Some attempts at the preparation of a silicon-carbon double bond.

Robert J. Seidewand

University of Windsor

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SOME ATTEMPTS AT THE PREPARATION OF
A SILICON-CARBON DOUBLE BOND

BY

ROBERT J. SEIDEWAND

A DISSERTATION
Submitted to the Faculty of Graduate Studies through the Department of Chemistry in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario
1972
This thesis is dedicated to my family:

Betsy, Michael and Derek
ABSTRACT

The pyrolysis of silyl hydrogen phthalates has been proposed as a possible low temperature means of producing silico-olefins (Si=C). Various attempts at the synthesis of a silyl hydrogen phthalate have afforded mixtures of the silyl hydrogen phthalate and the corresponding disilyl phthalate ester. The reaction of diphenylmethylchlorosilane (2) with potassium hydrogen phthalate (1) or with phthalic acid and of diphenylmethysilsilane (7) with phthalic acid (catalyzed by Pd-C) have all yielded mixtures. Attempted synthesis of silver hydrogen phthalate, to use as a substitute for 1, by reaction of 1 with silver nitrate afforded mainly the disilver salt of phthalic acid.

Pyrolysis of diphenylmethysilsilyl methyl phthalate (10), trimethysilyl methyl phthalate (11), trimethysilyl 2-octyl phthalate (16) and benzylidiphenylsilyl methyl phthalate (19) does not lead to silico-olefins, but does afford phthalic anhydride and silyl ethers. Diphenylmethysilyl t-butyl phthalate (22) and trimethysilyl t-butyl phthalate (23) are postulated to thermally decompose to a silyl hydrogen phthalate which further decomposes to phthalic anhydride and a silyl alcohol. The mechanisms of the transformations are discussed along with the results of the pyrolysis of optically active 16.
Various attempts to dehydrochlorinate benzhydryldiphenylchlorosilane (26) with triethylamine, DBN and n-butyllithium, and benzylidiphenylchlorosilane (18) with t-butyllithium led to mixtures composed primarily of silanol and siloxane material. The formation of these mixtures is discussed as arising from base-promoted hydrolysis of the Si-Cl bond. Reaction of 2 with n-butyllithium afforded diphenyldimethylsilane (25) after addition of methyl iodide, and attempted dehydrogenation of benzyl-diphenylsilane (22) with DDQ yielded unreacted starting material.

A convenient procedure was developed for the synthesis of (α-trimethylsilylbenzyl)diphenylchlorosilane (30) and (α-trimethylsilylbenzyl)diphenylmethoxysilane (31) by deprotonation of the appropriate activated organosilane by t-butyllithium and in situ silylation by trimethylchlorosilane. Pyrolytic decomposition of 31 above 300° (30 was inert) afforded trimethylmethoxysilane (14) and a residue. The possible intermediacy of a Si=C species was not established.
ACKNOWLEDGEMENT

I wish to express my sincere gratitude to Dr. K. G. Rutherford for his patient guidance, his kind understanding and his enthusiasm throughout the course of these studies.

A word of appreciation is also due Drs. L. K. Lam, J. M. McIntosh, and H. H. Holton for many stimulating and beneficial discussions.

Finally, a special thank-you to my wife, Betsy; my parents, Mr. and Mrs. Edward Seidewand; my grandparents, Mr. and Mrs. Joseph Schafer; my parents-in-law, Mr. and Mrs. Edward Baumer and also Mrs. Sharon Schneider, for their unfailing support and encouragement during this entire project.

To all these special people, I am indebted.

-RJS
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INTRODUCTION

Since the 1940's, there has been a considerable amount of research and development of silicone polymers. The interest has been due mainly to their more favorable thermal and oxidative stability as compared to organic polymers. The present day silicone polymers (Figure 1)

\[
\begin{array}{c}
\text{Si} \\
\text{O} \\
\end{array}
\]

\[n\]

**Figure 1 -- Silicone Polymer**

are composed primarily of polymethyl- and polyphenyl-siloxanes which are obtained from hydrolysis of the corresponding silyl chlorides and polymerization thereof. Since both carbon-carbon and silicon-oxygen polymers display very desirable properties, a natural outgrowth would be the study of a hybrid heteropolymer containing alternating silicon and carbon atoms (Figure 2). One of the ways that

\[
\begin{array}{c}
\text{Si} \\
\text{C} \\
\end{array}
\]

\[n\]

**Figure 2 -- A Silicon-Carbon Heteropolymer**
can be readily envisaged for the production of such a chain would be the polymerization of the corresponding silicon-carbon double-bonded monomer (Si=C).

In contrast, however, to the abundance and importance of unsaturation in carbon compounds, there has been no authenticated report of the isolation of any kind of stable multiple-bonded silicon compound.

One of the first compounds postulated to have silicon multiply bonded was a material described as "diphenyl-diethylsilicoethylene." F. S. Kipping, a pioneer in the organosilicon field, mentioned it in a brief note in his early papers but never referred to it again. Throughout the succeeding years other postulated examples of (p-p)\( \equiv \) bonded silicon compounds have appeared and some of these are listed in Table I along with their probable or established structures.

One of the reasons advanced to explain why the polymeric siloxanes are more stable relative to their analogous Si=O monomers is the availability of (d-p)\( \equiv \) bonding in the polymeric species (Figure 3). While this

\[
\begin{align*}
R_2Si=0 & \quad \to \quad \left[ \begin{array}{c}
\text{R} \\
\text{Si=O}
\end{array} \right]_n \\
\end{align*}
\]

Figure 3 -- (d-p)\( \equiv \) Bonding in Siloxanes
# TABLE I

**Proposed (p-p)\(\uparrow\uparrow\)** Bonded Organosilicon Compounds

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<td>PhEtSi=SiEtPh</td>
<td>3</td>
<td>cyclo(PhEtSi-)(_n)</td>
<td>6</td>
</tr>
<tr>
<td>(Ph(_3)Ge)(_2)Si=Si(GePh(_3))(_2)</td>
<td>7</td>
<td>(Ph(_3)GeSiGePh(_3))(_n)</td>
<td>5</td>
</tr>
<tr>
<td>H(_2)Si=0</td>
<td>8</td>
<td>(-H(_2)Si-()(_n)</td>
<td>8,9</td>
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<tr>
<td>Me(_2)Si=CHSiMe(_3)</td>
<td>10</td>
<td>Me(<em>2)Si(</em>\uparrow\uparrow)CH(_2)SiMe(_2)</td>
<td>11,12</td>
</tr>
<tr>
<td>Ph(_2)Si=CH(_2)</td>
<td>13</td>
<td>(MePh(_2)Si)(_2)O</td>
<td>14</td>
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</table>

May seem like a reasonable explanation, in view of evidence supporting d orbital bonding in organosilicon compounds, it cannot explain why polymeric (Si-C)\(_n\) compounds (in which there is no (d-p)\(\uparrow\uparrow\) bonding) are found in contrast to the corresponding Si=C species.

Various other theories have been advanced to rationalize the general lack of stable (p-p)\(\uparrow\uparrow\) multiple bonds among Group IV (and second row) elements. It has been suggested by Pitzer, after considering bond energies and molecular...
geometry, that the absence of multiple bonds was due to
the greater interatomic repulsion by either the filled
inner shells or repulsion between these inner shells and
electrons in the bonding orbitals. In the formation, for
instance, of a multiple bond between two silicon atoms
(electronic configuration: 1s^2 2s^2 2p^6 3s^2 3p^2) the p_z orbitals
(after sp^2 hybridization) must approach sufficiently close
for overlap and effective achievement of this is sup-
posedly prevented by the repulsive effect of the large
inner shells.\(^{16}\) It has also been suggested \(^{17}\) that (p-p) overlap is less favorable because the np orbitals (n > 2)
are larger and more diffuse. This type of reasoning, however,
does not suffice to explain systems such as P=O (Ph_3PO),
S=O (SO_2) and C=S (CS_2) although Pitzer \(^{15}\) has pointed out
(in the first two cases) that the stability inherent in
these systems may be the consequence of the relative sizes
and shapes of the atomic orbitals involved. The results of
Mulliken's overlap integral calculations, using Slater
and SCF orbitals, were somewhat ambiguous since the integrals
for (p-p) overlap were higher for the second row atoms than
for the first. More recently, an equivalent orbital method
of calculation, using a semiempirical choice of parameters,
has indicated that the (p-p) overlap interaction for a Si-Si (p-p)
overlap bond is about half that for carbon. If this calculation
is fairly accurate then the energetics and kinetics of the
system may well favor the single-bonded over the double-bonded species.

Recently, considerable interest has been developing concerning the possible existence of \( \text{Si}(3p)\cdots\text{C}(2p) \) bonded species as reaction intermediates. Disilanes of the following type (Figure 4) were shown by Kumada to undergo cleavage with sodium ethoxide in ethanol to yield a silyl ether.

\[ \text{EtO} \rightarrow \begin{array}{c} \text{Me} \end{array} \begin{array}{c} \text{Si} \end{array} \begin{array}{c} \text{Me} \end{array} \begin{array}{c} \text{Si} \end{array} \begin{array}{c} \text{CH}_2 \end{array} \rightarrow \begin{array}{c} X \end{array} \]

\[ \begin{array}{c} \text{EtO} \rightarrow \begin{array}{c} \text{Me} \end{array} \begin{array}{c} \text{Si} \end{array} \begin{array}{c} \text{CH}_2 \end{array} \begin{array}{c} \text{R}^2 \end{array} \rightarrow \begin{array}{c} \text{Me} \end{array} \begin{array}{c} \text{Si} \end{array} \begin{array}{c} \equiv \text{CH}_2 \end{array} \leftrightarrow \begin{array}{c} \text{Me} \end{array} \begin{array}{c} \text{Si} \end{array} \begin{array}{c} \equiv \text{CH}_2 \end{array} \leftrightarrow \begin{array}{c} \text{Me} \end{array} \begin{array}{c} \text{Si} \end{array} \begin{array}{c} \equiv \text{CH}_2 \end{array} \end{array} \]

\[ \begin{array}{c} \text{EtOH} \end{array} \rightarrow \begin{array}{c} \text{Me} \end{array} \begin{array}{c} \text{Si} \equiv \text{CH}_2 \end{array} \begin{array}{c} \text{R}^2 \end{array} \]

\( R^1, R^2 = \text{Me and Ph} \)

\( X = \text{Cl, Br} \)

**Figure 4** -- Cleavage of 1-Halomethyl-1-phenyldisilanes by Sodium Ethoxide
The manner of addition of ethanol to the proposed intermediate is consistent with carbon being more electronegative (2.5) than silicon (1.8). The results also indicate that the cleavage reaction is favored over a competing intramolecular rearrangement when \( R^2 \) is phenyl, probably because of stabilization of the intermediate.

Reduction of triphenylchlorosilane with dimethyldeuteriosilylmethylmagnesium bromide gave two main products which were postulated as arising through a mechanism that involved the formation of a silicon-carbon double-bonded intermediate (Figure 5).

\[
\begin{align*}
\text{Br} & \quad \text{Mg} \\
\text{Cl} & \quad \text{CH}_2 \\
\text{Ph}_3\text{Si} & \quad \text{SiMe}_2 \\
& \quad \text{D} \\
\end{align*}
\rightarrow \quad \left[ \text{Me}_2\text{Si} = \text{CH}_2 \right] + \text{Ph}_3\text{SiD}
\]

\[\text{Me}_2\text{SiDCH}_2\text{MgBr} \]

\[\text{Me}_2\text{SiDCH}_2\text{SiMe}_2\text{CH}_3 \xleftarrow{H_2O} \text{Me}_2\text{SiDCH}_2\text{SiMe}_2\text{CH}_2\text{MgBr} \]

**Figure 5 -- Reduction of Triphenylchlorosilane**

Gas-phase thermolysis of 1,1-disubstituted-1-sila-cyclobutanes has afforded the corresponding substituted
1,3-disilacylclobutanes and ethylene. A kinetic study of the decomposition (400-460°) of 1,1-dimethyl-1-silacylclobutane indicated a reversible initial reaction to give an unstable intermediate containing a silicon-carbon double bond (Figure 6).

