g, 0.16 mol) and 200 mL of anhydrous ether were activated with 2 mL of 1,2-dibromoethane for 3 h. A solution of 1,5-dibromo-3-methylpentane (15.0 g, 0.061 mol) in 350 mL of anhydrous ether was added slowly to the activated magnesium turning over 8 h. The reaction mixture was refluxed for an additional 8 h, then cooled to room temperature. Methylphenyldichlorosilane (11.74 g, 0.061 mol) in 150 mL of anhydrous ether was added dropwise to the diGrignard solution. After the addition was complete the reaction
mixture was heated to reflux for 18 h, then cooled to room
temperature. Saturated ammonium chloride was added slowly
under cooling by an ice cold water bath to maintain the
temperature around 24-30°C, until two layers were clearly
formed. An additional 50 mL of ice cold water was added.
This mixture was transferred to a separatory funnel, the
ethereal layer separated and washed with (2x150 mL) of
distilled water, then dried over anhydrous magnesium
sulfate for 3 h. The drying agent was filtered off, ether
removed by distillation, and the remaining liquid
distilled under vacuum to yield product boiling at 100-
101°C/1 mm, 7.5 g (60%). GC indicated a 58/42 mixture of
cis and trans isomers of 1,4-dimethyl-1-phenyl-1-
silacyclohexane.

$^1$H NMR: $\delta$ 0.18 (s, 3H, Si-Me equatorial),
0.29 (s, 3H, Si-Me axial),
0.30-0.80 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.95-2.20 (m, 10H, -CH$_2$-CH-CH$_2$-),
0.84 (d:J=6.300 Hz, 3H, C-Me),
0.91 (d:J=6.100 Hz, 3H, C-Me), 7.23-7.65 (m, 5H, Ar-H).
$^{13}$C NMR (CDCl$_3$): trans (minor):  -5.62 (s, 1C, SiMe),
12.19 (s, 2C, C$_2$ and C$_6$), 23.35 (s, 1C, c-Me),
32.79 (s, 2C, C$_3$ and C$_5$), 35.62 (s, 1C, C$_4$),
127.73 (s, 1C, Si-C$_1$'), 128.89 (s, 2C, C$_2$' and C$_6$'),
133.86 (s, 2C, C$_3$' and C$_5$'), 139.08 (s, 1C, C$_4$'). Cis
(major): -2.16 (s, 1C. SiMe), 11.67 (s, 2C, C$_2$ and C$_6$),
22.87 (s, 1C, c-CH₃), 32.57 (s, 2C, C₃ and C₅),
35.23 (s, 1C, C₄), 127.73 (s, 1C, Si-C₁⁻),
128.75 (s, 2C, C₂⁻ and C₆⁻),
133.86 (s, 2C, C₃⁻ and C₅⁻),
138.89 (s, 2C, C₄⁻). IR: 2960, 2900, 2870, 2850, 1460,
1430, 1410, 1380, 1260, 1180, 1130, 1000, 930, 850, 810,
800, 770, 740, 710. MS: cis isomer (major): 204(6),
190(3), 189(12), 162(6), 161(46), 159(9), 148(7), 147(19),
145(8), 135(7), 134(16), 133(7), 127(14), 126(100),
122(6), 121(58), 120(13), 119(19), 111(37), 107(12),
106(5), 105(44), 103(4), 99(4), 98(14), 97(5), 95(5),
93(7), 91(6), 83(4), 79(7), 53(6), 43(7). Trans isomer
(minor): 204(2), 190(4), 189(18), 162(6), 161(40),
159(9), 148(7), 147(22), 145(7), 135(8), 134(17), 133(8),
128(5), 127(14), 126(100), 122(7), 121(64), 120(14),
119(20), 112(5), 111(43), 106(7), 105(53), 99(5), 98(13),
97(5), 95(7), 93(11), 91(7), 83(7), 83(7), 79(10), 59(6),

7. Preparation of N-Benzoyl-2,6-dimethylpiperididine.

A solution of sodium hydroxide pellets (52.5 g, 1.3
mol) and 400 mL of distilled water was placed in a three­
necked round-bottomed flask equipped with a mechanical
stirrer, an addition funnel, reflux condenser, nitrogen
inlet system, and ice cold water bath to maintain the
reaction temperature around room temperature. 2,6-Dimethylpiperidine (113 g, 1.0 mol) was poured into the sodium hydroxide solution, and the mixture stirred for 15 min. Benzoyl chloride (140.0 g, 1.00 mol) was placed in an addition funnel and added dropwise to the piperidine/sodium hydroxide solution over a period of 2 h. The temperature was maintained around 25-35°C by using an ice cold water bath. After the addition was complete, the reaction mixture was stirred for an additional 2 h. Benzene (500 mL) was added to dissolve all the product. The organic layer, the top layer, was separated and dried over anhydrous calcium chloride. Benzene was removed, and the product was collected as a white solid 180 g (86%), m.p. 110-111°C (lit 104 110-112°C). \(^1\)H NMR: 
\[ \delta \quad 1.26 \ (d: J=7.100 \text{ Hz}, \ 6\text{H, C-Me}), \]
\[1.04-2.10 \ (m, \ 6\text{H, -CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{2}-}), \]
\[4.30-4.70 \ (m, \ 4\text{H, -N-CH-}), \]
\[7.35 \ (s, \ 5\text{H, Ar-H}). \]

MS: 217(12), 216(5), 202(9), 105(100), 77(28). Anal. Calcd. for C\textsubscript{14}H\textsubscript{19}ON: C, 71.41; H, 8.75; N, 6.45. Found: C, 71.50; H, 8.67; N, 6.50.

8. Preparation of 2,6-Dibromoheptane.

A solution of N-benzoyl-2,6-dimethylpiperidine (100 g, 0.46 mol) in 250 mL of carbon tetrachloride was cooled in an ice cold water bath to control the reaction temperature and stirred until all the solid was dissolved.
Phosphorus tribromide (125.0 g, 0.46 mol) was added dropwise to the N-benzoyl-2,6-dimethylpiperidine with the reaction temperature maintained in the range 24-34°C. The reaction mixture became a dark yellow solution. After the addition was complete, bromine (73.6 g, 0.46 mol) was added very slowly. This was an exothermic reaction, and the reaction temperature was carefully controlled. It took about 3 h to complete the addition. The mixture was cooled to room temperature without using any ice water bath and then warmed up to 60-65°C for a period of 30 min to remove the fumes. Carbon tetrachloride was removed by simple distillation and the mixture was co-distillate at 130-140°C/5 mm. The distillate, which contained phosphoryl bromide, phenyl cyanide, and 1,5-dibromoheptane, was poured into a beaker which contained 500 g of crushed ice and allowed to stand for 2 h. The precipitate was discarded and the liquid layer was extracted with (2x250 mL) of ligroine. The ligroine solution was washed very carefully with (10x40 mL) of concentrated sulfuric acid in order to oxidize phenyl cyanide to benzoic acid. The organic layer was neutralized with (2x100 mL) of dilute sodium hydroxide solution, dried over anhydrous calcium chloride anhydrous for 1 h, and the drying agent filtered. Ligroine was removed by simple distillation, and the residue was vacuum distilled to give a colorless
oily liquid boiling at 110–111°C/10 mm (lit104 121–123°C/25mm) 40.5 g (34%).

\(^1\text{H NMR:} \delta 1.74 (d: J=6.814 \text{ Hz}, 6\text{H, C-Me}),
\ 1.30-2.51 (m, 6\text{H, }-\text{CH}_2-\text{CH}_2-\text{CH}_2-),
\ 3.99-4.34 (m, 2\text{H, }-\text{CH-Br}).

\text{MS:} \ 260(0.4), 258(0.8), 256(0.4), 179(58), 177(63),
\ 98(11), 97(100), 67(12), 55(25). \ \text{IR:} \ 2960, 2950, 2915,
\ 2870, 2840, 1460, 1450, 1445, 1440, 1380, 1290, 1280,
\ 1230, 1210, 1160, 1140, 810. \ \text{Anal. Calcd. for } \text{C}_7\text{H}_{14}\text{Br}_2:
\ C, 32.56; \ H, 5.43; \ Br, 62.01. \ \text{Found: } \ C, 32.65; \ H, 5.51.

9. \text{Preparation of 1,1,2,6-Tetramethyl-1-silacyclopheXane.}

Magnesium turnings (1.15 g, 0.05 mol) in 75 mL of anhydrous ether were activated with 0.5 mL of 1,2-dibromoethane for 3 h, then cooled to room temperature. A solution of 2,6-dibromoheptane and 150 mL of anhydrous ether was added slowly to the activated magnesium. After finishing the addition the mixture was refluxed for 10 h and cooled to room temperature. From a second addition funnel, a solution of dimethyldichlorosilane (2.56 g, 0.02 mol) in 75 mL of ether was added slowly to the diGrignard solution. After the addition was completed, the reaction mixture was refluxed for an additional 30 h, then cooled to room temperature. Saturated ammonium chloride was added slowly (an ice cold water bath was used during this
addition) until two layers were formed clearly, then 20 mL of distilled water was added. After transfer to a separatory funnel, the organic layer was separated, washed with (2x25 mL) of distilled water, and dried over anhydrous magnesium sulfate for 2 h. The drying agent was filtered and the ether was removed by distillation. The residue was distilled under reduced pressure in a short-path still to give a colorless oily liquid boiling at 97-98°C/70 mm 1.1 g (32%). A 50/50 mixture of 1,1,2,6-tetramethyl-1-silacyclohexane was indicated by GC analysis.

$^1$H NMR: 0.05 (s, 3H, Si-Me), 0.06 (s, 6H, Si-Me), 0.08 (s, 3H, Si-Me), 0.88 (d: J=7.392 Hz, 6H, C-Me), 0.97 (d: J=7.135 Hz, 6H, C-Me), 0.12-0.85 (m, 4H, -CH-Si-CH_), 1.00-2.20 (m, 12H, -CH$_2$-CH$_2$-).

IR: 2960, 2930, 2910, 2850, 2830, 1445, 1430, 1410, 1380, 1260, 1210, 1170, 850, 820, 810, 740. MS: cis isomer: 156(53), 141(23), 127(3), 115(12), 114(61), 113(36), 102(4), 101(20), 100(65), 99(64), 97(12), 96(8), 95(6), 87(18), 86(83), 85(100), 83(6), 81(23), 73(39), 72(18), 71(9), 67(4), 59(39), 58(12), 55(6), 43(7), 41(4). Trans isomer: 156(45), 141(17), 127(4), 116(4), 115(12), 114(64), 113(36), 101(19), 100(61), 99(66), 97(14), 96(9), 95(9), 92(7), 91(11), 88(5), 87(21), 86(93), 85(100).
83(7), 82(4), 81(26), 74(6), 73(7), 72(24), 71(18), 72(24), 71(18), 69(6), 67(6), 60(5), 59(65), 58(24), 57(8), 55(11), 45(5), 43(13), 41(9). Anal. Calcd. for C₉H₂₀Si: C, 69.23; H, 12.82; Si, 17.95. Found: C, 69.15; H, 12.73.


3,3-Dimethylglutaric acid (40 g, 0.25 mol), 150 mL of dry methanol, 250 mL of dry benzene and 5.0 mL of concentrated sulfuric acid were placed in a round-bottomed flask equipped with magnetic stirrer and reflux condenser. The mixture was heated to reflux at a very gentle rate for 12 h. The reaction mixture was cooled to room temperature, and then neutralized with 10% sodium carbonate. Benzene and unreacted methanol were removed by distillation. The residue was extracted with (3x200 mL) of ether and dried over anhydrous sodium sulfate for 2 h. Ether was removed by fraction distillation, and the residue was distilled under reduced pressure to give a colorless oily product boiling at 115-117°C/25 mm 47.0 g (78%).

¹H NMR: δ 1.12 (s, 6H, C(CH₃)₂); 2.43 (s, 4H, -CH₂-CH₂-); 3.66 (s, 6H, -CO₂-CH₃).

11. Preparation of 3,3-Dimethyl-1,5-pentanediol.

To a mixture of lithium aluminum hydride (15.2 g, 0.3 mol) in 250 mL of dry THF, dimethyl 3,3-dimethylglutarate
(38.2 g, 0.22 mol) in 250 mL of dry THF was added dropwise to the lithium aluminum hydride solution. The temperature increased slowly, and an ice cold water bath was used to maintain the reaction temperature around room temperature. After finishing the addition, the reaction mixture was heated to reflux overnight, then cooled to room temperature. The excess lithium aluminum hydride was destroyed by adding 100 mL of ethyl acetate, 50 mL of water, and 50 mL of dilute HCl. The mixture was now extracted in a soxhlet extractor with THF for two days. After drying over anhydrous magnesium sulfate for 3 h, THF was removed by distillation, and the remaining liquid was vacuum distilled gave a colorless thick oily liquid boiling at 135-136°C/0.5 mm 26.5 g (95%).

