1964

Strained cyclic organosilicon compounds

William Henry Atwell
Iowa State University

Recommended Citation

Atwell, William Henry, "Strained cyclic organosilicon compounds " (1964). *Retrospective Theses and Dissertations*. 3835.
https://lib.dr.iastate.edu/rtd/3835

ATWELL, William Henry, 1936–
STRAINED CYCLIC ORGANOSILICON COMPOUNDS.

Iowa State University of Science and Technology
Ph.D., 1964
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

STRAINED CYCLIC ORGANOSILICON COMPOUNDS

by

William Henry Atwell

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

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1964

TABLE OF CONTENTS

INTRODUCTION

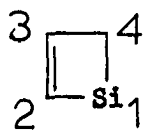
At the time of this author's initial investigations, the area of strained cyclic organosilicon compounds was populated by only a few silacyclobutane derivatives, by a single 1,3-disilacyclobutane type, and by an unusual cyclosilane compound; namely, octaphenylcyclotetrasilane. In addition, the general lack of information on the reactivity of the above silacycloalkanes toward a variety of synthetically useful reagents precluded their use for the preparation of the corresponding unsaturated derivatives. During the course of this work, convincing evidence was reported for the intermediate formation of silacyclopropane derivatives. The synthesis of the highly reactive 7-silanorbornadiene derivatives further broadened this area of research.

The first objective of the work presented here was to study the synthesis and chemical reactivity of the saturated four-membered cyclic organosilicon compounds for the purpose of correlating both their reactivity and the factors contributing to this reactivity. Inherent in this study was a comparison of the properties of the homologous four- and five-membered cyclic derivatives.

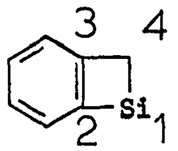
Subsequent to the successful completion of the first phase of the investigation, it would then be possible to utilize this newly acquired information for the synthesis of silacyclobutene and related compounds. It is hoped that this presentation will instill interest in a new, unusual and rapidly growing area of organosilicon research.

NOMENCLATURE

In naming the organosilicon compounds prepared herein, the rules of nomenclature recommended by the Commission of Nomenclature of Organic Chemistry of the I. U. P. A. C., and adopted by the American Chemical Society, will be employed. The numbering of the cyclic systems is typified by the following examples.



1-silacyclobut-2-ene



2:3-benzo-1-silacyclobut-2-ene

Exceptions to the above will be noted with octaphenylcyclotetrasilane (1-4) and its derivatives. These compounds will be named according to a previously described (4) system. Thus, H(SiPh$_2$)$_4$H will be designated as 1*H*, 4*H*-octaphenyltetrasilane rather than 1,1,2,2,3,3,4,4-octaphenyltetrasilane, in order to avoid unwieldy sequences of numbers. It should be stressed that the nomenclature being employed is unambiguous since the polysilane compounds discussed here do not contain branched-chains.

The abbreviation Ph for the phenyl (C_6H_5) group will be used throughout this work. All other groups will be designated by their structural formulas. Exceptions to this latter statement will be noted in the case of Et for the ethyl (C_2H_5) group in solvents and to call attention to the role of the solvents in various mechanistic interpretations.

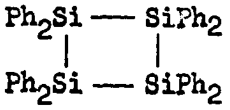
Finally, the following designations will be used throughout this thesis. 1) THF = tetrahydrofuran; 2) LAH = lithium aluminum hydride; 3) NBS = N-bromosuccinimide; 4) n.m.r. = nuclear magnetic resonance; and 5) ether = diethyl ether.

HISTORICAL

Four-Membered Rings

Octaphenylcyclotetrasilane

Among the compounds isolated by Kipping from the reaction of dichlorodiphenylsilane with sodium, was a material which he designated as compound "A" (1). In order to explain the high reactivity of this compound in free radical-type reactions, he assigned to compound "A" a biradical structure [...$SiPh_2SiPh_2SiPh_2SiPh_2$...] (1,2). However, this compound has recently been shown to be octaphenylcyclotetrasilane [I]

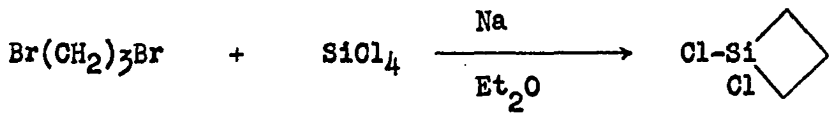


I

(3). Compound [I] and other organic substituted cyclosilanes have been the subject of a recent review, and for further information the reader is referred to this comprehensive work (4).

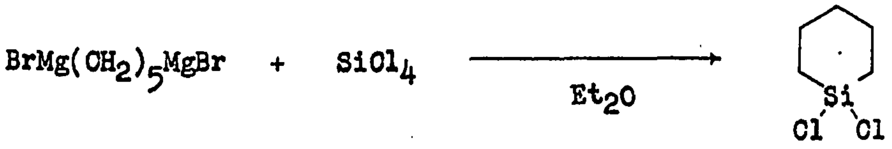
Silacyclobutanes

The first preparation of a silacyclobutane derivative was reported by Hart (5) in 1887. He isolated from the reaction of 1,3-dibromopropane, silicon tetrachloride and sodium, a material which he designated as 1,1-dichloro-1-silacyclobutane [II]. In 1926 Widdowson (6), on the suggestion of Kipping and under his supervision, attempted without success to duplicate some of Hart's results. Although no attempt was made to resynthesize



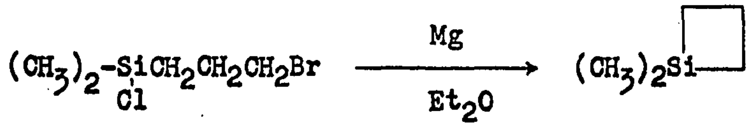
II

the silacyclobutane [II], Widdowson suggested that the silicon-containing compounds reported by Hart be deleted from the chemical literature. Confirmation of the meager evidence presented by Hart for the formation of [II] is still non-existent; however, his controversial report was actually the stimulus for the first successful preparation of a cyclic organosilicon compound by Bygden (7). The latter, also doubtful of Hart's results, employed one mole of 1,5-pentamethylenedimagnesium dibromide and one mole of silicon tetrachloride to prepare 1,1-dichloro-1-silacyclohexane [III].



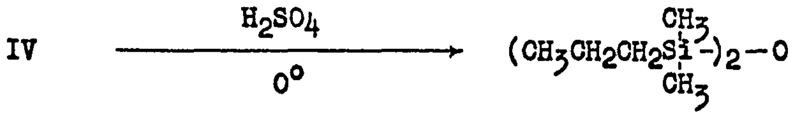
III

The interest in silacyclobutanes remained dormant until 1954 when Sommer and Baum reported (8) the preparation of 1,1-dimethyl-1-silacyclobutane [IV]. The procedure used for the preparation of [IV] involved several synthetic steps. Demethylation of 3-bromopropyltrimethylsilane with sulfuric acid followed by reaction of the resulting symmetrical disiloxane with ammonium chloride-sulfuric acid mixture gave 3-bromopropyldimethylsilane [V]. Treatment of [V] with magnesium in ether gave the silacyclobutane [IV].



V IV

The silacyclobutane ring system proved to be extremely susceptible to cleavage by polar reagents. Simply mixing [IV] with 1*N* potassium hydroxide at room temperature gave a highly exothermic reaction (8). Further contrast to ordinary tetraalkylsilanes is evident from the reported violent reaction of [IV] with sulfuric acid at room temperature in spite of the heterogeneous nature of the reaction. This latter reaction was used as a proof of structure since the product was the expected di-*n*-propyltetramethyldisiloxane [VI]. The reaction of [IV] with both acid and base proceeded without gas evolution in accord with the occurrence of ring opening.



$$\text{IV} \xrightarrow[0^{\circ}]{H_2SO_4} (CH_3CH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}-)_2-O$$

VI

Calculation of the bond angles in [IV] was carried out (8) using the following assumptions:

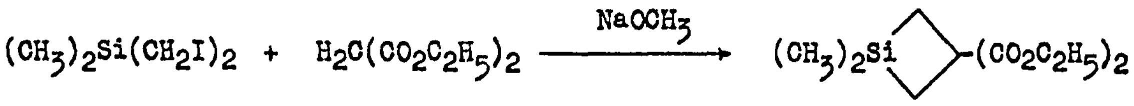
a) that the silacyclobutane ring is planar and that the C-C-C angle is tetrahedral (at least to a first approximation);

b) that 1.94 Å and 1.54 Å are the lengths of the C-Si and C-C bonds, respectively.

This calculation gave 80°48' for the C-Si-C bond angle and 84°52' for each of the two C-C-Si bond angles. It follows therefore that, in a planar structure, the C-Si-C angle cannot be significantly increased without expansion of the C-C-C angle beyond the tetrahedral value.

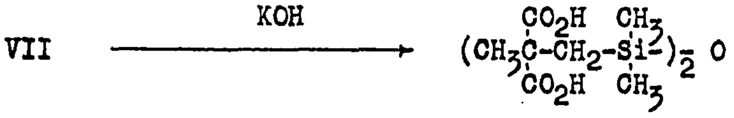
In 1955, West (9) reported the synthesis of another silacyclobutane;

namely, 3,3-dicarbethoxy-1,1-dimethyl-1-silacyclobutane [VII] using an entirely different approach. His method involved a ring closure between bis(iodomethyl)dimethylsilane and diethyl malonate effected with sodium methoxide.



VII

Attempted basic hydrolysis of [VII] resulted in ring opening with subsequent formation of sym-bis(2,2-dicarboxypropyl)tetramethyldisiloxane [VIII].



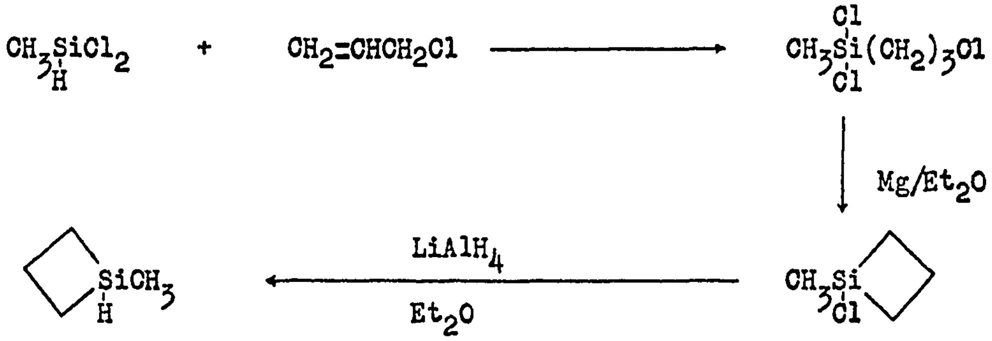
$$\mathrm{VII} \xrightarrow{\mathrm{KOH}} (\mathrm{CH_3}\overset{\mathrm{CO_2H}}{\underset{\mathrm{CO_2H}}{\mathrm{C}}}\mathrm{-CH_2-}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{-})_2\ \mathrm{O}$$

VIII

With regard to the reactivity of silacyclobutanes, West (9) suggested that in spite of the additional size of the silicon, the total angular strain is probably no greater in silacyclobutanes than in cyclobutanes due to the ready ability of silicon to deform its bond angles (9). Since silacyclobutanes are cleaved more readily than cyclobutanes, he held that ring opening of the former was facilitated because it had available to it mechanisms not available in the case of the latter.

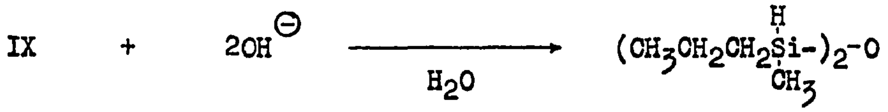
Incidental to the preparation of 4,4-dimethyl-4-silacyclohexanone, Benkeser and Bennett (10) isolated a compound identical with that reported by West (9). It was stated (10) that the cyclization to [VII] was surprisingly facile even in the presence of a large excess of diethyl malonate.

In 1957, Sommer and co-workers (11) synthesized 1-methyl-1-silacyclobutane [IX] for the purpose of comparing the reactivity with hydroxide ion of a four-membered ring silicon hydride, relative to that of acyclic and other previously known cyclic silicon hydrides. The synthetic steps employed were as follows (12):



IX

In 95% ethanol at 35° with an ammonia-ammonium iodide buffer, [IX] was found to give 60% of the theoretical hydrogen at an extremely fast rate which corresponded to a reasonable half-life of 7.5 minutes. The same reagent gave no hydrogen in a comparative time with the highly reactive triphenylsilane (13). Also, 40% of the theoretical hydrogen was evolved at a different rate smaller than the first by a factor of ten. This latter rate has been shown to comprise hydrogen evolution from sym-di-n-propyldimethyldisiloxane [X]. This compound is formed via



$$\text{IX} + 2OH^{\ominus} \xrightarrow[H_2O]{} (CH_3CH_2CH_2\overset{H}{\underset{CH_3}{Si}}\text{-})_2\text{-}O$$

X

ring opening of [IX] in a reaction quite competitive with the evolution of hydrogen from the silacyclobutane [IX].

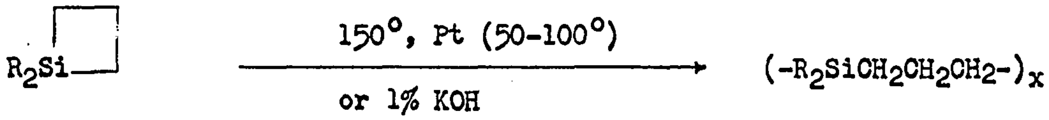
Thus, the displacement of hydride ion by hydroxide ion was found to proceed much more readily at four-membered ring silicon atoms than at silicon in other five- and six-membered ring silicon hydrides (14). In this respect, cyclic silicon hydrides exhibit a complete reversal of the structure-reactivity relationships observed for displacements at carbon (15). To explain the enhanced reactivity of the four-membered ring silicon hydrides, Sommer and co-workers (11) invoked the I-strain (internal strain) theory (16). A more detailed consideration of their arguments will be presented in the Discussion section.

In addition to the forgoing, several other silacyclobutane derivatives; namely, 1-chloro-1-ethyl-, 1-chloro-1,3-dimethyl-, and 1-ethyl-1-methyl-1-silacyclobutane were prepared (17) during this period (see Table 1). However, no reactions of these compounds were reported.

Smith (18) has calculated the bond refractions of the cyclotri-, cyclotetra-, and cyclopentamethylene groups bonded to silicon, in addition to the bond dispersions of the latter groups. He has shown that a ring refraction is present in the four- and five-membered rings but not in the six. He stated that these results are in agreement with those of an inspection of the molecular models; a strain free structure can be obtained only in the case of the six-membered ring. He also stated that the results are in accord with the unusual reactivity of the silacyclobutanes. It should be mentioned that in the cyclobutanes, cyclopentanes and cyclohexanes the latter two are without ring refractions (19). A more complete examination of the ring refractions in silacyclobutanes has been carried out by Vdovin, *et al*. (20).

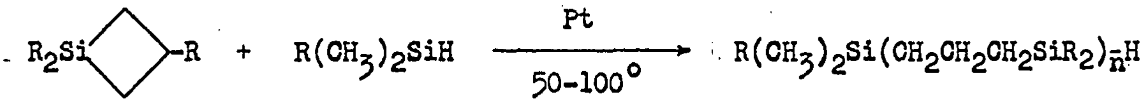
Equipped with the above information, together with the reported preparation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (see Historical section on Disilacyclobutanes), the present author initiated his studies of strained cyclic organosilicon compounds.

More recently, the preparation (20,21,22) and polymerization (21,22) of numerous silacyclobutanes has been reported. The polymerization reactions are induced thermally above 150° (21,22) or by platinum[1] or basic (23) catalysts.



At the present time, it is not known whether the platinum-catalyzed polymerization of these silacyclobutanes involves an alkyl-alkyl exchange or a slow rearrangement to an allylsilane followed by the more rapid alkyl-hydrogen exchange.

The platinum-catalyzed interaction of silicon hydrides with silacyclobutanes has also been described[1]. Under the influence of platinum catalysts (Pt/C or H_2PtCl_6) a series of telomeric products is obtained;

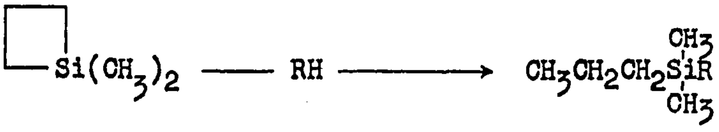


however, no reaction similar to that illustrated occurs in the absence of the metal catalyst.

---

[1] D. R. Weyenberg and L. E. Nelson, Dow Corning Corporation, Midland, Michigan. Information on the preparation and polymerization of silacyclobutanes. Private communication. 1964.

The ring opening of 1,1-dimethyl-1-silacyclobutane /IV/ with a variety of reagents has been reported recently (24). The conditions necessary for ring opening and the yields of the corresponding open chain



IV

where R= -Cl, -OH, n-$C_7H_{15}O$-, or CH_3CO_2-

products were dependent on the nature of the R group.

Finally, reaction of 1-chloro-1-methyl-1-silacyclobutane /XI/ with numerous RH reagents leads to a variety of silicon substituted silacyclobutanes /XII/ (21,24). Without the addition of pyridine ring cleavage products were obtained.

XI XII

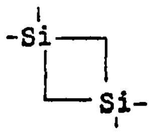
where R= -Cl, CH_3CO_2-, n-$C_7H_{15}O$-, $(C_2H_5)_2N$-, and $(C_4H_9)_2N$-

A list of all known silacyclobutanes together with their boiling points, refractive indexes, and appropriate references is given in Table 1.

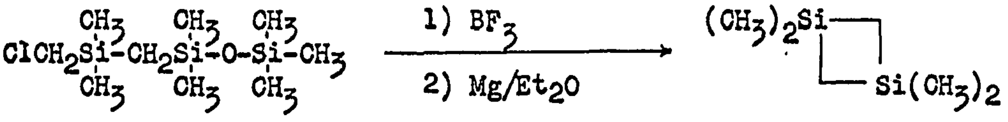
Disilacyclobutanes

Two distinct disilacyclobutane derivatives are possible; namely, a 1,2-disilacyclobutane and a 1,3-disilacyclobutane. While no derivatives of the 1,2-type have been reported, derivatives of the latter type have been prepared.


1,2-


1,3-

The preparation of the first 1,3-disilacyclobutane; namely, 1,1,3,3-tetramethyl-1,3-disilacyclobutane /XIII/ was reported by Knoth and Lindsey (25) in 1958. In their unique preparation, chloromethylpentamethyldisiloxane was converted to the Grignard reagent and coupled with (chloromethyl)dimethylchlorosilane to give 1-chloro-2,2,4,4,6,6-hexamethyl-5-oxa-2,4,6-trisilaheptane /XIV/. The siloxane linkage was then cleaved by boron trifluoride in ether to give 1-chloro-4-fluoro-2,2,4-trimethyl-2,4-disilapentane which was then cyclized with magnesium to give the desired /XIII/.



XIV XIII

The original interest in /XIII/ was to attempt its pyrolysis to $(CH_3)_2Si{=}CH_2$, which Knoth and Lindsey hoped to trap by rapid quenching[1]. However, /XIII/ was found to exhibit remarkable thermal stability, and passage of this compound through a tube packed with quartz helices at pressures of 4-5 mm. (with short contact times) gave no decomposition up to 850°. Above this temperature /XIII/ decomposed completely, and

---

[1] W. H. Knoth, Jr., E. I. Du Pont de Nemours and Co., Wilmington, Delaware. Information on the pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Private communication. 1962.

Table 1. Known Silacyclobutanes[a]

Formula	Name	B.p., °C ($n^{20}D$)	Reference
$C_3H_6Cl_2Si$	1,1-Dichloro-1-silacyclobutane	114.5-114.8 (1.4620)	(20)
C_4H_9ClSi	1-Chloro-1-methyl-1-silacyclobutane	103.5-104 (1.4482)	(20,24)
C_4H_9DSi	1-Methyl-1-silacyclobutane-1-D	62.5-63.5 (1.4318)[b]	(12)
$C_4H_{10}Si$	1-Methyl-1-silacyclobutane	63/733mm. (1.4313)	(11,12)
$C_5H_{11}ClSi$	1-Chloro-1,3-dimethyl-1-silacyclobutane	118/740mm. (1.4428)	(17)
$C_5H_{11}ClSi$	1-Chloro-1-ethyl-1-silacyclobutane	133.5/747mm. (1.4570)	(17)
$C_5H_{12}Si$	1,1-Dimethyl-1-silacyclobutane	81/730mm. (1.4270)	(8,20)
$C_6H_{12}O_2Si$	1-Acetoxy-1-methyl-1-silacyclobutane	62-63/30mm. (1.4322)	(22,24)
$C_6H_{14}Si$	1-Ethyl-1-methyl-1-silacyclobutane	65.5-66/100mm. (1.4552)	(20)
$C_6H_{14}Si$	1,1,3-Trimethyl-1-silacyclobutane	94/723mm. (1.4232)	(26)
$C_6H_{14}Si$	1-Ethyl-1-methyl-1-silacyclobutane	109/745mm. (1.4388)	(17)

---

[a] Compounds prepared in this work not included.

[b] Determined at 24.5°.

Table 1. (continued)

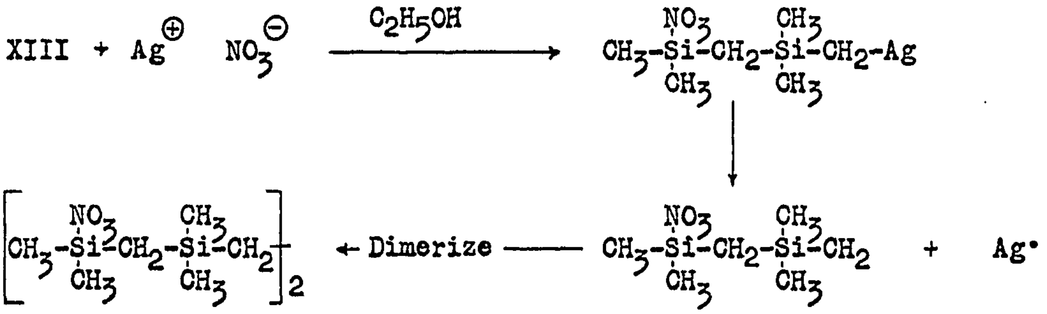
Formula	Name	B.p.,°C ($n^{20}D$)	Reference
$C_7H_{14}Si$	1-Allyl-1-methyl-1-silacyclobutane	53/50mm. (1.4571)	(21)
$C_8H_{18}NSi$	1-(N,N-Diethylamino)-1-methyl-1-silacyclobutane	76-77/37mm. (1.4518)	(22,24)
$C_8H_{24}Si$	1-Butyl-1-methyl-1-silacyclobutane	65.5-66/25mm. (1.4455)	(20)
$C_{10}H_{14}Si$	1-Methyl-1-phenyl-1-silacyclobutane	61.5-62/5mm. (1.5349)	(20)
$C_{10}H_{14}OSi$	1-Methyl-1-phenoxy-1-silacyclobutane	84-84.5/5mm. (1.5139)	(22,24)
$C_{11}H_{16}Si$	1,3-Dimethyl-1-phenyl-1-silacyclobutane	131-132/49mm. (1.5192)^c	(Footnote pg.9)
$C_{11}H_{16}Si$	1-Benzyl-1-methyl-1-silacyclobutane	73.5-74/5mm. (1.5313)	(20)
$C_{11}H_{24}OSi$	1-(n-Heptoxy)-1-methyl-1-silacyclobutane	87.5-88/6.5mm. (1.4412)	(22,24)
$C_{12}H_{27}NSi$	1-(N,N-Dibutylamino)-1-methyl-I-silacyclobutane	90-91/2.5mm. (1.4552)	(22,24)

---

[c] Determined at 25°.

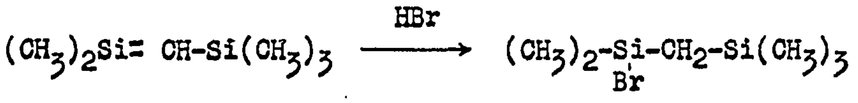
the only products that could be identified were ethylene and acetylene.

Compound [XIII] was found (25,27) to decolorize a solution of bromine in carbon tetrachloride at room temperature and to reduce ethanolic silver nitrate solutions, often with the formation of a silver mirror. The reactions with bromine (25,28,29) and silver nitrate (25,30) are reported to proceed with ring-opening. A recent examination (30) of the reaction between [XIII] and ethanolic silver nitrate is consistent with the following scheme;



The Si-NO_3 groups would react further with the solvent, presumably with the formation of SiOH or Si-O-Si linkages.

From the pyrolysis of tetramethylsilane, Fritz and Grobe (31) reported the preparation of a compound, $C_6H_{16}Si_2$, to which they ascribed the silaolefin structure [XV] on the basis of its extreme reactivity toward a variety of reagents. Thus, [XV] reacted with bromine in carbon tetrachloride at room temperature, reduced an acid solution of silver ion, and reacted with hydrogen bromide to give the monobromo compound [XVI].

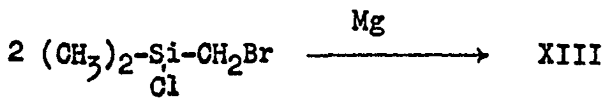


$$(CH_3)_2Si{=}CH\text{-}Si(CH_3)_3 \xrightarrow{HBr} (CH_3)_2\text{-}\underset{Br}{Si}\text{-}CH_2\text{-}Si(CH_3)_3$$

XV XVI

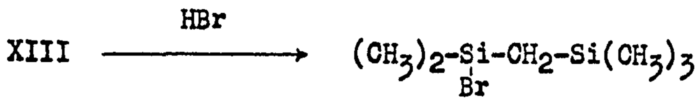
A reexamination (32) of this problem by the original authors showed that the compound believed to be [XV] was actually 1,1,3,3-tetramethyl-1,3-disilacyclobutane [XIII]. It is indeed somewhat ironic that Fritz and Grobe mistook [XIII] for a silaolefin since [XIII] was originally prepared as a possible precursor to a silaolefin.

A one step preparation of [XIII] has been reported (29). This procedure involved the addition of (bromomethyl)dimethylchlorosilane [XVII] to magnesium in ether and only a low yield (4%) of the 1,3-disilacyclobutane [XIII] was realized. The ring-opening of [XIII] with hydrogen bromide has also been observed (29,32).



$$2\ (CH_3)_2\text{-}\underset{\displaystyle Cl}{Si}\text{-}CH_2Br \xrightarrow{Mg} \text{XIII}$$

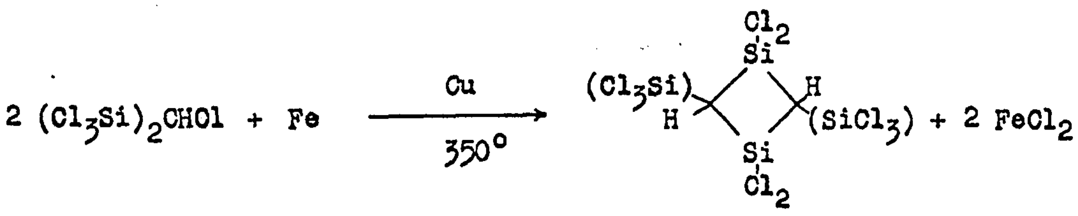
XVII



$$\text{XIII} \xrightarrow{HBr} (CH_3)_2\text{-}\underset{\displaystyle Br}{Si}\text{-}CH_2\text{-}Si(CH_3)_3$$

XVI

Some unusual and highly chlorinated 1,3-disilacyclobutanes have been prepared (33,34). Treatment of bis(trichlorosilyl)chloromethane [XVIII] with an iron-copper powder mixture gives 1,1,3,3-tetrachloro-2,4-bis(trichlorosilyl)-1,3-disilacyclobutane [XIX] (34), whereas tris-(trichlorosilyl)chloromethane upon similar treatment gave 1,1,3,3-tetrachloro-2,2,4,4-tetrakis(trichlorosilyl)-1,3-disilacyclobutane [XX] (33,34).

