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MONOMERIC ORGANOSILICON COMPOUNDS WITH POLYFUNCTIONAL GROUPS

by

Dwain R Chapman

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Approved:

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Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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INTRODUCTION

Previous interest in organosilicon chemistry has been largely dominated by certain polymeric compounds containing alternate silicon atoms such as the so-called silicones. Studies of the chemistry of silicon have dealt with relatively few compounds containing more than two silicon atoms bonded to each other. However, in recent years technical skills have enabled investigators to prepare and characterize an increasing number of polysilanes of chain lengths seemingly limited only to the present skill and modes available.

At the time this investigation was begun several organic substituted cyclosilanes had been characterized and were readily available. Some investigations had been made in the use of these compounds as precursors to formerly unavailable organosilicon compounds. Only a few heterocyclic compounds containing silicon-silicon bonds had been prepared and little or no study had been made of the reactions of these compounds.

It had been observed that the presence of a silicon atom in a cyclic compound gave a reactivity to that compound unlike analogous linear compounds. It had also been demonstrated that the reactivity with certain reagents was dependent on ring size.

The present investigation was begun to make use of some readily available cyclosilanes and heterocyclic polysilane compounds in a further investigation of their reactivity and, if possible, to initiate studies of linear polysilanes containing various functional groups by heretofore unused or unknown routes. Such new compounds afford the opportunity of expanding the present knowledge of the physical properties as well as contributing to the spectrographic studies of organopolysilane compounds. Attention was directed toward the ultraviolet and infrared properties of compounds containing the silicon-silicon bond.

NOMENCLATURE[1]

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. However, Rule 70.15 of the so-called Amsterdam report, which enables us to give the compound $Cl-SiPh_2SiPh_2-O-SiPh_2SiPh_2-Cl$ the name 1,5-dichloro-1,1,2,2,4,4,5,5-octaphenyl-3-oxapentasilane, also carries the footnote "This rule is subject to the possible extensions of the oxa-aza convention which are now being considered by the commission".

The I.U.P.A.C. Commissions on Nomenclature of Organic Chemistry and of Inorganic Chemistry held joint sessions in 1962 and 1963 and it was tentatively decided that the names of all structures should be based on the name of the corresponding hydrocarbon even when there is little or no carbon present. Following this change, the name for the above compound would be 1,5-dichloro-1,1,2,2,4,4,5,5-octaphenyl-3-oxa-1,2,4,5-tetrasilapentane.

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[1] The author is grateful to Dr. L. T. Capell of The Ohio State University and former Nomenclature Director and Executive Consultant of The Chemical Abstracts Service of The American Chemical Society for his assistance with the nomenclature.

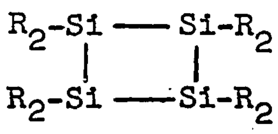
Rule 70.7 of the Amsterdam report states "Open-chain compounds which have the requirements for more than one of the structures as defined (i.e., siloxane, silthiane, silazane or silane) will be named, if possible, in terms of the silane, silazane, silthiane or siloxane containing the largest number of silicon atoms". Application of this rule would name the above compound 1,3-bis (chlorodiphenylsilyl)-1,1,3,3-tetraphenyldisiloxane.

Following the above suggestions, compounds named in this thesis will predominantly follow rule 70.7 with the exception of certain polysilanes containing hetero atoms in the chain which seem more suitably adapted to the oxa-aza convention. Exceptions will be noted in discussing certain α,ω-disubstituted polysilanes in which a seemingly unambiguous nomenclature given in recent reviews (2, 3) will be used (e.g., the compound $H-(SiMe_2)_3-Cl$ will be named 1H,3-chlorohexamethyltrisilane). Most of the compounds discussed are straight-chain polysilanes containing phenyl or methyl groups on each silicon atom with varying groups only on the terminal silicon. To avoid unwieldy sequences of numbers, these organic substituents will not be numbered in every instance a compound is discussed when the shorter name appears unambiguous. The abbreviation Ph for the phenyl (C_6H_5) group, Me for the methyl (CH_3) group and ether for diethyl ether will be used throughout this thesis.

HISTORICAL

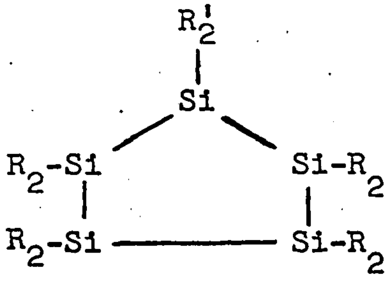
Cyclosilanes

Several organic substituted cyclosilanes have been prepared. The known compounds are tetra-, penta- or hexacyclic and are represented by structures I-III.



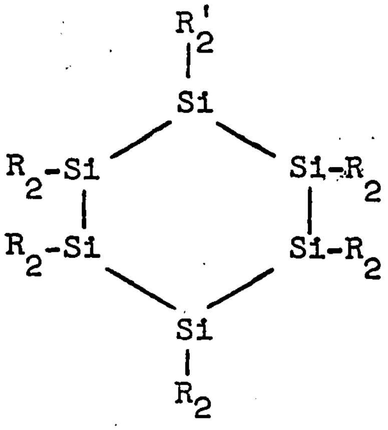
I

a R = Ph
b R = p-MePh



II

a R = R' = Ph
b R = Ph, R' = Me
c R = R' = p-MePh



III

a R = R' = Me
b R = Ph, R' = Me
c R = R' = Ph

The first preparation of a cyclosilane was carried out by Kipping from the reaction of dichlorodiphenylsilane and sodium (4). Three crystalline compounds were obtained which have only recently been fully characterized and identified as octaphenylcyclotetrasilane (Ia) (5), decaphenylcyclopentasilane (IIa) (6) and dodecaphenylcyclohexasilane (IIIc) (7). Later preparations by Kipping (8) have been tentatively assigned structures Ib and IIc by analogy with the phenylated series (2). Compounds IIb and IIIb have been prepared by the reaction of dichlorodimethylsilane with 1,4-dilithiooctaphenyltetrasilane (3) and 1,5-dilithiodecaphenylpentasilane, respectively (9).

The first permethylated cyclosilane, dodecamethylcyclohexasilane (IIIa), was made from the reaction of dichlorodimethylsilane and sodium (10a) or lithium (10b). More recent investigations of Ia (9), IIa (9), and IIIa (11) have provided means of preparing these compounds in yields of 60-70% using lithium in tetrahydrofuran with the appropriate dimethyl- or diphenyldichlorosilane.

Reactions of Cyclosilanes

Reactions of cyclosilanes known prior to this study will be discussed in general terms with the recommendation that the reader seek further detailed information from a recent review (2) which also includes some of the results reported herein.

Ia and IIa are readily cleaved by lithium metal in tetrahydrofuran to give silyllithium compounds (12-14). Whereas, 1,5-dilithiodecaphenylpentasilane could be obtained in high yield (9), the 1,4-dilithiooctaphenyltetrasilane compound was determined to be present in only 27% yield (12). IIIa does not react with lithium alone in tetrahydrofuran but the presence of a catalytic amount of triphenylsilyllithium causes extensive reaction and cleavage (2).

Ring-opening of the cyclosilanes with halogens has been very useful in the characterization of the cyclic compounds. Kipping was first to observe the rather surprising reaction of Ia with iodine (4, 12) to form the easily hydrolyzed 1,4-diiodooctaphenyltetrasilane. He reported that under comparable conditions IIa did not react with iodine. Bromine is more reactive with Ia (12) and if two moles of bromine are added, 1,2-dibromotetraphenyldisilane can be isolated in 85% yield (9). IIa, by careful addition of an equivalent amount of bromine, gives a high yield of 1,5-dibromodecaphenylpentasilane (9, 12, 14). Mixed products are obtained with an excess of bromine (4).

Organic halides, inorganic halides and certain metal salts have proven useful in the preparation of 1,4-dihalooctaphenyltetrasilane compounds. 1,1,2,2-Tetrachloroethane (4) and a large variety of halogenated hydrocarbons (2) have been used to prepare 1,4-dihalooctaphenyltetrasilane from their reaction with Ia. 1,2-Dibromoethane has been used to obtain 1,4-dibromooctaphenyltetrasilane (15). Mercuric chloride reacts with Ia to give a 92% yield of the 1,4-dichlorooctaphenyltetrasilane and 94% mercurous chloride (16). Mercuric bromide, mercuric iodide and stannic chloride react in a similar manner (16). Inorganic halides such as phosphorus pentachloride, sulfuryl chloride and thionyl chloride have also been used to give favorable yields of 1,4-dichlorooctaphenyltetrasilane

(17). Prior to this investigation IIa was not known to react with any of the above reagents.

The first reported cleavage of IIIa was with iodine (18). Mercuric chloride cleaves IIIa in tetrahydrofuran to give a mixture of dichlorosilanes, with evidence for compounds containing one, two, and three silicon atoms (19). During the course of this investigation, and following methods described herein, IIIa was cleaved by 1,1,2,2-tetrachloroethane to yield 1,6-dichlorododecamethylhexasilane in ca. 40% yield (11). Also used was phosphorus pentachloride (20) and chlorine.[1] However, cleavage reactions of the resulting linear polysilane, after initial ring-opening, becomes competitive and a multiple of compounds of varying chain length is obtained. Compounds in the series $Cl-(SiMe_2)_n-Cl$, where n = 2, 3, 4 or 6, have been obtained (19).