$^1$H NMR: $\delta$ 0.95 (s, 6H, C(CH$_3$)$_2$), 3.70 (t, 4H, -CH$_2$-OH), 1.61 (t, 4H, -CH$_2$-CH$_2$-), 2.10 (broad, 2H [OH]). MS: 115(4), 114(45), 113(12), 100(6), 99(100), 95(3), 86(4), 83(3), 81(14), 71(10), 70(14), 69(91), 68(18), 67(1), 59(2), 58(2), 57(11), 56(29), 55(19), 53(2), 43(10), 41(14), 40(3), 34(5).

12. Preparation of 1,5-Dibromo-3,3-dimethylpentane.

3,3-Dimethyl-1,5-pentanediol (20.0 g, 0.15 mol) was placed in a three-necked round-bottomed flask equipped with a magnetic stirrer, an addition funnel, a reflux condenser and nitrogen inlet system. From an addition funnel
phosphorus tribromide (41.0 g, 0.15 mol) was added drop-wise to the diol while stirring with a magnetic stirrer and maintaining the temperature at about 0-15°C by using an ice cold water bath. After the addition was complete the reaction was stirring for an additional 6 h at room temperature and for 30 minutes in a steam bath (using a beaker containing hot water so that the temperature was not more than 100°C). After cooling, the reaction mixture was poured into a beaker which contained 300 g of crushed ice and then extracted with (3x100 mL) of benzene. The organic layer was washed with cold portions of dilute sulfuric acid and one portion of cold water. The benzene solution was dried over anhydrous magnesium sulfate for 2 h. The drying agent was filtered off. Benzene was removed by simple distillation, and the residue was distilled under reduced pressure to give a colorless liquid boiling at 116-117°C/8 mm yielded 24.5 g (66%).

$^1$H NMR: δ 0.92 (s, 6H, C(CH$_3$)$_2$);
1.81-2.50 (m, 4H, -CH$_2$-C-CH$_2$-), 3.35-3.85 (m, 4H, CH$_2$-Br).
13. **Preparation of 1,1,4,4-Tetramethyl-1-silacyclohexane.**

Magnesium turnings (3.5 g, 0.14 mol) in 150 mL of anhydrous ether were placed in a three-necked round-bottomed flask. The magnesium turnings were activated with 1.0 mL of 1,2-dibromoethane for 3 h. A solution of 1,5-dibromo-3,3-dimethylpentane (15 g, 0.059 mol) in 200 mL of anhydrous ether was placed in an addition funnel and added slowly to the activated magnesium turnings. After finishing the addition the reaction mixture was refluxed for an additional 8 h then cooled to room temperature. From a second addition funnel, a solution of dimethyldichlorosilane (7.55 g, 0.085 mol) in 100 mL of anhydrous ether was added dropwise to the diGrignard solution. After the addition was complete, the reaction mixture was refluxed for 24 h, then cooled to room temperature. Saturated ammonium chloride was added slowly (an ice cold water bath was used to maintain the reaction temperature around 25°C) until two layers were formed clearly, then an additional 70 mL of cold water was added. After transfer to a separatory funnel, the organic layer was separated, washed with 100 mL of distilled water and dried over anhydrous magnesium sulfate for 3 h. The drying agent was filtered off. Ether was removed by distillation, and the residue was distilled under reduced pressure to give a colorless oily liquid boiling at 91-92°C/90 mm 3.5 g (46%).
1H NMR: \( \delta 0.01 (s, 6H, Si(CH_3)_2); \)
0.85 (s, 6H, C(CH_3)_2), 0.46-0.64 (m, 4H, -CH_2-Si-CH_2-),
1.30-1.52 (m, 4H, -CH_2-C-CH_2). IR: 2960, 2950, 2930,
2870, 1480, 1470, 1460, 1400, 1380, 1340, 1250, 1120,
1060, 1050, 930, 850, 770, 690. MS: 156(13), 142(4),
141(28), 129(10), 128(65), 114(17), 113(50), 111(2),
101(9), 100(75), 99(33), 97(7), 87(14), 86(17), 85(47),
74(8), 73(60), 72(61), 71(15), 70(7), 69(8), 67(6), 60(9),
59(100), 58(43), 57(8), 55(27), 53(11), 45(3), 43(7),
41(4). Anal. Calcd. for C_{19}H_{20}Si: C, 69.23; H, 12.82;
Si, 17.95. Found: C, 69.08; H, 12.67.

14. Reduction of 1-Chloro-1,4-dimethyl-1-silacyclo-
hexane (Cis/Trans = 33/67) with Lithium
Aluminum Hydride.

Lithium aluminum hydride (233.8 mg, 6.15 mmol) and 40 mL of anhydrous ether were placed in a three-necked round-
bottomed flask equipped with a magnetic stirrer, an addition funnel, a reflux condenser, and nitrogen inlet system
and stirred. From an addition funnel a solution of a 35:65 mixture of cis and trans isomers of 1-chloro-1,4-
dimethyl-1-silacyclohexane (1.00 g, 6.15 mmol) in 20 mL of anhydrous ether was added dropwise to the lithium
aluminum hydride solution. After the addition was completed, the reaction mixture was refluxed while stirring
at a very gentle rate under nitrogen for 8 h, then cooled
to room temperature. The ethereal layer was separated. The precipitate was washed with (2x15 mL) of anhydrous ether. All the ethereal layers were combined in a flask and placed in an ice cooling bath, and water was added to decompose any LiAlH₄ left over from the reaction mixture. The ether layer was separated and the residue was extracted with (3x15 mL) of ether. The ether solution was dried over anhydrous magnesium sulfate for 1 h. Drying agent was filtered off. Ether was removed by distillation and the residue was distilled under reduced pressure in a short-path still at 57-58°C/71 mm, to give 0.72 g (91%) of a 66:34 mixture of 1,4-dimethyl-1-silacyclohexane as a colorless oily liquid.

$^1$H NMR: δ 0.06 (d: J=3.486 Hz, 3H, Si-Me equatorial), 0.11 (d: J=3.524 Hz, 3H, Si-Me axial), 0.26-0.80 (m, 4H, -CH₂-Si-CH₂-), 0.86 (d: J=6.200 Hz, 6H, C-Me), 0.90-2.20 (m, 10H, -CH₂-CH-CH₂-), 3.78 (m, 1H, Si-H axial), 3.85 (m, 1H, Si-H equatorial).

15. Free Radical Chlorination of 1,4-Dimethyl-1-silacyclohexane (Cis:Trans = 66/34) with CCl₄/BPO.

Benzoyl peroxide (18.9 mg, 0.0078 mmol) in 30 mL of dry carbon tetrachloride was placed in a three-necked round-bottomed flask equipped with a magnetic stirrer, a
reflux condenser, an addition funnel, and nitrogen inlet system and stirred. From an addition funnel, a solution of 66:34 mixture of cis and trans isomers of 1,4-dimethyl-1-silacyclohexane (1.0 g, 7.8 mmol) was poured into the CCl₄/BPO while stirring under nitrogen at room temperature for 3 min, and then the reaction mixture was heated to 82°C for 2 h. After cooling to room temperature, CCl₄ was removed by distillation, and the product was distilled under reduced pressure in a short-path still at 94-95°C/55 mm to give 0.83 g (66%) of a 65:35 mixture of cis and trans 1-chloro-1,4-dimethyl-1-silacyclohexane.

1H NMR: δ 0.41(s, 3H, Si-Me equatorial),
0.44 (s, 3H, Si-Me axial);
0.21-0.80 (m, 8H, -CH₂-Si-CH₂-),
0.91 (d: J=6.200 Hz, 6H, C-Me),
0.93-2.25 (m, 10H, -CH₂-CH-CH₂).

16. **Reduction of 1-Chloro-1,4-dimethyl-1-silacyclohexane** (Cis/Trans = 65/35) with Lithium Aluminum Hydride in Ether.

The general procedure [14] was followed. Lithium aluminum hydride (210 mg, 5.50 mmol) and 40 mL of anhydrous ether were placed in a round-bottomed flask. From an addition funnel a 65:35 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-silacyclohexane (1.0 g, 6.15 mmol) was added dropwise to the lithium aluminum
hydride solution. Vacuum distillation at 57-58°C/71 mm,
gave 0.66 g (94%) of a 34:66 mixture of cis and trans 1,4-
dimethyl-l-silacyclohexane as a colorless oily liquid.

$^1$H NMR:  0.06 (d:J=3.512 Hz, 3H, Si-Me equatorial),
0.10 (d:J=3.540 Hz, 3H, Si-Me axial),
0.86 (d:J=6.197 Hz, 6H, C-Me),
0.26-0.80 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.90-2.20 (m, 10H, -CH$_2$-CH-CH$_2$-),
3.76 (m, 1H, Si-H axial), 3.86 (m, 1H, Si-H equatorial).

17. Free Radical Chlorination of 1,4-dimethyl-l-
silacyclohexane (Cis:Trans = 34/66) with
CCL$_4$/BPO.

Following the general procedure [15]; benzoyl peroxide (9.0 mg, 0.0037 mmol) and 30 mL of dry carbon
tetrachloride were placed in a three-necked round-bottomed flask. From an addition funnel, a 34:66 mixture of cis
and trans isomers of 1,4-dimethyl-1-silacyclohexane (0.50
0.50 g, 3.9 mmol) was poured into the CCL$_4$/BPO. Vacuum distil-
lration at 94-95°C/55 mm, gave 0.83 g (66%) of a 35:65 mixture of cis and trans 1-chloro-1,4-dimethyl-1-
silacyclohexane.

$^1$H NMR:  0.41 (s, 3H, Si-Me equatorial),
0.45 (s, 3H, Si-Me axial),
0.21-0.81 (m, 8H, -CH$_2$-Si-CH$_2$),
0.91 (d: J=6.200 Hz, 6H, C-Me),
0.92-2.22 (m, 10H, -CH₂-CH-CH₂⁻).

18. Fluorination of 1-Chloro-1,4-dimethyl-1-
silacyclohexane (Cis/Trans = 35/65) with
Ammonium Hydrogen Difluoride.

A 35/65 mixture of cis and trans isomers of 1-chloro-
1,4-dimethyl-1-silacyclohexane (500 mg, 3.07 mmol) and
anhydrous ammonium hydrogen difluoride (200 mg, 3.50 mmol)
was placed in a round-bottomed flask equipped with a mag-
netic stirrer, a short path distillation head, and
nitrogen inlet system and stirred at room temperature for
5 min. Distillation under reduced pressure in a short-
path still gave a colorless oily liquid boiling at 54-
55°C/55 mm, and yielded 0.44 g (98%) of a 65:35 mixture of
cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacy-
clohexane.

1H NMR: 6 0.19 (d: J=7.310 Hz, 3H, Si-Me equatorial),
0.31-1.07 (m, 8H, -CH₂-Si-CH₂⁻),
0.88 (d: J=6.505 Hz, 6H, C-Me),
1.07-2.17 (m, 10H, -CH₂-CH-CH₂⁻).

IR: 2950, 2920, 2910, 2905, 2870, 2850, 1460, 1405, 1480,
1300, 1260, 1210, 1180, 1100, 1070, 1030, 930, 910, 870,
830, 785, 750. MS: cis (major): 146(40), 131(63),
120(4), 119(11), 118(100), 105(3), 104(4), 103(38),
91(24), 90(87), 89(36), 79(3), 78(7), 77(63), 76(41),
19. Fluorination of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 35/65) with Zinc Difluoride.

Following the general procedure [18], a 35:65 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-silacyclohexane (200 mg, 1.23 mmol) and zinc difluoride (129.1 g, 1.25 mmol) were placed in a round-bottomed flask and stirred at room temperature for 8 min. Distillation at boiling 54-55°C/55 mm, yielded 145 mg (81%) of a 65:35 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane. $^1$H NMR: $\delta$
0.19 (d:J=7.312 Hz, 3H, Si-Me equatorial), 0.26 (d:J=7.509 Hz, 3H, Si-Me axial).