![Chemical Reaction Diagram]

**Figure 6 -- Pyrolysis of 1,1-Dimethyl-1-silacylclobutane**

The rate of decomposition of the monosilacylclobutane was decreased by ethylene and propene which is in agreement with the supposition that the initial step giving Me₂Si=CH₂ and ethylene is reversible. When the pyrolysis was carried out in the presence of water vapor or ammonia no formation of the disilacylclobutane occurred (the disilacylclobutane was
shown to be unreactive towards water and ammonia under the same conditions. The products isolated with water and ammonia lend credulity to the proposed double-bonded structure. Further evidence for the intermediacy of Me₂Si=CH₂ during the pyrolysis of both allyltrimethylsilane and 1,1-dimethyl-1-silacyclobutane was obtained by Bailey in a Diels-Alder trapping experiment with 2,3-dimethyl-1,3-butadiene (Figure 7).

\[
\begin{align*}
& \text{CH}_2=\text{CH}\text{-CH}_3(\text{H}) \\
& \text{Me}_2\text{Si} \xrightarrow{600^\circ} \left[\text{Me}_2\text{Si}=\text{CH}_2\right] \xleftarrow{} \text{Me}_2\text{Si} \\
& \text{Me}_2\text{Si} \quad \text{Me}_2\text{Si} \\
& \text{Me} \quad \text{Me} \\
& \text{Me} \quad \text{Me} \\
& \text{SiMe}_2
\end{align*}
\]

**Figure 7 -- Pyrolysis of Allyltrimethylsilane**

Mass spectral evidence for the occurrence of disila-28,29 cyclobutanes was obtained from the pyrolysis of trimethylsilane (Figure 8).
Figure 8 -- Pyrolysis of Trimethylsilane

A nonchain mechanism involving radical disproportionations was postulated to yield silicon-carbon double-bonded species which dimerized to the cyclic silanes (Figure 9).

Figure 9 -- Postulated Decomposition Path During Pyrolysis of Trimethylsilane
Pyrolysis of tetramethyldisilane yielded 1,1,3,3-tetramethyl-1,3-disilacyclobutane (Figure 10) as one of the major products as well as higher molecular weight products that appear to be built up primarily of Me₂Si=CH₂ units. From the results of kinetic calculations a minimum stabilization of 17 kcal/mol was estimated for the Si=C double bond.

\[
\begin{align*}
\text{Me}_4\text{Si} & \underset{537-707^\circ}{\longrightarrow} \text{Me}_3\text{Si}^* + \text{Me}^* \\
\text{Me}^* + \text{Me}_4\text{Si} & \longrightarrow \text{CH}_4 + \text{Me}_3\text{Si}-\text{CH}_2^* \\
\text{Me}_3\text{SiCH}_2^* & \longrightarrow \text{Me}^* + \text{Me}_2\text{Si}=\text{CH}_2 \\
2 \text{Me}_2\text{Si}=\text{CH}_2 & \longrightarrow \text{Me}_2\text{Si} - \text{SiMe}_2
\end{align*}
\]

**Figure 10 -- Pyrolysis of Tetramethyldisilane**

Walsh has recently analyzed the thermochemical and kinetic data from the pyrolysis of 1,1-dimethyl-1-sila-cyclobutane (Figure 6) and from trimethyldisilane (Figure 8). Calculations reported to rest on reasonable kinetic and thermochemical assumptions have yielded a \(\text{T}-\)bond energy, \(D_{\text{T}}\), of ca. 33±5 kcal/mol for methylene-dimethyldisilane (Me₂Si=CH₂) and methylenemethyldisilane (MeHSi=CH₂). This is very similar to an estimate of ca.
28 kcal/mol based on the dissociation energy of the diatomic molecule SiC. For comparative purposes, the \( ^1 \Pi \)-bond energy in the analogous isobutene (\( \text{Me}_2\text{C} = \text{CH}_2 \)) is ca. 60 kcal/mol. Preliminary calculations suggest that the \( ^1 \Pi \)-bond energy in silico-ketones (\( \text{R}_2\text{Si}=\text{O} \)) is also approximately 1/2 the value for ketones.

On the basis of the thermochemical calculations and the results of the various trapping experiments, it appears likely that the silicon-carbon double bond system is capable of existence but that due to the weakness of the \( ^1 \Pi \)-bond linkage (ca. 1/2 the values for olefins), the silico-olefins are very reactive in bimolecular reactions with themselves and with other appropriate molecules.

In assimilating the above results and trying to assess how one might design a synthetic pathway to prepare a monomeric Si=C system, two obvious obstacles would appear to need elimination. First, the high temperatures employed in the pyrolytic studies are obviously a serious deterrent to being able to isolate a monomer and control the reaction of such a reactive intermediate. The second obstacle involves the undesirability of various kinds of solvents, such as alcohols, which readily intercept the reactive species and render it, at least at first glance, unsuitable for polymerization purposes.
Over the past ten years, our laboratory has been engaged in an exhaustive study on the pyrolysis of hydrogen phthalate esters of tertiary alcohols. It has been found that such esters decompose at relatively low temperatures (100-150°) to give excellent yields of olefins (Figure 11).

![Chemical Structure](image)

**Figure 11 -- Pyrolysis of Tertiary Hydrogen Phthalates**

Isotope studies have shown that the reaction proceeds through a reversibly formed ion pair and that ortho carboxyl proton participation aids in the rate of decomposition of the esters.

A natural extrapolation would be to study the pyrolysis of tertiary silyl hydrogen phthalates (Figure 12). There is, however, a scarcity of such derivatives in the literature. Gilman recorded an unsuccessful attempt at the preparation of a silyl hydrogen phthalate upon reacting triphenylsilanol
Figure 12 -- Proposed Pyrolysis of Tertiary Silyl Hydrogen Phthalates

with phthalic anhydride. A patent reference reports the chloroplatinic acid catalyzed preparation of silyl derivatives of dicarboxylic acids, including phthalic acid, although the report indicates that a mixture of silyl hydrogen phthalate and disilyl ester was produced. It thus appeared desirable to devise a practical route to synthesize pure silyl hydrogen phthalates and then to ascertain if their pyrolytic decomposition would be a feasible route for the production of monomeric Si=C compounds.

A different type of pyrolytic pathway that might lead us to our objective involves the exceptional reactivity of \( \beta \)-haloalkylsilanes. A few representative compounds shown in Figure 13 decomposed upon attempted distillation to produce a silyl halide and an olefin.
\[
\begin{align*}
\text{Et}_3\text{SiCH}_2\text{CH}_2\text{Cl} & \quad 80^\circ \rightarrow \quad \text{Et}_3\text{SiCl} + \text{CH}_2=\text{CH}_2 \\
\text{Me}_3\text{SiCH}_2\text{CHBrCH}_3 & \quad 40^\circ \rightarrow \quad \text{Me}_3\text{SiBr} + \text{CH}_2=\text{CHCH}_3 \\
\text{Me}_3\text{SiCH}_2\text{CHClCH}_3 & \quad 90^\circ \rightarrow \quad \text{Me}_3\text{SiCl} + \text{CH}_2=\text{CHCH}_3
\end{align*}
\]

**Figure 13 -- Thermal Cleavage of \(_\beta\)-Haloalkylsilanes**

The elimination reactions have been postulated to proceed through a four-centred activated complex (Figure 14), promoted by overlap of the lone pair of electrons on the \(_\beta\)-heteroatom with the vacant d-orbitals of silicon.

\[
\text{R}_3\text{Si-CH}_2 \quad \Delta \quad \begin{bmatrix} \text{R}_3\text{Si--CH}_2 \\ \text{X-CH}_2 \end{bmatrix} \rightarrow \quad \text{R}_3\text{SiX} + \text{CH}_2=\text{CH}_2
\]

**Figure 14 -- Proposed Mechanism for \(_\beta\)-Haloalkylsilane Cleavage**

In addition to halogen substituents, the cleavage reaction also occurs when there is a \(_\beta\)-oxygen atom (Figure 15) capable of being transferred, apparently in a \textit{cis}-like manner, to silicon via a four-centred transition state.
Further examples (Figure 16) of this thermal 1,4 cleavage are provided by the decomposition of phosphonates, ketene silyl acetalts and N-silylated urethanes and carbamoyl chlorides.

It can readily be seen from the various examples that the migration of a $\text{Si} - \text{halo}$ or oxygenated substituent to the silicon atom, with concomitant elimination of a multiple-bonded fragment, could conceivably lead one into the $\text{Si}=\text{C}$ system if the necessary precursors were available. A second alternative to attaining our goal was therefore the synthesis of the following system (Figure 17) which incorporates the 1,4 juxtaposition of silicon and chlorine (or methoxy). An added advantage is that the trimethylsilyl fragment would be volatile (bp $57^\circ$ in both cases).
\[ \text{Me}_3\text{Si-CH}_2\text{PO(OMe)} \xrightarrow{207^\circ} \text{Me}_3\text{SiOMe} + \text{CH}_2=\text{PO(OMe)} \]

\[ \text{Ph}_2\text{C}=\text{C} \xrightarrow{180^\circ} \text{Me}_3\text{SiOMe} + \text{Ph}_2\text{C}=\text{C}=\text{O} \]

\[ \text{R}-\text{C} \xrightarrow{110^\circ} \text{Me}_3\text{SiOR} + \text{RN}=\text{C}=\text{O} \]

\[ \text{R}-\text{C} \xrightarrow{-20-0^\circ} \text{Me}_3\text{SiCl} + \text{RN}=\text{C}=\text{O} \]

**Figure 16 -- Thermal Decomposition of Various β-substituted Silanes**

\[ \text{R}_2\text{Si-CH}_2 \xrightarrow{\Delta} ? \xrightarrow{\text{X} \rightarrow \text{SiMe}_3} \text{R}_2\text{Si}=\text{CH}_2 + \text{Me}_3\text{SiX} \]

\( X = \text{Cl}, \text{OCH}_3 \)

**Figure 17 -- Proposed 1,4 Cleavage Route to the Si=C System**
A third possible route to the Si=С system involves classical methods such as dehydrohalogenation, dehydration and dehydrogenation. West was unable to dehydrogenate silacyclohexane over a platinum or palladium catalyst at temperatures up to 500°. F. S. Kipping tried to dehydrate tribenzylsilanol and to dehydrochlorinate tribenzylchlorosilane (Figure 18) with no reported success.

\[
\begin{align*}
(\text{PhCH}_2)_2\text{Si}-\text{CH}_2\text{Ph} \quad & \xrightarrow{\text{P}_2\text{O}_5} \quad (\text{PhCH}_2)_2\text{Si}-\text{CH}_2\text{Ph} \\
\text{OH} \quad & \quad \text{or ZnCl}_2 \\
& \quad \text{or (CH}_3\text{CO)}_2\text{O} \\
(\text{PhCH}_2)_2\text{Si}-\text{CH}_2\text{Ph} \quad & \xrightarrow{\text{Quinoline}} \quad (\text{PhCH}_2)_2\text{Si}-\text{CH}_2\text{Ph} \\
\text{Cl} \quad & \quad \text{or PhNMe}_2
\end{align*}
\]

Figure 18 — Kipping's Attempted Preparation of Si=С

The dehydration route would appear the least promising since silanols, in general, condense \((2\text{R}_3\text{SiOH} \rightarrow \text{R}_3\text{SiOSiR}_3 + \text{H}_2\text{O})\) readily to the corresponding disiloxane. In the case of the dehydrogenation route, it was decided to explore the possibility of using high potential quinones such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). It was also
proposed to try and improve the dehydrohalogenation route by employing stronger bases that might allow the proposed elimination of HX to occur at low temperatures, perhaps even below 0°C.