Ia has also been cleaved with mercuric acetate to give 1,4-diacetoxyoctaphenyltetrasilane which can also be prepared by the reaction of mercuric acetate on 1H,4H-octaphenyltetrasilane or by the reaction of acetic anhydride on 1,4-dichlorooctaphenyltetrasilane. No reaction occurred between IIa or hexaphenyldisilane and mercuric acetate. No attempted reaction of mercuric acetate with IIIa has been recorded.

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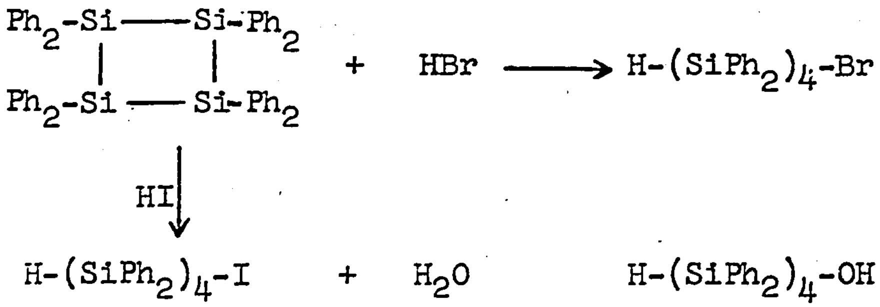
[1] P. K. Sen and R. A. Tomasi, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of chlorine with dodecamethylcyclohexasilane. Private communication. 1964.

A previously unprecedented cleavage of a silicon-silicon bond is observed in the cleavage of Ia with hydrogen bromide and hydrogen iodide (9). Attempted cleavage of Ia with hydrogen chloride or IIa with hydrogen halides under comparable conditions resulted only in recovery of the starting material. Hydrogen iodide and hydrogen bromide react with octaphenylcyclotetrasilane in refluxing benzene to give 1-iodo-1,1,2,2,-3,3,4,4-octaphenyltetrasilane and 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane (85%), respectively. One hour and four hours, respectively, were required to bring about complete disappearance of Ia. The iodosilane was not isolated, but was hydrolyzed and characterized as 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol (27%) (9).



Addition of phenyllithium to Ia in a tetrahydrofuran-ether mixture gave after five hours a 55% recovery of the starting material and an 18.5% yield of decaphenylcyclopentasilane (20). Using a fivefold excess of phenyllithium, no starting material was recovered and the products were hexaphenyldisilane (19%) and pentaphenyldisilane (36%) (20).

A similar 1:1 molar treatment of IIa with phenyllithium for five hours gave a 95% recovery of the starting material (20). A ninefold excess of phenyllithium added to IIa subsequent to hydrolysis gave pentaphenyldisilane (62%) as the only identifiable product.

Ia reacts with methyllithium in a tetrahydrofuran-ether mixture to give 1-lithio-4-methyloctaphenyltetrasilane (66%) (2). In the presence of excess methyllithium further cleavage of the polysilane is observed to give 1H,2-methyltetraphenyldisilane as the major product (65%) after acid hydrolysis (2). IIa reacts with a five mole excess of methyllithium to give 1-lithio-2-methyltetraphenyldisilane which was characterized as 1,2-dimethyltetraphenyldisilane[1] with trimethyl phosphate.

Triphenylsilyllithium reacts with Ia to give, after acid hydrolysis, IIa and 1H-nonaphenyltetrasilane. Excess triphenylsilyllithium gave hexaphenyldisilane and pentaphenyldisilane (20). The reaction of triphenylsilyllithium and IIa over extended periods gives a 79% yield of pentaphenyldisilane after acid hydrolysis (20). Similar disilanes have been obtained with methyldiphenylsilyllithium (13) and dimethylphenylsilyllithium (21).

Excess methyllithium with IIIa gives a complex mixture which, upon treatment with chlorotrimethylsilane, gives

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[1] K. Y. Chang, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of methyllithium on octaphenylcyclotetrasilane decaphenylcyclopentasilane. Private communication. 1964.

permethylated polysilanes containing three to eight silicon atoms (11). Only decamethyltetrasilane (22, 23) and dodecamethylpentasilane were isolated in a relatively pure state (2).

Other nucleophilic reagents capable of cleaving Ia are lithium aluminum hydride (24) and hydroxylic bases (4). Methylenetriphenylphosphorane cleaves Ia to give, after acid hydrolysis, 4H-octaphenyltetrasilane-1-ol (25).

Cleavage of a silicon-silicon bond in many reactions may be considered as an oxidation. However, specific oxidation of Ia has been observed with oxygen and oxygen-containing compounds. Kipping prepared octaphenyloxatetrasilacyclopentane by direct oxidation of Ia with air at room temperature (15). The cyclic monoxide, octaphenyl-1,4-dioxatetrasilacyclohexane, and varying amounts of viscous polymers were obtained from Ia and air in toluene at 100°C, ozonized oxygen in carbon tetrachloride, benzaldehyde, benzyl alcohol, acetophenone, paraldehyde and amyl nitrite (15). Octaphenyl-1,4-dioxatetrasilacyclohexane has also been obtained by the reaction of nitric acid on octaphenyloxatetrasilacyclopentane (4) and by the hydrolysis of 1,2-dibromotetraphenyldisilane (26). The reaction of Ia is rapid in refluxing nitrobenzene to give a second dioxide (4) which has been suggested to be octaphenyl-1,3-dioxatetrasilacyclohexane. IIa was found to be unreactive toward such oxidizing agents under comparable conditions.

In the presence of chromium-containing catalysts, such as a "copper chromite", at 150°C and 800 psi pressure, hydrogenolysis of Ia takes place to give 42-48% of diphenylsilane and 5-12% of 1H,4H-octaphenyltetrasilane (24). Under like conditions, hexaphenyldisilane gives 17% triphenylsilane and a 59% recovery of starting material. IIa is more resistant than hexaphenyldisilane using the same conditions.

Dodecaphenylcyclohexasilane (IIIc) is prepared in very low yield as a by-product from the general preparation of octaphenylcyclotetrasilane (Ia) and decaphenylcyclopentasilane (IIa) (4, 9). Shielded by bulky phenyl groups, it is the most stable and unreactive cyclosilane known. Cleavage reactions occur only under strong forcing conditions which cause multiple cleavages (7, 9). No significant study has been made on other cyclosilanes known at this time.

Reactions of the Silicon-Silicon Bond

All of the reactions of cyclosilanes presently studied involve ring opening to form an α,ω-disubstituted polysilane. The resulting compound is subject to further silicon-silicon bond cleavage depending upon the reactivity of the compound and reagent in the media used. The chemistry involved in initial ring opening of a cyclosilane is dependent upon the substituents, the ring size and steric factors.

The significance of factors controlling the reactivity of the above cyclosilanes will best be understood in terms of analogous silicon-silicon bond cleavage of linear organosilanes. Therefore, a brief review of some of the general reactions of organodisilane systems will be considered. Further detailed treatment has been the subject of some interest in recent years (2, 3, 27).

Aryl substituted disilanes are cleaved by alkali metals in ether solvents (28-30). Sodium-potassium alloy, rubidium, and cesium cleave the silicon-silicon bonds of arylated disilanes to give the corresponding silylmetallic compounds (31-35). As a method of choice, silyllithium compounds are prepared by the cleavage of a disilane with lithium in tetrahydrofuran (36-38). They are generally easily handled and reasonably stable (39).

The cleavage of disilanes with phenyllithium is generally slow and requires tetrahydrofuran as the solvent and a large excess of phenyllithium to ensure complete reaction. The treatment of hexaphenyldisilane with phenyllithium in diethyl ether for five days resulted in a 93% recovery of the starting material and a 5% yield of tetraphenylsilane. A tenfold excess of phenyllithium in tetrahydrofuran after 24 hours gave a 50% recovery of the hexaphenyldisilane and an 89% yield of tetraphenylsilane (based on unrecovered starting material) (40). A comparable treatment of hexaphenyldisilane with methyllithium resulted in an 84% recovery of starting material and the formation of a small amount of triphenylsilanol.[1]

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[1] K. Y. Chang, op. cit., p. 10.

Excess benzyllithium in a mixture of ether and tetrahydrofuran cleaves hexaphenyldisilane completely within one hour at room temperature (41). The reactions of the unsymmetrical disilanes, chloropentaphenyldisilane, ethoxypentaphenyldisilane and pentaphenyldisilane with phenyllithium in ether resulted in no cleavage products (42). In each instance excellent yields of hexaphenyldisilane were reported.

A recent study made during the course of the present work exemplifies the complexity of the reaction of alkyllithium compounds on polysilanes (9). A reaction of _n_-decyllithium with 1_H_,4-bromooctaphenyltetrasilane in ether gave as products: Ia (22%), IIa (1%), 1_H_,4-_n_-decyloctaphenyltetrasilane (2.3%) and a trace of 1,4-_n_-decyloctaphenyltetrasilane. Treatment of 1_H_,4-bromooctaphenyltetrasilane with _n_-decylmagnesium bromide initially in refluxing ether and finally in refluxing toluene resulted in no reaction. A reaction of _n_-decyllithium with 1_H_,4-chlorooctaphenyltetrasilane in a mixture of benzene and ether gave as products: _n_-decyldiphenylsilane (40%), 1_H_,4_H_-octaphenyltetrasilane (7.5%), Ia, and a trace of _n_-decyltriphenylsilane (9).

The variety of products obtained demonstrates the diversity of the reactions which are involved. Apparently there have occurred silicon-silicon bond cleavage, silicon-phenyl bond cleavage, halogen-metal interconversion and simple displacement of hydrogen or halogen to give the direct coupling product. The isolation of _n_-decyltriphenylsilane can be explained by the cleavage of the polysilane chain by phenyllithium to give the triphenylsilyl group. The phenyllithium most probably arose through displacement by n-decylithium. Reactions of this type have been observed in the past in the cleavage of phenyl groups from silicon by 1,4-dilithiobutane (43).