20. Fluorination of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 35/65) with Cesium Fluorine.

Following the general procedure [18], a 35:65 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-
silacyclohexane (300 mg, 1.85 mmol) and cesium fluoride (0.3 g, 2.0 mmol) was placed in a round-bottomed flask and stirred at room temperature for 10 min. Distillation at boiling 54-55°C/55 yielded 230 mg (86%) of a 64:36 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane. $^1$H NMR:

\[ \delta 0.19 \text{ (d: } J=7.310 \text{ Hz, } 3\text{H, Si-Me equatorial)}, \]

\[ 0.26 \text{ (d: } J=7.507 \text{ Hz, } 3\text{H, Si-Me axial}). \]

21. **Fluorination of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 35/65) with Potassium Fluoride.**

Following the general procedure [18], a 35:65 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-silacyclohexane (400 mg, 2.46 mmol) and potassium fluoride (145 mg, 2.5 mmol) was placed in a round-bottomed flask and stirred at room temperature for 10 min. Distillation at boiling 54-55°C/55 mm yielded 320 mg (89%) of a 63:37 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-silacyclohexane. $^1$H NMR: $\delta$

\[ 0.19 \text{ (d: } J=7.310 \text{ Hz, } 3\text{H, Si-Me equatorial)}, \]

\[ 0.26 \text{ (d: } J=7.505 \text{ Hz, } 3\text{H, Si-Me axial}). \]
22. **Fluorination of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 35/65) with Sodium Tetrafluoroborate in Acetone.**

A 35:65 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-silacyclohexane (200 mg, 1.23 mmol) and sodium tetrafluoroborate (143 mg, 6 mmol) in 6 mL of dry acetone were placed in a round-bottomed flask and stirred at room temperature for 15 min. After removal of acetone, the remaining liquid was distilled under reduced pressure at boiling 54-55°C/55 mm to yield 150 mg (84%) of a 61:39 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane. \(^1\)H NMR: \(\delta\)

0.19 (d:J=7.320 Hz, 3H, Si-Me equatorial),
0.26 (d:J=7.521 Hz, 3H, Si-Me axial).

23. **Reduction of 1-Fluoro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 65/35) with Lithium Aluminum Hydride.**

The reaction was carried out in a three-necked round-bottomed flask which was equipped with a magnetic stirrer, a reflux condenser, an addition funnel and nitrogen inlet system. Lithium aluminum hydride (380 mg, 10.0 mmol) and 30 mL of anhydrous ether were placed in the flask. From an addition funnel of 65:35 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane (500 mg, 3.42 mmol) in 30 mL of ether was added slowly to the
lithium aluminum hydride solution. After the addition was completed, the reaction mixture was refluxed under nitrogen for 17 h and cooled to room temperature. The ethereal layer was separated, and the precipitate was washed with (3x10 mL) of ether. All the ethereal layers were combined in a flask and which placed in an ice cold water bath. Water was added to decompose any lithium aluminum hydride left over from the reaction mixture. The ethereal layer was isolated and the residue was washed carefully with (3x15 mL) of ether. The combined ethereal were dried over anhydrous magnesium sulfate for 3 h. Drying agent was filtered off. Ether was removed by fractional distillation, and the residue was distilled under reduced pressure in a short-path still to give a colorless oily liquid boiling at 57-58°C/71 mm (0.43 mg, 98%). The product was a 35/65 mixture of cis and trans isomers of 1,4-dimethyl-1-silacycloclohexane.

\( ^1\text{H NMR: } \delta \ 0.06 \ (d:J=3.490 \text{ Hz}, \ 3\text{H}, \ \text{Si-Me equatorial}), \ 0.10 \ (d:J=3.510 \text{ Hz}, \ 3\text{H}, \ \text{Si-Me axial}), \ 0.30-0.80 \ (m, \ 8\text{H}, \ \text{-CH}_2-\text{Si-CH}_2-), \ 0.86 \ (d:J=5.980 \text{ Hz}, \ 6\text{H}, \ \text{C-Me}), \ 0.91-2.15 \ (m, \ 10\text{H}, \ \text{-CH}_2-\text{CH-CH}_2-). \ 3.76 \ (m, \ 1\text{H}, \ \text{Si-H axial}); \ 3.86 \ (m, \ 1\text{H}, \ \text{Si-H equatorial}). \)
24. **Fluorination of 1-Chloro-1,4-dimethyl-l-silacyclohexane (Cis/Trans = 64/36) with Ammonium Hydrogen Difluoride.**

Following the general procedure [18], a 64:36 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-l-silacyclohexane (200 mg, 1.23 mmol) and anhydrous ammonium hydrogen difluoride (71.3 mg, 1.25 mmol) were placed in a round-bottomed flask and stirred for 5 min. Distillation at 54-55°C/55 mm, yielded 175 mg (98%) of a 35:65 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-l-silacyclohexane. $^1$H NMR:

$\delta$ 0.19 (d:J=7.311 Hz, 3H, Si-Me equatorial), 0.26 (d:J=7.511 Hz, 3H, Si-Me axial).

25. **Fluorination of 1-Chloro-1,4-dimethyl-l-silacyclohexane (Cis/Trans = 64/36) with Zinc Difluoride.**

Following the general procedure [18], a 64:36 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-l-silacyclohexane (150 mg, 0.92 mmol), and zinc difluoride (129.2 g, 1.25 mmol) were placed in a round-bottomed flask and stirred for 8 min. Distillation at 54-55°C/55 mm yielded 115 mg (86%) of a 35:65 mixture cis and trans isomers of 1-fluoro-1,4-dimethyl-l-silacyclohexane. $^1$H NMR:

$\delta$ 0.19 (d:J=7.312 Hz, 3H, Si-Me equatorial), 0.26 (d:J=7.509 Hz, 3H, Si-Me axial).
26. **Fluorination of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 64/36) with Cesium Fluoride.**

Following the general procedure [18], a 64:36 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-silacyclohexane (200 mg, 1.23 mmol) and cesium fluoride (190 mg, 1.25 mmol) were placed in a round-bottomed flask and stirred for 10 min. Distillation at 54-55°C/55 mm yielded 160 mg (89%) of a 38:62 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane.

\[ ^1H \text{ NMR:} \]
\[ \delta 0.19 (d:J=7.310 \text{ Hz, } 3H, \text{ Si-Me equatorial}), \]
\[ 0.26 (d:J=7.507 \text{ Hz, } 3H, \text{ Si-Me axial}). \]

27. **Fluorination of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 64/36) with Potassium Fluoride.**

A 61:39 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-silacyclohexane (200 mg, 1.25 mmol) and potassium fluoride (75.5 mg, 1.3 mmol) were placed in a round-bottomed flask and stirred for 10 min. Distillation at 54-55°C/55 mm, yielded 160 mg (88%) of a 39:61 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane. \[ ^1H \text{ NMR:} \]
\[ \delta 0.19 (d:J=7.320 \text{ Hz, } 3H, \text{ Si-Me equatorial}), \]
\[ 0.26 (d:J=7.520 \text{ Hz, } 3H, \text{ Si-Me axial}). \]
28. **Fluorination of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 64/36) with Sodium Tetrafluoroborate in Acetone.**

Following the general procedure [18], a 64:36 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-silacyclohexane (200 mg, 1.23 mmol) and sodium tetrafluoroborate (143 mg, 1.3 mmol) in 6 mL of dry acetone were placed in a round-bottomed flask and stirred at room temperature for 15 minutes. After removal of acetone, the remaining liquid was distilled under reduced pressure at 54-55°C/55 mm yield 150 mg (83%) of a 39:61 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane. $^1$H NMR:

$\delta 0.19$ (d: $J=7.320$ Hz, 3H, Si-Me equatorial),

$\delta 0.26$ (d: $J=7.505$ Hz, 3H, Si-Me axial).

29. **Reduction of 1-Fluoro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 35/65) with Lithium Aluminum Hydride.**

Following the general procedure [23], lithium aluminum hydride (380 mg, 10 mmol) and 30 mL of anhydrous ether were placed in the round-bottomed flask. From an addition funnel a 35/65 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane (260 mg, 6.8 mmol) in 30 mL of ether was added slowly to the lithium aluminum hydride solution. The product was distilled at
57-58°C/71 mm to yielded 0.82 g (94%) of a 65:35 mixture of cis and trans isomers of 1,4-dimethyl-1-silacyclohexane. $^1$H NMR:

$\delta$ 0.06 (d: J=3.486 Hz, 3H, Si-Me equatorial),

0.11 (d: J=3.524 Hz, 3H, Si-Me axial),

0.31-0.78 (m, 8H, -CH$_2$-SI-CH$_2$-),

0.86 (d: J=6.030 Hz, 6H, C-Me),

0.90-2.13 (m, 10H, -CH$_2$-CH-CH$_2$-),

3.76 (m, 1H, Si-H axial); 3.86 (m, 1H, Si-H equatorial).

30. **Bromination of 1,4-Dimethyl-1-silacyclohexane**

(Cis:Trans = 65/35) with Bromine in Carbon Tetrachloride.

A 65:35 mixture of cis and trans isomers of 1,4-dimethyl-1-silacyclohexane (400 mg, 3.12 mmol) was placed in a three-necked round-bottomed flask equipped with a magnetic stirrer, an addition funnel, a reflux condenser and nitrogen inlet system and stirred. From an addition funnel a solution of bromine in carbon tetrachloride (0.56 g of bromine in 10 mL of carbon tetrachloride) was added dropwise to the 1,4-dimethyl-1-silacyclohexane while stirring. A dry ice-acetone bath was used to maintain the reaction mixture at -50°C to -60°C. After the addition was complete, nitrogen was passed through the reaction while it was stirring for 15 min to remove any excess fumes. The reaction mixture was warmed up to room temperature.
Carbon tetrachloride was removed by distillation, and the residue was distilled under reduced pressure in a short-path still to give a colorless oily liquid boiling at 67-68°C/15 mm (220 mg, 91%). The product was a 65:35 mixture of cis and trans isomers of 1,4-dimethyl-1-silacycloc-hexane. \(^1\)H NMR:

\[\delta 0.57 \text{ (s, 3H, Si-Me equatorial),} \]
\[0.60 \text{ (s, 3H, Si-Me axial),} \]
\[0.89 \text{ (d: J=6.559 Hz, 3H, C-Me),} \]
\[0.91 \text{ (d: J=6.105 Hz, 3H, C-Me),} \]
\[0.64-2.10 \text{ (m, 18H, ring-H).} \]

IR: 2930, 2880, 2850, 2840, 1460, 1450, 1400, 1380, 1300, 1260, 1210, 1180, 1100, 1070, 1020, 1000, 930, 910, 850, 820, 790, 750, 730, 630. MS: cis (major): 208(57), 206(60), 194(4), 193(39), 192(5), 191(33), 180(95), 178(80), 167(2), 166(4), 165(36), 164(5), 163(41), 152(100), 151(55), 150(97), 149(33), 139(51), 138(62), 137(46), 136(61), 135(7), 127(18), 126(17), 125(63), 124(39), 123(71), 121(4), 111(34), 109(60), 107(53), 99(21), 98(8), 97(24), 95(6), 71(10), 69(6), 67(19), 66(3), 59(8), 58(4), 57(4), 56(8), 55(22), 53(13), 45(8), 43(26), 42(7), 41(13). Trans (minor): 208(50), 206(52), 194(3), 193(40), 192(4), 191(41), 180(91), 178(93), 165(38), 163(40), 152(99), 151(40), 150(100), 149(30), 139(48), 138(60), 137(40), 136(60), 135(6), 127(17), 126(19), 125(60), 124(35), 123(63), 121(2), 111(35), 109(55), 107(50), 99(17), 98(11), 97(13), 95(5), 71(8), 69(5), 67(17), 66(2), 59(7), 58(2), 57(3), 56(7), 55(20),
31. Bromination of 1,4-Dimethyl-1-silacyclohexane (Cis/Trans = 65/35) with Bromoform and Benzoyl Peroxide

A solution of 3 mL of bromoform and benzoyl peroxide (2.88 mg, 0.00117 mmol) was placed in a round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, an addition funnel and nitrogen inlet system and was stirred. From an addition funnel, a 65:35 mixture of cis and trans isomers of 1,4-dimethyl-1-silacyclohexane (150.0 mg, 1.17 mmol) was poured into the bromoform solution. The reaction was stirred for 5 min, and then heated to reflux gently for 15 min. After cooling to room temperature, excess bromoform was distilled off under nitrogen, and the remaining liquid was distilled under vacuum in a short-path still to give a colorless oily liquid boiling at 58-68°C/15 mm (220 mg, 92%). A 66:34 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-1-silacyclohexane was obtained. $^1$H NMR:

δ 0.57 (s, 3H, Si-Me equatorial),
0.60 (s, 3H, Si-Me axial),
0.91 (d: J=5.980 Hz, 3H, C-Me),
0.89 (d: J=6.559 Hz, 3H, C-Me),
0.61-2.07 (m, 18H, ring-H).
32. Reduction of 1-Bromo-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 65/35) with Lithium Aluminum Hydride.