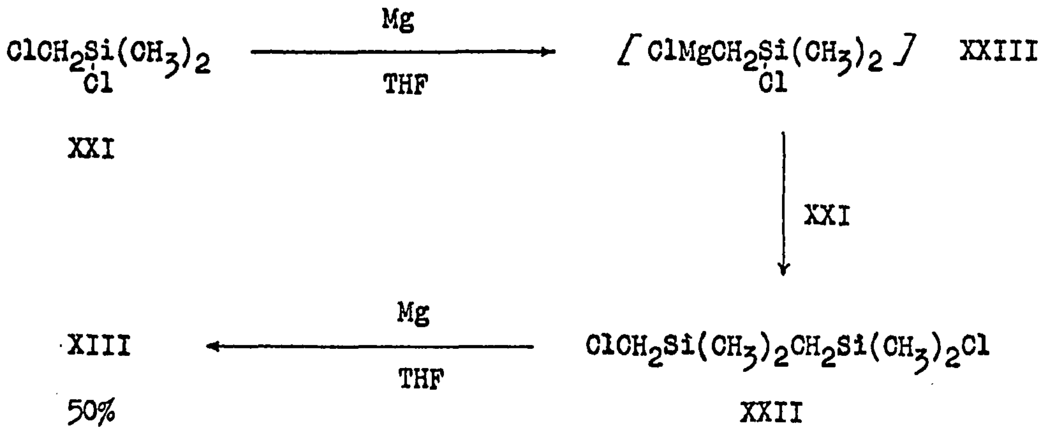


XVIII XIX

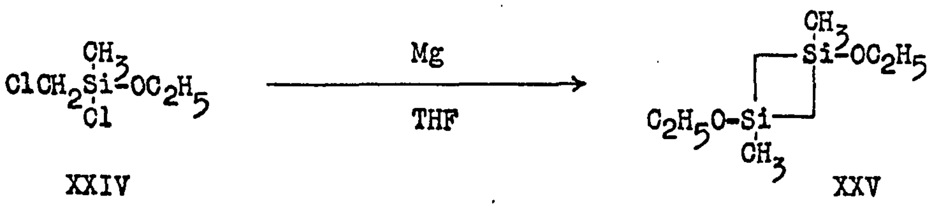
These disilacyclobutanes also react with polar reagents such as hydrogen chloride (34). In addition, the infrared spectra of /XIX/ and /XX/ have been reported (34).

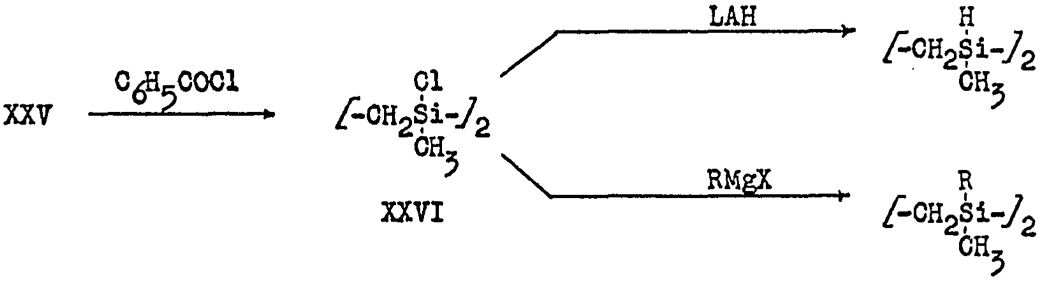
$$\begin{tikzcd}
XIX + 2\ HCl \arrow[r, "C_6H_5N(CH_3)_2"] \arrow[d, "HCl"] & 2\ (Cl_3Si)_2CH_2 \\
(Cl_3Si)_2CH\text{-}SiCl_2\text{-}CH_2\text{-}SiCl_3 &
\end{tikzcd}$$

One of the most useful methods for the synthesis of 1,3-disilacyclobutanes was developed recently by Kriner (35). This latter method was essentially the same as that employed by Mueller except that Kriner added magnesium to a (chloromethyl)dimethylchlorosilane /XXI/-tetrahydrofuran (THF) mixture (i.e. inverse addition). The success of this method is attributed to the favored production of 1,4-dichloro-1,1,3,3-tetramethyl-1,3-disilabutane /XXII/, since only small amounts of the intermediate Grignard /XXIII/ will be formed in an enviroment rich in /XXI/. This will hold until the concentration of /XXII/ becomes appreciable. On the contrary, the normal addition method produces a relatively high concentration of the intermediate Grignard /XXIII/, resulting in a preponderance of intermolecular chain lengthening reactions.



Advantages of Kriner's method include increased yields and the ability to synthesize a variety of silicon-functional 1,3-disilacyclobutanes. Thus, reaction of (chloromethyl)ethoxymethylchlorosilane [XXIV] with magnesium gave 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane [XXV]. Treatment of [XXV] with benzoyl chloride gave 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane [XXVI]. Further, treatment of [XXVI] with either lithium aluminum hydride (LAH) or Grignard reagents gave other silicon-functional 1,3-disilacyclobutanes.





A study of the infrared spectra of the Si-CH_2-Si band frequencies in a number of 1,3-disilacyclobutanes indicates that a shifting of this band to lower frequencies occurs with these compounds (35). Thus, while linear and six-membered ring compounds containing the Si-CH_2-Si linkage absorb in the 1040-1065 cm.$^{-1}$ region, 1,3-disilacyclobutanes absorb in the 935-955 cm.$^{-1}$ region. This shift can be attributed to the strained ring structure of these compounds, and may be compared to the similar shifts of the Si-O-Si frequency which have been observed (36, 37) in several strained cyclic siloxanes. The infrared, Raman and n.m.r. spectra of 1,1,3,3-tetramethyl-1,3-disilacyclobutane have been reported previously (32).

A tabulation of the reported 1,3-disilacyclobutane derivatives is given in Table 2, together with their physical properties and references to the researchers who isolated and characterized them.

Silacyclobutenes

While no preparations nor attempted preparations of a silacyclobutene derivative have been reported, the attempted preparation of a pseudo-silacyclobutene; namely, 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene /XXVII/ has been described. Thus, treatment of (o-bromobenzyl)diphenylsilane or (o-chlorobenzyl)diphenylsilane with sodium gave none of the desired /XXVII/, and only a low yield of a product tentatively identified as the

Table 2. Known 1,3-Disilacyclobutanes[a]

Formula	Name	B.p.,(m.p.),°C $[n^{25}_{D}]$	Reference
$C_2Cl_{16}Si_6$	1,1,3,3-Tetrachloro-2,2,4,4-tetrakis(trichlorosilyl)-1,3-disilacyclobutane	(276-278, sublimes)	(33,34)
$C_2H_2Cl_{10}Si_4$	1,1,3,3-Tetrachloro-2,4-bis(trichlorosilyl)-1,3-disilacyclobutane	150-152/7mm. (87-88)	(34)
$C_4H_{10}Cl_2Si_2$	1,3-Dichloro-1,3-dimethyl-1,3-disilacyclobutane	59/20mm. [1.4729]	(35)
$C_4H_{12}Si_2$	1,3-Dimethyl-1,3-disilacyclobutane	96 [1.4546]	(35)
$C_5H_{13}ClSi_2$	1-Chloro-1,3,3-trimethyl-1,3-disilacyclobutane	67.5-68/59mm. [1.4568]	(35)
$C_6H_{15}Cl_3Si_3$	1-Methyldichlorosilicomethylene-3-chloro-1,3-dimethyl-1,3-disilacyclobutane	131/20mm. [1.4901]	(35)
$C_6H_{16}Si_2$	1,1,3,3-Tetramethyl-1,3-disilacyclobutane	60.5-61/100mm. (-9 to -8.5) [1.4401]	(23,25,27, 28,30,32, 35,38,39)
$C_7H_8OSi_2$	1-Ethoxy-1,3,3-trimethyl-1,3-disilacyclobutane	71/40mm. [1.4364]	(35)
$C_8H_{20}O_2Si_2$	1,3-Diethoxy-1,3-dimethyl-1,3-disilacyclobutane	78-79/16mm. [1.4336]	(35)

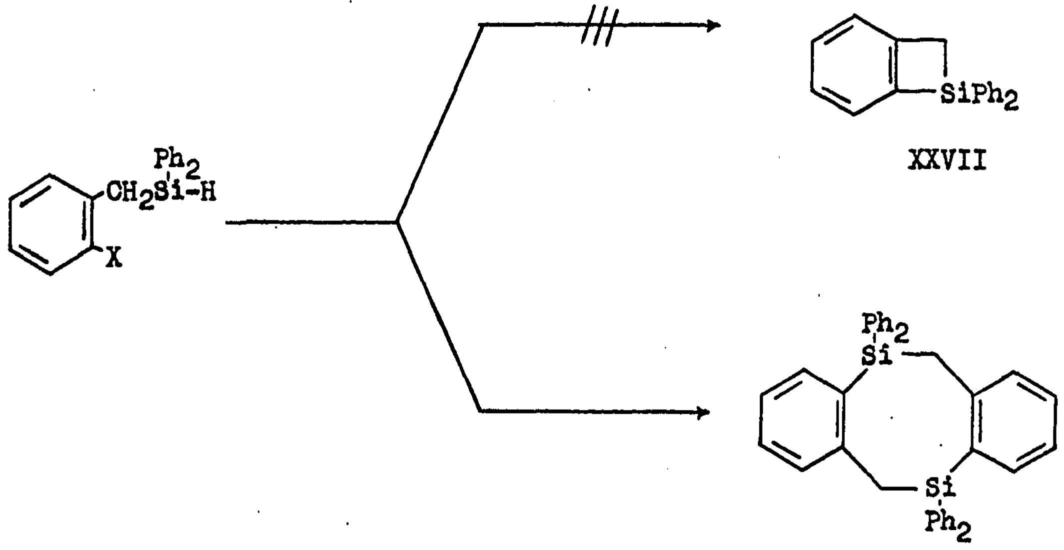
---

[a] Compounds prepared in this work not included.

Table 2. (Continued)

Formula	Name	B.p.,(m.p.),°C [$n^{25}D$]	Reference
$C_9H_{24}Si_3$	1-Trimethylsilmethyl-1,3,3-trimethyl-1,3-disilacyclobutane	112.5-113/50mm. [1.4578]	(35)
$C_{10}H_{36}OSi_4$	Bis(1,3,3-trimethyl-1,3-disilacyclobutyl)-1-siloxane	[1.4525]	(35)
$C_{16}H_{20}Si_2$	1,3-Dimethyl-1,3-diphenyl-1,3-disilacyclobutane	99/1.1mm. [1.5727]	(35)

dimer [XXVIII] could be isolated (40).



XXVII

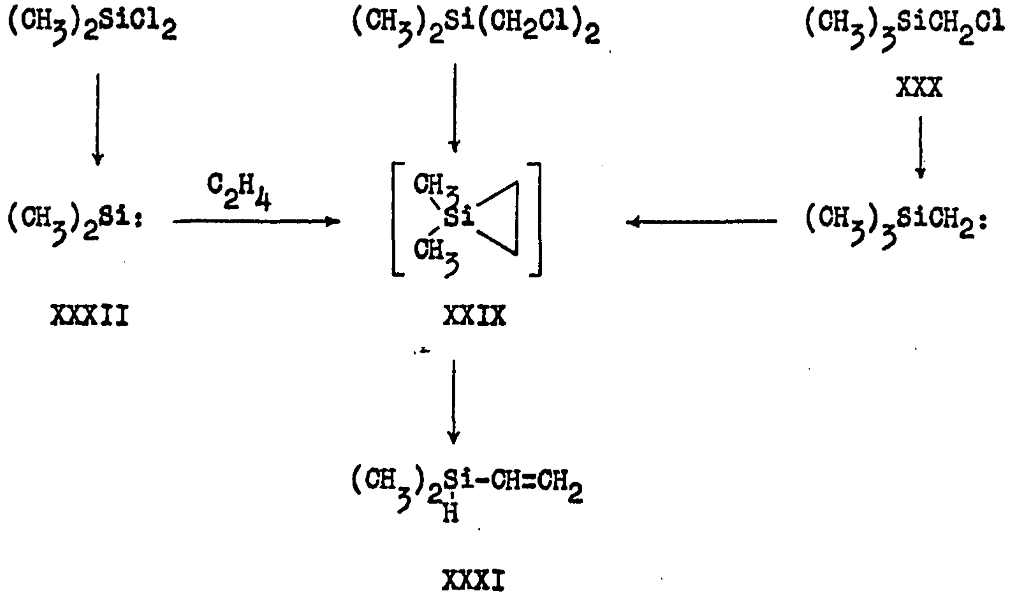
XXVIII

Three-Membered Rings

Silacyclopropanes

An attempted preparation of 1,1-dimethyl-1-silacyclopropane [XXIX] was reported by Roberts and Dev in 1951 (41). The approach used by these workers involved the reaction of bis(halomethyl)dimethylsilanes with zinc and magnesium under conditions which were known to give good yields of cyclopropanes. However, none of the desired silacyclopropane [XXIX] was isolated, and only (chloromethyl)trimethylsilane, tetramethylsilane and polymeric products could be separated. Their results indicate that bis-(halomethyl)dimethylsilanes show no tendency to undergo the Freund reaction with zinc or magnesium.

Recently, convincing evidence for the intermediate formation of [XXIX] was reported by Skell and Goldstein (42). Treatment of dichloro-



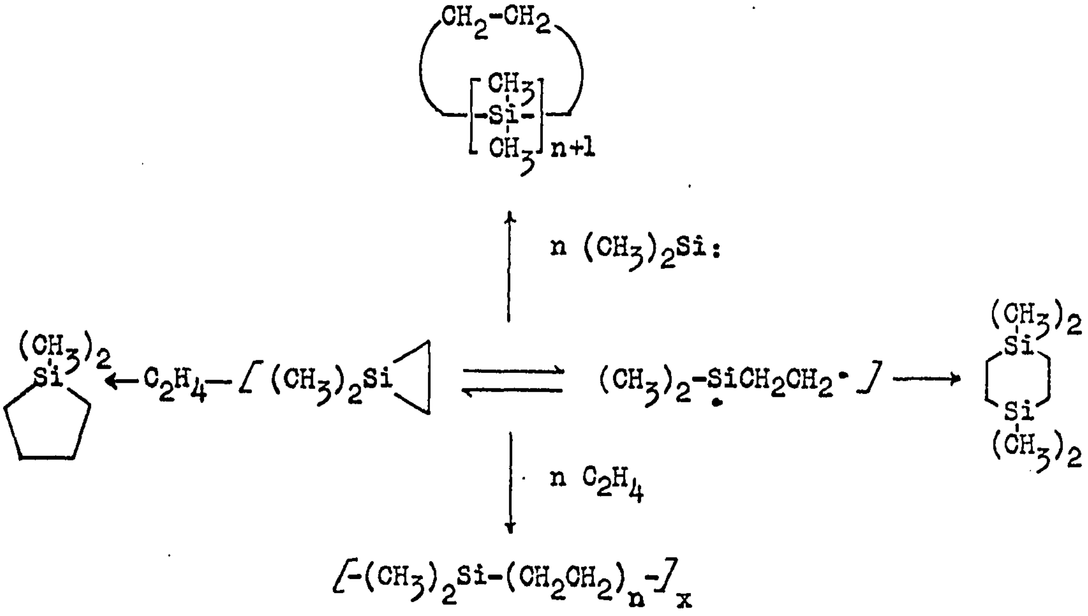
dimethylsilane, bis(chloromethyl)dimethylsilane or (chloromethyl)trimethylsilane [XXX] (carried in a stream of helium) with sodium-potassium alloy vapor at 260-280° gave dimethylvinylsilane [XXXI]. Other evidence has been presented for the existence of dimethylsilylene [XXXII] (42). Thus, silacyclopropanes appear to undergo rearrangement to vinylsilanes, analogous to the rearrangement of cyclopropane to propylene. The energy of activation for this silacyclopropane thermolysis was calculated (42) as 36 kcal. mole^{-1} and the C-Si-C angle as approximately 48°.

Urry and Connolly (43) have reported that the reaction of (chloromethyl)trimethylsilane [XXX] with alkali metals in hydrocarbon or tetrahydrofuran (THF) solvent gave a material believed to be crude [XXIX]. This crude material exhibited an infrared absorption at the same frequency (1030 cm.$^{-1}$) and with the same shape as the ring deformation mode of cyclopropane. This material could not be purified further by vacuum line, gas chromatographic or chemical separation techniques. In addition, other products formed in these reactions were best explained by postulation of the intermediate formation of the silacyclopropane [XXIX].

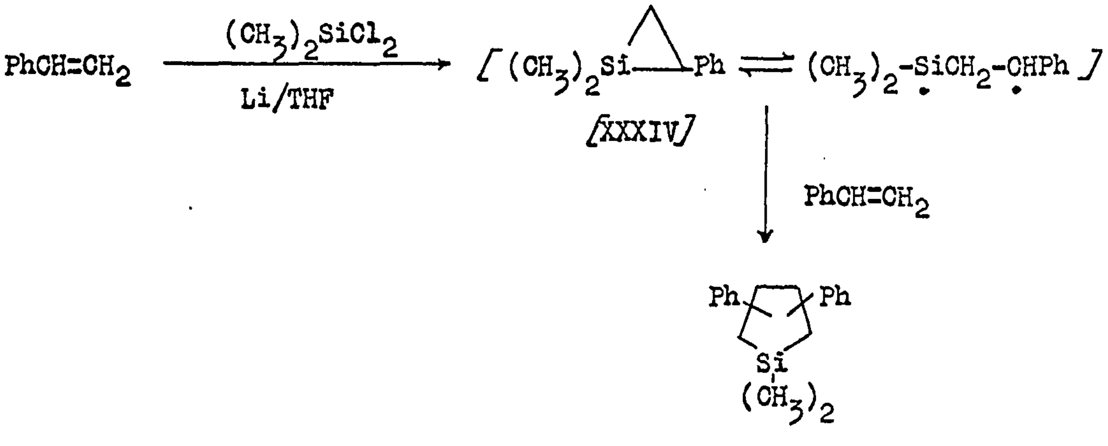
Nefedov and Manakov have proposed (44) the intermediate formation of [XXIX] in the reaction of dichlorodimethylsilane and lithium. Using

$$(CH_3)_2SiCl_2 \xrightarrow[THF]{Li} \underset{XXXII}{(CH_3)_2Si:} \xrightarrow{C_2H_4} [XXIX]$$

ethylene as a trapping agent the final products isolated in their reaction are compatible with the dimerization of [XXIX] together with its reaction with dimethylsilylene [XXXII] and ethylene. In the absence of dichlorodimethylsilane, lithium and ethylene do not react.

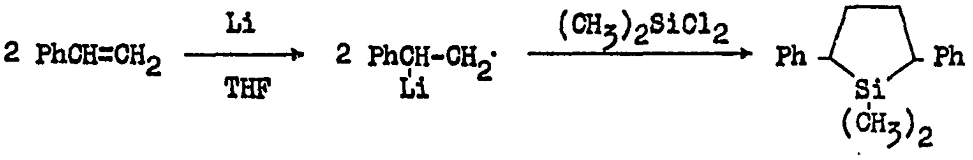


In related reactions of dichlorodimethylsilane, lithium and phenyl-substituted olefins (styrene, stilbene, tetraphenylethylene, etc.), silacyclopentane derivatives are also obtained as the final products (45).



XXXIII

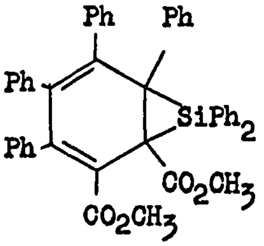
For example, with styrene the product isolated was designated as 1,1-dimethyl-x,x'-diphenyl-1-silacyclopentane [XXXIII], and the intermediate formation of the silacyclopropane [XXXIV] was suggested. However, independent workers (46,47) have shown that the final product is 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane [XXXV] (cis-trans-mixture) and that this product is best explained by a trapping of the styrene radical-anion by dichlorodimethylsilane.



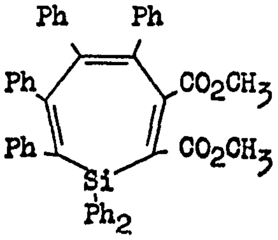
XXXV

Some evidence which is consistent with the formation of silacyclopropane intermediates by the capture of diphenylsilylene ($Ph_2Si:$) with olefins having reactive groups in the allylic position has also been reported (48).

Finally, a compound which contains either a silacyclopropane structure [XXXVI] or a silacycloheptatriene structure [XXXVII] has been isolated (49) from the ethanol-induced isomerization of dimethyl 7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene-2,3-dicarboxylate (the chemistry of 7-silanorbornadienes will be discussed in the next section). A differen-



XXXVI

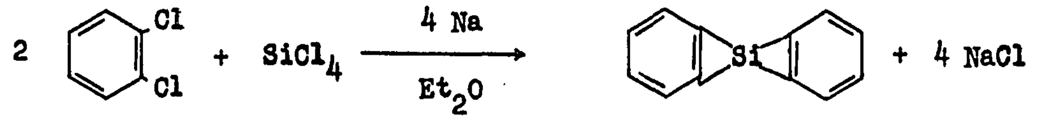


XXXVII

tiation between these two structures was not possible in view of the formal analogy to the norcaradiene $\rightleftharpoons$ cycloheptatriene problem.

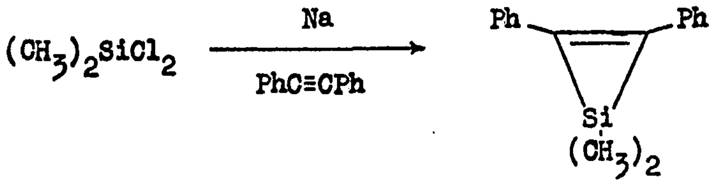
Silacyclopropenes

The preparation of a pseudo-silacyclopropene was claimed by Hart in 1887 (5). He isolated from the reaction of o-dichlorobenzene, sodium and silicon tetrachloride, a material to which he assigned the spiro structure [XXXVIII]. Attempts by Widdowson (6) to duplicate the preparation of [XXXVIII] failed, and it was suggested that this compound be deleted from the chemical literature.



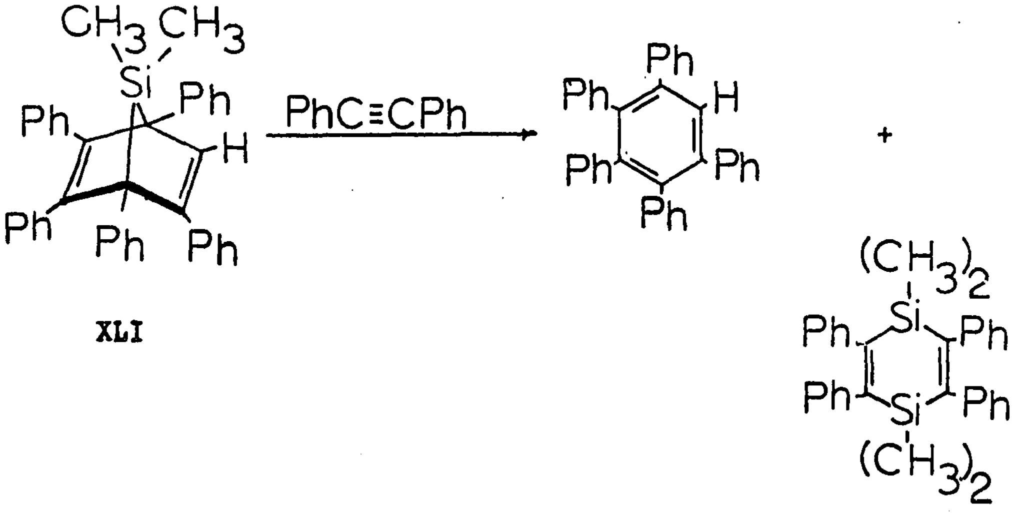
XXXVIII

In 1962, Vol'pin and co-workers (50) reported that the reaction of dichlorodimethylsilane and sodium, in the presence of diphenylacetylene, gave a product identified as 1,1-dimethyl-2,3-diphenylsilacyclopropene [XXXIX]. However, a reinvestigation of this work by West and Bailey (51) showed that both molecular weight measurements and mass spectral data indicated that the product believed to be [XXXIX] was actually the dimeric compound, 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene [XL]. Attempts to prepare [XXXIX] by the pyrolysis of



XXXIX

7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene [XLI], in the presence of diphenylacetylene, also resulted in the formation of [XL] (52). Thus, at the present time no compounds containing the silacyclopropene ring system have been isolated.



