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Preparation and stability of phenylated polysilanes

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PREPARATION AND STABILITY OF PHENYLATED POLYSILANES

by

Gerald Lee Schwebke

A Dissertation Submitted to the
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DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1964

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INTRODUCTION

Interest in polysilane compounds stems from the possibility of using the silicon chain as the backbone of potentially useful polymers. Misconceptions based on observations on unsubstituted polysilanes have arisen concerning the relative stability of such compounds as a function of the silicon chain length. Appropriately substituted polysilanes, however, should possess a greater degree of stability and the paucity of such compounds can be laid rather to problems in methods of preparation.

Therefore, the purpose of the work presented here was to investigate methods of preparation of organically substituted polysilanes, more particularly, phenyl substituted compounds having silicon functional moieties in terminal positions.

Entrance into the area of phenyl substituted polysilanes is most easily gained through the perphenylated cyclosilanes, initially studied by F. S. Kipping and his co-workers in the decade following 1920. These compounds have been subject to considerable investigation and deliberation concerning their constitution and structure, both by Kipping and by workers in These Laboratories. Particular emphasis has been placed on the compound, decaphenylcyclopentasilane, in confirming its structure and in investigating its derivatives as intermediates in the synthesis of other polysilanes.

NOMENCLATURE

In naming organosilicon compounds having silicon chains, 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 (1), will be used with the exceptions noted below. Organosilicon compounds having open silicon atom chains will be named as derivatives of compounds of the general formula $H_3Si(SiH_2)_nSiH_3$ and will be called disilanes, trisilanes, tetrasilanes, etc. The generic name of such compounds is silanes. For designating the position of substituents in compounds named as silanes, each member will be numbered from one terminal silicon atom to the other. Because the compounds discussed here are highly substituted straight-chain silanes bearing generally the same organic substituents on each silicon atom, with varying terminal groups, the position of these organic substituents will not be numbered in order to avoid unwieldy sequences of numbers. Therefore, the compound of the formula $BrSiPh_2(SiPh_2)_3SiPh_2Br$[1] will be named

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[1] The abbreviation Ph for the phenyl (C_6H_5) group will be used throughout this thesis. All other groups will be designated by their structural formulas.

1,5-dibromodecaphenylpentasilane, instead of 1,5-dibromo-1,1,2,2,3,3,4,4,5,5-decaphenylpentasilane. The numbering of the phenyl groups is unnecessary, as the shorter name is unambiguous. Also, again to avoid long series of numbers for silane derivatives containing the Si-H group, the naming is accomplished by prefixing to the rest of the name a position symbol, followed by italic capital *H*, for each such group. Therefore, $HSiPh_2(SiPh_2)_5SiPh_2H$ will be named 1*H*,7*H*-tetradecaphenylheptasilane, and $HSiPh_2(SiPh_2)_2SiPh_2OH$ will be 4*H*-octaphenyltetrasilan-1-ol.

Organosilicon compounds containing chains of silicon atoms in a cycle will be named as derivatives of cyclic silicon compounds having the formula $(SiH_2)_n$ and will be called cyclotrisilanes, cyclotetrasilanes, etc., according to the number of members in the ring; they will have the generic name *cyclosilanes*. Cyclosilanes will be numbered in the same way as are carbon compounds of a similar nature. Therefore, the compound $\overline{Si(CH_3)_2SiPh_2(SiPh_2)_3Si}Ph_2$ will be named 1,1-dimethyldecaphenylcyclohexasilane.

Other groups and radicals which are substituents will be named as they are in carbon chemistry. For example, *n*-$C_4H_9SiPh_2(SiPh_2)_3SiPh_2C_4H_9$-*n* will be named 1,5-di-*n*-butyldecaphenylpentasilane.

HISTORICAL

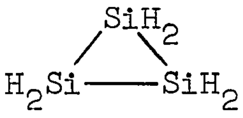
Polysilanes

One property shared by both carbon and silicon is the ability to form stable covalent atom-to-atom bonds, i.e., $\equiv C-C \equiv$ and $\equiv Si-Si \equiv$. The catenation of carbon is well known and is exemplified in its straight-chain paraffinic compounds. The first four members of the analogous series of silanes (Si_nH_{2n+2}), prepared by the acid hydrolysis of magnesium silicide, were initially characterized by Stock (2). With the advent of gas chromatography, such hydrolysis mixtures were shown to contain at least twenty-one components with polysilanes of chain lengths as long as eight silicon atoms being tentatively identified (3). Chlorine-substituted polysilanes and their corresponding hydrolysis products with chain lengths of ten silicon atoms have been characterized (4, 5). Although the polysilanes appear to be less stable than their carbon counterparts (6), they are certainly sufficiently stable to make their isolation and characterization possible.

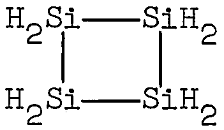
Recently, the structure and chemistry of materials of the type $(SiH_2)_n$ and $(SiH)_n$ have been investigated and reviewed (7). However, these compounds cannot be considered analogous to the alkene or alkyne series in carbon chemistry because of their polymeric nature. The inability of silicon to form multiple bonds with itself or other elements is well known, but perhaps not easily explained (8, 9). It might be pointed out that none of the elements below the second period in the periodic table appears to form stable double bonds with themselves. For example, the compounds "phosphobenzene" and "arsenobenzene," supposedly analogues of azobenzene, are better described as tetraphenylcyclotetraphosphine (10) and hexaphenylcyclohexaarsine (11), respectively. Also, sulfur, under ordinary conditions, exists as a cyclic octamer.

Organic substituted polysilanes are known and will be reviewed in connection with the cyclosilanes. Other elements of Group IVb have a tendency toward catenation, and organic derivatives of polygermanes and polystannanes of chain lengths up to nine are known (12-15). The tendency toward catenation decreases in going from silicon to lead, and no organic lead compounds are known with more than two lead atoms bound together in a chain (7).

A class of polysilanes which can be envisioned as analogous to the cycloalkanes is the cyclosilanes, of which cyclotrisilane (I), cyclotetrasilane (II), cyclopentasilane (III), and cyclohexasilane (IV) would be examples. Although existence of these simple cyclosilanes has not been documented in the literature to date, they



I



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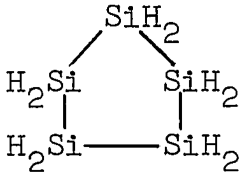

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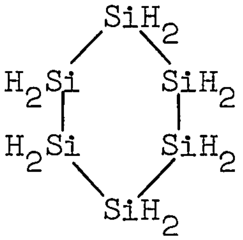
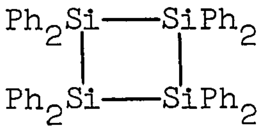


IV

cannot be ruled out as minor products or possible intermediates in the acid hydrolysis of magnesium silicide (2, 3). Attempts to prepare compounds of the silylene type, $(SiH_2)_x$, either by hydrolysis of the calcium silicide, CaSi (16), or by reaction of dichlorosilane with sodium amalgam (17), resulted in the isolation of polymeric materials with less than the required stoichiometric amount of hydrogen. The fact that the simple cyclosilanes are unknown may very well be due, not to the lack of stability of these compounds, but to the lack of synthetic methods.

However, cyclosilanes which are completely substituted with organic groups are known (18-29). These compounds conform to the general formula $(SiR_2)_n$, consisting of a cycle of n silicon atoms, each of which bears two organic groups. At present, the known organic substituted cyclosilanes consist of four-, five-, or six-membered rings which are substituted by phenyl, p-tolyl or methyl groups. Thus, the following compounds (V-IX) have been prepared and their structures have been elucidated, either by direct examination, or by analogy to the phenylated series (V-VI). Also, in the phenylated series a third compound is known; however, its structure has not yet been determined. It is possibly the next member (X) in the homologous series.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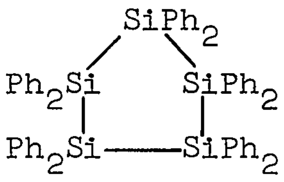
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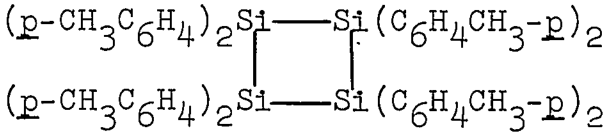
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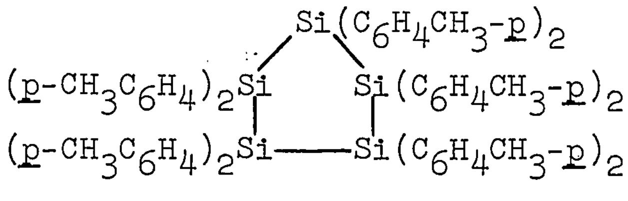
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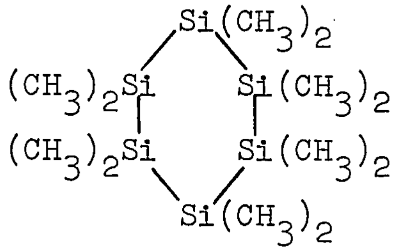
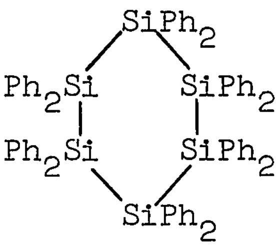


IX



X

Structure and Properties of the Cyclosilanes

Organic substituted cyclosilanes were first recognized as products of reactions designed to prepare compounds containing silicon-silicon double bonds. It would appear that the first substituted cyclosilane or possible mixture of cyclosilanes was prepared by F. S. Kipping by the reaction of dichloroethylphenylsilane with sodium to give a material described as "diphenyldiethylsilicoethylene" (30). Only a few properties of this substance were given. It was described as a vitreous, easily fusible solid which was soluble in common organic solvents except alcohols. Although this material was not recognized as such, it may have been a cyclosilane because the reaction of dichlorosilanes with alkali metals has since been recognized as resulting in cyclosilanes, and because of the fact that silicon is not known to form stable double bonds with another silicon atom, as carbon does with itself in ethylene compounds.

The first examples of well-defined cyclosilanes, also reported by Kipping, were products obtained from the reaction of sodium with dichlorodiphenylsilane in boiling toluene (18). Three distinct crystalline compounds were isolated which were designated as Compound A (18), Compound B (18), and Compound C (19).

In addition to the crystalline cyclosilanes isolated from the reaction of dichlorodiphenylsilane with sodium, there was obtained an amorphous, extremely insoluble, apparently polymeric material designated as Compound D (19). Rather large quantities of viscous liquids which have not as yet been fully characterized were also isolated (31). Partial resolution of these oils was achieved by fractionation from acetone. Some of the less soluble portions appeared to be made up of only diphenylsilylene materials, as indicated by elemental analysis. Cryoscopic determinations of various fractions indicated multiples of the $SiPh_2$ group ranging from seven to nine, and chemical evidence seemed to indicate that the materials were closed chain silanes (31). Compound A could also be prepared in comparable yield from chlorophenoxydiphenylsilane and sodium (32).

The determination of the structures of Compound A and

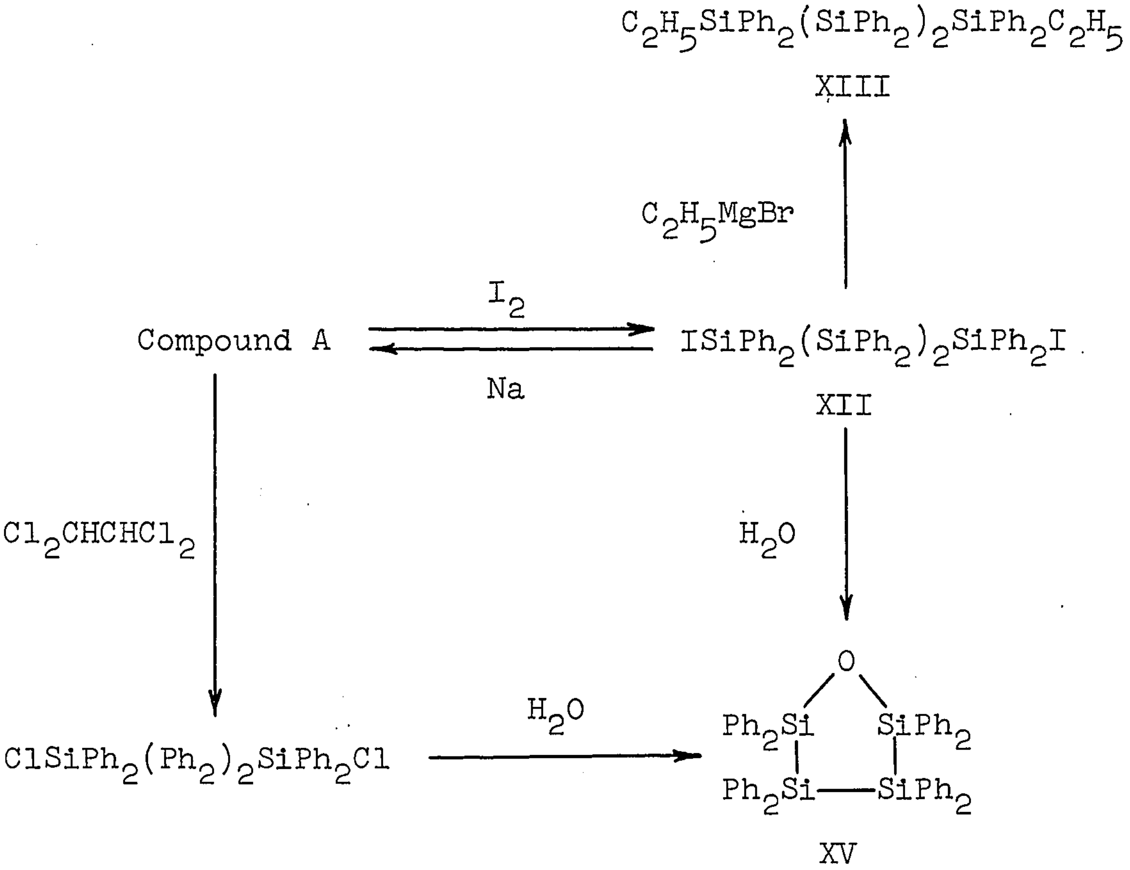
Compound B presented a very interesting problem, which has been resolved only recently. Inaccurate data obtained for the molecular weight of Compound B led to a difficulty concerning the relationship of the two compounds.

Both materials were shown by elemental analysis and hydrogen value determinations (33, 34) to be of the general formula $(SiPh_2)_n$ (18). Also, both compounds upon hydrolysis with aqueous piperidine gave only diphenylsilanediol (XI), or its condensation products. The disturbing fact was that molecular weight determinations appeared to indicate that the two compounds were isomers of the formula $(SiPh_2)_4$.

$$Si_4Ph_8 + 8H_2O \xrightarrow{\text{Piperidine}} \underset{\text{XI}}{4Ph_2Si(OH)_2} + 4H_2$$

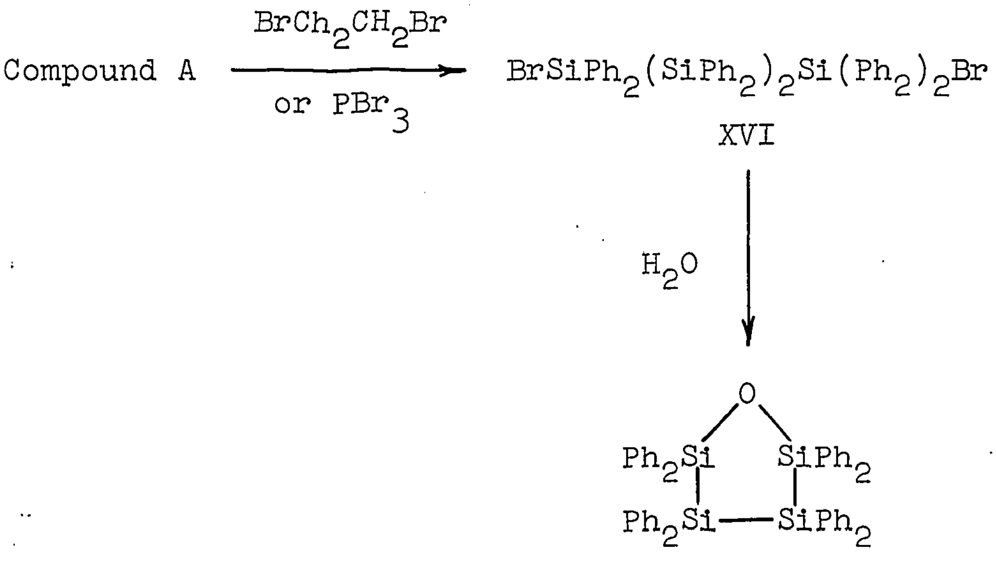
Molecular weights obtained for Compound A were 637 and 699, while those for Compound B were recorded as 734, 718, and 718 (18). Both were determined cryoscopically in benzene, with molecular weights for the former compound being more suspect due to its low solubility in benzene. The calculated molecular weight for Si_4Ph_8 is 729, while those for the next lower and next higher homologue are 547 and 911, respectively. Although the observed molecular weight for Compound B corresponded closely to that expected for a tetrasilane, Kipping was unable to obtain any characteristic derivatives of it due to its stability to the reagents which were tried (18, 19).

On the other hand, Compound A, melting at about 335°, was characterized by its extreme reactivity in comparison to B, resulting in derivatives which indicated very definitely that A was a tetrasilane. Thus, Compound A readily reacted with iodine to give 1,4-diiodooctaphenyltetrasilane (XII), which could be reconverted to A by sodium in refluxing toluene (18). The diiodo derivative could also be converted to 1,4-diethyloctaphenyltetrasilane (XIII) by means of ethylmagnesium bromide (35). Phenylmagnesium bromide did not react similarly, and this was attributed to steric factors. Compound A also reacted with _sym_-tetrachloroethane to give 1,4-dichlorooctaphenyltetrasilane, which was shown to be analogous to the diiodo derivative by conversion to the common hydrolysis product, octaphenyloxacyclopentasilane (XV) (18). Refluxing with 1,2-dibromoethane or phosphorus tribromide transformed A into 1,4-dibromooctaphenyltetrasilane (XVI), which was not isolated but converted directly to the cyclic oxide (XV) by aqueous acetone (36). Compound A was decomposed readily with oxygenating agents, such as refluxing nitrobenzene (18), benzaldehyde and amyl nitrite (36), as well as oxygen and ozone, to give several oxygenated products in varying amounts (36). Compound B, a material of rather greater



solubility than A and not melting below 360°, was found to be generally unreactive with all these reagents under similar conditions.

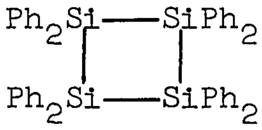
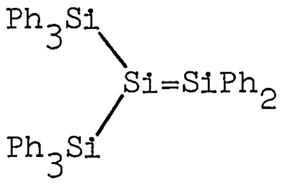
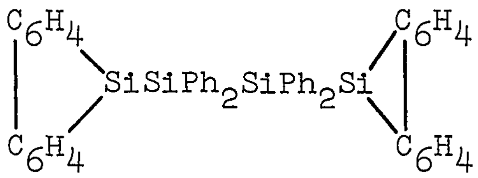
Kipping was then left with assigning a structure to each of the significantly different compounds, each of which appeared to be an octaphenyltetrasilane. Several possible structures were considered for Compound A, which was termed by Kipping as "unsaturated" (18).

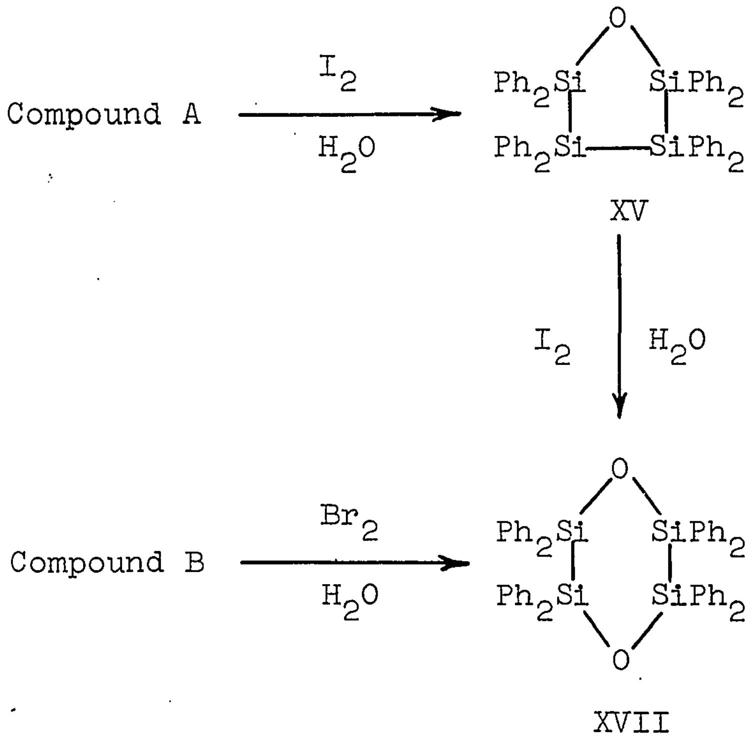


XV

Structure I, Table 1, was quickly dismissed because of the reaction of A with iodine, and because of the experimental molecular weight. While structure II, Table 1, was tenable for the "unsaturated" compound, this structure was desired by him for Compound B. A number of factors ruled against isomers III, IV, and V, Table 1, including the improbability of their formation in the reaction mixture producing A; the fact that no triphenylsilanol was obtained from the hydrolysis of A; and the fact that the same cyclic dioxide (XVII) (37) could be obtained starting with either A or B (18). Hydrogen value, hydrolysis products and behavior toward iodine eliminated isomers VI and VII, Table 1.

Table 1. Structures considered by Kipping for Compound A (18)

Number	Structure
I	$Ph_2Si{=}SiPh_2$
II	
III	$Ph_3SiSiPh{=}SiPh{-}SiPh_3$
IV	$Ph_3SiSiPh_2SiPh{=}SiPh_2$
V	
VI	$C_6H_4{=}SiPhSiPh_2SiPh_2SiPh{=}C_6H_4$
VII	
VIII	$\cdot SiPh_2SiPh_2SiPh_2SiPh_2\cdot$



Kipping also suggested that the two compounds were possibly both octaphenylcyclotetrasilane, one with all four silicons in a plane while, in the other, the silicons were in a tetrahedral arrangement (18). However, recognizing that ready reaction with iodine and with oxidizing agents was reminiscent of the free radical species of carbon, Kipping assigned to Compound A, although it was colorless, an open chain structure of four diphenylsilylene units with terminal tervalent silicon atoms, $\cdot SiPh_2SiPh_2SiPh_2SiPh_2\cdot$ (36). To Compound B, because of its relative stability to a variety of reagents, he assigned the closed chain structure, octaphenylcyclotetrasilane (V) (36).

Based on these conclusions, Compound A might be expected to be converted into Compound B simply by heating; however, it appeared to be stable to heat. When A was melted (about 335°) in a sealed exhausted tube for twenty hours and then allowed to cool, the pale yellow oil crystallized almost immediately and appeared to be unchanged A (36). In the work of Schlenk and Mark (38), Kipping found support for a postulate that the structure of Compound A containing tervalent silicon need not be prone to cyclize or polymerize. Those workers had found that the free radical species, triphenylmethyl and pentaphenylethyl, did not combine to give octaphenylpropane, nor did pentaphenylethyl dimerize to produce decaphenylbutane.

Six years later Kipping had occasion to publish results of the reaction of dichlorodi-p-tolylsilane with sodium in refluxing toluene (20) which gave a mixture of products, two of which were recognized as being analogous to compounds A and B. Therefore, to the less soluble material, melting at 290-293°d, Kipping assigned the structure of octa-p-tolyltetrasilane, with two tervalent silicon atoms. This material readily reacts with iodine to give 1,4-diiodoocta-p-tolyltetrasilane which is in turn hydrolyzed to octa-p-tolyloxacyclopentasilane. It also undergoes other reactions characteristic of Compound A. The second compound, designated as octa-p-tolylcyclotetrasilane, by analogy to Compound B, was found not to react with iodine, sym-tetrachloroethane or nitrobenzene.

In 1937, when Kipping summarized his work in the field of organosilicon chemistry (39), he still felt, justifiably, that the structures which he had assigned to Compounds A and B and their p-tolyl analogues were correct and in accord with the evidence which had been accumulated.

In 1930 Kraus and Brown (40) obtained from the reaction of diphenyldichlorogermane with sodium in refluxing xylene a product designated by them as "diphenylgermanium." This compound, which melted at 294-296°, was insoluble in common organic solvents and readily reacted with sodium in liquid ammonia to give germylmetallic compounds. The molecular weight of the compound, determined ebullioscopically in benzene, corresponded to a tetramer, $(Ph_2Ge)_4$. These workers, however, cite no analogy between this compound and Kipping's Compound A.

The problem lay dormant until 1960, when, in connection with a study of the direct preparation of organosilyllithium compounds from chlorosilanes (41, 42), it was found that appreciable quantities of 1,4-dilithiooctaphenyltetrasilane were produced when an excess of lithium was reacted with dichlorodiphenylsilane in tetrahydrofuran (43).

It was also recognized that a compound identical with Kipping's Compound A was an intermediate in the reaction. An investigation of this material was undertaken, and electron paramagnetic resonance studies of it, both in the solid state and in toluene solution, failed to detect unpaired electrons (25). The structure therefore assigned to Kipping's Compound A is octaphenylcyclotetrasilane (V), and its reactivity is explained as due to ring strain in the cyclic structure (25). Subsequently, it was discovered that the silicon-silicon bond in octaphenylcyclotetrasilane would react with a variety of halogenating agents, both organic and inorganic, with organolithium and organosilyllithium reagents as well as hydrogen chloride, hydrogen bromide and hydrogen iodide. It might be pointed out that the reactivity of the silicon-silicon bond in octaphenylcyclotetrasilane is qualitatively of the order of that found in the unstrained systems of hexaphenylditin and hexaphenyldilead (7), which react with halogens, alkali metals and oxidizing agents. Hexaethylditin and hexaethyldilead have both been shown to react with 1,2-dibromoethane (44), as does Compound A.

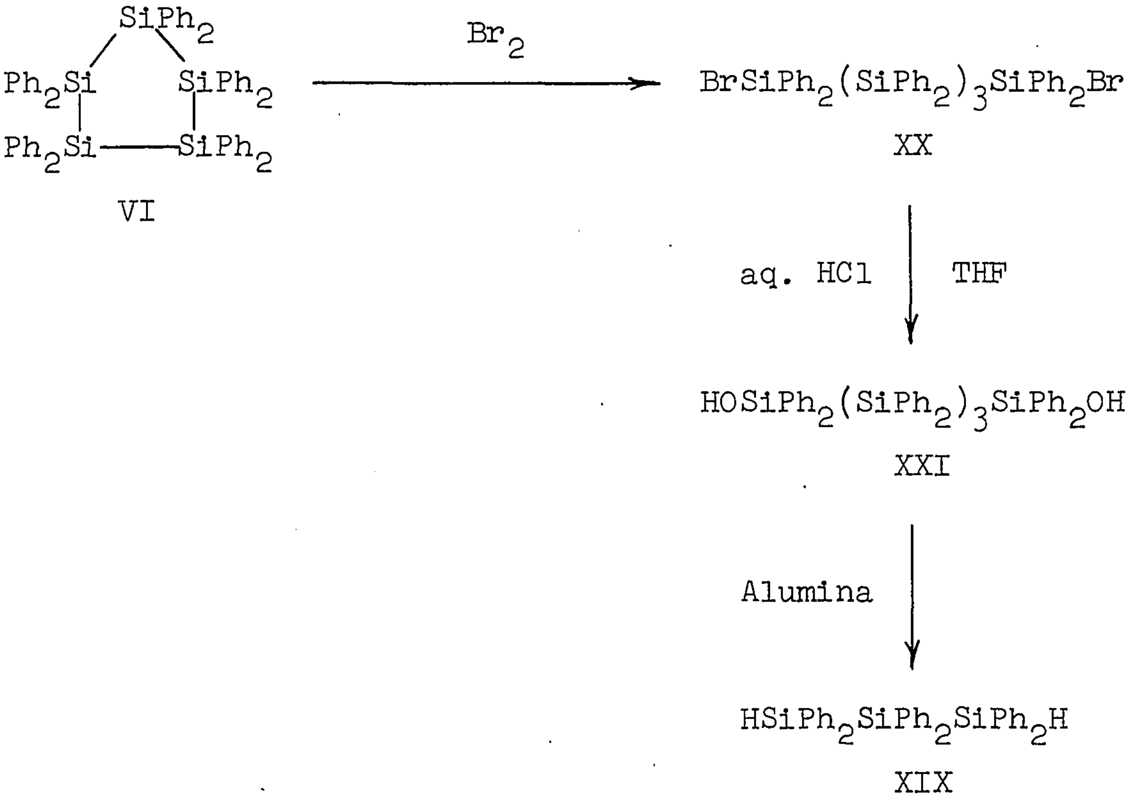
This then leaves the problem of the structure for Compound B, which Kipping considered to be the cyclic tetramer.

As implied previously, Kipping had obtained inaccurate data which forced him into the position concerning Compound A outlined above. This concerned the molecular weight of Compound B, the only evidence Kipping possessed which indicated that the compound was a tetrasilane. He had little chemical evidence for this assumption. The molecular weight did, in fact, appear to be a point of concern, because it was redetermined by him cryoscopically in both benzene and camphor (19), but again a tetrasilane was indicated. Kipping, however, did point out that experimentally determined molecular weights of hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane were 15 to 20% low in benzene (45). Kipping did not follow this implication, first of all, because the deviation of the molecular weight from a tetrasilane was not very great and, secondly, because he assumed that a difference in ring size would not explain sufficiently the great difference in reactivity of the two compounds.