Aqueous or methanolic alkali (44-47) and alkali in hexanol (10) causes cleavage of a silicon-silicon bond to give a silanol and hydrogen gas. These reactions can be considered as an attack of a base or nucleophilic species. That a silicon hydride can be an intermediate in such reactions is shown in the cleavage of polysilanols by alumina (14, 48) which can be considered to be a mildly basic reagent. Silicon hydrides containing one less silicon atom are obtained. It appears that inductive withdrawing substituents such as chlorine atoms or hydroxyl groups (14, 42, 48) aid nucleophilic attack on an adjacent silicon atom.

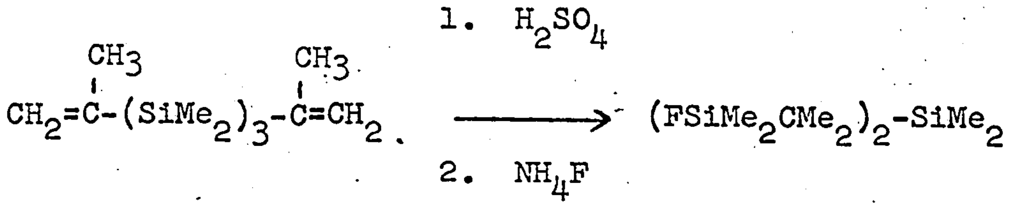
Depending on the substituents, halogens cleave organodisilanes with varying ease. The relative reactivity of the halogens appears to be $Cl_2 > Br_2 > I_2$ (49).

Hexaaryldisilanes are resistant to silicon-silicon cleavage (34, 50-52), although hexaphenyldisilane is slowly cleaved by bromine in carbon tetrachloride (50). Hexaalkyldisilanes are rather easily cleaved by halogens (49, 53, 54). However, halogen substitution on the disilane reduces the rate of cleavage (54), e.g., 1,2-dichlorotetramethyldisilane is cleaved by bromine approximately 100 times slower than hexamethyldisilane under the same conditions (49).

Polysilanes have been generally considered to be quite resistant to acid cleavage of silicon-silicon bonds. Extensive studies have been made of the desilylation (55) of aryl substituted silanes with hydrogen halides (27, 56-58). Alkyl cleavage of alkylsilanes is brought about by hydrogen halides in the presence of aluminum halides, presumably by the strong acid $HAlX_4$ (27, 59). Extensive studies have been made on the effect of substituents on the leaving group and on silicon (27). Aryl substitution decreases with increasing negative character of the substituents on silicon and also with electron-withdrawing substituents on the aryl group (60-62). The proposed mechanism involves electrophilic attack at carbon. When the R group in $C_6H_5SiR_3$ is varied in the series methyl, ethyl, _i_-propyl, the ease of cleavage of the phenyl group falls in the ratio of 100:48:6 which suggests a steric hindrance effect. The order of the inductive effect in the series should facilitate cleavage by stabilizing the positively-charged transition state (63). Under pressure, in the absence of catalysts, hydrogen halides cause the halogenation of silane and monoalkylsilanes (64). Concentrated sulfuric acid has been used to cleave methyl groups from permethylated polysilanes to obtain, after treatment with an ammonium halide salt, α-halo- or α,ω-dihalomethylpolysilanes (54). No silicon-silicon bond cleavage was observed.

Upon passing hydrogen chloride gas over $Me_3SiSiMe_3$, $Me_3SiSiMe_2Cl$, $Me_3SiCH_2SiMe_2Cl$, $Me_3SiCH_2SiCl_3$ and $Me_3SiCH_2SiMe_3$ at 350 to 700°C, it was found that the yields obtained by breaking silicon-silicon or silicon-methylene bonds decreased in the given order with the latter two being equivalent (65). In a recent preparation of pentamethyldisilanylferrocene and 1,1'-bis(pentamethyldisilanyl)ferrocene, cleavage of the silicon-silicon bond was found to be facile in very dilute solutions of hydrogen chloride in methanol or ethanol (66). This was cited as the first published example of acid cleavage of a silicon-silicon bond under mild conditions. A possible intermediate was postulated as involving filled d-orbitals of iron with vacant p-orbitals of silicon which facilitated the rapid electrophilic cleavage observed (66). Comparable conditions with pentamethylphenyldisilane, heptamethylphenyltrisilane and cyclopentadienylpentamethyldisilane gave no silicon-silicon acid cleavage. Hydrogen chloride has been found to rapidly cleave certain perchlorinated polysilanes (67) and mixtures of methylchlorodisilanes (68) in the presence of amine catalysts.

Several reagents are capable of causing an intramolecular rearrangement of certain organosilanes to form disilylmethane derivatives. Rearrangement products have been obtained from isopropenylpentamethyldisilane, 1,2-diisopropenyltetramethyldisilane and 1,3-diisopropenylhexamethyltrisilane with concentrated sulfuric acid, subsequent to treatment with ammonium fluoride (69).



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-(SiMe_2)_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow[2.\ NH_4F]{1.\ H_2SO_4} (FSiMe_2CMe_2)_2-SiMe_2$$

(Chloromethyl)pentamethyldisilane undergoes intramolecular rearrangement with aluminum chloride (54) and also with a nucleophilic reagent, sodium ethoxide in ethyl alcohol (70). The phenomenon of intramolecular rearrangement to form disilylmethane derivatives has also been observed with hexamethyldisilane which readily undergoes rearrangement at 600°C to give 2,2,4-trimethyl-2,4-disilapentane (71).

A direct analogy with the reactivity of cyclosilanes of varying ring size can be made by comparing the silicon-methylene cleavage reactions of silacyclobutane and silacyclopentane derivatives. The silacyclobutane ring system has been shown to be very susceptible to cleavage by polar reagents. Facile ring opening has been observed with ethanolic base (72, 73), sulfuric acid (73), ethanolic silver nitrate (74), bromine (74, 75) and hydrogen halides (75-77). A recent study of 1,1-triphenyl-1-silacyclobutane found that facile ring opening also occurred with lithium aluminum hydride and with basic alumina chromatography (78). The five-membered ring homolog, 1,1,2-triphenyl-1-silacyclopentane, was found to be quite unreactive under conditions where the silacyclobutane was readily cleaved. It did not react with bromine, ethanolic silver salts, lithium aluminum hydride or with basic alumina (78). The compound 1-methyl-1-silacyclopentane was found to be 10^3 to 10^4 times less reactive in hydrolysis reactions than its four-membered ring homolog (72).

The enhanced reactivity of the four-membered ring vs. the five-membered ring is proposed to be a combination of increased ground state energy, due to ring strain, and a decreased transition state energy due to the geometry of the four-membered ring. An attacking species is able to form a pentacovalent addition complex with the four-membered ring resulting in less angular motion in going from a strained tetrahedral sp^3 hybrid to an essentially less strained trigonal bipyramid dsp^3 hybrid (17, 78). On the other hand, the five-membered ring, due to less ring strain, would enjoy a lower ground state energy and the corresponding pentacoordinate transition state would require a greater angular motion in rehybridization from a nearer tetrahedral configuration to the pentacovalent complex. The stability and formation of pentacoordinate organosilicon transition states, intermediates and compounds have been the subject of recent interest (79, 80).

An analogous comparison has been made recently of the relative reactivity of cyclosilanes such as octaphenylcyclotetrasilane (Ia) and decaphenylcyclopentasilane (IIa) (2).

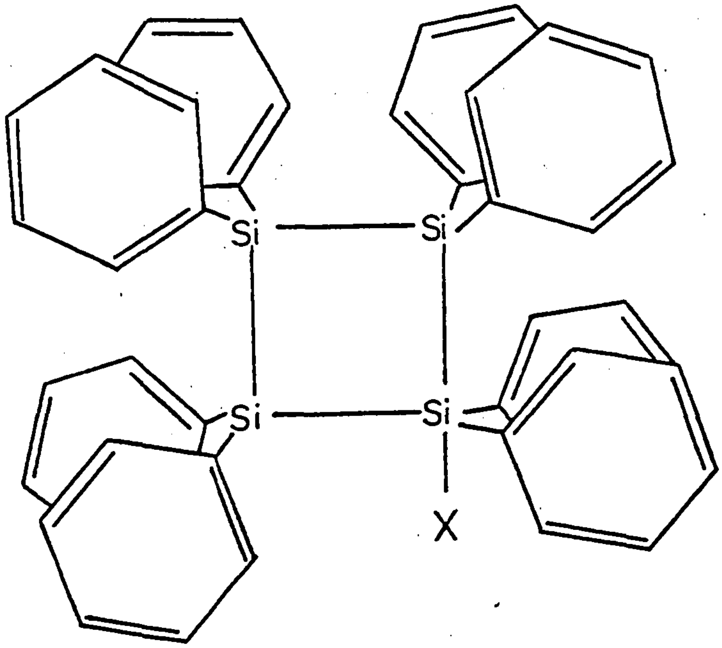


Figure 1. Pentacovalent intermediate involved in the attack of octaphenylcyclotetrasilane by various reagents

Figure 1 demonstrates the formation of the pentacovalent complex as it might be applicable to reactions of Ia. It is suggested 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, e.g., the greater reactivity of bromine with IIa over that of hexaphenyldisilane (2).