XLI

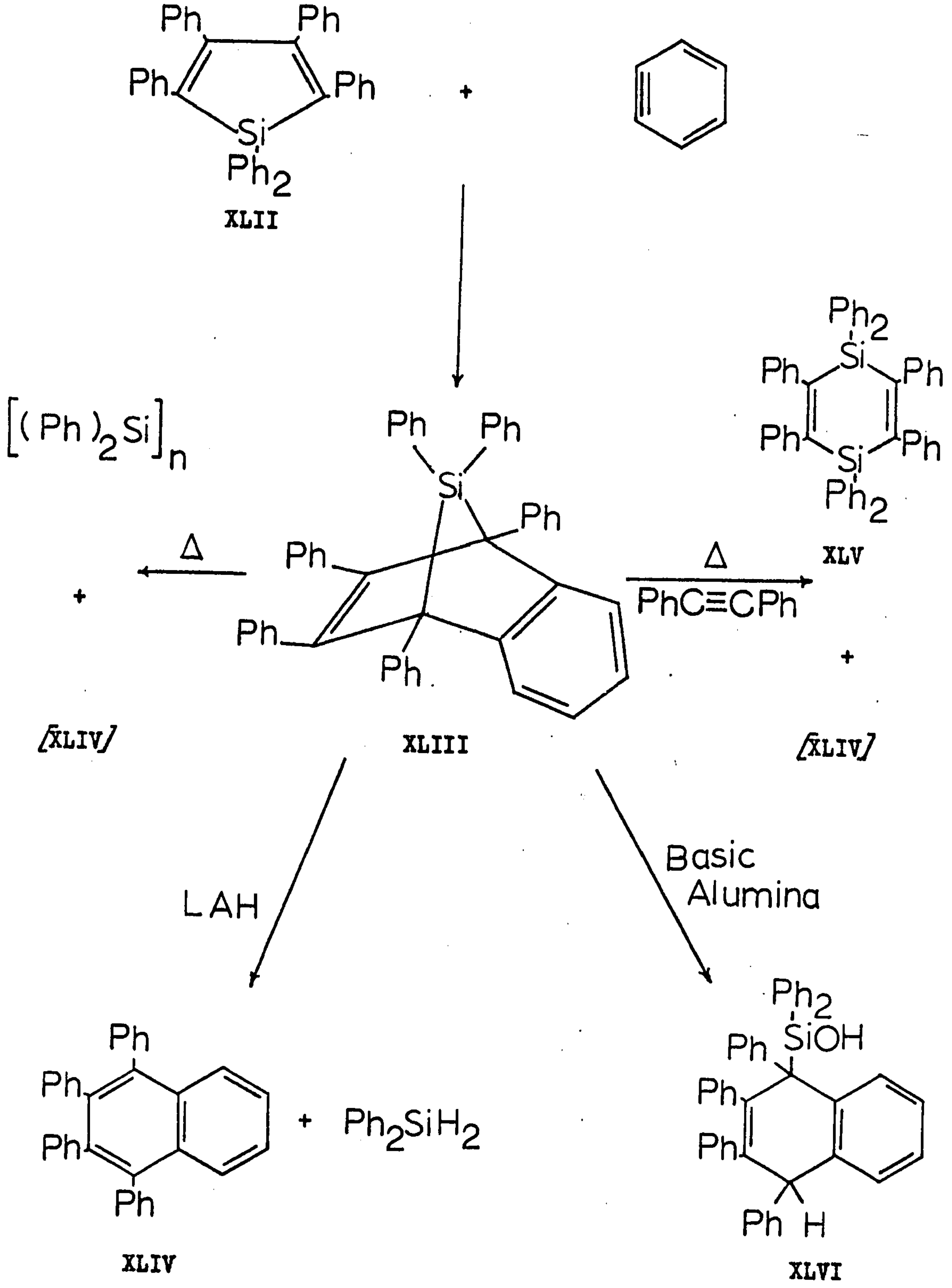
XL

Bicyclic Compounds

7-Silanorbornadienes

The 7-silanorbornadienes are the newest and probably the most unusual type of strained ring organosilicon compounds, and only a few derivatives of this type are known (49,52). In general, much of the reactivity characteristic of these bicyclic compounds is reminiscent of that observed with silacyclobutanes to be discussed later in this thesis.

The preparation of 7-silanorbornadienes is readily accomplished by a Diels-Alder reaction between silacyclopentadiene derivatives and acetylenic dienophiles. Thus, reaction of 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene [XLII] and benzyne gave 1,4-dihydro-1,2,3,4,9,9-


XLII
XLIII
Δ
[(Ph)$_2$Si]$_n$
+
[XLIV]
Δ
PhC≡CPh
XLV
+
[XLIV]
LAH
Basic Alumina
+ Ph$_2$SiH$_2$
XLIV
XLVI

hexaphenyl-1,4-silanonaphthalene /XLIII/ (49). A trivial yet more informative name for this compound is 2:3-benzo-1,4,5,6,7,7-hexaphenyl-7-silanorbornadiene. Unfortunately, I.U.P.A.C. Rules do not provide for the fusion type names with bicyclo ring names, but instead consider such systems to be bridged ortho-fused systems.[1]

Reaction of /XLIII/ with lithium aluminum hydride (LAH) under mild conditions, gave 1,2,3,4-tetraphenylnaphthalene /XLIV/ and diphenylsilane. The pyrolysis of /XLIII/ at 300° gave, in addition to /XLIV/, a diphenylsilylene polymer. When the pyrolysis reaction was carried out in the presence of diphenylacetylene, the products were /XLIV/ and 1,1,2,3,4,4,5,6-octaphenyl-1,4-disilacyclohexadiene /XLV/. Finally, when an attempt was made to chromatograph /XLIII/ on a basic alumina column an exothermic reaction ensued, and elution of the column gave the silanol /XLVI/. While similar reactions would be expected to occur with other 7-silanorbornadienes, the chemistry of these compounds has not been fully investigated.

---

[1] L. T. Capell, Chemical Abstracts Service, The Ohio State University, Columbus, Ohio. Information on the naming of some cyclic organosilicon compounds. Private communication. 1963.

EXPERIMENTAL

The solvents and reagents used in these experiments were commercially available materials. The tetrahydrofuran was dried by refluxing for 24 hours over sodium metal followed by distillation from lithium aluminum hydride immediately before use. An anhydrous grade of diethyl ether was used subsequent to storage over sodium wire.

The organosilicon halides were purchased from Dow Corning Corporation and used without further purification.

The magnesium metal (turnings) employed was a Grignard grade obtained from Mallinkrodt Chemical Works. Lithium wire was obtained from Lithium Corporation of America.

The basic alumina was purchased from Chicago Apparatus Co., Chicago, Illinois. The neutral and acidic alumina was made by Woelm and purchased from Alupharm Chemicals, New Orleans, Louisiana.

In most experiments the apparatus employed consisted of a three-necked flask of suitable size equipped with ground glass joints, fitted with a Trubore stirrer, condenser and addition funnel. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. The glassware was oven-dried and purged while hot with nitrogen.

Silicon analyses were carried out according to a published procedure (53). Color Test I was used as a qualitative test for organometallic reagents (54).

All melting points reported are uncorrected. The cited values were determined using either a Mel-Temp apparatus or an electrically heated oil-bath.

Molecular weight determinations were obtained with a vapor pressure osmometer Model 301A, manufactured by Mechrolab. Inc., Mountain View, California. For hydrogenation work a Paar hydrogenation shaker manufactured by the Paar Instrument Co., Moline, Illinois; Hydrogenation Apparatus Model CA No. 314 was employed.

Infrared spectra were routinely determined using a Perkin-Elmer, Model 21, spectrophotometer. For the identification of structual features due to the presence of silicon, the infrared correlations of Smith (55) were used. For the correlation of spectral properties of organic groups the works of Bellamy (56) and Nakanishi (57) were consulted. The intensity of the infrared bands are reported as: s (strong), m (medium), and w (weak). The ultraviolet spectra were determined with a Beckman DK-2A spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian Associates High Resolution Spectrometer, Model HR-60, operating at 60 Mc./sec.

Reactions of Octaphenylcyclotetrasilane and Related Compounds

Octaphenylcyclotetrasilane and phosphorus pentachloride

To a suspension of 6.0 g. (8.2 mmoles) of octaphenylcyclotetrasilane in 30 ml. of benzene was added 1.70 g. (8.2 mmoles) of phosphorus pentachloride (weighed out under a layer of benzene). After 25 min. of reflux the reaction mixture was homogeneous. Concentration of the solution and addition of petroleum ether (b.p. 60-70°) gave 6.0 g. (92%) of 1,4-dichlorooctaphenyltetrasilane, m.p. 183-186°. Recrystallization from benzene-petroleum ether (b.p. 60-70°) gave 5.8 g. of pure product, m.p. 186-187° (89%). A mixture melting point with an authentic sample (58) was not depressed and the infrared spectra were superimposable.

Octaphenylcyclotetrasilane and sulfuryl chloride

Six grams (8.2 mmoles) of octaphenylcyclotetrasilane and 1.21 g. (9.0 mmoles) of sulfuryl chloride were refluxed in 40 ml. of benzene. Subsequent to 30 min. of refluxing, the homogeneous reaction mixture was filtered and concentrated. Addition of petroleum ether (b.p. 60-70°) gave 5.5 g. of 1,4-dichloroootaphenyltetrasilane, m.p. 184-186° (83.5%).

Octaphenylcyclotetrasilane and thionyl chloride

A mixture of 6.0 g. (8.2 mmoles) of octaphenylcyclotetrasilane and 1.10 g. (9.0 mmoles) of thionyl chloride in 50 ml. of benzene was refluxed for 5 hours. Filtration gave a trace of recovered octaphenylcyclotetrasilane. Concentration of the filtrate and addition of petroleum ether (b.p. 60-70°) gave 2.0 g. (62%) of crude product, m.p. 178-186°. Recrystallization raised the melting point to 184-186° (36%).

1,4-Diacetoxyoctaphenyltetrasilane

From octaphenylcyclotetrasilane and mercuric acetate. Fifteen grams (0.02 mole) of octaphenylcyclotetrasilane and 1.31 g. (0.041 mole) of mercuric acetate in *ca.* 150 ml. of sodium-dried benzene were heated at reflux temperature of the solvent for 24 hours. A small amount of mercury was observed on the bottom of the reaction flask. The tan reaction mixture was cooled and filtered. Evaporation of the solvent gave 16.62 g. (95.8%) of a light-yellow solid, m.p. 212-234°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60-70°) gave 13.1 g. (79%) of a white solid, m.p. 233-235°. This material was heated under reduced pressure at 100° for 1 hour prior to analysis.

Anal. Calcd. for $C_{52}H_{46}O_4Si_4$: C, 73.79; H, 5.43; Si, 13.26. Found: C, 73.97, 73.98; H, 5.63, 5.54; Si, 13.20, 13.15.

The infrared spectrum showed the bands at 5.8 and 8.2 microns characteristic of the acetate group. The n.m.r. spectrum gave a ratio of aromatic to aliphatic protons of 6.57 (calculated value, 6.67). The methyl groups gave the expected singlet which appeared at 8.28τ.

From 1H, 4H-octaphenyltetrasilane and mercuric acetate. A mixture of 3.0 g. (4.1 mmole) of 1*H*, 4*H*-octaphenyltetrasilane (48) and 2.58 g. (8.2 mmole) of mercuric acetate in 100 ml. of glacial acetic acid was refluxed for 12 hours. Filtration of the cooled reaction mixture gave 1.3 g. (79%) of mercury and 3.3 g. (95.5%) of a white solid, m.p. 205-230°. Recrystallization of this material from benzene-petroleum ether (b.p. 60-70°) afforded 2.5 g. (72%) of product, m.p. 233-235°. A mixture melting point with an authentic sample of 1,4-diacetoxyoctaphenyltetrasilane was not depressed and the infrared spectra were superimposable.

From 1,4-dichlorooctaphenyltetrasilane and acetic anhydride. A mixture of 5.0 g. (6.25 mmole) of 1,4-dichlorooctaphenyltetrasilane in 50 ml. of acetic anhydride was refluxed for 24 hours. Filtration gave 4.0 g. (80%) of unreacted starting material, m.p. 185-187° (mixture m.p.). Evaporation of the solvent from the filtrate gave 0.85 g. (16%)

of white solid, m.p. 230-235°. Recrystallization from benzene-petroleum ether (b.p. 60-70°) afforded 0.75 g. (14%) of product, m.p. 233-235° (mixture m.p.).

Hydrolysis of 1,4-diacetoxyoctaphenyltetrasilane

A mixture of 3.0 g. (3.5 mmoles) of 1,4-diacetoxyoctaphenyltetrasilane and 50 ml. of ca. 0.5N hydrochloric acid was refluxed for 48 hours. Filtration gave 2.5 g. (91.2%) of white solid, m.p. 230-234°. Recrystallization from benzene-petroleum ether (b.p. 60-70°) raised the melting point to 234-236° (87%). A mixture melting point with an authentic sample of octaphenyloxacyclopentasilane was not depressed. The infrared spectrum showed the strong band at 10.45 microns previously reported for this strained cyclic siloxane (37).

Hexaphenyldisilane and mercuric acetate (attempted)

A mixture of 5.2 g. (0.01 mole) of hexaphenyldisilane and 6.37 g. (0.02 mole) of mercuric acetate in 100 ml. of sodium-dried benzene was refluxed for 72 hours. Filtration gave 8.0 g. of solid, m.p. 270° dec. This material was extracted with hot water and filtered to give 5.0 g. (96%) of recovered starting material, m.p. 365-367° (mixture m.p.).

Decaphenylcyclopentasilane and mercuric acetate (attempted)

A mixture of 10.0 g. (0.011 mole) of decaphenylcyclopentasilane (59) and 7.01 g. (0.022 mole) of mercuric acetate in 100 ml. of sodium-dried benzene was refluxed for 72 hours. Filtration gave 11.0 g. of solid, m.p. 275° dec. Extraction of this material with acetone followed by filtration gave 8.5 g. (85%) of recovered starting material, m.p. 456-462° (mixture m.p.). No other pure materials could be isolated.

(2,2-Dicarbethoxypropyl)ethoxydimethylsilane and Related Compounds

(2,2-Dicarbethoxypropyl)ethoxydimethylsilane

Sodium, 7.3 g. (0.318 g.-atom), was treated with 100 ml. of absolute ethanol. To the cooled mixture was added 152.9 g. (0.954 mole) of diethyl malonate (200% excess). The mixture was then heated at reflux temperature as 25 g. (0.0159 mole) of bis(chloromethyl)dimethylsilane in 40 ml. of absolute ethanol was added slowly. Subsequent to refluxing for 24 hours, 100 ml. of ethanol was removed by distillation and replaced with 200 ml. of water. The mixture was extracted several times with ether and dried over sodium sulfate. Following the removal of solvent and excess diethyl malonate by distillation, there was obtained 28.5 g. (92.5%, based on the g.-atoms of sodium employed), of product, b.p. 79-81°/0.25 mm., $n^{20}D$ 1.4345, d_{20}^{20} 1.0101 (lit. value (14) b.p. 141-143°/15 mm., $n^{25}D$ 1.4318, d_4^{25} 0.997).

The infrared spectrum of this compound as a capillary cell contained the pertinent absorption bands listed in Table 3.

The reaction residue consisted of 3.5 g. of red oil. Distillation of this residue under vacuum gave a small amount of material (ca. 0.5 g.), b.p. 140-142°/0.005 mm., $n^{20}D$ 1.4500. Benkeser and Bennett (10) have reported the isolation of a material believed to be sym-tetramethyldi-(2,2-dicarbethoxy)propyldisiloxane, b.p. 155-161°/0.05 mm., $n^{24}D$ 1.4468. The infrared spectrum of this material contained a band at 9.55 microns indicative of the Si-O-Si linkage and was tentatively identified as the above siloxane.

Table 3. Infrared Spectral Data for (2,2-Dicarbethoxypropyl)ethoxydimethylsilane

Band Position (microns)	Intensity	Characteristic
3.35, 3.44	m,w	Aliphatic C-H
5.78	s	CO_2R
7.80	m	-----
8.00	m	$Si-CH_3$
8.20	s	CO_2R
8.50, 8.62	m,m	Possibly Si-alkyl
9.12, 9.27, 10.58	s,m,m	$Si-O-O_2H_5$
11.94, 12.67	s,m	$Si-CH_3$

Hydrolysis of (2,2-dicarbethoxypropyl)ethoxydimethylsilane

A mixture of 3.0 g. (0.1 mole) of sodium hydroxide, 5.0 g. (0.0172 mole) of (2,2-dicarbethoxypropyl)ethoxydimethylsilane and 50 ml. of ethanol was refluxed for 5 hours. The precipitated potassium salt was removed by filtration and the filtrate discarded. The crude potassium salt was dissolved in 10 ml. of warm water and made just acidic with concentrated hydrochloric acid. The acidified solution was extracted with four 30 ml. portions of ether and dried over sodium sulfate. Evaporation of the solvent gave a white solid which was taken up in ethyl acetate. Addition of petroleum ether (b.p. 60-70°) gave 1.76 g. (62%) of sym-bis(2,2-dicarboxypropyl)tetramethyldisiloxane, m.p. 133-135° dec. (lit. value (10) m.p. 131-133° dec.).

The infrared spectrum of this compound as a potassium bromide pellet contained the pertinent absorption bands listed in Table 4.

Table 4. Infrared Spectral Data for sym-Bis(2,2-dicarboxypropyl)tetramethyldisiloxane

Band Position (microns)	Intensity	Characteristic
2.75 to 4.15	broad	CO_2H
5.76, 5.82	s,s	CO_2H
7.80	m	-----
8.00	m	$Si-CH_3$
8.40	m	Possibly Si-alkyl
9.65	s	Si-O-Si
11.91, 12.35, 12.55	s,s,m	$Si-CH_3$

1,1,2-Triphenyl-1-silacyclobutane and Related Compounds

(3-Phenylpropyl)diphenylsilane

The Grignard reagent prepared from 119.4 g. (0.6 mole) of 3-phenylpropyl bromide and 24.32 g. (1.0 g.-atom) of magnesium in ca. 300 ml. of ether was added to 113.3 g. (0.57 mole) of chlorodiphenylsilane in 200 ml. of ether. Color Test I was negative immediately after addition. The reaction mixture was poured upon crushed ice acidified with 5<u>N</u> hydrochloric acid. Subsequent to extraction with ether and drying over anhydrous sodium sulfate, the solvent was removed with the aid of a steam-bath. Distillation of the residual oil gave 131 g. (76%) of clear colorless liquid, b.p. 147-150°/0.02 mm., $n^{20}D$ 1.5897.

<u>Anal</u>. Calcd. for $C_{21}H_{22}Si$: Si, 9.29; Found: Si, 9.10, 9.15.

The infrared spectrum as a capillary cell showed the prominent absorption bands listed in Table 5.

Table 5. Infrared Spectral Data for (3-Phenylpropyl)diphenylsilane

Band Position (microns)	Intensity	Characteristic
3.25, 3.30	w,w	Aromatic C-H
3.40, 3.48	w,w	Aliphatic C-H
4.72	s	Si-H
6.24, 6.30, 6.67	w,w,m	Ph-
6.87	m	Possibly Si-alkyl
7.00	s	Ph-
8.45, 8.66	w,w	Possibly Si-alkyl
8.99	s	Si-Ph
9.40, 9.74, 10.04	w,w,w	Ph-
12.43	s	Si-H

Bromo(3-bromo-3-phenylpropyl)diphenylsilane (attempted)

A solution of 15.1 g. (0.05 mole) of (3-phenylpropyl)diphenylsilane and 17.81 g. (0.1 mole) of N-bromosuccinimide in 125 ml. of carbon tetrachloride was stirred for 5 min. At this time, a considerable amount of heat was evolved and the mixture turned bright orange. After the initial reaction had subsided, the orange mixture was irradiated for 10-15 min. with a General Electric Sun Lamp. The orange color disappeared and the mixture turned light yellow. Subsequent to cooling and filtration under nitrogen, there was obtained 10.9 g. (94%) of succinimide, m.p. 124-126°. The solvent was removed from the filtrate under reduced pressure using a maximum oil-bath temperature of 50°. There was obtained 22.5 g. (98%) of light yellow oil which could not be induced to crystallize. Except for the absence of absorption bands at 4.72 and 12.43 microns, the infrared spectrum of the crude dibromo-compound as a capillary cell was identical to that of (3-phenylpropyl)diphenylsilane.

Distillation of the crude dibromo-compound resulted in a considerable amount of decomposition. However, there was obtained 5.0 g. of liquid, b.p. 172-173°/0.02 mm. which solidified on cooling, m.p. 77-78°. This material was identified on the basis of its silicon analysis and its infrared and n.m.r. spectra as bromo(3-phenyl-2-propenyl)diphenylsilane (yield 24.3%).

Anal. Calcd. for $C_{21}H_{29}BrSi$: Si, 7.41; Found: Si, 7.60, 7.70.

The infrared spectrum as a capillary cell showed no absorptions due to the Si-H group. The spectrum contained a weak band at 6.08 microns characteristic of the phenyl-conjugated double bond stretching vibrations and also a strong absorption at 10.44 microns indicative of a trans-double bond.

Reaction of crude (undistilled) bromo(3-bromo-3-phenylpropyl)diphenylsilane with magnesium (attempted)

The crude bromo(3-bromo-3-phenylpropyl)diphenylsilane obtained from 15.1 g. (0.05 mole) of (3-phenylpropyl)diphenylsilane and 17.8 g. (0.1 mole) of N-bromosuccinimide was dissolved in 100 ml. of ether and added to 2.43 g. (0.2 g.-atom) of magnesium and 10 ml. of ether containing a trace of iodine. The mixture was refluxed for 48 hours. The ether was removed by distillation and replaced as needed with petroleum ether (b.p. 60-70°). The solution was then filtered under nitrogen. The solvent was removed under vacuum and the residual oil was distilled to give 4.5 g. (24%) of liquid, b.p. 177-178°/0.4 mm. This material solidified upon cooling (m.p. 77-78°) and a mixture melting point with a known sample of bromo(3-phenyl-2-propenyl)diphenylsilane was not depressed. In addition, the infrared spectra were superimposable.

1,1,2-Triphenyl-1-silacyclobutane

The crude bromo(3-bromo-3-phenylpropyl)diphenylsilane obtained from 60.4 g. (0.02 mole) of (3-phenylpropyl)diphenylsilane and 71.34 g. (0.04 mole) of N-bromosuccinimide was dissolved in 250 ml. of tetrahydrofuran (THF). The THF solution was added slowly to 7.3 g. (0.3 g.-atom) of magnesium. A brown color developed as the exothermic reaction proceeded. After stirring for 24 hours, the mixture was decanted from excess magnesium into a mixture of ice and 5N hydrochloric acid. Subsequent to extraction with ether and drying over anhydrous sodium sulfate, the solvents were removed on a steam-bath to give a brown viscous oil. Distillation gave 36.5 g. (60%) of viscous liquid, b.p. 155-158°/0.03 mm. Upon cooling, this material solidified, m.p. 64-66°. Recrystallization from petroleum ether (b.p. 28-38°) gave 31 g. (51.6%) of pure material, m.p. 67-68°.

Anal. Calcd. for $C_{21}H_{20}Si$: C, 84.05; H, 6.66; Si, 9.32; Mol. Wt. 300.3; Found: C, 84.29, 84.50; H, 6.63, 6.74; Si, 9.40, 9.43; Mol. Wt. 304.3 (osmometer in benzene).

Pure 1,1,2-triphenyl-1-silacyclobutane was best obtained by passing a petroleum ether (b.p. 60-70°) solution of crude material through an acidic or neutral alumina column. Material obtained in this manner was stable for months. However, crude material tended to decompose slowly and carbonyl absorptions could be detected in the infrared spectra of the resulting mixtures. Although the mechanism of this decomposition was not investigated, it appears to be an oxidative process.

The infrared spectrum of pure 1,1,2-triphenyl-1-silacyclobutane in carbon tetrachloride and in carbon disulfide was quite similar to that of (3-phenylpropyl)diphenylsilane except for the absence of Si-H absorption bands. In addition, the spectrum of 1,1,2-triphenyl-1-silacyclobutane contained a strong absorption at 11.52 microns not present in (3-phenylpropyl)diphenylsilane.

Reaction of 1,1,2-triphenyl-1-silacyclobutane with lithium aluminum hydride (LAH) in ether

One gram (3.3 mmole) of 1,1,2-triphenyl-1-silacyclobutane dissolved in 30 ml. of ether was slowly added to an excess (0.76 g., 0.02 mole) of LAH and 20 ml. of ether. The mixture was stirred for 1 hour and then hydrolyzed with 5N hydrochloric acid. Subsequent to the usual work-up, evaporation of the solvent gave 0.92 g. (92%) of clear oil, $n^{20}D$ 1.5892. The infrared spectrum of this material was superimposable with that of a pure sample of (3-phenylpropyl)diphenylsilane.

When the above reaction was repeated using refluxing tetrahydrofuran as solvent, secondary cleavages became more prominent and the yield of (3-phenylpropyl)diphenylsilane was reduced to 41%, b.p. 130-131°/0.005 mm., $n^{20}D$ 1.5896.

Chromatography of 1,1,2-triphenyl-1-silacyclobutane (attempted)

A petroleum ether (b.p. 60-70°) solution containing 0.8 g. (2.7 mmole) of 1,1,2-triphenyl-1-silacyclobutane (m.p. 67-68°) was adsorbed on an alumina column. Elution with the same solvent and also with cyclohexane and benzene did not yield any products. Elution with ethanol gave a clear viscous oil which could not be induced to crystallize. The infrared spectrum as a capillary cell showed the absence of Si-H and Si-O-Si absorption bands. The presence of bands at 3.0 and 12.0 microns characteristic of -O-H and Si-O- stretch, respectively, indicated the presence of an Si-OH group. The remainder of the spectrum was quite similar to that of (3-phenylpropyl)diphenylsilane. In view of the anticipated high boiling point of this compound and the possibility of decomposition, no attempt was made to purify this material further.

(3-Phenylpropyl)triphenylsilane

A solution of phenyllithium prepared from 3.14 g. (0.02 mole) of bromobenzene in 50 ml. of ether was added to 5 g. (0.0165 mole) of (3-phenylpropyl)diphenylsilane in 20 ml. of ether. After stirring for 1 hour, the mixture was acid hydrolyzed using 5N hydrochloric acid. Following the usual work-up there was obtained a viscous oil. Chromatography on alumina gave, using petroleum ether (b.p. 60-70°) as eluent, 6.0 g. of oil which solidified upon treatment with ethanol, m.p. 69-71°. Recrystallization from the same solvent gave 5.4 g. (87.3%) of solid product, m.p. 70-71°.

Anal. Calcd. for $C_{27}H_{26}Si$: Si, 7.42; Found Si, 7.35, 7.40.

The infrared spectrum of this material in carbon tetrachloride did not contain absorption bands characteristic of the Si-H group and was very similar to that of (3-phenylpropyl)diphenylsilane.

Reaction of 1,1,2-triphenyl-1-silacyclobutane with lithium

A solution of 2 g. (6.7 mmoles) of 1,1,2-triphenyl-1-silacyclobutane and 40 ml. of tetrahydrofuran was slowly added to 0.42 g. (0.06 g.-atom) of finely cut lithium wire. A yellow color developed and the resulting mixture was allowed to stir for 3 hours. At this time, Color Test I was still negative. Subsequent to acid hydrolysis and the usual work-up, the solvent was removed on a steam-bath to give a non-crystallizing polymeric oil. The infrared spectrum in carbon tetrachloride showed no

Si-H absorption bands. The spectrum was in other respects quite similar to that of (3-phenylpropyl)diphenylsilane.

Reaction of 1,1,2-triphenyl-1-silacyclobutane with phenyllithium

1:6 Ratio. One gram (3.3 mmole) of 1,1,2-triphenyl-1-silacyclobutane in 25 ml. of ether was slowly added to 0.02 mole of phenyllithium prepared in ether. The ether solution began to reflux gently. After stirring for 1 hour, hydrolysis was effected by pouring the reaction mixture upon crushed ice acidified with 5N hydrochloric acid. Subsequent to the usual work-up, there was obtained an oil which was chromatographed on an alumina column. Elution with petroleum ether (b.p. 60-70°) gave only a trace (less than 1%) of (3-phenylpropyl)triphenylsilane identified by mixture melting point and comparison of infrared spectra. Further elution afforded only a glass-like polymeric material. The infrared spectrum of this material in carbon tetrachloride showed no Si-H absorptions and was very similar to that of the polymeric material obtained from the reaction of 1,1,2-triphenyl-1-silacyclobutane with lithium.

1:9 Ratio. A solution of 2.0 g. (6.7 mmole) of 1,1,2-triphenyl-1-silacyclobutane in 25 ml. of ether was slowly added to 0.06 mole of phenyllithium in *ca.* 50 ml. of ether. The mixture was allowed to stir for 3 hours and then worked up as described above. Chromatography of the reaction residue gave 1.0 g. (40%) of pure (3-phenylpropyl)triphenylsilane, m.p. and mixture m.p. 70-71°.