The problem of the molecular weight and structure of Compound B was investigated in our Laboratories (28) after the structure of octaphenylcyclotetrasilane had been assigned to Compound A. The molecular weight was initially determined cryoscopically in perylene and by isothermal distillation methods. By the perylene method, a range of 830 to 1270 was obtained for seven determinations with an average value of 1085. This molecular weight indicated that Compound B was dodecaphenylcyclohexasilane. The isothermal distillation method also indicated a hexasilane, with values of 1025, 1120, and 1225 being obtained. Three derivatives of Compound B were also obtained; they were compounds assigned the structures 1,6-dimethyldodecaphenylhexasilane, 1,6-dibromododecaphenylhexasilane and its hydrolysis product, dodecaphenylhexasilane-1,6-diol (28). Attempts to prepare the first of these compounds by methods not involving Compound B and its derivatives were inconclusive. It might be pointed out that the elemental analysis of these compounds is also not conclusive evidence for their structure.

After the above information was published concerning Compound B (28), an investigation into the cleavage of the silicon-silicon bond adjacent to an hydroxy group in polysilanols was carried out (46). It had been shown previously that when the hydrolysis product of 1,4-dichlorooctaphenyltetrasilane was simply chromatographed on alumina, 1*H*,2*H*-tetraphenyldisilane could be obtained (47). This reaction appears to be general, because, as an example, 4*H*-octaphenyltetrasilan-1-ol (XVIII), when chromatographed on alumina, gives 1*H*,3*H*-hexaphenyltrisilane (XIX) (46). However, when the dihydroxy derivative of Compound B was submitted to this treatment, the product was again 1*H*,3*H*-hexaphenyltrisilane (XIX), indicating that the compound was actually decaphenylpentasilane-1,5-diol (XXI) (46), and that Compound B is decaphenylcyclopentasilane (VI).

$$\underset{\text{XVIII}}{HSiPh_2(SiPh_2)_2SiPh_2OH} \xrightarrow{\text{Alumina}} \underset{\text{XIX}}{HSiPh_2SiPh_2SiPh_2H}$$

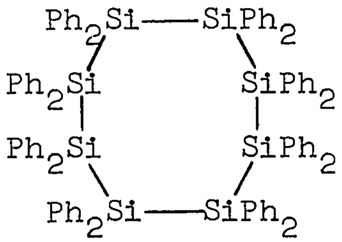


VI

$$\xrightarrow{Br_2} \underset{\text{XX}}{BrSiPh_2(SiPh_2)_3SiPh_2Br} \xrightarrow[\text{THF}]{\text{aq. HCl}} \underset{\text{XXI}}{HOSiPh_2(SiPh_2)_3SiPh_2OH} \xrightarrow{\text{Alumina}} \underset{\text{XIX}}{HSiPh_2SiPh_2SiPh_2H}$$

Compound C was the third crystalline compound isolated by Kipping (19). It was usually obtained in a mixture with octaphenylcyclotetrasilane, from which Compound C was separated either by fractional crystallization or by conversion of the octaphenylcyclotetrasilane to its more soluble 1,4-diiodide or 1,4-dichloride. Kipping found that Compound C did not react with the reagents which attach octaphenylcyclotetrasilane. Compound C was described as a crystalline material which, when heated in a test tube, did not melt at high temperatures, charred slightly and gave vapors which took fire with distinct explosion (19).

The structure of Compound C has not yet been established. Kipping suggested that C, due to its unreactivity, resembled Compound B (decaphenylcyclopentasilane), but was probably more complex. He proposed as possible structures dodecaphenylcyclohexasilane (X) or hexadecaphenylcyclooctasilane (XXII) (19). The former is a very likely structure, because it is the next in the homologous series of phenylated cyclosilanes and is not an unexpected product in the reaction of dichlorodiphenylsilane with metals.



XXII

The structures and properties of the phenylated cyclic polysilanes have been treated in detail because, in addition to being polysilanes themselves, they are also the starting point for the synthesis of a number of open chain compounds. It might be pointed out that, by analogy to octaphenylcyclotetrasilane and decaphenylcyclopentasilane, corrected structures for the corresponding p-tolyl derivatives reported by Kipping (39) may also be assigned. Therefore, the less soluble, reactive compound melting at 290-293° (decomp.) was probably octa-p-tolylcyclotetrasilane (VII), while the more soluble, less reactive material was probably deca-p-tolylcyclopentasilane (VIII).

One other organic substituted cyclosilane derivative has been reported in the literature. C. A. Burkhard prepared dodecamethylcyclohexasilane (IX) by the reaction of dichlorodimethylsilane with sodium in hydrocarbon solvents (21). Under these conditions, the cyclosilane was formed in rather low yield along with polymeric materials, one of which was characterized as a dimethylsilylene polymer with an average degree of polymerization of 55 units. The cyclosilane has also been prepared from dichlorodimethylsilane with sodium or lithium (22) in tetrahydrofuran. Modifications of these reactions have resulted in high yields of the cyclosilane (23, 24).

Dodecamethylcyclohexasilane was characterized by analysis and molecular weight, and was reported to have a crystal transition temperature of 74° (21). It readily sublimes at 100° and melts at 250-252° in a sealed tube. It appears that several crystal changes occur when a sample is heated slowly from room temperature to 200°. Molecular weight determination using the vapor pressure osmometer gave a value of 349, to be compared with a theoretical value of 348.9 (24). The cyclosilane has also been prepared from 1,2-dichlorotetramethyldisilane with sodium-potassium alloy in tetrahydrofuran (23). In addition, it was obtained from the treatment of 1,1,1,3,3,3-hexaphenyldimethyltrisilane with lithium in the same solvent (24).

Chemistry of the Silicon-Silicon Bond

To present a brief survey of the chemistry of the organic substituted silicon-silicon bond, as it bears on the reactions of cyclosilanes and polysilanes which have been investigated, some general reactions of the organodisilane linkage will be considered. Some of the reactions which the disilane system undergoes may be grouped in several classes: cleavage by alkali metals; cleavage by bases, including organometallic and organosilylmetallic reagents; and cleavage by halogens.

Organic substituted disilanes containing aryl groups are cleaved by alkali metals in ethereal solvents (48-50).

Sodium-potassium alloy, rubidium, and cesium will cleave the silicon-silicon bond in arylated disilanes in diethyl ether to give the corresponding silylmetallic compounds (51-55). In ethylene glycol dimethyl ether, sodium and lithium are effective cleaving agents (56). However, the method of choice for preparing silyllithium compounds is the cleavage of a disilane with lithium in tetrahydrofuran (41, 57, 58). Such solutions are easily handled and are reasonably stable (59). This system has been used quite extensively to investigate the perphenylated cyclosilanes.

Although silicon-silicon bond cleavage of halogenated polysilanes by organometallic reagents has long been known (60), the cleavage of hexaaryldisilanes, by organolithium compounds, even though it has been observed to take place (61), cannot be considered a facile reaction. The reactions of hexaalkylated disilanes with organometallic reagents has not as yet been adequately investigated. Arylated disilanes are also cleaved by silyllithium compounds (55) and by lithium aluminum hydride in tetrahydrofuran (62).

Scission of the silicon-silicon bond of disilanes is also achieved through the agency of aqueous or methanolic alkali (2, 63), aqueous piperidine (33, 34) and alkali in hexanol (21). All of these reactions can be considered as an attack of a basic or nucleophilic species and are represented generally by the following:

$$R_3Si\text{-}SiR_3 + R'^- \longrightarrow R_3SiR' + R_3Si^-$$

$$R_3Si\text{-}SiR_3 + R'_3Si^- \longrightarrow R_3Si\text{-}SiR'_3 + R_3Si^-$$

$$R_3Si\text{-}SiR_3 + H^- \longrightarrow R_3Si\text{-}H + R_3Si^-$$

$$R_3Si\text{-}SiR_3 + OH^- \longrightarrow R_3SiOH + R_3Si^-$$

The last reaction is carried out in hydroxylic media, which results in immediate hydrolysis of the intermediate silyl anion to an Si-H compound which is in turn hydrolyzed to a silanol with evolution of hydrogen (64, 65).

$$R_3Si^- + ROH \longrightarrow R_3SiH + RO^-$$

$$R_3SiH + ROH \longrightarrow R_3SiOR + H_2$$

That a silicon hydride can be an intermediate in such reactions is shown in the cleavage of polysilanols on alumina (46, 47), which can be considered to be a mildly basic reagent.

Not considering resonance effects, it would appear that inductively withdrawing substituents such as chlorine or hydroxy groups (46, 47, 66) on a silicon atom aid in nucleophilic attack at this site.

Halogens cleave the Si-Si bond of disilanes with varying ease, depending upon the substituents on silicon and upon the halogen undergoing reaction. Thus, the relative reactivity of halogens with a given silicon-silicon bond appears to be Cl>Br>I (67). This order of reactivity is probably due to the relative coordinating ability of the halogens with silicon in a pentacovalent state, possibly due to steric limitations.

Hexaryldisilanes are fairly resistant to halogens (54, 68-70); however, hexaphenyldisilane is cleaved slowly by bromine in carbon tetrachloride (70). Hexaalkyldisilanes, on the other hand, are rather easily cleaved by halogens (53, 67, 71). Also, substitution of alkyl groups by halogen on the disilane linkage reduces the rate of cleavage to a marked degree (67). For example, the cleavage of 1,2-dichlorotetramethyldisilane by bromine is about 100 times slower than that of hexamethyldisilane under the same conditions (67).

In contrast to the analogous hexaarylethanes, hexaaryldisilanes show no tendency to dissociate into radicals (8) and, therefore, do not react with oxygen, with oxidizing agents such as selenium dioxide and lead tetraacetate, or with iodine in boiling xylene (54, 69, 70, 72, 73).

Derivatives of Octaphenylcyclotetrasilane

Octaphenylcyclotetrasilane reacts readily with lithium metal in tetrahydrofuran solvent to give a mixture of silyllithium compounds (27). No starting material is recovered; however, treatment of such solutions with trimethyl phosphate (74) provided only 27% of 1,4-dimethyloctaphenyltetrasilane (XXIII) (27, 75), indicating a fairly low yield of 1,4-dilithiooctaphenyltetrasilane. The 1,4-dimethyl derivative (XXIII) was also obtained from the reaction of methyldiphenylsilyllithium with 1,2-dichlorotetraphenyldisilane (27); this reaction provided a structure proof for the dimethyl compound.

$$2CH_3SiPh_2Li + ClSiPh_2SiPh_2Cl \longrightarrow \underset{\text{XXIII}}{CH_3SiPh_2(SiPh_2)_2SiPh_2CH_3}$$

Decaphenylcyclopentasilane is the major product obtained when dichlorodiphenylsilane is added to the lithium cleavage products of octaphenylcyclotetrasilane.[1] Although this result is not unexpected, its significance regarding

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[1] H. J. S. Winkler, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the conversion of octaphenylcyclotetrasilane to decaphenylcyclopentasilane. Private communication. 1960.

the relationship of octaphenylcyclotetrasilane and decaphenylcyclopentasilane is lessened by the fact that the cleavage of the cyclotetrasilane results in a variety of silyllithium compounds, including 1,4-dilithiooctaphenyltetrasilane (XXIV). Also, 1H,4H-octaphenyltetrasilane (XXV) and 1H,6H-dodecaphenylhexasilane (XXVI) have been obtained in yields of about 25% by treating the silyllithium compounds produced in the lithium cleavage with dilute hydrochloric acid (43) and with chlorodiphenylsilane,[1] respectively. That other disilanyllithium compounds are present in these solutions is indicated by the isolation, in low yields, of 1H,2H-tetraphenyldisilane (76) from the reaction mixture hydrolyzed with acid; and 1H,5H-decaphenylpentasilane from the reaction with chlorodiphenylsilane (77). The residues from such reactions consisted of intractable mixtures of polysilanes.

The variety of products isolated from such reactions can be explained by the ready reaction of octaphenylcyclotetrasilane with silyllithium compounds (78). Thus, 1,4-dilithiooctaphenyltetrasilane (XXIV) formed by the initial lithium cleavage of octaphenylcyclotetrasilane is able to

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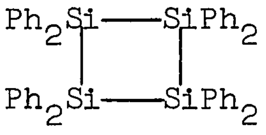
[1] R. Harrell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the cleavage of octaphenylcyclotetrasilane. Private communication. 1962.



V

$$\xrightarrow[\text{THF}]{\text{Li}} \quad LiSiPh_2(SiPh_2)_2SiPh_2Li$$

XXIV

$$XXIV + (CH_3O)_3PO \longrightarrow CH_3SiPh_2(SiPh_2)_2SiPh_2CH_3$$

XXIII

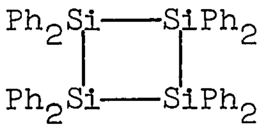
$$XXIV + H_3O^+ \longrightarrow HSiPh_2(SiPh_2)_2SiPh_2H$$

XXV

$$XXIV + ClSiPh_2H \longrightarrow HSiPh_2(SiPh_2)_4SiPh_2H$$

XXVI

cleave more octaphenylcyclotetrasilane. Also, cleavage of the α,ω-dilithio compounds by lithium can increase the variety of disilanyllithium compounds, which can in turn cleave octaphenylcyclotetrasilane, leading to a wide distribution of polysilanes.



V

$$+ \; LiSiPh_2(SiPh_2)_2SiPh_2Li \longrightarrow$$

XXIV

$$LiSiPh_2(SiPh_2)_6SiPh_2Li \xrightarrow{\text{V or Li}} \text{Polysilanes}$$

1,4-Dilithiooctaphenyltetrasilane (XXIV) can also be prepared directly from dichlorodiphenylsilane and an excess of lithium in tetrahydrofuran, probably through octaphenylcyclotetrasilane as an intermediate (43). The disilanyllithium compound prepared in this manner was derivatized with n-butyl chloride, with dimethyl sulfate, and with chlorotrimethylsilane to give 1,4-di-n-butyloctaphenyltetrasilane, 1,4-dimethyloctaphenyltetrasilane, and 1,1,1,6,6,6-hexamethyloctaphenylhexasilane, respectively. None of these compounds was isolated in yields greater than 33% (43).

That octaphenylcyclotetrasilane reacts readily with halogens was first discovered by Kipping, who observed the rather surprising reaction with iodine (18, 27). Some inorganic halides and metal salts in which the central atom can possess different oxidation states have the ability to break the silicon-silicon bond in octaphenylcyclotetrasilane. Thus, mercuric chloride reacts with the cyclotetrasilane in benzene to give 92% of 1,4-dichlorooctaphenyltetrasilane (XIV) and 94% of mercurous chloride (79). Mercuric bromide, mercuric iodide and stannic chloride have been observed to react in a similar manner to give the corresponding 1,4-dihalo derivatives (79).

Octaphenylcyclotetrasilane is cleaved by phenyllithium in a tetrahydrofuran-ether mixed solvent system (78). When

V

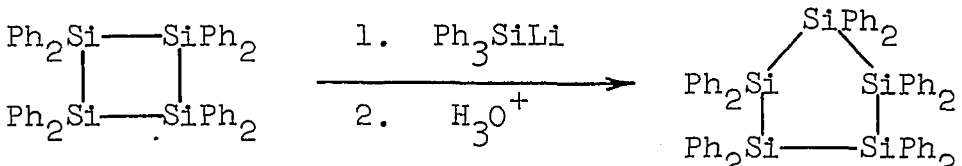
XIV

equimolar quantities of the reactants are stirred together for 5 hours, 55% of the octaphenylcyclotetrasilane is recovered and decaphenylcyclopentasilane is obtained in 18% yield.

However, when five equivalents of phenyllithium are used for extended reaction times, the major product isolated after hydrolysis is pentaphenyldisilane (78). Of course, in these reactions, as in the lithium cleavage of octaphenylcyclotetrasilane, a great variety of polysilanyllithium compounds is possible.

Methyllithium also cleaves octaphenylcyclotetrasilane in tetrahydrofuran-ether solvent. Two equivalents of methyllithium bring about cleavage within 30 minutes to give 1-lithio-4-methyloctaphenyltetrasilane in yields up to 66%, as indicated by treating the reaction solution with trimethyl phosphate to obtain 1,4-dimethyloctaphenyltetrasilane. Acid hydrolysis of the reaction mixture leads to 1<u>H</u>-4-methyloctaphenyltetrasilane in comparable yield. The use of a longer reaction time and a large excess of methyllithium leads to 1<u>H</u>-2-methyltetraphenyldisilane as the major product after acid hydrolysis.[1]

Octaphenylcyclotetrasilane reacts with triphenylsilyllithium to give, subsequent to acid hydrolysis, decaphenylcyclopentasilane and a product tentatively identified as 1H-nonaphenyltetrasilane (XXVII) (78). Excess triphenylsilyllithium and extended reaction time provided hexaphenyldisilane and pentaphenyldisilane (XXVIII) in moderate yield (78). The products isolated from these reactions indicate that secondary cleavage reactions have taken place under the conditions used.



V VI

$$+\ Ph_3Si(SiPh_2)_2SiPh_2H\ +\ Ph_3SiSiPh_2H$$

XXVII XXVIII

Octaphenylcyclotetrasilane (V) also reacts with methylenetriphenylphosphorane with ring opening to give as

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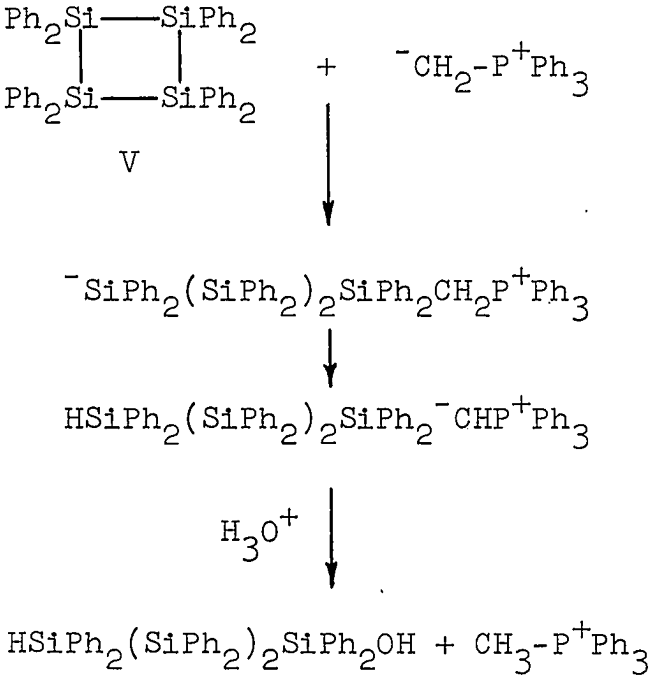
[1] H. Gilman and K. Y. Chang, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the cleavage of octaphenylcyclotetrasilane. Private communication. 1962.

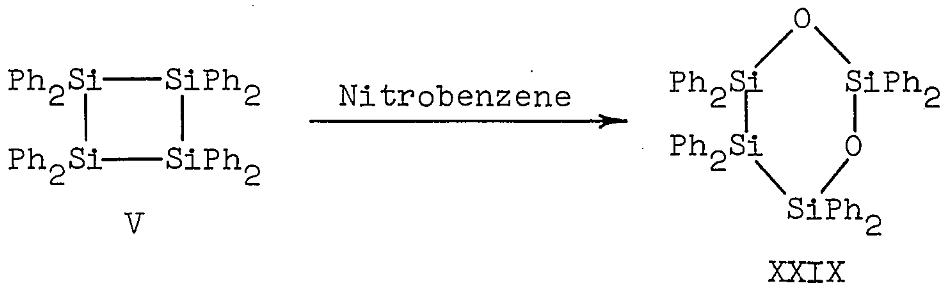
a product after acid hydrolysis 4H-octaphenyltetrasilan-1-ol (XVIII) (80). This product is depicted as arising through the following reaction scheme.



V

XVIII

Oxidation of octaphenylcyclotetrasilane has been observed with oxygen and oxygen-containing compounds. Kipping found that octaphenylcyclotetrasilane is rapidly attacked by refluxing nitrobenzene to give a dioxide (18) as the major product which has since been suggested to be octaphenyl-1,3-dioxacyclohexasilane (37). The ease of oxidation is demonstrated by the fact that the cyclosilane is oxidized by air at room temperature to give octaphenyloxacyclopentasilane and a glue-like polymer, evidently siloxanes (36). Octaphenylcyclotetrasilane is oxidized by air in toluene at 100° and by ozonized oxygen in carbon tetrachloride or carbon disulfide. From these reactions there was isolated the oxidation products, octaphenyloxacyclopentasilane and octaphenyl-1,4-dioxacyclohexasilane (36).

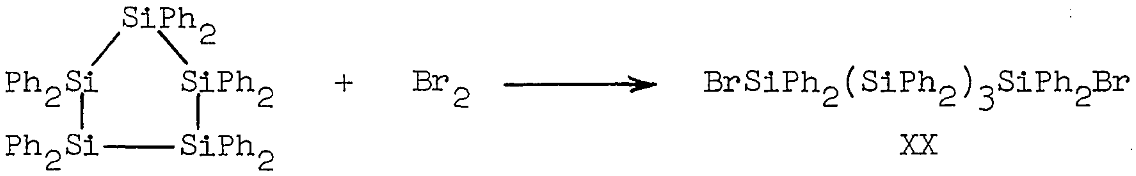


Benzaldehyde causes rapid oxidation of octaphenylcyclotetrasilane, while benzyl alcohol, acetophenone, paraldehyde and amyl nitrite react slowly. Again, the products from these reactions are the cyclic monoxide and dioxide along with varying amounts of viscous polymers (36). Octaphenylcyclotetrasilane appears to be stable to aqueous oxidizing agents such as potassium permanganate and dichromate; however, this may be due to the insolubility of the compound.

Hydrogenolysis of octaphenylcyclotetrasilane occurs under conditions of relatively high temperature and pressure in the presence of chromium-containing catalysts (62).

Polysilanes Derived from Decaphenylcyclopentasilane

Kipping reported that Compound B (decaphenylcyclopentasilane) reacted with bromine to give a mixture of products, which were subsequently hydrolyzed and a cyclic dioxide isolated (18). This compound has more recently been shown to be octaphenyl-1,4-dioxacyclohexasilane (37). It has also been found that careful addition of an equivalent amount of bromine to decaphenylcyclopentasilane (VI) in benzene results in a high yield of 1,5-dibromodecaphenylpentasilane (XX) (28). This dibromo compound was one of the important links in the chain of evidence leading to the correct structure of decaphenylcyclopentasilane.



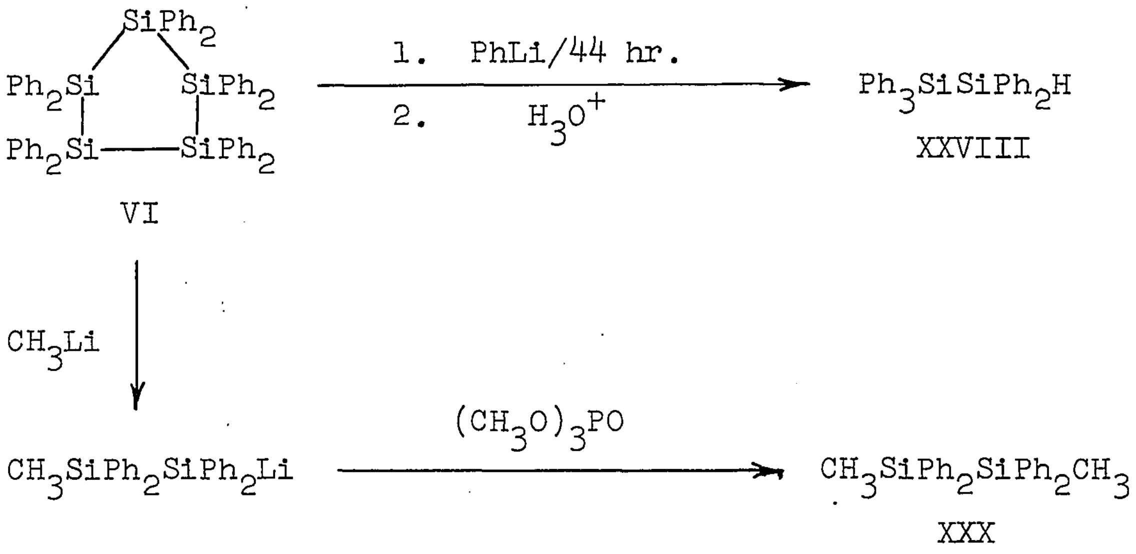
$$+ \ Br_2 \longrightarrow BrSiPh_2(SiPh_2)_3SiPh_2Br$$

VI

XX

When decaphenylcyclopentasilane is heated strongly in the absence of air, the compound decomposes to give tetraphenylsilane, triphenylsilane and a resinous material (81a). If the decomposition is attempted under low pressure, the compound only sublimes. Tetraphenylsilane and triphenylsilane are also products of the thermal decomposition of octaphenylcyclotetrasilane; however, no decaphenylcyclopentasilane was found (81a).

Phenyllithium slowly cleaves decaphenylcyclopentasilane in tetrahydrofuran-ether to give, with excess organometallic compound and extended reaction times, pentaphenyldisilane (XXVIII) (69) as the major product after acid hydrolysis (78). Decaphenylcyclopentasilane reacts with a five-molar excess of methyllithium to give 1-lithio-2-methyltetraphenyldisilane, characterized as 1,2-dimethyltetraphenyldisilane (XXX).[1]



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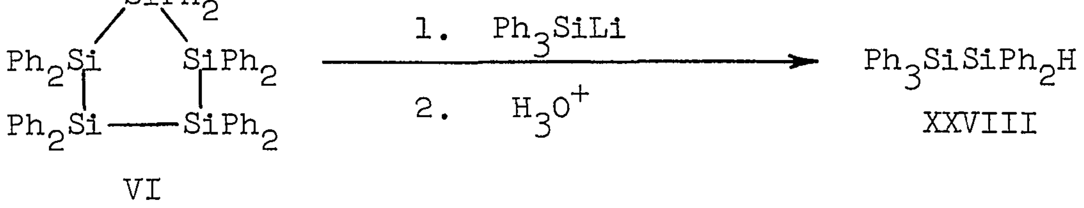
[1] H. Gilman and K. Y. Chang, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the cleavage of decaphenylcyclopentasilane. Private communication. 1962.

Organosilyllithium compounds react, over extended periods, with decaphenylcyclopentasilane to give disilanyllithium compounds (78) which have been used to prepare a variety of organic substituted disilanes. For example, triphenylsilyllithium reacts to give a 79% yield of pentaphenyldisilane (XXVIII) after acid hydrolysis (78). Methyldiphenylsilyllithium (28) and dimethylphenylsilyllithium (81b) have been used to cleave decaphenylcyclopentasilane to give 1*H*-2-methyltetraphenyldisilane (XXXI) and 1*H*-2,2-dimethyltriphenyldisilane, respectively. The last-named compound was converted to the corresponding chlorosilane (XXXII) with phosphorus pentachloride (81b).

Decaphenylcyclopentasilane, like octaphenylcyclotetrasilane, is readily cleaved by lithium in tetrahydrofuran (28, 29), to give good yields of 1,5-dilithiodecaphenylpentasilane. Treatment of this dilithium compound with trialkyl phosphates provided the corresponding 1,5-dialkyldecaphenylpentasilanes (28, 29). 1,5-Dilithiodecaphenylpentasilane has also been subjected to acid hydrolysis to give 1*H*,5*H*-decaphenylpentasilane (77).



$$\mathrm{VI} \xrightarrow[2.\quad H_3O^+]{1.\quad CH_3SiPh_2Li} CH_3SiPh_2SiPh_2H$$

XXXI

$$\begin{tikzcd}
\mathrm{VI} \arrow[r, "1.\quad (CH_3)_2SiPhSi", "2.\quad H_3O^+"'] & (CH_3)_2SiPhSiPh_2H \; \mathrm{XXXII} \arrow[d, "PCl_5"'] \\
 & (CH_3)_2SiPhSiPh_2Cl \; \mathrm{XXXIII}
\end{tikzcd}$$

EXPERIMENTAL

The reagents and solvents used in the following experiments were commercially available materials. Unless otherwise stated, the tetrahydrofuran was dried by refluxing at least 24 hours over sodium metal followed by distillation from lithium aluminum hydride immediately before use. Anhydrous diethyl ether used for reaction purposes was stored over sodium wire.

The organosilicon halides were purchased from Dow Corning Corporation.

In general, the experimental apparatus consisted of a three-necked flask of appropriate size with ground glass joints, fitted with a Trubore stirrer, a Friedrichs condenser and an addition funnel. The condenser and addition funnel were topped with nitrogen inlets when reactions involving organometallic or organosilylmetallic compounds or in some cases halosilanes were carried out. All glassware was oven-dried before use and purged while hot with dry oxygen-free nitrogen before reactants were introduced.

Lithium metal was obtained commercially as wire from Lithium Corporation of America and was wiped free of its protective coating and cut into small pieces into the nitrogen filled reaction flask. Magnesium metal was Grignard grade turnings obtained from Mallinkrodt Chemical

Works.

Quantitative titrations of organometallic and organosilylmetallic solutions were carried out in a manner similar to a published procedure employing the double titration technique using either benzyl chloride (82) or allyl bromide.[1] Silicon analyses were carried out according to a published procedure (83). Color Test I was used as a qualitative test for organometallic and organosilylmetallic reagents (84).

All melting points are uncorrected. For compounds melting above 100° melting points were determined with a Mel-Temp apparatus; all others were determined in an electrically heated oil bath. Infrared spectra were routinely determined using the Perkin-Elmer, model 21, spectrophotometer, and proton magnetic resonance spectra obtained from a Varian Associates High Resolution Spectrophotometer, model HR-60, at 60 Mc/sec.

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[1] F. K. Cartledge and S. Y. Sim, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the double titration technique using allyl bromide. Private communication. 1962.

Stability of Alkyllithium Compounds in Mixed Solvent Systems

Preparation of *n*-butyllithium in diethyl ether

n-Butyllithium was prepared from *n*-butyl bromide and lithium in diethyl ether using a previously described procedure (85).