The Ultraviolet Absorption Properties of Polysilanes

The ultraviolet properties of numerous monosilane derivatives have been previously reported (27, 81). Only recently has a study of the spectral properties of polysilanes been examined (3). Hague and Prince (81) have reported that Group IVB compounds of the type Ph_3MMPh_3 (M = Si, Ge, Sn and Pb) show ultraviolet maxima in the 239-248 mμ region (ϵ = 30,400 to 33,900). Thus, hexaphenyldisilane has λmax. 246.5 mμ (ϵ = 32,600). It was suggested that an intense interaction between phenyl groups on different M atoms through the M-M bond occurred. Conjugation was considered to occur through overlap of $p\pi$ orbitals with suitable vacant d-orbitals on the M atom, i.e., $p\pi$ -d or $d\pi$ -d interactions. Other studies soon followed on the effects of replacing the phenyl substituents of the disilane with methyl or vinyl groups (82-84) and extending the perphenylated silicon-silicon chain (85, 86). An examination (87) of a homologous series of α,ω-diphenyl-permethylated polysilanes, Ph-$(SiMe_2)_n$-Ph (where n = 2 to 6), gave maxima in the 236 to 265 mμ region (ε = 18,200 to 30,500). Studies of a family of permethylated linear polysilanes, Me-$(SiMe_2)_n$-Me, implied that the polysilane chain itself absorbs ultraviolet radiation without the presence of phenyl groups (82). The intense absorption of organopolysilanes has been observed to be present in cyclic (10b, 86) and branched (88, 89) compounds, although the absorption maxima appear at lower wavelengths than their linear analogs. The ultraviolet spectra of some cyclosilane compounds have been reported to show absorptions as given in Table 1 (86).

Table 1. Ultraviolet spectral data for some cyclosilanes (86)

Compound		$\lambda_{Max.}$, mμ	Molar absorbtivity ε
$(SiPh_2)_4$	Ia	234	64,500
$(SiPh_2)_5$	IIa	270, 251 (sh)	33,000, 60,000
$Me_2Ph_8Si_5$	IIb	240(sh)	41,000
$(SiPh_2)_6$	IIIc	248(sh)	60,000
$Me_2Ph_{10}Si_6$	IIIb	250(sh)	56,800
$(SiMe_2)_6$	IIIa	232, 255 (sh)	5,800, 2,000

Present studies on the ultraviolet properties of polysilanes have led to the following observations (3).

a) Phenyl-containing monosilanes exhibit only the benzenoid fine-structure of B-bands having low molar absorbtivities (27, 81).

b) With polysilanes, intense absorption maxima are observed and the $\lambda_{Max.}$ increases with increasing chain length.

c) The molar absorbtivities also increase with increasing chain length. These compounds appear to obey Beers-Law.

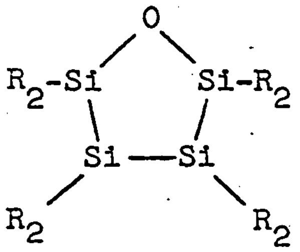
d) Substituents such as phenyl and vinyl cause an increase in $\lambda_{Max.}$, while chloro-, hydroxyl and H- appear to have little effect on the band position.

e) Cyclic and branched polysilanes absorb at lower wavelengths than their corresponding open-chain analogs.

Heterocyclic Polysilanes

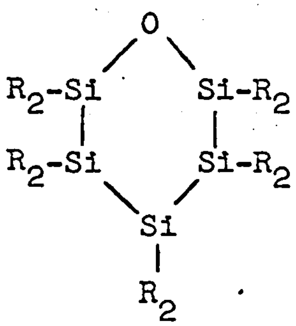
The term heterocyclic as it applies to polysilanes in this discussion will be limited to those compounds containing at least one silicon-silicon bond. This eliminates compounds such as silacyclobutane in which we would properly consider silicon as the hetero atom. Also this would not include cyclotri- or cyclotetrasiloxanes which are not monosilanes but do not contain two adjacent silicon atoms. As mentioned previously, numerous compounds such as siloxanes, silazanes or silthianes containing alternate silicon atoms have been prepared and studied extensively (27, 90).

Only a few heterocyclic compounds containing the silicon-silicon bond have been prepared and little or no study has been made on the reactions of these compounds. Most of the known compounds contain oxygen as the hetero atom. Derivatives having structures IV-IX have been prepared. The present discussion will be



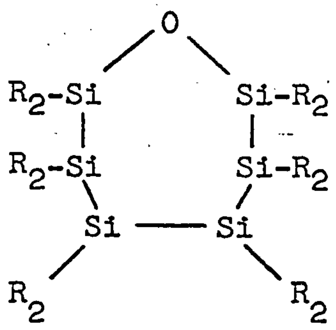
IV

R = Ph



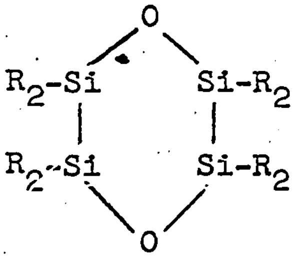
V

R = Ph



VI

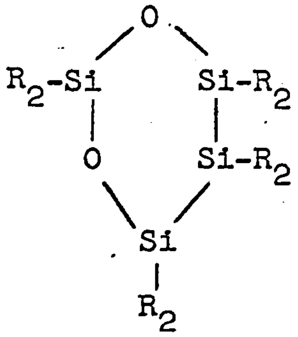
R = Me



VII

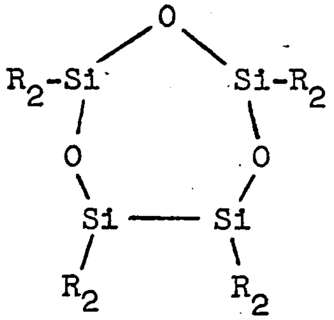
a R = Ph

b R = Me



VIII

R = Ph



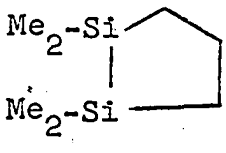
IX

a R = Ph

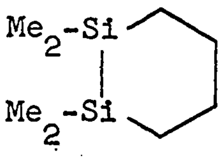
b R = Me

confined to the preparation and reactions of some of these compounds.

To demonstrate the limited number of heterocyclic compounds prepared, most of the known compounds are listed below with the preparation reference in parenthesis.



(91)



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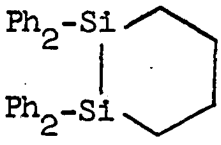
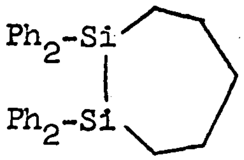


(17)



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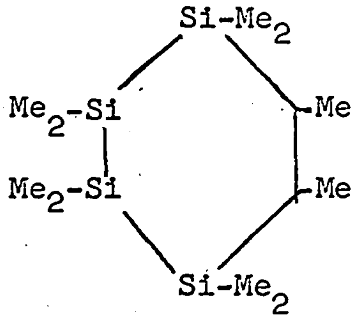

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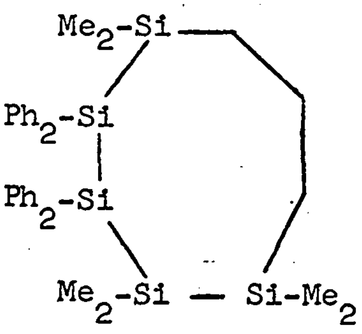

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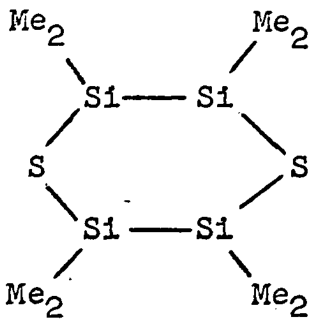

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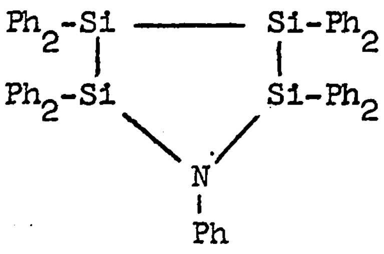

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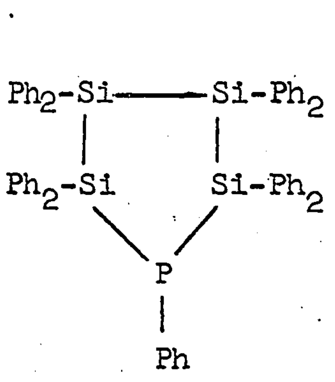

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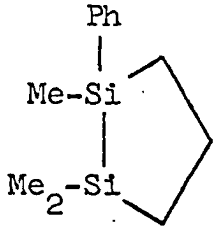

(96)

Kipping prepared IV by direct oxidation of Ia and by hydrolysis of the dihalo derivatives of Ia (4). He also obtained two compounds having the general formula $Ph_8Si_4O_2$ for which he proposed structures VIIa and VIII, but he was unable to characterize either compound (4). One of these compounds was prepared by the oxidation of IV with nitric acid. The same compound was prepared by the dehydration of 1,1,2,2-tetrasilane-1,2-diol, showing the compound to be VIIa (26). The other isomer obtained by the reaction of nitrobenzene on Ia was assumed to be VIII (26). Kumada has reported the preparation of VIIb from the hydrolysis of 1,2-dihalo- and 1,2-diethoxytetramethyldisilanes (97), and of IXb from the cohydrolysis of diethoxydimethylsilane and 1,2-diethoxytetramethyldisilane (98). Compounds V and VI have been obtained by dehydration of the corresponding α,ω-diols.[1] V was obtained in very low yields.

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[1] S. Inoue, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Private communication. 1963.