Reaction of 1,1,2-triphenyl-1-silacyclobutane with hydrogen

At room temperature and 45 p.s.i.g. Two grams (6.7 mmoles) of 1,1,2-triphenyl-1-silacyclobutane and 0.5 g. (25% by weight) of 10% palladium-on-charcoal catalyst was added to 50 ml. of cyclohexane. The mixture was placed in a Paar hydrogenation shaker and the system was flushed several times with hydrogen. Finally, the pressure was adjusted to ca. 45 p.s.i.g. and the mixture was shaken for 18 hours. Filtration of the resulting mixture followed by removal of the solvent gave a viscous oil. The infrared spectrum of this oil in carbon tetrachloride contained a weak absorption at 4.72 microns indicative of the Si-H groupings. The remainder of the spectrum was very similar to that of the starting material and contained a strong 11.52 micron band.

At 75° and 45 p.s.i.g. The recovered material from above was redissolved in cyclohexane and prepared as described above using fresh catalyst. The pressure was adjusted to 45 p.s.i.g. and heated at 70-80° for 24 hours. After work-up as described above, the infrared spectrum of the residual oil showed only a slight increase in intensity of the 4.72 micron band. This increase was accompanied by a slight decrease in intensity of the 11.52 micron band.

Reaction of 1,1,2-triphenyl-1-silacyclobutane with phenylmagnesium bromide (attempted)

A solution of 1 g. (3.3 mmole) of 1,1,2-triphenyl-1-silacyclobutane and 20 ml. of tetrahydrofuran (THF) was added to 0.4 mole of phenylmagnesium bromide prepared in THF. The mixture was stirred for 24 hours and then hydrolyzed with 5N hydrochloric acid. Extraction with ether followed by removal of the solvents on a steam-bath gave a viscous oil. Treatment of the oil with ethanol gave 0.85 (85%) of solid, m.p. 66-68°. A mixture melting point with an authentic sample of 1,1,2-triphenyl-1-silacyclobutane was not depressed, and the infrared spectra were superimposable.

4-Phenyl-1-butanol

The Grignard reagent from 91.5 g. (0.5 mole) of 2-phenylethyl bromide and 19.5 g. (0.8 g.-atom) of magnesium prepared in 250 ml. of ether was cooled by the use of an ice-bath. A three-fold excess of ethylene oxide dissolved in 100 ml. of ether was slowly introduced with rapid stirring. After stirring for 2 hours and allowing the mixture to warm to room temperature, Color Test I was negative. Acid hydrolysis followed by the usual work-up and distillation of the resulting oil gave 36.5 g. (49%) of product, b.p.88-90°/0.3 mm., $n^{20}D$ 1.5210 [lit. value (60), b.p. 125-126° (8.0 mm.), $n^{20}D$ 1.5220]. The infrared spectrum of this material as a capillary cell contained strong bands at 3.0 and 9.4 microns characteristic of the -C-H and -C-OH stretch, respectively.

1-Bromo-4-phenylbutane

To 36.35 g. (0.242 mole) of 4-phenyl-1-butanol was added 54.2 g. (0.2 mole) of phosphorus tribromide. The reaction mixture was kept at ice-bath temperature during the addition. Following the addition, the mixture was allowed to come to room temperature and then refluxed for 1 hour at ca. 100°. The solution was cooled, acid hydrolyzed , extracted with ether and the organic layer dried over anhydrous sodium sulfate. Evaporation of the solvents and distillation of the residual oil afforded

36.7 g. (71.5%) of product, b.p. 68-69°/0.1 mm., $n^{20}D$ 1.5397 [lit. value (60), b.p. 129-130°/12 mm., $n^{20}D$ 1.5400]. The infrared spectrum of this material as a capillary cell showed an absence of the characteristic -OH bands.

(4-Phenylbutyl)diphenylsilane

An ether solution of 0.085 mole of 4-phenylbutylmagnesium bromide was added to 18.62 g. (0.085 mole) of chlorodiphenylsilane in 150 ml. of ether. Color Test I was negative immediately after addition. Acid hydrolysis followed by the usual work-up gave a viscous oil. Distillation of this crude material gave 21.6 g. (80%) of clear colorless product, b.p. 136-138°/0.004 mm., $n^{20}D$ 1.5792.

Anal. Calcd. for $C_{22}H_{24}Si$: Si, 9.17; Found: Si, 9.16, 9.10.

The infrared spectrum of this material as a capillary cell was very similar to that of the previously described (3-phenylpropyl)diphenylsilane.

1,1,2-Triphenyl-1-silacyclopentane

A solution of 18.95 g. (0.06 mole) of (4-phenylbutyl)diphenylsilane and 21.4 g. (0.12 mole) of N-bromosuccinimide in 100 ml. of carbon tetrachloride was stirred in a 250 ml. three-necked round-bottomed flask. After several minutes, a yellow-orange color developed as the exothermic reaction proceeded. After the initial reaction had subsided, the orange reaction mixture was allowed to cool and then irradiated with a General Electric Sun Lamp. Within several minutes, the orange color had disappeared. The reaction mixture was cooled and filtered under nitrogen. Evaporation of the solvent under vacuum gave the crude bromo(4-bromo-4-

phenylbutyl)diphenylsilane. The infrared spectrum of this crude material did not contain bands indicative of the Si-H group.

The crude (undistilled) dibromo compound was diluted with 200 ml. of tetrahydrofuran (THF) and added to 2.19 g. (0.09 g.-atom) of magnesium in 15 ml. of THF. The mixture was stirred for 24 hours. Acid hydrolysis followed by the usual work-up gave a viscous oil. Distillation gave 10 g. (53%) of product, b.p. 163-165° (0.06 mm.) which solidified upon standing, m.p. 85-86°. A recrystallization from n-propanol did not alter the melting point.

Anal. Calcd. for $C_{22}H_{22}Si$: C, 84.10; H, 7.00; Si, 8.94; Found: C, 84.50, 84.60; H, 7.11, 7.26; Si, 8.88, 8.65.

The infrared spectrum of this material was quite similar to the four-membered ring homolog; however, there was no maximum at 11.52 microns previously observed in the spectrum of the latter compound. It should be mentioned that there was an additional band present in the spectrum of 1,1,2-triphenyl-1-silacyclopentane at 9.60 microns. This band was sharp and of medium intensity and was absent in the spectrum of 1,1,2-triphenyl-1-silacyclobutane.

Chromatography of a pure sample of 1,1,2-triphenyl-1-silacyclopentane on an alumina column gave a near quantitative recovery of material of equal purity.

Reaction of 1,1,2-triphenyl-1-silacyclopentane with lithium aluminum hydride (LAH) (attempted)

A mixture of 1.0 g. (3.2 mmoles) of 1,1,2-triphenyl-1-silacyclopentane and 0.3 g. (8.0 mmoles) of LAH in 30 ml. of tetrahydrofuran was refluxed for 8 hours. Acid hydrolysis followed by the usual work-up gave 0.9 g. (90%) of solid, m.p. 83-86°. A mixture melting point with the starting material was not depressed and the infrared spectra were superimposable.

2,3-Benzo-1-silacyclobut-2-enes and Related Compounds

o-Bromobenzyl bromide (CAUTION LACHRYMATOR)

N-Bromosuccinimide (NBS) 178 g. (1.0 mole), and 171 g. (1.0 mole) of *o*-bromotoluene in *ca.* 600 ml. of carbon tetrachloride was irradiated with a General Electric Sun Lamp. Refluxing occurred shortly thereafter as the exothermic reaction proceeded. The reaction mixture was cooled, filtered under nitrogen and the solvent removed with the aid of a steam-bath. Distillation of the residual oil gave 160 g. of product, b.p. 66-69°/0.2 mm. (64%) [lit. value (61) b.p. 136°/16 mm.].

Diphenyl-o-tolylsilane

The Grignard reagent prepared from 137 g. (0.8 mole) of *o*-bromotoluene and 24.32 g. (1.0 g.-atom) of magnesium in 350 ml. of ether, was added to 166.2 g. (0.76 mole) of chlorodiphenylsilane in 150 ml. of the same solvent. Color Test I was negative immediately after addition. Acid hydrolysis followed by the usual work-up gave a viscous oil. The oil was dissolved in ethanol and seeded with a known sample (62) of this material to give 179 g. (85.6%) of solid product, m.p. 44-46°. This material was identified by mixture melting point and comparison of the infrared spectrum with that of a known sample.

The infrared spectrum of diphenyl-o-tolylsilane in both carbon tetrachloride and carbon disulfide showed the absorption bands listed in Table 6.

Table 6. Infrared Spectral Data for Diphenyl-o-tolylsilane

Band Position (microns)	Intensity	Characteristic
3.26, 3.30	m,m	Aromatic C-H
3.42, 3.50	w,w	Aliphatic C-H
4.71	s	Si-H
6.31, 6.74, 6.81	w,w,w	Ph-
6.90	m	Possibly Si-alkyl
7.01, 7.81, 7.95	s,w,w	Ph-
8.33, 8.44, 8.65	w,w,w	Possibly Si-alkyl
8.90 (shoulder)	s	------
9.00	s	Si-Ph
9.32, 9.74, 10.03	w,w,w	Ph-
12.20, 12.45, 12.67	s,s,s	Si-H
13.45	s	o-Disubstitution
13.70, 14.07, 14.38	s,s,s	Ph-

Bromo(α-bromo-o-tolyl)diphenylsilane

A mixture of 27.4 g. (0.1 mole) of diphenyl-o-tolylsilane, 35.6 g. (0.2 mole) of NBS and 250 ml. of carbon tetrachloride was stirred in a one-liter three-necked round-bottomed flask. After an induction period, which varied slightly from run to run (20 min.) an exothermic reaction occurred and an orange color developed. When the initial heat of reaction had dissipated the mixture was irradiated with a General Electric Sun Lamp. The orange color faded and the final reaction mixture was yellow-white. Subsequent to cooling, filtration under nitrogen gave 21 g. (90.5%) of succinimide, m.p. 124-126° (mixture m.p.). The solvent was completely evaporated from the filtrate to give a viscous oil which solidified upon treatment with sodium-dried petroleum ether (b.p. 60-70°). Recrystallization from the same solvent gave 37 g. (86%) of pure product, m.p. 93-94°.

Anal. Calcd. for $C_{19}H_{16}Br_2Si$: Si, 6.50; Found: 6.50, 6.71.

The infrared spectrum of this material in carbon tetrachloride showed the absence of Si-H absorptions and was quite similar to that of diphenyl-o-tolylsilane.

The purification of this readily hydrolyzable material was found to be tedious and generally unnecessary. In future reactions involving this dibromo compound the crude product was used immediately after its preparation.

o-Bromobenzyldiphenylsilane

The Grignard reagent, o-bromobenzylmagnesium bromide (63) prepared from 50 g. (0.2 mole) of o-bromobenzyl bromide and 9.72 g. (0.4 g.-atom) of magnesium in 200 ml. of ether (titration yield, 83%), was added to 36.2 g. (0.165 mole) of chlorodiphenylsilane in 200 ml. of ether. Color Test I was negative immediately after addition. Acid hydrolysis followed by the usual work-up gave a viscous oil. Distillation of this residual oil gave 35.4 g. of light yellow liquid, b.p. 158-160°/0.05 mm., $n^{20}D$ 1.6260 /lit. (40), b.p. 148-150°/0.02 mm., $n^{20}D$ 1.6268/. The infrared spectrum of this material was identical with that of a known sample (40).

Diphenyl-o-tolylsilanol

One gram (3.65 mmoles) of diphenyl-o-tolylsilane was added to an aqueous silver nitrate-pyridine solution (64). Heat was evolved and a brown color developed. After stirring for 1 hour the mixture was extracted with ether. Removal of the solvents gave an oil which was chromatographed on an alumina column. Elution with petroleum ether (b.p. 60-70°) gave 0.76 g. (66%) of solid, m.p. 123-125°. Recrystallization from the same solvent raised the melting point to 126-127° (50%).

Anal. Calcd. for $C_{19}H_{18}OSi$: Si, 9.72; Mol. Wt. 290.3; Found: Si, 9.50, 9.58; Mol. Wt. 294.4 (osmometer in benzene).

The infrared spectrum of diphenyl-o-tolylsilanol in carbon tetrachloride showed bands at 2.73 and 12.45 microns indicative of the C-H and Si-O stretch, respectively. The remainder of the spectrum was very similar to that of diphenyl-o-tolylsilane.

Preparation of 2:3-benzo-1-silacyclobut-2-ene

From bromo(α-bromo-o-tolyl)diphenylsilane. The crude bromo(α-bromo-o-tolyl)diphenylsilane prepared from 27.43 g. (0.1 mole) of diphenyl-o-tolylsilane and 35.6 g. (0.2 mole) of NBS, was dissolved in 200 ml. of tetrahydrofuran and added slowly to 6.0 g. (0.25 g.-atom) of magnesium. An exothermic reaction occurred as a dark brown color developed. The mixture was allowed to stir overnight and then hydrolyzed with 5N hydrochloric acid. Subsequent to the usual work-up there was obtained a viscous oil which was extracted with petroleum ether (b.p. 60-70°). The petroleum ether extracts were distilled to give 3.0 g. of viscous oil, b.p. 135-150°/0.01 mm. Addition of petroleum ether (b.p. 28-38°) to the distillate gave 0.75 g. of solid, m.p. 124-126°. The infrared spectrum of this material was identical to that of diphenyl-o-tolylsilanol and a mixture melting point was not depressed (yield 2.6%).

The petroleum ether filtrate was concentrated and addition of ethanol gave 1.3 g. of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene, m.p. 75-76° (4.8%).

Anal. Calcd. for $C_{19}H_{16}Si$: C, 83.80; H, 5.87; Si, 10.32; Mol. Wt., 272.3; Found: C, 83.92, 83.70; H, 5.96, 6.09; Si, 10.16, 10.06; Mol. Wt., 274.3 (osmometer in benzene).

From (o-bromobenzyl)chlorodiphenylsilane. A mixture of 20.3 g. (0.0575 mole) of (o-bromobenzyl)chlorodiphenylsilane and 50 ml. of carbon tetrachloride was added slowly to 120 g. (0.576 mole) of phosphorus pentachloride in 75 ml. of the same solvent. The reaction was heated for 2 hours and the solvent removed under vacuum with the aid of a steam-bath. The infrared spectrum of the residual oil determined as a capillary cell showed the absence of any Si-H absorption bands and was quite similar to that of o-bromobenzyldiphenylsilane.

The crude (o-bromobenzyl)chlorodiphenylsilane was dissolved in 100 ml. of tetrahydrofuran and added to 2.43 g. (0.1 g.-atom) magnesium in 25 ml. of the same solvent. The reaction mixture was heated gently for 3 hours, and hydrolyzed with 5N hydrochloric acid. Subsequent to the usual work-up and evaporation of the solvents there was obtained a viscous residue. Distillation gave 4.4 g. (28.2%) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene, b.p. 130-134°/0.06 mm., which solidified upon standing, m.p. 74-75°. A mixture melting point with a known sample was not depressed and the infrared spectra were superimposable.

The infrared spectrum of this material determined in both carbon tetrachloride and carbon disulfide showed the absorption bands given in Table 7.

Table 7. Infrared Spectral Data for 2:3-Benzo-1,1-diphenyl-1-silacyclobut-2-ene.

Band Position (microns)	Intensity	Characteristic
3.25, 3.30	m,w	Aromatic C-H
3.42	w	Aliphatic C-H
6.31, 6.72, 6.89	w,w,w	Ph-
6.95	m	Possibly Si-alkyl
7.00	s	Ph-
7.16	w	-----
7.80, 7.95	w,w	Ph-

Table 7. (continued)

Band Position (microns)	Intensity	Characteristic
8.43	w	Possibly Si-alkyl
8.99	s	Si-Ph
9.35, 9.73, 10.04	w,w,w	Ph-
9.62	m to s	See Discussion Section
12.85	s	-----
13.47	s	o-Disubstitution
13.64, 13.87, 14.40	s,s,s	Ph-

From dichlorodiphenylsilane, o-bromobenzyl bromide, and magnesium in ether. A solution of 25.0 g. (0.1 mole) of o-bromobenzyl bromide diluted to 100 ml. with ether was slowly added to 9.27 g. (0.4 g.-atom) of magnesium in 20 ml. of the same solvent. When the formation of o-bromobenzylmagnesium bromide (63) was initiated the simultaneous addition of 25.3 g. (0.1 mole) of dichlorodiphenylsilane was begun. In order to allow simultaneous addition of this type, a four-necked round-bottomed flask was used. The rate of addition of the dichlorodiphenylsilane was faster than that of the o-bromobenzyl bromide.

The reaction mixture was refluxed during the addition of the chlorosilane (2 hours) and then for an additional 48-72 hours. At this time Color Test I was negative and the formation of considerable amounts of inorganic salts was observed. Subsequent to acid hydrolysis and the usual work-up, the dried ether layer was evaporated. Addition of 75 ml. of cyclohexane gave 7.2 g. of diphenylsilanediol, m.p. 160-162° dec. (33.3%). The filtrate was evaporated, taken up in petroleum ether (b.p. 60-70°) and chromatographed on an acidic alumina column. Elution with the same solvent gave 7.5 g. (27.2%, based on the o-bromobenzyl bromide employed) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene, m.p. 73-75° (mixture m.p.). This compound was observed to be entirely stable when chromatographed on either acidic or neutral alumina.

Although crude samples of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene, decomposed slowly upon standing, pure samples are very stable and show no change in melting point after one year in a closed vial.

A solution of 1.0 g. (3.67 mmoles) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene (m.p. 74-75°) in 5 ml. of petroleum ether (b.p. 60-70°) was chromatographed on a basic alumina column. Elution with the same solvent gave 0.4 g. of solid, m.p. 126-127° (38%). This material was identified as diphenyl-o-tolylsilanol by mixture melting point and by comparison of the infrared spectrum with that of an authentic sample.

Reaction of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene with phenyllithium

To a solution of 54 mmoles of phenyllithium (prepared in ether) was added 1.0 g. (3.67 mmoles) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene in 20 ml. of the same solvent. After stirring for 1 hour the reddish-brown reaction mixture was hydrolyzed with 5N hydrochloric acid. Extraction with ether followed by the usual work-up gave a viscous oil. This oil solidified upon addition of ethanol to give 0.4 g. of solid, m.p.

170-180° (30%). Recrystallization from the same solvent gave 0.3 g. (22.5%) of pure product, m.p. 187-189°. A mixture melting point with a known sample of o-tolyltriphenylsilane (65) was not depressed and the infrared spectra were superimposable.

Reaction of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene with phenylmagnesium bromide (attempted)

A solution of 27 mmoles of phenylmagnesium bromide (prepared in tetrahydrofuran) was added rapidly to 1.0 g. (3.67 mmoles) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene in 20 ml. of ether. After stirring for 16 hours the mixture was hydrolyzed with 5N hydrochloric acid. The usual work-up followed by removal of the solvents gave a viscous oil. Addition of ethanol gave 0.85 g. (85%) of recovered starting material, m.p. 73-75°.

Reaction of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene with lithium aluminum hydride (LAH)

In ether at room temperature. A solution of 1.0 g. (3.67 mmoles) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene in 35 ml. of ether was slowly added to 0.76 g. (20 mmoles) of LAH in 30 ml. of the same solvent. The solution was stirred for 7 hours and then hydrolyzed with 5N hydrochloric acid. The usual work-up gave a viscous oil which was chromatographed on an acidic alumina column. Elution with petroleum ether (b.p. 60-70°) gave 0.20 g. (20%) of slightly impure diphenyl-o-tolylsilane, m.p. 39-42° (mixture m.p.) and comparison of the infrared spectrum with that of a known sample. Further elution of the column gave 0.5 g. of very viscous oil which could not be induced to crystallize. The infrared spectrum of this latter material in carbon tetrachloride was very similar to that of diphenyl-o-tolylsilane.

In refluxing tetrahydrofuran (THF). A solution of 1.0 g. (3.67 mmoles) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene in 25 ml. of THF was slowly added to 0.76 g. (20 mmoles) of LAH in 30 ml. of refluxing THF. Subsequent to 24 hours of reflux, the reaction mixture was acid hydrolyzed. The usual work-up gave a viscous oil. Addition of petroleum ether (b.p. 60-70°) gave 0.4 g. of solid, m.p. 295-310°. Recrystallization from benzene-petroleum ether (b.p. 60-70°) gave 0.12 g. (12%) of crystalline solid, m.p. 314-316°. This compound was identified as 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene by mixture melting point and by comparison of the infrared spectrum with that of a known sample (40).

Anal. Calcd. for $C_{38}H_{32}Si_2$: Mol. Wt. 544.8; Found: 540.0 (osmometer in benzene).

The infrared spectrum of this dimer determined in carbon disulfide showed the absorption bands listed in Table 8.

The filtrate was concentrated and chromatographed on an acidic alumina column. Elution with petroleum ether (b.p. 60-70°) gave diphenyl-o-tolylsilane as a viscous oil which solidified upon treatment with ethanol; 0.26 g. (26%), m.p. 41-43°.

When the reflux time was extended to 48 hours, the yields of 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene and diphenyl-o-tolylsilane were 10% and 20%, respectively.

Table 8. Infrared Spectral Data for 2:3,6:7-Dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene

Band Position (microns)	Intensity	Characteristic
3.27, 3.33	m,m	Aromatic C-H
3.46	w	Aliphatic C-H
7.93	w	Ph-
8.35, 8.70	w,m	Possibly Si-alkyl
9.05	s	Si-Ph
9.74	w	Ph-
12.14, 12.88	w,s	-----
13.07, 13.18 (shoulder)	s,s	o-Disubstitution
13.56, 13.72, 14.35	s,s,s	Ph-

In refluxing THF (inverse addition). A solution of 0.76 g. (20 mmoles) of LAH in 60 ml. of THF was filtered under nitrogen to give a clear solution. This LAH solution was added dropwise to 2.0 g. (7.4 mmoles) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene in 25 ml. of refluxing THF. An orange color developed rapidly. Subsequent to 48 hours of reflux the mixture was acid hydrolyzed. Extraction with ether and evaporation of the solvents gave a sticky solid mass which resisted all crystallization attempts. The residue was dissolved in carbon tetrachloride and chromatographed on a neutral alumina column. No diphenyl-*o*-tolylsilane was eluted with either petroleum ether (b.p. 60-70°) or cyclohexane. However, elution with a 50:50 carbon tetrachloride-benzene mixture gave 0.20 g. of solid, m.p. 300-310°. Recrystallization from a large volume of cyclohexane gave 0.15 g. (7.5%) of dimer, m.p. 310-313° (mixture melting point).

Reaction of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene with maleic anhydride

In refluxing carbon tetrachloride (attempted). A solution of 1.0 g. (3.67 mmoles) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene and 0.36 g. (3.67 mmoles) of maleic anhydride in 25 ml. of carbon tetrachloride was refluxed for 48 hours. Evaporation of the solvent gave a semi-solid mass. Addition of petroleum ether (b.p. 28-38°) gave 0.88 g. of recovered starting material, m.p. and mixture m.p. 74-76° (88%).

In a sealed tube at ca. 150°. One gram (3.67 mmoles) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene and 0.36 g. (3.67 mmoles) of maleic anhydride was heated in a sealed tube at 150-160°/0.5 mm. for 3 hours. The resulting solid pellet was dissolved in hot benzene and chromatographed on an acidic alumina column. Elution of the column gave only a glass-like polymeric material which could not be induced to crystallize.

Reaction of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene with dimethyl acetylenedicarboxylate (attempted)

One gram (3.67 mmoles) of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene and 1.0 g. (7.1 mmoles) of dimethyl acetylenedicarboxylate were heated at 100-110° (under a nitrogen atmosphere) for 18 hours. Cooling gave a yellow oil which resisted crystallization attempts. This oil dissolved in petroleum ether (b.p. 60-70°) and was chromatographed on an acidic alumina column. Elution with the same solvent gave 0.8 g. (80%) of recovered starting material, m.p. and mixture m.p. 73-75°. Further elution gave only small amounts of yellow oil.

Methylphenyl-o-tolylsilane

A solution of o-tolylmagnesium bromide, prepared from 68.4 g. (0.4 mole) of o-bromotoluene and 14.4 g. (0.6 g.-atom) of magnesium in 200 ml. of ether, was added to 56.4 g. (0.36 mole) of chloromethylphenylsilane in 200 ml. of the same solvent. Color Test I was negative immediately after addition. Subsequent to the usual work-up the residue was distilled to give 63.8 g. (83.6%) of product, b.p. 82-84°/0.25 mm., $n^{20}D$ 1.5740 [lit. value (62) b.p. 83-84°/0.2 mm.].

The infrared spectrum of this material as a capillary cell showed the bands listed in Table 9.

(o-Bromobenzyl)methylphenylsilane

The Grignard reagent, o-bromobenzylmagnesium bromide, prepared from 50 g. (0.2 mole) of o-bromobenzyl bromide and 9.72 g. (0.4 g.-atom) of magnesium in 200 ml. of ether, was added to 29.6 g. (0.19 mole) of chlorodiphenylsilane in 150 ml. of ether. Color Test I was negative immediately after addition. Acid hydrolysis followed by the usual work-up gave a viscous oil. Distillation of this residual oil gave 27.3 g. of colorless product, b.p. 116-118°/0.5 mm., $n^{20}D$ 1.5998 (47%).

Anal. Calcd. for $C_{14}H_{15}BrSi$: Si, 9.61; Found: Si, 9.70, 9.80.

Table 9. Infrared Spectral Data for Methylphenyl-o-tolylsilane

Band Position (microns)	Intensity	Characteristic
3.25, 3.32	m,w	Aromatic C-H
3.36, 3.45	w,w	Aliphatic C-H
4.71	s	Si-H
6.29, 6.73, 6.80	w,w,w	Ph-
6.90	m	Possibly Si-alkyl
7.00, 7.80, 7.93	s,w,w	Ph-
8.00	m	Si-CH_3
8.87	s	Possibly Si-alkyl
9.02	s	Si-Ph
9.30, 9.74, 10.03	w,w,w	Ph-
11.63	s	Si-CH_3
12.00	s	Si-H
13.45 (shoulder)	s	o-Disubstitution
13.60, 13.90, 14.45	s,s,s	Ph-

2:3-Benzo-1-methyl-1-phenyl-1-silacyclobut-2-one

From (o-bromobenzyl)chloromethylphenylsilane. A solution of 26.1 g. (0.097 mole) of (o-bromobenzyl)methylphenylsilane in 75 ml. of carbon tetrachloride was slowly added to 20.1 g. (0.097 mole) of phorphorus pentachloride in 125 ml. of the same solvent. An exothermic reaction occurred, and the homogeneous mixture was stirred for 8 hours. The solvent was removed completely using a rotary evaporator to give a light yellow viscous oil. The infrared spectrum of this material as a capillary cell showed the absence of Si-H absorptions, but was in other respects quite similar to that of (o-bromobenzyl)methylphenylsilane.

The residual oil was dissolved in 200 ml. of tetrahydrofuran and added to 4.86 g. (0.2 g.-atom) of magnesium in 20 ml. of the same solvent. The reaction mixture was heated gently throughout the addition. Acid hydrolysis followed by the usual work-up gave a viscous residue. Distillation of this residue gave 4.5 g. of 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene, b.p. 97.5-98°/0.5 mm., $n^{20}D$ 1.5937 (22.5%).

Anal. Calcd. for $C_{14}H_{14}Si$: C, 80.07; H, 6.67; Found: C, 79.60, 79.80; H, 6.66, 6.61.