It was further proposed to employ in the various schemes, if necessary, appropriately substituted starting materials that would yield a monomeric Si=C compound which may be stable by a combination of steric and resonance effects. A logical starting point would be the utilization of strategically placed phenyl groups which could provide both advantages.
RESULTS AND DISCUSSION

Synthesis of a Silyl Hydrogen Phthalate

Silyl esters have been prepared by a variety of routes. One of the first pathways (Figure 19) envisioned for the synthesis of a silyl hydrogen phthalate involved the reaction of a silyl chloride, such as diphenylmethylchlorosilane (2), with potassium hydrogen phthalate (1).

\[
\begin{align*}
\text{CO}_2\text{K} & + \text{Ph}_2\text{MeSiCl} & \xrightarrow{\text{C}_6\text{H}_6} & \text{CO}_2\text{SiMePh}_2 \text{H} & + \text{CO}_2\text{SiMePh}_2 \\
1 & & & 2 & 3 \\
& & & + \text{Ph}_2\text{MeSiOH} & 4 \\
& & & & 5
\end{align*}
\]

*Figure 19 -- Reaction of Potassium Hydrogen Phthalate with Diphenylmethylchlorosilane*

The reaction afforded a mixture of three products, subsequently identified as the silyl hydrogen phthalate 2 (17%), the disilyl phthalate 4 (75%), and the silanol 5 (8%). Specified yields were determined by nmr integration.

Diphenylmethylsilyl hydrogen phthalate (3) and its corresponding disilyl phthalate ester (4) were tentatively
identified on the basis of spectral results. The infrared spectrum of the mixture revealed the presence of an ester group (5.85, 7.67 \( \mu \)) and little, if any, of the typical broad O-H stretching (3.3-4.0 \( \mu \)) normally associated with a carboxylic acid. Nmr inspection indicated the absence of an acid proton but did reveal two CH\(_3\)Si singlets at \( \sim 8.96 \) and 9.08 which were assigned to 2 and 4, respectively. Comparison of the corresponding ir and nmr data of other routes (which follow subsequently) aimed at obtaining 2 as the sole or major product revealed similar mixtures which showed a slight broadening in the acid region (3.3-4.0 \( \mu \)) of the ir as the CH\(_3\)Si singlet (\( \sim 9.08 \)) ascribed to 4 decreased at the expense of the singlet (\( \sim 8.96 \)) due to the silyl hydrogen phthalate (2). The appearance of the acid proton of 2 could likewise be observed by nmr as 2 became a more significant amount of the mixture. The presence of diphenylmethylsilanol 5 was deduced on the basis of spectral comparison with authentic material.

Further evidence to support the postulated structures comes from the slow hydrolysis of the two esters (2, 4) which can be readily followed by nmr. The decrease in the singlets at \( \sim 8.96 \) and 9.08 and the concomitant increase (\( \sim 9.28 \)) of the silanol 5, and the presence of phthalic acid, is in accord with the well-known ease of hydrolysis of silyl esters. The fact that the diester 4 predominates, even
with an excess of 1, may be the consequence of a faster homogeneous rate of reaction of the silyl chloride 2 with the acid group of 3 than with more unreacted potassium hydrogen phthalate which is relatively insoluble in the reaction medium.

Another possible approach, which would still incorporate the attractiveness of being able to remove excess insoluble starting material and inorganic salt by-product, would be the similar reaction sequence utilizing the silver salt of 1. Since silver salts of acids are generally more reactive than alkali metal salts, it appeared to be a possible way to circumvent the problem encountered with 1. Although the preparation and use of silver hydrogen phthalate does not appear to be reported in the literature, we attempted to prepare the salt according to a general procedure for obtaining silver salts of organic acids. Reaction of potassium hydrogen phthalate with silver nitrate yielded, in all cases, a water insoluble salt. Addition of 2 to this silver salt gave a mixture of four products: 3 (22%), 4 (45%), 5 (20%), and 6 (13%). The last product 6 was identified as sym-tetra phenyldimethyldisiloxane (Ph₂MeSiOSiMePh₂) by comparison with a synthetic sample. This material presumably arises from the well-known ease of condensation of silanols to siloxanes.
The reaction of the silver salt with methyl iodide afforded dimethyl phthalate rather than the expected methyl hydrogen phthalate.

Hydrolysis of a weighed quantity of what was presumed to be monosilver salt with hydrochloric acid and then, addition of sodium hydroxide to solubilize the phthalic acid, afforded a quantity of silver chloride consistent with the salt being mainly the disilver salt of phthalic acid (Figure 20).

\[
\text{CO}_2\text{Ag} + \text{HCl} \xrightarrow{\text{H}_2\text{O}} \text{CO}_2\text{H} + \text{AgCl} \downarrow \\
\text{NaOH}/\text{H}_2\text{O}
\]

**Figure 20 -- Hydrolysis of Silver Phthalate**

For the moment, the isolation of what appears to be mainly a disilver salt from reaction of equimolar quantities of silver nitrate with potassium hydrogen phthalate lacks a satisfactory explanation. It is possible that silver hydrogen phthalate may be the first intermediate formed (Figure 21).
Although silver salts of acids are generally water insoluble, it appears probable that this particular salt has sufficient solubility to allow further selective reaction with silver nitrate.

Examination of other possible homogeneous reactions which yield silyl esters led us to consider the pyridine catalyzed reaction of an acid with a silyl chloride (Figure 22).

$$\text{RCO}_2\text{H} + R_3\text{SiCl} \xrightarrow{\text{C}_5\text{H}_5\text{N}} \text{RCO}_2\text{SiR}_3 + \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$$
Employment of this type of reaction using phthalic acid and silyl chloride afforded a mixture of products, even with an excess of phthalic acid, in which the desired monosilyl hydrogen phthalate ester was still the minor component: 2 (19%), 4 (32%), and 6 (49%).

The transition metal (Group VIII) catalyzed reaction of an organosilicon hydride with an organic acid has been developed as a convenient procedure for the synthesis of silyl esters (Figure 23).

$$\text{RCO}_2\text{H} + \text{R}_3\text{SiH} \xrightarrow{\text{M}} \text{RCO}_2\text{SiR}_3 + \text{H}_2$$

**Figure 23 -- Transition Metal Catalyzed Substitution Reaction of a Silyl Hydride**

Use of this type of reaction with phthalic acid and diphenylmethylsilane (2) in the presence of 10% palladium on carbon (Figure 24) afforded a familiar mixture: 2 (22%), 4 (34%), 5 (33%), and 6 (11%).

$$\text{CO}_2\text{H} + \text{Ph}_2\text{MeSiH} \xrightarrow{\text{Pd-C}} 2 + 4 + 5 + 6 + \text{H}_2$$

**Figure 24 -- Palladium Catalyzed Reaction Between Phthalic Acid and Diphenylmethylsilane**
In assessing the relative merits of other possible reaction schemes which could lead to a silyl hydrogen phthalate, there arose the possibility that this particular species might thermally decompose to give a silyl alcohol rather than the desired silico-olefin. Although tertiary hydrogen phthalates are known to decompose to olefins, secondary alkyl hydrogen phthalates have been shown to yield olefin-alcohol mixtures. Optically active 2-octyl phthalate, for example, decomposes with retention of configuration to give 2-octanol as the major product (Figure 25).

\[
\begin{align*}
\text{COC}^*_{\text{B}_{17}} \quad \xrightarrow{\Delta} \quad \text{O} & + \quad \text{HOC}^*_{\text{B}_{17}} \\
\text{C-O-H} & 
\end{align*}
\]

**Figure 25 -- Pyrolysis of Optically Active 2-Octyl Hydrogen Phthalate**

The likelihood of this reaction path being followed in the silyl hydrogen phthalate system can be envisioned if one considers the results supporting the intermediacy of ion pairs in the pyrolytic decomposition of tertiary hydrogen phthalates coupled with the fact that condensed phase tricoordinate siliconium ions analogous to carbonium ions
are not well established. The possibility, of course, still exists that a silyl hydrogen phthalate might thermally decompose to a silyl olefin without the intermediacy of an ion pair. The obvious way to circumvent the possible carboxylic acid induced displacement reaction involved replacement of the carboxyl proton by a methyl group (Figure 26).

![Chemical Structure]

**Figure 26 -- General Structure of Desired Triorganosilyl Methyl Phthalate**

Further examination of the possible nature of the transition state, if silyl olefin formation were to be realized, indicated that a slight amount of positive charge might develop at the silicon center through elongation of the silicon-oxygen linkage (a). It therefore appeared advantageous to study the effect of both phenyl and methyl substitution at the silicon atom.
Synthesis and Pyrolysis of Monosilyl Phthalate Esters

Diphenylmethyllumethyl phthalate (10) and trimethylsilyl methyl phthalate (11) were prepared from potassium methyl phthalate (8) and the appropriate silyl chloride. Deprotonation of methyl hydrogen phthalate by potassium 2,6-di-t-butylphenoxide \(^{64}\) provided a convenient procedure for preparation of anhydrous 8 (Figure 27).

\[
\text{CO}_2\text{CH}_3 + \text{Ph}_2\text{CO}_2\text{H} \xrightarrow{\text{THF}} \text{CO}_2\text{CH}_3 + \text{Ph}_2\text{CO}_2\text{K}
\]

\[
8 + \text{Ph}_2\text{CH}_3\text{SiCl} \xrightarrow{\text{Et}_2\text{O}} \text{CO}_2\text{CH}_3 + \text{Ph}_2\text{CO}_2\text{SiPh}_2
\]

\[
8 + (\text{CH}_3)_3\text{SiCl} \xrightarrow{\text{Et}_2\text{O}} \text{CO}_2\text{CH}_3 + (\text{CH}_3)_2\text{Si(CH}_3)_2
\]

Figure 27 -- Synthesis of Diphenylmethyllumethyl and Trimethylsilyl Methyl Phthalate
The silyl esters 10 and 11, as well as subsequently prepared silyl esters, displayed definitive spectral properties as outlined in the Experimental Section and all were hydrolyzed by moisture to the expected alkyl hydrogen phthalate and the appropriate silanol. The silanol was invariably contaminated with the corresponding disiloxane, consistent with the known ease of condensation of triorganosilanols. All silyl esters synthesized also gave satisfactory elemental analyses.

Thermal decomposition of 10 could be slowly effected at 250° to give phthalic anhydride (12) and diphenylmethylmethoxysilane (13) as the major products (Figure 28).

![Chemical Diagram]

Figure 28 -- Pyrolysis of 10 and 11
A more expedient route to the same products could be
realized simply by pyrolysis with a Bunsen flame. Silyl
ester 11 decomposed in a similar manner over the temperature
range 400-470° to give 12 and trimethylmethoxysilane (14).
No silico-olefin nor products which could be construed as
arising from a silico-olefin intermediate were observed in
any of the attempted pyrolyses.

The identification of the silyl ethers 13 and 14 was
based on comparison of ir and nmr spectral data as well as
gas chromatographic retention time with synthetic samples.
All subsequent silyl ester pyrolyses were characterized in
a similar manner as detailed in the Experimental Section.

Isolation of silyl ethers from the pyrolysis of 10
and 11 contrasts with the pyrolysis of methyl alkyl phthalates
which give the appropriate alkene, methanol, and phthalic
anhydride. The reaction is postulated to initially involve
the formation of alkene and methyl hydrogen phthalate,
followed by decomposition of the acid ester to methanol and
phthalic anhydride.

Trimethyldisilyl 2-octyl phthalate (16) was next prepared
(Figure 29) since it incorporates the bulkier C8 fragment
which could conceivably hinder the silyl ether formation and
perhaps, favor silyl olefin formation. The pyrolysis of 16
(400-470°), however, still yielded phthalic anhydride and
silyl ether 17 as the major products (Figure 29).
Figure 29 -- Synthesis and Pyrolysis of Trimethylsilyl 2-Octyl Phthalate

In order to provide some idea of the stereochemical aspects of this transformation, the optically active trimethylsilyl 2-octyl phthalate (16a) was prepared and pyrolyzed (Figure 30).