Preparation of *n*-decyllithium and *n*-tetradecyllithium in diethyl ether

These two long chain alkyllithium compounds were prepared in a similar manner. In a typical procedure, ten milliliters of a solution of 250.0 g. (1.13 moles) of *n*-decyl bromide dissolved in 850 ml. of diethyl ether was added to 18.8 g. (2.71 g.-atoms) of lithium metal suspended in 100 ml. of diethyl ether. After stirring for 15 min. at room temperature, the mixture became cloudy and Color Test I was positive. The stirred reaction mixture was cooled by means of a Dry Ice-acetone bath to -10° and the remainder of the *n*-decyl bromide solution was added dropwise over a period of 5 hours, with the temperature being maintained at $-10 \pm 5^{\circ}$. The resulting solution was stirred for an additional 2 hours at 0°, and then was transferred to a graduated addition funnel with filtration through glass wool to remove the excess lithium. The yield of n-decyllithium, determined by the method of double titration (benzyl chloride), was 0.922 mole (81.5%) in 1071 ml. of solution.

Preparation of n-decyllithium in tetrahydrofuran (attempted)

Attempts to prepare n-decyllithium from n-decyl bromide in tetrahydrofuran were essentially unsuccessful. The reaction would not start nor proceed at low temperatures. The n-decyl bromide appeared to freeze out of solution. At higher temperatures coupling became the predominant reaction. For example, when ten milliliters of a solution of 21.9 g. (0.099 mole) of n-decyl bromide in 180 ml. of tetrahydrofuran was added to 2.07 g. (0.298 g.-atom) of lithium suspended in 30 ml. of tetrahydrofuran at -10°, the reaction started within a minute. Dropwise addition was continued and shortly a precipitate began to form. Allowing the temperature of the reaction mixture to rise a few degrees caused dissolution of the precipitate. However, with continued addition the precipitate again formed and finally the reaction mixture had to be maintained at 0° to be kept homogenous. The addition was complete in 2 hours, and the yield of n-decyllithium was only 3.9%. Hydrolysis of the reaction mixture and subsequent work-up afforded 10.6 g. (75.3%) of crude eicosane. Recrystallization from absolute ethyl alcohol gave 7.50 g. (53.7%) of eicosane, m.p. 35.5-36.5° (mixed m.p.).

Relative stabilities of n-butyllithium in ether-tetrahydrofuran, ether-tetrahydropyran, and ether-2,2,4,4-tetramethyltetrahydrofuran

One hundred milliliters of a 0.972 M solution of n-butyllithium in diethyl ether was added each to 100 ml. of tetrahydrofuran, tetrahydropyran, and 2,2,4,4-tetramethyltetrahydrofuran. Each mixture was refluxed and required 24 hours, one week, and three weeks, respectively, to give a negative Color Test I.

Decomposition of n-butyllithium in ether-tetrahydrofuran

To 90 ml. of tetrahydrofuran was added 100 ml. of a 0.810 M solution of n-butyllithium in diethyl ether. After stirring the mixture for 24 hours at room temperature, Color Test I was negative. The reaction mixture was hydrolyzed, and the aqueous layer saturated with sodium chloride and extracted with ether. After drying, the organic layers were distilled to give 3.60 g. (96%) of ethyl alcohol, b.p. 75-77°, n_D^{20} 1.3640, identified by means of its 3,5-dinitrobenzoate, m.p. 92-93.5° (mixed m.p.).

Decomposition of n-tetradecyllithium in ether-tetrahydrofuran

To 65 ml. of tetrahydrofuran was added 198 ml. of a 0.691 M solution of n-tetradecyllithium in diethyl ether. After stirring for 16 hours at room temperature and 24 hours at reflux, Color Test I was negative. Hydrolysis with a saturated ammonium chloride solution followed by extraction with ether and then removal of the solvents gave a pale yellow oil, which was distilled under reduced pressure. At 10 mm. 15.83 g. (58%) of crude tetradecane (n_D^{20} 1.4302), boiling over the range 120-148°, was obtained. A redistillation seemed to do little to purify it further [13.9 g. (51%), n_D^{20} 1.4302, b.p. 115-117°/10 mm.]. Chromatography of the distillation residue afforded 0.65 g. of octacosane m.p. 60-61.5° (mixed m.p.) and a small amount of tetradecanol, m.p. 37-38°.

Decomposition of n-decyllithium in ether-tetrahydrofuran

One hundred and seventy-eight milliliters of a 0.647 M solution of n-decyllithium in diethyl ether was added to 65 ml. of tetrahydrofuran. A negative Color Test I was obtained after 48 hours of reflucing of the stirred mixture. Hydrolysis followed by the usual extractive procedure led to an oil which was distilled through a packed column to give 12.79 g. (78.2%) of n-decane, b.p. 170-171.8°, n_D^{20} 1.4119. Fractional distillation at reduced pressure of the residue resulted in 0.92 g. (5.8%) of less pure n-decane, b.p. 59-62°/11 mm., n_D^{20} 1.4128.

Relative stability of n-decyllithium in mixed solvents

Two hundred and sixty-five milliliters of a 0.860 M solution of n-decyllithium in diethyl ether was added each to 225 ml. of tetrahydropyran, and 2,2,4,4-tetramethyltetrahydrofuran, and 139 ml. of a 1.08 M solution of n-decyllithium in diethyl ether to 139 ml. of tetrahydrofuran. The mixtures were stirred at room temperature and periodically aliquots were taken to determine the total base and alkyllithium content of each mixture. The data obtained are summarized in Table 3 and are graphically represented in Figure 1 (see Discussion).

Stability of n-decyllithium in diethyl ether

To 129 ml. of diethyl ether was added 100 ml. of a 1.06 M n-decyllithium solution in diethyl ether. The reaction mixture was stirred at room temperature and titrated periodically. After 72 hours a heavy white precipitate formed and persisted until after Color Test I was negative (3 1/2 weeks). The precipitate appeared to be a complex containing the alkyllithium compound because during the latter stages of the reaction Color Test I was positive for the precipitate but negative for the supernatant liquid.

Derivatization of *n*-decyllithium in ether-tetrahydropyran

At 22 hours a 50 ml. aliquot (0.00985 mole of RLi) of the reaction of *n*-decyllithium solution in ether-tetrahydropyran solution used above in the stability study was removed and added to 2.91 g. (0.00985 mole) of chlorotriphenylsilane dissolved in 50 ml. of diethyl ether cooled to ice bath temperature. After 7 hours Color Test I was negative. The usual work-up followed by chromatography on an alumina column resulted in 2.05 g. (52%) of crude *n*-decyltriphenylsilane m.p. 46-55°. The infrared spectrum of this material was the same as a spectrum of authentic *n*-decyltriphenylsilane, however attempts to purify it were unsuccessful.

Derivatization of *n*-decyllithium in ether-2,2,4,4-tetramethyltetrahydrofuran

After 66 hours a 50 ml. aliquot (0.00995 mole) of the reaction mixture of n-decyllithium with ether-2,2,4,4-tetramethyltetrahydrofuran was treated with an equivalent amount of chlorotriphenylsilane dissolved in 50 ml. of ether. The mixture was stirred at room temperature for 24 hours and then worked up in a manner similar to the previous reaction. Again a crude n-decyltriphenylsilane (3.0 g., 75%) melting over the range 40-60° was obtained and could not be purified by rechromatography, recrystallization, or sublimation. The infrared spectrum of this material and that of n-decyltriphenylsilane were superimposable.

Preparation of n-decyltriphenylsilane

n-Decyllithium was prepared by a published procedure (86). A solution of 0.086 mole of n-decyllithium in 100 ml. of diethyl ether was added to 25.35 g. (0.086 mole) of chlorotriphenylsilane dissolved in 100 ml. of ether at ice-bath temperature. After seven hours of stirring at room temperature, Color Test I was negative. After hydrolysis with water the reaction mixture was worked up in the usual manner. Unfortunately, a small ether fire caused the loss of a considerable part of the product. However, 8.72 g. (25.3%) of crude n-decyltriphenylsilane, m.p. 64-69°, was salvaged. One recrystallization from ethanol afforded pure product, m.p. 68-69.5° (mixed m.p.).

Preparation and Reactions of Benzyllithium

Benzyllithium from benzyl methyl ether (run 3, Table 2)

To a stirred mixture of 10.4 g. (1.50 g. atoms) of finely cut lithium wire in 60 ml. of tetrahydrofuran cooled to -10° was added 12.2 g. (0.10 mole) of benzyl methyl ether (Eastman white label) dissolved in 30 ml. of diethyl ether at a rate of 30 drops per minute. Ten minutes after the addition was begun, the solution became green, slowly turning to dark brown as the addition was continued. The internal temperature of the reaction mixture was maintained between -5° and -15° by manipulation of a Dry Ice-acetone bath used for cooling, while the rate of addition was kept constant. Subsequent to the addition, the mixture was stirred for another hour at -10°.

The resulting benzyllithium solution was filtered through glass wool into an addition funnel provided with an outer glass shell into which a cooling mixture of Dry Ice and acetone at -10° was placed. Aliquots were taken and the yield, determined by double titration (benzyl chloride) was 0.0672 mole (67.0%) of organometallic compound in 88 ml. of solution, corresponding to a 0.76 molar solution. The benzyllithium was derivatized by adding to 29.5 g. (0.10 mole) of chlorotriphenylsilane dissolved in

50 ml. of tetrahydrofuran cooled to Dry Ice-acetone temperature. The stirred reaction mixture was allowed to warm to room temperature and then was hydrolyzed by pouring into distilled water. The organic and ether extraction layers were combined, dried over anhydrous sodium sulfate and the solvents stripped off, leaving a white solid which when recrystallized from methanol gave 16.5 g. (75.0%) of benzyltriphenylsilane, m.p. and mixed m.p. 95-96°.

Benzyllithium from benzyl ethyl ether (run 8, Table 2)

To 6.94 g. (1.0 g.-atom) of finely cut lithium wire suspended in 60 ml. of tetrahydrofuran cooled to -10° was added 20.4 g. (0.15 mole) of benzyl ethyl ether dissolved in 30 ml. of diethyl ether at a rate of 20 drops per minute. The reaction started 15 min. after the beginning of the addition as evidenced by coloration of the solution. On two occasions the lithium clumped into a single ball which dispersed on continued stirring. Upon completion of the addition the mixture was stirred for one hour at -10°. The benzyllithium solution was filtered through glass wool into an addition funnel, cooled to -10° as previously described. The yield, determined by double titration, was 0.124 mole (83.0%) of benzyllithium in 107 ml., corresponding to a 1.16 molar solution.

Table 2. Preparation of benzyllithium from benzyl alkyl ethers in tetrahydrofuran-ether solvent system at -10±5°

Run[a]	Moles of the benzyl ether	Excess of lithium	Solvent tetrahydrofuran/ether (ml/ml)	Rate of addition	% yield of organometallic[b]	Molarity
1	0.046	7.8	Tetrahydrofuran only	40 drops per min.	67	0.27
2	0.10	7.5	58/48	40	45	0.39
3	0.10	7.5	58/30	30	67	0.76
4	0.15	5.0	60/30	20	68	1.05
5	0.15	3.3	60/30	20	83	1.16

[a] In run 5 benzyl ethyl ether was used; in all others benzyl methyl ether was used.

[b] Yield of benzyllithium determined by the method of double titration, using benzyl chloride.

The benzyllithium solution (0.117 mole) was added to 22.7 g. (0.124 mole) of benzophenone dissolved in 50 ml. of diethyl ether at ice-bath temperature. Throughout the addition the reaction mixture remained dark green until the final milliliter had been added, at which time the solution became purple in color. The mixture was allowed to stir for 45 min. and then was hydrolyzed by pouring onto crushed ice. The subsequent work-up gave a pale yellow oily solid after the solvents had been removed. Recrystallization of the solid from petroleum ether (b.p. 60-70°) afforded 27.2 g. (85.0%) of benzyldiphenylcarbinol, m.p. and mixed m.p. 87-88° [lit. (87) 87-88°].

Cleavage of hexaphenyldisilane with benzyllithium

Run 1 To 5.18 g. (0.01 mole) of hexaphenyldisilane suspended in 50 ml. of tetrahydrofuran at -10° was added 91 ml. of benzyllithium solution (0.957 mole). The reaction mixture was stirred for 30 min. at -10° and then allowed to warm to room temperature over a period of one hour. At this time no hexaphenyldisilane was observed suspended in the reaction mixture. After an additional hour of stirring at room temperature, the mixture was hydrolyzed by pouring onto crushed ice. Some ether was added and the two-phase mixture was filtered, giving no recovered hexaphenyldisilane. The layers were separated and worked up in the usual manner. Removal of the solvents left an oily solid which was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Elution with the same solvent gave small amounts of oils which were not identified. Elution of the column with benzene afforded 2.79 g. (85.0%) of crude benzyltriphenylsilane, m.p. 80-92°. Two recrystallizations from methanol gave 1.90 g.

(54%) of pure benzyltriphenylsilane, m.p. and mixed m.p. 94-95°.

Run 2 Ninety-six milliliters of a tetrahydrofuran-ether solution of 0.0934 mole of benzyllithium was added to 5.18 g. (0.01 mole) of hexaphenyldisilane suspended in 50 ml. of tetrahydrofuran at -10°. The stirred mixture was allowed to warm to room temperature over a period of 60 min., at which time no hexaphenyldisilane was present. The mixture was hydrolyzed by addition of 150 ml. of distilled water. The layers were separated and the organic layer washed several times with water and dried over anhydrous sodium sulfate. Removal of the solvent left an oily solid which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60-70°) gave in the first fractions a small amount of oil whose infrared spectrum indicated the presence of Si-H linkages; however, no pure compounds were isolated. Further elution with the same solvent afforded 3.73 g. (106%) of benzyltriphenylsilane, m.p. 95-96°. The excess benzyltriphenylsilane possibly arose from a secondary reaction, such as the cleavage of unreacted benzyl methyl ether by triphenylsilyllithium. Elution with benzene and with ethyl acetate gave only small amounts of intractable tars.

An attempt to duplicate the above reaction resulted in a 108% yield of crude benzyltriphenylsilane, m.p. 65-90°.

However, recrystallization afforded only 90% of the compound (m.p. 94-96°), of similar purity as that of the previous reaction.

Run 3 Benzyllithium (0.021 mole) was added to 5.18 g. (0.01 mole) of hexaphenyldisilane suspended in 50 ml. of tetrahydrofuran cooled to -10°. The stirred mixture was allowed to warm to room temperature over a period of 90 min., at which time no hexaphenyldisilane could be observed in the reaction mixture. The usual chromatographic work-up gave 2.70 g. (77%) of crude benzyltriphenylsilane, m.p. 88-94°. Recrystallization from petroleum ether (b.p. 60-70°) left 2.30 g. (66.0%) of pure compound, m.p. 92-94° (mixed m.p.). No other products were isolated.

Preparation of Phenylated Cyclosilanes

Octaphenylcyclotetrasilane

To 14.0 g. (2.02 g.-atoms) of lithium metal was added 1.0 g. of dichlorodiphenylsilane dissolved in 20 ml. of tetrahydrofuran. Within 5 min. the reaction initiated and with rapid stirring (Herschberg) a solution of 256 g. (1.01 moles) of dichlorodiphenylsilane was added at a rate so as to maintain a slight yellow color (silyllithium). The reaction proceeded with vigorous refluxing. Addition took 50 min. and for the last quarter of the addition the reaction flask was insulated with a heating mantle. After completion of the addition the mixture was stirred for 15 min., and then allowed to cool to room temperature. Filtration, followed by extraction of the insoluble material twice with 300 ml. of hot benzene, twice with methanol-water (300 ml./100 ml.) and then with acetone afforded 107.7 g. (58.0%) of octaphenylcyclotetrasilane, m.p. and mixed m.p. 318-323°.

Decaphenylcyclopentasilane

A mixture of 14.38 g. (2.07 g.-atoms) of lithium metal and 1.0 g. (0.004 mole) of dichlorodiphenylsilane dissolved in 20 ml. of sodium-dried tetrahydrofuran was stirred (Hershberg) at room temperature for 1 min. The reaction mixture became warm and a red-brown color (silyllithium) developed.

To the reaction mixture initiated in this manner was added 254.7 g. (1.01 moles) of dichlorodiphenylsilane dissolved in 300 ml. of sodium-dried tetrahydrofuran. The addition was carried out in such a manner that a light yellow coloration was maintained. Under these conditions the reaction was very exothermic throughout the addition, which was complete within 1 hour. Subsequently, the reaction mixture was stirred at reflux for 4 hours, which resulted in a dark brown color. Then 6.1 g. (0.024 mole) of dichlorodiphenylsilane was added to react with the silyllithium compounds present.

The white suspension which resulted was hydrolyzed by addition to ice water to dissolve the lithium chloride which had formed. Filtration provided 176.6 g. (93.8%) of crude decaphenylcyclopentasilane, m.p. 440-455°. The dried crude product was dissolved in about 2 liters of benzene and allowed to stand for several days. The solution was filtered periodically to remove precipitated Compound C, 5.0 g. (2.7%), melting over the range 490-500°. Recrystallization of this material from tetralin raised its melting point to 502-504° (inserted into the melting point block at 480°).

When Compound C would no longer precipitate, the benzene solution was concentrated to about 300 ml. and added to 1 liter of hot petroleum ether (b.p. 60-70°). There precipitated 142.2 g. (76.5%) of pure crystalline decaphenylcyclopentasilane, m.p. 466-470° (mixed m.p.).

Although decaphenylcyclopentasilane of this quality was considered pure and subsequently used for various reactions, as an added measure of confidence of the purity of the compound, two additional recrystallization steps were carried out for analytical samples. The decaphenylcyclopentasilane obtained as described above was recrystallized once from cyclohexane and once from ethyl acetate and then dried in vacuo in a drying pistol at 140°. No alteration in the melting point characteristics was noted. Infrared was utilized to check the complete removal of the ethyl acetate solvent.

Anal. Calcd. for $C_{60}H_{50}Si_5$: Mol. wt., 911.45. Found: Mol. wt. 912 (Vapor pressure osmometer in benzene with benzil as standard; see Discussion part).

Compound C

To 15.3 g. (2.2 g.-atom) of lithium metal was added 2 g. of dichlorodiphenylsilane dissolved in 20 ml. of sodium-dried tetrahydrofuran. The reaction started within a few minutes, as indicated by the evolution of heat and formation of the usual silyllithium color.

To this rapidly stirred mixture was added 253 g. (1.01 moles total) of dichlorodiphenylsilane dissolved in 300 ml. of tetrahydrofuran. The rate of addition was regulated to maintain a low concentration of silyllithium compounds and a vigorous, spontaneous reflux. The addition was complete within 2 hours and the resulting reaction mixture was stirred with refluxing for 48 hours. At the end of this time one milliliter of water was added to decompose the silyllithium compounds present.

The insoluble material was removed by filtration and boiled with 200 ml. of a methanol-water mixture. After drying, the water insoluble material (52.2 g.) was extracted four times with cold benzene to leave 5.7 g. (3.1%) of Compound C, m.p. 500-504° (decomp.). From the benzene and tetrahydrofuran soluble materials was isolated 92 g. (50%) of decaphenylcyclopentasilane, m.p. 460-464°.

The final reaction residue, soluble in acetone and n-propanol was subjected to vacuum distillation. The fraction boiling 140-146°/0.01 mm. was redistilled to give 11.04 g. (4.3%) of 2,2-diphenyl-1-oxa-2-silacyclohexane, b.p. 112-113/0.002 mm., n_D^{20} 1.5753 and d_{20}^{20} 1.094. N.m.r. absorptions at 6.09 τ (triplet), 8.35 τ (multiplet), and 8.91 τ (triplet) as well as in the phenyl region were in a ratio of 1.95:4.00:2.02:10, respectively.

Anal. Calcd. for $C_{16}H_{18}OSi$: C, 75.54; H, 7.13; Si, 11.03; Mol. wt., 254.4; MR_D, 77.98. Found: C, 75.35, 75.47; H, 6.86, 6.70; Si, 10.71, 10.71; Mol. wt., 259, 255 (vapor pressure osmometer in benzene); MR_D, 76.87.

Purification of Compound C

For the purpose of study and reactions, Compound C was prepared as described above or was collected from the several preparations of decaphenylcyclopentasilane which were carried out and from reactions of unpurified octaphenylcyclotetrasilane with various halogenating agents and hydrogen halides. Purification of the compound can be carried out by several crystallization methods.

Small amounts of Compound C can be recrystallized from benzene, in which it is very sparingly soluble (about 0.35 g./100 ml.). From this solvent the compound can be obtained in much better crystal form than others which have been investigated. Larger amounts of Compound C can be recrystallized from refluxing tetralin (3 g./100 ml.) or from refluxing benzyl alcohol, in which the compound is significantly more soluble.

The most efficient method employed was one of Soxhlet extraction with benzene employing an apparatus in which the extracting mixture could be efficiently stirred.

The pure Compound C obtained by any of these methods melted, when placed in the melting point block at 490°, at 502-504°, decomposing to a lemon yellow froth or liquid with condensation of a colorless material in the upper part of the melting zone. Compound C maintained at temperatures above 450°, but below its melting point, for extended periods underwent significant sintering and softening.

Dodecaphenylcyclohexasilane

From dichlorodiphenylsilane and 1,5-dilithiodecaphenylpentasilane To 4.04 g. (0.0159 mole) of dichlorodiphenylsilane dissolved in 200 ml. of tetrahydrofuran was added dropwise 166 ml. of a tetrahydrofuran solution containing 0.0157 mole of 1,5-dilithiodecaphenylpentasilane. After about three-fourths of this solution had been added, the silyllithium color began to persist in the reaction mixture. Therefore, an additional 1.21 g. (0.0048 mole) of dichlorodiphenylsilane was introduced and the addition of silyllithium solution completed. A slight orange-yellow color remained at the end of the addition. After stirring overnight the reaction mixture was colorless.

Hydrolysis with 1N hydrochloric acid caused the precipitation of 1.50 g. (13.1%) of octaphenylcyclotetrasilane, m.p. 307-317° (mixed m.p.). The usual work-up provided a residue which was treated with benzene to give 0.4 g. (2.7%) of crude Compound C, melting with decomposition over the range 470-500°. Recrystallization from tetralin raised its melting point to 500° (mixed m.p.).

Concentration of the benzene soluble portion of the reaction residue and addition of petroleum ether (b.p. 60-70°) provided 3.50 g. (24.5%) of decaphenylcyclopentasilane, m.p. 435-445°.

<u>From 1,3-dichlorohexaphenyltrisilane and sodium</u> A mixture of 3.09 g. (0.005 mole) of 1,3-dichlorohexaphenyltrisilane, 0.25 g. (0.0109 g.-atom) of sodium metal and 50 ml. of sodium-dried xylene was refluxed for 5 hours with the formation of a blue colored precipitate.

After allowing it to stand overnight the reaction mixture was treated with 20 ml. of ethanol to destroy excess sodium. The reaction mixture was then filtered and the insoluble material was treated with water. The water insoluble material amounted to 0.70 g. melting over the range 360-380° (decomp.). Extraction of this with 200 ml. of boiling benzene left 0.40 g. (14.7%) of a tan solid melting 370-377° (decomp.). This material did not alter the melting point characteristics of a sample of Compound D[1] when the two were admixed.

The benzene soluble material precipitated upon cooling of the solution to room temperature. There was obtained 0.25 g. (9.2%) of pure Compound C, m.p. 502-504° (mixed m.p.).

From the original xylene soluble material there was obtained 0.41 g. (15%) of decaphenylcyclopentasilane,

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[1] This material can be obtained from the reaction of dichlorodiphenylsilane with sodium in refluxing toluene and is apparently similar to the amorphous, highly insoluble substance first characterized by Kipping (19).

which melted 430-440° (mixed m.p.) after recrystallization from benzene-petroleum ether (b.p. 60-70°). A trace of octaphenylcyclotetrasiloxane, m.p. 188-189° (mixed m.p.) was also isolated.

From 1,3-dichlorohexaphenyltrisilane and magnesium Magnesium metal (1.00 g., 0.041 g.-atom) and a small crystal of iodine was treated with 10 ml. of a solution of 3.09 g. (0.005 mole) of 1,3-dichlorohexaphenyltrisilane in 56 ml. of tetrahydrofuran at the reflux temperature for half an hour. Apparently the reaction did not initiate. The remainder of the chlorosilane solution was added along with a second iodine crystal, and the reaction mixture was refluxed overnight producing a slight green color.

A third crystal of iodine was added and the reaction mixture was refluxed for an additional 24 hours with no change in its appearance.

Work-up was effected with 1N hydrochloric acid followed by the usual extractive procedure yielding 2.38 g. (82%) of hexaphenyltrisilane-1,3-diol, m.p. 145-147°. Recrystallization from petroleum ether (b.p. 60-70°) gave the pure product, m.p. 146.5-148° (mixed m.p.). No other products were isolable.

From 1,3-dihalohexaphenyltrisilane and sodium-potassium alloy One milliliter of sodium-potassium alloy suspended in 20 ml. of tetrahydrofuran was treated over a period of 2 1/2 hours with slight warming with 4.00 g. (0.00567 mole) of the dihalo-compound prepared by the reaction of N-bromosuccinimide with 1H,3H-hexaphenyltrisilane in carbon tetrachloride. At the end of this time the reaction solution was bright red in color and Color Test I was positive. The mixture was stirred for an additional 2 hours at room temperature and then about 15 g. of mercury metal was added to amalgamate the excess alloy.

After stirring this mixture overnight the silylmetallic solution, along with an insoluble solid material, was decanted from the amalgam. Analysis by double titration (allyl bromide) indicated the presence of 0.0126 mole of silylmetallic content.

The resulting solution was added rapidly to 3.36 g. (0.0126 mole) of tri-n-butyl phosphate and after 15 min. Color Test I was negative. Hydrolysis with 200 ml. of 1N hydrochloric acid and the usual work-up provided a residual oil from which was isolated by trituration with petroleum ether (b.p. 60-70°) 0.51 g. (16%) of decaphenylcyclopentasilane, melting after recrystallization from ethyl acetate at 460-464° (mixed m.p.).

The petroleum ether soluble material was chromatographed on alumina to give 0.43 g. (8.6%) of 1,2-di-n-butyltetraphenyldisilane, m.p. 97-98° (mixed m.p.) after recrystallization from ethanol. Also isolated was 0.37 g.

(8.3%) of 1,3-di-n-butylhexaphenyltrisilane, m.p. 145-147° (mixed m.p.) after recrystallization from benzene-ethanol. No other products were obtained.

Tetradecaphenylcycloheptasilane (attempted)

Eight grams (0.0153 mole) of 1,2-dibromotetraphenyldisilane suspended in 10 ml. of tetrahydrofuran was treated in a dropwise manner with 0.014 mole of 1,5-dilithiodecaphenylpentasilane in 155 ml. of tetrahydrofuran solution. At no time during the addition was Color Test I observed to be positive. The reaction mixture was stirred overnight at room temperature and then hydrolyzed (1N hydrochloric acid). The usual work-up provided octaphenylcyclotetrasilane (14.5%), m.p. 322-328° (mixed m.p.) and decaphenylcyclopentasilane (31.9%), m.p. 460-466° (mixed m.p.) as the only isolable products.

Reaction of dichlorodimethylsilane with lithium

A solution of 32.67 g. (0.253 mole) of dichlorodimethylsilane in 150 ml. of tetrahydrofuran was added dropwise to 3.47 g. (0.50 g.-atom) of lithium metal suspended in 50 ml. of the same solvent. Turbidity developed immediately and heat was evolved. A heavy white precipitate had formed by the time the addition was completed.

The mixture was refluxed for several days with aliquots being taken periodically and titrated (hydrolyzable chlorine) to determine the extent of reaction. After one week of refluxing the titration indicated the reaction to be 94% complete.

After cooling to room temperature, the mixture was filtered to remove insoluble solids. These solids were treated first with ethanol and then with water to give 5.29 g. (36%) of water insoluble amorphous polymer, melting over the range 370-390°. Attempts to crystallize this material from various solvents failed due to its extreme insolubility. The polymer is apparently similar to that obtained previously by Burkhard (21) and consists of an unknown and probably variable number of dimethylsilylene units. Its infrared spectrum (KBr) shows only absorption bands attributable to a structure of this type.

The tetrahydrofuran soluble portion of the reaction residue was an oil from which precipitated a crystalline solid. The mixture of solid and oil was triturated with a small amount of ethanol to give 4.03 g. (29.5%) of white crystalline solid, melting over the range 236-245° with extensive presoftening. This compound was dissolved in hot ethanol and filtered to remove a small amount of gum-like substance. Concentration of the solution and cooling gave pure dodecamethylcyclohexasilane. This material sublimed above 100° and possessed a crystal transition temperature of 73.5°. The melting point did not appear to be improved over that of the crude material; however, in a sealed capillary tube the melt solidified over a narrow range (251.5-249.5°). This material then melted at 251.5-252.5°.

Attempts to use more forcing conditions for this reaction, namely, refluxing of the reaction mixture during the addition of the dichlorosilane to the lithium metal, resulted in much shorter reaction times (5-6 hours); however, under these conditions much more of the polymer (80%) was obtained with a concomitant decrease in the yield of the cyclic product (2.8%).

Derivatives of Octaphenylcyclotetrasilane

Octaphenylcyclotetrasilane with anhydrous hydrogen bromide

Anhydrous hydrogen bromide was bubbled at a moderate rate through a mildly refluxing stirred suspension of 7.29 g. (0.010 mole) of octaphenylcyclotetrasilane in 150 ml. of sodium-dried benzene. After four hours only a small amount of suspended material remained and the solution had become slightly yellow in color. The benzene solution was concentrated and 100 ml. of sodium-dried petroleum ether (b.p. 77-115°) was added. A fine white precipitate, melting with decomposition above 475°, was removed by filtration. This operation was repeated until no more high melting precipitate formed upon concentration of the solution.

Final concentration of the petroleum ether solution provided 6.89 g. (85.0%) of crude 1*H*-4-bromooctaphenyltetrasilane, melting over the range 161-168°. Recrystallization (decolorizing charcoal) from petroleum ether (b.p. 77-115°) gave 5.68 g. (70%) of pure product, m.p. 166-167°.