Although the distillate was colorless immediately after distillation, this material rapidly discolored upon exposure to air. Redistillation of samples of this material which had been stored for one week in a closed vial gave only 60-70% recovery of pure 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene.

The infrared spectrum of this material as a capillary cell contained the pertinent absorption bands listed in Table 10.

From dichloromethylphenylsilane, o-bromobenzyl bromide, and magnesium. The preparation of this compound was accomplished using the procedure previously described for 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene. The reactants, o-bromobenzyl bromide (25 g., 0.1 mole), magnesium (9.72 g.,

Table 10. Infrared Spectral Data for 2:3-Benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene

Band Position (microns)	Intensity	Characteristic
3.28, 3.35	m,w	Aromatic C-H
3.40, 3.45	w,m	Aliphatic C-H
6.32, 6.74, 6.91	m,w,m	Ph-
6.97	m	Possibly Si-alkyl
7.02	s	Aromatic C-H
7.20	w	Aliphatic C-H
7.83, 7.95	m,w	Ph-
8.00	s	Si-CH_3
8.95	s	Possibly Si-alkyl
9.04	s	Si-Ph
9.38, 9.75, 10.04	w,w,m	Ph-
9.63	m to s	See Discussion Section
12.25, 12.45	s,s	Si-CH_3
12.85, 13.10	s,s	-----
13.45	s	o-Disubstitution
13.65, 13.92, 14.40	s,m,s	Ph-

0.4 g.-atom), and dichloromethylphenylsilane (19.1 g., 0.1 mole), were added according to this procedure and the reaction mixture was refluxed for 24-36 hours. At this time Color Test I was negative. Acid hydrolysis followed by the usual work-up gave a viscous oil. Distillation gave 6.45 g. of pure product, b.p. 119-120°/1.25 mm., $n^{20}D$ 1.5939 (30.6%). The infrared spectrum of this material was identical with that of a previously prepared sample of 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene.

Reaction of 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene with lithium aluminum hydride (LAH)

In ether at room temperature. A solution of 2.09 g. (0.01 mole) of 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene in 60 ml. of ether was slowly added to 0.76 g. (0.02 mole) of LAH in 30 ml. of the same solvent. The mixture was stirred for 4 hours and then hydrolyzed with 5*N* hydrochloric acid. The usual work-up gave 2.0 g. of clear colorless oil. Distillation gave 0.8 g. of methylphenyl-*o*-tolylsilane, b.p. 81-83°/0.25 mm., $n^{20}D$ 1.5740 (38.2%). The infrared spectrum of this material was superimposable with that of a previously prepared sample. The distillation residue was non-volatile at 130°/0.25 mm. and quite viscous.

In refluxing tetrahydrofuran (THF). A solution of 2.09 g. (0.01 mole) of 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene in 40 ml. of THF was slowly added to 0.76 g. (0.02 mole) of LAH in 30 ml. of refluxing THF. Subsequent to 72 hours of reflux, the reaction mixture was acid hydrolyzed. The usual work-up gave a viscous oil. This residual oil was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on a neutral alumina column. Elution with the same solvent gave 0.2 g. of crude methylphenyl-*o*-tolylsilane (10%), $n^{20}D$ 1.5720. Elution with cyclohexane and carbon tetrachloride gave 0.27 g. of 2:3,6:7-dibenzo-1,5-dimethyl-1,5-diphenyl-1,5-disilacycloocta-2,6-diene, m.p. 168-178°. Recrystallization from petroleum ether (b.p. 60-70°) gave 0.15 g. (9%) of pure product, m.p. 176.5-177.5°.

Anal. Calcd. for $C_{28}H_{28}Si_2$: C, 80.00, H, 6.65; Found: C, 80.05, 79.98; H, 6.61, 6.58.

The infrared spectrum of this material in carbon disulfide showed the pertinent absorption bands listed in Table 11.

Table 11. Infrared Spectral Data for 2:3,6:7-Dibenzo-1,5-dimethyl-1,5-diphenyl-1,5-disilacycloocta-2,6-diene

Band Position (microns)	Intensity	Characteristic
3.27, 3.33	m,w	Aromatic C-H
3.80, 3.45, 7.14	w,w,w	Aliphatic C-H
7.75, 7.93	m,s	Ph-
8.04	s	$Si-CH_3$
8.35, 8.72, 8.84	m,s,w	Possibly Si-alkyl
9.06	s	Si-Ph
12.16, 12.37, 12.66	s,s,s	Possibly $Si-CH_3$
13.10	s	o-Disubstitution
13.58, 13.80, 14.30	s,s,s	Ph-

Evaporation of the mother liquor gave 0.1 g. of crystalline solid. The majority of this material melted at 133-135°; however, continued heating of this melt-solid mixture caused this material to resolidify and remelt sharply at 157-158°. Several additional recrystallizations failed to alter these unusual melting characteristics, and a mixture melting point with the previously isolated product (m.p. 176.5-177.5°) melted at 120-145°. The infrared spectrum of this lower melting material was, except for slight differences in the 12-15 micron region, identical with that of the high melting product (m.p. 176.5-177.5).

1,1,2-Triphenyl-1-silacyclobut-2-ene and Related Compounds

2-Bromo-1,1,2-triphenyl-1-silacyclopentane

A mixture of 3.14 g. (0.01 mole) of 1,1,2-triphenyl-1-silacyclopentane, 1.78 g. (0.01 mole) of N-bromosuccinimide (NBS) and a catalytic amount of benzoyl peroxide in 40 ml. of carbon tetrachloride was heated at reflux temperature. The reaction course was followed by observing the appearance of succinimide, and prolonged heating was avoided. Subsequent to cooling, filtration, and evaporation of the solvent, there was obtained 3.5 g. (90%) of product, m.p. 98-100° dec. Recrystallization from petroleum ether (b.p. 60-70°) raised the melting point to 101-103° dec. (79%).

Anal. Calcd. for $C_{22}H_{21}BrSi$: C, 67.18; H, 6.36; Si, 7.14; Found: C, 69.01, 69.00; H, 5.52, 5.71; Si, 7.21, 7.22.

2-Bromo-1,1,2-triphenyl-1-silacyclopentane decomposed upon standing in a closed vial. The silicon analysis was carried out immediately after purification whereas the carbon-hydrogen analysis was carried out at a later date. In view of the ease of decomposition of this material, subsequent reactions employing this compound were carried out on the crude product immediate after preparation.

The infrared spectrum of this material was very similar to that of 1,1,2-triphenyl-1-silacyclopentane except for the absence of the 9.60 micron band.

1,1,2-Triphenyl-1-silacyclopent-2-ene

The crude 2-bromo-1,1,2-triphenyl-1-silacyclopentane was prepared (as described above) from 6.28 g. (0.02 mole) of 1,1,2-triphenyl-1-silacyclopentane and 3.56 g. (0.02 mole) of NBS was dissolved in 70 ml. of ethanol. Four grams (0.04 mole) of potassium acetate and 6 ml. of glacial acetic acid were added and the mixture was refluxed for 12 hours. The resulting mixture was cooled and filtered to give 4.8 g. of product, m.p. 119-120° (76.5%). Recrystallization from absolute ethanol gave no change in melting point. 1,1,2-Triphenyl-1-silacyclopent-2-ene was completely stable when chromatographed on a basic alumina column.

Anal. Calcd. for $C_{22}H_{20}Si$: C, 84.60; H, 6.41; Si, 9.00; Found: C, 84.48, 84.30; H, 6.47, 6.57; Si, 8.90, 9.10.

The infrared spectrum of this compound in carbon tetrachloride contained the absorption bands listed in Table 12.

Table 12. Infrared Spectral Data for 1,1,2-Triphenyl-1-silacyclopent-2-ene

Band Position (microns)	Intensity	Characteristic
3.27, 3.30	m,w	Aromatic C-H
3.44, 3.52	m,w	Aliphatic C-H
6.25, 6.69	w,m	Ph-
6.35	w	Possibly SiC=C- (66)
6.93	m	Possibly $-CH_2-$
7.00	s	Ph-
7.95, 8.42, 8.85	m,w,s	Possibly Si-alkyl
9.00	s	Si-Ph
9.34, 9.72, 10.03	w,m,w	Ph-
10.66, 10.80, 11.02	m,s,w	See Discussion Section

Hydrogenation of 1,1,2-triphenyl-1-silacyclopent-2-ene

A mixture of 0.2 g. (0.637 mmole) of 1,1,2-triphenyl-1-silacyclopent-2-ene and a catalytic amount of 10% palladium-on-charcoal in 15 ml. of cyclohexane was hydrogenated at 1 atm. At the end of 2 hours approximately 1 equivalent of hydrogen uptake was observed. Filtration followed by evaporation of the solvent gave a viscous oil which crystallized upon addition of ethanol to give 0.15 g. (75%) of 1,1,2-triphenyl-1-silacyclopentane, m.p. and mixture m.p. 84-86°.

2-Bromo-1,1,2-triphenyl-1-silacyclobutane

A mixture of 2 g. (6.7 mmole) of 1,1,2-triphenyl-1-silacyclobutane and 1.2 g. (6.7 mmole) of NBS in 40 ml. of carbon tetrachloride was irradiated with a General Electric Sun Lamp for 10-15 min. Cooling followed by filtration gave 0.6 g. (91%) of succinimide, m.p. 124-126° (mixture m.p.). Evaporation of the solvent under vacuum gave a light yellow oil. This oil was taken up in petroleum ether (b.p. 60-70°) and after standing for six days the reaction product crystallized. Filtration gave 2.4 g. of solid, m.p. 67-69°. Several recrystallizations from the same solvent raised the melting point to 69-70° (40%).

Anal. Calcd. for $C_{21}H_{19}BrSi$: Si, 7.41; Found: Si, 7.52, 7.56.

The infrared spectrum of this material in carbon tetrachloride was quite similar to that of 1,1,2-triphenyl-1-silacyclobutane except that in the former the 11.52 micron band was extremely weak. The n.m.r. spectrum of the crude 2-bromo-1,1,2-triphenyl-1-silacyclobutane (oil obtained upon evaporation of the carbon tetrachloride) was essentially identical with the spectrum of the pure material (see Discussion Section). This result indicates that the yield of 2-bromo-1,1,2-triphenyl-1-silacyclobutane was essentially quantitative rather than the 40% isolated. Since this material was observed to decompose rapidly upon standing in a closed vial, subsequent reactions were carried out using the crude product shortly after its preparation.

(3-Ethoxy-3-phenylpropyl)diphenylsilanol

The crude 2-bromo-1,1,2-triphenyl-1-silacyclobutane prepared (as described previously) from 4.0 g. (0.0134 mole) of 1,1,2-triphenyl-1-silacyclobutane and 2.38 g. (0.0134 mole) of NBS was reacted with 1.30 g. (0.0134 mole) of potassium acetate and 2-3 ml. of glacial acetic acid in 50 ml. of ethanol. An exothermic reaction ensued and the mixture was then refluxed for 4-5 hours. The reaction mixture was evaporated to dryness, petroleum ether (b.p. 60-70°) was added and the mixture was filtered to give a trace of solid, m.p. 120-126°. The infrared spectrum of this material (carbon tetrachloride) contained bands at 8.65, 9.28, and 10.55 microns indicative of the SiOEt group. No SiOH bands could be detected. The filtrate was chromatographed on a basic alumina column. Ethyl acetate eluates gave 1.10 g. of product, m.p. 119-123° (22.2%). Recrystallization from carbon tetrachloride-petroleum ether (b.p. 60-70°) gave 0.90 g. of pure product, m.p. 129-130° (18.4%).

Anal. Calcd. for $C_{23}H_{27}O_2Si$: C, 75.98; H, 7.49; Found: C, 75.88, 75.66; H, 7.05, 6.91.

The infrared spectrum of this compound in carbon tetrachloride contained bands at 2.70 and 2.92 microns characteristic of the free-OH and hydrogen bonded-OH, respectively. A strong band at 9.05 microns indicative of the Si-phenyl linkage and a strong to medium intensity band at 9.20 microns (C-O-C linkage) are structurally important.

1,1,2-Triphenyl-1-silacyclobut-2-ene

Crude 2-bromo-1,1,2-triphenyl-1-silacyclobutane, prepared from 8.0 g. (0.027 mole) of 1,1,2-triphenyl-1-silacyclobutane and 4.76 g. (0.0268 mole) of NBS as described previously, was dissolved in 100 ml. of ether. Phenylmagnesium bromide (0.027 mole) was added slowly to the ethereal solution of 2-bromo-1,1,2-triphenyl-1-silacyclobutane so that little or no refluxing occurred. The separation of magnesium bromide was readily apparent during the reaction. The reaction mixture was hydrolyzed quickly with 5<u>N</u> hydrochloric acid, extracted with ether and the extracts dried over sodium sulfate. Subsequent to evaporation of solvent the residue was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on an acidic alumina column. Elution with the same solvent gave 5.0 g. of viscous oil. Distillation of this oil gave, in addition to a small amount of bibenzyl, 3.0 g. of 1,1,2-triphenyl-1-silacyclobut-2-ene, b.p. 149-151°/0.005 mm. This material solidified slowly upon treatment with a small amount of petroleum ether (b.p. 60-70°), m.p. 50-53° (37.5%). The purity of this material was sufficient for further reactions. An analytical sample was obtained by careful recrystallization from a large volume of absolute ethanol, m.p. 54-55°.

Anal. Calcd. for $C_{21}H_{18}Si$: C, 84.58; H, 6.03; Found: C, 84.36, 84.40; H, 6.26, 6.10.

An infrared spectrum of this olefin in carbon tetrachloride and bromotrichloromethane showed the prominent bands listed in Table 13.

Reaction of 1,1,2-triphenyl-1-silacyclobut-2-ene with basic alumina

A petroleum ether (b.p. 60-70°) solution of 1,1,2-triphenyl-1-silacyclobut-2-ene (0.5 g.) was adsorbed on a basic alumina column (exothermic reaction). Elution with ethanol gave (3-phenyl-2-propenyl)diphenyl-

Table 13. Infrared Spectral Data for 1,1,2-triphenyl-1-silacyclobut-2-ene

Band Position (microns)	Intensity	Characteristic
3.25, 3.30	s,m	Aromatic C-H
3.40, 3.50	s,m	Aliphatic C-H
6.26, 6.72, 7.0	w,m,s	Ph-
6.38	w	Possibly SiC=C (66)
6.92	m	Possibly $-CH_2-$
7.95, 8.23, 8.43	m,m,w	Possibly Si-alkyl
9.0 (split)	s	Si-Ph-
9.37, 9.73, 10.04	m,m,w	Ph-
10.42, 10.68, 11.02	m,m,w	See Discussion Section

silanol as a viscous oil; 0.35 g., (70%). The infrared spectrum of this material (capillary cell) showed the absence of SiH and SiOSi absorption bands. The presence of bands at 3.0 and 12.0 microns characteristic of the OH and SiO stretch, respectively, indicated the presence of an SiOH group. A medium intensity band at 10.45 microns was indicative of the presence of a <u>trans</u>-double bond. A weak band at 6.08 microns characteristic of the phenyl-conjugated double bond stretching vibrations was also present. The ultraviolet spectrum contained a typical styrene-type absorption band at 259 mμ. In view of the anticipated high boiling point of this compound and the possibility of decomposition, no attempt was made to purify this material further.

Reaction of 1,1,2-triphenyl-1-silacyclobut-2-ene with phenyllithium

1,1,2-Triphenyl-1-silacyclobut-2-ene (0.25 g., 8.34 mmoles) was dissolved in 30 ml. of ether and added to 30 mmoles of phenyllithium (prepared in ether). Subsequent to 2 hours of stirring the mixture was acid hydrolyzed. After the usual work-up the reaction mixture was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on an acidic alumina column. Elution with the same solvent gave 0.1 g. of slightly crude 1-phenyl-1-(triphenylsilyl)propene-1, m.p. 161-164°. Recrystallization from ethanol raised the melting point to 166-168°.

Anal. Calcd. for $C_{27}H_{24}Si$: C, 86.13; H, 6.37: Found: C, 85.70, 85.82; H, 6.32, 6.22.

(3-Phenyl-2-propenyl)triphenylsilane

A tetrahydrofuran solution of 1.0 g. (2.63 mmoles) of bromo(3-phenyl-2-propenyl)diphenylsilane was added to an excess of phenylmagnesium bromide (10.0 mmoles). The mixture was refluxed for 2 hours, acid hydrolyzed, extracted with ether and the extracts dried over sodium sulfate. Subsequent to removal of the solvents the residue was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on basic alumina. Elution with the same solvent gave 0.4 g. of crude product, m.p. 89-95°

(40.4%). Recrystallization from petroleum ether (b.p. 60-70°)-ethanol raised the melting point to 96.5-97.5° (27%).

Anal. Calcd. for $C_{27}H_{24}Si$: C, 86.13; H, 6.37; Found: C, 86.31, 86.31; H, 6.35, 6.32.

The infrared spectrum of this compound in carbon tetrachloride contained a weak band at 6.08 microns characteristic of the phenyl-conjugated double bond and also a strong absorption at 10.44 microns indicative of a *trans*-double bond. Thus, (3-phenyl-2-propenyl)diphenylsilanol, (3-phenyl-2-propenyl)triphenylsilane, and bromo(3-phenyl-2-propenyl)-diphenylsilane all show similar infrared properties characteristic of the phenyl-conjugated *trans*-double bond.

The ultraviolet spectrum of (3-phenyl-2-propenyl)triphenylsilane contained a typical styrene-type absorption band at 261 mμ.

Hydrogenation of 1,1,2-triphenyl-1-silacyclobut-2-ene

In the presence of Pd/C or PtO at room temperature (attempted). A mixture of 1,1,2-triphenyl-1-silacyclobut-2-ene (0.2 g., 0.67 mmole), 15 ml. of cyclohexane and 0.1 g. of 10% palladium-on-charcoal was subjected to hydrogenation conditions (H_2, 1 atm.) for 1 hour, with little hydrogen uptake being observed. Filtration followed by evaporation of the solvent gave 0.18 g. (90%) of recovered starting material, m.p. and mixture m.p. 53-55°.

When the above conditions were repeated using a platinum oxide catalyst, 85% of recovered starting material was obtained, m.p. 53-55°.

In the presence of PtO at 40-50 p.s.i.g. and room temperature (attempted). 1,1,2-Triphenyl-1-silacyclobut-2-ene (0.2 g., 0.67 mmole), 30 ml. of cyclohexane and 0.1 g. of PtO were placed in a Paar hydrogenation shaker and the system was flushed several times with hydrogen. Finally, the pressure was adjusted to ca. 40-50 p.s.i.g. and the mixture was shaken for 2 hours. Filtration of the resulting mixture followed by removal of the solvent gave 0.18 g. (90%) of recovered starting material, m.p. and mixture m.p. 53-55°.

Studies with 1,1,3,3-Tetramethyl-1,3-disilacyclobutane

1,1,3,3-Tetramethyl-1,3-disilacyclobutane

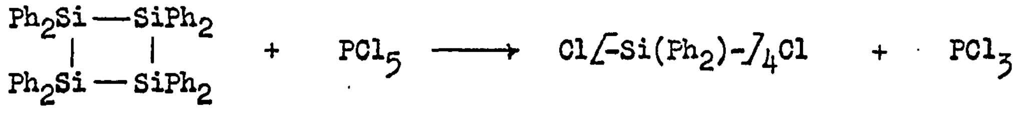
A solution of 30.6 g. (0.2 mole) of (chloromethyl)dimethylchlorosilane in 90 ml. of tetrahydrofuran was slowly added to 9.73 g. (0.4 g.-atom) of magnesium in 20 ml. of the same solvent. The mixture was heated gently during the addition and finally refluxed for an additional 12 hours. The reaction mixture was decanted away from the excess magnesium into crushed ice acidified with 5N hydrochloric acid. The hydrolyzed mixture was extracted with three 75 ml. portions of ether, and the organic layer dried over anhydrous sodium sulfate. Subsequent to removal of the solvents, distillation of the residue gave 2.9 g. (20%) of product, b.p. 115-117°, $n^{20}D$ 1.4412 [lit. value (25) b.p. 117-119°, $n^{27}D$ 1.4380].

DISCUSSION

Studies with Octaphenylcyclotetrasilane and Related Compounds

While the preparation of octaphenylcyclotetrasilane /I/ was reported more than forty years ago (1,4), it was not until recently that the structure of this compound was completely elucidated (3,4). Since the initial preparation of this compound in This Laboratory (48), octaphenylcyclotetrasilane has been the subject of numerous investigations, most of which have been summarized recently (4). At the time of his initial investigations, the present author was aware of the facile reactions of octaphenylcyclotetrasilane with halogens, hydrogen halides, polyhalo organic compounds, organometallic reagents, lithium, oxidizing agents, metal hydrides and metal halides (4). The reaction of octaphenylcyclotetrasilane with inorganic metal halides is a particularly unique observation which appeared worthy of further investigation.

The author's initial investigations with octaphenylcyclotetrasilane were concerned with its reactivity toward inorganic non-metallic halides, such as phosphorus pentachloride, sulfuryl chloride and thionyl chloride. Phosphorus pentachloride proved to be a particularly effective chlorinating agent, and high yields of 1,4-dichlorooctaphenyltetrasilane /XLVII/



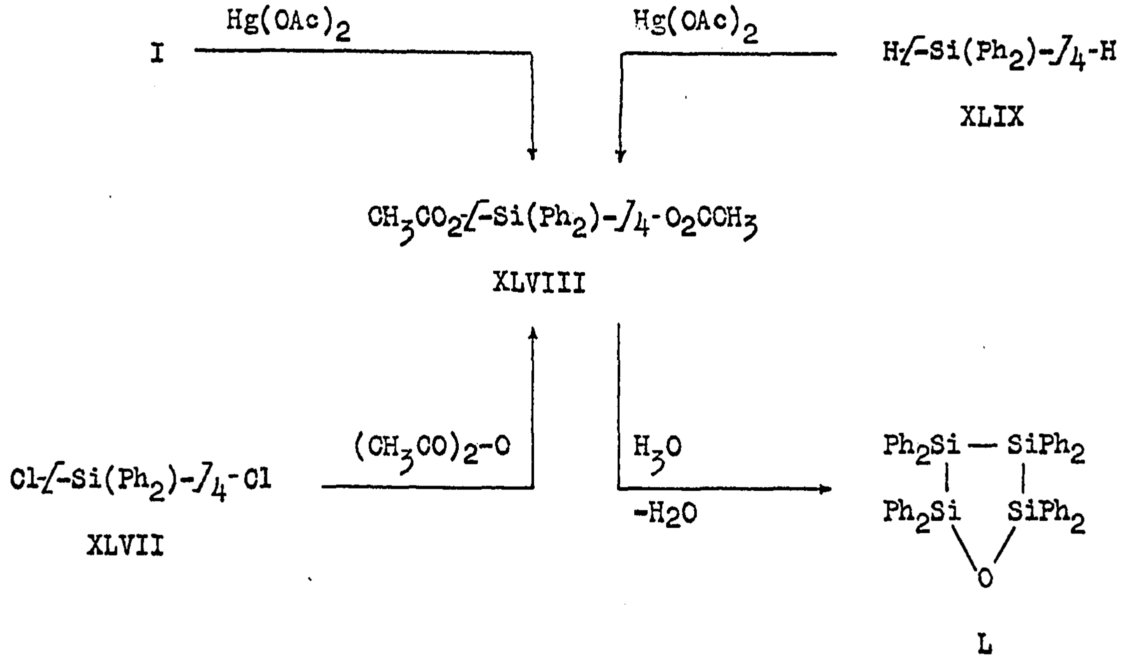
$$\begin{array}{c} Ph_2Si - SiPh_2 \\ | \quad\quad | \\ Ph_2Si - SiPh_2 \end{array} + PCl_5 \longrightarrow Cl/\text{-}Si(Ph_2)\text{-}/_4Cl + PCl_3$$

I XLVII

were obtained. The advantages of this reagent for the preparation of [XLVII] include: (a) the availability and cost of phosphorus pentachloride; (b) the ease of isolation of [XLVII] in a highly purified state; and (c) the stability of [XLVII] under the reaction conditions. On the other hand, while the reactions with sulfuryl chloride and thionyl chloride were successful, the yields of [XLVII] were appreciably lower. In view of this latter fact, together with the inconveniences encountered in handling these latter chlorinating agents, these reagents are less synthetically useful than phosphorus pentachloride.

The reaction of [I] with other non-halogen containing inorganic salts was also briefly investigated. Compound [I] was found to reduce an ethanolic solution of silver nitrate at room temperature. This reaction was quite facile in spite of the insolubility of [I] in the reaction medium. This reactivity is in agreement with that observed for 1,1,3,3-tetramethyl-1,3-disilacyclobutane [XIII] (25,27,28,30,32). Under the same conditions, no reaction was obtained with decaphenylcyclopentasilane (59) in spite of the greater solubility of this material.

Reaction of [I] with mercuric acetate in benzene solvent gave 1,4-diacetoxyoctaphenyltetrasilane [XLVIII]. An alternate synthesis of [XLVIII] was achieved by heating 1*H*, 4*H*-octaphenyltetrasilane [XLIX] (48, 67) with mercuric acetate in glacial acetic acid. Similar reactions have been reported previously for monosilanes (68). In addition, [XLVIII] was obtained by refluxing 1,4-dichlorooctaphenyltetrasilane [XLVII] in acetic anhydride. Further proof of the structure of [XLVIII] was obtained by hydrolysis to octaphenyloxacyclopentasilane [L] (37). The infrared and n.m.r. spectra of [XLVIII] were also examined and found to be in agreement with the proposed structure (see Experimental section).

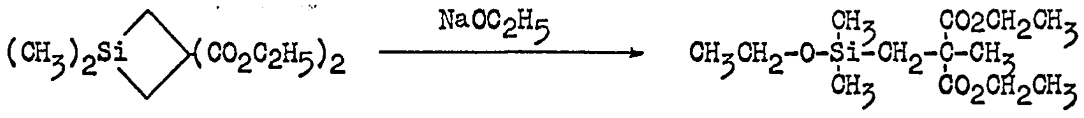


When either hexaphenyldisilane or decaphenylcyclopentasilane was treated with mercuric acetate under even more forcing conditions, the starting materials were recovered in good yields.

Studies with (2,2-Dicarbethoxypropyl)ethoxydimethylsilane and Related Compounds

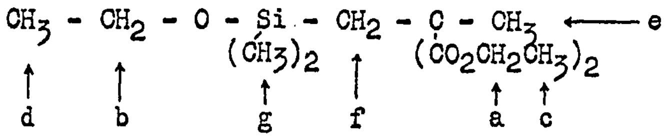
In view of the unusual reactivity of octaphenylcyclotetrasilane, a program concerned with the preparation, properties and reactions of strained cyclic organosilicon compounds was undertaken. In connection with this program, it became advantageous to repeat the preparation of a compound previously designated as 3,3-dicarbethoxy-1,1-dimethyl-1-silacyclobutane [VII]. This compound was reported first by West (9) and later by Benkeser and Bennett (10). The general method utilized was a ring closure reaction of bis(halomethyl)dimethylsilane and diethyl malonate effected with sodium alkoxide. Since the yield obtained by Benkeser and Bennett was somewhat better than that obtained by West, the procedure given by the former was employed in this work.