Figure 30 -- Preparation and Pyrolysis of Optically Active 16a
(R)-trimethylsilyl 2-octyl phthalate (16a) afforded the optically active silyl ether 17a ([\alpha]^{24}_{D} -17.4^\circ). Assignment of the R configuration to (-)-17a was provided by preparation of (R)-(−)-17a ([\alpha]^{24}_{D} -16.1^\circ) from (R)-(−)-2-octanol (Figure 31).

\[
\begin{align*}
\text{OH} & \quad \text{(R)-(−)} \\
\text{CH}_3\text{CH(CH}_2_5\text{CH}_3 + (\text{CH}_3)_3\text{SiCl}} & \xrightarrow{\text{C}_6\text{H}_5\text{N}} \quad \text{OSi(CH}_3)_3
\\
\text{Ether} & \quad \text{CH}_3\text{CH(CH}_2_5\text{CH}_3}
\end{align*}
\]

\[\text{Figure 31 -- Preparation of (R)-(−)-17a}\]

The pyrolytic transformation thus occurs in a stereospecific fashion with retention of configuration at the optically active carbon centre. Further studies to determine the stereochemistry at the silicon centre and determination of which oxygen is realized in the silyl ether have not been pursued.

Consideration of the $^{18}_0$ results from the pyrolysis of diphenylketene methyl trimethylsilyl acetal (Figure 16) and the relative ease of displacement of -OCOR groups from acyloxysilanes have led us to favor (as illustrated for the pyrolysis of 16a) the following pathway for the transformation of our silyl alkyl phthalates to phthalic anhydride and the corresponding silyl ethers (Figure 32).
Figure 32 -- Postulated Thermal Decomposition Pathway of Silyl Alkyl Phthalates

Benzylidiphenylsilyl methyl phthalate (12) was synthesized in order to ascertain if the more reactive benzyl carbon-hydrogen linkage might enhance the possibility of silyl olefin formation (Figure 33).

\[
\text{PhCH}_2\text{MgCl} + \text{Ph}_2\text{SiCl}_2 \xrightarrow{\text{Et}_2\text{O}} \text{Ph}_2\text{SiC(CH}_3\text{)}_2\text{Ph}
\]

(18)

\[
\text{CO}_2\text{K} + 18 \xrightarrow{\text{Et}_2\text{O}} \text{Ph}(\text{CO}_2\text{C(OEt)}_2\text{SiPh}_2\text{)}
\]

(19)
Figure 33 -- Synthesis and Pyrolysis of Benzyl Diphenyl-Silyl Methyl Phthalate

Thermolysis (400°) of 12, however, proceeded in an analogous fashion to afford phthalic anhydride (12) and silyl ether 20.

Consideration of what effect a tertiary alkyl group might have on hindering the coupling reaction prompted us to prepare diphenylmethyldimethyl t-butyl phthalate (22) and trimethylsilyl t-butyl phthalate (23) (Figure 34).
\[21 + 2 \xrightarrow{\text{Et}_2\text{O}} \begin{align*}
&\text{CO}_2\text{Si}(\text{CH}_3)_3 \\
&\text{CO}_2\text{CMe}_3 \\
\end{align*}
\]

**Figure 34 -- Synthesis of Diphenylmethylsilyl and Trimethylsilyl t-Butyl Phthalate**

Pyrolysis (Bunsen flame) of 22 afforded a mixture of diphenylmethyldimethylsiline (5), sym-tetraphenyldimethyldisiloxane (6) and 12. The silyl ester 23 yielded hexamethyldisiloxane (24) and 12 (Figure 35).

\[\begin{align*}
\Delta \rightarrow &\ 12 + \text{Ph}_2\text{SiOH} + (\text{Ph}_2\text{Si}^-)_2\text{O} \\
&\ 5 \ 6 \\
+ &\left[\text{CH}_2=\text{C}(\text{CH}_3)_2\right] \\
\end{align*}\]

**Figure 35 -- Pyrolysis of Diphenylmethylsilyl and Trimethylsilyl t-Butyl Phthalate**
The mechanism of formation of the decomposition products can be readily rationalized as occurring through the intermediacy of a silyl hydrogen phthalate (Figure 36) that apparently decomposes exclusively by silyl alcohol formation.

\[
\begin{align*}
\text{COSiR}_3 & \xrightarrow{\Delta} \text{C-OSiR}_3 \\
\text{C}_2\text{O-CH}_2(\text{CH}_3) & \xrightarrow{} \text{C-OH} \\
\text{(R}_3\text{Si-)}_2 & \xrightarrow{} \text{R}_3\text{SiOH} + 12
\end{align*}
\]

**Figure 36 -- Proposed Decomposition of Silyl t-Butyl Phthalates**

From the above, it would appear that in situ preparations of silyl hydrogen phthalates may well be realized since t-butyl esters are known to decompose readily at 210°, well below our pyrolysis conditions, to isobutylene and the corresponding carboxylic acid.
Attempted Dehydrohalogenation of Silyl Chlorides as a Potential Route to Silico-Olefins

Consideration of other possible routes that might provide us entry into the Si=C system led us to attempt the dehydrohalogenation of the readily available diphenylmethylchlorosilane (2). Reaction of 2 with n-butyllithium at -78°C and then, addition of methyl iodide to quench any reactive lithium species afforded a crude mixture of three major products (83, 10 and 5%) as indicated by gc analysis. Diphenyldimethylsilane (25), identified by spectral comparison with authentic material, was isolated as the major product by preparative gc (Figure 37).

\[
\text{Ph}_2\text{Si-CH}_3 + \text{n-BuLi } \xrightarrow{\text{Et}_2\text{O}, -78^\circ} \left[ \text{Ph}_2\text{Si-CH}_3 + \text{Li} \right] \xrightarrow{\text{CH}_3\text{I}} \text{Ph}_2\text{Si-CH}_3
\]

Figure 37 -- Reaction of Diphenylmethylchlorosilane with n-Butyllithium

Although the combination of organolithium reagents and silyl chlorides normally yield coupling products and, in some instances, metatation of a silyl methyl group, it seems likely that a metal-halogen interconversion route has been followed in which the intermediate diphenylmethylsilyl-
lithium is trapped by the added methyl iodide. Assignment of a structure to the other two products was not possible although infrared analysis indicated one of the products (10%) to be a siloxane species (see Experimental Section).

Benzhydryldiphenylchlorosilane (26) was synthesized (Figure 38) since it incorporates the more acidic $\alpha$-benzhydryl proton as well as providing the desired Si=C species with the possible advantages of resonance stabilization and steric hindrance to further reaction.

$$\begin{align*}
\text{Ph}_2\text{CH}_2 + \text{n-BuLi} & \xrightarrow{\text{Et}_2\text{O}} \text{Ph}_2\text{CHLi} \\
\text{Ph}_2\text{CHLi} + \text{Ph}_2\text{SiCl}_2 & \xrightarrow{\text{Et}_2\text{O}} \text{Ph}_2\text{Si-CHPh}_2 \\
& \quad \quad \text{Cl} \\
\end{align*}$$

Figure 38 -- Synthesis of Benzhydryldiphenylchlorosilane

Attempted dehydrochlorination of 26 with triethylamine and with the more reactive 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) led to mixtures of unreacted starting material, corresponding silanol and the disiloxane derived from 26. The product mixture was tentatively identified by ir and nmr analysis and the Si-O species seem most reasonably rationalized as arising from amine promoted hydrolysis of
the silyl chloride by traces of moisture which were not rigorously eliminated from the reaction environment. Reaction of silyl chloride 26 with n-butyllithium led to a complex mixture of at least seven products which were not further characterized.

Consideration of the possible problems that might be encountered in trying to initially assess the presence, by ir and nmr, of a species such as Ph₂Si=CH₂ prompted us to continue our investigations with a slightly different system.

Benzylidiphenylchlorosilane (18), obtained from the reaction of benzylmagnesium chloride with diphenylidichlorosilane (Figure 33), was considered an attractive silyl chloride for dehydrochlorination studies. The silyl olefin derivable from this compound, Ph₂Si=CHPh, contains in addition to the desired phenyl groups, an olefinic CH group which should be easy to distinguish by ir and nmr analysis. Reaction of the silyl chloride 18 with t-butyllithium, a strong hindered base, afforded a deep orange solution (upon mixing at -78°C) which persisted for over 4 hr after warming to room temperature. Ir and nmr inspection of the residue obtained after removal of insoluble salts and volatile reaction solvents indicated the absence of 18 and the presence of a complex mixture. Infrared analysis indicated silanol (2.73 and 12.2 μ) and siloxane (9.1-10 μ)
material as the major identifiable species.

Metalation of the benzyl group by t-butyllithium appears reasonable in view of the deeply colored solution obtained. Highly colored solutions are well-known for carbanions which are stabilized by aromatic resonance. Traces of moisture probably slowly reprotoxate the metalated centre and base catalyzed hydrolysis of the silyl chloride could then occur (Figure 39).

\[
\begin{align*}
\text{Ph}_2\text{Si-CH}_2\text{Ph} + \text{t-BuLi} & \xrightarrow{\text{THF}} \left[ \text{Ph}_2\text{Si-CPh} \right]_1^1 \\
\text{Cl} & \quad \text{Cl Li} \\
\text{18} & \quad \text{H}_2\text{O} \\
\text{Ph}_2\text{Si-CH}_2\text{Ph} & \xleftarrow{\text{LiOH}} \text{Ph}_2\text{Si-CH}_2\text{Ph} \\
\text{OH} & \quad \text{H}_2\text{O} \\
\text{Cl} &
\end{align*}
\]

**Figure 39** -- Possible Reaction of Benzylidiphenylchlorosilane with t-Butyllithium

The spectral results, however, indicate that the reaction is more complex than that depicted in Figure 39. This may well be due to an unknown amount of the silylorganolithium intermediate reacting further with another silylorganolithium intermediate (and further repetition of this) to yield higher homologues which could likewise decompose to silanol and siloxane material.
Attempted Synthesis of Diphenylchloromethylidiphenylsilane

The possibility of utilizing diphenylchloromethyl-diphenylsilane (28) as a silyl olefin precursor was not further investigated after initial attempts at its synthesis met with little success. Diphenylchloromethyllithium, which has been reported to react readily at low temperatures (ca. -100°C) with carbon dioxide presumably via a nucleophilic attack by the chloro carbanion was expected to couple readily with diphenylchlorosilane (27) to afford 28 (Figure 40).

\[
\begin{align*}
\text{Ph}_2\text{CCL}_2 + \text{n-BuLi} & \xrightarrow{\text{THF, -100°C}} \text{Ph}_2\text{CCLi} \\
\text{Ph}_2\text{CCLi} + \text{Ph}_2\text{SiHCl} & \xrightarrow{\text{THF, -100°C}} \text{Ph}_2\text{Si-CHPh}_2 + \text{Ph}_2\text{C}=\text{CPh}_2 \\
& \quad \text{Cl} \\
\text{Ph}_2\text{Si-CHPh}_2 + \text{Cl} & \quad \text{H Cl}
\end{align*}
\]

Figure 40 -- Attempted Synthesis of Diphenylchloromethylidiphenylsilane
The two products which were isolated and characterized were silyl chloride 26 (46%) and tetraphenylethylene (8%). A small amount (7%) of a third product was isolated and characterized by IR as a SiH (4.65 and 11.95 μ) compound but the data were insufficient to warrant assignment of structure 26.

The formation of tetraphenylethylene has been postulated as arising from decomposition of the α-chloroalkyl-lithium above -65° to lithium chloride and diphenylcarbene which can then dimerize to tetraphenylethylene. Kobrich, however, has pointed out that dimerizing α-elimination may be considered as arising from a reaction in which one carbenoid molecule acts as a nucleophile and the other as an electrophile, followed by β-elimination of lithium chloride. The formation of silyl chloride 26 appears most readily explained as occurring through the intermediacy of a carbenoid species, electrophilic in character, which inserts into the Si-H bond.