Anal. Calcd. for $C_{48}H_{41}BrSi_4$: Si, 13.86; hydrogen value, 111 ml./g. Found: Si, 13.76, 13.72; hydrogen value, 109 ml./g.

Octaphenylcyclotetrasilane with anhydrous hydrogen iodide

Anhydrous hydrogen iodide was prepared by dropwise addition of a solution of 125 g. of iodine in 70.5 g. of 47% hydriodic acid to an excess of red phosphorus in a two-necked flask provided with a gas outlet tube. Between the hydrogen iodide flask and the reaction flask was a drying tube containing phosphorus pentoxide. The gas generated in this manner was bubbled through a suspension of 7.29 g. (0.010 mole) of octaphenylcyclotetrasilane in 150 ml. of refluxing benzene. Within one hour all of the cyclosilane had gone into solution. Dry nitrogen was then passed through the cooled solution. Removal of the benzene by distillation left a gray gummy mass to which chloroform was added. A small amount of white insoluble material was filtered off. Dry ether was added to the chloroform solution which was then cooled to 0°. Only a small quantity of white solid precipitated which melted over a wide range above 400°.

Because the iodo compound appeared to be decomposing (depositing of iodine) in solution, it was hydrolyzed. Work-up of the hydrolysis product afforded 3.50 g. (47%) of white crystalline material, m.p. 177-183°. Recrystallization from benzene-petroleum ether (b.p. 77-115°) gave 2.00 g. (27%) of pure 4*H*-octaphenyltetrasilanol-1, m.p. 183-185°, whose infrared spectrum possessed absorption bands at 2.80 μ and 4.79 μ, indicative of SiOH and SiH, respectively.

Anal. Calcd. for $C_{48}H_{42}OSi_4$: Si, 15.0. Found: Si, 15.0, 14.9.

Octaphenylcyclotetrasilane with anhydrous hydrogen chloride

Into a refluxing suspension of 7.29 g. (0.01 mole) of octaphenylcyclotetrasilane in 150 ml. of benzene was introduced anhydrous hydrogen chloride over a period of six hours. At the end of this time the reaction was allowed to cool and dry nitrogen was bubbled through it to remove excess hydrogen chloride. Work-up gave 6.90 g. (95%) of recovered starting material, m.p. 305-310° (mixed m.p.). The remainder of the reaction mixture was a brown gum from which no products could be isolated.

1,2-Dibromotetraphenyldisilane

To 50.0 g. (0.0686 mole) of octaphenylcyclotetrasilane suspended in 160 ml. of sodium-dried benzene was added in a dropwise manner 11.0 g. (0.069 mole) of bromine dissolved in 100 ml. of benzene. The bromine reacted rapidly as evidenced by the decolorization of the reaction mixture. Then an additional 11.0 g. (0.069 mole) of bromine dissolved in 40 ml. of benzene was added and the resulting mixture was stirred at room temperature for 72 hours.

The benzene solution was warmed slightly to bring about dissolution of some of the insoluble material present. Filtration removed 3.69 g. (7.4%) of high melting material (crude Compound C). Benzene was stripped off under reduced pressure and the residue recrystallized from sodium-dried petroleum ether (b.p. 60-70°) to give 53.6 g. (74.6%) of 1,2-dibromotetraphenyldisilane, m.p. 157-158° (mixed m.p.). An additional 5.22 g. (7.3%) of less pure product (m.p. 143-150°) was isolated from the mother liquor.

1,4-Dibromooctaphenyltetrasilane

A suspension of 2.00 g. (0.00275 mole) of octaphenylcyclotetrasilane in 100 ml. of sodium-dried benzene was brought to the reflux temperature. A solution of 0.00276 mole of bromine in 10 ml. of benzene was added in a dropwise fashion. Instant decolorization occurred throughout the addition.

Subsequently, the benzene solvent was removed by distillation leaving a solid residue of 2.32 g. (95%) of crude 1,4-dibromooctaphenyltetrasilane, m.p. 210-215°. One recrystallization from benzene-petroleum ether (b.p. 60-70°) gave the pure product, m.p. 222-224° (mixed m.p.).

n-Decyllithium with 1*H*-4-bromooctaphenyltetrasilane

n-Decyllithium was prepared in 81.7% yield (benzyl chloride double titration) from 25.0 g. (0.113 mole) of *n*-decyl bromide and 1.80 g. (0.259 g.-atom) of lithium metal in 90 ml. of diethyl ether. Twenty-nine milliliters (0.0257 mole) of this solution was added slowly to a refluxing solution of 10.08 g. (0.0124 mole) of 1*H*-4-bromooctaphenyltetrasilane in 450 ml. of diethyl ether.

After the first few milliliters of the organolithium solution had been added the reaction mixture became bright yellow in color and remained so throughout the addition. Color Test I was strongly positive upon completion of the addition but was negative after overnight refluxing. Hydrolysis of the reaction mixture with saturated ammonium chloride solution provided 2.0 g. (22%) of octaphenylcyclotetrasilane, melting over the range 303-325°. Recrystallization from xylene raised its melting point to 320-325° (mixed m.p.).

The ether soluble portion of the reaction products was subjected to the usual work-up to provide an oil which was completely soluble in petroleum ether (b.p. 60-70°). Chromatography on alumina yielded, in addition to large amounts of intractable oils, a trace of somewhat impure 1,4-di-_n_-decyloctaphenyltetrasilane, m.p. 66-68° (mixed m.p.), and 0.25 g. (2.3%) of 1_H_-4-decyloctaphenyltetrasilane, m.p. 61-63°, after recrystallization from ethanol.

Anal. Calcd. for $C_{58}H_{62}Si_4$: Si, 12.89. Found: Si, 12.77, 12.72.

Benzene elution afforded 0.15 g. of decaphenylcyclopentasilane, which melted at 430-440° (mixed m.p.) after two recrystallizations from ethyl acetate. Other fractions from the chromatography consisted of intractable viscous oils, whose infrared spectra showed the presence of Si-H, Si-phenyl and aliphatic C-H groups.

n-Decylmagnesium bromide with 1H-4-bromooctaphenyltetrasilane

n-Decylmagnesium bromide was prepared according to the usual procedure in a 90.8% yield (simple base titration) from 11.06 g. (0.050 mole) of n-decyl bromide and 1.31 g. (0.054 g.-atom) of magnesium metal in 30 ml. of diethyl ether.

To 9.36 g. (0.0115 mole) of 1H-4-bromooctaphenyltetrasilane suspended in 150 ml. of diethyl ether was added 10 ml. of the Grignard solution (0.0124 mole) prepared above. After the reaction mixture had been refluxed for five hours Color Test I was still strongly positive. Therefore, the ether was replaced with toluene until the reflux temperature of the reaction mixture had reached 105°. Continued refluxing for 36 hours provided a negative color test.

Hydrolysis of the reaction mixture with dilute acid followed by the usual work-up afforded 5.33 g. (62%) of crude 4H-octaphenyltetrasilan-1-ol, melting over the range 165-180°. Several recrystallizations of this material from benzene-petroleum ether (b.p. 60-70°) gave the pure compound, m.p. 183-185° (mixed m.p.).

n-Decyllithium with 1,4-dichlorooctaphenyltetrasilane

A solution of 8.00 g. (0.010 mole) of 1,4-dichlorooctaphenyltetrasilane in 100 ml. of sodium-dried benzene was treated with 0.022 mole of n-decyllithium in 27 ml. of diethyl ether solution at room temperature. After 12 hours of stirring of the reaction mixture Color Test I was negative and a white precipitate had formed. Hydrolysis with 200 ml. of 1N hydrochloric acid caused the precipitate to dissolve (lithium halide).

Treatment of the reaction residue with petroleum ether (b.p. 60-70°) provided 0.90 g. (12%) of octaphenyloxacyclopentasilane, m.p. 223-225° (mixed m.p.). Alumina chromatography afforded as the only tractable product 0.66 g. (6.5%) of 1,4-di-n-decyloctaphenyltetrasilane, m.p. 70.5-71.5° after recrystallization from acetone.

Anal. Calcd. for $(n\text{-}C_{10}H_{21})_2Ph_8Si_4$: aliph. H/arom. H 42/40. Found: aliph. H/arom. H, 42.3/40 (n.m.r.).

n-Decyllithium with 1H-4-chlorooctaphenyltetrasilane

To a solution of 15.3 g. (0.02 mole) of 1H-4-chlorooctaphenyltetrasilane in 100 ml. of sodium-dried benzene was added 27 ml. of n-decyllithium (0.022 mole) diethyl ether solution. A bright yellow color developed and shortly a precipitate began to form. Color Test I was positive after 18 hours-stirring time. After additional hours of refluxing the color test was only slightly positive. Hydrolysis with 200 ml. of 1N hydrochloric acid provided an insoluble material, which was removed from the hydrolysis mixture by filtration. It proved to be octaphenylcyclotetrasilane, m.p. 323-330° (mixed m.p.).

Work-up of the organic soluble material afforded 14.8 g. of a viscous oil which was dissolved in petroleum ether (b.p. 60-70°). Overnight there precipitated 1.1 g. (7.5%) of crude 1H,4H-octaphenyltetrasilane, m.p. 150-165°. Recrystallization of this material from petroleum ether (b.p. 60-70°) gave 0.43 g. of pure compound, m.p. 163-164° (mixed m.p.).

Chromatography of the petroleum ether soluble material on alumina with the same solvent as eluent provided 2.59 g. (39.9%) of crude n-decyldiphenylsilane. Fractional distillation at reduced pressure gave 1.15 g. (17.7%) of pure product, b.p. 134-136°/0.007 mm. and n_D^{20} 1.5248. (Lit. (88) b.p. 164-168°/1.5 mm., n_D^{20} 1.5253)

Continued elution with petroleum ether yielded a trace of n-decyltriphenylsilane, which after recrystallization from ethanol melted at 67-68.5° (mixed m.p.). Elution with cyclohexane and carbon tetrachloride gave viscous fractions (7.38 g.) which proved to be intractable mixtures.

1,4-Di-n-butyloctaphenyltetrasilane (attempted)

To 8.00 g. (0.010 mole) of 1,4-dichlorooctaphenyltetrasilane dissolved in 50 ml. of tetrahydrofuran was added 0.040 mole of n-butylmagnesium bromide in 104 ml. of tetrahydrofuran solution. The resulting mixture was stirred for 24 hours at the reflux temperature. Color Test I was negative at the end of this time. Hydrolysis was effected with 200 ml. of 1N hydrochloric acid and the usual work-up was employed.

There was isolated in three fractions 5.72 g. (75%) of octaphenyltetrasilane-1,4-diol, m.p. 213-215° (mixed m.p.). No other products were isolated from the residue.

Derivatives of Decaphenylcyclopentasilane

1,5-Dibromodecaphenylpentasilane

From decaphenylcyclopentasilane and bromine To 10.00 g. (0.011 mole) of decaphenylcyclopentasilane dissolved in 100 ml. of sodium-dried benzene, cooled to ice-bath temperature, was added dropwise a solution of 1.76 g. (0.011 mole) of bromine in 30 ml. of benzene. The addition took one hour. After stirring for an additional 6 hours at room temperature, the pale yellow solution was distilled to remove the solvent, the final traces being removed at reduced pressures. There was obtained a sticky froth which solidified when digested with petroleum ether (b.p. 60-70°). Removal of the crystalline solid by filtration provided 10.90 g. (94.4%) of 1,5-dibromodecaphenylpentasilane, m.p. 202-207°. Recrystallization from cyclohexane-benzene raised the melting point to 207-209° (mixed m.p.).

From 1*H*,5*H*-decaphenylpentasilane and phosphorus pentabromide To 1.5 g. (0.0016 mole) of 1*H*,5*H*-decaphenylpentasilane dissolved in 30 ml. of carbon tetrachloride was added dropwise a solution of 1.42 g. (0.0033 mole) of phosphorus pentabromide in 70 ml. of the same solvent. After stirring overnight at room temperature, the pale yellow reaction mixture was distilled to remove the solvent.

The residue was recrystallized from cyclohexane to give 1.20 g. (67%) of crude 1,5-dibromodecaphenylpentasilane, m.p. 185-200°. Recrystallization of the crude product from benzene-cyclohexane raised its melting point to 203-205° (mixed m.p.).

1H,5H-Decaphenylpentasilane

Four grams (0.0037 mole) of 1,5-dibromodecaphenylpentasilane suspended in 50 ml. of diethyl ether was treated with 0.30 g. (0.0075 mole) of lithium aluminum hydride. After 10 min. of stirring the dibromo compound appeared to be dissolving. However, upon continued stirring a heavy white precipitate began to form. After refluxing the reaction mixture gently for 2.5 hours, it was hydrolyzed by addition to ice water which had been acidified with hydrochloric acid. The insoluble material recovered from the ether solution provided 3.24 g. (95.3%) of 1H,5H-decaphenylpentasilane, m.p. 147-149°.

Recrystallization of this material from acetone raised the melting point to 151-151.5°. The mixed melting point and the infrared spectrum of this compound are consistent with the compound obtained from the acid hydrolysis of the dilithio derivative of Compound B (decaphenylcyclopentasilane) (77).

1H-5-Bromodecaphenylpentasilane (attempted)

Anhydrous hydrogen bromide was bubbled slowly through a refluxing mixture of 21.88 g. (0.24 mole) of decaphenylcyclopentasilane and 400 ml. of sodium-dried xylene for a period of five hours. Upon cooling to room temperature, the reaction mixture was concentrated and treated with petroleum ether (b.p. 60-70°) to give a total of 17.65 g. (80.6%) of recovered decaphenylcyclopentasilane, m.p. 440-450°. The final residue was an intractable brown oil, the infrared spectrum of which showed the presence of SiH, SiOH and SiOSi groupings.

1*H*-5-Chlorodecaphenylpentasilane (attempted)

A solution of 21.88 g. (0.024 mole) of decaphenylcyclopentasilane in 400 ml. of *o*-dichlorobenzene was treated at the reflux temperature with a slow stream of anhydrous hydrogen chloride for eight hours. The solvent was removed by distillation and 50 ml. of petroleum ether (b.p. 60-70°) was added to the residue. Decaphenylcyclopentasilane, m.p. 440-450°, was recovered in two crops in 83% yield. No other products could be isolated.

In a second experiment treatment of 2.19 g. (0.0024 mole) of decaphenylcyclopentasilane suspended in 10 ml. of *o*-dichlorobenzene with excess anhydrous hydrogen chloride in a sealed tube at 260-290° resulted in the recovery of 98% of the starting material.

1,5-Dibromodecaphenylpentasilane with n-decylmagnesium bromide in tetrahydrofuran

A mixture of 7.3 g. (0.30 g.-atom) of magnesium metal and 20 ml. of tetrahydrofuran was treated with 10 ml. of a solution of 25.0 g. (0.113 mole) of n-decyl bromide in 80 ml. of tetrahydrofuran. After a few minutes the reaction mixture became warm and darkened in color. Dropwise addition was continued over a period of one hour. After the heat of reaction had subsided stirring was continued for two hours at room temperature. The Grignard solution was filtered from excess magnesium through glass wool into an addition funnel. Titration of an aliquot indicated the presence of 0.101 mole (89.4%) of n-decylmagnesium bromide.

Twenty-two milliliters of this solution (0.020 mole) was added to 10.7 g. (0.010 mole) of 1,5-dibromodecaphenylpentasilane dissolved in 90 ml. of tetrahydrofuran. The stirred reaction was heated at reflux for 10 days before a negative Color Test I was obtained. Hydrolysis with 1N hydrochloric acid and the usual work-up afforded 12.0 g. of turbid oil, from which was isolated by trituration with petroleum ether, 5.5 g. (58.3%) of decaphenylpentasilane-1,5-diol, m.p. 170-173° (mixed m.p.). No further products were isolable from the viscous residue either by fractional crystallization or by chromatography.

Decaphenylpentasilane-1,5-diol

One hundred milliliters of 1N hydrochloric acid was added to 30.0 g. (0.028 mole) of 1,5-dibromodecaphenylpentsilane dissolved in 200 ml. of tetrahydrofuran. The two-phase reaction mixture was stirred overnight at room temperature.

The organic layer was separated from the aqueous layer, which was also extracted with several portions of diethyl ether. The combined organic layers were dried (sodium sulfate) and the solvents were evaporated. The residue was dissolved in boiling cyclohexane and upon cooling there precipitated 25.35 g. (95.7%) of decaphenylpentasilane-1,5-diol, m.p. 172-174° (mixed m.p.).

1H,3H-Hexaphenyltrisilane

Decaphenylpentasilane-1,5-diol was prepared as described above from 29.5 g. (0.0275 mole) of 1,5-dibromodecaphenylpentasilane. The crude reaction product was dissolved in benzene and chromatographed on a 5 x 50 cm. basic alumina column (Alcoa activated alumina F-20). Elution of the column with about 12 liters of benzene over a period of four days yielded 11.92 g. (79.0%) of crude 1H,3H-hexaphenyltrisilane.

Recrystallization of this material from benzene-ethanol provided 10.76 g. (71.3%) of pure 1H,3H-hexaphenyltrisilane, m.p. 95.5-97° (mixed m.p.). Stripping the column with a mixture of acetic acid and tetrahydrofuran (1:5) provided viscous polyphenylsiloxane polymer from which was isolated some diphenylsilanediol, m.p. 148-153° decomp. and a trace of hexaphenylcyclotrisiloxane, m.p. 187-189° (mixed m.p.).

1H,3H-Hexaphenyltrisilane with N-bromosuccinimide in carbon tetrachloride

A stirred mixture of 6.00 g. (0.0109 mole) of 1H,3H-hexaphenyltrisilane, 3.90 g. (0.0219 mole) of N-bromosuccinimide and 100 ml. carbon tetrachloride was subjected to ultraviolet light (G.E. Sunlamp) for 30 min. At this time a flocculent precipitate was floating in the clear reaction solution.

Filtration of the mixture gave 2.17 g. (100%) of succinimide, m.p. 121-124° (mixed m.p.). The filtrate, which became red in contact with air, was evaporated and the residue recrystallized from sodium-dried petroleum ether (b.p. 60-70°). There was obtained 4.70 g. (65%) of a product, m.p. 137-138°.

Anal. Calcd. for $C_{36}H_{30}Br_2Si_3$: Si, 11.92. Calcd. for $C_{36}H_{30}BrClSi_3$: 12.71. Found: Si, 12.54, 12.45.

The infrared spectrum of this material indicated the presence of only Si-phenyl, but not SiOH or SiOSi groupings. It is possible that chlorine from the solvent is in some manner incorporated into the compound.

A repeat of this reaction was carried out completely under nitrogen, including crystallization and filtration of the pur product and resulted in the same product, m.p. 137-138° (mixed m.p.).

Anal. Found: Si, 12.37, 12.52.

1,3-Dibromohexaphenyltrisilane

To 4.00 g. (0.00728) of 1H,3H-hexaphenyltrisilane dissolved in 50 ml. of sodium-dried benzene, cooled to ice-bath temperature, was added slowly a solution of 2.34 g. (0.0146 mole) of bromine in 50 ml. of benzene. The bromine decolorized immediately upon addition. A light red-brown color persisted after the addition was complete. An aspirator vacuum was applied to remove excess bromine and hydrogen bromide which had formed and then the benzene was removed by distillation at atmospheric pressure. The residue was digested with 20 ml. of sodium-dried petroleum ether (b.p. 60-70°) and then allowed to cool to room temperature. Up to this point all steps had been carried out under a nitrogen atmosphere.

Filtration gave 3.72 g. (72.5%) of gray crystalline material, m.p. 151-153°. A mixed melting point of this product with 1,2-dibromotetraphenyldisilane, m.p. 153-154.5°, was depressed to 128-140°. Purification of the compound was accomplished by dissolving it under nitrogen in benzene, adding charcoal and filtering after warming for a few minutes. The solution thus obtained was distilled to remove most of the benzene and then 20 ml. petroleum ether was added giving white crystalline pure 1,3-dibromohexaphenyltrisilane, m.p. 153-154°.

Anal. Calcd. for $C_{36}H_{30}Br_2Si_3$: Br, 22.6. Found: Br, 22.2, 22.3.

1,5-Dilithiodecaphenylpentasilane

To a stirred mixture of 14.6 g. (0.016 mole) of decaphenylcyclopentasilane and 1.1 g. (0.16 g.-atom) of lithium metal was added about 10 ml. of tetrahydrofuran. Within one minute the reaction mixture became yellow and 150 ml. of tetrahydrofuran was added dropwise over a period of 45 min. The mixture was stirred for an additional 75 min. at room temperature and then filtered through glass wool into an addition funnel. Analysis of the solution (166 ml.) by the double titration technique using allyl bromide indicated the presence of 0.0321 mole (100%) of silyllithium content.

This method of preparation of 1,5-dilithiodecaphenylpentasilane was used to prepare several polysilanes as is subsequently described. Shorter reaction times led to recovered decaphenylcyclopentasilane, while longer times gave lower yields of 1,5-disubstituted derivatives and increased quantities of shorter chain cleavage products.

1,5-Di-*n*-butyldecaphenylpentasilane

Eighty milliliters of a tetrahydrofuran solution of 1,5-dilithiodecaphenylpentasilane (0.0155 mole of SiLi) obtained from the lithium cleavage of decaphenylcyclopentasilane was added rapidly to 4.40 g. (0.0165 mole) of tri-*n*-butyl phosphate dissolved in 20 ml. of tetrahydrofuran. Within 15 min. the reaction mixture was practically colorless and Color Test I was negative. Hydrolysis was effected by addition to 200 ml. of 1*N* hydrochloric acid. The usual work-up, followed by removal of the solvents by distillation, provided the crude reaction product, which was digested with ethanol. Removal of the insoluble material by filtration gave 5.82 g. (73.2%) of crude 1,5-di-*n*-butyldecaphenylpentasilane, melting over the range 153-161°. Recrystallization from benzene-petroleum ether (b.p. 60-70°) raised its melting point to 162.5-164°.

Anal. Calcd. for $(n\text{-}C_4H_9)_2Ph_{10}Si_5$: Si, 13.70;

arom. H/aliph. H, 50/18. Found: Si, 13.66, 13.61; arom. H/aliph. H, 51.5/18 (n.m.r.).

The remainder of the reaction residue was chromatographed on alumina to give 0.035 g. (0.9%) of 1,2-di-*n*-butyltetraphenyldisilane which melted at 101-102° (mixed m.p.) after recrystallization from ethanol; 0.115 g. (2.2%) of 1,3-di-*n*-butylhexaphenyltrisilane which melted at 147-149° after recrystallization from petroleum ether.

Anal. Calcd. for $(n\text{-}C_4H_9)_2Ph_6Si_3$: Si, 12.75; arom. H/aliph. H, 30/18. Found: Si, 12.60, 12.72; arom. H/aliph. H, 30.0/18.

There was also isolated 0.62 g. (7.9%) of 1,5-di-*n*-butyldecaphenylpentasilane, m.p. 160-162°, and 0.14 g. (2.0%) of decaphenylcyclopentasilane, m.p. 430-445°.

1,2-Di-*n*-butyltetraphenyldisilane

n-Butylmagnesium bromide was prepared in 94.4% yield from 3.42 g. (0.025 mole) of *n*-butyl bromide and 2.43 g. (0.10 g.-atom) of magnesium metal in 50 ml. of tetrahydrofuran. Forty-four milliliters of this solution, containing 0.020 mole of Grignard reagent, was added to 5.24 g. (0.01 mole) of 1,2-dibromotetraphenyldisilane dissolved in 50 ml. of tetrahydrofuran. After stirring at room temperature for 24 hours Color Test I was negative. Hydrolysis and the usual work-up gave 4.9 g. of an oil which was chromatographed on an alumina column. There was isolated 0.94 g. (19.6%) of 1,2-di-n-butyltetraphenyldisilane, which melted at 101-102° after recrystallization from ethanol.

Anal. Calcd. for $C_{32}H_{38}Si_2$: Si, 11.72. Found: Si, 11.74, 11.54.

1,5-Dimethyldecaphenylpentasilane

From 1,5-dilithiodecaphenylpentasilane and trimethyl phosphate To 2.30 g. (0.0165 mole) of trimethyl phosphate dissolved in 20 ml. of tetrahydrofuran was added rapidly 0.0075 mole of 1,5-dilithiodecaphenylpentasilane in 80 ml. of tetrahydrofuran solution. The red-brown color of silyllithium disappeared immediately, and heat evolution caused quite vigorous refluxing of the reaction mixture. Color Test I was negative, and after stirring for 15 min., the mixture was hydrolyzed with 200 ml. of 1N hydrochloric acid.

Following the usual work-up, 5.50 g. (75.5%) of crude product, m.p. 183.5-188°, was isolated. Recrystallization from benzene-petroleum ether (b.p. 60-70°) raised the melting point to 189-190° (mixed m.p.).

Anal. Calcd. for $(CH_3)_2Ph_{10}Si_5$: arom. H/aliph. H, 52/6; mol. wt., 941.5. Found: arom. H/aliph. H, 51.2/6; mol. wt., 938 (vapor pressure osmometer in benzene with decaphenylcyclopentasilane as standard).

From 1,5-dibromodecaphenylpentasilane and methylmagnesium iodide Methylmagnesium iodide was prepared in the conventional way from 28.4 g. (0.20 mole) of methyl iodide and 10.0 g. (0.41 g.-atom) of magnesium metal in 250 ml. of diethyl ether in 97% yield. Twenty milliliters of this solution, containing 0.0173 mole of methylmagnesium iodide, was added to 8.90 g. (0.00831 mole) of 1,5-dibromodecaphenylpentasilane dissolved in 150 ml. of tetrahydrofuran. Color Test I was negative after three hours. A second 20 ml. of the Grignard reagent was added to the reaction mixture which was then stirred overnight at room temperature and for 5 hours at the reflux temperature. Color Test I remained positive.

Work-up was effected by hydrolysis with 1N hydrochloric acid, followed by the usual extractive procedure. Removal of the ether and tetrahydrofuran resulted in a residue which, after treatment with cyclohexane, provided 7.52 g. (96.2%) of crude product, m.p. 180-185°. Recrystallization from benzene-petroleum ether (b.p. 60-70°) gave pure 1,5-dimethyldecaphenylpentasilane, m.p. 186-188° (mixed m.p.).

An attempt to prepare 1,5-dimethyldecaphenylpentasilane by this method employing the dibromo compound and the Grignard reagent in a 1:2 mole ratio at room temperature failed. There was isolated after hydrolysis 75.4% of decaphenylpentasilane-1,5-diol, and, by chromatography of the mother liquor, a trace of 1*H*-4-methyloctaphenyltetrasilane, m.p. 171-174° (mixed m.p.).

From 1-lithio-2-methyltetraphenyldisilane and dichlorodiphenylsilane   1-Lithio-2-methyltetraphenyldisilane was prepared according to a published procedure (28) from 4.19 g. (0.0046 mole) of decaphenylcyclopentasilane dissolved in 40 ml. of tetrahydrofuran and 0.0231 mole of methyldiphenylsilyllithium in 59 ml. of tetrahydrofuran. After stirring for 48 hours, analysis by double titration (allyl bromide) indicated that the silyllithium content of the solution had decreased only about 4%.

Eighty-eight milliliters of this solution, containing 0.0195 mole of silyllithium compounds and 0.0254 mole of total base, was added to 3.21 g. (0.0127 mole) of dichlorodiphenylsilane. Within one hour after the addition was complete Color Test I was negative. Acid hydrolysis and the usual work-up resulted in an oil which resisted crystallization from petroleum ether or from ethanol.

However, there was isolated by fractional crystallization from ethyl acetate and alumina chromatography 3.10 g. (28.6%) of crude 1,5-dimethyldecaphenylpentasilane, which melted at 188-189° (mixed m.p.) after recrystallization from ethyl acetate.

1,1,1,7,7,7-Hexamethyldecaphenylheptasilane

To 3.42 g. (0.0316 mole) of chlorotrimethylsilane dissolved in 50 ml. of tetrahydrofuran was added, over a period of 15 min., 0.0075 mole of 1,5-dilithiodecaphenylpentasilane in 83 ml. of tetrahydrofuran. Fifteen min. after completion of the addition the reaction mixture was clear and colorless. Hydrolysis was effected with ice water, and after work-up there was isolated 6.77 g. (83%) of crude product, m.p. 194-198°.

Recrystallization from petroleum ether (b.p. 60-70°) gave pure 1,1,1,7,7,7-hexamethyldecaphenylheptasilane, m.p. 197-199°. The n.m.r. spectrum of this compound showed absorption for phenyl and methyl (10.4 τ) protons in a ratio of 50:18.2 (theory 50:18).

Anal. Calcd. for $C_{66}H_{68}Si_7$: C, 74.96; H, 6.48. Found: C, 74.84, 74.87; H, 6.32, 6.40.

1*H*,7*H*-Tetradecaphenylheptasilane

To 10.1 g. (0.045 mole) of rapidly stirred chlorodiphenylsilane at room temperature was added in a dropwise fashion 0.0152 mole of 1,5-dilithiodecaphenylpentasilane in 170 ml. of tetrahydrofuran. The red silyllithium color disappeared immediately upon mixing. Color Test I was negative upon completion of the addition.

Acid hydrolysis and work-up gave an oily solid which was digested with boiling petroleum ether (b.p. 60-70°). Filtration of the hot petroleum ether suspension afforded 15.72 g. (82.0%) of white powder, m.p. 195-200°. When this material was recrystallized from benzene-propanol and from benzene-cyclohexane there was obtained pure 1*H*,7*H*-tetradecaphenylheptasilane, m.p. 203-204°.

Anal. Calcd. for $C_{84}H_{72}Si_7$: Si, 15.39. Found: Si, 15.31, 15.39.