From the reaction of bis(chloromethyl)dimethylsilane, diethyl malonate and sodium ethoxide, a compound was obtained whose properties were in excellent agreement with those previously reported (9,10). The infrared spectrum of this material (see Experimental section) was identical with that of a known sample graciously supplied by Dr. Benkeser. However, an examination of the n.m.r. spectrum of this material showed that it was not the previously reported silacyclobutane [VII], but rather a ring opened product; namely, (2,2-dicarbethoxypropyl)ethoxydimethylsilane [LI]. The formation of [LI] can be explained in terms of a cleavage of [VII] by sodium ethoxide.



VII LI

The n.m.r. spectrum of [LI] contained a pair of quartets centered at 5.92 (J= 7.2 c.p.s.) and 6.43τ (J= 7.2 c.p.s.) assigned to the protons (a) and (b), respectively. The (c) and (d) protons appeared as a pair of triplets centered at 8.78 (J= 7.2 c.p.s.) and 8.89τ (J= 7.2 c.p.s.), respectively. The pair of triplets overlapped giving rise to four peaks of unequal intensity. The remainder of the spectrum consisted of singlets



$$\underset{\underset{d}{\uparrow}}{CH_3} - \underset{\underset{b}{\uparrow}}{CH_2} - O - \underset{\underset{g}{\uparrow}}{\underset{(CH_3)_2}{Si}} - \underset{\underset{f}{\uparrow}}{CH_2} - \underset{(\underset{\underset{a}{\uparrow}}{CO_2CH_2}\underset{\underset{c}{\uparrow}}{CH_3})_2}{C} - CH_3 \longleftarrow e$$

centered at 8.62, 8.81 and 9.92 τ assigned to the (e), (f) and (g) protons, respectively. The relative areas of all peaks were in agreement with the proposed structure.

It was previously reported (9) that the basic hydrolysis of [VII] proceeded with ring opening to yield sym-bis(2,2-dicarboxypropyl)tetramethyldisiloxane [LII]. Although the reactivity of other known silacyclobutanes (8,11,25) would predict such behavior for [VII], the above observation can also be explained in terms of this proposal. Thus, hydrolysis of [LI] under similar conditions yields [LII]. On the basis of the physical, chemical, and spectral evidence presented this author feels

$$LI \longrightarrow (CH_3-\overset{CO_2H}{\underset{CO_2H}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{Si}}-)_2O$$

LII

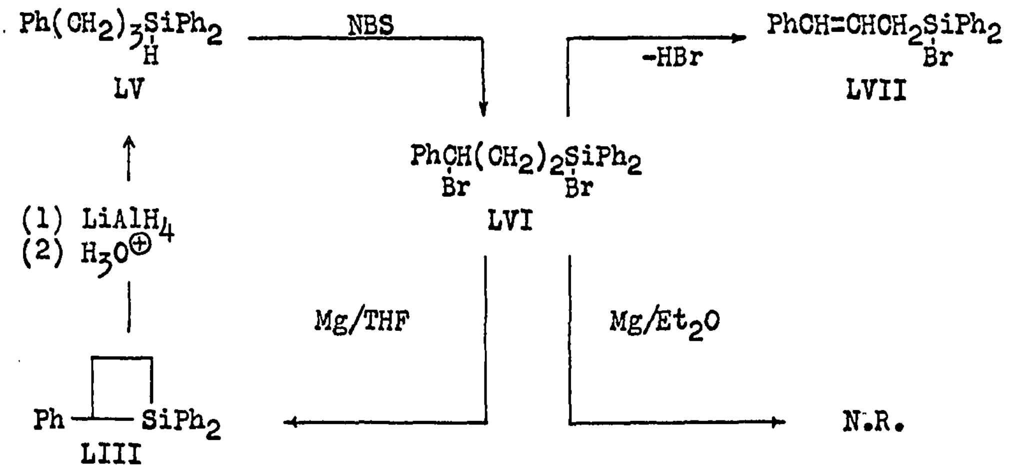
certain that the compound previously designated as 3,3-dicarbethoxy-1-silacyclobutane [VII] is in reality (2,2-dicarbethoxypropyl)ethoxydimethylsilane [LI]. It seems equally certain, however, that [VII] was a precursor to [LII] and the formation of this silacyclobutane must be quite facile even in the presence of a large excess of diethyl malonate.

Studies with 1,1,2-Triphenyl-1-silacyclobutane and Related Compounds

A search of the literature showed that relatively few silacyclobutane compounds had been prepared, and that little information was available concerning the reactivity of these compounds. The silacyclobutane ring system has been shown to be extremely susceptible to cleavage by polar reagents. Facile ring opening has been observed with the following: (a) ethanolic base (8,11); (b) sulfuric acid (8); (c) ethanolic silver nitrate (25); and (d) bromine (25). This phase of the investigations of strained cyclic organosilicon compounds is concerned with the synthesis of 1,1,2-triphenyl-1-silacyclobutane /LIII/, and 1,1,2-triphenyl-1-silacyclopentane /LIV/, and a qualitative comparison of the reactivities of these two compounds toward a variety of reagents.

The ability of N-bromosuccinimide (NBS) to effect bromination of silicon hydrides (69-71) as well as allylic bromination (72) was utilized in the preparation of /LIII/ and /LIV/. The synthetic method employed for the preparation of /LIII/ and /LIV/ was essentially the same and will be described in detail for the former.

(3-Phenylpropyl)diphenylsilane /LV/ was treated with NBS to give bromo(3-bromo-3-phenylpropyl)diphenylsilane /LVI/. Attempts to purify this latter material by distillation resulted in decomposition with the subsequent isolation of bromo(3-phenyl-2-propenyl)diphenylsilane /LVII/. However, reaction of crude (undistilled) /LVI/ with magnesium in tetrahydrofuran (THF) afforded /LIII/ in yields ranging from 40-55%.



Surprisingly, no reaction could be observed when ether was substituted for THF as the solvent in the cyclization step.

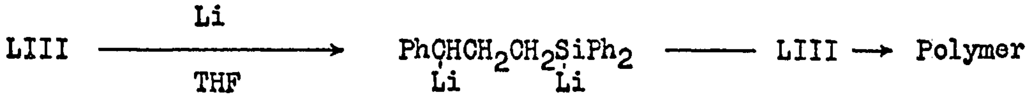
Cleavage of the silacyclobutane /LIII/ with lithium aluminum hydride was found to occur under mild conditions giving high yields of the initial starting material /LV/. This appears to be the first reported cleavage of a silacyclobutane using lithium aluminum hydride, and this reagent promises to be of general utility for the proof of structure of such compounds.

Compound /LIII/ was found to decolorize a solution of bromine in carbon tetrachloride slowly at room temperature and to reduce ethanolic solution of silver salts, such as silver nitrate and silver acetate, often with the formation of a silver mirror. These observations are in agreement with the high degree of reactivity previously reported for other silacyclobutane compounds (25).

In addition to the above, /LIII/ was found to undergo exothermic ring opening on a basic alumina column. On the basis of infrared analysis and by analogy with the lithium aluminum hydride cleavage, the product of this reaction is believed to be (3-phenylpropyl)diphenylsilanol. Although the cleavage of silicon-silicon bonds has been observed (4,73) to occur on an alumina column of this type, no cleavages of silacyclobutanes have been previously reported.

During the initial studies the high boiling point and low melting point of /LIII/, together with the inability to chromatograph this compound, complicated the isolation and purification of products both in its preparation and its reactions. However, continued investigation revealed that this silacyclobutane was completely stable when chromatographed on an acidic or neutral alumina column. In this manner, pure /LIII/ is readily obtained, and the technique promises to be extremely useful in studies of silacyclobutane compounds.

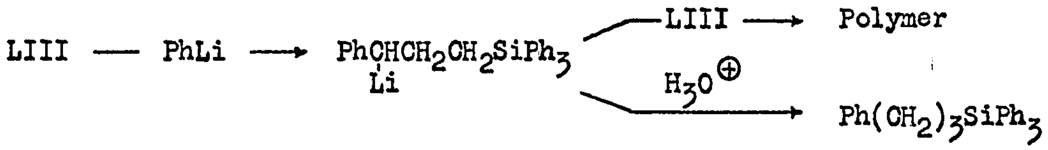
The cleavage of benzyl groups from silicon employing lithium (74) and sodium-potassium alloy (75) has been reported. It seemed reasonable that the cleavage of /LIII/ by lithium should occur even more readily in view of the apparent ring strain present in this compound. Reaction of /LIII/ with lithium in THF proceeded with the formation of a light yellow solution. However, Color Test I remained negative throughout the reaction indicating the absence of detectable amounts of any organo- or silyllithium compound. Work-up <u>via</u> acid hydrolysis yielded a material which appeared to be polymeric in nature. The infrared spectrum of this material showed no absorption in the 4.6-4.8 micron region characteristic of the silicon-hydrogen group (55) which would result from acid hydrolysis of any silyllithium compound present (56,76,77). It appears that the cleavage of /LIII/ by lithium is substantially slower than its cleavage by the initially formed dilithio compound /LVIII/.



$$\text{LIII} \xrightarrow[\text{THF}]{\text{Li}} \underset{\text{Li}}{\text{PhCH}}\text{CH}_2\text{CH}_2\underset{\text{Li}}{\text{Si}}\text{Ph}_2 \text{ —— LIII} \longrightarrow \text{Polymer}$$

LVIII

This conclusion was substantiated to a degree when it was observed that the addition of /LIII/ to a five-equivalent excess of phenyllithium gave only a trace of the expected (3-phenylpropyl)triphenylsilane /LIX/. The major portion of the reaction product again appeared to be polymeric



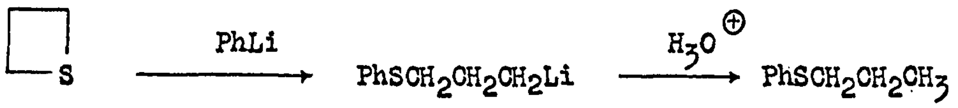
$$\text{LIII — PhLi} \longrightarrow \underset{\text{Li}}{\text{PhCH}}\text{CH}_2\text{CH}_2\text{SiPh}_3 \begin{cases} \text{— LIII} \longrightarrow \text{Polymer} \\ \xrightarrow{\text{H}_3\text{O}^{\oplus}} \text{Ph(CH}_2)_3\text{SiPh}_3 \end{cases}$$

LX LIX

in nature, and its infrared spectrum was quite similar to that of the product from the lithium cleavage. However, when the reaction was repeated using an eight-equivalent excess of phenyllithium the yield of /LIX/ was increased to 40%. The above results can best be explained in terms of a competitive cleavage of /LIII/ by phenyllithium and the more reactive intermediate /LX/. In direct contrast, however, /LIII/ was not cleaved by the less reactive phenylmagnesium bromide in THF at room temperature.

An authentic sample of (3-phenylpropyl)triphenylsilane /LIX/ was prepared by the reaction of phenyllithium with (3-phenylpropyl)diphenylsilane (see Experimental Section).

The above results are analogous to those observed with thiacycloalkanes. Thus, thiacyclobutane [LXI] has been observed (78) to undergo reaction with phenyllithium to yield, among other products, phenylpropylsulfide [LXII].



LXI LXII

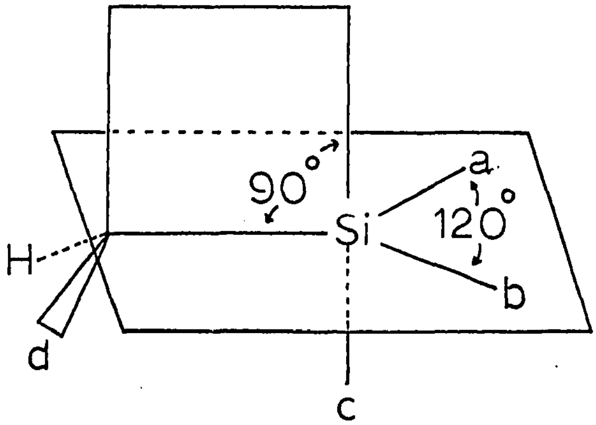
The reaction of [LIII] with hydrogen in the presence of palladium-on-charcoal was also investigated. At room temperature and employing a pressure of 45 p.s.i.g., [LIII] exhibited a resistence to cleavage as evidenced by the weakness of the silicon-hydrogen absorption band in the infrared spectrum of the crude reaction product. Essentially the same results were obtained when a reaction temperature of 75° was employed. The stability of this silacyclobutane under hydrogenolysis conditions appears to be comparable to that exhibited by cyclobutanes (79).

In order to validly compare the reactivity of this silacyclobutane with that of larger cyclic organosilicon compounds, its five-membered ring homolog 1,1,2-triphenyl-1-silacyclopentane [LIV] was prepared. The preparation employed (4-phenylbutyl)diphenylsilane as starting material and was similar to that previously described for [LIII]. The five-membered ring [LIV] was found to be quite nonreactive under conditions where [LIII] was readily cleaved. Thus, [LIV] did not react with the following reagents: (a) bromine in carbon tetrachloride; (b) ethanolic silver salts; (c) lithium aluminum hydride (LAH) in THF; and (d) basic alumina chromatography.

In attempts to explain the facile ring opening of silacyclobutanes earlier workers have proposed several theories. The first of such proposals (8) attributed the enhanced reactivity of silacyclobutanes to the angular strain present in the ring. The second (9) stated that in spite of the additional size of silicon, the angular strain in silacyclobutanes is probably no greater than in cyclobutanes since the tetrahedral angle of silicon is reported (9) to be more easily deformed than that of carbon. In view of the fact that silacyclobutanes are cleaved more readily than cyclobutanes, it was postulated that ring opening of the former was facilitated because it had available to it mechanisms not available in the case of the latter. While it is reasonable that ring strain may increase the reactivity of silacyclobutanes, this author feels that the magnitude of this effect need not be greater than that observed in carbon chemistry (80). In addition, this author believes that the second proposal is essentially correct and that this difference in reactivity is associated with the participation of the d-orbitals of silicon during the substitution reaction, resulting in the formation of a pentacovalent addition complex (81).

With regard to the difference in reactivity of the silacyclobutane /LIII/ and its five-membered ring homolog /LIV/, however, a similar reasoning cannot be employed since the d-orbital participation should be operative in both compounds. At the present time, the observed difference in reactivity between /LIII/ and /LIV/ (strained-silicon *versus* unstrainedsilicon) can be explained by a qualitative consideration of both the ground and the transition state energies of these two compounds. In view of the apparent distortion of bond angles resulting in the formation of a considerably strained ring system (8), [LIII] should possess a more energetic ground state than its ring homolog. This would favor ring opening of the former in preference to the latter.

A theoretical consideration of the transition state of a silacyclobutane derivative in a nucleophilic displacement reaction has been previously reported by Sommer (11). He has explained the high reactivity of 1-methyl-1-silacyclobutane [IX] in hydrolysis reactions by a consideration of the structure-reactivity relations resulting from steric factors. Compound [IX] has been observed to be 10^3-10^4 times more reactive in hydrolysis reactions than the five-membered ring homolog 1-methyl-1-silacyclopentane (11). By analogy, the geometry of the pentacovalent addition complex resulting from the reaction of [LIII] with phenyllithium would ideally approximate a structure of the type [LXIII], with ring opening being the predominent reaction.



LXIII, a=b=c=d=Ph-

With 1,1,2-triphenyl-1-silacyclobutane [LIII] the structure-reactivity relations resulting from steric factors can also be explained in terms of the three considerations first proposed by Sommer and co-workers (11).

First, since the ring substituents in [LIII] are "pulled back" (relative to [LIV]) away from the path of the attacking reagent, the formation of [LXIII] should be greatly facilitated. Secondly, the C-Si-C angle in [LXIII] would be expected to be about 90°. Since the ring-angle in [LIII] should be close to this value, much less internal strain (I-strain) (16) should be introduced during formation of the complex from [LIII] than would be the case with the five-membered ring homolog [LIV]. Thirdly, due to an increased crowding of the ring substituents in [LVIII] relative to [LIII], an increase in steric strain should result during the formation of the former. All of the above points indicate that the formation of a complex of the type [LXIII] from [LIII] would be energetically more favorable than formation of a similar complex from [LIV]. Thus, the relative magnitude of both the ground and transition state energies are consistent with the observed reactivity of [LIII] and [LIV].

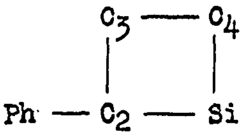
Several important observations should be noted. First, although the concept of I-strain appears to have been replaced in some cases (82,83), with that of a change of orbital hybridization brought about by the change in angular requirements in forming different sized rings, the basic features involved in this theory seem to be quite applicable to organosilicon chemistry (81). Secondly, the arguments presented above assume the formation of a pentacovalent-silicon complex involving dsp^3 hybridization of the silicon orbitals. However, even incomplete hybridization of this type would decrease the energy necessary to reach the transition state during a substitution reaction (81). Finally, phenyllithium was chosen for use in the illustration /LXIII/ merely because of the symmetry of the resulting complex, and the conclusions reached should be applicable to reactions with other reagents.

In general, the infrared spectra of 1,1,2-triphenyl-1-silacyclobutane /LIII/ and 1,1,2-triphenyl-1-silacyclopentane /LIV/ were quite similar to those of their open chain analogs. A radical departure from this general observation was found in the spectrum of /LIII/. The spectrum of /LIII/ in carbon disulfide or carbon tetrachloride contained a strong, sharp band at 11.52 microns. This band was absent in the spectrum of the five-membered ring homolog /LIV/ and in the spectra of all the open chain compounds prepared and described in this section. At the present time, this band appears to be characteristic of the 2-phenyl-1-silacyclobutane ring system. A band at 8.9 microns has been previously reported to be present in four silacyclobutanes prepared by Sommer (11). The presence of such a band in the spectrum of /LIII/ could not be detected due to the intense silicon-phenyl absorption in this area. The infrared data of all pertinent compounds are given at the end of the experimental section concerned with their preparation.

The structures of all pure compounds prepared in this section were confirmed by analysis of their n.m.r. spectra. The n.m.r. data are given in Table 14. The aromatic proton shielding values are not included in the table as the protons were represented by a multiplet in all cases.

The following are illustrations of the numbering system used for this spectral tabulation of the open chain and cyclic compounds.

$\mathrm{Ph\text{-}C_4\text{-}C_3\text{-}C_2\text{-}Si}<$



It is interesting to note that although the τ values in the spectra of [LIII] and [LIV] show appreciable paramagnetic shifts when compared with the open chain compounds, (3-phenylpropyl)diphenylsilane [LV] and (4-phenylbutyl)diphenylsilane, respectively, the differences are much greater in the case of [LIII]. Even more striking is the shift observed for the benzylic proton of [LIII] relative to [LIV].

2:3-Benzo-1,1-diphenyl-1-silacyclobut-2-ene and Related Compounds

Following the synthesis and study of 1,1,2-triphenyl-1-silacyclobutane [LIII], attention was focused on the preparation of unsaturated derivatives of this type. Since no silacyclobutene derivatives have been reported, initial investigations were concerned with the synthesis of a pseudo-silacyclobutene; namely, 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene [XXVII]. The attempted preparation of [XXVII] from (o-halophenyl)diphenylsilanes and sodium has been discussed (see Historical Section).

Compound [XXVII] was prepared by three independent synthetic methods.

Table 14. N.m.r. Data for 1,1,2-Triphenyl-1-silacyclobutane and Related Compounds[a]

A) 1,1,2-Triphenyl-1-silacyclobutane [LIII]
B) (3-Phenylpropyl)diphenylsilane [LIV]
C) (3-Phenylpropyl)triphenylsilane [LIX]
D) Bromo(3-phenyl-2-propenyl)diphenylsilane [LVII]
E) 1,1,2-Triphenyl-1-silacyclopentane [LIV]
F) (4-Phenylbutyl)diphenylsilane

Compound	Si-H[b]	C_2-H[b]	C_3-H[b]	C_4-H[b]	C_5-H[b]	Ratio, Aryl C-H:Alkyl C-H	
						Theo.	Found
A		6.64 (4) [1]	7.62 (m) [2]	8.50 (m) [2]		3.00	3.15
B	5.08 (3) [1]	9.02 (m) [2]	8.21 (m) [2]	7.37 (3) [2]		2.14	2.09
C		8.31 (m) [4]	8.31 (m) [4]	7.40 (3) [2]		3.33	3.25
D		7.47 (m) [2]	3.89 (m) [4]	3.89 (m) [4]		3.75	3.87
E		7.31 (4) [1]	7.94 (m) [4]	7.94 (m) [4]	8.70 (m) [2]	2.15	2.11
F	5.10 (3) [1]	8.73 (m) [2]	8.38 (m) [4]	8.38 (m) [4]	7.52 (3) [2]	1.88	1.80

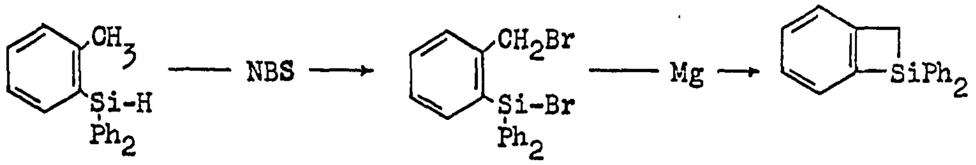
---

[a] Run at 60 Mc. in CCl_4.

[b] Values are given in τ units. Number in parenthesis represents peak multiplicity, (m) signifies a multiplet, where the number of peaks could not be counted accurately. The number in brackets indicates the relative peak areas.

Treatment of diphenyl-o-tolylsilane [LXIV][1] with N-bromosuccinimide (NBS) [Method A] gave bromo(α-bromo-*o*-tolyl)diphenylsilane [LXV].

Method A



LXIV LXV XXVII

Reaction of [LXV] with magnesium in tetrahydrofuran (THF) gave the desired benzosilacyclobutene [XXVII]. The yields of [XXVII] obtained by Method A were quite low (4-5%) and highly dependent upon small changes in the reaction conditions.

The yield of [XXVII] was significantly improved by employing Method B. *o*-Bromobenzyldiphenylsilane [LXV] (40) was converted to (*o*-bromobenzyl)chlorodiphenylsilane [LXVI] by the use of phosphorus pentachloride[2]. Reaction of this crude chlorosilane with magnesium in THF gave [XXVII] (28%). Although Method B enjoyed the advantage that increased and consistant yields of [XXVII] were obtained, it was somewhat

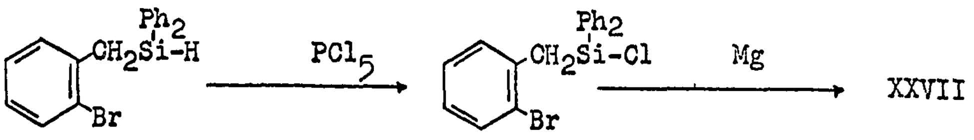
---

[1] Diphenyl-*o*-tolylsilane has been reported (62) to be a liquid, b.p. 138-140°/0.046 mm., $n^{20}D$ 1.6113. However, a sample of this previously prepared material was found to contain small crystals and cooling caused this material to solidify, m.p. 43-45°.

[2] S. Cooper, G. R. Chainani, R. A. Tomasi, K. Y. Chang and H. Gilman, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the conversion of silicon hydrides to chlorosilanes using phosphorus pentachloride. Private communication. 1962.

unattractive because of the number of synthetic steps involved.

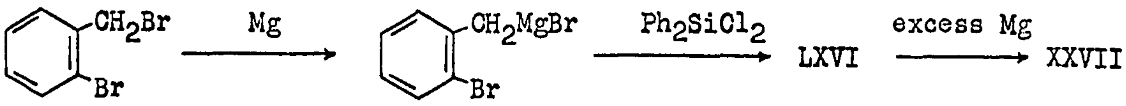
Method B



LXV LXVI

It seemed likely that the *in situ* formation of [LXVI] in the presence of excess magnesium should also yield compound [XXVII], and this constituted the basis for Method C. *o*-Bromobenzyl bromide [LXVII] has been

Method C



LXVII LXVIII

reported (63) to react with magnesium in ether to give high yields of *o*-bromobenzylmagnesium bromide [LXVIII]. Addition of dichlorodiphenylsilane to an *o*-bromobenzylmagnesium bromide-magnesium mixture gave 25-30% yields of [XXVII].

Method C was further simplified by employing the simultaneous addition of [LXVII] and dichlorodiphenylsilane to magnesium in ether, thereby eliminating the preparative step involving the prior formation of [LXVIII].

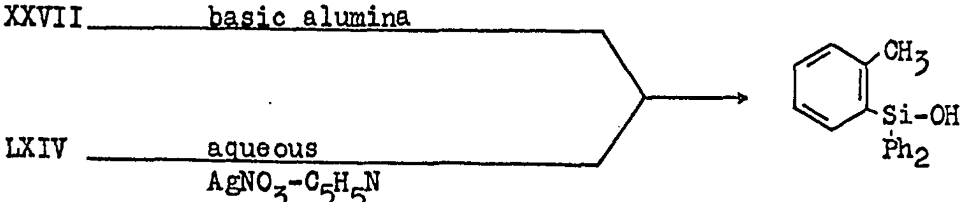
Benzosilacyclobutene [XXVII] is a crystalline solid, m.p. 75-76° which can be readily distilled at low pressure without decomposition, b.p. 130-134°/0.06 mm.

The infrared spectrum of [XXVII] was quite similar to that of the previously described 2:3-benzo-1,1-diphenyl-1-silacyclopent-2-ene (40). However, the spectrum of [XXVII] contained a sharp band at 9.65 microns not present in the spectrum of the five-membered ring homolog. Since ring opening of [XXVII] results in the disappearance of this 9.65 micron band, it appears that this band is associated with the strained benzosilacyclobutene system.

Compound [XXVII] exhibited a light blue fluorescence in the solid state in the presence of ultraviolet light. The ultraviolet spectrum of [XXVII] (ethanol) gave the following maxima in $m\mu$ ($\log \varepsilon$): 263.5 (3.230), 269.5 (3.342), and 276.5 (3.243). These ultraviolet properties are quite similar to those reported (84) for benzocyclobutene, $\lambda_{max}^{ethanol}$ ($\log \varepsilon$): 260 (3.09), 265.5 (3.28), and 271.5 (3.27).

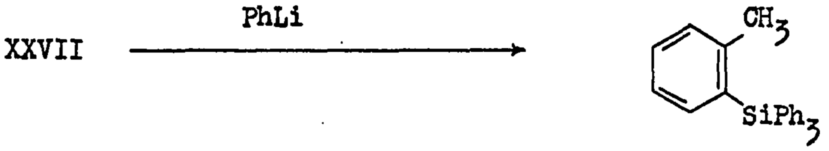
The n.m.r. spectrum of [XXVII] (in carbon tetrachloride) contained a sharp singlet centered at 7.54 τ due to the two equivalent benzylic protons (aromatic/aliphatic proton ratio= 7.09; calcd. 7.00). For comparison purposes, the benzylic protons of benzyltriphenylsilane fall at 7.20 τ.

Compound [XXVII] exhibited the high degree of reactivity previously reported for other silacyclobutanes. Thus, [XXVII] rapidly decolorized solutions of bromine in carbon tetrachloride at room temperature, and reduced ethanolic solutions of silver nitrate, often with the formation of a silver mirror. Chromatography of [XXVII] on a basic alumina column gave diphenyl-o-tolylsilanol [LXIX]. The assignment of structure [LXIX] was based on analytical data and molecular weight determinations. In addition, the infrared spectrum of this material was found to be identical with that of an authentic sample of [LXIX] prepared by the reaction of diphenyl-o-tolylsilane [LXIV] with an aqueous silver nitrate-pyridine mixture (64).