**Attempted Pyrolytic Elimination of HCl from Benzhydryl-diphenylchlorosilane**

Vigorous heating of silyl chloride 26 with a Bunsen flame for 5 min resulted in no detectable decomposition. This result contrasts with the easy dehydrohalogenation of compounds such as EtMeCBr(CH2Ph), which cannot be distilled even under low pressure.
Attempted Dehydrogenation of Benzylidiphenyilsilane

Benzyldiphenyilsilane (29) was readily obtained from lithium aluminum hydride reduction of benzyldiphenyl-chlorosilane (18). Attempted dehydrogenation of 29 using the high potential quinone, 2,3-dichloro-5,6-dicyano-quinone (DDQ), led only to recovery of 29 (Figure 41).

\[
\text{Ph}_2\text{Si-CH}_2\text{Ph} + \text{LiAlH}_4 \xrightarrow{\text{Et}_2\text{O}} \text{Ph}_2\text{Si-CH}_2\text{Ph} \\
\text{Cl} \quad \text{H} \quad 8 \quad 29
\]

\[
\text{Ph}_2\text{Si-CH}_2\text{Ph} + \text{DDQ} \xrightarrow{\text{p-dioxane} \quad 105^\circ} 29 \\
\text{H} \quad 29
\]

**Figure 41 -- Preparation and Attempted Dehydrogenation of Benzyldiphenyilsilane**

Synthesis and Pyrolysis of \(\alpha\)-Trimethylsilylorganosilanes

It has been reported that various trimethylsilyl derivatives can be metalated in the methyl group by the strong hindered base, t-butyllithium. \(^{69}\) Trimethylchlorosilane, for example, can be metalated and then trapped by excess chlorosilane (Figure 42).
Me₃SiCl + t-BuLi $\xrightarrow{\text{THF}, -78^\circ}$ [LiCH₂SiMe₂Cl] $\xrightarrow{}$ Me₃SiCH₂SiMe₂Cl

*Figure 42 -- Reaction of t-Butyllithium with Trimethylchlorosilane*

From our results on the probable metalation of benzyl-diphenylchlorosilane (18) with t-butyllithium, it appeared feasible to selectively lithiate the benzylsilane 18 in the presence of trimethylchlorosilane (2) and then have the diphenylchlorosilylbenzyl lithium trapped by the chlorosilane 2.

Addition of t-butyllithium to a mixture of silyl chlorides 2 and 18 proved to be an expedient procedure for the synthesis of (α-trimethylsilylbenzyl)diphenylchlorosilane (30). An analogous reaction of t-butyllithium with a mixture of 2 and benzylidiphenylmethoxysilane (20) (obtained from methanalysis of 18) conveniently afforded (α-trimethylsilyl)diphenylmethoxysilane (31) (Figure 43).

Ph₂Si-CH₂Ph $\xrightarrow{\text{t-BuLi/THF}, -78^\circ}$ [Ph₂Si-CHPh] $\xrightarrow{2}$ Ph₂Si-CHPh

18 30
Figure 43 -- Selective Lithiation by t-Butyllithium and in situ Trapping by Trimethylchlorosilane

Both of these compounds now provide us with the desired 1,4-juxtaposition of silicon and a heteroatom substituent (Figure 17).

Attempted pyrolytic elimination of trimethylchlorosilane from (α-trimethylsilyl)diphenylchlorosilane (30) at temperatures up to 470°C resulted only in recovery of starting material. The pyrolysis of (α-trimethylsilyl)diphenylmethoxysilane (31) in the temperature range 300-470°C did result in complete decomposition of 31 and furnished trimethylmethoxysilane (14) in a 50% yield (Figure 44).

Figure 44 -- Pyrolytic Decomposition of (α-Trimethylsilyl)diphenylmethoxysilane
Go, ir and nmr analysis of the brown glue-like pot residue indicated a complex mixture which is very likely polymeric and consisting, to a great extent, of siloxane material.

The nature of the route leading to the trimethyl-methoxysilane \((\text{14})\) can only be speculated but, if it does involve the formation of \(\text{Ph}_2\text{Si} = \text{CHPh}\), the high temperatures employed probably favor, to a large extent, intermolecular processes leading to a complex high molecular weight residue.

The reason for the stability of silyl chloride \(\text{30}\), when under the same conditions silyl ether \(\text{31}\) completely decomposes, remains rather obscure at this point. Consideration of the bond energies listed in Table II enables a crude calculation of the energetics involved in the desired reaction leading to extrusion of silyl chloride \(\text{2}\) from \(\text{30}\) (and silyl ether \(\text{14}\) from \(\text{31}\)) and formation of the silyl olefin, \(\text{Ph}_2\text{Si} = \text{CHPh}\). The crude calculation indicates that the desired transformation would be ca. 43 kcal/mol endothermic in both cases.
### TABLE II

**Bond Energies (kcal/mol)**

<table>
<thead>
<tr>
<th>Silicon</th>
<th></th>
<th>Carbon</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Si</td>
<td>51</td>
<td>C-C</td>
<td>83</td>
</tr>
<tr>
<td>Si-C</td>
<td>76</td>
<td>C-Si</td>
<td>76</td>
</tr>
<tr>
<td>Si-O</td>
<td>106</td>
<td>C-O</td>
<td>86</td>
</tr>
<tr>
<td>Si-H</td>
<td>76</td>
<td>C-H</td>
<td>99</td>
</tr>
<tr>
<td>Si-Cl</td>
<td>91</td>
<td>C-Cl</td>
<td>81</td>
</tr>
<tr>
<td>Si-F</td>
<td>135</td>
<td>C-F</td>
<td>111</td>
</tr>
<tr>
<td>Si-I</td>
<td>56</td>
<td>C-I</td>
<td>51</td>
</tr>
</tbody>
</table>

Si=C \( \overline{\text{bond energy}}: 33 \pm 5 \)
SUMMARY

All attempts to generate a Si=C system by pyrolytic routes have led either to a different pathway being followed (Figures 32 and 36) or, in the case of 31, decomposition to a high molecular weight residue. The nature of the temperature employed (>300°) for the decomposition of 31 also mitigates against the possible isolation or use of a Si=C species, if indeed this were formed during the thermolysis of 31.

Attempts to prepare a stable Si=C system by dehydrohalogenation and dehydrogenation techniques were also unfruitful. A convenient procedure for the synthesis of α-trimethylsilylorganosilanes, by deprotonation of activated organosilanes and in situ silylation by trimethylchlorosilane, did arise out of this research investigation.
SUGGESTIONS FOR FURTHER RESEARCH

Consideration of the crude calculation of the energetics (ca. 43 kcal/mol endothermic) for the transformation of (α-trimethylsilyl)diphenylchlorosilane (30) and (α-trimethylsilyl)diphenylmethoxysilane (31) to Ph₂Si=CHPh and the corresponding trimethylsilyl fragment indicates the obvious desirability of utilizing a system which would be less endothermic. This could well lead to a lower rearrangement temperature and aid us in either isolating a Si=С species or perhaps being able to control and utilize this species for synthetic purposes.

Synthesis of the following system (Figure 45) is proposed since a crude calculation, using the bond energies found in Table II, indicates that the desired transformation would be ca. 8 kcal/mol endothermic for X = Cl and ca. 2 kcal/mol exothermic for X = OCH₃.

\[
\begin{align*}
\text{R}_2\text{Si-CH}_2' \quad \Delta \quad \text{R}_2\text{Si=CH}_2' + \text{Me}_3\text{SiX} \\
\text{Me}_3\text{Si} \quad X
\end{align*}
\]

\[
X = \text{Cl, OCH}_3
\]

**Figure 45** -- Further Proposed Route for the Generation of a Silico-Olefin

48
EXPERIMENTAL

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on Beckman IR-10 and IR-12 spectrometers in chloroform or deuterochloroform solutions unless otherwise noted. Nuclear magnetic resonance spectra were obtained with a Jeolco C-60 HL spectrometer in deuterochloroform with methylene chloride as an internal standard (\textit{\(\tau\)} 4.70) unless otherwise specified. Optical rotation measurements were determined with a Rudolph Model 80 polarimeter equipped with a sodium lamp (\(\lambda\) 589 nm) using 2 dm polarimeter tubes. Gas chromatography (go) was performed on Hewlett Packard 720 and 5750 instruments. Columns utilized were as follows: 6 ft X 1/4 in. 10% SE 30 on 60-80 Chromosorb W, 8 ft X 1/4 in. 20% SE 30 on 60-80 Chromosorb W, 8 ft X 3/8 in. 10% SE 30 on 60-80 Chromosorb W and 6 ft X 1/4 in. 10% Dextil 300 on 60-80 Chromosorb W. All nonaqueous reactions were run in dried apparatus under an atmosphere of nitrogen and the silyl chlorides utilized were distilled prior to use. All ethereal solvents were purified by distillation from lithium aluminum hydride and pyridine was distilled from calcium hydride. Anhydrous sodium sulfate was used for all drying operations unless otherwise noted. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. and A. B. Gygli Microanalyses Laboratory, Toronto, Ontario.
Characterization of the Mixtures Obtained in the Attempted Synthesis of Diphenylmethyilsilyl Hydrogen Phthalate. -- All attempted procedures to produce diphenylmethyilsilyl hydrogen phthalate led to a similar mixture of three or four components in varying amounts. Specified yields were determined by nmr integration. Compounds 5 and 6 of the mixture were identified by comparison with infrared and nmr spectra of synthetic material. The infrared spectra of the various mixtures all revealed, in addition to the absorptions ascribed to 5 and/or 6, an ester species (5.35 and 7.67 μ) and a general lack of the typical broad O-H stretching band of a carboxylic acid in the 3.3 to 4.0 μ region. The nmr revealed an aromatic multiplet (τ 2.5) and four CH3-Si singlets (when both 5 and 6 were present). The signals at τ 9.28 and 9.35 were identified as those of 5 and 6, respectively, and those at 8.96 and 9.08 were tentatively identified as those of 2 and 4, respectively. Comparison of the corresponding ir and nmr spectra revealed that as the τ 9.08 singlet (4) decreased and the 8.96 (2) singlet increased there was a concomitant slight broadening in the 3.3 - 4.0 μ carboxylic acid region of the ir. In the cases where 4 was calculated to be less than twice the amount of 2, there was observed an average nmr absorption position that appears consistent with the rapid chemical exchange
of the hydroxyl and carboxyl protons of 2 and 5. Exposure of the various mixtures to moisture resulted in decomposition giving phthalic acid and a mixture of 4 and 5.

Reaction of Potassium Hydrogen Phthalate (1) with Diphenylmethylichlorosilane (2). -- To 2.04 g (10 mmol) of 1 in 25 ml of benzene (distilled from sodium) was added dropwise 1.03 ml (5 mmol) of 2 in 5 ml of benzene and the resulting solution was stirred for 24 hr. The solution was filtered and concentrated overnight at 35° (0.5 mm) to give 1.45 g of a viscous pearly liquid which contained 2 (17%), 4 (75%), and 5 (8%).

Attempted Preparation of Silver Hydrogen Phthalate. -- A typical procedure involved the dropwise addition of 3.5 g (50 mmol) of silver nitrate in 20 ml of double distilled water to 10.2 g (50 mmol) of 1 in 300 ml of double distilled water and stirring the heterogeneous mixture for 10 to 30 min. The material was filtered and washed with water and dried in vacuo at 60° to give 5 to 7 g of a white solid: ir 6.33 and 7.1 μ.

Treatment of 1 g of the above with 12 N HCL (pH ≤ 2) to convert the silver salt of the acid to phthalic acid and silver chloride and addition of 3 N sodium hydroxide (pH ≥ 9) to solubilize the phthalic acid as its sodium salt gave silver chloride which was filtered and dried in vacuo. The yields of silver chloride obtained varied from 0.65 g
to 0.75 g. The theoretical yield of silver chloride expected from silver phthalate is 0.76 g while that from silver hydrogen phthalate would be 0.53 g. Similar results were found from material obtained using an excess of 1.