1,1-Dimethyldecaphenylcyclohexasilane

To 2.15 g. (0.015 mole) of dichlorodimethylsilane dissolved in 200 ml. of tetrahydrofuran was added dropwise 0.0144 mole of 1,5-dilithiodecaphenylpentasilane in 166 ml. of tetrahydrofuran. After about 120 ml. of this solution had been added the silyllithium color began to persist. The final 50 ml. was added slowly. The solution became clear on continued stirring.

Hydrolysis with acidified ice water caused the precipitation of 0.55 g. (5.2%) of octaphenylcyclotetrasilane, m.p. 318-324°. The tetrahydrofuran soluble material was crystallized from benzene-petroleum ether (b.p. 60-70°) to give 5.0 g. (37%) of 1,1-dimethyldecaphenylcyclohexasilane, m.p. 472-476°. Recrystallization from benzene did not alter the melting point.

The compound obtained in this manner retained benzene of crystallization as shown by the fact that refluxing a sample of the compound with carbon tetrachloride and distilling the resulting solution gave benzene in the distillate as shown by ultraviolet. There was indicated to be more than two moles of benzene per mole of 1,1-dimethyldecaphenylcyclohexasilane by this method. The elemental analysis also indicates this fact.

<u>Anal</u>. Calcd. for $C_{62}H_{56}Si_6$: C, 76.80; H, 5.82; Si, 17.38. Found: C, 79.60, 79.39; H, 6.07, 6.06; Si, 14.55, 14.56.

The n.m.r. spectrum of the compound possessed absorption for methyl (9.46 τ) and for aromatic protons in a ratio of about 74:6. In addition to the usual monosubstituted phenyl absorptions, the infrared spectrum contained bands at 8.07 μ, 11.95 μ, and 12.53 μ characteristic for dimethylsilane compounds as well as absorption at 9.68 μ and 14.90 μ indicative of the presence of benzene. Drying of a sample of the compound at 135° for 48 hours indicated the presence of about 2.7 molecules of benzene per molecule of 1,1-dimethyldecaphenylcyclohexasilane. A silicon analysis on the dried sample gave a value of 17.52% silicon.

Decaphenylcyclopentasilane with lithium in the presence of chlorotrimethylsilane

Twenty milliliters of tetrahydrofuran was added to 14.6 g. (0.016 mole) of decaphenylcyclopentasilane and 1.6 g. (0.23 g.-atom) of lithium metal. After 5 min. of stirring, 4.32 g. (0.0398 mole) of chlorotrimethylsilane dissolved in 140 ml. of tetrahydrofuran was added over a period of 30 min. The silyllithium color remained throughout the addition and began to darken perceptibly after the addition was complete. Therefore, the filtered reaction mixture was added to 2.60 g. (0.0239 mole) of chlorotrimethylsilane. The color discharged immediately.

Acid hydrolysis and the usual work-up gave a residue from which was isolated by treatment with benzene-petroleum ether (b.p. 60-70°) 4.2 g. (29%) of decaphenylcyclopentasilane, m.p. 470-474° (mixed m.p.). The soluble portion was chromatographed on alumina. Elution of the column with petroleum ether gave first an oil from which there was isolated by distillation 1.47 g. (14.1%) of 1,1,1,3,3,3-hexamethyldiphenyltrisilane, b.p. 131-133°/0.55 mm., n_D^{20} 1.5717. Redistillation of this material gave the pure product, b.p. 105.5-106°/0.2 mm., n_D^{20} 1.5736.

Anal. Calcd. for $C_{18}H_{28}Si_3$: C, 65.78; H, 8.59. Found: C, 65.94, 65.97; H, 8.32, 8.30.

Secondly, there was obtained 1.04 g. (6.4%) of crude 1,1,1,4,4,4-hexamethyltetraphenyltetrasilane, m.p. 255-260°. Recrystallization from ethanol gave the analytical sample, m.p. 261.5-263°.

Anal. Calcd. for $C_{30}H_{38}Si_4$: C, 70.50; H, 7.49. Found: C, 70.42, 70.30; H, 7.26, 7.14.

Continued elution with petroleum ether gave 1.98 g. (17.9%) of a third compound, m.p. 289-297°. Recrystallization of this material from ethyl acetate and from benzene-ethanol gave pure 1,1,1,5,5,5-hexamethylhexaphenylpentasilane, m.p. 315-320°.

Anal. Calcd. for $C_{42}H_{48}Si_5$: C, 72.76; H, 6.98. Found: C, 72.98, 73.05; H, 6.67, 6.82.

With cyclohexane there was isolated from the column 0.72 g. (5.1%) of crude 1,1,1,6,6,6-hexamethyloctaphenylhexasilane, which melted at 293-296° (mixed m.p.) after recrystallization from benzene-petroleum ether. Carbon tetrachloride eluted 3.66 g. (21.6%) of crude 1,1,1,7,7,7-hexamethyldecaphenylheptasilane. Recrystallization from ethyl acetate gave the pure compound, m.p. 197-198° (mixed m.p.).

Reactions of Compound C

Lithium cleavage of Compound C

Reaction with trimethyl phosphate   Two grams (0.00183 mole of $(SiPh_2)_6$) of Compound C and 0.52 g. (0.075 g.-atom) of lithium metal were treated with a few milliliters of tetrahydrofuran. After stirring for 7 hours the reaction started, as indicated by a yellow color in the mixture. The remainder of the tetrahydrofuran (50 ml.) was added slowly and the silyllithium color deepened as the addition progressed. Then the reaction mixture was stirred at room temperature for 14 hours. At the end of this time a simple base titration indicated the presence of 0.0071 mole of silyllithium compounds.

The solution was filtered through glass wool and then added to 1.20 g. (0.086 mole) of trimethyl phosphate dissolved in 50 ml. of tetrahydrofuran. After acid hydrolysis there was recovered 0.1 g. (5%) of Compound C, m.p. 496° decomp. Work-up of the organic solvent soluble material by chromatography on an alumina column, provided 0.20 g. (14.9%) of 1,2-dimethyltetraphenyldisilane, which melted at 141-143° (mixed m.p.) after recrystallization from petroleum ether (b.p. 60-70°).

Cyclohexane eluted 1.09 g. (55.6%) of crude 1,3-

dimethylhexaphenyltrisilane, m.p. 90-93°. This material was recrystallized from ethanol to give the pure compound, m.p. 92-93° (mixed m.p.). There was also isolated a trace of 1,4-dimethyloctaphenyltetrasilane, m.p. 217-220° (mixed m.p.). The yields cited here are based on unrecovered Compound C. No other products were isolated.

Reaction with tri-n-butyl phosphate To 3.5 g. (0.0032 mole) of Compound C and 0.60 g. (0.086 g.-atom) of lithium metal was added sufficient tetrahydrofuran to form a thin paste. This mixture was stirred for half an hour at slight reflux before the reaction started. The remainder of the tetrahydrofuran (100 ml.) was added dropwise while the reaction mixture was warmed gently. After stirring the resulting mixture for 13 hours at slight reflux, double titration (allyl bromide) indicated the presence of 0.0105 mole of silyllithium.

The reaction mixture, filtered free of lithium, was added to 3.42 g. (0.0128 mole) of tri-n-butyl phosphate. After Color Test I was negative, hydrolysis with 200 ml. of 1 N hydrochloric acid was carried out to provide 0.20 g. (5.7%) of insoluble Compound C, m.p. 498-500° decomp. Alumina chromatography of the ether soluble residue provided 0.58 g. (21.7%) of crude 1,2-di-n-butyltetraphenyldisilane, which melted at 98-100° (mixed m.p.) after recrystallization from ethanol. Also isolated with petroleum ether (b.p. 60-70°) as the eluent was 1.06 g. (28.7%) of 1,3-di-n-butylhexaphenyltrisilane, m.p. 146-147.5°, after it was recrystallized from petroleum ether.

A second reaction employing 8 hours cleavage time at room temperature yielded 11.4% of recovered Compound C, 13.4% of 1,2-di-n-butyltetraphenyldisilane and 39.2% of 1,3-di-n-butylhexaphenyltrisilane. In a third run for 5 hours at room temperature there was obtained 42% of recovered Compound C, 4.5% of 1,2-di-n-butyltetraphenyldisilane and 41.5% of 1,3-di-n-butylhexaphenyltrisilane. All product yields are based on unrecovered Compound C.

Short contact time followed by trimethyl phosphate

Into a reaction flask provided with a sintered glass filter and stopcock at the bottom was introduced 5.00 g. (0.0046 mole) of Compound C and 2.0 g. (0.29 g.-atom) of lithium metal. A few milliliters of tetrahydrofuran was introduced and after 10 min. of stirring the reaction began. The silyllithium compounds thus formed were filtered through the sintered glass employing a slight vacuum into a lower reaction flask which contained 4.2 g. (0.03 mole) of trimethyl phosphate. Over a period of three and one-half hours 120 ml. of tetrahydrofuran was added to the cleavage mixture and the solution of silyllithium compounds thus formed was subsequently removed and allowed to react with the trimethyl phosphate.

Subsequent to acid hydrolysis, 1.2 g. (24%) of Compound C was recovered. The remainder of the reaction residue was chromatographed on alumina to give 0.1 g. (2.4%) of crude 1,2-dimethyltetraphenyldisilane, m.p. 119-130°. It was recrystallized from petroleum ether (b.p. 60-70°) to give the pure product, m.p. 140-142° (mixed m.p.).

Cyclohexane elution of the column provided 1.71 g. (43%) of 1,3-dimethylhexaphenyltrisilane, which melted at 92-93° (mixed m.p.) after recrystallization from petroleum ether. With carbon tetrachloride there was eluted 0.05 g. (1.3%) of crude 1,6-dimethyldodecaphenylhexasilane, melting over the range 190-200°. Two recrystallizations from petroleum ether raised its melting point to 205-207° (mixed m.p.).

In a second reaction using the same apparatus 6.00 g. (0.0055 mole) of Compound C was cleaved with 0.85 g. (0.12 g.-atom) of lithium metal. The silyllithium compounds were allowed to react with 3.66 g. (0.026 mole) of trimethyl phosphate. One liter of tetrahydrofuran was added to the cleavage mixture and the resulting solution removed over a period of 7 hours. Compound C (54.3%) was recovered from the reaction mixture. Also isolated were 0.35 g. of diphenylsilanediol, m.p. 136-140° and, by fractional crystallization, 0.15 g. (5.3%) of crude

1,6-dimethyldodecaphenylhexasilane, m.p. 195-200°. Recrystallization of the crude product from petroleum ether gave white crystals, m.p. 206-208° (mixed m.p.).

Anal. Calcd. for $C_{74}H_{66}Si_6$: mol. wt., 1124. Found: mol. wt., 1155, 1141 (vapor pressure osmometer in benzene with decaphenylcyclopentasilane as standard).

Short contact time followed by tri-n-butyl phosphate In an apparatus similar to that described for the previous reactions, but with a finer sintered glass filter, 8.00 g. (0.0073 mole) of Compound C was cleaved with 2.00 g. (0.288 g.-atom) of lithium metal using 1250 ml. of tetrahydrofuran over a period of 9 hours. At the end of this time only a small amount of dark brown insoluble material remained in the upper reaction flask.

The solution from the lower flask was hydrolyzed by addition to one liter of distilled water containing 15 ml. of concentrated hydrochloric acid. After the addition of some diethyl ether the water layer was removed and the organic layer filtered to give 0.50 g. (6.2%) of recovered Compound C, m.p. 495-500° decomp.

The ether solution was dried with anhydrous sodium sulfate and the solvent removed by evaporation. The residue which resulted was chromatographed on an alumina column. There was isolated from the petroleum ether (b.p. 60-70°) eluates 1.91 g. (21.5%) of crude 1,3-di-n-butylhexaphenyltrisilane, which melted at 145-147° (mixed m.p.) after recrystallization from petroleum ether. Continued elution with the same solvent afforded 0.30 g. (5.2%) of 1,4-di-n-butyloctaphenyltetrasilane, m.p. 217-220°. When recrystallized from benzene-petroleum ether the compound melted at 221-222° (mixed m.p.).

Elution of the column with carbon tetrachloride provided 0.29 g. (5.1%) of decaphenylcyclopentasilane, m.p. 450-460° (mixed m.p.), and benzene and ethyl acetate eluted 2.11 g. (27%) of crude tri-n-butyl phosphate. No significant quantities of material were eluted with tetrahydrofuran or ethanol.

Finally the alumina column was stripped with a 5% solution of acetic acid in tetrahydrofuran to give 4.45 g. (about 55%) of very viscous siloxane polymer, the infrared spectrum of which showed the presence of SiOH and SiOSi groupings in addition to the Si-phenyl group.

A repeat of this reaction under the same conditions, but using 8.87 g. (0.096 mole) of n-butyl chloride for the formation of the derivatives, resulted in the recovery of 0.35 g. (4.2%) of Compound C and the isolation of 0.30 g. (3.6%) of diphenylsilanediol, m.p. 151-155° (mixed m.p.) prior to the chromatographic step. In this case the only product isolated by chromatography with petroleum ether and with cyclohexane was 2.59 g. (28.0%) of 1,3-di-n-butylhexaphenyltrisilane, m.p. 145-147° (mixed m.p.). The chromatography was continued no further.

Compound C with phosphorus pentachloride in sym-tetrachloroethane

A stirred mixture of 2.00 g. (0.0018 mole) of Compound C, 0.82 g. (0.0039 mole) of phosphorus pentachloride and 75 ml. of sym-tetrachloroethane was heated to 135° for 2 hours. No detectable change in the appearance of the reaction mixture occurred during this time. An additional 1.64 g. (0.0078 mole) of phosphorus pentachloride was introduced and the mixture was heated at 135° for 5 hours to give a clear solution.

The solvent was removed at reduced pressure and the residue was treated with sodium-dried petroleum ether (b.p. 60-70°) to give 0.30 g. (15%) of recovered Compound C, m.p. 495-500° decomp. The residual oil failed to crystallize from petroleum ether; only an oil formed when the solution was cooled.

The petroleum ether was evaporated and the oil was recrystallized from acetone to give 0.19 g. (15%) of a compound, m.p. 217-221°. Recrystallization of this compound from benzene-petroleum ether afforded pure octaphenyl-1,4-dioxacyclohexasilane, m.p. 223-225° (mixed m.p.). The infrared spectrum of the compound and that of an authentic sample of octaphenyl-1,4-dioxacyclohexasilane were superimposable. No other products were isolable.

When Compound C was refluxed with sym-tetrachloroethane alone for 48 hours, 98% of the starting material was recovered.

Compound C with mercuric chloride

In benzene A mixture of 1.99 g. (0.0073 mole) of mercuric chloride, 2.00 g. (0.0018 mole) of Compound C and 100 ml. of sodium-dried benzene was stirred at the reflux temperature for 18 hours. Filtration of the mixture provided 2.76 g. of insoluble material which was treated with hot water, to give 1.84 g. (92%) of recovered Compound C, m.p. 500-503°.

In tetrahydrofuran A suspension of 2.00 g. (0.0018 mole) of Compound C in 75 ml. of tetrahydrofuran was refluxed with 1.99 g. (0.0073 mole) of mercuric chloride for 24 hours with no appreciable change in the appearance of the reaction mixture. There was recovered 1.85 g. (92.5%) of Compound C, m.p. 498-500° decomp.

Compound C with chlorine

Several reactions of Compound C with chlorine gas were attempted in either benzene, carbon tetrachloride or o-dichlorobenzene, with the recovery of varying amounts of Compound C. The compound does react with chlorine at elevated temperatures, but the complexity of the mixture of products made isolation by the usual techniques impossible. In order to cause significant amounts of Compound C to react, large excesses of chlorine had to be used, which evidently caused secondary cleavage reactions with whatever products had initially been formed.

Compound C with bromine

A mixture of 1.5 g. (0.0014 mole) of Compound C and 0.0028 mole of bromine in 110 ml. of sodium-dried benzene was refluxed for 5 hours. The red-brown color of the bromine remained. Filtration of the cooled reaction mixture afforded 1.44 g. (96%) of recovered Compound C, m.p. 502-504°.

Compound C with methyllithium

Two grams (0.0018 mole) of Compound C suspended in 100 ml. of tetrahydrofuran was stirred at room temperature for 24 hours with 0.0146 mole of methyllithium prepared in diethyl ether. Hydrolysis and filtration afforded 1.91 g. (96%) of recovered Compound C, m.p. 495-500°.

Compound C with benzyllithium

To 4.00 g. (0.0036 mole) of Compound C suspended in 50 ml. of tetrahydrofuran was added 0.051 mole of benzyllithium in 45 ml. of solution. The mixture was stirred for 15 hours at room temperature and then hydrolyzed with 200 ml. of 1*N* hydrochloric acid.

Filtration of the hydrolysis mixture provided 2.86 g. (71.5%) of recovered Compound C, m.p. 500-502°. From the organic layer the only product which could be isolated was a trace of diphenylsilanediol, m.p. 160-162°. This product was insoluble in carbon tetrachloride and carbon disulfide, but the infrared spectrum (KBr) was identical with that of an authentic sample of diphenylsilanediol.

DISCUSSION

Stability of Some n-Alkyllithium Compounds in Mixed Solvent Systems

The use of tetrahydrofuran as a solvent for organolithium reagents is known to enhance the reactivity of these compounds in metalation (89-91) and displacement reactions (92). In general, the organolithium compounds used in these studies were prepared in diethyl ether and the metalation or displacement reaction was subsequently carried out in tetrahydrofuran. This procedure resulted in a mixed solvent system of ether and tetrahydrofuran. Organolithium compounds can be prepared in tetrahydrofuran at low temperatures (93), however, n-alkyllithium compounds have been found to be unstable in tetrahydrofuran at room temperature. n-Butyllithium under these conditions decomposes completely within two hours, as indicated by the color test for organometallic compounds (93).

Although organolithium compounds in ether-tetrahydrofuran have been used for metalation reactions, the stability of these compounds in the mixed solvent has not been investigated quantitatively. The problem of stability is important with respect to the efficiency of metalation or displacement reactions in this solvent.

With a view towards using alkyllithium compounds subsequently for coupling reactions with phenylated halopolysilanes, the stability of some model compounds in mixtures of tetrahydrofuran and diethyl ether (about 1:1 by volume) was investigated. For purposes of comparison, mixtures of diethyl ether and tetrahydropyran and diethyl ether and 2,2,4,4-tetramethyltetrahydrofuran were also investigated. Utilizing the semiquantitative method of the color test, it was found that n-butyllithium was completely decomposed in ether-tetrahydrofuran within twenty-four hours at the reflux temperature. Negative color tests were obtained for n-butyllithium in ether-tetrahydropyran and ether-2,2,4,4-tetramethyltetrahydrofuran under the same conditions after one week and three weeks, respectively. Tetrahydrofuran therefore enhances the decomposition of n-butyllithium to a very marked degree.

When n-tetradecyllithium and n-decyllithium were refluxed in ether-tetrahydrofuran for forty-eight hours to give a negative color test, the major products isolated in each case were n-tetradecane and n-decane, respectively, indicating that the major course of decomposition was one involving a metalation reaction. Organolithium compounds react with common alkyl ethers having β hydrogen atoms to give an olefin product along with an alkoxide (94) according to the general formula:

$$RCH_2CH_2OR' + R''Li \longrightarrow RCH{=}CH_2 + LiOR' + R''H$$

An attempt was made to form derivatives with partly decomposed n-decyllithium in ether-tetrahydropyran and in ether-2,2,4,4-tetramethyltetrahydrofuran with chlorotriphenylsilane. There was isolated impure n-decyltriphenylsilane which could not be purified by fractional crystallization techniques. This might indicate that organolithium compounds other than n-decyllithium had in some manner formed in the solution. In the case of the decomposition of n-butyllithium in ether-tetrahydrofuran, ethanol was isolated in high yield. Therefore, the pathway of decomposition in these solvent systems is most probably not an extraordinary one.

A kinetic study concerning the stability of n-decyllithium in the three mixed solvent systems as well as in diethyl ether was carried out. The study was concentrated on this particular compound because in the projected coupling reactions this reagent could possibly confer desirable properties on the products, namely, lowered melting points. Phenylated polysilanes tend to be high melting compounds.

The stability of n-decyllithium in each of the solvents was determined by titrating each reaction mixture periodically, employing the method of double titration using benzyl chloride (82). The kinetic data obtained from these experiments are graphically represented in Figure 1 and are summarized in Table 3.

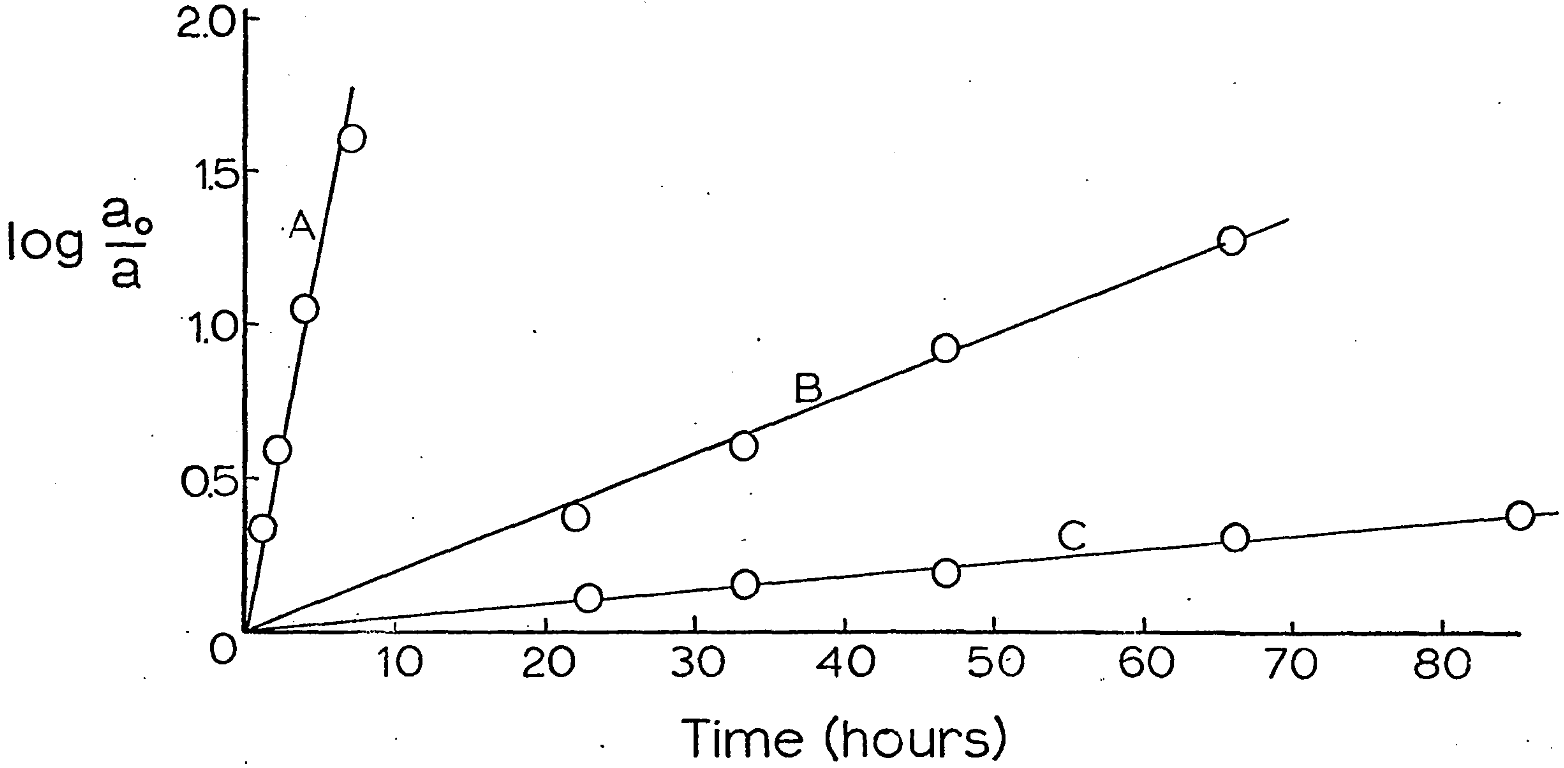
Table 3. Stability of n-decyllithium in mixed solvent systems at room temperature

Solvent	k_1 (hours^{-1})	$t_{\frac{1}{2}}$ (hours)
Diethyl ether-tetrahydrofuran	0.598	1.2
Diethyl ether-tetrahydropyran	0.0450	15
Diethyl ether-2,2,4,4-tetramethyltetrahydrofuran	0.0104	67
Diethyl ether	0.0096	72

The decomposition of n-decyllithium in each of the solvents is first order in organolithium compound concentration over at least 80% of the reaction, with the decomposition being sixty times faster in diethyl ether-tetrahydrofuran than in diethyl ether alone.

Of main interest here is the low order of stability of the alkyllithium compounds in ether-tetrahydrofuran with the formation of alkoxides and the possibility of

Figure 1. Log $\frac{a_o}{a}$ vs. time for n-decyllithium at room temperature in diethyl ether-tetrahydrofuran (A), diethyl ether-tetrahydropyran (B), and diethyl ether-2,2,4,4-tetramethyltetrahydrofuran (C)


log $\frac{a_o}{a}$
2.0
1.5
1.0
0.5
0
A
B
C
10
20
30
40
50
60
70
80
Time (hours)

inseparable impurities in the final coupling products with chlorosilanes. These factors militate against the use of this system in the formation of alkyl-substituted polysilanes. Therefore, these solvent systems were not used in the projected reactions. As will be discussed later organolithium compounds in diethyl ether alone or in diethyl ether-benzene mixtures, or alkylmagnesium halides in diethyl ether, were used in efforts to make phenylated alkylpolysilanes.

Preparation and Some Reaction of Benzyllithium

The utilization of the diethyl ether-tetrahydrofuran solvent system has proved of value in the preparation of benzyllithium. The direct preparation of benzyllithium as a useful intermediate is beset with difficulties which require special techniques. The organolithium compound can not be prepared in substantial quantities by the reaction of a benzyl halide with lithium metal in a suitable solvent such as diethyl ether. With dioxane as solvent, only 1.4% of phenylacetic acid could be obtained from the carbonation of the reaction mixture from benzyl chloride and lithium ribbon (95). Due to the reactivity of benzyllithium, coupled with the ease with which benzyl halides undergo displacement of the halide ion by organometallic compounds (96, 97), the preparation leads mainly to the coupling product, bibenzyl (95, 98). Halogen-metal interconversion is also to no avail for the same reasons (99). Benzyllithium has been prepared in the past by the reaction of either lithium metal or organolithium compounds with other organometallic compounds such as dibenzylmercury (100) and benzylmagnesium chloride (101) or organometalloidal compounds such as tribenzylantimony (102). Benzyllithium has also been obtained in moderate yields from the metalation of toluene with n-butyllithium in diethyl ether-tetrahydrofuran solvent (103).

A procedure for the direct preparation of benzyllithium in good yields in tetrahydrofuran from lithium metal and alkyl benzyl ethers has been reported (104, 105). However, a difficulty still present in these preparations is one of solubility. A 0.1 normal solution of benzyllithium in diethyl ether is supersaturated (106). In the case of tetrahydrofuran, attempts to prepare benzyllithium solutions greater than 0.3 normal resulted in the formation of gelatinous precipitates (105). The use of such solutions for large scale preparations requires a large volume of solvent.

A method for the preparation of benzyllithium in solutions of high concentrations has been developed (107).

The two solvents were utilized in such manner that at the beginning of the preparation the reaction solution would have a high tetrahydrofuran concentration, and at the end, when the benzyllithium concentration was high, the reaction solution would be diluted with diethyl ether. This was accomplished by adding to a suspension of small pieces of lithium metal in tetrahydrofuran, a solution of the alkyl benzyl ether in diethyl ether. By this method solutions of benzyllithium of concentrations as high as 1.16 normal were obtained in yields of up to 83%. No limiting concentration was determined. Although all preparations were carried out and the resulting solutions kept at -10° prior to reaction, this may not have been entirely necessary, due to the fact that benzyllithium is relatively stable in tetrahydrofuran alone, even more so than methyllithium (93, 105, 108).

Treatment of the benzyllithium solutions with benzophenone and with chlorotriphenylsilane provided good yields of benzyldiphenylcarbinol and benzyltriphenylsilane, respectively. A significant fact in these experiments is that no identifiable amounts of bibenzyl were found in the chromatographic work-up as was the case when benzyllithium prepared in tetrahydrofuran alone was derivatized with benzophenone (108).

The cleavage of hexaphenyldisilane with phenyllithium in a diethyl ether-tetrahydrofuran mixed solvent system has been reported (61). When a mixture of two volumes of ether to one of tetrahydrofuran, with phenyllithium in ten-fold excess, was employed, the cleavage of hexaphenyldisilane was 90% complete after two days of refluxing. In this study it was found that when a mixture of about one volume of ether to four of tetrahydrofuran and a 9.3-fold excess of benzyllithium (XXXIV) was used, hexaphenyldisilane (XXXV) was completely cleaved within an hour at temperatures between -10° and room temperature. An essentially quantitative yield of benzyltriphenylsilane (XXXVI)

$$\underset{\text{XXXIV}}{PhCH_2Li} + \underset{\text{XXXV}}{Ph_3SiSiPh_3} \longrightarrow \underset{\text{XXXVI}}{PhCH_2SiPh_3} + Ph_3SiLi$$

could be isolated. When a 2.1-fold excess of benzyllithium was employed the cleavage was complete within ninety minutes as evidenced by the disappearance of hexaphenyldisilane to give 66% of benzyltriphenylsilane (XXXVI).

It is evident that the use of benzyllithium in reactions involving polysilanes would be severely hampered by the possibility of indiscriminate cleavage of silicon-silicon bonds.

Formation of the Phenylated Cyclosilanes

The classical methods for building carbon chains generally involve compounds having unsaturation. However, because silicon appears to be incapable of forming multiple bonds with itself or other atoms, the majority of the chain extending reactions available in carbon chemistry have no analogy in silicon chemistry. The most common method employed for the formation of the silicon-silicon bond is a Wurtz coupling of halosilanes with alkali metals such as sodium. However, preparations of polysilanes with more

$$2R_3SiCl + 2Na \longrightarrow R_3SiSiR_3 + 2NaCl$$

than two silicon atoms by an analogous coupling reaction would require halopolysilanes which are often difficult to prepare and are limited in variety, and would generally provide nonfunctional derivatives.