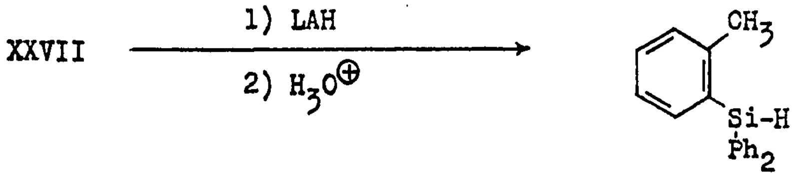
LXIX

Compound [XXVII] was readily cleaved by phenyllithium to give, subsequent to acid hydrolysis, o-tolyltriphenylsilane [LXX] (65). None of the ring opened product [LXX] could be isolated from [XXVII] and phenylmagnesium bromide at room temperature. Work-up of the reaction under these conditions gave only the recovered starting material.



LXX

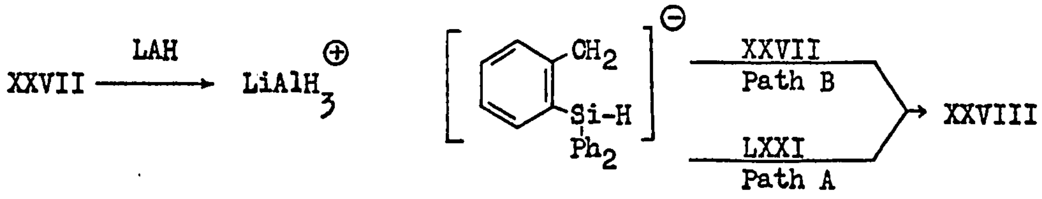
Cleavage of [XXVII] with lithium aluminum hydride (LAH) in ether followed by acid hydrolysis gave the expected ring cleavage product, diphenyl-o-tolylsilane [LXIV].



LXIV

An unusual and unexpected dimerization was observed when [XXVII] was added to LAH in refluxing tetrahydrofuran (THF). Under these conditions diphenyl-o-tolylsilane [LXIV] was obtained in 26% yield. In addition a crystalline solid, m.p. 314-316°, was also obtained. This material was observed to be identical in all respects with the previously prepared (40) 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene [XXVIII].

It is quite reasonable to expect that the diphenyl-o-tolylsilane [LXIV] isolated in the above cleavage reactions is formed by acid hydrolysis of an initially formed complex of the type [LXXI]. The isolation of both the dimer [XXVIII] and [LXIV] under these conditions suggested the possibility that [LXXI] is also an intermediate in the formation of [XXVIII].



LXXI

Two distinct pathways can be envisioned for the formation of the dimer from [LXXI]. First, the reaction of [LXXI] in an intermolecular "head to tail" manner (Path A) would yield the observed dimeric product [XXVIII]. Alternately, cleavage of [XXVII] by [LXXI] (Path B) would also be expected to give [XXVIII]. This investigation indicates that the most probable reaction mechanism is that outlined in Path B. The evidence supporting this choice follows:

(a) No increase in the yield of dimer [XXVIII] was observed when the reaction time was doubled, indicating that the latter is not formed by a slow intermolecular condensation of [LXXI].

(b) Inverse addition (i.e. addition of the LAH to [XXVII]) resulted in the formation of comparable yields of [XXVIII]. Most important, however, no diphenyl-*o*-tolylsilane could be isolated under these conditions suggesting a rapid cleavage of [XXVII] by [LXXI].

(c) Compounds of the type $LiAlR_4$ have been observed to have an initial reactivity comparable to that of organolithium compounds (85,86) and a reactivity greater than that of LAH would be expected for [LXXI]. The cleavage of 1,1,2-triphenyl-1-silacyclobutane with LAH has been previously observed to give lower yields of the ring opened product, (3-phenylpropyl)diphenylsilane if refluxing tetrahydrofuran is used as reaction solvent, apparently due to competitive cleavage of this silacyclobutane by the resulting $LiAlH_3R$ complex. The ability of organolithium compounds to effect ring opening has also been previously demonstrated.

(d) Although Path B (or Path A) indicates that the dimerization could be achieved with a catalytic amount of LAH, inverse addition (see point b above) results in the formation of considerable amounts of polymer suggesting that intermolecular polymerization is more rapid than intermolecular cyclization to [XXVIII]. When o-bromobenzyldiphenylsilane (rather than o-chlorobenzyldiphenylsilane) is reacted with sodium the yield of recovered starting material is decreased; however, the yield of [XXVIII] remains low (40), supporting the conclusion that intermolecular polymerization is more favorable than intermolecular cyclization.

Examination of the eight-membered ring structure [XXVIII] using Stuart-Briegleb models shows that two nonplanar structures are possible for the unsubstituted basic ring system. Although a model of only one of the two possible conformations can be constructed with the tetraphenyl-substituted derivative, [XXVIII] is most likely inverting between the two possible forms. Further examination of these two conformations showed that the environments of the protons in a methylene group are nonequivalent, and the n.m.r. spectrum of [XXVIII] (in carbon disulfide) contained two bands at 7.23 (2 units) and 7.40 τ (2 units) due to the two pairs of nonequivalent methylene protons (aromatic/aliphatic proton ratio = 6.90; calcd. 7.00). In view of the insolubility of the dimer [XXVIII] in carbon disulfide and other solvents (such as chloroform, deuterochloroform, and cyclohexane), further refinement of the fine splitting of these two bands was not possible. The dimeric structure of [XXVIII] was also substantiated by molecular weight determinations.

Benzocyclobutene and its derivatives have been reported (87,88) to undergo ring expansion with dienophiles such as maleic anhydride and N-phenylmaleimide. However, similar ring expansions of [XXVII] with either maleic anhydride or dimethyl acetylenedicarboxylate could not be obtained.

The facile ring openings observed with [XXVII] can be readily explained in terms of the factors which have been previously described as contributing to the enhanced reactivity of 1,1,2-triphenyl-1-silacyclobutane and other silacyclobutanes.

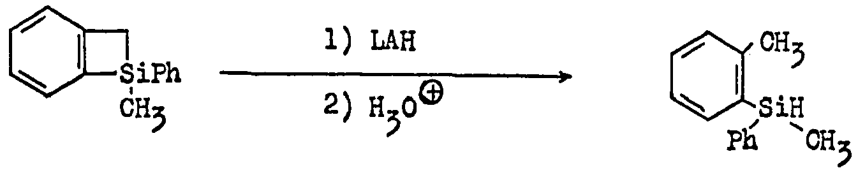
The synthesis of an additional benzosilacyclobutene derivative; namely, 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene [LXXII] was undertaken in order to clarify several points of interest. First, it was of considerable importance to demonstrate the general synthetic utility of Methods B and C. Secondly, the synthesis of a second derivative of this type would allow a more valid comparison and assignment of spectral features. Finally, a comparison of the chemical reactivity of two benzosilacyclobutene derivatives was of fundamental interest.

Reaction of (*o*-bromobenzyl)chloromethylphenylsilane with magnesium in THF (Method B) gave the desired benzosilacyclobutene [LXXII] in a 22% yield. Further, reaction of dichloromethylphenylsilane, *o*-bromobenzyl bromide, and magnesium in THF (Method C) gave a slightly better yield of [LXXII] (30.6%).

Compound [LXXII] is a colorless liquid (b.p. 97.5-98°/0.5 mm.) which, contrary to the diphenyl derivative, exhibits only moderate stability in air (see Experimental section). The infrared spectrum of [LXXII] contained the band at 9.65 microns, previously attributed to the strained benzosilacyclobutene system. Like the diphenyl analog, ring opening of [LXXII] caused the disappearance of this band. The ultraviolet spectrum of [LXXII] (in ethanol) was essentially identical with that of its diphenyl derivative, and contained the following maxima in mμ: 262.5, 269, 276, again substantiating that these spectral properties are characteristic of the strained benzosilacyclobutene system.

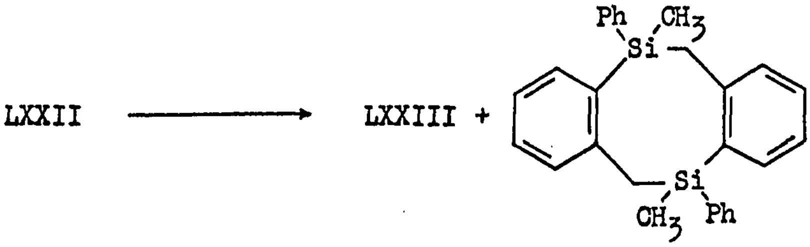
The n.m.r. spectrum of [LXXII] (in carbon tetrachloride) contained, in addition to the aromatic multiplet, two sharp singlets centered at 7.44 and 9.34τ, assigned to the methylene and Si-methyl protons, respectively. The aromatic/aliphatic proton ratio was 1.79 (calcd. 1.80). It is somewhat unusual that while the two methylene protons in [LXXII] would seem to be in different environments, the band due to these protons appeared as a very sharp singlet.

Compound [LXXII] exhibited chemical reactivity comparable to the analogous diphenyl derivative. Thus, reactions with both ethanolic silver nitrate and bromine in carbon tetrachloride were observed with [LXXII] at room temperature. Treatment of [LXXII] with lithium aluminum hydride (LAH) in ether gave the expected methylphenyl-_o_-tolylsilane [LXXII]. In addition, when the reaction of [LXXII] and LAH was carried out in reflux-



LXXII LXXIII

ing THF, the products were [LXXIII] and the anticipated dimer, 2:3, 6:7-dibenzo-1,5-dimethyl-1,5-diphenyl-1,5-disilacycloocta-2,6-diene [LXXIV].



LXXIV

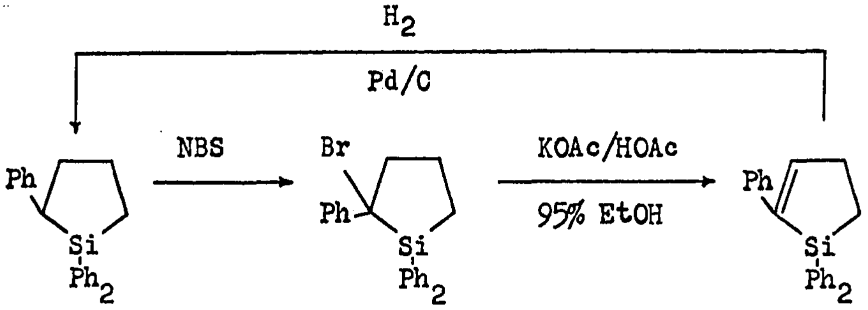
In spite of the possibility for <u>cis-trans</u>-isomerism, only one form of compound [LXXIV] could be isolated in the pure state (m.p. 176.5-177.5) and a sterochemical assignment was not possible.

The n.m.r. spectrum of [LXXIV] (in carbon tetrachloride) showed a typical AB pattern consisting of a pair of doublets of unequal intensity at 7.16 and 7.51 τ. In addition to the above chemical shift values, analysis of the spectrum according to a published procedure (89) gave a value of 13.5 c.p.s. for the coupling constant J_{AB}.

Studies with 1,1,2-Triphenyl-1-silacyclobut-2-ene and Related Compounds

Encouraged by the successful preparation of the previously mentioned silacyclobutane and pseudo-silacyclobutene derivatives, attention was directed toward the synthesis of 1,1,2-triphenyl-1-silacyclopent-2-ene [LXXV] and 1,1,2-triphenyl-1-silacyclobut-2-ene, [LXXVI].

Compound [LXXV] was prepared by a two step synthesis starting with the previously described 1,1,2-triphenyl-1-silacyclopentane [LIV]. Reaction of [LIV] with N-bromosuccinimide (NBS) gave 2-bromo-1,1,2-triphenyl-1-silacyclopentane [LXXVII] in a 79% yield.



LIV LXXVII LXXV

The n.m.r. spectrum of [LXXVII] (in carbon tetrachloride) contained a multiplet centered at 8.65 τ assigned to the methylene protons adjacent to silicon. In addition to the low field aromatic multiplet, the remainder of the spectrum showed a broad band centered at 7.60 τ due to the four remaining methylene protons. The ratio of aromatic/aliphatic protons was 2.50 (calcd. 2.50).

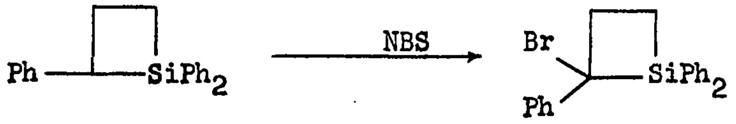
Treatment of [LXXVII] with a potassium acetate-acetic acid mixture in refluxing ethanol gave the desired olefin [LXXV] (77%). Compound [LXXV] is a stable, colorless crystalline solid, m.p. 119-120°. This compound exhibited a light blue fluorescence in ultraviolet light in the solid state and showed the following ultraviolet absorption maximum: $\lambda_{max}^{ethanol}$ 255 mμ (log ε = 4.065). These results are in excellent agreement with those reported (90) for 1-phenylcyclopentene: $\lambda_{max}^{ethanol}$ 255 mμ (log ε = 4.030).

The n.m.r. spectrum of [LXXV] contained two multiplets at 8.73 and 7.22 τ assigned to the protons of the methylene group adjacent to silicon and the olefinic bound methylene group, respectively. These values are similar to those reported (66) for the corresponding protons in 1,1-dichloro-1-silacyclopent-2-ene. The olefinic proton could not be observed in the spectrum and the aromatic/aliphatic proton ratio was in poor agreement with the theoretical value when the aromatic area was assumed to be equivalent to fifteen protons. It appeared reasonable that the olefinic proton band could lie beneath the aromatic absorption since this latter band was quite broad and extended to 3.15 τ. Indeed this appeared to be the case since a recalculation of the above ratio using an aromatic area based on sixteen protons gave a value of 4.0 (calcd. 4.0). In addition, the olefin [LXXV] was quite readily hydrogenated to give 1,1,2-triphenyl-1-silacyclopentane [LIV].

The infrared spectrum of [LXXV] (in carbon tetrachloride) was significantly different from that of the saturated material [LIV]. The spectrum of [LXXV] showed a complete absence of the 9.60 micron band present in [LIV]. Of particular interest is the fact that the spectrum of [LXXV] showed three bands at 10.66 (m), 10.80 (s), and 11.02 (w) microns. At the present time these bands appear to be associated with the cyclic olefin system. The infrared spectrum of 1-phenylcyclopentene contains only a single absorption in this region at 10.48 microns (90).

Compound [LXXV] did not react with ethanolic solutions of silver nitrate and was recovered quantitatively when chromatographed on acidic, neutral and basic alumina.

The preparation of 1,1,2-triphenyl-1-silacyclobut-2-ene [LXXVI] was considerably more involved. Reaction of 1,1,2-triphenyl-1-silacyclobutane [LIII] with NBS gave a monobromo compound ($C_{21}H_{19}BrSi$) which was assigned structure [LXXVIII]. The structural assignment was based on analytical, spectral and chemical evidence.



LIII LXXVIII

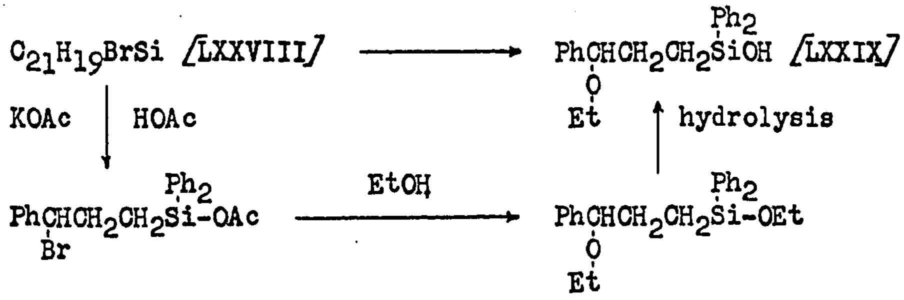
In view of the complexity of the n.m.r. spectrum of [LXXVIII] and the unexpected area ratios obtained, a detailed analysis of this spectrum was necessary. A published (91-93) inerative method for calculating accurate parameters from high resolution spectra (adapted for use with the IBM 7074 computer) was employed[1]. An expansion of the aliphatic proton bands of the observed spectrum together with the calculated spec-

---

[1] L. Rodewald, Iowa State University of Science and Technology, Ames, Iowa. Information on the computer analysis of the n.m.r. spectrum of 2-bromo-1,1,2-triphenyl-1-silacyclobutane. Private communication. 1964.

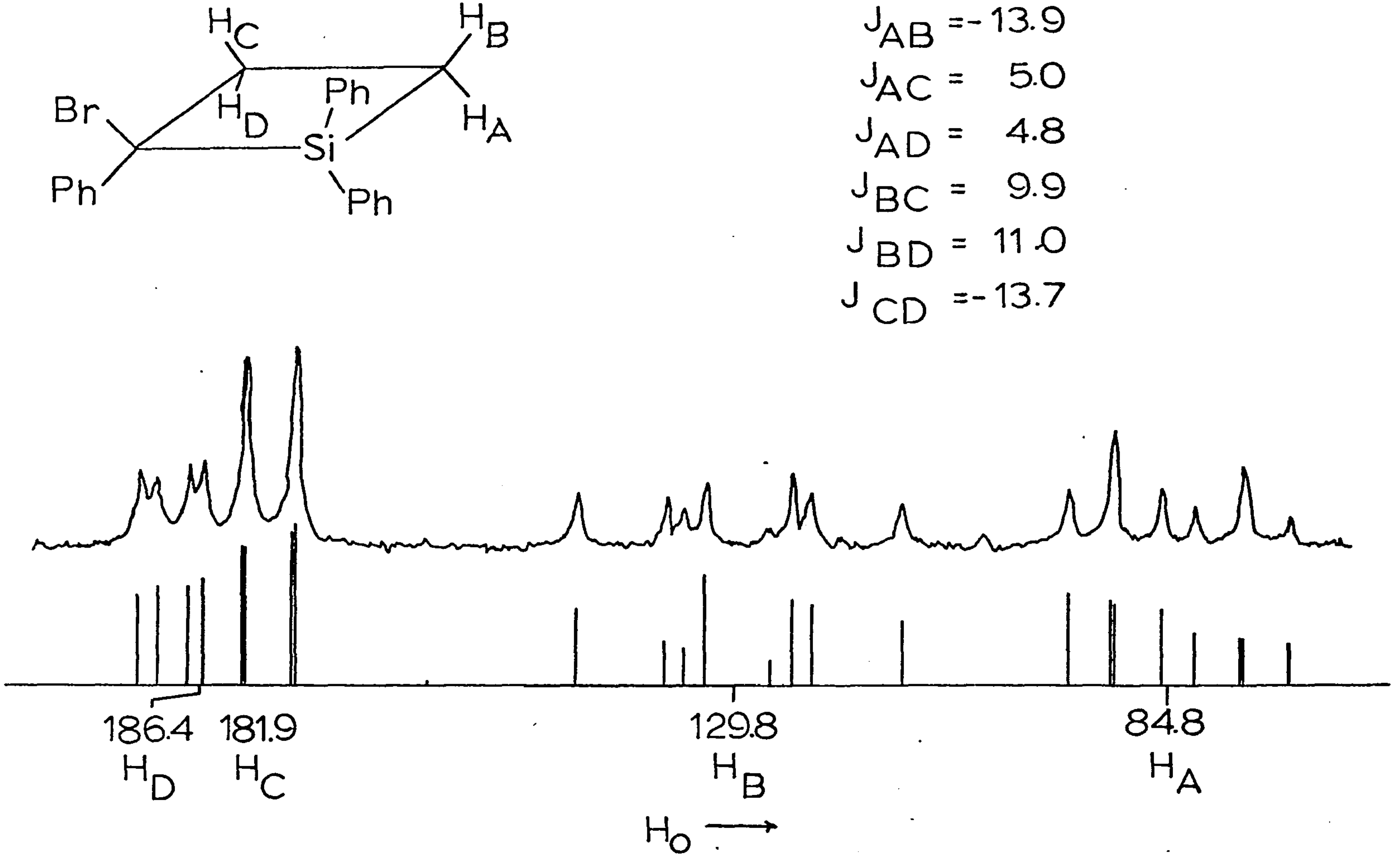
trum is given in Figure 1. A tabulation of the observed line frequencies together with the calculated frequencies and intensities is presented in Table 15. The compatibility of the observed spectrum and the structural assignment is clearly indicated by an examination of Figure 1 and Table 15.

In addition to the n.m.r. spectrum, strong chemical evidence was obtained which supported the conclusion that the monobromo compound is [LXXVIII]. Reaction of the $C_{21}H_{19}BrSi$ compound with a potassium acetate-acetic acid mixture in refluxing ethanol gave (3-ethoxy-3-phenylpropyl)-diphenylsilanol [LXXIX]. The silanol [LXXIX] is believed to result from;



[LXXX] [LXXXI]

(a) the cleavage of the silacyclobutane [LXXVIII] by acetate ion giving [LXXX]; (b) reaction of [LXXX] with ethanol to give the diethoxy compound [LXXXI]; and finally (c) hydrolysis of the SiOEt to SiOH during work-up. The initial cleavage of [LXXVIII] by acetate ion is consistent with the facile ring opening of silacyclobutanes observed with other nucleophiles. Additional evidence was observed for the intermediacy of the diethoxy compound [LXXXI]. In one experiment, the infrared spectrum (in carbon tetrachloride) of the crude product from the reaction of [LXXVIII] with



$J_{AB} = -13.9$
$J_{AC} = 5.0$
$J_{AD} = 4.8$
$J_{BC} = 9.9$
$J_{BD} = 11.0$
$J_{CD} = -13.7$

Figure 1. Aliphatic proton spectrum of 2-bromo-1,1,2-triphenyl-1-silacyclobutane. All values in c.p.s.
(Above) observed spectrum - (Below) calculated spectrum.

Table 15. N.m.r. Spectral Data for 2-Bromo-1,1,2-triphenyl-1-silacyclobutane /LXXVIII/

Observed Frequency	Calculated Frequency[a]	Calculated Intensity[b]
71.57	71.62	0.61
76.71	76.70	0.70
76.71	76.79	0.70
81.81	81.73	0.80
85.40	85.36	1.18
90.44	90.24	1.28
90.44	90.63	1.29
95.34	95.36	1.41
112.86	112.83	1.00
122.07	121.99	1.22
124.17	123.96	1.29
126.73	126.57	0.37
133.32	133.18	1.68
135.41	135.44	0.58
0.00	137.00	0.02
137.64	137.90	0.70
0.00	140.94	0.01
146.90	146.81	1.19
164.30	163.79	0.07
0.00	168.52	0.05
0.00	172.70	0.05
177.03	177.07	2.53
177.03	177.27	2.39
0.00	177.73	0.04
182.12	182.15	2.13
182.12	182.20	2.21
186.37	186.14	1.70
188.13	188.44	1.56
0.00	190.55	0.06
191.48	191.32	1.57
193.27	193.38	1.48
0.00	195.82	0.05
0.00	201.88	0.05
0.00	206.97	0.04

---

[a] The average deviation between the observed and the calculated frequency is 0.14 (only observed frequencies are included in this average).

[b] Bands with an intensity lower than 0.07 are not included in the calculated spectrum in Figure 1.

ethanol contained bands at 8.65, 9.28, and 10.55 microns, indicative of the SiOEt linkage (in compound /LXXXI/). No SiOH bands could be detected in the latter spectrum before chromatographic work-up.

The assignment of structure /LXXIX/ follows from an examination of the infrared (see Experimental section) and n.m.r. spectra. The pertinent n.m.r. spectral data for /LXXIX/ are listed in Table 16. An interesting feature observed in this spectrum was the presence of a double quartet

Table 16. N.m.r. Data for (3-Ethoxy-3-phenylpropyl)-diphenylsilanol /LXXIX/[a,b]

Band Position (in τ values)	Relative Intensity	Band Assignment
5.83 (t)[c]	(1)	$\text{H}-\overset{\overset{\text{O}}{\vert}}{\text{C}}-\text{C}\leqq$
6.32 (s)[d]	(1)	$\geqq\text{SiO-H}$
6.74 (dq)[e]	(2)	$\geqq\text{C-CH}_2\text{-O-}$
8.19 (m)[f]	(2)	$\geqq\text{C-CH}_2\text{-C}\leqq$
8.87 (m)[f]	(5)	$\text{CH}_3\text{-C}\leqq$ and $\geqq\text{C-CH}_2\text{-Si}\leqq$

---

[a] Deuterochloroform solvent.

[b] Aromatic region excluded.

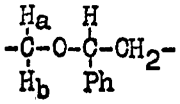
[c] t= Triplet, J= 6.7 c.p.s.

[d] Broad singlet.

[e] Double quartet separated by ca. 2.6 c.p.s. (J= 6.7 c.p.s.).

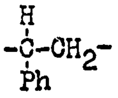
[f] m= Multiplet where the number of peaks could not be counted accurately.

at 6.74 τ (see Table 16, footnote e). It appears that the nonequivalence of the protons in the methylenoxy group results from an intrinsic asymmetry of the ether grouping [LXXXII]. Examples of this phenomenon have been observed previously (89,94,95). To the protons H_a and H_b of the methylenoxy group, the attached group [LXXXIII] is asymmetric and each



$$\text{-}\overset{H_a}{\underset{H_b}{C}}\text{-O-}\overset{H}{\underset{Ph}{C}}\text{-CH}_2\text{-}$$

LXXXII



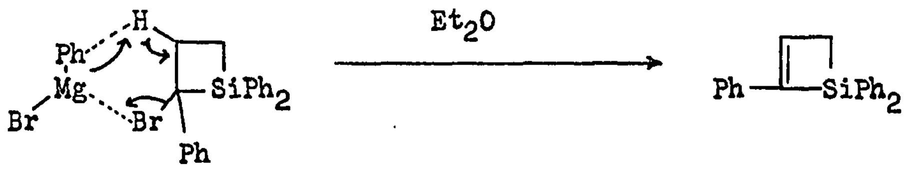
$$\text{-}\overset{H}{\underset{Ph}{C}}\text{-CH}_2\text{-}$$

LXXXIII

proton experiences a different average environment. To what extent restricted rotation may be contributing to the nonequivalence was not studied.

The environment about the benzylic carbon atom was further confirmed by a double resonance (96) experiment. Irradiation of the methylene protons ($\text{Ph-}\overset{H}{\underset{O}{C}}\text{-CH}_2\text{-}$) 136 c.p.s. upfield from the benzylic proton triplet collapsed the latter to a broad singlet. Finally, it should be noted that the position of the ethoxy group in the silanol [LXXIX] lends considerable support to the conclusion that the bromo substituent in [LXXVIII] was located on the benzylic carbon.

The main difficulty involved in the preparation of a silacyclobutene derivative is the susceptibility of the four-membered silicon rings to nucleophilic ring opening. Thus, a great majority of the known dehydrohalogenation techniques are of little use. The successful synthesis of 1,1,2-triphenyl-1-silacyclobut-2-ene [LXXVI] involved the treatment of 2-bromo-1,1,2-triphenyl-1-silacyclobutane [LXXVIII] with an ethereal solution of phenylmagnesium bromide (ratio 1:1). By analogy with previously reported (97) dehydrohalogenations of this type we have suggested that this bimolecular reaction proceeds through a cyclic mechanism. At the present time the successful synthesis of [LXXVI] is attributed to the stability of the silacyclobutane and silacyclobutene ring to phenylmagnesium bromide and to steric conditions (in [LXXVIII]) resulting in a slow "condensation" reaction (97).