Lithium aluminum hydride (186.2 mg, 4.9 mol) and 40 mL of anhydrous ether were placed in a three-necked, round-bottomed flask equipped with a magnetic stirrer, an addition funnel, a reflux condenser and nitrogen inlet system. From an addition funnel, a 65:35 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-1-silacyclohexane (1.0 g, 4.9 mol) in 30 mL of anhydrous ether was added slowly to the lithium aluminum hydride solution while stirring. After the addition was complete the reaction mixture was refluxed while stirring under nitrogen for 3 h, then cooled to room temperature. The ethereal layer was separated, and the residue was washed very carefully with 2x30 mL of anhydrous of ether. All the ether layers were combined in a flask, and it was placed in an ice cold water bath. Water was added slowly to the ether solution to decompose any lithium aluminum hydride left over from the reaction mixture, while an ice cooling bath was used to maintain the solution temperature around 25°C. The ether layer was separated and the precipitate was extracted carefully with (3x15 mL) of ether. The ether solution was dried over anhydrous magnesium sulfate for 2 h. The drying agent was filtered off. Ether was removed by fractional distillation, and the remaining liquid was
distilled under vacuum in a short-path still to give a colorless oily liquid boiling at 58-59°C/71 mm (0.60 g, 95%). A 35:65 mixture of cis and trans isomers of 1,4-dimethyl-l-silacyclohexane was obtained.

$^1$H NMR:

$\delta$ 0.06 (d:J=3.538 Hz, 3H, Si-Me equatorial),
0.11 (d:J=3.664 Hz, 3H, Si-Me axial),
0.27-0.82 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.86 (d:J=6.027 Hz, 6H, C-Me),
0.92-2.11 (m, 10H, -CH$_2$-CH-CH$_2$-),
3.78 (m, 1H, Si-H axial), 3.86 (m, 1H, Si-H equatorial).

33. Bromination of 1,4-Dimethyl-l-silacyclohexane (Cis/Trans = 35/65) with Bromine in Carbon Tetrachloride.

Following the general procedure [30], a 35:65 mixture of cis and trans isomers of 1,4-dimethyl-l-silacyclohexane (300 mg, 3.12 mmol) was placed in a round-bottomed flask, and bromine in carbon tetrachloride (0.42 g of bromine in 10 mL of carbon tetrachloride) was added. Distillation at 67-68°C/25 mm yielded 0.44 g (91%) of a 35:65 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-l-silacyclohexane. $^1$H NMR:

$\delta$ 0.57 (s, 3H, Si-Me equatorial),
0.60 (s, 3H, Si-Me axial),
0.90 (d:J=6.700 Hz, 3H, C-Me),
34. **Bromination of 1,4-Dimethyl-1-silacyclohexane**  
(Cis/Trans = 35/65) with Bromoform and Benzoyl Peroxide.

Following the general procedure [31], a solution of 3 mL of bromoform and benzoyl peroxide (3.78 mg, 0.00156 mol) was placed in a round-bottomed flask under nitrogen. A 35:65 mixture of cis and trans isomers of 1,4-dimethyl-1-silacyclohexane (200 mg, 1.56 mmol) was poured into the bromoform solution while stirring. Distillation under vacuum at 67-68°C/15 mm yielded 300 mg (94%) of a 34:66 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-1-silacyclohexane. \(^1\)H NMR:

\(\delta\) 0.57 (s, 3H, Si-Me equatorial),

0.60 (s, 3H, Si-Me axial),

0.91 (d: J=6.057 Hz, 3H, C-Me),

0.89 (d: J=6.540 Hz, 3H, C-Me),

0.61-2.10 (m, 18H, ring-H).

35. **Reduction of 1-Bromo-1,4-dimethyl-1-silacyclohexane** (Cis/Trans = 34/66) with Lithium Aluminum Hydride.

Following the general procedure [32], lithium aluminum hydride (138.2 mg, 3.65 mmol) and 30 mL of
anhydrous ether were placed in a round-bottomed flask. From an addition funnel a 34:66 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-1-silacyclohexane (0.75 g, 3.65 mmol) in 30 mL of anhydrous ether was added slowly to the lithium aluminum hydride solution while stirring. Distillation under reduced pressure at 58-59°C/71 mm yieldd 0.44 g (94%) of a 65:35 mixture of cis and trans isomers of 1,4-dimethyl-1-silacyclohexane.

$^1$H NMR:

© 0.06 (d:J=3.538 Hz, 3H, Si-Me equatorial),
0.11 (d:J=3.720 Hz, 3H, Si-Me axial),
0.27-0.82 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.86 (d:J=6.027 Hz, 6H, C-Me),
0.92-2.11 (m, 10H, -CH$_2$-CH-CH$_2$-),
3.78 (m, 1H, Si-H axial),
3.86 (m, 1H, Si-H equatorial).

36. **Bromination of 1,4-Dimethyl-1-phenyl-1-silacyclohexane (Cis/Trans = 60/40) with Bromine in Carbon Tetrachloride.**

In three-necked round-bottomed flask equipped with an addition funnel, a reflux condenser, a magnetic stirrer, and nitrogen inlet system was placed a 60:40 mixture of cis and trans of isomers of 1,4-dimethyl-1-phenyl-1-silacyclohexane (1.5 g, 7.35 mmol) and 2 mL of dry carbon tetrachloride. From an addition funnel a solution of 3%
bromine in carbon tetrachloride (13.6 mL) was added slowly to the solution of 1,4-methyl-1-phenyl-1-silacyclohexane while stirring. A dry ice-acetone bath was used to maintain the reaction temperature at -50° to -60°C. After the addition was complete, nitrogen was passed through the reaction mixture while stirring for 15 min. Then the reaction mixture was warmed to room temperature under stirring. Carbon tetrachloride was removed by distillation, and the residue was distilled under vacuum at 67°C/15 mm to yield 1.0 g (95%) of a 61:39 mixture of cis and trans isomers of 1-bromo-1-methyl-1-silacyclohexane. 

$^1$H NMR:

$\delta$ 0.57 (s, 3H, Si-Me equatorial),
0.60 (s, 3H, Si-Me axial),
0.90 (d: J=6.544 Hz, 3H, C-Me),
0.94 (d: J=6.000 Hz, 3H, C-Me),
0.61-2.17 (m, 18H, Ar-ring-H).

37. Bromination of 1,4-Dimethyl-1-phenyl-1-silacyclohexane (Cis/Trans = 38/62) with Bromine in Carbon Tetrachloride.

Following the general procedure [36], a 38:62 mixture of cis and trans of 1,4-dimethyl-1-phenyl-1-silacyclohexane (1.0 g, 4.9 mmol) was placed in a round-bottomed flask. From an addition funnel, bromine in carbon tetrachloride (0.78 g, in 8.5 mL of CC1$_4$) was added dropwise to
the methylphenylsilane solution. Distillation under vacuum in a short-path still at 66-67°C/15 mm yielded 0.95 g (94%) of a 60/40 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-1-silacyclohexane.

$^1$H NMR:

$\delta$ 0.57 (s, 3H, Si-Me equatorial),
0.60 (s, 3H, Si-Me axial).

38. Fluorination of 1-bromo-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 40/60) with Ammonium Hydrogen Difluoride.

A solution of a 40:60 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-1-silacyclohexane (200 mg, 0.97 mmol) and anhydrous ammonium hydrogen difluoride (60.0 g, 1.05 mmol) was placed in a round-bottomed flask equipped with a magnetic stirrer and a short path distillation head and stirred at room temperature under nitrogen for 5 min. Distillation under reduced pressure gave a colorless oily liquid boiling at 54-55°C/55 mm (1.25 g, 88%) which was a 60:40 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane.

$^1$H NMR:

$\delta$ 0.19 (d:J=7.300 Hz, 3H, Si-Me equatorial),
0.26 (d:J=7.505 Hz, 3H, Si-Me axial),
0.31-1.02 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.88 (d: J=6.479 Hz, 6H, C-Me),
1.07-2.17 (m, 10H, ring-H).

39. Fluorination of 1-Bromo-1,4-dimethyl-1-
silacyclohexane (Cis/Trans = 62/38) with
Ammonium Hydrogen Difluoride.

Following the general procedure [38], a 62:38 mixture
of cis and trans isomers of 1-bromo-1,4-dimethyl-1-
silacyclohexane (200 mg, 0.97 mmol), and ammonium hydrogen
difluoride (60.0 g, 1.05 mmol) was placed in a round-
bottomed flask and stirred at room temperature for 5 min,
and then distilled under reduced pressure at 55°C/50 mm to
give 1.2 g (85%) of a 38:62 mixture of cis and trans
isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane as a
colorless oily liquid.

\[ \text{\textsuperscript{1}H NMR:} \]
\[ \delta 0.19 (d: J=7.301 \text{ Hz}, 3\text{H}, \text{Si-Me equatorial}), \]
\[ 0.26 (d: J=7.505 \text{ Hz}, 3\text{H}, \text{Si-Me axial}). \]

40. Fluorination of 1-Bromo-1,4-dimethyl-1-
silacyclohexane (Cis/Trans = 35/65) with Zinc
Difluoride.

Following the general procedure [38], a 35:65 mixture
of cis and trans isomers of 1-bromo-1,4-dimethyl-1-
silacyclohexane (200 mg, 0.97 mmol) and anhydrous zinc
difluoride anhydrous (103 mg, 1.0 mmol) were combined in a
flask. Distillation under reduced pressure at 54-55°C/55 mm gave 1.25 g (88%) of a 65:35 mixture of 1-fluoro-1,4-dimethyl-1-silacyclohexane.

1H NMR:
δ 0.19 (d: J=7.312 Hz, 3H, Si-Me equatorial),
0.26 (d: J=7.511 Hz, 3H, Si-Me axial),
0.31-1.07 (m, 8H, -CH₂-Si-CH₂-),
0.88 (d: J=6.504 Hz, 6H, C-Me),
1.08-2.17 (m, 10H, -CH₂-CH-CH₂-).

41. Fluorination of 1-Bromo-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 62/38) with Zinc Difluoride.

Following the general procedure [38], a 62:38 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-1-silacyclohexane (200 mg, 0.97 mmol), and anhydrous zinc difluoride (103 mg, 1.05 mmol) were placed in a round-bottomed flask. Distillation under vacuum at 55°C/55 mm yielded 124 mg (88%) of a 38:62 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane.

1H NMR:
δ 0.19 (d: J=7.312 Hz, 3H, Si-Me equatorial),
0.26 (d: J=7.500 Hz, 3H, Si-Me axial),
0.88 (d: J=6.493 Hz, 6H, C-Me),
0.30-1.07 (m, 8H, -CH₂-Si-CH₂-),
1.07-2.17 (m, 10H, -CH₂-CH-CH₂-).
42. Methylation of 1-Chloro-1,4-dimethyl-silacyclohexane with MeLi in Ether.

The reaction was run in a three-necked round-bottomed flask equipped with a magnetic stirrer, an addition funnel, a reflux condenser, and nitrogen inlet system. A 1.5 N solution of MeLi in ether (9.3 mL, 14.0 mmol) was added dropwise and with stirring during 30 min to a cold (5-15°C) solution of a 65/35 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-silacyclohexane (2.0 g, 12.3 mmol) in 40 mL of anhydrous ether. After completing the addition, the reaction mixture was refluxed for 4 h. It was warmed to room temperature and treated with 4 mL of distilled water and then partitioned between ether and aqueous ammonium chloride solution. The ethereal layer was washed with aqueous sodium chloride and dried over anhydrous magnesium sulfate for 3 h. Ether was removed by distillation and the residue was distilled in a short-path still under reduced pressure at 63°C/40 mm to give 1.55 g (86%) of 1,1,4-trimethyl-1-silacyclohexane as a colorless oily liquid. $^1$H NMR:

$\delta$ -0.03 (s, 3H, Si-Me equatorial),
0.02 (s, 3H, Si-Me axial), 0.30-0.83 (m, 4H, -CH$_2$-CH$_2$-),
0.86 (d:J=6.100 Hz, 3H, C-Me),
0.90-2.25 (m, 5H, -CH$_2$-CH$_2$-CH-).
43. Methylation of 1-Chloro-1,4-dimethyl-1-silacyclohexane with MeMgBr in Ether.

Following the general procedure [42], a 3.2 M solution of methyl magnesium bromide in ether (2.03 mL, 6.5 mol) was added dropwise and with stirring during 30 min to a 65:35 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-silacyclohexane (1.0 g, 6.15 mmol) in 20 mL of anhydrous ether. After completing the addition the reaction mixture was refluxed for 6 h. After worked up as before, distillation at 62-63°C/40 mm gave 71 mg (82%) of 1,1,4-trimethyl-1-silacyclohexane as a colorless oily liquid. 1H NMR:
S-0.03 (s, 3H, Si-Me equatorial);
0.02 (s, 3H, Si-Me); 0.31-0.83 (m, 4H, -CH$_2$-Si-CH$_2$-);
0.86 (d:J=6.03 Hz, 3H, C-Me),
0.91-2.25 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-).