EXPERIMENTAL

The reagents, solvents and gases used in the following experiments were commercially available materials. All hydrocarbons and ether solvents used in a reaction were stored over sodium wire. Other reagents and gases were used as they were obtained commercially or freshly distilled if there was any question of water or oxygen-containing contaminants. Tetrahydrofuran used with organometallic reagents was dried by refluxing for 24 hours over sodium followed by distillation from lithium aluminum hydride. The organosilicon halides were obtained from Dow Corning Corporation and Union Carbide Corporation. Lithium metal from Lithium Corporation of America was obtained as wire. It was washed free of oils with hydrocarbons and cut small pieces into a nitrogen-filled reaction flask. Organometallic solutions were quantitatively titrated according to a published double titration technique using allyl bromide or 1,2-dibromoethane (99, 100). Color Test I was used as a qualitative test for organometallic reagents (101). The molar refractance (MR), boiling-point number (B.P.N.) and calculated boiling points were obtained using data from a recent publication (27) and from studies in These Laboratories.[1] The yields of crude products or unidentified

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[1] J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on group boiling-point numbers of polysilanes. 1965.

solids are based on the weight of the starting material to give crude approximations of the material balance.

In general, the experimental apparatus consisted of a four-necked standard taper flask equipped with a thermometer, a Trubore stirrer, a Friedrichs condenser and, as required, an addition funnel or gas inlet tube which usually extended below the liquid level. A safety flask having the same or a larger volume than the reaction vessel was placed between it and the gas source. The gases were metered by passing them through a 1 mm. capillary 3 cm. long. The pressure drop across this orifice was measured with a manometer filled with carbon tetrachloride. The calibration was based on the water displacement of air in an inverted 500 ml. graduate. A high speed, air-driven motor was used for most reactions. A wire flail attached to the paddle in reactions using lithium metal increased the agitation and was generally felt to be helpful in obtaining high yields. All glassware was oven-dried before use and purged while hot with dry, oxygen-free nitrogen. All external outlets were fitted with nitrogen inlets to exclude air. Pressure reactions were carried out in a 1 liter stainless steel Parr Pressure Reaction Apparatus, item No. 4511, under atmospheres of oxygen-free, dry nitrogen. Temperatures were uncorrected and melting points above 100°C were obtained with a Mel-Temp apparatus. Lower melting points were determined in an electrically heated oil bath.

Infrared spectra were determined using a Perkin Elmer

Model 21 Spectrophotometer. A Beckman IR-7 Spectrophotometer with sodium chloride optics was used for spectra in the 400 to 1200 cm^{-1} region with KBr cells. Ultraviolet spectra were obtained with a Beckman-DK-2A Spectrophotometer. Letters indicate the relative intensity of absorption bands: s = strong, m = medium, w = weak, sh = shoulder. Proton magnetic resonance (NMR) spectra were obtained with a Varian A-60 Spectrometer or a Varian High Resolution Spectrophotometer, model HR-60, at 60 Mc/sec.

Vapor phase chromatographic (VPC) analyses were carried out with an F & M Model 500 Gas Chromatograph, using a column packed with silicon gum rubber S E 30 on Chromosorb W (1:20). Molecular weight determinations were made with a Mechrolab Model 301-A Vapor Pressure Osmometer. Benzil was used as a standard with benzene as solvent.

Preparation of Cyclosilanes

Octaphenylcyclotetrasilane

Following a previously described synthesis (9), 14 gm. (2.02 gm.-atom) of lithium metal, 50 ml. of tetrahydrofuran and 1 ml. of dichlorodiphenylsilane were placed in a reaction flask. In a few minutes the reaction became hot and, with rapid stirring, a solution of 278 gm. (1.1 moles) of dichlorodiphenylsilane in 200 ml. of tetrahydrofuran was added in 75 minutes at a rate which maintained a slight yellow color (silyllithium) in the reaction mixture. The reaction proceeded with vigorous refluxing except for the last few minutes when heating was required.

The mixture was then cooled and filtered. The insoluble material was extracted twice with hot benzene and twice with a methanol-water mixture to obtain 137 gm. (68%) of Ia, m.p. and mixture m.p. 318-324°C. Concentration of the benzene liquor and addition of petroleum ether (b.p. 60-70°C) gave 3-4 gm. (2%) of IIa, m.p. 460-468°C.

Decaphenylcyclopentasilane (IIa)

Dichlorodiphenylsilane, 1 ml., was added to 14.4 gm. (2.04 gm.-atoms) of lithium metal in 20 ml. of tetrahydrofuran to initiate a reaction. To a rapidly stirred mixture was added, over 30-45 minutes, 255 gm. of dichlorodiphenylsilane in 300 ml. of tetrahydrofuran. The rate of addition was such as to maintain a light yellow color. The mixture was then refluxed for 4 hours and the color became dark brown. Addition of 6-8 ml. of dichlorodiphenylsilane then stopped the reaction by reacting with the silyllithium and excess lithium present. After cooling and hydrolyzing in cold water, the mixture was filtered and the residue washed with 3 l. of acetone to yield 167 gm. (91%) of crude product, m.p. 440-450°C. The dried crude product was then dissolved in 2 l. of benzene and allowed to stand for several days. Approximately 2-3 gm. of dodecaphenylcyclohexasilane (IIIc) was slowly precipitated in this manner. After removal of IIIc, the solvent was concentrated and petroleum ether (b.p. 60-70°C) added to yield 150 gm. (81%) of pure IIa, m.p. and mixture m.p. 472-476°C.

Dodecamethylcyclohexasilane

Using a slightly modified procedure from that described (11), 5 gm. of hexaphenyldisilane was added to 45.5 gm. of dry lithium wire. Rapid stirring for 10 minutes caused a thorough coating of the disilane on the lithium metal. Tetrahydrofuran, 50 ml., was then added and a dark brown mixture of triphenylsilyllithium appeared after 30 minutes of rapid stirring. In two additions a total of 360 ml. (3.0 moles) of dichlorodimethylsilane in 750 ml. of tetrahydrofuran was added in 14 to 20 hours. The first solution contained 180 ml. of dichlorodimethylsilane in 450 ml. of tetrahydrofuran. The second solution, which was added to the funnel when the addition of the first portion was almost complete, contained 180 ml. of dichlorodimethylsilane in 300 ml. of tetrahydrofuran.

The mixture was heated as the reaction subsided during the latter half of the additions. The light yellow color of the active silyllithium compounds was difficult to discern in this reaction due to the light brown color of the salts. Using "High Sodium" (0.1%) lithium (Lithium Corporation of America) improved the color but seemed to have little or no effect on the yield of IIIa. As soon as the addition was complete, the mixture was cooled and poured through an open Buchner funnel into 400 ml. of ice water containing 100 ml. of *N* HCl. The organic material was extracted twice with ether which was then washed twice with distilled water and dried with anhydrous sodium sulfate. The ethers were then removed by evaporation on a rotary evaporator under reduced pressure and the residue washed with 50 ml. of cold acetone. The crude product, 130 gm. (75%), was recrystallized from hot acetone to obtain a 125 gm. (72%) yield of IIIa, m.p. and mixture m.p. 252-256°C.

Reactions of Octaphenylcyclotetrasilane

Octophenylcyclotetrasilane with phosphorus pentachloride

In benzene. To a suspension of 3 gm. (0.004 mole) of Ia in 50 ml. of benzene was added 0.94 gm. (0.0045 mole, 10% excess) of phosphorus pentachloride. The mixture was refluxed with stirring for 1 hour. The homogeneous reaction mixture was concentrated and, upon the addition of petroleum ether (b.p. 60-70°C), 3.02 gm. (92%) of yellow-white solids, m.p. 183-186°C, was obtained. One recrystallization from benzene-petroleum ether (b.p. 60-70°C) gave 2.7 gm. (83%) of pure material, m.p. and mixture m.p. 186-187°C. Small amounts of nonresolvable crystalline solids were isolated.

A similar reaction involving 44.0 gm. (0.06 mole) of Ia, 13.6 gm. (0.065 mole) of phosphorus pentachloride and 150 ml. of benzene provided 44.7 gm. (93%) of 1,4-dichlorooctaphenyltetrasilane, m.p. 185-187°C, upon recrystallization.

In xylene A third reaction was made using 10.0 gm. (0.013 mole) of Ia, 90 ml. of xylene and 3.13 gm. (0.015 mole) of phosphorus pentachloride. The mixture was refluxed for 2 hours, cooled and filtered. The filtrate was distilled to yield approximately 1 ml. (90%) of phosphorus trichloride, b.p. 76-80°C., n_D^{20} 1.5077 (ref. sample 1.5138). An infrared spectrum of the distillate was superimposable with the spectrum of a freshly distilled sample of the trichloride. Work-up as above gave 1.7 gm. (17%) of recovered Ia, m.p. 315-320°C and 8.2 gm. (73.5%) of 1,4-dichlorooctaphenyltetrasilane, m.p. 185-187°C.

Octaphenylcyclotetrasilane with phosphorus trichloride (attempted)

Phosphorus trichloride, 2.1 gm. (0.015 mole), Ia, 10.0 gm. (0.013 mole), and 90 ml. of xylene were refluxed for 2 hours. Upon filtering, 9.85 gm. (98.5%) of starting material was recovered, m.p. 318-322°C.

Octaphenylcyclotetrasilane with chlorine

In carbon tetrachloride A series of reactions was carried out in which Ia, 10.0 gm. (0.011 mole), was dissolved in 100 ml. of carbon tetrachloride and the rapidly stirred suspension was treated with chlorine gas at a constant rate (approximately 200 ml./min.) for a specified time. The reaction was then quenched by the rapid removal of excess chlorine under reduced pressure. The solvent was also removed in this manner. The products were isolated by crystallization of the residues from benzene-petroleum ether (b.p. 60-70°C) mixtures. The results are summarized in Table 2.