**Reaction of the Silver Salt with Diphenylmethylchlorosilane (2).** — To 2.73 g (10 mmol, calcd. for a monosilver salt) of the silver salt in 100 ml of benzene was added dropwise 1.03 ml (5 mmol) of 2 in 20 ml of benzene and the resulting solution was stirred in the dark for 24 hr. The solution was filtered and concentrated overnight at 35° (0.5 mm) to give 1.4 g of a viscous pale yellow liquid which contained 3 (32%), 4 (45%), 5 (20%) and 6 (13%). Repetition of the above procedure using ether as solvent gave ca. the same relative amounts of 3 and 4.

Use of triphenylchlorosilane gave spectral results indicating mainly a disilyl ester.

**Reaction of the Silver Salt with Methyl Iodide.** — To 1.36 g (5 mmol, calcd. for a monosilver salt) of the silver salt in 40 ml of benzene was added dropwise 0.44 ml (7 mmol) of methyl iodide in 10 ml of benzene and the solution was stirred for 24 hr. The solution was filtered and concentrated to give 0.4 g of a liquid characterized by its ir and nmr spectra as dimethyl phthalate.
Pyridine-Promoted Reaction of Diphenylmethylchlorosilane (2) with Phthalic Acid. -- To 1.66 g (10 mmol) of phthalic acid and 0.4 ml (5 mmol) of pyridine in 50 ml of 1,2-dimethoxyethane (DME) was added 1.03 ml (5 mmol) of 2. The resulting solution was stirred for 4 hr and then permitted to stand without stirring for 4 hr. The solution was filtered through Super Cel and concentrated. Methylene chloride was added and the solution was refiltered and concentrated and the procedure repeated to give 0.54 g of a viscous pale yellow liquid which contained 3 (19%), 4 (32%), and 6 (49%).

Palladium-Catalyzed Reaction of Diphenylmethylsilane (7) with Phthalic Acid. -- To 0.99 g (5 mmol) of 2 and 150 mg of 10% Pd-C in 10 ml of DME was added dropwise 1.66 g (10 mmol) of phthalic acid in 35 ml of DME. After hydrogen evolution ceased (ca. 20 min), the solution was stirred for an additional 2 hr and then permitted to stand without stirring for 2 hr. The solution was filtered through Super Cel and concentrated. Methylene chloride was added and the solution was refiltered and concentrated to give 0.87 g of a viscous pale yellow liquid which contained 3 (22%), 4 (34%), 5 (33%), and 6 (11%).

Diphenylmethylsilanol (5). -- Diphenylmethylchlorosilane (2) (3.9 g) was converted by the method of Dauudt and
Hyde\textsuperscript{77} into \( \mathcal{Z} \) (2.7 g, 75\%): bp 99-100\(^{\circ}\) (0.005 mm) \([\text{lit.}\textsuperscript{77} \text{ bp 184-187}^{\circ}\) (24 mm)]\).

\textbf{Sym-Tetraphenyldimethyldisiloxane (6).} -- Diphenylmethylsilanol (\( \mathcal{Z} \)) was converted by the method of Daudt and Hyde\textsuperscript{77} into \( \mathcal{Z} \): mp 45-46\(^{\circ}\) \([\text{lit.}\textsuperscript{77} \text{ mp 50}^{\circ}\)]\).

\textbf{Diphenylmethylsilane (7).} -- Diphenylmethylchlorosilane \( \mathcal{Z} \) (9.3 g) was converted by the method of Benkeser and Foster\textsuperscript{78} into \( \mathcal{Z} \) (6.3 g, 80\%): bp 93-94\(^{\circ}\) (0.85 mm); \( n^\text{20D} = 1.5721 \) \([\text{lit.}\textsuperscript{78} \text{ bp 82}^{\circ}\) (0.15 mm); \( n^\text{20D} = 1.5747 \)]. The nmr spectrum was identical with that published.\textsuperscript{79}

\textbf{Methyl Hydrogen Phthalate.} -- Phthalic anhydride \( \text{74 g} \) and absolute methanol \( \text{50 ml} \) were combined according to the procedure of Eliel and Burgstahler\textsuperscript{80} to give 82 g (91\%) of methyl hydrogen phthalate: mp 80.5-81.5\(^{\circ}\) \([\text{lit.}\textsuperscript{80} \text{ mp 82-82.5}^{\circ}\)]\).

\textbf{Potassium Methyl Phthalate (8).} -- To \( 3.9 \text{ g (100 mg-atoms) of potassium in 20 ml of tetrahydrofuran (THF) cooled to } 0^{\circ} \text{ was added dropwise 24.7 g (120 mmol) of 2,6-di-t-butylphenol}^\text{64} \text{ in 200 ml of THF. Following the initial vigorous reaction, the mixture was refluxed for 1 hr to complete the reaction. The solution of potassium 2,6-di-t-butylphenoxide was then cooled to } 0^{\circ} \text{ and 21.6 g (120 mmol) of methyl hydrogen phthalate in 200 ml of THF was added and the resulting solution}
was stirred for 1 hr after warming to room temperature. The mixture was filtered and the white solid was washed with four 50-ml portions of THF and dried in a vacuum oven at 50° to give 20 g (92%) of 8: IR (KBr) 5.78, 6.25 and 7.12 μ; NMR (D2O - TSP) 2.4 (m, 4) and 6.09 (s, 3, OCH3).

**Diphenylmethylsilyl Methyl Phthalate (10).** -- To 1.09 g (5 mmol) of 8 in 50 ml of ether was added 0.83 ml (4 mmol) of 2 and the resulting heterogeneous mixture was vigorously stirred for 4 hr at room temperature and then allowed to stand without stirring for 4 hr. The mixture was filtered through Super Cel under an atmosphere of nitrogen and concentrated overnight at 35° (1 mm) to give 1.2 g (82%) of 10 as a pale yellow viscous liquid: IR 5.78, 5.85 and 8.93 μ (PhSi); NMR 2.4 (m, 14), 6.34 (s, 3, OCH3) and 8.98 (s, 3, CH3Si).

**Anal.** Calcd for C22H20O4Si: C, 70.18; H, 5.35; Si, 7.46. Found: C, 70.13; H, 5.41; Si, 7.55.

**Trimethylsilyl Methyl Phthalate (11).** -- To 3.27 g (15 mmol) of 8 in 80 ml of ether was added 1.53 ml (12 mmol) of trimethylchlorosilane (2) and the resulting heterogeneous mixture was vigorously stirred for 4 hr and then allowed to stand without stirring for 4 hr. The mixture was filtered through Super Cel under an atmosphere of nitrogen and concentrated overnight at 40° (0.5 mm) to give 2.4 g (80%)
of 11 as a yellow liquid: ir 5.78, 5.85 and 11.7 μ (CH$_3$Si);
nmr δ 2.4 (m, 4), 6.1 (s, 3, OCH$_3$) and 9.61 (s, 9, CH$_3$Si).

Anal. Calcd for C$_{12}$H$_{16}$O$_4$Si: C, 57.11; H, 6.39;
Si, 11.13. Found: C, 57.48; H, 6.55; Si, 11.21.

General Pyrolysis Procedure. -- The thermal rearrangements were effected either by a calibrated variac-controlled heating mantle or by the use of a Bunsen flame. The sample was placed in a dried single-neck flask which was attached to a cooled flask for trapping of volatile products. All pyrolyses were conducted under an atmosphere of nitrogen. After the pyrolysis assembly cooled, pentane was added, and the insoluble phthalic anhydride was filtered, washed with pentane, dried and identified by comparison of its infrared spectrum and its melting point with authentic material. The combined pentane fractions were concentrated to yield oils. The components which constituted the oils were identified by ir, nmr and gc (retention time) comparison with authentic material and the relative amounts were calculated by nmr integration.

Pyrolysis of Diphenylmethylsilyl Methyl Phthalate (10). --
Pyrolysis of 1.1 g of 10 with a Bunsen flame for 15 min and then for 3 min (0.5 mm) to remove volatile material from the pyrolysis flask gave phthalic anhydride (12) (0.4 g, 88%) and a yellow oil (0.64 g) which contained four components as indicated by ir and nmr inspection. The components were
identified as diphenylmethyldimethoxysilane (13) (85%),
6 (7%), methyl hydrogen phthalate (2%) and 10 (6%).
The presence of 6 and 13 in ca. the same relative amounts
was also found by gc analysis.

Pyrolysis at 250° indicated ca. 90% decomposition of
10 after 6 hr.

Pyrolysis of Trimethylsilyl Methyl Phthalate (11). —
Pyrolysis of 2.3 g of 11 at 400° (1 hr) and then at 470°
(0.5 hr) gave 12 (0.65 g, 48%) and trimethylmethoxysilane (14)
(0.37 g, 38%). The remaining material (0.86 g), from con-
centration of the pentane layer, was shown by ir and nmr
inspection to consist of methyl hydrogen phthalate along
with small amounts of trimethylsilanol, hexamethyldisiloxane
(24) and 11 and 12.

Diphenylmethyldimethoxysilane (13). — Diphenylmethyldi-
chlorosilane (2) (4.5 g) was converted by a procedure
81 analogous to Sommer et al. into 13 (2.3 g; 53%):
bp 87-90° (0.075 mm); n²⁵D 1.5531 [lit. 82 n²⁵D 1.5510].

Trimethylmethoxysilane (14). — Trimethylchlorosilane (9)
(12.8 g) was converted by the method of Sauer 83 into 14 (2.2 g,
18%): bp 57-55°; n²⁰D 1.3675 [lit. 83 bp 57°; n²⁰D 1.3678].

2-Octyl Hydrogen Phthalate (15). — Phthalic anhydride (12)
(37 g) and 2-octanol (32.5 g) were reacted according to the
procedure of Kenyon to give 57.4 g (83%) of 15: mp 52.5-54.0° [lit. mp 55°].

**Trimethylsilyl 2-Octyl Phthalate (16).** -- To 8.3 g (30 mmol) of 15 in 125 ml of ether was added 2.7 ml (33 mmol) of pyridine and 4.9 ml (33 mmol) of 2 and the solution was stirred for 4 hr and then allowed to stand without stirring for 4 hr. The solution was filtered through Super Cel under an atmosphere of nitrogen and concentrated. Pentane (40 ml) was added and the solution was refiltered and concentrated overnight at 40° (0.4 mm) to give 7.6 g (72%) of 16 as a colorless liquid: ir 5.83 and 11.7 μ; nmr (CDCl3-p-dioxane) 2.5 (m, 4), 4.85 (broadened sextet, 1, CH3), 8.7 (m, 16) and 9.6 (m, 9, CH3Si).

**Pyrolysis of Trimethylsilyl 2-Octyl Phthalate (16).** -- Pyrolysis of 7.5 g of 16 at 400° (2 hr) and then at 470° (15 min) gave 12 (2.9 g, 90%) and a colorless volatile liquid (2.0 g) which contained five components by spectral and gc analysis. The components were identified as 2-octyltrimethylsilyl ether (17) (major component), 2-octanol, hexamethyldisiloxane (24), trimethylsilanol, and a mixture of octenes.
2-Octyltrimethylsilyl Ether (17). -- Trimethylchlorosilane (2) (14.5 g) was converted by the method of Fertig, Gerrard and Herbst,\textsuperscript{85} using ether as solvent, into 17 (26 g, 64%): bp 99.0-99.5\degree (30 mm); \(\eta^\text{20} = 1.4127\) [lit.\textsuperscript{85} bp 91\degree (22 mm); \(\eta^\text{20} = 1.4124\)].

(R)-(−)-2-Octyl Hydrogen Phthalate (15a). -- Phthalic anhydride (12) (18.5 g) and (R)-(−)-2-octanol\textsuperscript{86-88} (16.25 g) were reacted according to the procedure of Kenyon\textsuperscript{84} to give 26 g (74%) of 15a: mp 69-71\degree; \([\alpha]_D^{24} = -44.8\degree\) (c 3.4, abs ethanol) [lit.\textsuperscript{84} mp 75\degree; \([\alpha]_D = -48.4\degree\)].