44. Methylation of 1-Fluoro-1,4-dimethyl-1-silacyclohexane with MeLi in Ether.

Following the general procedure [42], a solution of 1.5 N of MeLi in ether (9.0 mL, 13.6 mmol) was added dropwise and with stirring during 30 min to a cold solution of a 65:35 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane (2.0 g, 13.6 mmol) in 40 mL of anhydrous ether. After the addition was complete, the
reaction mixture was refluxed for 8 h. Vacuum distillation in a short-path still at 62-63°C/40 mm yielded 1.6 g (84%) of 1,1,4-trimethyl-1-silacyclohexane as a colorless oily liquid. \(^1\)H NMR:

\(\delta-0.03\) (s, 3H, Si-Me equatorial),
0.02 (s, 3H, Si-Me axial), 0.30-0.83 (m, 4H, -CH\(_2\)-CH\(_2\)-),
0.86 (d, \(J=6.100\) Hz, 3H, C-Me),
0.90-2.25 (m, 5H, -CH\(_2\)-CH\(_2\)-CH\(_-\)).

45. Methylation of 1-Fluoro-1,4-dimethyl-1-silacyclohexane with MeMgBr in Ether.

Following the general procedure [42], a 3.2 M solution of methylmagnesium bromide in ether (0.78 mL, 2.5 mmol) was added dropwise and with stirring during 10 min to a cold (5-15°C) solution of a 65:35 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane (0.3 g, 2.05 mmol) in 10 mL of anhydrous ether. When the addition was complete the reaction mixture was refluxed for 10 h. Vacuum distillation in a short-path still at 62-63°C/40 mm gave 0.24 g (83%) of 1,1,4-trimethyl-1-silacyclohexane as a colorless oily liquid.

\(^1\)H NMR:

\(\delta-0.03\) (s, 3H, Si-Me equatorial),
0.02 (s, 3H, Si-Me axial),
0.31-0.83 (m, 4H, -CH\(_2\)-Si-CH\(_2\)-),
0.86 (d:J=6.037 Hz, 3H, C-Me),
0.91-2.25 (m, 6H, -CH₂-CH₂-CH₂-).

46. Methylation of 1-Bromo-1,4-dimethyl-1-
silacyclohexane with MeLi in Ether.

Following the general procedure [42], a 1.5 N solution of MeLi in ether (5.33 mL, 8.0 mmol) was added dropwise and with stirring during 30 min to a cold solution of a 65/35 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-1-silacyclohexane (1.5 g, 7.28 mmol) in 40 mL of anhydrous ether. When the addition was complete, the reaction mixture was refluxed for 4 h. Vacuum distillation in a short path still at 63°C/40 mm yielded 59 mg (86%) of 1,1,4-trimethyl-1-silacyclohexane.

¹H NMR: δ -0.03 (s, 3H, Si-Me equatorial),
0.02 (s, 3H, Si-Me axial), 0.30-0.83 (m, 4H, -CH₂-CH₂-),
0.86 (d:J=6.100 Hz, 3H, C-Me),
0.90-2.25 (m, 5H, -CH₂-CH₂-CH-).

47. Methylation of 1-Bromo-1,4-dimethyl-1-
silacyclohexane with MeMgBr in Ether.

Following the general procedure [42], a 3.2 M solution of methylmagnesium bromide in ether (3.1 mL, 10.0 mol) was added dropwise and with stirring during 30 min to a cold solution of a 65/35 mixture of cis and trans isomers of 1-bromo-1,4-dimethyl-1-silacyclohexane (2.0 g,
9.7 mmol) in 30 mL of anhydrous ether. When the addition was complete the reaction mixture was refluxed for 6 h. Vacuum distillation at 62-63°C/40 mm gave 1.12 g (81%) of 1,1,4-trimethyl-1-silacyclohexane. 1H NMR:

δ -0.03 (s, 3H, Si-Me equatorial),
0.02 (s, 3H, Si-Me axial),
0.31-0.83 (m, 4H, -CH₂-Si-CH₂-),
0.8612 (d, J=6.037 Hz, 3H, C-Me),
0.91-2.25 (m, 6H, -CH₂-CH₂-CH₂-).

48. Phenylation of 1-Chloro-1,4-dimethyl-1-
silacyclohexane (Cis/Trans = 65/35) with Phenyllithium (2M) in Ether.

The reaction was carried out in a three-necked round-bottomed flask under nitrogen, and a magnetic stirrer was used. A 2 M solution of PhLi (in 75:35 benzene:ether) (7 mL, 14 mmol) was placed in an addition funnel and added dropwise to a cold (5-15°C) solution of 1.7 g (10.5 mmol) of a 65/35 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-silacyclohexane in 30 mL of anhydrous ether. After stirring under refluxed for 6 h, the reaction mixture was hydrolyzed with 5 mL of saturated NH₄Cl. The ether layer was separated, washed with (2x3 mL) of distilled water and dried over anhydrous magnesium sulfate. After removing the solvent, the remaining liquid was distilled under reduced pressure in a short-path still
at 111-112°C/3 mm to give 1.4 g (65%) of a 38:62 mixture of cis and trans isomers of 1,4-dimethyl-1-phenyl-1-silacyclohexane was a colorless oily liquid. 

\(^1\)H NMR: \( \delta \) 0.18 (s, 3H, Si-Me equatorial), 0.29 (s, 3H, Si-Me axial).

49. Phenylation of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 35/65) with Phenyllithium (2M) in Ether.

Following the procedure [48], to 1.8 g (11.0 mmol) of a 35/65 mixture of cis and trans isomers 1-chloro-1,3-dimethyl-1-silacyclohexane in 40 mL of ether was added dropwise to a 2 M solution of PhLi (7.5 mL, 15 mmol). Distillation under vacuum at 112°C/3 mm gave 1.4 g (63%) of a 61:39 mixture of cis and trans isomers of 1,4-dimethyl-1-silacyclohexane. \(^1\)H NMR: \( \delta \) 0.18 (s, 3H, Si-Me equatorial), 0.29 (s, 3H, Si-Me axial).

50. Phenylation of 1-Fluoro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 65/35) with Phenyllithium (2M) in Ether.

The reaction was carried out in a three-necked round-bottomed flask, under nitrogen and a magnetic stirrer was used. A 2 M solution of MeLi (in 75:35 benzene:ether) (4.5 mL, 9.0 mmol) was placed in an addition funnel and
added dropwise to a cold (5-15°C) solution of 1.0 g (6.84 mmol) of a 65/35 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane in 20 mL of anhydrous ether. After stirring under reflux for 12 h, the reaction mixture was hydrolyzed with 4 mL of saturated NH₄Cl. The ether layer was separated, washed with (2x2 mL) of distilled water and dried over anhydrous magnesium sulfate. After removing the solvent, the remaining liquid was distilled under reduced pressure in a short-path still at 111-112°C/3 mm to yield 0.8 g (57%) of a 38:62 mixture of cis and trans isomers of 1,4-dimethyl-1-phenyl-1-silacyclohexane as a colorless thick oily liquid.

\[ ^1H \text{NMR: } \delta \ 0.18 \text{ (s, 3H, Si-Me equatorial)}; \ 0.29 \text{ (s, 3H, Si-Me axial)}. \]

51. **Phenylation of 1-Fluoro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 35/65) with Phenyllithium (2M) in Ether.**

Following the procedure [50], a solution of 2 M of PhLi (6.5 mL, 13.0 mol) was added dropwise to 1.5 g (10.3 mmol) of a 35/65 mixture of cis and trans isomers of 1-fluoro-1,3-dimethyl-1-silacyclohexane in 40 mL of ether and stirred reflux for 12 h. Distillation under reduced pressure at 111-112°C/3 mm yielded 1.3 g (60%) of a 61:39 mixture of cis and trans isomers of 1,4-dimethyl-1-phenyl-1-silacyclohexane. \[ ^1H \text{NMR:} \]
δ 0.18 (s, 3H, Si-Me equatorial);
0.29 (s, 3H, Si-Me axial).

52. Phenylation of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 65/35) with Phenylmagnesium Bromide (3M) in Ether.

The reaction was carried out in a three-necked round-bottom flask, under nitrogen, and a magnetic stirrer was used. To 2.5 g (15.4 mmol) of a 65/35 mixture of cis and trans isomers of 1-chloro-1,4-dimethyl-1-silacyclohexane in 35 mL of anhydrous ether was added dropwise a 3 M solution of phenylmagnesium bromide in ether (6.0 mL, 18.0 mmol). After stirring under reflux for 8 h, the reaction mixture was hydrolyzed with 5 mL of saturated NH₄Cl. The ether layer was washed with water (2x3 mL) and dried over anhydrous magnesium sulfate. After removing the solvent, the remaining liquid was distilled under reduced pressure in a short-path still at 111-112°C/3 mm to yield 2.0 g (64%) of a 40:60 mixture of cis and trans isomers of 1,4-dimethyl-1-phenyl-1-silacyclohexane.

¹H NMR: δ 0.18 (s, 3H, Si-Me equatorial);
0.29 (s, 3H, Si-Me axial).
53. Phenylation of 1-Chloro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 35/65) with Phenylmagnesium Bromide (3M) in Ether.

Following the procedure [52], to (2.0 g, 12.3 mmol) of a 35/65 mixture of cis and trans isomer of 1-chloro-1,3-dimethyl-1-silacyclohexane in 35 mL of ether was added dropwise a 3 M solution of phenylmagnesium bromide in ether (5.0 mL, 15.0 mmol), and the mixture was stirred under reflux for 8 h. The product was distilled under reduced pressure at 112°C/3 mm to yield 1.7 g (68%) of a 61/39 mixture of cis and trans isomers of 1,4-dimethyl-1-silacyclohexane as a colorless oily liquid.

\[ ^1H \text{NMR: } \delta \text{ 0.18 (s, 3H, Si-Me equatorial), 0.29 (s, 3H, Si-Me axial).} \]

54. Phenylation of 1-Fluoro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 65/35) with Phenylmagnesium Bromide (3M) in Ether.

The reaction was carried out in a three-necked round-bottomed flask under nitrogen, and a magnetic stirrer was used. To 1.5 g (10.3 mmol) of a 65/35 mixture of cis and trans isomers of 1-fluoro-1,4-dimethyl-1-silacyclohexane in 40 mL of anhydrous ether was added dropwise a solution of 3 M of phenyl magnesium bromide in ether (3 mL, 12.0 mmol). After stirring under reflux for 8 h, the reaction mixture was hydrolyzed with 5 mL of saturated \( \text{NH}_4\text{Cl}. \) The
ether layer was washed with water (2x3 mL) and dried over anhydrous magnesium sulfate. After removing the solvent, the remaining liquid was distilled under reduced pressure using a short-path still at 112°C/3 mm to give 1.5 g (71%) of a 38:62 mixture of cis and trans isomers of 1,4-dimethyl-1-phenyl-1-silacyclohexane. $^1$H NMR:
$\delta$ 0.18 (s, 3H, Si-Me equatorial);
0.29 (s, 3H, Si-Me axial).

55. Phenylation of 1-Fluoro-1,4-dimethyl-1-silacyclohexane (Cis/Trans = 35/65) with Phenylmagnesium Bromide (3M) in Ether.

Following the procedure [54], to 1.0 g (6.85 mmol) of a 35/65 mixture of cis and trans isomers of 1-fluoro-1,3-dimethyl-1-silacyclohexane in 35 mL of ether was added dropwise to 3 M solution of phenylmagnesium bromide in ether (2.5 mL, 7.5 mmol). Distillation under vacuum at 112-113°C/3 mm yielded 0.95 g (68%) of a 63/37 mixture of cis and trans isomers of 1,4-dimethyl-1-silacyclohexane as a colorless oily liquid. $^1$H NMR:
$\delta$ 0.18 (s, 3H, Si-Me equatorial);
0.29 (s, 3H, Si-Me axial).