In ether Octaphenylcyclotetrasilane, 10.0 gm. (0.014 mole), suspended in 80 ml. of ether was treated with chlorine

Table 2. Reaction of octaphenylcyclotetrasilane with chlorine

Time min.	Temp.[a] °C	Starting material (%)	Dichloro derivatives (%)[b,c]	
			1,4-	1,2-
2.5	20 - 29	---	96.7	---
5	25 - 33	---	89	1.7
10	24 - 31	---	85	8.5
15	25 - 35	---	71.6	25.4
20	25 - 30	---	56.6	33
30	25 - 30	---	30.6	37
40	28 - 30	---	---	34
70	26 - 36	---	---	43

[a] Temperature control was maintained with an ice-bath.

[b] Based on unrecovered starting material.

[c] The remainder of the reaction residue consisted of high boiling, unidentified, viscous oils.

gas at 200 ml./min. for 10 minutes in the manner described in the previous experiment. The temperature was held at 18-22°C by means of an ice-bath. The reaction mixture was then filtered to yield 10.4 gm. (94.7%) of 1,4-dichlorooctaphenyltetrasilane, m.p. and mixture m.p. 187-188°C. Evaporation of the filtrate yielded an additional 0.3 gm. (2.7%) of product, m.p. 184-186°C, and 0.2 gm. of an unidentified material melting at 179-180°C.

A similar reaction, with chlorine addition for 1 hour, provided 10.5 gm. (95.7%), m.p. 188-189°C, and 0.3 gm. (2.7%) of 1,4-dichlorooctaphenyltetrasilane, m.p. 186-188°C.

In petroleum ether (b.p. 60-70°C) Chlorine gas was added at approximately 200 ml./min. for 15 minutes (3 l., 0.12 mole) to a suspension of 21.9 gm. (0.03 mole), in 150 ml. of petroleum ether (b.p. 60-70°C). The temperature was maintained at 15-25°C with an ice-bath. The excess of chlorine was removed under reduced pressure and the solids were filtered off to provide 24.0 gm. (100%) of 1,4-dichlorooctaphenyltetrasilane, m.p. and mixture m.p. 186-187°C.

In n-pentane A 22 gm. (0.03 mole) sample of Ia suspended in 150 ml. of *n*-pentane was treated with chlorine gas for 13 minutes at 200 ml./min. (2.6 l., 0.11 mole) in the manner described. After removal of excess chlorine, the suspension was filtered to obtain 23.7 gm. (97.3%) of 1,4-dichlorooctaphenyltetrasilane, m.p. and mixtures m.p. 184-185°C.

In ether containing hydroquinone Chlorine gas was added at approximately 200 ml./min. for 3 min. (0.6 l., 0.025 mole) to a mixture containing 5 gm. (0.007 mole) of Ia, 80 ml. of ether and 1 gm. (0.009 mole) of hydroquinone, m.p. 175-177°C. The temperature was kept at 15-17°C with an ice-bath. Excess chlorine was removed under reduced pressure and the suspension filtered to give 4.6 gm. (92%) of recovered Ia, m.p. and mixture m.p. 321-328°C. Concentration of the solvent gave 0.3 gm. (5.5%) of 1,4-dichlorooctaphenyltetrasilane and 0.3 gm. (30%) of hydroquinone, m.p. 172-174°C and mixture m.p. 174-177°C.

Octaphenylcyclotetrasilane with anhydrous hydrogen chloride

Octaphenylcyclotetrasilane was treated with anhydrous hydrogen chloride under a variety of conditions with regard to solvent, temperature and duration of reaction (Table 3). Depending on the conditions the yield of 1-chloro-1,1,2,2,3,3,-4,4-octaphenyltetrasilane ranged from 2 to 92%. Details of the reaction in benzene are given, together with the work-up of the products as a general procedure.

A mixture of 14.6 gm. (0.02 mole) of Ia and 250 ml. of benzene was heated to the reflux temperature and anhydrous hydrogen chloride was added continuously above the liquid level for 6 hours. An additional 200 ml. of benzene was introduced and the admission of gas continued for 6 hours. After standing overnight at room temperature, the reaction mixture was filtered to give 12.6 gm. (86.3%) of crude starting material, m.p. 308-320°C. Concentration of the filtrate gave in two crops an additional 1.9 gm. (13.4%) of recovered octaphenylcyclotetrasilane.

The final filtrate was then evaporated to dryness at reduced pressure with the aid of a steam bath. The residue was dissolved in 2 ml. of benzene and the addition of 20 ml. of petroleum ether (b.p. 60-70°C) caused the precipitation of 0.30 gm. of solid, m.p. 156-158°C. Recrystallization of this material provided 0.28 gm. (2.0%) of pure 1-chloro-1,1,2,2,3,-3,4,4-octaphenyltetrasilane, m.p. 161-163°C. Mixture melting

Table 3. Reactions of octaphenylcyclotetrasilane (Ia) with hydrogen chloride

Solvent (ml.)	Ia (mole)	Temp. (°C)	Time (hours)	Recovered (Ia)	Product[a]
Benzene[b] (450)	0.02	78	12	89%	2%
Xylene (300)	0.02	138	6	62	33
Xylene (350)	0.04	138	13	55	33
Xylene (750)	0.04	138	17	70	21
o-Dichlorobenzene (300)	0.04	175	2.0	1.4	81
o-Dichlorobenzene (300)	0.04	175	1.5	3	88
o-Dichlorobenzene (400)	0.08	175	1.75	1.2	91
o-Dichlorobenzene (400)	0.08	175	3	1.3	93

[a] 1*H*,4-Chlorooctaphenyltetrasilane.

[b] With the exception of the reaction in benzene the hydrogen chloride was admitted below the liquid level at all times.

point determinations of this compound with 1*H*,4*H*-octaphenyltetrasilane, m.p. 160-161°C, and with 1*H*,4-bromooctaphenyltetrasilane, m.p. 161-162°C, were not depressed. However, an infrared spectrum of the product (in carbon disulfide) using potassium bromide cells showed a silicon-hydrogen absorption at 795 cm^{-1} as well as absorptions at 560 and 523 cm^{-1} attributable to the silicon-chloride bond (102) (see discussion).

Anal. Calcd. for $C_{48}H_{41}ClSi_4$: Si, 14.68. Found: Si, 14.58, 14.48%. The ultraviolet absorption spectrum in cyclohexane gave $\lambda_{max.}$ 253 mμ (w sh).

Octaphenylcyclotetrasilane with β,β'-dichlorodiethyl ether A mixture of 14.6 gm. (0.02 mole) of Ia and 100 ml. of β,β'-dichlorodiethyl ether was refluxed for 1.5 hours. After standing overnight, 2.2 gm. (15%) of starting material, m.p. 318-330°C was obtained. The solvent was removed by distillation under reduced pressure with a steam bath and the residue dissolved in 10-15 ml. of benzene. Addition of 30-40 ml. of petroleum ether (b.p. 60-70°C) provided 4.2 gm. (29%) of a crude product, m.p. 173-176°C. Evaporation of the filtrate to approximately 20 ml. provided an additional 0.6 gm. (4.1%), m.p. 153-155°C. Repeated recrystallization provided no pure products. Using KBr cells, an infrared spectrum (in CS_2) of the lowest melting fraction obtained showed strong absorptions at 790, 560 and 523 cm^{-1} and was superimposable with the spectrum of 1H,4-chlorooctaphenyltetrasilane. A spectrum of the higher melting fraction, m.p. 170-175°C, showed a weak absorption at 790 cm^{-1} and strong absorptions at 523, 545 and 560 cm^{-1}. This spectrum was superimposable with the spectrum of 1,4-dichlorooctaphenyltetrasilane.

Octaphenylcyclotetrasilane with a hexachlorocyclohexane

Decalin, 100 ml., containing 80 gm. (0.11 mole) of Ia and 11.7 gm. (0.04 mole) of 1,2,3,4,5,6-hexachlorocyclohexane, m.p. 111-113°C, was heated at 185°C for 5 hours. The solvent was then removed with a rotary evaporator under reduced pressure and the residue, except for 18.9 gm. (24%) of Ia, m.p. 328-332°C, was dissolved in hot benzene. Concentration of the solvent and addition of petroleum-ether (b.p. 60-70°C) provided 41.7 gm. (52% based on starting material) of solids melting over the range 175-180°C and 2.4 gm. (3%) of solids, m.p. 150-154°C. Repeated recrystallization from benzene-petroleum ether (b.p. 60-70°C) mixtures gave no pure fractions but mixture melting points and infrared spectra comparisons with high melting, 178-180°C, fractions and low melting, 160-162°C, fractions as in the previous reaction indicated the products to be mixtures of 1,4-dichloro- and 1*H*,4-chlorooctaphenyltetrasilane.

Octaphenylcyclotetrasilane with t-butyl chloride

In xylene   A mixture of 22 gm. (0.03 mole) of Ia, 200 ml. of xylene and 5 ml. (0.046 mole) of t-butyl chloride was heated for 24 hours at 133-138°C. *t*-Butyl chloride, 5 ml. (0.046 mole), was then added and heating continued for 23 hours at 132°C. Upon cooling, 7.0 gm. (31%) of starting material, m.p. 327-332°C, was obtained. Concentration of the solution and addition of petroleum ether (b.p. 60-70°C) several times provided the following solid fractions: 12.3 gm. (53%) of 1*H*,4-chlorooctaphenyltetrasilane, m.p. and mixture m.p. 161-

162°C; 1.0 gm. (4.3%), m.p. 156-160°C; and 0.3 gm. (1.4%), melting over the range 158-176°C. A vapor trap immersed in a dry ice-acetone bath attached to the condenser trapped a mixture of liquids and solids. This mixture was then warmed and the vapors placed in a gas cell. An infrared spectrum showed absorptions which differed from the spectrum of *t*-butyl chloride at 1660 and 888 cm^{-1}. This is believed to be due to isobutylene formed by dehydrohalogenation of the *t*-butyl chloride (103).