As outlined in the historical section silicon functional polysilanes are available through the organic substituted cyclosilanes, which have been prepared successfully by the treatment of dichlorodiorganosilanes with alkali metals or magnesium. The method of choice for the preparation of the perphenylated cyclosilanes is the reaction of dichlorodiphenylsilane with lithium metal in tetrahydrofuran, from which yields of up to 40% of octaphenylcyclotetrasilane can be obtained (27).

An improved technique has been developed in which either octaphenylcyclotetrasilane or decaphenylcyclopentasilane can be prepared in high yield.[1] The technique involves the maintenance of a small amount of silyllithium species throughout the preparation. Under these conditions, when an equivalent amount of dichlorodiphenylsilane is added to lithium, the reaction is exothermic and octaphenylcyclotetrasilane can be isolated in yields up to 60%. If a slight excess of lithium is used under the same conditions and the reaction mixture is refluxed for three hours subsequent to combining the reactants, octaphenylcyclotetrasilane is converted to decaphenylcyclopentasilane. The product is obtained in nearly quantitative yield. Small amounts (about 3%) of Compound C can usually be isolated from these reactions.

A number of precursory compounds can be visualized in the formation of octaphenylcyclotetrasilane and the higher cyclosilanes from the reaction of dichlorodiphenylsilane with a metal such as lithium and these are listed in Table 4.

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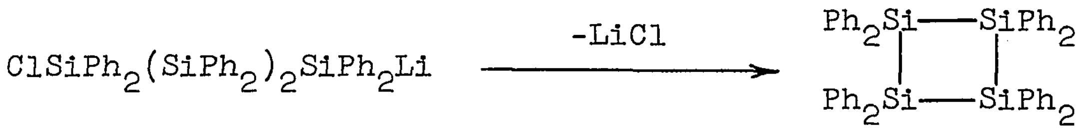
[1] J. M. Kraemer, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the preparation of octaphenylcyclotetrasilane and decaphenylcyclopentasilane. Private communication. 1960.

Table 4. Possible intermediates in the formation of octaphenylcyclotetrasilane

$Ph_2SiClLi$	$ClSiPh_2SiPh_2SiPh_2Cl$
Ph_2Si	$ClSiPh_2SiPh_2SiPh_2Li$
Ph_2SiLi_2	$LiSiPh_2SiPh_2SiPh_2Li$
$ClSiPh_2SiPh_2Cl$	$ClSiPh_2SiPh_2SiPh_2SiPh_2Cl$
$ClSiPh_2SiPh_2Li$	$ClSiPh_2SiPh_2SiPh_2SiPh_2Li$
$LiSiPh_2SiPh_2Li$	$LiSiPh_2SiPh_2SiPh_2SiPh_2Li$

One of the simplest intermediates is chlorodiphenylsilyllithium ($Ph_2SiClLi$). This compound may undergo a variety of reactions, among which are the following: (a) reaction with itself to give 1-chloro-2-lithiotetraphenyldisilane; (b) reaction with dichlorodiphenylsilane to give 1,2-dichlorotetraphenyldisilane; (c) reaction with many of the other suggested possibilities in Table 4, providing a chain-lengthening scheme in which the final step leading to octaphenylcyclotetrasilane is most probably ring closure of 1-chloro-4-lithiooctaphenyltetrasilane. Chlorodiphenylsilyllithium can be depicted in other conversions such as: (d) reaction with lithium metal to give dilithiodiphenylsilane (Ph_2SiLi_2), a species of undoubtedly high reactivity,



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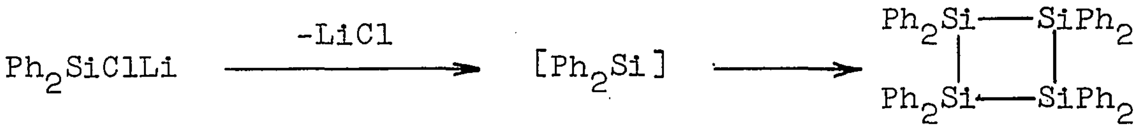
which could undergo the same type of silicon chain propagating steps described for chlorodiphenylsilyllithium; (e) elimination of lithium chloride to give diphenylsilylene (Ph_2Si), which might in turn "polymerize" to octaphenylcyclotetrasilane. Some studies are in progress in our



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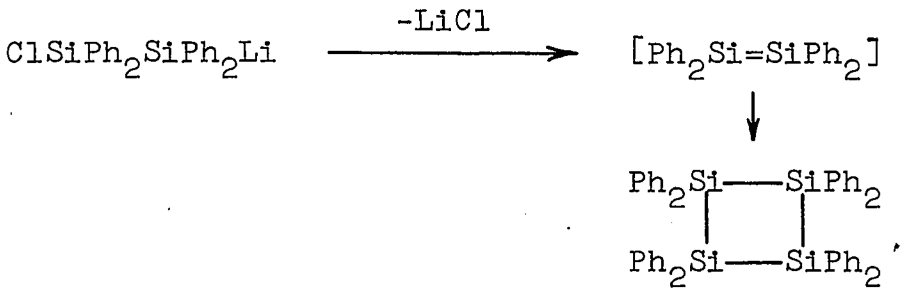
laboratories on the trapping of a diphenylsilylene species; and an interpretation of some of these reactions does not exclude the possibility that diphenylsilylene may be formed transitorily.

There also exists the remote possibility of the intermediate formation of a Si=Si type which might be expected to dimerize to octaphenylcyclotetrasilane. Other possibilities for the formation of octaphenylcyclotetrasilane involve not only interaction of some combinations of the compounds in Table 4, but also reactions of some of them

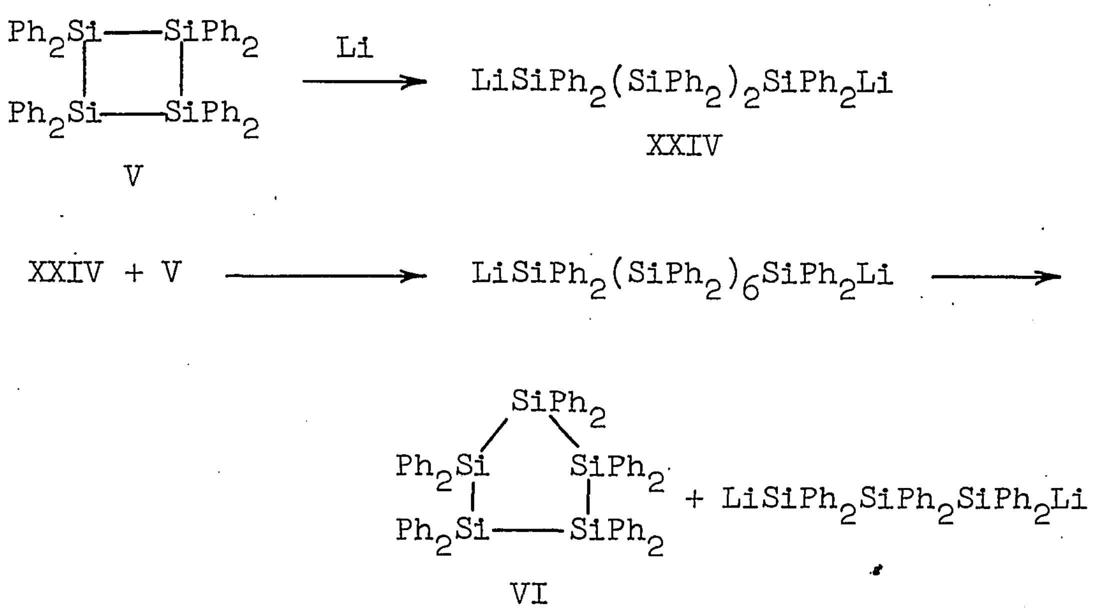


V

with dichlorodiphenylsilane or with lithium metal.

Whatever the mode of formation of octaphenylcyclotetrasilane, it appears that this compound can be a precursor of decaphenylcyclopentasilane. In the preparation of the latter compound the same conditions prevail in the first stages as in the preparation of octaphenylcyclotetrasilane. At this point the slight excess of lithium metal converts octaphenylcyclotetrasilane (V) into decaphenylcyclopentasilane (VI), evidently through steps involving intramolecular cyclization.

In the determination of the structure of Compound B (decaphenylcyclopentasilane) molecular weight data have led in the past on the one hand to the view that the compound was octaphenylcyclotetrasilane, and on the other hand to the conclusion that it was dodecaphenylcyclohexasilane. However, recent chemical evidence indicated that Compound B is decaphenylcyclopentasilane. Therefore, it



was necessary to obtain an experimental molecular weight which was consistent with the indicated structure.

These data were obtained with a vapor pressure osmometer[1] and agree excellently with the structure, decaphenylcyclopentasilane (VI). Using benzil as the standard, the molecular weight of the compound was determined in benzene at several concentrations (Table 5), and extrapolated graphically to zero concentration (Figure 2). The experimental molecular weight by this method was found to be 912 which is to be compared with theoretical value of 911.4 for decaphenylcyclopentasilane. The molecular

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[1] Manufactured by Mechrolab, Inc., Mountain View, California.

Figure 2. Molecular weight of decaphenylcyclopentasilane determined at several concentrations and extrapolated to infinite dilution

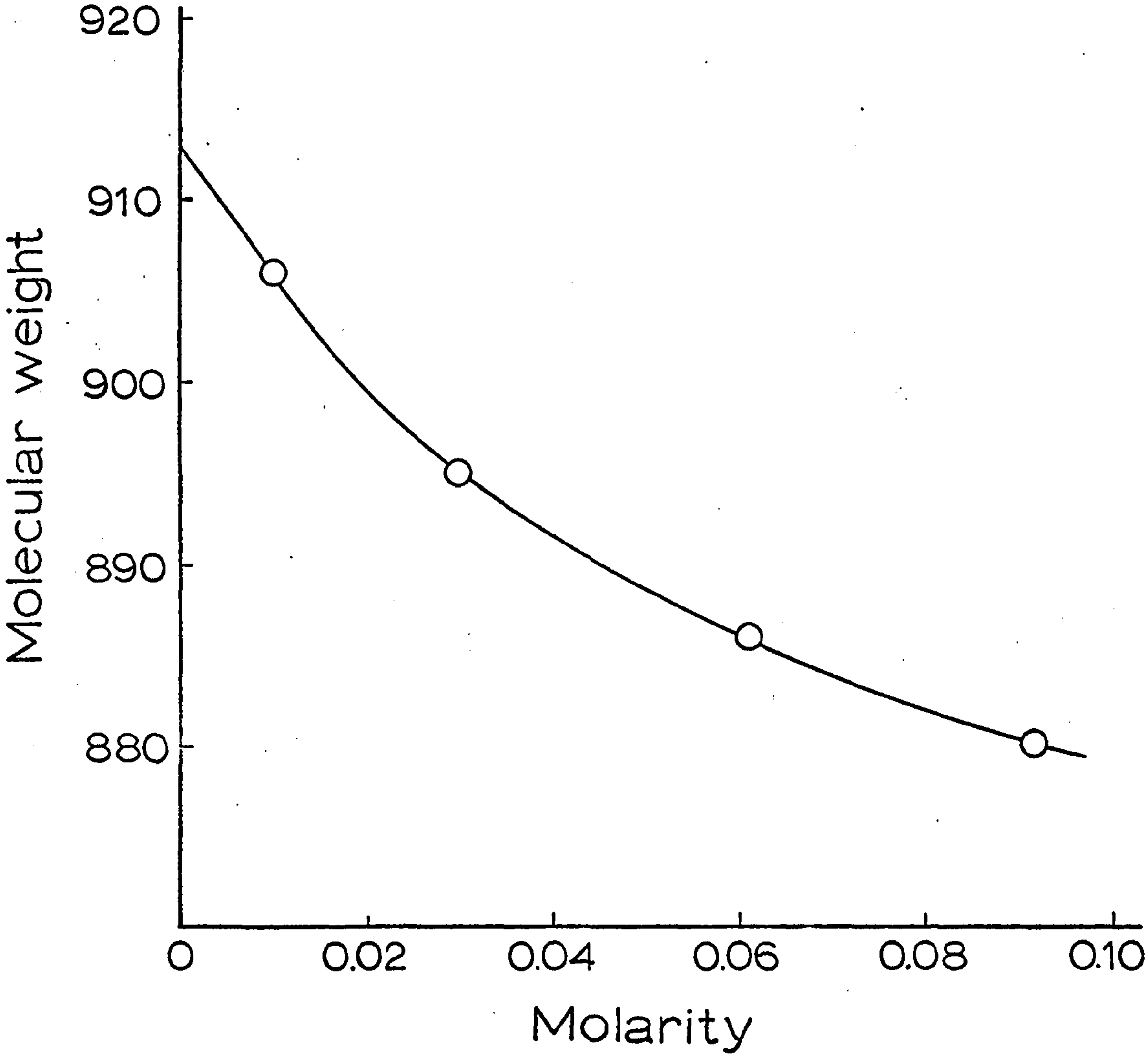
920
910
900
890
880
Molecular weight
0
0.02
0.04
0.06
0.08
0.10
Molarity

Table 5. Molecular weight of decaphenylcyclopentasilane in benzene at 37.0° (vapor pressure osmometer)[a]

Concentration (gm/liter)	Concentration (Molar, obs.)	Molecular weight
9.056	0.0100	906
26.58	0.0296	895
54.04	0.0610	886
80.57	0.0915	880

[a] Benzil was used as standard.

weight of decaphenylcyclopentasilane has also been determined for us ebullioscopically in toluene (109) using octaphenylcyclotetrasilane as a standard,[1] and by an X-ray diffraction study and density determination of crystalline decaphenylcyclopentasilane.[2] The former method gave a value of 921 (average of four values) for the molecular weight of decaphenylcyclopentasilane. The X-ray analysis was performed on crystals grown from a mixture of benzene

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[1] Determined by Dr. C. A. Glover, Tennessee Eastman Company Research Laboratories.

[2] Determined by Dr. H. W. Patton, Tennessee Eastman Company Research Laboratories.

and alcohol, from which the cyclopentasilane crystallizes with one molecule of benzene for each Si_5Ph_{10} unit. The value for the molecular weight obtained by this method was 983, which is in good agreement with a value of 989 calculated for decaphenylcyclopentasilane plus one molecule of benzene.

Since the structures of Compound A and Compound B have been determined to be octaphenylcyclotetrasilane and decaphenylcyclopentasilane, respectively, it might be concluded that the third crystalline compound (Compound C) from the reaction of dichlorodiphenylsilane with metals is dodecaphenylcyclohexasilane. However, proving this assumption has been a problem which has not as yet been satisfactorily accomplished.

Ebullioscopic measurements in toluene gave values ranging from 1180 to 1240 for the molecular weight of Compound C. The theoretical value for dodecaphenylcyclohexasilane is 1093.7 and that for the cycloheptasilane is 1276.0. With the knowledge of the past difficulties in determining molecular weights of compounds of this type and the fact that solubility problems make these values suspect, faith in the experimental values cannot be too firm.

An attempt to prepare dodecaphenylcyclohexasilane by treatment of dichlorodiphenylsilane with 1,5-dilithiodecaphenylpentasilane resulted in octaphenylcyclotetrasilane and decaphenylcyclopentasilane in moderate yields. Compound C was isolated in 2.7% yield. This quantity is about the same order as that encountered in the preparations of octaphenylcyclotetrasilane and decaphenylcyclopentasilane, and therefore, does not necessarily indicate that the compound is dodecaphenylcyclohexasilane.

From the reaction of 1,3-dichlorohexaphenyltrisilane with sodium metal in refluxing toluene Compound C was isolated in 9.2% yield, along with 15% of decaphenylcyclopentasilane and 14.7% of a material apparently similar to Kipping's Compound D. Attempted reactions of 1,3-dichlorohexaphenyltrisilane with magnesium and of 1,3-dihalohexaphenyltrisilane with sodium-potassium alloy were of no value, due to no reaction in the first case, and excessive silicon-silicon bond cleavage leading to silylmetallic compounds in the second case.

An effort to improve the yield of Compound C from the reaction of dichlorodiphenylsilane with a slight excess of lithium by extended refluxing periods resulted in only 3.1% of the desired compound. Apparently the silyllithium compounds slowly consume themselves by cleavage of the tetrahydrofuran in a manner similar to other silyllithium compounds (110, 111). This is indicated by the isolation of 2,2-diphenyl-1-oxa-2-silacyclohexane in low yield. An attempt to prepare tetradecaphenylcycloheptasilane from 1,2-dibromotetraphenyldisilane and 1,5-dilithiodecaphenylpentasilane resulted in octaphenylcyclotetrasilane and decaphenylcyclopentasilane as the only identifiable products.

Dodecamethylcyclohexasilane was prepared in moderate yield by the reaction of dichlorodimethylsilane with lithium metal in tetrahydrofuran. Recent modifications of this reaction have improved the yield of the cyclosilane at the expense of the dimethylsilylene polymer which is usually formed in the reaction (23, 24).

Concerning the relative yields of the phenylated cyclosilanes, some speculation may be raised. By analogy to carbon chemistry, if there are reaction pathways available, it might be expected that cyclohexasilanes would be the most favored product. This is evidently the case with the permethylated compounds, where dodecamethylcyclohexasilane is the major cyclic product. However, in the case of the perphenylated compounds this apparently is not true. Compound C, assuming that it is dodecaphenylcyclohexasilane, is formed in only small quantities. Decaphenylcyclopentasilane appears to be the most stable homologue under the reaction conditions. Even in reactions designed for the preparation of dodecaphenylcyclohexasilane the five-membered ring compound was the major product.

These results of course do not indicate that dodecaphenylcyclohexasilane is less stable than the lower homologues, but that it is less easily formed. Consideration of a Stuart-Briegleb model of the cyclohexasilane reveals a compact and tight arrangement due to the bulkiness of the phenyl groups. Because of this the orientation of all groups in the immediate precursor to Compound C might be extremely critical in going to the cyclic product.

One other piece of information has been gathered concerning the structures of the three perphenylated cyclosilanes. Their infrared spectra in the 2-15 μ range are for all practical purposes identical. The absorption near 9.15 μ does show a slight shift to longer wave lengths with increasing ring size. However, the spectra are quite characteristic in the 700-200 cm^{-1} region. The infrared spectra (Figures 3 and 4) of these cyclosilanes, and also of 1,5-di-n-butyldecaphenylpentasilane, were determined in this region as Nujol mulls using cesium iodide optics (Beckman IR7). All four compounds possess an absorption band at about 476 cm^{-1} which is split into a doublet. Absorption in this region has been attributed to a silicon-phenyl grouping (112). The three cyclosilanes also have an absorption centered at 333 cm^{-1}. In octaphenylcyclotetrasilane it appears as a sharp singlet; in decaphenylcyclopentasilane it appears as a reasonably symmetrical

Figure 3. (A) Infrared spectrum of octaphenylcyclotetrasilane from 700 to 200 cm^{-1} (Nujol mull); (B) Infrared spectrum of decaphenylcyclopentasilane from 2 to 10.5 μ (CCl_4), from 10.5 to 15 μ (CS_2) and from 700 to 200 cm^{-1} (Nujol mull)

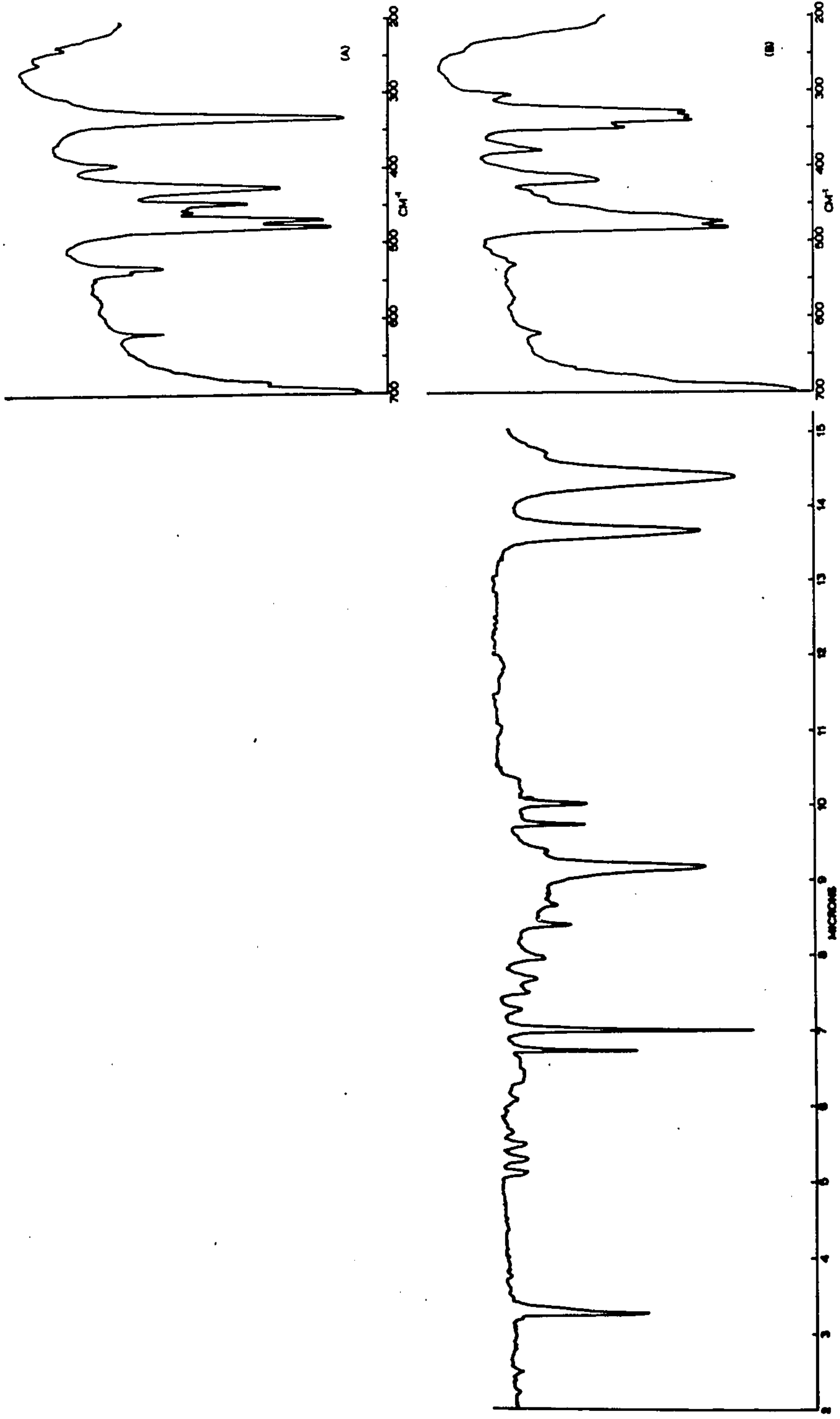
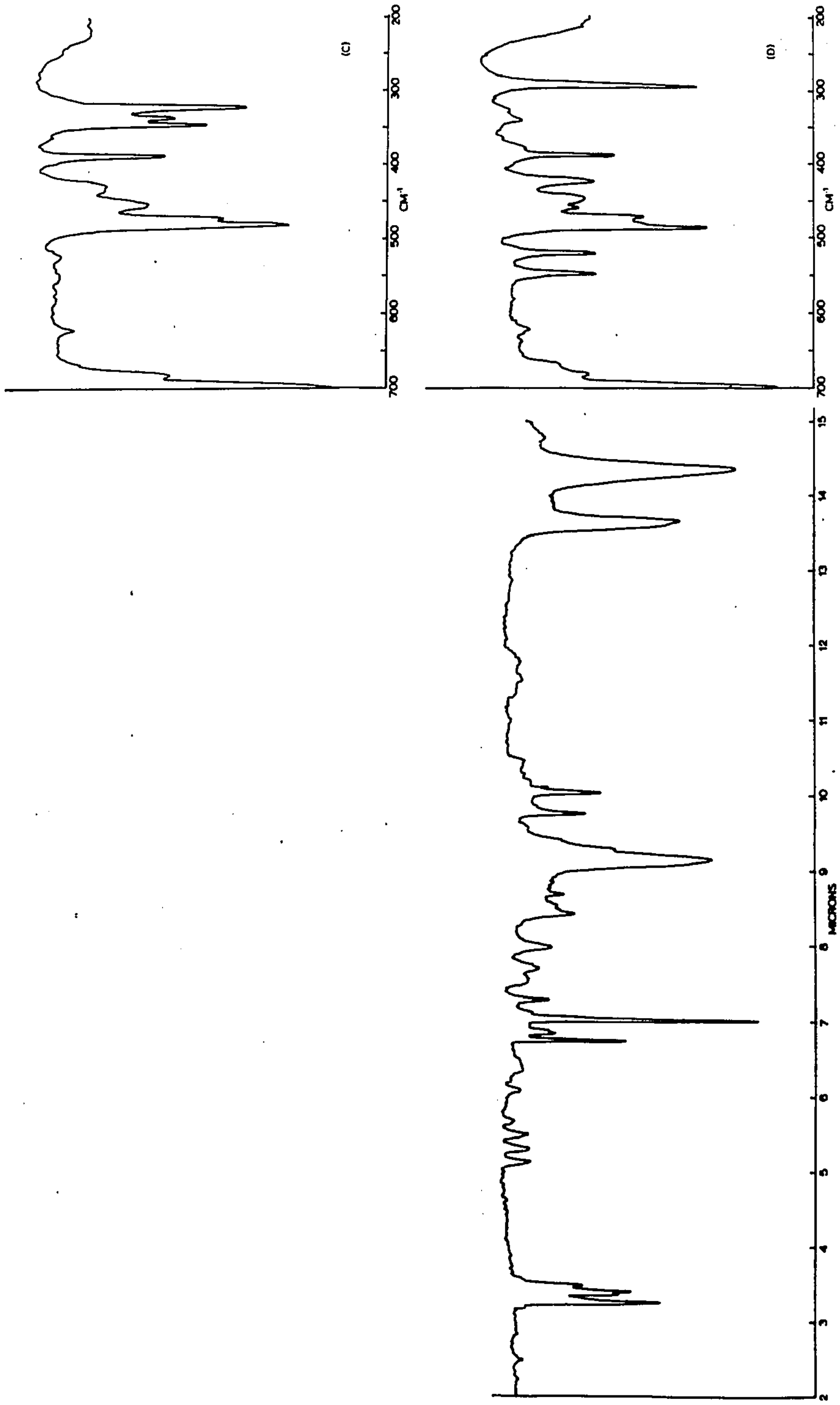

(A)
(B)
200
300
400
500
600
700
CM⁻¹
2
3
4
5
6
7
8
9
10
11
12
13
14
15
MICRONS

Figure 4. (C) Infrared spectrum of Compound C from 700 to 200 cm^{-1} (Nujol mull); (D) Infrared spectrum of 1,5-di-n-butyldecaphenylpentasilane from 2 to 10.5 μ (CCl_4), from 10.5 μ to 15 μ (CS_2) and from 700 to 200 cm^{-1} (Nujol mull)

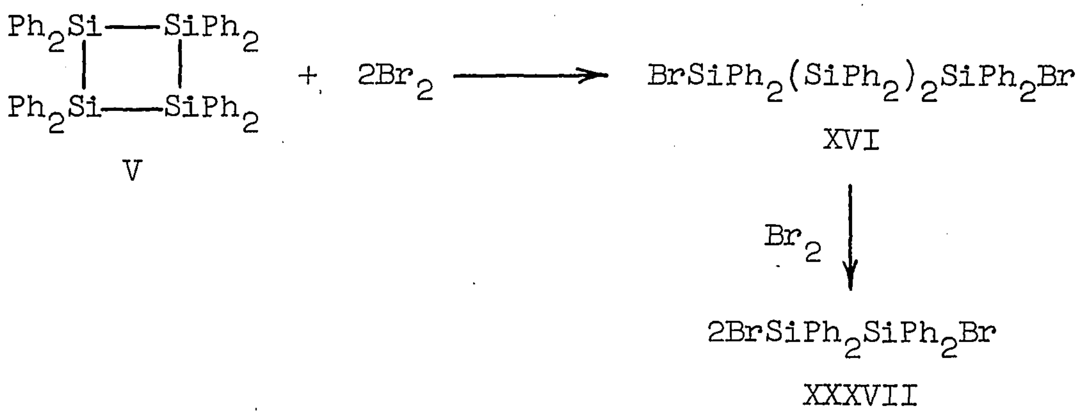

(C)
(D)
CM⁻¹
200
300
400
500
600
700
MICRONS
2
3
4
5
6
7
8
9
10
11
12
13
14
15

multiplet; and in Compound C it is a triplet. In 1,5-di-n-butyldecaphenylpentasilane absorption at this point is lacking; however, a new strong absorption band appears at 294 cm^{-1}. Absorption in this region has been attributed, in the case of hexaphenyldisilane, to axial deformation of the two silicon atoms (112). Whether the observed data correspond to the same type of absorption is not certain; but, in any case, the spectra seem to indicate similarities between the three cyclosilanes as well as some definite differences.