56. Preparation of 1-Chloromethyl-1,2-dimethyl-1-silacyclopentane.

Magnesium turnings (5.0 g, 0.210 mol) in 150 mL of anhydrous ether were placed in a three-necked, round-
bottomed flask equipped with a mechanical stirrer, an addition funnel, a reflux condenser and nitrogen inlet system, and were activated by stirring with 2 mL of 1,2-dibromoethane for 3 h. From an addition funnel, a solution of 1,4-dibromopentane (20 g, 0.87 mol) and 300 mL of anhydrous ether was added slowly to the activated magnesium turnings. After the addition was complete, the reaction mixture was refluxed gently under nitrogen for 8 h, cooled to room temperature, and filtered under nitrogen. A second three-necked round-bottomed flask was charged with chloromethylmethylidichlorosilane (14.2 g, 0.087 mol) in 150 mL of anhydrous ether. To this solution the diGrignard reagent was added dropwise over a 4 h period. The reaction mixture was refluxed for 25 h and then cooled to room temperature. Saturated ammonium chloride was added under cooling with an ice bath, followed by addition of distilled water. The aqueous layer was removed and the ether layer washed with water (2x100 mL), dried over anhydrous magnesium sulfate and filtered. The ether was removed by distillation, and the residue was vacuum distilled at 106-107°C/70 mm to yield 7.5 g (53%) of a 61:39 mixture of cis and trans isomers of 1-chloromethyl-1,2-dimethyl-1-silacyclohexane as a colorless oil. ¹H NMR:

δ 0.16 (s, 3H, Si-Me cis), 0.21 (s, 3H, Si-Me trans), 0.25-1.01 (m, 6H, \(-\text{CH}_2\)-Si-CH-), 1.05 (m, 6H, -C-\text{CH}_3),
1.07-2.25 (m, 8H, -CH$_2$-CH$_2$-),
2.84 (s, 2H, -CH$_2$-Cl cis), 2.86 (s, 2H, -CH$_2$-Cl trans).
IR: 2930, 2920, 2910, 2850, 1465, 1435, 1410, 1400, 1390,
1260, 1180, 930, 880, 840, 800, 790, 670. MS: minor:
(149 M$^+$-15, 13), 147(M$^+$-15, 28), 123(4), 122(9), 121(23),
120(23), 119(39), 115(3), 114(10), 113(100), 111(19),
107(7), 106(7), 105(16), 99(1), 98(1), 97(9), 96(2),
95(15), 94(31), 93(29), 92(80), 91(5), 87(4), 86(9),
85(94), 83(6), 81(12), 80(4), 79(32), 78(11), 77(4),
73(2), 71(9), 69(4), 67(8), 66(4), 65(24), 64(4), 63(39),
59(34), 57(3), 45(4), 43(16), 42(5), 41(6), 39(6). Major:
149(M$^+$-15, 12), 147(M$^+$-15, 34), 123(3), 122(8), 121(11),
119(37), 115(4), 114(10), 113(92), 111(18), 107(7),
106(7), 105(15), 99(1), 98(1), 97(7), 96(2), 95(14),
94(27), 93(31), 92(74), 91(6), 87(4), 86(10), 85(100),
83(6), 81(10), 80(6), 79(33), 78(9), 77(6), 73(2), 71(9),
69(4), 67(9), 66(4), 65(22), 64(5), 63(40), 60(3), 59(53),
for C$_7$H$_{15}$SiCl: C, 51.69; H, 9.23; Cl, 21.84; Si, 17.23.
Found: C, 51.46; H, 9.41.

57. Thermal Rearrangement of a 61:39 Mixture of Cis and Trans Isomers of 1-Chloromethyl-1,2-dimethyl-1-silacyclopentane.

In a thick-wall NMR tube was placed a 61:39 mixture of cis and trans isomers of 1-chloromethyl-1,2-dimethyl-1-
silacyclopentane (20.0 mg, 0.123 mmol) and 0.40 mL of CDCl$_3$. The tube was sealed under nitrogen and was placed into an oil bath at 149-150°C for 3 h. $^1$H NMR indicated that was small amount of rearrangement product, 1-chloro-1,3-dimethyl-1-silacyclohexane was formed. The temperature was increased to 200°C and the NMR tube was left in the oil bath for 4 h. $^1$H NMR then showed that the amount of rearrangement product had increased, to approximately 80%, and a 43:57 mixture of cis and trans isomers of 1-chloro-1,3-dimethyl-1-silacyclohexane was obtained. $^1$H NMR:

$\delta$ 0.41 (s, 3H, Si-Me equatorial),
0.44 (s, 3H, Si-Me axial), 0.98 (d, $J$=6.618 Hz, 6H, C-Me),
0.44-0.95 (m, 6H, $-\text{CH}_2\text{-Si-CH}_2$-),
1.10-2.25 (m, 10H, $-\text{CH}_2\text{-CH}_2\text{-CH}_2$-).

58. Reaction of a 61:39 Mixture of Cis and Trans Isomers of 1-Chloromethyl-1,2-dimethyl-1-silacyclopentane with ammonium hydrogendifluoride.

In a round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, and nitrogen inlet system was placed a solution of a 61:39 mixture of cis and trans isomers of 1-chloromethyl-1,2-dimethyl-1-silacyclohexane (1.0 g, 6.15 mmol) in 50 mL of acetonitrile and anhydrous ammonium hydrogendifluoride (0.40 g, 7.0 mmol). The
reaction mixture was refluxed while stirring under nitrogen for 3 days. After cooling to room temperature, the acetonitrile was removed by distillation. The residue was distilled under reduced pressure in a short-path still to give a colorless oily liquid boiling at 60°C/50 mm (0.20 g, 22%). A 45:55 mixture of cis and trans isomers of 1-fluoro-1,3-dimethyl-1-silacyclohexane was obtained.

$^1$H NMR:
$\delta$ 0.19 (d: $J$=7.519 Hz, 3H, Si-Me equatorial),
0.26 (d: $J$=7.326 Hz, 3H, Si-Me axial);
0.97 (d: $J$=6.0940 Hz, 6H, C-Me),
0.32-0.94 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.99-2.20 (m, 10H, -CH$_2$-CH$_2$-CH-).
Spectroscopic Data

1. N-Benzoylpiperidine.

$^1H$ NMR: δ 1.20-1.65 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-),
3.20-3.65 (broad, 4H, -CH$_2$-N-CH$_2$-), 7.30 (s, 5H, Ar-H).

MS: 189(35), 188(100), 105(83), 77(50), 51(9).

2. 1,5-Dibromopentane.

Bp 111-112°C/15 mm Hg (lit$^{141}$ 108-110°C/20 mm)

$^1H$ NMR: δ 1.30-2.40 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-),
3.31-3.60 (m, 4H, -CH$_2$-Br).

IR: 3000, 2960, 2930, 2860, 2850, 1460, 1450, 1440, 1430,
1290, 1230, 1130, 760. MS: 232(5.5), 230(11), 228(5.8),
151(71), 149(70), 69(100), 41(40).

3. 1,1-Dimethyl-1-silacyclohexane.

$^1H$ NMR: δ 0.01 (s, 6H, Si-Me);
0.45-0.49 (m, 4H, -CH$_2$-Si-CH$_2$-),
1.40-2.00 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-).

$^{13}C$ NMR (CDCl$_3$): -2.96 (s, 2C, Si-Me),
14.49 (s, 2C, C$_2$ and C$_6$), 24.63 (s, 2C, C$_3$ and C$_5$),
30.33 (s, 1C, C$_4$). IR: 2950, 2900, 2870, 2870, 2850,
1450, 1410, 1300, 1260, 1190, 1000, 920, 850, 810, 740,
700. MS: 128(26), 115(4), 114(7), 113(100), 111(2),
100(4), 99(2), 97(2), 87(4), 86(11), 85(85), 84(2), 83(2), 73(3), 72(12), 71(5), 66(2), 59(21), 58(4), 55(2), 45(2), 43(4).

4. 1-Methyl-1-silacyclopentane.
$^1$H NMR: $\delta$ 0.09 (d: $J$= 3.742 Hz, 3H, Si-Me),
0.41-1.13 (m, 4H, -CH$_2$-Si-CH$_2$-),
1.17-2.15 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-),
3.81-4.00 (m, 1H, Si-H). MS: 114(43), 113(27), 112(5), 110(2), 99(17), 98(3), 97(21), 87(13), 86(100), 85(34), 83(4), 73(9), 72(24), 71(48), 70(6), 69(4), 68(2), 67(5), 66(2), 60(3), 59(16), 58(43), 57(5), 55(7), 53(4), 45(9), 44(4), 43(14), 42(3).

5. 1-Methyl-1-Chloro-1-silacyclopentane.
$^1$H NMR: $\delta$ 0.42 (s, 3H, Si-Me),
0.50-1.16 (m, 4H, -CH$_2$-Si-CH$_2$-),
1.20-2.20 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-).
MS: 150(13), 148(27), 136(3), 135(27), 134(8), 133(45), 131(2), 124(2), 123(3), 122(30), 121(10), 120(89), 119(7), 113(5), 112(7), 111(2), 109(5), 108(8), 107(40), 106(24), 105(100), 104(2), 103(2), 99(3), 98(7), 97(79), 96(2), 95(9), 94(38), 93(22), 92(92), 91(7), 85(7), 84(6), 83(4), 81(25), 80(12), 79(64), 78(23), 77(4), 69(3), 68(3),
67(7), 66(4), 65(27), 64(5), 63(54), 59(2), 55(4), 53(3), 43(6), 41(3), 39(4).

6. 1-Methyl-1-phenyl-1-silacyclohexane.

$^1$H NMR: $\delta$ 0.25 (s, 3H, Si-Me),
0.51-1.10 (m, 4H, -CH$_2$-Si-CH$_2$-),
1.20-2.11 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-),
7.23-7.60 (m, 5H, Ar-H).

$^{13}$C NMR (CDCl$_3$): $\delta$ 3.96 (s, 1C, Si-Me),
12.98 (s, 2C, C$_2$ and C$_6$), 24.52 (s, 2C, C$_3$ and C$_5$),
30.10 (s, 1C, C$_4$), 127.52 (s, 1C, Si-C$_1$'),
128.82 (s, 2C, C$_2$' and C$_6$'), 133.64 (s, 2C, C$_3$' and C$_5$'),
138.96 (s, 1C, C$_4$'). IR: 2950, 2910, 2900, 2850, 1450, 1430, 1400, 1260, 1190, 1110, 990, 910, 810, 780, 740, 700. MS: 190(11), 176(9), 175(65), 162(1), 148(7), 147(44), 135(3), 134(10), 133(6), 123(3), 122(11), 121(71), 120(9), 119(16), 114(4), 113(12), 112(100), 107(15), 106(6), 105(54), 103(4), 99(2), 98(4), 97(53), 95(6), 93(8), 91(6), 85(5), 84(1), 83(1), 81(3), 79(5), 67(3), 59(3), 57(1), 55(1), 43(3), 41(1).

7. 1-Bromo-1-methyl-1-silacyclohexane.

$^1$H NMR: $\delta$ 0.57 (s, 3H, Si-Me),
0.60-1.55 (m, 4H, -CH$_2$-CH$_2$-),
1.60-2.21 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-),
MS: 194(54), 192(54), 179(75), 177(80), 166(69), 164(59), 151(69), 149(60), 138(52), 136(48), 123(50), 125(45), 113(46), 112(27), 111(10), 109(53), 107(50), 98(10), 97(100), 86(23), 84(11), 83(7), 69(4). Anal. Calcd. for C$_6$H$_{13}$SiBr: C, 37.50; H, 6.82; Si, 14.57; Br, 41.10. Found: C, 37.35; H, 6.98.

8. 1-Fluoro-1-methyl-1-silacyclohexane.
$^1$H NMR: δ 0.22 (d, J=7.370 Hz, 3H, Si-Me), 0.30-1.06 (m, 4H, -CH$_2$-Si-CH$_2$-), 1.16-2.16 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-). IR: 2990, 2950, 2910, 2890, 1460, 1450, 1410, 1260, 1190, 1010, 920, 860, 830, 800. MS: 132(49), 118(3), 117(3), 106(3), 105(8), 104(81), 103(8), 101(2), 92(2), 91(22), 90(17), 89(100), 87(2), 85(2), 78(4), 77(20), 76(73), 75(7), 65(2), 64(2), 63(29), 62(9), 61(2), 49(2), 47(14), 39(1). Anal. Calcd. for C$_6$H$_{13}$F: C, 54.55; H, 9.85; Si, 21.21; F, 14.39. Found: C, 54.45; H, 9.80.

$^1$H NMR: δ 1.20 (d, J=6.500 Hz, 3H, C-Me), 1.60 (m, 6H, -CH$_2$-CH$_2$-CH$_2$-), 2.80-3.20 (m, 1H, CH-Br), 3.70-4.60 (m, 2H, CH$_2$-Br), 7.32 (s, 5H). IR: 3500, 3050, 2970, 2940, 2860, 1760, 
1.5-Dibromohexane.