(R)-Trimethylsilyl 2-Octyl Phthalate (16a). -- Optically active ester 16a was obtained from 15a by the same procedure used for the synthesis of inactive ester.

Anal. Calcd for C\textsubscript{19}H\textsubscript{30}O\textsubscript{4}Si: C, 65.10; H, 8.62.
Found: C, 65.24; H, 8.50.

Pyrolysis of (R)-Trimethylsilyl 2-Octyl Phthalate (16a). -- Pyrolysis of 5.5 g of 16a at 400\degree (1.5 hr) and then at 470\degree (0.5 hr) gave 12 (2.2 g, 93%) and a colorless volatile liquid (2.6 g) which contained five components by gc analysis. The products were separated by preparative gc and were identified by spectral comparison and gc retention times with authentic samples. The first two components were identified as trimethylsilanol (1%) and hexamethyldisiloxane (24) (2%). The third peak (4%) consisted of at least three components tentatively
identified as a mixture of octenes by gc and spectral comparison with an authentic sample of 1-octene. The fourth compound (10%) was identified as 2-octanol: $\left[\alpha\right]_{D}^{24} -8.8^\circ$ (c, 1.7, abs ethanol). The last component (83%) was identified as (R)-(−)-2-octyltrimethylsilyl ether (17a): $\left[\alpha\right]_{D}^{24} -17.4^\circ$ (c, 3.4, isooctane).

(R)-(−)-2-Octyltrimethylsilyl Ether (17a). -- The optically active ether 17a was prepared by the same procedure as the inactive ether in a 75% yield: bp 89-90° (18 mm); $\left[\alpha\right]_{D}^{24} -16.1^\circ$ (c, 3.4, isooctane).

Benzylidiphenylchlorosilane (18). -- Benzylmagnesium chloride $^{39}$ (200 mmol) in 150 ml of ether and diphenyldichlorosilane (53.2 g, 210 mmol) in 125 ml of ether were stirred for 15 min at 0° and then refluxed for 2 hr. Upon cooling, the solution was filtered through Super Cel under an atmosphere of nitrogen with the aid of another 150 ml of ether and the filtrate was concentrated. Methylene chloride (50 ml) was added and the solution was refiltered and concentrated to a pale yellow liquid. Short-path distillation gave 40.9 g (66%) of 18: bp 147-150° (0.003 mm); mp 52-57°; $\left[\beta\right]_{D}^{25} 1.6085$; ir 7.0, 8.97 and 19.0 $\mu$ (SiCl); nmr $\tau$ 2.7 (m, 15) and 7.2 (s, 2).

Anal. Calcd for C$_{19}$H$_{17}$ClSi: C, 73.87; H, 5.54; Cl, 11.47. Found: C, 73.76; H, 5.58; Cl, 11.38.
Benzylidiphenylsilyl Methyl Phthalate (19). -- To 1.09 g (5 mmol) of 8 in 50 ml of ether was added 1.23 g (4 mmol) of 18 in 1 ml of ether and the mixture was stirred for 4 hr and then allowed to stand without stirring for 4 hr. The mixture was filtered through Super Cel under an atmosphere of nitrogen and concentrated overnight at 45° (0.3 mm) to give 1.4 g (78%) of 19 as a pale yellow viscous liquid: ir 5.78, 5.84 and 8.90 μ (PhSi); nmr T 2.6 (m, 19), 6.38 (s, 3, OCH3) and 6.85 (s, 2, CH2Ph).

Anal. Calcd for C28H24O4Si: C, 74.30; H, 5.34; Si, 6.20; Found: C, 74.48; H, 5.45; Si, 5.90.

Pyrolysis of Benzylidiphenylsilyl Methyl Phthalate (19). --

Pyrolysis of 0.96 g of 19 at 400° (1 hr) and then with a Bunsen flame for 3 min (0.5 mm) gave 12 (0.28 g, 90%) and a yellow oil (0.24 g) which was identified as benzylidiphenylmethoxysilane (20) along with small traces of 12 and starting material. Go analysis on an SE 30 column likewise confirmed the methoxysilane as the main product. The brown nonvolatile material in the pyrolysis flask (0.34 g) displayed a strong broad ir stretching band (9.1-9.8 μ), characteristic of siloxanes (SiO-Si).90 Partial moisture hydrolysis of 19 either before or during pyrolysis to give a silanol which readily condenses under the pyrolysis conditions to a disiloxane could account for the siloxane material observed. This material was not further characterized.
Benzylidiphenylmethoxysilane (20). -- Benzylidiphenyl-chlorosilane (18) (5.17 g) was converted by the method of Sauer into 20 (3.9 g, 76%): bp 142-144° (0.005 mm); \( \text{NMR} \) 1.5923; \( \text{IR} \) 3.52, 7.0, 8.93 and 9.17 \( \mu \); \( \text{nmr} \) \( \text{T} \) 2.7 (m, 15), 6.42 (s, 3) and 7.24 (s, 2).

Anal. Calcd for \( \text{C}_{20}\text{H}_{20}\text{OSi} \): C, 78.89; H, 6.62; Si, 9.22. Found: C, 78.55; H, 6.78; Si, 8.90.

Potassium t-Butyl Phthalate (21). -- To 11.2 g (10 mmol) of potassium t-butoxide in 400 ml of THF was added rapidly a solution of 14.8 g (10 mmol) of 12 in 150 ml of THF. After ca. 5 min of stirring, an additional 250 ml of THF was added to facilitate stirring. The mixture was stirred for 3 hr and the white mass was then filtered and washed with three 50-ml portions of THF and three 50-ml portions of ether and dried in a vacuum oven at 65° to give 19.4 g (75%) of 21: \( \text{IR (KBr)} \) 5.80, 6.25 and 7.1 \( \mu \); \( \text{nmr (D}_{2}\text{O - TSP)} \) \( \text{T} \) 2.5 (m, 4) and 8.4 (s, 9).

Diphenylmethysilyl t-Butyl Phthalate (22). -- To 1.04 g (5 mmol) of 21 in 40 ml of ether was added 0.7 ml (3.4 mmol) of 2 and the mixture was vigorously stirred for 4 hr and then allowed to stand without stirring for 4 hr. The mixture was filtered through Super Cel under an atmosphere of nitrogen and concentrated overnight at 40° (0.5 mm) to give 1.17 g (83%) of 22 as a viscous liquid: \( \text{IR} \) 5.83 and 8.9 \( \mu \); \( \text{nmr} \)
τ 2.4 (m, 14), 8.45 (s, 9) and 8.9 (s, 3, CH₃Si).

Anal. Calcd for C₂₅H₂₆O₄Si: C, 71.73; H, 6.26; Si, 6.71. Found: C, 71.58; H, 6.38; Si, 6.55.

Trimethylsilyl t-Butyl Phthalate (23). -- To 9.1 g (35 mmol) of 21 in 80 ml of ether was added 4 ml (32 mmol) of 2 and the solution was stirred for 4 hr and then allowed to stand without stirring for 4 hr. The mixture was filtered through Super Cel under an atmosphere of nitrogen and concentrated overnight at 35° (0.75 mm) to give 5.9 g (64%) of 22 as a pale yellow viscous oil: ir 5.83 and 11.7 μ; nmr τ 2.4 (m, 4), 8.4 (s, 9) and 9.6 (s, 9, CH₃Si).


Pyrolysis of Diphenylmethyilsilyl t-Butyl Phthalate (22). -- Pyrolysis of 0.6 g of 22 with a Bunsen flame for 5 min gave 12 (0.21 g, 98%) and a yellow oil (0.25 g) which contained 5 (36%) and 6 (64%).

Pyrolysis of Trimethylsilyl t-Butyl Phthalate (23). -- Pyrolysis of 5.7 g of 23 with a Bunsen flame for 20 min gave 12 (2.8 g, 98%) and, after careful removal of pentane, hexamethyldisiloxane (24) (0.87 g, 56%). The material (23 mg) that remained in the pyrolysis flask was a black char.
Hexamethyldisiloxane (24). -- Trimethylchlorosilane (9) (8.1 g) was converted by the method of Sauer\textsuperscript{83} into 24 (4 g, 55%).

Trimethylsilanol. -- Trimethylchlorosilane (9) was hydrolyzed by water into a mixture\textsuperscript{83} of trimethysilanol and 24 as indicated by ir and nmr analysis.

Reaction of n-Butyllithium with Diphenylmethylchlorosilane (2). -- To 2.55 ml (12.2 mmol) of 2 in 50 ml of ether at -78° was added dropwise 7.65 ml (12.3 mmol) of 15% n-butyllithium in hexane and the deep yellow solution was stirred for 1.5 hr. Methyl iodide (1.86 ml, 30 mmol) was added and the resulting milky solution was stirred for 0.5 hr and then allowed to warm to room temperature. After the solution was filtered through Super Cel and the filtrate concentrated, petroleum ether (30-60°) was added and the solution was refiltered and concentrated to give a yellow-brown liquid (2.35 g). Gc analysis indicated three major components (83, 10 and 5%). Vacuum transfer (200°/0.003 mm) yielded 1.1 g of a yellow oil. Preparative gc afforded the major component (83%) which was characterized as diphenyl-dimethylsilane (25): \textsuperscript{91} ir 7.0, 7.93, 9.0, 12.0 and 12.2 μ; nmr 2.5 (m, 10) and 9.34 (s, 6, CH₃Si). Preparative gc of the nonvolatile residue afforded the two nonvolatile products. The 10% product appears to be siloxane (SiOSi)
in nature: ir 7.0, 7.87, 8.88 and 9.26 μ (broad, strong); nmr 2.3 (m, 9.5), 9.38 (s, 2) and 9.63 (s, 4). The third product (5%) was isolated in an insufficient amount to permit characterization. A weak ir indicated the material to be devoid of phenyl-silicon groups.

**Benzhydryldiphenylchlorosilane (26).** -- To 25 g (0.1 mol) of diphenyldichlorosilane in 200 ml of ether was added dropwise 280 ml of an ethereal solution of benzhydryllithium\(^{92}\) (0.1 mol) and the pasty mass was refluxed for 1.5 hr. The solution was filtered of lithium chloride and the filtrate was concentrated. Pentane was added and the heterogeneous solution was refluxed (2 hr) and filtered. The residue was washed with warm pentane and dried to give 15 g of white powder: mp 119-121\(^{0}\). Recrystallization from petroleum ether (bp 65-110\(^{0}\)) afforded 26 as small white crystals (98% purity by gc): mp 122-123\(^{0}\); ir 7.0, 9.0, 18.2 and 18.9 μ; nmr (CDCl\(_3\) - TMS) \(\sim\) 2.55 (m, 20) and 5.6 (s, 1).

**Reaction of 26 with Triethylamine.** -- To 385 mg (1 mmol) of 26 in 10 ml of benzene was added 0.14 ml (1 mmol) of triethylamine and the solution was refluxed for 48 hr. The solution was filtered of 33 mg of triethylamine hydrochloride and concentration of the filtrate afforded 312 mg of a brown solid. Infrared analysis indicated the material to be a mixture of 26 and presumably the silanol (2.7-3.1 and 12.0 μ).
derived from 26 along with a small amount of triethylamine hydrochloride.

Reaction of 26 with 1,5-Diazabicyclo[4.3.0]non-5-ene. --
To 124 mg (1 mmol) of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in 1 ml of chloroform was added 385 mg (1 mmol) of 26 in 2 ml of chloroform and the solution was stirred for 20 hr and then refluxed for 4 hr. The solution was concentrated to a residue which, by ir inspection, appeared to be a mixture of DBN and its hydrochloride as well as a Si-O-Si species (9-10 μ). Recrystallization of the residue from nitromethane gave a white solid (mp 181-183°). The infrared spectrum indicated strong broad SiOSi stretching (9-10 μ) and the nmr revealed an aromatic multiplet (Ț 2.8) and a singlet (Ț 5.94) in a ratio of ca. 20:1. A small amount of 26 and an alcoholic component (SiOH) also appeared to be present in the recrystallized material.