In decalin A mixture of Ia, 22 gm. (0.03 mole), *t*-butyl chloride, 28 gm. (0.3 mole), and 100 ml. of freshly distilled decalin was heated at the reflux temperature (83-95°C) for 72 hours. Concentration of the solvent gave a 21.8 gm. (99%) recovery of Ia, m.p. 332-334°C.

To a second reaction mixture containing 22 gm. (0.03 mole) of Ia in 100 ml. of decalin was added 5 ml. (4.35 gm., 0.046 mole) of *t*-butyl chloride. The mixture was then heated to a reflux temperature of 144°C which slowly rose to 170°C over 12 hours of heating. Addition of 5 ml. (4.35 gm., 0.046 mole) of *t*-butyl chloride then brought the reflux temperature down to 148°C. After an additional 11 hours of heating, the temperature had risen to 173°C and the reaction mixture was cooled and allowed to stand overnight. Work-up as above provided 18.6 gm. (80.6%) of crude 1*H*,4-chlorooctaphenyltetrasilane, m.p. 157-159°C. An infrared spectrum of the material was superimposable with that of an authentic sample.

Dehydrohalogenation of t-butyl chloride in decalin (attempted) A mixture of decalin, 75 ml., and t-butyl chloride, 10 ml., was refluxed for 24 hours. A dry ice-acetone trap connected to the condenser collected a small amount of t-butyl chloride containing no olefinic material as indicated by an infrared spectrum.

In o-dichlorobenzene Ia, 40 gm. (0.055 mole), and t-butyl chloride, 5 ml. (4.35 gm., 0.046 mole), were heated in 150 ml. of o-dichlorobenzene at 161-167°C for 1.75 hours. An additional 4 ml. (0.037 mole) of t-butyl chloride was added and heating continued at 157 to 180°C for 7.5 hours. Work-up as above gave 11.0 gm. (27%) of starting material, m.p. and mixture m.p. 229-231°C, and 29.4 gm. (70%) of 1H,4-chlorooctaphenyltetrasilane, m.p. and mixture m.p. 164-166°C.

Octaphenylcyclotetrasilane with 2-chlorobutane

Ten ml. (8.7 gm., 0.095 mole) of 2-chlorobutane was added slowly to 100 ml. of o-dichlorobenzene containing 7.3 gm. (0.01 mole) of Ia preheated to 180°C. The mixture was refluxed at 147-155°C for seven hours after which time an additional 4 ml. (3.5 gm., 0.04 mole) of 2-chlorobutane was added. Heating was continued at 146-150°C for an additional 9 hours. Work-up of the products as described gave a 6.2 gm. (85%) recovery of Ia and a 0.5 gm. (6.8%) yield of crude 1H,4-chlorooctaphenyltetrasilane, m.p. 156-159°C. Recrystallization of the crude material gave m.p. and mixture m.p. 164-166°C.

Octaphenylcyclotetrasilane with n-butyl chloride (attempted)

In xylene   A mixture containing 7.3 gm. (0.01 mole) of Ia in 100 ml. of xylene was heated under reflux. Over a 70 hour period, 8 ml. (0.074 mole) of *n*-butyl chloride was added in 2 ml. aliquots. The boiling point ranged from 129-133°C. Work-up gave a 99% recovery of Ia, m.p. and mixture m.p. 329-333°C.

In o-dichlorobenzene   A similar reaction was carried out with 7.3 gm. (0.01 mole) of Ia in 100 ml. of refluxing *o*-dichlorobenzene. Over a period of 67 hours, 9 ml. (0.085 mole) of *n*-butyl chloride was added. The temperature ranged from 157-158°C. Work-up gave 7.2 gm. (98%) of recovered Ia, m.p. and mixture m.p. 328-331°C.

Octaphenylcyclotetrasilane with t-butyl bromide

A mixture of Ia, 7.3 gm. (0.01 mole), *t*-butyl bromide, 5 ml. (0.044 mole), and 100 ml. of decalin was heated for 1 hour at 166°C. An additional 2 ml. (0.018 mole) of the bromide was then added and heating continued for 0.5 hours at 162°C. Upon cooling the solution and allowing it to stand for 36 hours, 6.25 gm. (77%) of solid, m.p. 174-177°C precipitated. Several recrystallizations from cyclohexane gave 0.1 gm. of white solid, m.p. 216-217°C. The melting point was not depressed by an authentic sample of 1,4-dibromooctaphenyltetrasilane. Concentration of the filtrate by distillation followed by addition of petroleum ether (b.p. 60-70°C) provided 1.3 gm.

(16%) of crystals, m.p. 161-163°C. It was not possible to determine if this fraction was 1*H*,4*H*-octaphenyltetrasilane, m.p. 160-161°C, or 1*H*,4-bromooctaphenyltetrasilane, m.p. 162-163°C, or a mixture of both as each of these compounds gave a mixture m.p. which was not depressed. An infrared spectrum of the last fraction obtained possessed a strong Si-O-Si absorption at 1045 cm^{-1} which indicated the presence of octaphenyloxatetrasilacyclopentane (26).

Octaphenylcyclotetrasilane and nitrobenzene

A 3.65 gm. (0.005 mole) sample of octaphenylcyclotetrasilane was added to 50 ml. of nitrobenzene and the mixture heated at reflux for 30 minutes. Cooling and addition of 75 ml. of ethyl alcohol gave no crystalline products. The solvents were then removed by distillation under reduced pressure. The residue was dissolved in acetone and 50 ml. of ethyl alcohol was added. Upon standing, 2.5 gm. (68%) of dark brown crystals precipitated, melting over the range 185-208°C. Recrystallization from acetone yielded 0.45 gm. (12%) of a compound having a constant m.p. of 245-246°C. This sample was used for an X-ray powder photograph which was found to be identical to the powder photograph of VIII, m.p. 256-257°C, obtained from the hydrolysis of XIII (see below). An ultraviolet spectrum of the above sample gave a $\lambda_{max.}$ (in cyclohexane) 245 mu (sh). The infrared spectrum gave absorptions (in CS_2) in μ at: 3.27 (m), 5.13, 5.30, 5.50, 7.3, 7.55, 7.72, 7.95 (w), 8.46 (m), 8.91, 9.0, 9.07 (s triplet), 9.43 (sh), 9.65, 9.71, 10.06 (m), 13.63, 14.00, 14.40 (s), 14.80 (m).

A second mixture of Ia, 21.9 gm. (0.3 mole), and 100 ml. of nitrobenzene was heated to 165°C. The reaction then became vigorously exothermic and the temperature rose to 208°C in less than one minute with a rapid reflux observed for several minutes. After heating at reflux for an additional 15 minutes the mixture was then cooled. Removal of the solvent by distillation under reduced pressure and addition of 50 ml. of acetone to the residue provided upon standing 4.9 gm. (22.4% based on starting material) of solid, m.p. 234-237°C. The addition of 30 ml. of ethyl alcohol gave an additional 6.2 gm. (28.3%) of a black crystalline solid. Repeated recrystallizations from acetone and from petroleum ether (b.p. 80-115°C) gave many fractions. Several grams were obtained which melted at 245-246°C. After several recrystallizations this m.p. rose to 248-250°C. The melting point of the major fraction was 245-247°C after seven recrystallizations. Small fractions having lower and higher melting points were obtained after each recrystallization. The infrared spectrum of the major fraction (in CS_2) gave absorptions in μ at 9.43 (sh), 9.65, 9.81 and 10.06 in the Si-O-Si band region. The absorptions at 9.65 and 10.06 μ are believed to be due to the silicon-phenyl vibrations. The band at 9.65 μ appears at 9.75 μ for larger ring siloxanes and is shifted to 9.65 μ for six-membered ring compounds showing an Si-O-Si absorption at 9.8-

9.9 μ. Lower melting pure fractions, 1.3 gm., m.p. 230-232°C, and 0.15 gm., m.p. 219-220°C, were obtained. A mixture m.p. with the higher melting fraction and IXa was not depressed. The infrared spectra of these two lower melting fractions (in CS_2) showed an Si-O-Si bond absorption at 9.43 μ identical to IXa.

A third reaction mixture of Ia, 21.9 gm. (0.03 mole), in 100 ml. of nitrobenzene was slowly heated to 140°C in 1.5 hours. The reaction was then cooled and 19.1 gm. (87%) of the starting material, m.p. 320-327°C, was recovered by filtration. Distillation of the filtrate under reduced pressure and addition of 15 ml. of acetone provided 0.7 gm. (3.2%) of solid melting over the range 262-280°C (block preheated to 250°C). Ethyl alcohol 20 ml., was then added and an additional 1.1 gm. (5%) of crystalline solid was obtained. The overall yield of solids based on starting material was 95%. Recrystallization of the last two fractions from acetone gave 0.7 gm. (3%) melting at 255-257°C (block preheated to 250°C), 0.25 gm. (1%) melting at 244-246°C and three other fractions totaling 0.6 gm. (2.5%), m.p. 252-255°C. A mixture m.p. with the first fraction and VIII, m.p. 256-257°C, was not depressed. The infrared spectrum (in CS_2) showed an Si-O-Si bond absorption at 9.80 μ characteristic of a six-membered ring (see Table 1). An infrared spectrum of the second fraction, m.p. 244-246°C, showed Si-O-Si bond absorptions at 9.43 (sh) and 9.80 μ similar to mixtures of IXa and VIII (see Table 14).