\(^1H\) NMR: \(\delta 1.72 (d: J=6.581 \text{ Hz}, 3\text{H}, \text{C-Me}),
1.33-2.37 (m, 6\text{H}, -\text{CH}_2-\text{CH}_2-\text{CH}_2-),
3.33-3.63 (d: J=6.600 \text{ Hz}, 2\text{H}, -\text{CH}_2-\text{Br}),
4.00-4.33 (m, 1\text{H}, -\text{CH}-\text{Br}). \text{ MS: 246(8), 244(16), 242(10), }\)
165(21), 163(23), 83(100), 69(2), 55(44). \text{ IR: 2990, 2980, 2930, 2910, 2890, 1450, 1390, 1290, 1270, 1250,}
1240, 1170, 740. \text{ Anal. Calcd. for } \text{C}_6\text{H}_{12}\text{Br}_2: \text{ C, 29.51; H, 4.92; Br, 65.57. }\text{ Found: C, 29.42; H, 4.97.}

1,2-Dimethyl-1-silacyclohexane.

\(^1H\) NMR:
\(\delta 0.08 (d: J=3.653 \text{ Hz}, 3\text{H}, \text{Si-Me equatorial}),
0.15 (d: J=3.712 \text{ Hz}, 3\text{H}, \text{Si-Me axial}),
0.94 (d: J=7.247 \text{ Hz}, 3\text{H}, \text{C-Me}),
1.09 (d: J=6.960 \text{ Hz}, 3\text{H}, \text{C-Me}),
0.21-1.12 (m, 6\text{H}, -\text{CH-Si-CH}_2-),
1.17-2.24 (m, 12\text{H}, -\text{CH}_2-\text{CH}_2-\text{CH}_2-),

1710, 1660, 1650, 1590, 1570, 1490, 1460, 1440, 1370,
1340, 1310, 1270, 1250, 1240, 1210, 1060, 1040, 1010, 790,
740, 710. \text{ MS: 203(19), 202(22), 188(25), 105(100),}
77(34), 51(8). \text{ Anal. Calcd. for } \text{C}_{13}\text{H}_{17}\text{ON}: \text{ C, 76.84; H, 8.37; N, 6.90; O, 7.88. }\text{ Found: C, 76.76; H, 8.52; N, 6.85.}
3.79 (m, 1H, Si-H), 3.98 (m, 1H, Si-H). IR: 2950, 2925, 2915, 2850, 2160, 1450, 1440, 1420, 1375, 1250, 1190, 1070, 970, 880, 840, 770. MS: cis isomer: 128(65), 127(6), 114(3), 113(33), 111(5), 102(4), 101(10), 100(100), 99(27), 98(5), 97(11), 95(2), 87(7), 86(23), 85(65), 83(8), 81(3), 74(5), 73(36), 72(74), 71(23), 70(4), 69(2), 67(4), 60(2), 59(19), 58(21), 57(3), 55(5), 53(2), 45(8), 43(6), 41(2). And trans isomer: 128(44), 127(2), 114(3), 113(31), 111(3), 102(4), 101(12), 100(100), 99(21), 98(3), 97(10), 87(5), 86(21), 85(58), 84(3), 83(7), 82(2), 81(2), 74(5), 73(28), 72(83), 71(23), 70(4), 69(3), 70(4), 69(3), 67(5), 59(15), 58(14), 57(3), 55(4), 45(6), 44(3), 43(6), 41(2). Exact Mass Calcd. for C7H16Si: 128.1021, found: first trans isomer: 128.0992; second cis isomer: 128.0993.

12. 1,1,2-Trimethyl-1-silacyclohexane.

1H NMR:

δ 0.01 (s, 3H, Si-Me equatorial),
0.06 (s, 3H, Si-Me axial), 0.25-0.90 (m, 3H, -CH-Si-CH2-),
0.96 (d; J = 7.075 Hz, 3H, C-Me),
1.03-2.15 (m, 6H, -CH2-CH2-CH2-).

IR: 2960, 2925, 2880, 2860, 1480, 1410, 1380, 1260, 1050, 990, 840, 820, 800, 700. MS: 142(42), 129(13), 128(6),
127(55), 116(4), 115(12), 114(88), 113(5), 112(2), 111(3), 110(6), 100(15), 99(100), 97(14), 95(3), 92(5), 91(9), 89(2), 88(4), 87(38), 86(57), 85(45), 84(4), 83(8), 82(2), 81(4), 79(2), 74(5), 73(34), 72(28), 71(11), 70(4), 69(3), 66(5), 61(3), 60(7), 59(6), 58(19), 57(4), 56(2), 55(7), 53(3), 45(5), 44(2), 43(12), 42(2), 41(4). Exact Mass Calcd. for C_{8}H_{18}Si: 142.1177. Found: 142.1166.

13. 1-Chloro-1,2-dimethyl-1-silacyclohexane.

$^1H$ NMR:

$\delta$ 0.39 (s, 3H, Si-Me equatorial);

0.43 (s, 3H, Si-Me axial);

0.95 (d: J=6.250 Hz, 3H, C-CH$_3$),

1.03 (d: J=7.025 Hz, 3H, C-Me),

0.45-0.91 (m, 6H, -CH-Si-CH$_2$-),

1.10-2.35 (m, 12H, -CH$_2$-CH$_2$-CH-). IR: 2960, 2950, 2930, 2910, 2860, 1460, 1410, 1430, 1260, 1180, 1110, 1080, 970, 800, 770. 750. MS: trans (major): 164(11), 162(31), 149(7), 148(3), 147(18), 137(3), 136(23), 135(13), 134(67), 133(13), 127(2), 122(4), 121(23), 120(9), 119(55), 117(4), 111(14), 110(3), 109(10), 108(35), 107(47), 106(100), 105(45), 99(4), 98(4), 97(23), 96(3), 95(29), 94(18), 93(63), 92(35), 91(7), 90(2), 83(7), 82(5), 81(30), 80(17), 79(72), 78(35), 77(3), 69(3), 68(5), 67(8), 65(10), 64(3), 63(24), 59(3), 55(7), 43(4),
14. 1,2-Dimethyl-1-phenyl-1-silacyclohexane.

$^1$H NMR:

$\delta$ 0.22 (s, 3H, Si-Me equatorial);
0.32 (s, 3H, Si-Me axial); 0.40-2.24 (m, 18H, ring-H),
0.83 (d, $J=6.577$ Hz, 6H, C-Me);

7.23-7.65 (m, 10H, Ar-H). IR: 2930, 2920, 2890, 2860,
2850, 1460, 1450, 1430, 1420, 1380, 1260, 1150, 1110,
1090, 790, 740, 710. MS: trans (minor): 204 (0.2),
190(4), 189(21), 162(5), 161(41), 159(6), 148(5), 147(33),
145(7), 136(1), 135(9), 134(20), 133(4), 128(4), 127(12),
126(100), 123(2), 122(6), 121(49), 120(7), 119(19),
117(2), 112(3), 111(21), 109(2), 107(10), 106(6), 105(42),
103(4), 99(3), 98(8), 97(3), 95(5), 93(4), 91(6), 85(4),
84(3), 83(4), 81(3), 79(6), 78(2), 77(2), 59(4), 55(4),
53(7), 45(2), 43(11), 42(2), 41(4), 39(3). Cis (major):
204(11), 190(10), 189(51), 162(12), 161(70), 159(12),
148(11), 147(65), 145(12), 136(3), 135(18), 134(40),
133(10), 128(5), 127(17), 126(98), 123(4), 122(14),
121(100), 120(14), 119(37), 117(4), 112(6),
111(49), 109(3), 107(18), 106(13), 105(93), 103(7), 99(6),
98(13), 97(6), 95(11), 93(18), 91(12), 85(8), 84(7),
83(8), 81(8), 79(13), 78(4), 77(5), 59(8), 58(2), 57(2),
55(10), 53(16), 45(6), 43(25), 42(6), 41(9), 39(8). Anal.
Calcd. for C_{13}H_{17}Si: C, 76.47; H, 9.80; Si, 13.71.
Found: C, 76.42; H, 9.90.

15. 1-Fluoro-1,2-dimethyl-1-silacyclohexane.

^{1}H NMR:
δ 0.20 (d: J=7.340 Hz, 3H, Si-Me equatorial),
0.25 (d: J=7.520 Hz, 3H, Si-Me axial);
0.30-0.93 (m, 6H, -CH₂-Si-CH⁻),
0.99 (d: J=6.925 Hz, 3H, C-Me),
1.06 (d: J=6.385 Hz, 3H, C-Me),
1.10-2.20 (m, 10H, -CH₂-CH₂-CH₂⁻).

IR: 2930, 2910, 2900, 2870, 1460, 1450, 1410, 1260, 945,
1040, 1010, 980, 940, 865, 800, 780. MS: cis (major):
146(15), 133(3), 132(10), 131(86), 118(3), 105(23),
104(44), 103(100), 101(5), 91(5), 90(8), 89(32), 78(5),
77(33), 76(64), 75(9), 63(32), 62(9), 49(5), 47(25),


\(^1\)H NMR: \( \delta 0.80 \) (d:J=6.100 Hz, 3H, C-Me), 1.00-2.10 (m, 5H, -CH\(_2\)-CH\(_2\)-CH-), 2.30-3.10 (m, 2H, -N-CH\(_2\)-), 3.60-4.40 (m, 2H, -CH\(_2\)-N-), 7.30 (s, 5H, Ar-H). IR: 3500, 3060, 3000, 2960, 2930, 2870, 2850, 1660, 1580, 1500, 1460, 1450, 1360, 1350, 1320, 1240, 1200, 1130, 1090, 1050, 970. MS: 203(27), 202(68), 188(14), 105(100), 77(39), 51(4). Anal. Calcd. for \( \text{C}_{13}\text{H}_{17}\text{ON} \): C, 76.84; H, 8.37; N, 6.90; O, 7.88. Found: C, 76.72; H, 8.60; N, 6.89.

17. 1,5-Dibromo-2-methylpentane.

Bp 110-112°C/5mm (lit\(^1\)42 98-99°C/11mm) \(^1\)H NMR: \( \delta 1.04 \) (d:J=6.632 Hz, 3H, C-Me), 1.24-2.11 (m, 5H, -CH\(_2\)-CH\(_2\)-CH-), 3.18-3.63 (m, 4H, -CH\(_2\)-Br). MS: 246(0.3), 244(1.1), 242(0.4), 165(22), 163(27), 83(100), 55(21). IR: 2970, 2940, 2890, 2870, 1460, 1450, 1430, 1360, 1330, 1300,
1280, 1260, 1240, 1220, 770. Anal. Calcd. for C₆H₁₂Br₂:
C, 29.51; H, 4.92; Br, 65.57. Found: C, 29.68; H, 5.04.

18. 1,3-Dimethyl-1-silacyclohexane.

¹H NMR:
$0.06 (D:J=3.572 Hz, 3H, Si-Me equatorial),$
0.11 (d:J=3.594 Hz, 3H, Si-Me axial),
0.13-0.93 (m, 8H, -CH₂-Si-CH₂-),
0.96 (d:J=6.443 Hz, 6H, -C-Me),
1.02-2.24 (m, 10H, -CH₂-CH₂-CH₃),
3.80 (m, 1H, Si-H axial), 3.99 (m, 1H, Si-H equatorial).
IR: 2950, 2920, 2870, 2850, 2110, 1460, 1450, 1410, 1380, 1340, 1260, 1210, 1180, 1060, 1050, 1020, 950, 890, 870, 800, 740, 730. MS: Cis isomer: 128(13), 127(6), 126(2), 115(4), 114(13), 113(100), 111(3), 101(2), 100(10), 99(9), 98(2), 97(4), 87(8), 86(24), 85(72), 84(3), 83(4), 73(3), 72(12), 71(12), 67(2), 59(15), 58(18), 57(2), 55(2), 45(2), 43(3), 40(2). Trans isomer: 128(18), 127(3), 115(4), 114(10), 113(100), 111(3), 101(2), 100(16), 99(8), 97(4), 87(8), 86(31), 85(63), 84(3), 83(4), 73(4), 72(12), 71(12), 69(2), 67(2), 60(2), 59(13), 58(22), 57(2), 55(2), 54(3), 45(3), 43(3). Exact Mass Calcd. for C₇H₁₆Si: 128.1021. Found: first isomer: 128.0986; second isomer: 128.0993.
19. **1,1,3-Trimethyl-1-silacyclohexane.**

$^1$H NMR:

$\delta$ -0.02 (s, 3H, Si-Me equatorial),

0.01 (s, 3H, Si-Me axial),

0.10–0.48 (m, 4H, Si-CH$_2$-),

0.94 (d; $J$=6.374 Hz, 3H, C-Me),

0.96–2.20 (m, 5H, -CH$_2$-CH$_2$-CH-).