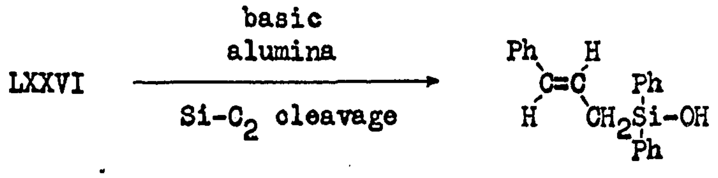
LXXVIII LXXVI

Compound [LXXVI] is a white, moderately stable solid, m.p. 54-55°, which can be distilled without apparent decomposition at low pressures (b.p. 149-150°/0.005 mm.). Pure 1-phenylcyclobutene, an oil of styrene like odor, sets to a gel (probably a polymer) on standing for several weeks. The ultraviolet spectrum of [LXXVI] (in ethanol) shows a maximum at 256 mμ ($\log \varepsilon = 4.194$). These values are in close agreement with those reported (98) for 1-phenylcyclobutene, $\lambda_{max}^{ethanol} = 251\text{-}255$ ($\log \varepsilon = 4.138\text{-}4.146$).

The infrared spectrum of [LXXVI] (in carbon tetrachloride) showed a complete absence of the 11.52 micron band previously reported in the saturated precursor, 1,1,2-triphenyl-1-silacyclobutane. In addition, the spectrum of [LXXVI] contained a trio of bands at 10.42 (m), 10.68 (m), and 11.02 (w) microns. While this latter pattern is similar to that observed in 1,1,2-triphenyl-1-silacyclopent-2-ene [LXXV] a shifting of the position of the first two bands is apparent.

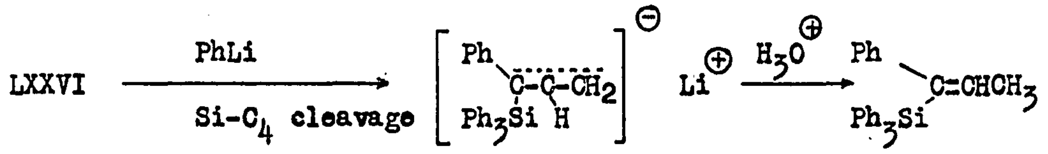
The n.m.r. spectrum of [LXXVI] contained a doublet centered at 8.10 τ (J= 2.0 c.p.s.). The magnitude of this coupling constant is of the order observed (99,100) for cyclobutene derivatives. As in the case of the five-membered ring homolog [LXXV], the olefinic band was not apparent and the remainder of the spectrum consisted of a broad aromatic region extending to 3.10 τ. Assuming an aromatic area of sixteen protons (olefinic included in this area) gave an aromatic/aliphatic ratio of 8.0 (calcd. 8.0). In case of [LXXVI] it became desirable (for reasons which will become apparent later) to confirm the existence of the olefinic proton. This was readily accomplished by a double resonance (96) experiment. Irradiation of the aromatic multiplet 329 c.p.s. downfield from the methylene doublet collapsed the latter to a sharp singlet. From the above information the position of the olefinic proton was calculated as 2.72 τ, well within the edge of the aromatic multiplet.

Compound [LXXVI] reduced an ethanolic solution of silver nitrate in agreement with previously reported silacyclobutane reactivity. Chromatography of [LXXVI] employing a basic alumina column resulted in ring opening. The infrared spectrum of the resulting product showed the presence of an SiOH group and a trans-double bond suggesting the formation of diphenyl(3-phenyl-2-propenyl)silanol [LXXXIV]. The ultraviolet spectrum of [LXXIV] contained a maximum at 259 $m\mu$ giving further support to the proposed structure.



LXXIV

An alternate mode of ring opening of [XXVI] was observed with phenyllithium. In this latter case the reaction product was 1-phenyl-1-(triphenylsilyl)propene-1 [LXXXV]. In view of the allylic nature of the



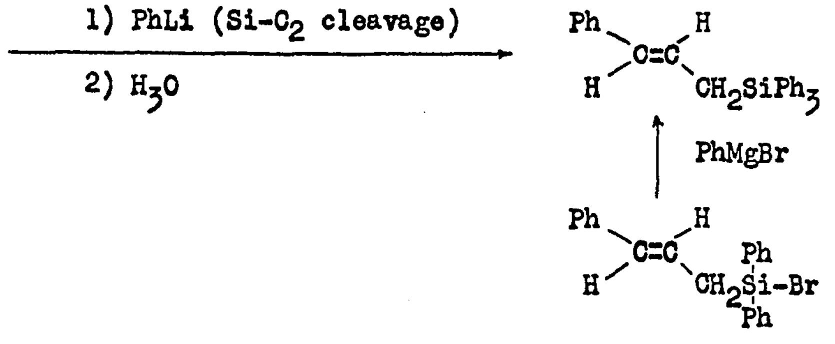
LXXXVII LXXXV

intermediate organometallic compound [LXXXVII], it was not possible to ascertain the stereochemistry of the olefin [LXXXV]. The n.m.r. spectrum of [LXXXV] (in carbon tetrachloride) showed, in addition to the aromatic multiplet, a doublet at 8.15τ (J= 6.5 c.p.s.) and a quartet at 3.59 (J= 6.5 c.p.s.), assigned to the methyl and methinyl protons, respectively.

The ultraviolet spectrum of [LXXXV] contained no maximum above 220 mμ. An examination of a molecular model (Stuart-Briegleb models) of [LXXXV] revealed that the bulky triphenylsilyl group prevents coplanarity of the phenyl group and the ethylenic bond, thus rationalizing the observed spectrum. No (3-phenyl-2-propenyl)triphenylsilane [LXXXVII], the product which would result from Si-C_2 cleavage, could be isolated. A known sample of [LXXXVII] was prepared from (3-phenyl-2-propenyl)-

diphenylsilane [LVII] and phenylmagnesium bromide ($\underset{H}{>C}=\overset{H}{C}<$ at 10.45 microns, Ph-C=CH- at 261 mμ).

LXXVI



LXXXVII

LVII

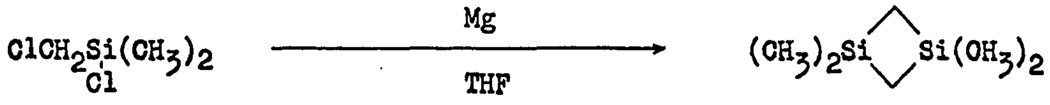
One of the most unexpected properties of [LXXVI] was its inertness to >C=C< hydrogenation. Although a variety of hydrogenation conditions were employed [LXXVI], contrary to its five-membered ring homolog [LXXV], resisted hydrogen uptake (hence the necessity for the double resonance experiment). It seems a logical assumption that this resistance to hydrogenation can be attributed to steric conditions resulting in inadequate contact between [LXXVI] and the catalyst surface. The same reasoning has been previously suggested (49) to explain the inertness of dimethyl 1,4,5,6,7,7-hexaphenyl-7-silanorbornadiene-2,3-dicarboxylate (another strained cyclic organosilicon compound) to >C=C< hydrogenation.

Studies with 1,1,3,3-Tetramethyl-1,3-Disilacyclobutane

The preparation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane [LXXXVIII] was undertaken in connection with a general study concerned with the preparation and properties of strained cyclic organosilicon compounds. Although a preparation of this compound had been previously described (25) that procedure involved a series of reaction steps (see Historical section) which made it tedious and unattractive.

The reaction of compounds of the general formula, $ClCH_2SiR_2Cl$, with metals has been reported (101) to give polymers of the type, $(-CH_2SiR_2-)_n$. It seemed likely that under suitable conditions, a reaction of this type could yield the desired disilacyclobutane /LXXXVIII/.

Reaction of (chloromethyl)dimethylchlorosilane /LXXXIX/ with magnesium in tetrahydrofuran (THF) gave /LXXXVIII/ in moderate yields (9-20%). The physical properties of this compound were in good agreement with those previously reported, and the infrared spectrum was identical



LXXXIX LXXXVIII

with that of a known sample (25).

During this investigation, a similarity was observed between the physical properties and chemical reactivity of /LXXXVIII/ and those of an isomeric compound previously reported (31) to be the silaolefin /XC/. Prompted by this observation, a detailed and elegant reexamination of

$$(CH_3)_2Si{=}CHSi(CH_3)_3$$

XC

this problem by the original authors (31) demonstrated that the compound believed to be the silaolefin [XC] was actually 1,1,3,3-tetramethyl-1,3-disilacyclobutane [LXXXVIII] (32)[1].

In view of the subsequent extensive investigations (25,27-32,35,38, 39) of [LXXXVIII], little work was devoted to a study of the chemical properties of this compound. However, dipole moment studies of [LXXXVIII] were carried out[2]. The absence of an observable dipole[2] eliminated the presence of a fixed nonplanar ring system in [LXXXVIII]. While the lack of such a dipole may be indicative of a planar structure, a rapidly inverting nonplanar configuration is also possible.

Compound [LXXXVIII] exhibited the high degree of reactivity toward bromine and ethanolic silver salt solutions previously reported (25). The reactions of silacyclobutanes with bromine (25,28-32) and silver nitrate (25,30) have been reported to proceed with ring opening. The ability to reduce ethanolic solutions of silver salts appears to be a characteristic of four-membered silicon-containing heterocycles. In addition to [LXXXVIII], the following compounds have been found to reduce such salt solutions: (a) octaphenylcyclotetrasilane [I]; (b) 1,1,2-triphenyl-1-silacyclobutane [LIII]; (c) 1,1,2-triphenyl-1-silacyclobut-2-ene [LXXVI]; (d) 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene [LXXVII];

---

[1] Dr. G. Fritz, Institute for Inorganic Chemistry, Justus Liebig University, Giessen, Germany. Information on the products resulting from the pyrolysis of tetramethylsilane. Private communication. 1962.

[2] Dr. H. K. Higgenbotham, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the dipole moment of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Private communication. 1964.

(e) 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene /LXXII/; and (f) 1,1-dimethyl-1-silacyclobutane /IV/ (25). This qualitative test must be applied with some caution, however, since Si-H compounds (64) and 1,1-dimethyl-1-silacyclopentadiene (102) have also been reported to reduce silver salts under comparable conditions.

Suggestions for Further Research

In such a new area of research, it is not unexpected that numerous research proposals are possible, many of them dealing with fundamental principles. Thus, while a qualitative comparison of the reactivity of the four- and five-membered rings has been accomplished in this thesis, no actual kinetic data (other than the excellent work of Sommer and co-workers) relating these species have been reported in the literature. Also, the study presented herein has provided little information concerning even the qualitative relative reactivities of 1,1,2-triphenyl-1-silacyclobutane, 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene, 2:3- benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene, 1,1,2-triphenyl-1-silacyclobut-2-ene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. A kinetic study of the relative reactivities of these compounds should be quite informative.

The susceptibility of the four-membered rings to nucleophilic attack suggests the possibility of ring expansion reactions with diazomethane. In the case of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene, the expected products would be nitrogen and the five-membered ring homolog, 2:3-benzo-1,1-diphenyl-1-silacyclopent-2-ene.

The inertness of 1,1,2-triphenyl-1-silacyclobut-2-ene to $>C=C<$

hydrogenation was quite unexpected. The synthesis of less hindered derivatives of this type would allow one to test the validity of the suggested steric origin.

The utilization of the benzosilacyclobutene derivatives for the preparation of more highly strained cyclic compounds, such as benzosilacyclobutenones, should also be investigated. A similar transformation; namely, that of benzyltriphenylsilane to benzoyltriphenylsilane, has been reported (81).

The question of the planarity or nonplanarity of the 1,3-disilacyclobutane ring system seems worthy of further investigation. A study of the equivalence of the methylene protons of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, as observed by low temperature n.m.r. techniques, should be informative.

Finally, the development of new methods for the synthesis of strained cyclic organosilicon compounds would greatly expedite investigations in this area.

SUMMARY

A review of the reported chemistry of strained cyclic organosilicon compounds has been presented. This review includes all cyclic compounds in which the silicon atom is connected to only carbon atoms in the ring system.

The reactions of octaphenylcyclotetrasilane with inorganic halogenating agents has been studied, and the yield of 1,4-dichlorooctaphenyltetrasilane was observed to decrease in the order: phosphorus pentachloride > sulfuryl chloride > thionyl chloride. An extension of this study described the reaction of this cyclosilane with mercuric acetate. The product of this latter reaction is 1,4-diacetoxyoctaphenyltetrasilane.

It has been shown, on the basis of chemical and spectral evidence, that the compound previously reported to be 3,3-dicarbethoxy-1,1-dimethyl-1-silacyclobutane is actually (2,2-dicarbethoxypropyl)ethoxydimethylsilane.

The preparation of 1,1,2-triphenyl-1-silacyclobutane and 1,1,2-triphenyl-1-silacyclopentane has been reported, together with a comparison of the reactivity of these compounds with: (a) basic alumina; (b) lithium aluminum hydride; (c) phenyllithium; and (d) phenylmagnesium bromide. A discussion of the factors contributing to the enhanced reactivity of silacyclobutanes has been presented.

The preparation of the first reported pseudo-silacyclobutene derivative; namely, 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene, by three independent synthetic methods has been accomplished. The reactivity of

this latter compound was found to be comparable to that of 1,1,2-triphenyl-1-silacyclobutane. However, when the lithium aluminum hydride cleavage of this benzosilacyclobutene derivative was carried out in tetrahydrofuran solvent, a dimeric product, 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene was obtained. Mechanistic details of this unusual and unexpected dimerization are given. The reactions observed with this benzosilacyclobutene were also exhibited by 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene. The preparation of this latter compound (by the same general methods) allowed a comparison of the spectral properties of these two derivatives.

Reaction of 1,1,2-triphenyl-1-silacyclobutane with N-bromosuccinimide gave 2-bromo-1,1,2-triphenyl-1-silacyclobutane. The structure of this compound was substantiated by chemical and spectral data. This latter data included a detailed analysis of the n.m.r. spectrum.

Treatment of 2-bromo-1,1,2-triphenyl-1-silacyclobutane with phenylmagnesium bromide gave 1,1,2-triphenyl-1-silacyclobut-2-ene. The spectral and chemical properties of this latter compound were compared with those of 1,1,2-triphenyl-1-silacyclopent-2-ene. One of the most unexpected properties observed for the silacyclobutene derivative was its inertness to $>C=C<$ hydrogenation.

A convenient one step method for the synthesis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane has been presented. The absence of an observable dipole moment indicates that this compound contains either a planar or a rapidly inverting nonplanar ring system.

LITERATURE CITED

1. F. S. Kipping and J. E. Sands, J. Chem. Soc., 119, 830, 848 (1921).
2. F. S. Kipping, J. Chem. Soc., 125, 2291 (1924).
3. A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson and H. Gilman, J. Am. Chem. Soc., 83, 1921 (1961).
4. H. Gilman and G. L. Schwebke. Organic Substituted Cyclosilanes. In F. G. A. Stone and R. West, eds. Advances in Organometallic Chemistry. Vol. 1, pp. 89-141. New York, New York, Academic Press. 1964.
5. W. B. Hart, Rep. Brit. Assoc. (Manchester), 1887, 661.
6. R. R. Widdowson, J. Chem. Soc., 1926, 958.
7. A. Bygden, Ber. Deut. Chem. Ges., 48, 1236 (1915).
8. L. H. Sommer and G. A. Baum, J. Am. Chem. Soc., 76, 5002 (1954).
9. R. West, J. Am. Chem. Soc., 77, 2339 (1955).
10. R. A. Benkeser and E. W. Bennett, J. Am. Chem. Soc., 80, 5414 (1958).
11. L. H. Sommer, U. F. Bennett, P. G. Campbell and D. R. Weyenberg, J. Am. Chem. Soc., 79, 3295 (1957).
12. D. R. Weyenberg. Studies on the Mechanism of the Base-Catalyzed Solvolysis of Triorganosilanes. Unpublished Ph.D. thesis. University Park, Pennsylvania, Library, The Pennsylvania State University. 1958.
13. L. Kaplan and K. E. Wilzbach, J. Am. Chem. Soc., 77, 1297 (1955).
14. R. West, J. Am. Chem. Soc., 76, 6015 (1954).
15. A. Streitwieser, Jr. Solvolytic Displacement Reactions. New York, New York, McGraw-Hill Book Co., Inc. 1962.
16. H. C. Brown and M. Borkowski, J. Am. Chem. Soc., 74, 1894 (1952).
17. A. D. Petrov, V. A. Ponomarenka, B. A. Sokolov and G. V. Odabashyan, Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci. (English translation), 1957, 1230.
18. B. Smith, Acta Chem. Scand., 9, 1286 (1955).

19. G. H. Jeffery and A. J. Vogel, J. Chem. Soc., 1948, 1804.

20. V. M. Vdovin, N. S. Nametkin and P. L. Grinberg, Proc. Acad. Sci. U. S. S. R., Div. Chem. Sci. (English translation), 150, 449 (1963).

21. V. M. Vdovin, K. S. Pushchevaya and A. D. Petrov, Proc. Acad. Sci. U. S. S. R., Div. Chem. Sci. (English translation), 141, 1203 (1961).

22. N. S. Nametkin and V. M. Vdovin, J. Polym. Sci., Part C (4), 1043 (1963).

23. N. S. Nametkin, V. M. Vdovin, and V. I. Zav'yalov, Izv. Akad. Nauk U. S. S. R., Ser. Khim., (1), 203 (1964). Original available but not translated; abstracted in Chem. Abstr., 60, 12117 (1964).

24. N. S. Nametkin, V. M. Vdovin, and P. L. Grinberg, Doklady. Akad. Nauk U. S. S. R., 155, 849 (1964). Original available but not translated; abstracted in Chem. Abstr., 60, 15901 (1964).

25. W. H. Knoth, Jr. and R. V. Lindsey, Jr., J. Org. Chem., 23, 1392 (1958).

26. P. G. Campbell. Synthesis and Chemistry of New Organosilicon Nitrites, Esters and Related Substances. Unpublished Ph.D. thesis. University Park, Pennsylvania, Library, The Pennsylvania State University. 1957.

27. W. H. Knoth, Jr. U. S. Patent 2,850,514. Sept. 2, 1958. Abstracted in Chem. Abstr., 53, 4166 (1958).

28. R. Mueller, R. Koehne and H. Beyer, Chem. Ber., 95, 3030 (1962).

29. G. Fritz and J. Grobe, Z. Anorg. Allgem. Chem., 315, 167 (1962).

30. R. Mueller, C. Dathe and R. Koehne, Z. Chem., 3, 427 (1963).

31. G. Fritz and J. Grobe, Z. Anorg. Allgem. Chem., 311, 325 (1961).

32. G. Fritz, H. J. Becker, E. A. V. Ebsworth, J. Grobe, W. Kemmerling and G. Sonntag, Z. Anorg. Allgem. Chem., 321, 10 (1963).

33. R. Mueller and W. Mueller, Chem. Ber., 96, 2894 (1963).

34. R. Mueller and W. Mueller, Chem. Ber., 97, 1111 (1964).

35. W. A. Kriner, J. Org. Chem., 29, 1601 (1964).

36. W. A. Piccoli, G. G. Haberland and R. L. Merker, J. Am. Chem. Soc., 82, 1883 (1960).

37. A. W. P. Jarvie, H. J. S. Winkler and H. Gilman, J. Org. Chem., 27, 614 (1962).

38. G. Greber and G. Degler, Makromol. Chem., 52, 174 (1962).

39. G. Fritz, Chimia, 16, 213 (1962).

40. H. Gilman and O. L. Marrs, I. Synthesis of 2:3-Benzo-1-silacycloalkenes, [to be published in J. Org. Chem., ca. (1964)].

41. J. D. Roberts and S. Dev, J. Am. Chem. Soc., 73, 1879 (1951).

42. P. S. Skell and E. J. Goldstein, J. Am. Chem. Soc., 86, 1442 (1964).

43. J. W. Connolly and G. Urry, J. Org. Chem., 29, 619 (1964).

44. O. M. Nefedov and M. N. Manakov, Angew. Chem. Intern. Ed. Engl., 3, 226 (1964).

45. O. M. Nefedov, M. N. Manakov and A. D. Petrov, Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci. (English translation), 1962, 152.

46. D. R. Weyenberg, L. H. Toporcer and M. J. Napoli, Abstr. Am. Chem. Soc., 140, 31Q (1961).

47. H. Gilman and W. H. Atwell, J. Organometal. Chem., 2, 291 (1964).

48. D. J. Peterson. Trapping of Organometallic and Organometalloidal Radicals. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1962.

49. H. Gilman, S. G. Cottis and W. H. Atwell, Some Diels-Alder Adducts of 1,1,2,3,4,5-Hexaphenyl-1-silacyclopentadiene, [to be published in J. Am. Chem. Soc., ca. (1964)].

50. M. E. Vol'pin, Yu. D. Koreshkov, V. G. Dulova and D. N. Kursanov, Tetrahedron, 18, 107 (1962).

51. R. West and R. E. Bailey, J. Am. Chem. Soc., 85, 2871 (1963).

52. H. Gilman, S. G. Cottis and W. H. Atwell, J. Am. Chem. Soc., 86, 1596 (1964).

53. H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, J. Am. Chem. Soc., 72, 5767 (1960).

54. H. Gilman and F. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

55. A. L. Smith, Spectrochim. Acta, 16, 87 (1960).

56. L. J. Bellamy. The Infrared Spectra of Complex Molecules. London, Methuen and Co., Ltd. 1954.

57. K. Nakanishi. Infrared Absorption Spectroscopy. San Francisco, California, Holden-Day, Inc., 1962.

58. H. Gilman and A. W. P. Jarvie, *Chem. Ind. (London)*, *1960*, 965.

59. H. Gilman and G. L. Schwebke, *J. Am. Chem. Soc.*, *86*, 2693 (1964).

60. W. E. Truce and J. P. Milionis, *J. Am. Chem. Soc.*, *74*, 974 (1952).

61. R. D. Gorsich. Some Cyclic Organosilicon Compounds and Derivatives. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.

62. H. G. Brooks. Synthesis and Reactions of Some Organosilicon Hydrides. Unpublished M.S. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

63. M. H. Beeby and F. G. Mann, *J. Chem. Soc.*, *1951*, 411.

64. H. Gilman, H. G. Brooks, Jr. and M. B. Hughes, *J. Org. Chem.*, *23*, 1398 (1958).

65. H. Gilman and G. N. R. Smart, *J. Org. Chem.*, *15*, 720 (1950).

66. R. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico, and P. H. Gund, *J. Am. Chem. Soc.*, *86*, 2446 (1964).

67. H. J. S. Winkler and H. Gilman, *J. Org. Chem.* *27*, 254 (1962).

68. B. N. Dolgov, N. P. Kharitanov and M. G. Voronkov, *J. Gen. Chem.*, (English translation), *24*, 861 (1954).

69. H. Gilman and W. J. Trepka, *J. Org. Chem.*, *27*, 1418 (1962).

70. H. Gilman and H. J. S. Winkler, *J. Org. Chem.*, *26*, 1265 (1961).

71. H. Hartman and C. Sarafidis, *Naturwissenschaften*, *21*, 494 (1962).

72. L. Horner and E. H. Winkelmann, *Angew. Chem.*, *71*, 349 (1959).

73. G. R. Chainani, S. Cooper and H. Gilman, *J. Org. Chem.* *28*, 2146 (1963).

74. H. Gilman, H. A. McNinch and D. Wittenberg, *J. Am. Chem. Soc.*, *23*, 2044 (1958).

75. R. A. Benkeser and R. G. Severson, *J. Am. Chem. Soc.*, *73*, 1424 (1951).

76. D. Wittenberg and H. Gilman, Quart. Rev., 13, 116 (1959).

77. H. Gilman and H. J. S. Winkler. Organosilylmetallic Chemistry. In H. Zeiss, ed. Organometallic Chemistry. pp. 270-345. New York, New York, Reinhold Publishing Corporation. 1960.

78. F. G. Bordwell, H. M. Anderson and B. M. Pitt, J. Am. Chem. Soc., 76, 1082 (1954).

79. J. Newham, Chem. Rev., 63, 123 (1963).

80. W. Huckel. Theoretical Principles of Organic Chemistry. Vol. 1. New York, New York, Elsevier. 1955.

81. C. Eaborn. Organosilicon Compounds. London, Butterworths Scientific Publications. 1960.

82. Sister M. Brandon, M. Tamres and S. Searles, Jr., J. Am. Chem. Soc., 82, 2129 (1960).

83. C. S. Foote, Tetrahedron Letters, No. 9, 579 (1963).

84. M. P. Cava and D. R. Napier, J. Am. Chem. Soc., 78, 500 (1956).

85. K. Ziegler. Organo-Aluminum Compounds. In H. Zeiss, ed. Organometallic Chemistry. pp. 194-269. New York, New York, Reinhold Publishing Corporation. 1960.

86. G. E. Coates. Organo-Metallic Compounds. pp. 126-144. New York, New York, John Wiley and Sons, Inc. 1960.

87. F. R. Jensen, W. E. Coleman and A. J. Berlin, Tetrahedron Letters, No. 1, 15 (1962).

88. F. R. Jensen and W. E. Coleman, J. Am. Chem. Soc., 80, 6149 (1958).

89. L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry. New York, New York, Pergamon Press. 1959.

90. W. H. Tallent, J. Org. Chem., 21, 862 (1956).

91. C. A. Reilly and J. D. Swalen, J. Chem. Phys., 32, 1378 (1960).

92. C. A. Reilly and J. D. Swalen, J. Chem. Phys., 34, 980 (1961).

93. C. A. Reilly and J. D. Swalen, J. Chem. Phys., 34, 2122 (1961).

94. J. A. Elvidge and R. G. Foster, J. Chem. Soc., 1964, 981.

95. G. M. Whitesides, D. Holtz, and J. D. Roberts, J. Am. Chem. Soc., 86, 2628 (1964).

96. R. Freeman, Mol. Phys., 3, 435 (1960).

97. M. S. Kharasch and O. Reinmuth. Grignard Reactions of Nonmetallic Substances, p. 1052. New York, New York, Prentice-Hall, Inc. 1954.

98. J. W. Wilt and D. D. Roberts, J. Org. Chem. 27, 3430 (1961).

99. O. L. Chapman, J. Am. Chem. Soc., 85, 2014 (1963).

100. G. U. S. Smith and H. Kriloff, J. Am. Chem. Soc., 85, 2016 (1963).

101. J. T. Goodwin, Jr., U. S. Patent 2,483, 972. Oct. 4, 1949. Abstracted in Chem. Abstr., 44, 2011 (1950).

102. J. Goubeau, T. Kolmar and H. Hofmann, Ann., 659, 39 (1962).

ACKNOWLEDGMENTS

The author expresses his sincere appreciation to Dr. Henry Gilman not only for his valuable research supervision, but also for his invaluable aid in all areas of graduate academic training.

The assistance of the author's research associates, especially Frank K. Cartledge for his critical reading of this manuscript, is greatly appreciated.

For her endless patience, sacrifices and assistance, of which the typing of this thesis is only an example, the author proudly acknowledges his wife, Barbara.

While it was only with the help of many others that the writing of this thesis was achieved, the author would be remiss if he did not express sincere gratitude to his parents.

This work was supported by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.