Some Reactions and Derivatives of Octaphenylcyclotetrasilane

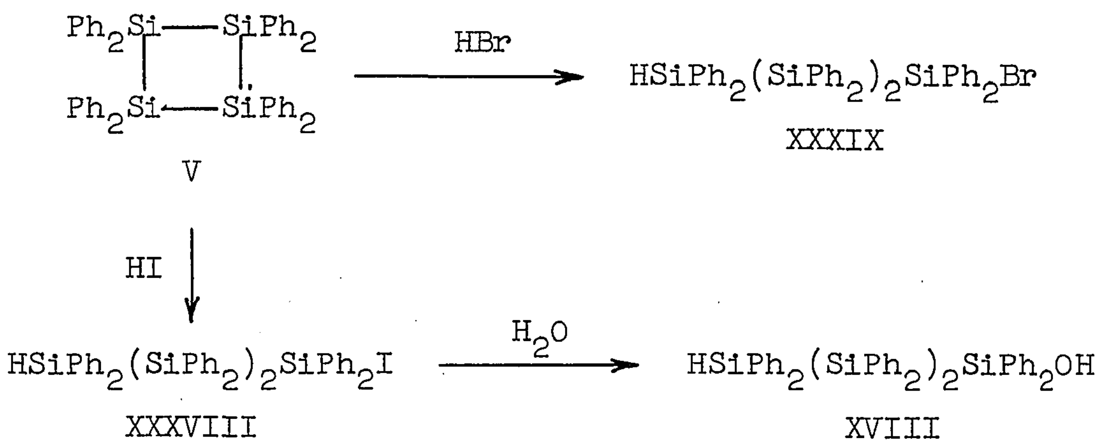
Halogenation of octaphenylcyclotetrasilane (V) has been accomplished with a variety of rather mild reagents ranging from iodine to sym-tetrachloroethane. Not surprisingly the cyclosilane has also been found to react with bromine. If equivalent amounts of reactants are used, the product is 1,4-dibromooctaphenyltetrasilane (XVI); however, if two equivalents of bromine to one of octaphenylcyclotetrasilane (V) are used, 1,2-dibromotetraphenyldisilane (XXXVII) can be isolated in yields up to 85%.

Octaphenylcyclotetrasilane is also cleaved by hydrogen



halides, although not with the facility observed with the halogens. Both hydrogen iodide and hydrogen bromide react with the cyclotetrasilane in refluxing benzene to give 1<u>H</u>-4-iodooctaphenyltetrasilane (XXXVIII) and 1<u>H</u>-4-bromooctaphenyltetrasilane (XXXIX), respectively. The iodosilane was not isolated, but was hydrolyzed and characterized as 4<u>H</u>-octaphenyltetrasilan-1-ol (XVIII). The bromosilane (XXXIX) is obtained in 85% yield. Under similar conditions hydrogen chloride did not react. The order of reactivity of the hydrogen halides with octaphenylcyclotetrasilane is apparently HI>HBr>HCl.

The reaction of hydrogen halides with a silicon-silicon bond is unprecedented, although in this case not entirely unexpected, due to the special properties of octaphenylcyclotetrasilane. As observed previously, halogenation of the compound is known with reagents,

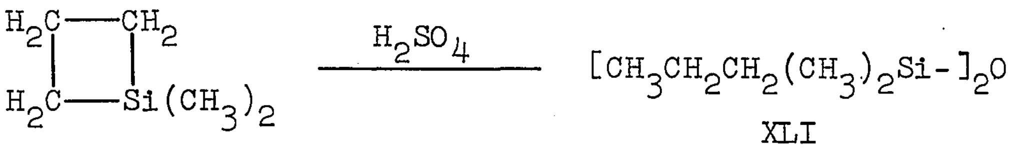


which would not be considered to be halogenating agents. These same reagents, as are the hydrogen halides, are ineffective in reactions with decaphenylcyclopentasilane.

The reactivity of octaphenylcyclotetrasilane has been attributed to "ring strain and the accompanying homolytic cleavage to a biradical" (27). This explanation may be an oversimplified statement of the mechanism of reaction involved in the ring opening, and it is not necessarily true that a biradical species is involved. First of all, to take a specific example, hexaphenyldisilane shows no tendency to dissociate into free radicals, as does hexaphenylethane, even though the silicon-silicon bond is considered to be inherently weak compared with a carbon-carbon bond (8). However, recent evidence (113) indicates that the dissociation energy of the silicon-silicon bond of disilane is 81.3 kcal. mole^{-1}, comparable to the dissociation energy of the carbon-carbon bond in ethane (83 kcal. mole^{-1}), rather than earlier values of about 50 kcal. mole^{-1}.

Secondly, granted that ring strain may increase the reactivity of octaphenylcyclotetrasilane due to distortion of the tetrahedral bond angles of silicon, this effect need not be so important as it is in carbon chemistry. The tetrahedral angle of silicon is believed to be more easily deformed than that of carbon (114). And, thirdly, if octaphenylcyclotetrasilane were incipiently disposed to dissociate into a biradical species under reasonably normal conditions due to ring strain, it might be expected to rearrange to a variety of products above its melting point because of the high reactivity of silyl radicals (8). However, as pointed out earlier, octaphenylcyclotetrasilane, when kept melted at 335° for twenty hours, in a sealed tube, apparently undergoes no change (36).

A possible explanation for the relatively great reactivity of octaphenylcyclotetrasilane, compared to the other perphenylated cyclosilanes and hexaphenyldisilane, concerns the molecular geometry of the compound, the fact that silicon can easily achieve a pentacovalent state, and steric factors. There is a lack of data concerning the reactivity of the silicon-silicon bond in a strained ring system, such as might be found in 1,2-disilacyclobutane derivatives; however, it has been found that silacyclobutane and 1,3-disilacyclobutane derivatives do undergo ring opening reactions easily with a variety of reagents. Thus, 1,1-dimethylsilacyclobutane (XL) undergoes a highly exothermic reaction with potassium hydroxide in ethanol and reacts violently with concentrated sulfuric acid at room temperature with no gas evolution, indicating ring opening (115). The resulting product is 1,3-di-*n*-propyltetramethyldisiloxane (XLI). Also, attempts to

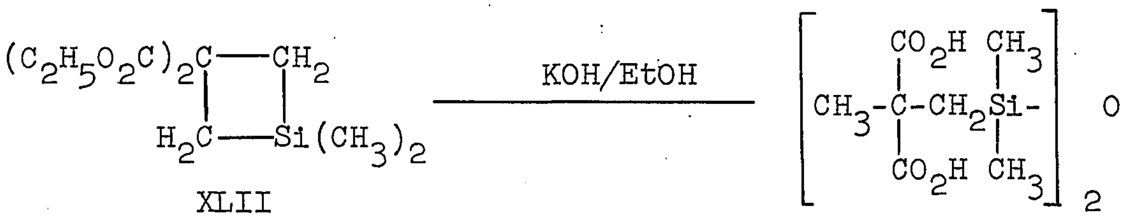


XL

$[CH_3CH_2CH_2(CH_3)_2Si-]_2O$

XLI

prepare the corresponding dicarboxylic acid from 3,3-dicarbethoxy-1,1-dimethylsilacyclobutane (XLII) by alkaline hydrolysis resulted in a ring-opened product (XLIII) (114).

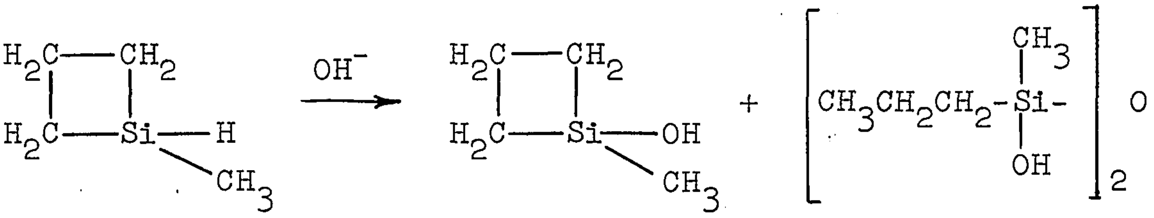


XLII

XLIII

1,1,3,3-Tetramethyl-1,3-disilacyclobutane reacts readily with silver nitrate in ethanol and with bromine in carbon tetrachloride as does 1,1-dimethylsilacyclobutane (XL) (116).

A significant competing reaction in the basic hydrolysis of 1-methylsilacyclobutane (XLIV) to give the corresponding silanol (XLV) is a ring opening to give 1,3-dihydroxy-1,3-dimethyl-1,3-di-n-propyldisiloxane (XLVI) as a final hydrolysis product (117). Sommer explained the high rate of hydrolysis of 1-methylsilacyclobutane (XLV) compared to higher homologues and to normal trialkylsilanes[1] by structure-reactivity relations resulting from <u>steric factors</u>, which can be applied directly to octaphenylcyclotetrasilane, with ring opening being the exclusive reaction.



XLIV XLV XLVI

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[1] The rate of hydrolysis of 1-methylsilacyclobutane (XLIV) to the corresponding silanol (XLV) is 10^4-10^5 times faster than the hydrolysis of triethylsilane to triethylsilanol (117).

Therefore, if the silicon atom of octaphenylcyclotetrasilane which is undergoing attack by a reacting species is considered to attain a pentacovalent configuration as depicted in Figure 5, the following three factors assist in the subsequent cleavage of a silicon-silicon bond: (a) ease of formation of pentacovalent silicon resulting from other groups being "pulled back" away from the path of reagent attack; (b) lack of angular strain[1] at the pentacovalent silicon atom relative to the tetracovalent state; (c) lack of appreciable added steric strain in the complex over that in the substrate, the added strain being less in a four-membered ring than in a larger one.

All of these factors would aid in the formation of the pentacovalent silicon atom, with ring strain in octaphenylcyclotetrasilane promoting formation of the complex rather than directly causing ring opening. For decaphenylcyclopentasilane, increased crowding of phenyl groups tends to prevent approach of reagents, internal strain would increase in the complex, and added steric interactions between phenyl groups in the complex would be appreciable. In hexaphenyldisilane, severe crowding of phenyl groups as

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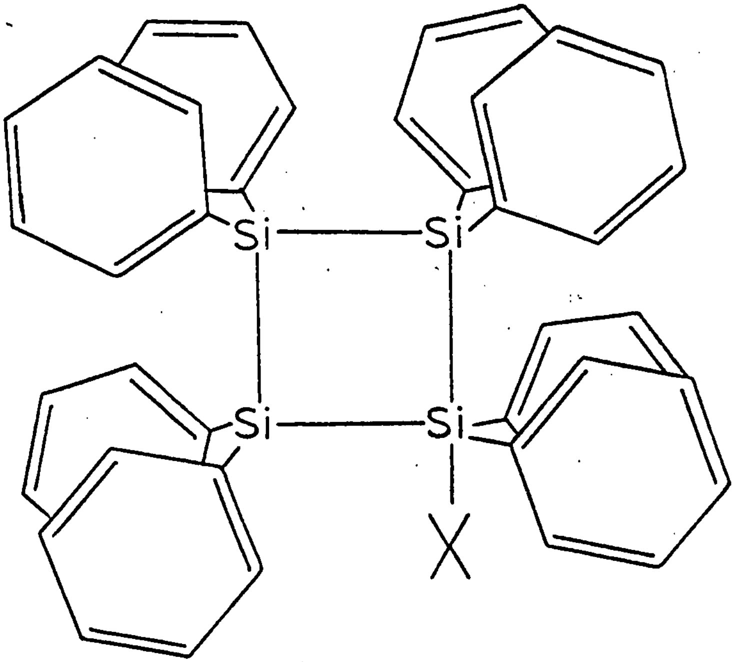
[1] The concept of internal strain or I-strain (118) appears to have been replaced in some cases with that of a change of orbital hybridization to compensate for geometrical requirements brought about by small ring formation (119, 120).

Figure 5. Pentacovalent intermediate involved in the attack of octaphenylcyclotetrasilane by various reactants


Si
Si
Si
Si
X

a pentacovalent state is approached might explain its relative inertness toward iodine and bases.

While this explanation assumes the formation of a discrete pentacovalent state, it might be pointed out that any mechanism which provides a closer approach to such an intermediate would permit a lower energy profile and, therefore, indicate a more facile reaction. This might explain, for example, all other factors being equal, the greater reactivity of decaphenylcyclopentasilane with bromine relative to hexaphenyldisilane.

With only poor success, attempts were made to prepare n-decyl-substituted polysilanes by the reaction of halopolysilanes with n-decyllithium and n-decylmagnesium bromide. The reaction of 1H-4-bromooctaphenyltetrasilane with n-decyllithium in diethyl ether resulted in only 2.3% of 1H-4-n-decyloctaphenyltetrasilane, along with a trace of 1,4-di-n-decyloctaphenyltetrasilane. Other than decaphenylcyclopentasilane, no other discrete compounds were isolable from the oily chromatography fractions. The reaction of n-decylmagnesium bromide with the same bromide resulted in no significant reaction. The only product isolated after hydrolysis was 4H-octaphenyltetrasilanol-1 in 62% yield. Similar negative results were obtained from the reaction of 1,4-dibromooctaphenyltetrasilane with n-butylmagnesium bromide in a mixture of tetrahydrofuran and ether.

Equimolar quantities of 1H-4-chlorooctaphenyltetrasilane and n-decyllithium were allowed to react in a mixture of diethyl ether and benzene to give octaphenylcyclotetrasilane, 1H,4H-octaphenyltetrasilane, n-decyltriphenylsilane and n-decyldiphenylsilane. The last named product was the major isolable product indicating that silicon-silicon bond cleavage is the predominant reaction.

The reaction of 1,4-dichlorooctaphenyltetrasilane with n-decyllithium in diethyl ether and benzene mixed solvent system, resulted in 6.5% of the desired 1,4-di-n-decyloctaphenyltetrasilane.

The various products isolated from these reactions involving n-decyllithium indicate the complexity of the reactions involved. Apparently there have occurred silicon-silicon bond cleavage, halogen-metal interconversion, silicon-phenyl bond cleavage along with the desired coupling reaction. Because of the rather poor results obtained, this area of investigation was terminated and attention was turned to decaphenylcyclopentasilane.

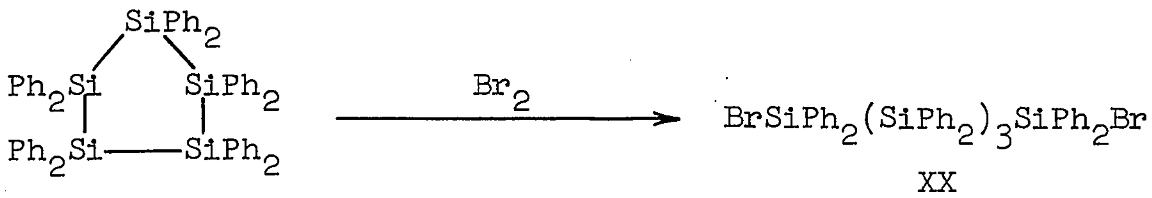
Derivatives of Decaphenylcyclopentasilane

Decaphenylcyclopentasilane has proved to be the most fruitful of the phenylated cyclosilanes for the preparation of various open-chain phenyl substituted polysilanes. The smooth silicon ring cleavages with either bromine or lithium have led to products which are important both in the verification of the structure of decaphenylcyclopentasilane and in providing intermediates which can be converted with a minimum of side reactions into further polysilane derivatives.

The bromine cleavage of decaphenylcyclopentasilane had previously been reported at a time when it was considered to be dodecaphenylcyclohexasilane (26, 28). Since that time the dibromo compound thus obtained has been shown quite conclusively to be a pentasilane (46) and was the first step in the revision of the view that Compound B was dodecaphenylcyclohexasilane.

The bromination reaction has been repeated with yields of 1,5-dibromodecaphenylpentasilane (XX) as high as 94% being obtained. 1,5-Dibromodecaphenylpentasilane was also obtained from the reaction of 1<u>H</u>,5<u>H</u>-decaphenylpentasilane (XLVII) with phosphorus pentabromide. The dibromo compound (XX) could be converted back to 1<u>H</u>,5<u>H</u>-decaphenylpentasilane by the action of lithium aluminum hydride in diethyl ether.

Contrary to the reaction of hydrogen halides with octaphenylcyclotetrasilane, hydrogen bromide and hydrogen chloride have little effect on decaphenylcyclopentasilane



VI

XX

$$\underset{\text{XLVII}}{\mathrm{HSiPh_2(SiPh_2)_3SiPh_2H}} \underset{\mathrm{LiAlH_4}}{\overset{\mathrm{PBr_5}}{\rightleftarrows}} \underset{\text{XX}}{\mathrm{BrSiPh_2(SiPh_2)_3SiPh_2Br}}$$

under similar conditions. Apparently hydrogen bromide reacts with the cyclosilane to some extent, however, no tractable products could be isolated.

An attempted preparation of di-n-decyldecaphenylpentasilane from 1,5-dibromodecaphenylpentasilane and n-decylmagnesium bromide in tetrahydrofuran resulted in decaphenylpentasilane-1,5-diol (XXI) as the only identifiable product after hydrolysis with hydrochloric acid. It was found that the diol could be prepared in 96% yield by the hydrolysis of 1,5-dibromodecaphenylpentasilane with aqueous hydrochloric acid in tetrahydrofuran.

Decaphenylpentasilane-1,5-diol (XXI), when chromatographed on basic alumina, gives rise to 1H,3H-hexaphenyltrisilane (XIX) and diphenylsilanediol (XI) in the form of its siloxane polymers. 1H,3H-Hexaphenyltrisilane was of interest because its conversion to 1,3-dibromohexaphenyl-

$$\underset{\text{XXI}}{HOSiPh_2(SiPh_2)_3SiPh_2OH} \xrightarrow{\text{Alumina}} \underset{\text{XIX}}{HSiPh_2SiPh_2SiPh_2H} + \underset{\text{XI}}{Ph_2Si(OH)_2}$$

trisilane could provide a useful intermediate in the preparation of dodecaphenylcyclohexasilane.

N-Bromosuccinimide (NBS) has been reported to convert triorganosilanes to their corresponding bromides (91, 121). The treatment of 1H,3H-hexaphenyltrisilane with N-bromosuccinimide in carbon tetrachloride, with initiation by ultraviolet light, resulted in a product which melted at 137-138°. A quantitative yield of succinimide was isolated. However, the silicon analysis of this material gave a value which was too high for 1,3-dibromohexaphenyltrisilane. A repeat of the reaction gave identical results.

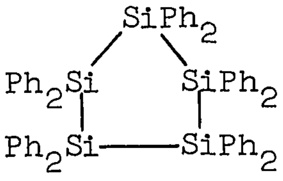
1,3-Dibromohexaphenyltrisilane was prepared by the reaction of 1H,3H-hexaphenyltrisilane with bromine in benzene. The product from this reaction melted at 151-153°. This apparent anomaly can possibly be explained by the observation that the triphenylsilyl radical is extremely reactive and will abstract chlorine from chlorobenzene (122, 123). If the bromination of 1H,3H-hexaphenyltrisilane with N-bromosuccinimide is considered to involve intermediately silyl radicals then by analogy it might be possible for them to abstract chlorine atoms from

$$\underset{\text{XIX}}{HSiPh_2SiPh_2SiPh_2H} \xrightarrow[CCl_4]{NBS} Br(\text{or } Cl)SiPh_2SiPh_2SiPh_2Br(\text{or } Cl)$$

$$\underset{\text{XIX}}{HSiPh_2SiPh_2SiPh_2H} \xrightarrow[\text{Benzene}]{Br_2} \underset{\text{XLVIII}}{BrSiPh_2SiPh_2SiPh_2Br}$$

carbon tetrachloride, giving a product or products having chlorosilane linkages. This would explain the high silicon analyses.

Decaphenylcyclopentasilane, like octaphenylcyclotetrasilane, is easily cleaved by lithium in tetrahydrofuran. However, in this case, the reaction is more straightforward than with octaphenylcyclotetrasilane. 1,5-Dilithiodecaphenylpentasilane (XLIX) is formed in good yields as indicated by double titration techniques and by the formation of derivatives with a variety of reagents.



VI

$$+ \ 2Li \longrightarrow \underset{\text{XLIX}}{LiSiPh_2(SiPh_2)_3SiPh_2Li}$$

Using trimethyl phosphate (74), tri-*n*-butyl phosphate (74), chlorotrimethylsilane and chlorodiphenylsilane, reagents which generally react with silyllithium compounds with a minimum of side reactions, resulted in 1,5-dimethyldecaphenylpentasilane (L), 1,5-di-n-butyldecaphenylpentasilane (LI), 1,1,1,7,7,7-hexamethyldecaphenylheptasilane (LII) and 1H,7H-tetradecaphenylheptasilane (LIII), respectively, in 80-85% yields.

$$\text{XLIX} + (CH_3O)_3PO \longrightarrow \underset{\text{L}}{CH_3SiPh_2(SiPh_2)_3SiPh_2CH_3}$$

$$\text{XLIX} + (\underline{n}\text{-}C_4H_9O)_3PO \longrightarrow \underset{\text{LI}}{\underline{n}\text{-}C_4H_9SiPh_2(SiPh_2)_3SiPh_2C_4H_9\text{-}\underline{n}}$$

$$\text{XLIX} + (CH_3)_3SiCl \longrightarrow \underset{\text{LII}}{(CH_3)_3SiSiPh_2(SiPh_2)_3SiPh_2Si(CH_3)_3}$$

$$\text{XLIX} + HSiPh_2Cl \longrightarrow \underset{\text{LIII}}{HSiPh_2(SiPh_2)_5SiPh_2H}$$

The lithium cleavage of decaphenylcyclopentasilane is complete in about two hours. Shorter reaction times lead to recovered starting material, while longer reaction times allow secondary cleavage reactions to occur. For example, using a four and a half-hour cleavage time, a 63% yield of 1,5-di-n-butyldecaphenylpentasilane (LI) and about 5% each of 1,2-di-n-butyltetraphenyldisilane (LIV) and 1,3-di-n-butylhexaphenyltrisilane (LV) were obtained subsequent to treating the reaction mixture with tri-n-butyl phosphate.

$$\mathrm{LiSiPh_2(SiPh_2)_3SiPh_2Li}$$

XLIX

$$\mathrm{Li}\Big\downarrow$$

$$\mathrm{LiSiPh_2SiPh_2Li + LiSiPh_2SiPh_2SiPh_2Li}$$

$$(\underline{n}\text{-}\mathrm{C_4H_9O})_3\mathrm{PO}\Big\downarrow$$

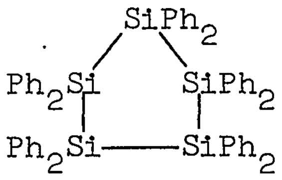
$$\underline{n}\text{-}\mathrm{C_4H_9SiPh_2SiPh_2C_4H_9}\text{-}\underline{n} + \underline{n}\text{-}\mathrm{C_4H_9SiPh_2SiPh_2SiPh_2C_4H_9}\text{-}\underline{n}$$

LIV LV

Evidently, the latter two products arise from lithium cleavage of 1,5-dilithiodecaphenylpentasilane (XLIX), a reaction which appears to be slow compared to lithium cleavage of decaphenylcyclopentasilane. Also, decaphenylcyclopentasilane has been shown to be relatively unreactive toward triphenylsilyllithium (78). This accounts for the high yield of the primary cleavage product, which is not effective in reacting further with decaphenylcyclopentasilane.

That 1,5-dilithiodecaphenylpentasilane is resistant to secondary lithium cleavage reactions, while other 1,5-disubstituted decaphenylpentasilanes are easily cleaved, is indicated in the reaction of decaphenylcyclopentasilane with lithium in the presence of chlorotrimethylsilane.

Chlorotrimethylsilane under these conditions does not react with lithium, but will react with any silyllithium compounds formed. Therefore, as 1,5-dilithiodecaphenylpentasilane (XLIX) is formed it is converted to 1,1,1,7,7,7-hexamethyldecaphenylheptasilane (LII), which is in turn cleaved by more lithium. The silyllithium compounds thus formed also react with chlorotrimethylsilane to give all the other possible products (LVI-LIX) resulting from the cleavage of silicon-silicon bonds of decaphenylcyclopentasilane.



VI

$$\xrightarrow{\text{Li, } (CH_3)_3SiCl}$$

$$(CH_3)_3SiSiPh_2(SiPh_2)_3SiPh_2Si(CH_3)_3 \xrightarrow{\text{Li, } (CH_3)_3SiCl}$$

LII

$$(CH_3)_3SiSiPh_2(SiPh_2)_2SiPh_2Si(CH_3)_3$$

LVI

$$+ \quad (CH_3)_3SiSiPh_2SiPh_2SiPh_2Si(CH_3)_3$$

LVII

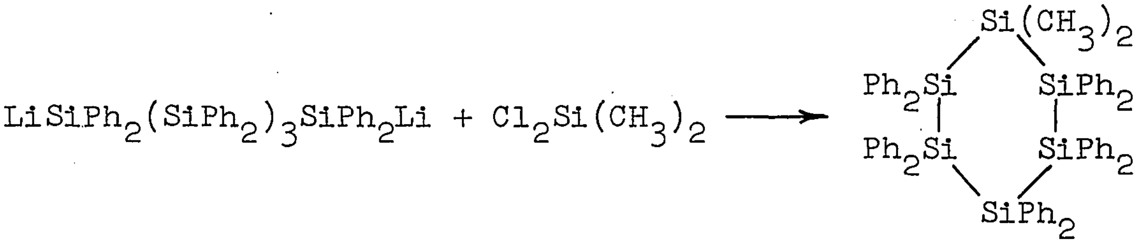
$$+ \quad (CH_3)_3SiSiPh_2SiPh_2Si(CH_3)_3$$

LVIII

$$+ \quad (CH_3)_3SiSiPh_2Si(CH_3)_3$$

LIX

The reaction of 1,5-dilithiodecaphenylpentasilane with dichlorodimethylsilane resulted in a 37% yield of 1,1-dimethyldecaphenylcyclohexasilane (LX). The formation of this compound indicates that highly phenylated cyclosilanes can be formed in moderate yields if steric requirements are not so great in the cyclization step. From this is further indication that the formation of dodecaphenylcyclohexasilane is hindered by stringent steric requirements in the cyclization reaction.



LX

The reactivity of the silicon-silicon bond in decaphenylcyclopentasilane is greatly reduced from that found in octaphenylcyclotetrasilane. An explanation for this lower reactivity can be seen as an extension of the arguments given for the four membered ring. In decaphenylcyclopentasilane the arrangement of groups around the silicon atom undergoing attack is less favorable for the formation of a pentacovalent transition state which would be of higher energy. Thus reactions would be slower or would not occur at all. Also, steric compression of phenyl groups would have a greater hindering effect to the formation of such a state and would, therefore, hinder reaction. Internal ring strain would increase in going to the pentacovalent complex.

Reactions of Compound C

As indicated earlier, physical evidence concerning the structure of Compound C is quite inconclusive although molecular weight values indicate that the compound probably contains no more than seven diphenylsilylene units. Several attempts to prepare dodecaphenylcyclohexasilane and tetradecaphenylcycloheptasilane were also inconclusive as to the identity of Compound C with either structure. Chemical reactions of Compound C also provide an indication that it is dodecaphenylcyclohexasilane, however, they do not prove this proposition beyond reasonable doubt.

Compound C is relatively nonreactive in comparison with octaphenylcyclotetrasilane and decaphenylcyclopentasilane. Thus, it does not react with iodine, sym-tetrachloroethane or refluxing nitrobenzene, nor does it react appreciably with alkali or aqueous piperidine (19).

Lithium reacts slowly with Compound C to give a mixture of disilanyllithium compounds. Treatment of these mixtures with trimethyl phosphate and with tri-*n*-butyl phosphate leads to 1,2- and 1,3-dialkyl compounds as the major products. The slowness of reaction might be attributed to a less reactive silicon-silicon bond; however, the insolubility of the compound in tetrahydrofuran is quite probably a contributing factor. Table 6 contains data concerning the lithium cleavage of Compound C over extended periods of time.

$$\text{Compound C} \xrightarrow[\text{2. } (\underline{n}\text{-}C_4H_9O)_3PO]{\text{1. Li}} \underline{n}\text{-}C_4H_9SiPh_2SiPh_2SiPh_2C_4H_9\text{-}\underline{n}$$

LIV

$$+\ \underline{n}\text{-}C_4H_9SiPh_2SiPh_2C_4H_9\text{-}\underline{n}$$

LV

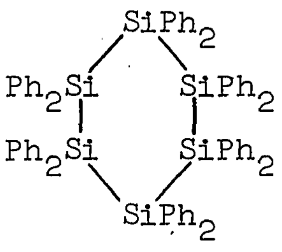
Table 6. Cleavage of Compound C by lithium in tetrahydrofuran

Time (hr)	Temperature	Treated with	Recovered C (%)	Derivatives (%)[a]	
				1,3-	1,2-
5	25°	$(\underline{n}\text{-}C_4H_9O)_3PO$	42.0	41.5	4.5
8	25°	$(\underline{n}\text{-}C_4H_9O)_3PO$	11.4	39.3	13.4
13	65°	$(\underline{n}\text{-}C_4H_9O)_3PO$	5.7	28.7	21.7
14	25°	$(CH_3O)_3PO$	5.0	55.6	14.9[b]

[a] Based on unrecovered C.

[b] A trace of 1,4-dimethyloctaphenyltetrasilane was also isolated.

If Compound C is dodecaphenylcyclohexasilane (X), then the cleavage with lithium may be represented as in the reaction scheme below. The 1,6-dilithiododecaphenylhexasilane (LXI) might be expected to undergo further


X

$$\xrightarrow{\text{Li}} \mathrm{LiSiPh_2(SiPh_2)_4SiPh_2Li}$$

LXI

$$\text{LXI} \xrightarrow{\text{Li}} \mathrm{2LiSiPh_2SiPh_2SiPh_2Li}$$

LXII

$$\text{LXI} \xrightarrow{\text{Li}} \mathrm{LiSiPh_2SiPh_2Li} + \mathrm{LiSiPh_2(SiPh_2)_2SiPh_2Li}$$

LXIII XXIV

cleavage with lithium to give 1,3-dilithiohexaphenyltrisilane (LXII). A less favorable cleavage would give 1,2-dilithiotetraphenyldisilane (LXIII) and 1,4-dilithiooctaphenyltetrasilane (XXIV).

When the lithium cleavage of Compound C was carried out in such a manner that prolonged contact of the silyllithium compounds formed with lithium metal was minimized, there could be isolated small quantities of 1,6-dimethyldodecaphenylhexasilane (LXIX) after the cleavage reaction

$$\text{LXI} + (CH_3O)_3PO \longrightarrow \underset{\text{LXIX}}{CH_3SiPh_2(SiPh_2)_4SiPh_2CH_3}$$

solution was treated with trimethyl phosphate. This is fairly good indication that Compound C is dodecaphenylcyclohexasilane. However, even under these special conditions the apparent yields of 1,6-dilithiododecaphenylhexasilane are low indicating that it undergoes secondary cleavage with great ease.