A tentative structure that might be considered would be the disiloxane, sym-tetraphenyl dibenzhydryldisiloxane. This is the expected product that would be obtained from hydrolysis of 26 to the silanol and then condensation to the corresponding disiloxane. Thin layer chromatography (tlc) using both silica gel (CCl₄) and neutral alumina (CH₂Cl₂) indicated one product. Gc analysis, however, at 350° on a 10% Dextril 300 column indicated three very high retention time components in ca.
the same relative amounts.

An analogous reaction carried out with benzene as solvent appeared to give similar results.

Reaction of 26 with n-Butyllithium. -- To 385 mg (1 mmol) of 26 in 5 ml of THF cooled to -78° was added dropwise 0.63 ml (1 mmol) of 15% n-butyllithium in hexane. The yellow solution turned colorless after 5 min and was stirred for 1 hr at -78° and then allowed to slowly warm to room temperature. After concentration of the solution, benzene was added, and the solution was filtered and reconcentrated to a residue which consisted of a mixture of at least seven products by gc analysis. The complex mixture was not further characterized.

Reaction of t-Butyllithium with 18. -- To 1.1 g (3.4 mmol) of 18 in 10 ml of THF at -78° was added dropwise 1.5 ml (3.6 mmol) of 2.26 M t-butyllithium in pentane in 8 ml of pentane and the resultant deep orange solution was stirred for 2 hr at -78° and 4 hr at room temperature. After standing overnight without stirring, the clear yellow solution was heated at 55° (1 hr) with no apparent visual change. Cyclohexane (5 ml) was added to facilitate the precipitation of lithium chloride, and the solution was refluxed for 1 hr. A small amount of white insoluble material was noted upon cooling. The solution was then concentrated, methylene chloride was added, and the solution was filtered through
Super Cel and concentrated to give 0.9 g of a yellow viscous liquid: ir 2.73, 7.0, 8.93, 9.4 and 12.2 μ; nmr \( \tau \) 2.8 (m, 15.7), 7.34 (s, 1), and a singlet (8.85) and three multiplets (6.25, 8.15 and 9.1), each of which amounted to less than half the amount of the singlet at 7.34 \( \tau \). No gc components could be observed on an SE 30 column up to 300°.

**Attempted Synthesis of Diphenylchloromethylidiphenylsilane (28).** -- To 2.37 g (10 mmol) diphenyl dichloromethane in 35 ml of THF cooled to -100° was added dropwise over 20 min 6.24 ml (10 mmol) of 15% n-butyllithium in hexane in 5 ml of THF. The solution was stirred at -100° for an additional 10 min. To the cold diphenylchloromethyl-lithium\(^{72}\) was added dropwise 2.19 g (10 mmol) of diphenylchlorosilane \((27)\) in 10 ml of THF and the resulting solution was stirred for 1 hr and then allowed to warm to room temperature. The THF was partially concentrated to enable removal of lithium chloride and the solution was then further concentrated to give 2.18 g of a semisolid residue. Gc analysis showed four products in addition to three low retention time components which amounted to ca. 30%. The four products were isolated by preparative gc.

The first product (8%) was identified as tetraphenylethylene: mp 226-229° \([\text{lit.}^{72} \text{ mp } 224-227°]\); ir 3.25-3.31,
6.25, 6.71, 6.91, 9.3 and 9.7 μ; nmr ~ 2.94 (s). The ir spectra was similar with that published. 93

The second product (7%) was characterized only as a SiH containing compound on the basis of its ir spectrum: ir 3.25-3.31, 4.65 (SiH), 7.0, 8.95 and 11.95 μ (SiH).

The major component (46%) was identified as benzylidyldiphenylchlorosilane (26). Its spectral properties were identical with those of a synthetic sample.

An insufficient amount of the fourth product (9%) was isolated to allow characterization.

Diphenylchlorosilane (27). -- Diphenylsilane (60 g) was converted by the method of Corey and West 94 into 27 (53 g, 76%): bp 105-106° (0.9 mm) [lit. 94 bp 99-101° (1 mm)].

Diphenylsilane. -- Diphenyldichlorosilane (127 g) was reduced by the method of Benkeser et al. 95 to diphenylsilane (74 g, 80%): bp 72-74° (0.25 mm) [lit. 95 bp 75-76° (0.5 mm)].

Attempted Pyrolytic Elimination of HCl from 26. -- 26 (397 mg) was heated vigorously under vacuum (0.01 mm) for 5 min with a Bunsen flame to give, after cooling, 383 mg of recovered 26.

Benzylidiphenylsilane (29). -- To 2.72 g (1.1 mol) of lithium aluminum hydride in 150 ml of ether was added 5.58 g (18 mmol) of 18 in 20 ml of ether. The resulting solution
was stirred for 5 min and then poured slowly into 600 ml of cold water that contained 40 ml of 12 N hydrochloric acid and extracted with ether. The ethereal extract was washed with water and dried. Short-path distillation afforded the hydride 29 (3.1 g, 62%): bp 130-132° (0.003 mm); mp 34-35°; \( \frac{d^2}{d} \) 1.6070; ir 4.7, 7.0, 8.94, 11.75 and 12.15 μ; nmr 2.7 (m, 15), 5.04 (t, 1, \( J = 6.3 \) Hz, SiH), and 7.3 (d, 2, \( J = 6.3 \) Hz, CH₂).

Anal. Calcd for C₁₉H₁₈S₁: C, 83.15; H, 6.61; S₁, 10.23. Found: C, 83.20; H, 6.71; S₁, 9.94.

Attempted Dehydrogenation of 29. -- To 640 mg (2.3 mmol) of 29 in 10 ml of p-dioxane was added 567 mg (2.5 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 10 ml of dioxane. The resulting clear red solution was stirred at 105° for 24 hr and then allowed to stand without stirring overnight at room temperature. The solution was filtered and the solid was washed with warm benzene (5 ml) and chloroform (20 ml) and dried to give 258 mg (48%) of 2,3-dichloro-5,6-dicyano-1,4-hydroquinone.

The filtrate and washings from the hydroquinone were combined and concentrated and the semisolid residue was dissolved in ethyl acetate (25 ml) and passed through a short column of 2 g of Woelm neutral alumina (activity grade 1). After elution with 100 ml of ethyl acetate, the eluate was concentrated to give 469 mg (73% recovery) of 29.
(d-Trimethylsilylbenzyl)diphenylchlorosilane (30). --

To 4 g (13 mmol) of 18 and 1.65 ml (13 mmol) of 2 in 25 ml of THF at -78° was added dropwise 6.2 ml (14 mmol) of 2.26 M t-butyl lithium in pentane in 25 ml of pentane. The resulting clear orange solution was stirred at -78° for 2 hr. The solution was then allowed to warm to room temperature, after addition of 0.26 ml (2 mmol) of 2, and stirred for 2 hr. Lithium chloride was filtered under nitrogen using Super Cel and the colorless filtrate was concentrated. Methylene chloride (20 ml) was added and the solution was refiltered, concentrated and distilled (short-path) to give 3.0 g of a colorless viscous oil: bp 154.5-155.5° (0.003 mm); n D 1.5877. Gc analysis showed 30 (94%), 18 plus a lower retention component (1%), and an unidentified high retention time component (5%). Preparative gc gave pure 30: ir 7.0, 9.03, 11.7 and 19.4 μ; nmr 2.6 (m, 15), 7.52 (s, 1, CH), and 10.1 (CH 3 Si).


(d-Trimethylsilylbenzyl)diphenylmethoxysilane (31). --

To 3.96 g (13 mmol) of 20 and 1.65 ml (13 mmol) of 2 in 25 ml of THF at -78° was added dropwise 6.2 ml (14 mmol) of 2.26 M t-butyl lithium in pentane in 20 ml of pentane. The resulting yellow solution was stirred at -78° for 2 hr. The solution was then allowed to warm to room temperature, after addition
of 0.26 ml (2 mmol) of \( \text{2} \), and stirred for 2 hr. Lithium chloride was filtered under nitrogen using Super Cel and the colorless filtrate was concentrated. Methylene chloride (20 ml) was added and the solution was refiltered, concentrated and distilled (short-path) to give 3.8 g of a colorless viscous oil: \( bp 151-153^\circ \) (0.005 mm); \( n^25^D \) 1.5757. Gc analysis revealed \( \text{31} \) (88\%) and an unresolved peak (12\%) at the same retention time as \( \text{20} \). Preparative gc gave pure \( \text{31} \): ir 3.53, 7.0, 8.98, 9.18, 11.7 and 19.2 \( \mu \); nmr \( \tau \) 2.6 (m, 15), 6.45 (s, 3, OCH\(_3\)), 7.75 (s, 1, OH) and 10.05 (s, 9, OCH\(_3\)Si).

**Anal.** Calcd for C\(_{23}\)H\(_{28}\)OSi\(_2\): C, 73.34; H, 7.49; Si, 14.91. Found: C, 73.39; H, 7.51; Si, 14.61.

**Pyrolysis of \( \text{30} \).** -- Pyrolysis of 1.39 g of \( \text{30} \) at 300\( ^\circ \) (1 hr), at 380\( ^\circ \) (1 hr) and then at ca. 470\( ^\circ \) (1 hr) yielded 29 mg of volatile material which was characterized by ir and nmr analysis as a mixture (1.6:1) of benzene and \( \text{24} \). The remaining yellow viscous liquid (1.31 g) in the pyrolysis flask was shown by ir, nmr and gc analysis to be starting material \( \text{30} \).

**Pyrolysis of \( \text{31} \).** -- Pyrolysis of 1.32 g of a 90:10 mixture of \( \text{31} \) and \( \text{20} \) at 300\( ^\circ \) (0.5 hr), at 380\( ^\circ \) (0.5 hr) and then at 470\( ^\circ \) (0.5 hr) gave 0.18 g (ca. 50\%) of trimethylmethoxysilane (14) which also contained a small amount of material tentatively identified as benzene. In the pyrolysis flask there remained a brown-yellow liquid phase and a very
tacky residue.

GC analysis of the liquid fraction (ca. 0.39 g) revealed the presence of 20 and a minimum of five faster eluting components, the total of which was less than that of 20. No other substantial component could be discerned upon programming up to 400°C on a Dextril 300 column. Infrared analysis (3.53, 7.0, 8.84, 9.27 and 11.8 μ) indicated absorptions due to 20 and to a trimethylsilyl group (11.8 μ) as well as a strong broad stretching band (9.27) characteristic of siloxanes (SiOSi). Nmr inspection revealed two high field singlets (9.8 and 9.9) and singlets at 9.5, 6.5, 7.0, 7.2 (unresolved singlet), 7.28 and 7.58 in addition to aromatic protons (2.6) and those attributable to 20 (6.4 and 7.2).

The tacky residue (ca. 0.76 g) was characterized mainly by its strong broad ir absorption (9.3 μ) usually attributed to siloxane material. Nmr inspection revealed a very broad aromatic multiplet (2.6) and two small singlets at 9.8 and 9.9.


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VITA AUCTORIS

Born:
August 1, 1944; Rochester, New York.

Education:
University of Windsor; Windsor, Ontario; 1962-1966.
Degree:  B.Sc., 1966.
Indiana University; Bloomington, Indiana, 1966-1969.
Degree:  M.Sc., 1969
University of Windsor; Windsor, Ontario; 1969-1972.
Graduate Studies leading to Ph.D.

Awards:
National Science Foundation Trainee 1966-1967.
Indiana University; Bloomington, Indiana

Honorary and Professional Societies:
The Chemical Institute of Canada
The American Chemical Society
Phi Lambda Upsilon

Marital Status:
Married August 6, 1966 to Elizabeth J. Baumer
Two Children:  Michael Robert; Born August 17, 1967
   Derek Daniel; Born March 26, 1972