IR: 2940, 2890, 2880, 2850, 2780, 1460, 1445, 1410, 1375, 1350, 1335, 1260, 1210, 1175, 1060 1040, 945, 910, 840, 810, 795, 735, 710. MS: 142(3), 129(2), 128(7), 127(50), 114(3), 101(7), 100(19), 99(100), 97(10), 87(5), 86(13), 85(69), 83(6), 82(2), 81(3), 74(3), 73(19), 72(53), 71(18), 70(4), 69(5), 67(7), 66(2), 61(2), 60(4), 59(58), 58(13), 57(7), 56(2), 55(11), 54(2), 53(5), 45(10), 44(8), 43(28), 42(8), 41(12). Exact Mass Calcd. for C$_8$H$_{18}$Si: 142.1177. Found: 142.1166.

20. **1-Chloro-1,3-dimethyl-1-silacyclohexane.**

$^1$H NMR: $\delta$ 0.41 (s, 3H, Si-Me axial),

0.44 (s, 3H, Si-Me equatorial),

0.45–2.20 (m, 18H, -CH$_2$-CH$_2$-CH-),

1.01 (d; $J$=6.384 Hz, 3H, C-Me),

0.98 (d; $J$=6.520 Hz, 6H, C-Me),

IR: 2945, 2920, 2900, 2810, 1455, 1405, 1340, 1260, 1210, 1180, 1060, 1040, 1020, 945, 905, 860, 840, 810, 770. MS:
cis isomer: 164(3), 162(7), 150(4), 149(34), 148(10), 147(100), 134(2), 123(5), 122(10), 121(40), 120(31), 119(72), 117(3), 112(3), 111(27), 109(2), 108(2), 107(10), 106(5), 105(26), 103(2), 99(2), 98(2), 97(3), 95(10), 94(26), 93(23), 92(66), 91(7), 85(2), 84(2), 83(6), 81(15), 80(8), 79(45), 78(13), 67(6), 65(17), 65(17), 63(38), 64(4), 55(4), 43(5), 41(5), 39(5). Trans isomer: 164(4), 162(14), 150(4), 149(35), 148(10), 147(100), 134(4), 123(9), 122(22), 121(57), 120(56), 119(96), 117(4), 112(3), 111(28), 109(3), 108(3), 107(14), 106(9), 105(35), 103(3), 97(4), 95(13), 94(35), 93(34), 92(98), 91(9), 85(3), 84(2), 83(7), 81(20), 80(10), 79(58), 78(16), 67(7), 65(23), 64(5), 63(50), 55(5), 45(2), 43(6), 41(7), 39(7). Anal. Calcd. for C_{7}H_{15}SiCl: C, 51.69; H, 9.23; Si, 17.23; Cl, 21.85. Found: C, 51.60; H, 9.35.

21. 1,3-Dimethyl-1-phenyl-1-silacyclohexane.

$^1H$ NMR:

0.18 (s, 3H, Si-Me equatorial),
0.30 (s, 3H, Si-Me axial),
0.30-0.90 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.97 (d: J=6.785 Hz, 3H, -C-CH$_3$)
1.00 (d: J=6.611 Hz, 3H, C-Me),
1.10-2.50 (m, 10H, -CH$_2$-CH$_2$-CH-),
7.23-7.65 (m, 10H, Ar-H). IR: 2950, 2910, 2890, 2850,
1460, 1435, 1260, 1210, 1180, 1120, 1060, 1050, 1020, 950, 890, 820, 740, 710. MS: Cis isomer: 204(0.2), 190(4), 189(21), 162(6), 161(37), 159(7), 148(5), 147(36), 145(7), 136(2), 135(9), 134(22), 133(6), 131(3), 128(5), 127(15), 126(100), 123(3), 122(7), 121(60), 120(10), 119(22), 117(3), 112(3), 111(28), 109(2), 107(12), 106(8), 105(59), 103(5), 99(3), 98(10), 97(3), 95(7), 93(12), 94(2), 91(8), 85(5), 84(4), 83(5), 81(4), 78(2), 79(9), 77(3), 59(4), 55(5), 53(9), 45(2), 43(9), 42(3), 41(4), 39(4). Trans isomer: 204(11), 190(11), 189(56), 162(10), 161(73), 159(11), 148(9), 147(58), 145(14), 136(3), 135(16), 134(36), 133(9), 131(6), 128(4), 127(12), 126(96), 123(4), 122(12), 121(99), 120(15), 119(41), 117(5), 112(5), 111(37), 109(3), 107(20), 106(14), 105(100), 103(8), 99(5), 98(10), 97(5), 95(10), 94(3), 93(21), 91(14), 85(7), 84(6), 83(7), 81(8), 79(14), 78(5), 77(6), 59(8), 55(9), 53(16), 45(4), 43(19), 42(5), 41(8), 39(7). Anal. Calcd. for C\textsubscript{13}H\textsubscript{17}Si: C, 76.47; H, 9.80; Si, 13.72. Found: C, 76.43; H, 9.89.

22. 1-Fluoro-1,3-dimethyl-1-silacyclohexane.

1H NMR:

δ 0.20 (d, J=7.349 Hz, 3H, Si-Me equatorial),
0.25 (d, J=7.535 Hz, 3H, Si-Me axial),
0.26-0.91 (m, 8H, -CH\textsubscript{2}-Si-CH\textsubscript{2}-),
0.97 (d: J = 6.594 Hz, 3H, C-Me),
1.01 (d: J = 6.212 Hz, 3H, C-me),
1.00-2.21 (m, 10H, ring-H). IR: 2940, 2920, 2860, 2850,
1460, 1450, 1410, 1380, 1340, 1280, 1260, 1210, 1180,
1060, 1040, 1020, 950, 910, 860, 840, 810, 780, 720. MS:
cis (major): 146(14), 133(4), 132(9), 131(100), 118(2),
105(16), 104(28), 103(85), 101(3), 91(3), 90(7), 89(3),
78(3), 77(16), 76(38), 75(4), 63(9), 62(2), 47(2). Trans
(minor): 146(19), 133(3), 132(8), 131(86), 118(3),
105(26), 104(49), 103(100), 101(5), 91(5), 89(35),
78(5), 77(26), 76(65), 75(6), 63(18), 62(4), 47(5). Anal.
Calcd. for C<sub>7</sub>H<sub>15</sub>FSi: C, 57.58; H, 10.27; F, 13.10; Si,
19.17. Found: C, 57.74; H, 10.34.

23. 1-Bromo-1,3-dimethyl-1-silacyclohexane.
<sup>1</sup>H NMR: <sup>§</sup> 0.57 (s, 3H, Si-Me equatorial),
0.59 (s, 3H, Si-Me axial), 1.10 (d: J = 6.134 Hz, 6H, C-Me),
0.37-2.19 (m, 18H, ring-H). IR: 2930, 2910, 2900, 2850,
1450, 1400, 1340, 1260, 1210, 1170, 1060, 1040, 1020, 940,
900, 890, 830, 800, 770, 730, 630. MS: cis (major):
208(10), 206(12), 194(10), 193(96), 192(10), 191(100),
167(11), 166(25), 165(61), 164(26), 163(52), 151(21),
149(21), 139(18), 138(60), 137(21), 136(60), 135(5),
127(6), 126(7), 125(44), 124(24), 123(56), 122(19),
121(5), 111(62), 110(8), 109(60), 108(7), 107(62), 99(7),
98(5), 97(15), 95(7), 71(6), 69(9), 67(12), 66(5), 59(9),
58(4), 57(4), 55(17), 53(12), 45(6), 43(32), 42(12),
41(20). Trans (minor): 208(9), 206(8), 194(7), 193(98),
192(11), 191(100), 167(8), 166(20), 165(63), 164(18),
163(61), 151(20), 149(20), 139(21), 138(53), 137(24),
136(55), 135(4), 127(8), 126(5), 125(45), 124(19),
123(54), 122(18), 121(20), 111(56), 110(7), 109(57),
108(5), 107(60), 99(4), 98(3), 97(13), 95(4), 71(3),
69(12), 67(10), 66(4), 59(7), 58(3), 57(5), 55(14),
53(10), 45(3), 43(30), 42(10), 41(16). Anal. Calcd. for
C$_7$H$_{15}$SiBr: C, 40.77; H, 7.33; Si, 13.58; Br, 38.31.
Found: C, 40.93; H, 7.25.

$^1$H NMR: $\delta$ 0.80 (d:J=6.200 Hz, 3H, C-Me),
0.92 (d:J=6.150 Hz, 3H, C-Me),
1.10-2.60 (m, 4H, -CH-CH$_2$-CH-),
2.80-3.50 (m, 2H, -CH$_2$-N-),
3.60-4.30 (m, 2H, -CH$_2$-N-), 7.35 (s, 5H, Ar-H).
MS: 217(45), 216(94), 202(37), 105(100), 77(34), 51(5).
Anal. Calcd. for C$_{14}$H$_{19}$ON: C, 77.41; H, 8.75; N, 6.45.
Found: C, 77.49; H, 8.63; N, 6.54.
25. \textit{1,5-Dibromo-2,4-dimethylpentane}.

BP 73-75°C/2 mm (lit 72-73°C/2 mm)

$^1$H NMR: \( \delta 1.06 \) (d: $J=6.668$ Hz, 6H, C-CH$_3$),
1.04-2.14 (m, 4H, -CH-CH$_2$-CH-),
3.17-3.60 (d: $J=5.807$ Hz, 4H, -CH$_2$-Br).

IR: 2980, 2930, 2920, 2880, 1460, 1440, 1390, 1320, 1290, 1270, 1240, 970, 920, 830, 750, 660. MS: 260(0.1), 258(0.3), 256(0.1), 179(1), 177(1), 98(6), 97(100), 67(1), 55(4). Anal. Calcd. for C$_7$H$_{14}$Br$_2$: C, 32.56; H, 5.43; Br, 62.0. Found: C, 32.60; H, 5.56.

26. \textit{1,1,3,5-Tetramethyl-1-silacyclohexane}.

$^1$H NMR: \( \delta 0.03 \) (s, 3H, Si-Me),
0.05 (s, 6H, Si-Me), 0.08 (s, 3H, Si-Me),
0.89 (d: $J=6.500$ Hz, 6H, C-CH$_3$),
0.93 (d: $J=6.810$ Hz, 6H, C-CH$_3$),
0.10-0.85 (m, 8H, -CH$_2$-Si-CH$_2$-),
0.98-2.10 (m, 8H, -CH-CH$_2$-CH-).

IR: 2950, 2920, 2910, 2860, 1460, 1435, 1380, 1260, 1230, 910, 880, 820, 690. MS: cis isomer: 156(18), 141(20), 129(5), 128(32), 114(18), 113(9), 103(3), 102(10), 101(75), 99(13), 97(1), 87(10), 86(2), 85(3), 83(2), 75(4), 74(5), 73(49), 72(2), 71(1), 61(4), 60(7), 59(100), 57(2), 56(1), 55(2), 45(3), 43(6), 41(3), 39(3). And trans isomer: 156(20), 141(19), 129(3), 128(20), 114(16),
113(8), 103(4), 102(10), 101(5), 99(14), 97(1), 87(8),
86(2), 85(4), 83(2), 75(2), 74(4), 73(61), 72(3), 71(2),
61(3), 60(8), 59(100), 57(3), 56(2), 55(3), 45(3), 43(6),
12.82; Si, 17.95.  Found:  C, 69.23; H, 12.71.
Binh Thanh Nguyen was born on August 5, 1952, in South Viet Nam. After graduation from Tay Ninh High School, he entered the University of Saigon, where he studied natural science and mathematics. In 1971, he voluntarily joined the military service and entered Nha-Trang Naval Academy. After graduation, he became a naval officer and served aboard several warships during the last years of the war. In 1975, after the Saigon government fell, he migrated to the United States. In August, 1975, he enrolled at New England College at Henniker, New Hampshire, where he studied chemistry under the direction of Dr. John J. Santos. On August 5, 1978, he married his classmate, the former Oanh Thi Vu. He and his wife entered the Graduate School at Pennsylvania State University Department of Chemistry and worked under the direction of Dr. Maurice Shamma. In August, 1980, he came to Baton Rouge and entered the Graduate School at Louisiana State University, where he is at the present a candidate for the degree of Doctor of Philosophy in the Department of Chemistry with a major in organic chemistry and a minor in inorganic chemistry. He performed his Ph.D. research under the direction of Prof. Frank K. Cartledge. He is now a U.S. citizen. He has accepted a
position as a postdoctoral fellowship with Prof. Frank K. Cartledge in the Department of Chemistry at Louisiana State University to begin January, 1986.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Binh Thanh Nguyen

Major Field: Organic Chemistry

Title of Dissertation: Synthesis, Reactivity And Stereochemistry Of Silacyclohexanes And Their Derivatives

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

November 20, 1985