In addition to the fact that Compound C does not react with iodine, it has been found that C does not add bromine in refluxing benzene. Under the same conditions, chlorine also does not react; however, when refluxing o-dichlorobenzene is used as the solvent, cleavage is complete within 5 minutes. The reaction products consist of a mixture of dichloropolysilanes and viscous polymers from which no materials of greater chain length than tetrasilanes could be isolated. Similar results were obtained from the extended reaction of phosphorus pentachloride with Compound C in refluxing sym-tetrachloroethane. Compound C was also found to be unreactive with mercuric chloride in refluxing benzene or tetrahydrofuran.

In contrast to octaphenylcyclotetrasilane and decaphenylcyclopentasilane, Compound C is resistant to methyllithium cleavage. Benzyllithium, which is known to cause rapid cleavage of hexaphenyldisilane (108), reacts only very slowly with C. The only product, other than recovered Compound C, isolated from this reaction was diphenylsilanediol.

Tabulation of Organopolysilanes

Many organic substituted compounds containing the silicon-silicon bond are known. The majority of these compounds are disilanes; however, highly phenylated organopolysilanes with definite chain lengths of at least nine silicon atoms are capable of existence. It would appear that chain length is not a limiting factor in the stability of these compounds. All of the compounds isolated do not undergo spontaneous decomposition and the majority of them are stable at their melting points. The reason for the paucity of organic substituted polysilanes appears then to be a lack of synthetic methods, rather than a lack of stability of such compounds.

In order to provide a convenient catalog of the compounds referred to in this dissertation, Table 7 lists these compounds, their melting point or boiling point, with reference to research workers who isolated and characterized them.

Table 7. Organopolysilanes

Formula	Name	M.P. (b.p.)	Reference
A. Disilanes			
$C_{20}H_{21}ClSi_2$	1-Chloro-2,2-dimethyltriphenyldisilane	(157/0.005mm)	(81b)
$C_{20}H_{22}Si_2$	1*H*-2,2-Dimethyltriphenyldisilane	(126-7/0.002mm)	(81b)
$C_{24}H_{20}Br_2Si_2$	1,2-Dibromotetraphenyldisilane	154.5-155.5	(34)
$C_{24}H_{20}Cl_2Si_2$	1,2-Dichlorotetraphenyldisilane	114.5-115	(34)
$C_{24}H_{21}ClSi_2$	1*H*-2-Chlorotetraphenyldisilane	45-50	(62)
$C_{24}H_{22}Si_2$	1*H*,2*H*-Tetraphenyldisilane	79-80	(34,76)
$C_{24}H_{22}O_2Si_2$	Tetraphenyldisilane-1,2-diol	139-140	(34)
$C_{25}H_{24}Si_2$	1*H*-2-Methyltetraphenyldisilane	71-73	(28)
$C_{26}H_{26}Si_2$	1,2-Dimethyltetraphenyldisilane	141-143	(124)
$C_{30}H_{25}ClSi_2$	1-Chloropentaphenyldisilane	154-155	(51)
$C_{30}H_{26}OSi_2$	Pentaphenyldisilan-1-ol	134-134.5	(66)
$C_{30}H_{26}Si_2$	1*H*-Pentaphenyldisilane	128-129	(66)
$C_{32}H_{38}Si_2$	1,2-Di-*n*-butyltetraphenyldisilane	101-102	(This work)
$C_{36}H_{30}Si_2$	Hexaphenyldisilane	368-370	(54)

Table 7. (Continued)

Formula	Name	M.P. (b.p.)	Reference
B. Trisilanes			
$C_{18}H_{28}Si_3$	1,1,1,3,3,3-Hexamethyldiphenyltrisilane	(105.5-106/0.2mm)	(This work)
$C_{36}H_{30}Cl_2Si_3$	1,3-Dichlorohexaphenyltrisilane	128.5-131	-[a]
$C_{36}H_{32}O_2Si_3$	Hexaphenyltrisilane-1,3-diol	146.5-148	(This work)
$C_{36}H_{32}Si_3$	1<u>H</u>,3<u>H</u>-Hexaphenyltrisilane	97-98	(43,46)
$C_{38}H_{36}Si_3$	1,3-Dimethylhexaphenyltrisilane	92-93	(This work)
$C_{38}H_{36}Si_3$	2,2-Dimethylhexaphenyltrisilane	223-227	(24)
$C_{44}H_{48}Si_3$	1,3-Di-<u>n</u>-butylhexaphenyltrisilane	147.5-149	(This work)
$C_{48}H_{40}Si_3$	Octaphenyltrisilane	260-262	(51)
C. Tetrasilanes			
$C_{30}H_{38}Si_4$	1,1,1,4,4,4-Hexamethyltetraphenyltetrasilane	261.5-263	(This work)

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[a] S. Cooper, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the conversion of silicon hydrides to chlorosilanes with phosphorus pentachloride. Private communication. 1962.

Table 7. (Continued)

Formula	Name	M.P. (b.p.)	Reference
$C_{48}H_{40}Br_2Si_4$	1,4-Dibromooctaphenyltetrasilane	220-221	(This work)
$C_{48}H_{40}Cl_2Si_4$	1,4-Dichloroctaphenyltetrasilane	185-186	(18,27)
$C_{48}H_{40}I_2Si_4$	1,4-Diiodooctaphenyltetrasilane	274-276	(18,27)
$C_{48}H_{40}Si_4$	Octaphenylcyclotetrasilane	313-316 dec.	(18,25,27)
$C_{48}H_{40}OSi_4$	Octaphenyloxacyclopentasilane	226-228	(18,37)
		234-236	(37)
$C_{48}H_{40}O_2Si_4$	Octaphenyl-1,3-dioxacyclohexasilane[b]	245-246	(18,37)
$C_{48}H_{40}O_2Si_4$	Octaphenyl-1,4-dioxacyclohexasilane	219-220	(37)
$C_{48}H_{41}BrSi_4$	1*H*-4-Bromooctaphenyltetrasilane	166-167	(This work)
$C_{48}H_{41}ClSi_4$	1*H*-4-Chlorooctaphenyltetrasilane	162-163	-[c]
$C_{48}H_{42}OSi_4$	4*H*-Octaphenyltetrasilan-1-ol	181-183	(This work)

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[b] Tentative structure.

[c] D. R. Chapman, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the cleavage of octaphenylcyclotetrasilane with hydrogen chloride. Private communication. 1962.

Table 7. (Continued)

Formula	Name	M.P. (b.p.)	Reference
$C_{48}H_{42}O_2Si_4$	Octaphenyltetrasilane-1,4-diol	212-214	(46)
$C_{48}H_{42}Si_4$	1*H*,4*H*-Octaphenyltetrasilane	160-162	(43)
$C_{49}H_{43}ClSi_4$	1-Chloro-4-methyloctaphenyltetrasilane	200-201	(Footnote, p. 34)
$C_{49}H_{44}Si_4$	1*H*-4-Methyloctaphenyltetrasilane	218-220	(Footnote, p. 34)
$C_{50}H_{46}Si_4$	1,4-Dimethyloctaphenyltetrasilane	220-222	(27)
$C_{52}H_{46}O_4Si_4$	1,4-Diacetoxyoctaphenyltetrasilane	233-235	(125)
$C_{56}H_{56}Si_4$	Octa-*p*-tolylcyclotetrasilane	290-293 dec.	(20)
$C_{56}H_{55}I_2Si_4$	1,4-Diiodoocta-*p*-tolyltetrasilane	300 dec.	(20)
$C_{56}H_{56}OSi_4$	Octa-*p*-tolyloxacyclopentasilane	228-229	(20)
$C_{56}H_{58}Si_4$	1,4-Di-*n*-butyloctaphenyltetrasilane	217-218	(This work)
$C_{60}H_{50}Si_4$	Decaphenyltetrasilane	358-360	(27)
$C_{68}H_{82}Si_4$	1,4-Di-*n*-decyloctaphenyltetrasilane	70-71	(This work)
D. Pentasilanes			
$C_{42}H_{48}Si_5$	1,1,1,5,5,5-Hexamethylhexaphenylpentasilane	315-320	(This work)

Table 7. (Continued)

Formula	Name	M.P. (b.p.)	Reference
$C_{60}H_{50}Br_2Si_5$	1,5-Dibromodecaphenylpentasilane	205-207	(28, This work)
$C_{60}H_{50}Cl_2Si_5$	1,5-Dichlorodecaphenylpentasilane	179-180	(46)
$C_{60}H_{50}Si_5$	Decaphenylcyclopentasilane	440-444	(18,28)
		466-470	(This work)
$C_{60}H_{52}O_2Si_5$	Decaphenylpentasilane-1,5-diol	169-170	(28,46)
$C_{60}H_{52}Si_5$	1*H*,5*H*-Decaphenylpentasilane	147-148	(77)
$C_{62}H_{56}Si_5$	1,5-Dimethyldecaphenylpentasilane	181-182	(28)
		189-190	(This work)
$C_{68}H_{68}Si_5$	1,5-Di-*n*-butyldecaphenylpentasilane	162-164	(This work)
$C_{70}H_{70}Si_5$	Deca-*p*-tolylcyclopentasilane	310	(20)
E. Hexasilanes			
$C_{12}H_{36}Si_6$	Dodecamethylcyclohexasilane	250-252	(21-24)
$C_{54}H_{58}Si_6$	1,1,1,6,6,6-Hexamethyloctaphenylhexasilane	295-297	(43)
$C_{62}H_{56}Si_6$	1,1-Dimethyldecaphenylcyclohexasilane	472-476	(This work)

Table 7. (Continued)

Formula	Name	M.P. (b.p.)	Reference
$C_{72}H_{60}Cl_2Si_6$	1,6-Dichlorododecaphenylhexasilane	234-237	(Footnote, p. 30)
$C_{72}H_{60}Si_6$	Dodecaphenylcyclohexasilane[b] (Compound C)	502-504 dec.	(19, This work)
$C_{72}H_{62}Si_6$	1_H_,6_H_-Dodecaphenylhexasilane	185-187	(Footnote, p. 30)
$C_{74}H_{66}Si_6$	1,6-Dimethyldodecaphenylhexasilane	205-207	(Footnote, p. 30)
F. Heptasilanes			
$C_{66}H_{68}Si_7$	1,1,1,7,7,7-Hexamethyldecaphenylheptasilane	197-199	(This work)
$C_{84}H_{72}Si_7$	1_H_,7_H_-Tetradecaphenylheptasilane	203-204	(This work)
G. Nonasilanes			
$C_{100}H_{92}Si_9$	1,1,9,9-Tetramethylhexadecaphenylnonasilane	230-232	(81b)

Suggestions for Further Research

Incidental to this work the relative stabilities of several n-alkyllithium compounds in mixed solvent systems have been studied. A more complete study in this area with respect to reaction rates and product formation with common alkyl and cyclic ethers would be of great value for determining the mode of decomposition and the value of such systems for preparative organic chemistry. New methods of analysis and product isolation could possibly give insights into the character of organolithium compounds in ether solutions and why, for example, tetrahydrofuran so greatly affects the reactivity of organolithium compounds.

The relative reactivities of the cyclosilanes as a function of ring size present an interesting test of the implications of higher coordination states as intermediates, in reactions involving attack on silicon. For example, ring cleavage reactions, such as halogenation, of a homologous series of these compounds should be studied with regard to reaction rates. Such a study should probably be carried out on a series other than the perphenylated cyclosilanes where vast differences in solubility would present experimental problems.

The formation of the cyclo- and polysilanes from lithium and dihalodiorganosilanes should be extended further to systems which might provide carbon functional groups more easily than do phenyl and methyl groups. Vinyl or allyl substituted polysilanes, as well as substituted-phenyl and benzyl compounds, would be of interest. Such substituents might well provide compounds interesting in their own right and having functional groups which could lead to cross-linked polymers involving polysilanes.

High molecular weight polysilane resins have been obtained from mixed coupling reactions of dichlorosilanes with sodium in aromatic hydrocarbons (126). Utilizing the improved conditions for the reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran, condensations of this type could be carried out to advantage.

Utilization of α,ω-dilithiopolysilanes for a variety of synthesis problems such as building higher polysilanes and cyclosilanes should be extended with emphasis on obtaining silicon functional compounds.

A complete investigation of the reaction of N-bromosuccinimide with silicon hydrides should be undertaken to determine the scope and limitations of this reaction. The implication of the intermediacy of silyl radicals, indicated in this work, should be substantiated.

SUMMARY

The route to phenylated polysilanes through the phenylated cyclosilanes has been investigated. The relative ease of formation of the phenylated cyclosilanes has been attributed to stringent steric requirements in rings larger than five silicon atoms. Therefore, decaphenylcyclopentasilane is the most accessible cyclosilane from the reaction of dichlorodiphenylsilane with lithium metal in tetrahydrofuran. Octaphenylcyclotetrasilane, a precursor of decaphenylcyclopentasilane, is also isolable in good yields from the same reaction when precautions are taken to minimize the concentration of silyllithium compounds during the course of the reaction, and to have the lithium metal completely consumed at the termination of the reaction. A slight excess of lithium metal is able to convert octaphenylcyclotetrasilane to decaphenylcyclopentasilane completely. The formation in low yield of Compound C, which is considered to be dodecaphenylcyclohexasilane, is attributed to rather severe steric requirements in going from an open-chain precursor to the cyclic product. However, Compound C, once it is formed, is apparently the most stable of this series of cyclosilanes to chemical attack.

Octaphenylcyclotetrasilane has been found to react

with hydrogen iodide and hydrogen bromide in refluxing benzene to give 1*H*-4-iodooctaphenyltetrasilane and 1*H*-4-bromooctaphenyltetrasilane, respectively. Hydrogen chloride reacts only slowly under similar conditions. The order of reactivity of the hydrogen halides with octaphenylcyclotetrasilane was observed to be HI>HBr>HCl. Decaphenylcyclopentasilane reacts only slowly, if at all, with hydrogen bromide and hydrogen chloride.

The high order of reactivity of octaphenylcyclotetrasilane has been attributed to ring strain and to the special geometry of the compound which minimizes steric interactions of phenyl groups on adjacent silicon atoms, with both factors promoting the formation of a pentacovalent intermediate. Formation of a similar intermediate for decaphenylcyclopentasilane is less favorable, while for dodecaphenylcyclohexasilane such an intermediate has little importance in reactions of the compound.

The structure of Compound B (decaphenylcyclopentasilane) has been shown conclusively to correspond to a five-membered ring. Molecular weight determinations by means of vapor pressure osmometry, X-ray analysis and ebullioscopic measurements are consistent with the proposed structure. Chemical proof for the structure was gained principally through examination of the derivatives formed from the lithium cleavage products. In all cases the major product was derived from 1,5-dilithiodecaphenylpentasilane, which is formed in yields of over 80%. Utilization of 1,5-dilithiodecaphenylpentasilane, which is apparently stable to cleavage by lithium metal, for the formation of a variety of open- and closed-chain polysilanes was investigated, and this compound was found generally to be a useful intermediate for the preparation of higher polysilanes.

Bromination of decaphenylcyclopentasilane provided high yields of 1,5-dibromodecaphenylpentasilane, which was converted into some of the products obtained from 1,5-dilithiodecaphenylpentasilane, showing the consistency of all products obtained from decaphenylcyclopentasilane. Hydrolysis of 1,5-dibromodecaphenylpentasilane gives decaphenylpentasilane-1,5-diol, which when chromatographed basic alumina gives high yields of 1<u>H</u>,3<u>H</u>-hexaphenyltrisilane, providing a convenient pathway to silicon functional phenylated trisilanes. Treatment of 1<u>H</u>,3<u>H</u>-hexaphenyltrisilane with N-bromosuccinimide in carbon tetrachloride gives a product which apparently contains chlorine. If silyl radicals are involved in this reaction it is reasonable that abstraction of chlorine atoms from the solvent has occurred. 1,3-Dibromohexaphenyltrisilane was prepared by the reaction of bromine with 1<u>H</u>,3<u>H</u>-hexaphenyltrisilane in benzene.

Although evidence for the structure of Compound C is not entirely conclusive, indications are that it is dodecaphenylcyclohexasilane. Molecular weight determinations by boiling point elevation of toluene point to either a six- or seven-membered ring. Chemically Compound C is quite inert to reagents which readily cleave octaphenylcyclotetrasilane and decaphenylcyclopentasilane. Thus, it does not react appreciably with mercuric chloride, bromine or alkyllithium compounds. Chlorine or phosphorus pentachloride under forcing conditions react with Compound C with excessive fragmentation of the silicon chain.

Lithium cleavage of Compound C over extended periods of time results in mainly 1,3-dilithiohexaphenyltrisilane, along with lesser amounts of 1,2-dilithiotetraphenyldisilane, both compounds being characterized as their dimethyl or di-n-butyl derivatives. When short contact times of lithium metal with the silyllithium compounds being formed were employed, small yields of 1,6-dimethyldodecaphenylhexasilane could be isolated after treatment of the reaction solution with trimethyl phosphate. This indicates that the major product, 1,3-dilithiohexaphenyltrisilane, is derived from 1,6-dilithiododecaphenylhexasilane, the primary cleavage product of Compound C. In contrast to 1,5-dilithiodecaphenylpentasilane, 1,6-dilithiododecaphenylhexasilane is very easily cleaved symmetrically by lithium metal.

The order of reactivity of these three cyclosilanes with a given reagent, as would be predicted by the ease of formation of a pentacovalent intermediate in each case, is octaphenylcyclotetrasilane>decaphenylcyclopentasilane> dodecaphenylcyclohexasilane.

LITERATURE CITED

1. Chem. Eng. News, 30, 4499 (1952).
2. A. Stock. Hydrides of boron and silicon. Ithaca, New York, Cornell University Press. 1933.
3. K. Borer and C. S. G. Phillips, Proc. Chem. Soc. (London), 1959, 189.
4. R. Schwarz and H. Meckbach, Z. Anorg. Allgem. Chem., 232, 241 (1937).
5. R. Schwarz and R. Thiel, Z. Anorg. Allgem. Chem., 235, 247 (1938).
6. F. G. A. Stone. Hydrogen compounds of the Group IV elements. Englewood Cliffs, New Jersey, Prentice-Hall, Inc. 1962.
7. G. Schott, Z. Chem., 2, 194 (1962).
8. C. Eaborn. Organosilicon compounds. London, England, Butterworths Publications, Ltd. 1960.
9. C. A. Coulson. Valence. 2nd ed. London, England, Oxford University Press. 1961.
10. F. Pass and H. Schindlbauer, Monatsh., 90, 148 (1958).
11. J. H. Burns and J. Waser, J. Am. Chem. Soc., 79, 859 (1957).
12. G. E. Coates. Organometallic compounds. 2nd ed. New York, New York, John Wiley & Sons, Inc. 1960.
13. W. P. Neumann, Angew. Chem., 74, 122 (1962).
14. W. P. Neumann and K. König, Angew. Chem., 74, 215 (1962).
15. W. P. Neumann, Angew. Chem., 75, 679 (1963).
16. R. Schwarz and F. Heinrich, Z. Anorg. Allgem. Chem., 221, 276 (1935).

17. A. Stock and C. Somieski, *Ber. Deut. Chem. Ges.*, *56B*, 132 (1923).

18. F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, *119*, 830 (1921).

19. F. S. Kipping, *J. Chem. Soc.*, *125*, 2291 (1924).

20. A. R. Steele and F. S. Kipping, *J. Chem. Soc.*, *1929*, 2545.

21. C. A. Burkhard, *J. Am. Chem. Soc.*, *71*, 963 (1949).

22. E. Hengge and H. Reuter, *Naturwissenschaften*, *49*, 514 (1962).

23. U. G. zu Stolberg, *Angew. Chem.*, *75*, 206 (1963).

24. H. Gilman and R. A. Tomasi, *J. Org. Chem.*, *28*, 1651 (1963).

25. H. Gilman, D. J. Peterson, A. W. P. Jarvie and H. J. S. Winkler, *J. Am. Chem. Soc.*, *82*, 2076 (1960).

26. H. Gilman, D. J. Peterson, A. W. Jarvie and H. J. S. Winkler, *Tetrahedron Letters*, *23*, 5 (1960).

27. A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc.*, *83*, 1921 (1961).

28. H. J. S. Winkler, A. W. P. Jarvie, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc.*, *83*, 4089 (1961).

29. H. Gilman and G. L. Schwebke, *J. Am. Chem. Soc.*, *85*, 1016 (1962).

30. F. S. Kipping, *Proc. Chem. Soc. (London)*, *27*, 143 (1911).

31. F. S. Kipping, *J. Chem. Soc.*, *1927*, 2719.

32. F. S. Kipping, *J. Chem. Soc.*, *1927*, 2728.

33. F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, *119*, 848 (1921).

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

35. F. S. Kipping, J. Chem. Soc., 123, 2598 (1923).

36. F. S. Kipping, J. Chem. Soc., 123, 2590 (1923).

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

38. W. Schlenk and H. Mark, Ber. Deut. Chem. Ges., 55B, 2285 (1922).

39. F. S. Kipping, Proc. Roy. Soc. (London), 159A, 139 (1937).

40. C. A. Kraus and C. L. Brown, J. Am. Chem. Soc., 52, 4031 (1930).

41. H. Gilman, D. J. Peterson and D. Wittenberg, Chem. Ind. (London), 1958, 1479.

42. M. V. George, D. J. Peterson and H. Gilman, J. Am. Chem. Soc., 82, 403 (1960).

43. D. J. Peterson. Trapping of organometallic and organometalloidal radicals. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1962.

44. G. A. Razuvayev, N. S. Vyanzankin and Y. I. Dergunov, Zh. Obshch. Khim., 30, 1310 (1960). Original available but not translated; abstracted in Chem. Abstr., 48, 12672 (1954).

45. F. S. Kipping, J. Chem. Soc., 101, 2113 (1912).

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

47. A. W. P. Jarvie and H. Gilman, Chem. Ind. (London), 1960, 1271.

48. 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.

49. H. Gilman and T. C. Wu, J. Am. Chem. Soc., 73, 4031 (1951).

50. D. Wittenberg and H. Gilman, *Quart. Revs.*, *13*, 116 (1959).

51. H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, *J. Am. Chem. Soc.*, *74*, 561 (1952).

52. H. Gilman and T. C. Wu, *J. Org. Chem.*, *18*, 753 (1953).

53. H. Gilman, R. K. Ingham and A. G. Smith, *J. Org. Chem.*, *18*, 1743 (1953).

54. H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, *75*, 3762 (1953).

55. H. Gilman, G. D. Lichtenwalter and D. Wittenberg, *J. Am. Chem. Soc.*, *81*, 5320 (1959).

56. A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, *76*, 278 (1954).

57. H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, *80*, 608 (1958).

58. H. Gilman and W. Steudel, *Chem. Ind.* (*London*), *1959*, 1094.

59. H. Gilman, R. A. Klein and H. J. S. Winkler, *J. Org. Chem.*, *26*, 2474 (1961).

60. H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, *24*, 1588 (1959).

61. B. J. Gaj and H. Gilman, *Chem. Ind.* (*London*), *1960*, 493.

62. R. A. Tomasi. Cleavage of organosilicon compounds. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1962.

63. G. Martin, *J. Chem. Soc.*, *107*, 1043 (1915).

64. G. Schott and C. Harzdorf, *Z. Anorg. Allgem. Chem.*, *306*, 180 (1960).

65. G. Schott and C. Harzdorf, *Z. Anorg. Allgem. Chem.*, *307*, 105 (1961).

66. H. Gilman and J. J. Goodman, *J. Am. Chem. Soc.*, *75*, 1250 (1953).

67. A. Taketa, M. Kumada and K. Tarama, *Nippon Kagaku Zasshi*, *78*, 999 (1957). Original available but not translated; abstracted in *Chem. Abstr.*, *52*, 8942 (1958).

68. F. S. Kipping, *J. Chem. Soc.*, *119*, 647 (1921).

69. H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, *73*, 5077 (1958).

70. T. C. Wu and H. Gilman, *J. Org. Chem.*, *23*, 913 (1958).

71. M. Kumada, J. Nakajima, M. Ishikawa and Y. Yamamoto, *J. Org. Chem.*, *23*, 292 (1958).

72. W. Schlenk, J. Renning and G. Racky, *Ber. Deut. Chem. Ges.*, *44*, 1178 (1911).

73. A. J. Petro and C. P. Smyth, *J. Am. Chem. Soc.*, *79*, 6147 (1957).

74. H. Gilman and B. J. Gaj, *J. Org. Chem.*, *26*, 247 (1961).

75. E. Hengge, H. Reuter and R. Petzold, *Angew. Chem.*, *75*, 677 (1963).

76. W. Steudel and H. Gilman, *J. Am. Chem. Soc.*, *82*, 6129 (1960).

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

78. A. W. P. Jarvie and H. Gilman, *J. Org. Chem.*, *26*, 1999 (1961).

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

80. H. Gilman and R. A. Tomasi, *J. Org. Chem.*, *27*, 3647 (1962).

81a. F. S. Kipping and A. G. Murray, *J. Chem. Soc.*, *1929*, 360.

81b. H. Gilman and R. A. Tomasi, *Chem. Ind. (London)*, *1963*, 945.

82. H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, *66*, 1515 (1944).

83. H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, *J. Am. Chem. Soc.*, *72*, 5767 (1950).

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

85. H. Gilman, J. A. Beel, C. G. Brannen, M. H. Bullock, G. E. Dunn and L. S. Miller, *J. Am. Chem. Soc.*, *71*, 1499 (1949).

86. H. Gilman, D. H. Miles, L. O. Moore and C. W. Gerow, *J. Org. Chem.*, *24*, 219 (1959).

87. H. Gilman, H. A. Pacevitz and O. Baine, *J. Am. Chem. Soc.*, *62*, 1514 (1940).

88. H. Gilman, R. D. Gorsich and B. J. Gaj, *U. S. Atomic Energy Commission Report*, *WADC 53-426*, Part V, 1 [Wright-Patterson AFB, Ohio] (1957).

89. H. Gilman and R. D. Gorsich, *J. Org. Chem.*, *22*, 687 (1957).

90. H. Gilman and S. Gray, *J. Org. Chem.*, *23*, 1476 (1958).

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

92. H. Gilman and B. J. Gaj, *J. Org. Chem.*, *22*, 447 (1957).

93. H. Gilman and B. J. Gaj, *J. Org. Chem.*, *22*, 1165 (1957).

94. R. L. Burwell, Jr., *Chem. Revs.*, *54*, 615 (1954).

95. H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, *77*, 3134 (1955).

96. E. Späth, *Monatsh.*, *34*, 1965 (1913).

97. R. C. Fuson, *J. Am. Chem. Soc.*, *48*, 2681 (1926).

98. K. Ziegler and H. Colonius, *Ann.*, *479*, 135 (1930).

99. G. Wittig and H. Witt, *Ber. Deut. Chem. Ges.*, *74B*, 1474 (1941).

100. Fr. Hein, E. Petzchner, K. Wagler and Fr. A. Segitz, Z. Anorg. Allgem. Chem., 141, 161 (1924).

101. K. Ziegler and F. Dersch, Ber. Deut. Chem. Ges., 64, 448 (1931).

102. T. V. Talalaeva and K. A. Kocheshkov, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (English translation), 1953, 263.

103. H. Gilman and B. J. Gaj, J. Org. Chem., 28, 1725 (1963).

104. H. Gilman, H. A. McNinch and D. Wittenberg, J. Org. Chem., 23, 2044 (1958).

105. H. Gilman and H. A. McNinch, J. Org. Chem., 26, 3723 (1961).

106. K. Ziegler and O. Schäfer, Ann., 479, 150 (1930).

107. H. Gilman and H. A. McNinch, J. Org. Chem., 27, 1889 (1962).

108. H. Gilman and G. L. Schwebke, J. Org. Chem., 27, 4259 (1962).

109. C. A. Glover and R. R. Stanley, Anal. Chem., 33, 447 (1961).

110. D. Wittenberg and H. Gilman, J. Am. Chem. Soc., 80, 2677 (1958).

111. D. Wittenberg, D. Aoki and H. Gilman, J. Am. Chem. Soc., 80, 5933 (1958).

112. L. A. Hurrah, M. T. Ryan and C. Tamborski, Spectrochim. Acta, 18, 21 (1962).

113. W. C. Steele and F. G. A. Stone, J. Am. Chem. Soc., 84, 3599 (1962).

114. R. West, J. Am. Chem. Soc., 77, 2339 (1955).

115. L. H. Sommer and G. A. Baum, J. Am. Chem. Soc., 76, 5002 (1954).

116. W. H. Knoth, Jr., and R. V. Lindsey, Jr., J. Org. Chem., 23, 1394 (1958).

117. L. H. Sommer, O. F. Bennet, P. G. Campbell and D. R. Weyenberg, J. Am. Chem. Soc., 79, 3295 (1957).

118. H. C. Brown, R. S. Fletcher and R. B. Johannesen, J. Am. Chem. Soc., 73, 212 (1951).

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

120. D. E. McLaughlin, M. Tamres and S. Searles, Jr., J. Am. Chem. Soc., 82, 5621 (1960).

121. H. Hartmann and C. Sarafidis, Naturwissenschaften, 21, 494 (1962).

122. J. Curtice, H. Gilman and G. S. Hammond, J. Am. Chem. Soc., 79, 4754 (1957).

123. L. E. Nelson, N. C. Angelotti and D. R. Weyenberg, J. Am. Chem. Soc., 85, 2662 (1963).

124. A. G. Smith. Some cleavage reactions of alkyl and aryl silanes. Unpublished M.S. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1953.

125. H. Gilman and W. H. Atwell, J. Org. Chem., 28, 2905 (1963).

126. H. A. Clark. U. S. Patent 2,563,005. Aug. 7, 1951. Abstracted in Chem. Abstr., 45, 10668 (1951).

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