α,ω-Octaphenyltetrasilane Derivatives

1H,4-Bromooctaphenyltetrasilane and t-butyl bromide

A mixture of 8.1 gm. (0.01 mole) of 1_H_,4-bromooctaphenyltetrasilane, 8.0 ml. (0.07 mole) of _t_-butyl bromide and 100 ml. of decalin was heated at 154°C for 12 hours. An additional 5 ml. (0.044 mole) of _t_-butyl bromide was added and heating was continued for 4 hours at 145°C. The solvent was removed by distillation under reduced pressure and the residue dissolved in benzene. The addition of petroleum ether (b.p. 60-70°C) provided 4.4 gm. (55%) of crude product, m.p. 200-202°C. Three recrystallizations from cyclohexane provided 1.9 gm. of a white solid, m.p. 219-221°C, the melting point of which was not depressed by an authentic sample of 1,4-dibromooctaphenyltetrasilane. Distillation of the filtrate and treatment with petroleum ether (b.p. 60-70°C) provided an additional 3.0 gm. (37%), m.p. 147-150°C, which was not characterized. Benzene was found to be unsuitable for the recrystallization of 1,4-dibromooctaphenyltetrasilane due to occlusion of the solvent in the crystal structure, giving a m.p. of 200-204°C instead of 223-224°C as obtained by the use of cyclohexane or petroleum ether (b.p. 90-115°C).

1,1,2,2,3,3,4,4-Octaphenyltetrasilan-1-ol

A mixture containing 15.3 gm. (0.02 mole) of 1_H_,4-chlorooctaphenyltetrasilane, 100 ml. of tetrahydrofuran and 50 ml. of _N_ hydrochloric acid was stirred at room temperature for 6 hours. The organic layer was separated from the aqueous layer and was washed several times with distilled water.

The solvent was evaporated from the extracted material and the residue was dissolved in 50 ml. of benzene. The resulting solution was dried with anhydrous sodium sulfate and after filtration was treated with 100 ml. of petroleum ether (b.p. 60-70°C) to yield 13.1 gm. (87%) of crude 1,1,2,2,3,3,-4,4-octaphenyltetrasilan-1-ol, m.p. 188-190°C. Partial evaporation of the filtrate provided an additional 1.6 gm. (10.7%) of product, m.p. 184-189°C. Recrystallization gave 13.35 gm. (89.5%) of the pure product, m.p. and mixture m.p. 185-187°C. An ultraviolet spectrum in cyclohexane gave $\lambda_{max.}$ 253 mμ (sh).

A sample of 1_H_,4-chlorooctaphenyltetrasilane treated in a similar manner in a mixture of benzene, ether and water showed no hydrolysis after 8 hours of stirring at 30°C.

1H,4-Methyloctaphenyltetrasilane

1_H_,4-Chlorooctaphenyltetrasilane, 4.8 gm. (0.063 mole), dissolved in 60 ml. of tetrahydrofuran was added slowly to a mixture of 7 ml. of a 0.81 M methylmagnesium iodide-ether solution (0.006 mole) and 40 ml. of tetrahydrofuran. Color Test I was negative 15 minutes after the addition and 10 ml. (0.008 mole) of the 0.81 M methylmagnesium iodide was added. After 1 hour the color test was again negative and an additional 5 ml. (0.004 mole) of the Grignard reagent was added. A color test after 30 hours of stirring was positive. The reaction mixture was then left to stand for three days after which time a solution of ammonium chloride in water was added. The two layers were separated with several washings of the aqueous layer with ether. After distillation of the organic layer under reduced pressure, the residue was dissolved in 25 ml. of benzene and 50 ml. of petroleum ether (b.p. 60-70°C) was added. Upon standing overnight, 3.1 gm. (66.5%) of a solid, m.p. 172-174°C was obtained. Evaporation of the solvent mixture provided an additional 0.7 gm. (15%), m.p. 171-173°C. The melting point of the first fraction when mixed with an authentic sample of 1-methyl-1,1,2,2,3,3,4,4-octaphenyltetrasilane was not depressed. An infrared spectrum (CS_2) of the product was very similar to the spectrum of the starting material with the exception of an absorption at 1240 cm^{-1} which is due to the silicon-methyl bond (102). An ultraviolet absorption spectrum gave $\lambda_{max.}$ 256.5 mμ (ε 35,260) in 1.35 x 10^{-5}M cyclohexane solution.

<u>1,4-Dipropoxyoctaphenyltetrasilane (attempted)</u>

An 8.0 gm. (0.01 mole) sample of 1,4-dichlorooctaphenyltetrasilane, m.p. 186-187°C, was stirred in 100 ml. of propyl alcohol at 37°C for 7 hours. After filtration, 7.9 gm. (99%) of solid melting at 179-181°C was obtained. Extraction with 100 ml. of hot petroleum ether (b.p. 80-115°C) left 1.0 gm. of insoluble material, melting over the range 206-222°C. The infrared spectrum of this latter fraction showed that octaphenyloxatetrasilacyclopentane was present (26). Infrared

spectra of all of the fractions obtained contained no absorptions in the region of aliphatic CH stretching vibrations as evidenced by other silylpropoxy compounds (see below).

1H,4-Propoxyoctaphenyltetrasilane

A 11.5 gm. (0.015 mole) sample of 1*H*,4-chlorooctaphenyltetrasilane was refluxed in 100 ml. of propyl alcohol for 4.5 hours. Filtration of the cooled mixture gave 7.3 gm. (62%) of crude product, m.p. 134-138°C. The alcohol was removed by distillation under reduced pressure and the residue dissolved in 5-10 ml. of benzene to which was then added 75 ml. of petroleum ether (b.p. 60-70°C). Upon standing, an additional 4.0 gm. (33%) of solids was precipitated. Recrystallization to a constant m.p. gave 5.6 gm. of pure 1*H*,4-propoxyoctaphenyltetrasilane, m.p. 140-141°C. An infrared spectrum of the material showed absorptions in the CH and COSi stretching regions at 3.38 and 9.31 u, respectively, consistant with the proposed structure (102, 103). The ultraviolet absorption spectrum in cyclohexane gave $\lambda_{max.}$ 253.0 mµ.

Anal. Calcd. for $C_{51}H_{48}OSi_4$: Si, 14.25 Found: Si, 14.28, 14.26%.

Condensation of 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol

In 90% formic acid (attempted) 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol 7.5 gm. (0.01 mole) was heated at 105°C in 100 ml. of 90% formic acid for 64 hours. After cooling, filtration of the mixture yielded 7.2 gm. (96%) of solids, m.p. 182-185°C. Recrystallization from benzene-petroleum ether (b.p. 60-70°C) gave 7.1 gm. (95%) of starting material, m.p. and mixture m.p. 187-189°C.

In 98% formic acid (attempted) As in the above reaction, 7.5 gm. (0.01 mole) of 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol was refluxed in 75 ml. of 98% formic acid for 3 days. Work-up gave 6.9 gm. (92%) of recovered starting material, m.p. and mixture m.p. 187-189°C.

A mixture of 7.5 gm. (0.01 mole) of the tetrasilanol in 50 ml. of benzene and 50 ml. of 98% formic acid was heated for 87 hours. Work-up gave 2.4 gm. (32%) of starting material, m.p. 185-187°C, and the following crude solids: 2.0 gm., melting over the range 80-110°C; 0.25 gm., melting over the range 156-162°C; and 0.2 gm., m.p. 170-172°C. Attempted fractional crystallization gave no pure compounds. An infrared spectrum (in CS_2) of the crude fractions showed weak absorptions at 9.3-9.4 μ, indicative of SiOSi bonds (103).

1H,4-Chlorooctaphenyltetrasilane with phenyllithium

In tetrahydrofuran at room temperature Three aliquots, 10, 3 and 2 ml., of 0.4 M phenyllithium-ether (0.006 mole) were added over a period of 20 minutes to 4.6 gm. (0.006 mole) of 1*H*,4-chlorooctaphenyltetrasilane dissolved in 75 ml. of tetrahydrofuran. Addition of each aliquot produced a bright orange color which rapidly faded except for the last addition in which the color did not fade after stirring for 30 minutes.

The reaction mixture was then hydrolyzed with water, extracted with ether, the solvent removed by distillation under reduced pressure and the residue dissolved in benzene. Fractionation from a benzene-petroleum ether (b.p. 60-70°C) mixture provided five fractions which melted either in the range of 198-230°C or 430-490°C. Recrystallization of the fractions provided 1.75 gm. (40%) of IIa, m.p. 469-472°C, and 0.4 gm. (8.3%) of tetraphenylsilane, m.p. 236-238°C. Identification was achieved by a mixed melting point with an authentic sample. The remainder of the reaction residue was a yellow oil. An infrared spectrum of the oil showed a strong absorption in the Si-H region at 4.72 μ (102). At no time during the reaction was Color Test I positive.

<u>In tetrahydrofuran at -30°C</u> 1<u>H</u>,4-Chlorooctaphenyltetrasilane, 7.65 gm. (0.01 mole), in 75 ml. of tetrahydrofuran was treated with 25 ml. of 0.485 M phenyllithium (0.012 mole) in ether at -30°C. After 45 minutes of stirring, the reaction mixture was rapidly hydrolyzed and the products isolated as described in the previous experiment to give 2.0 gm. (27%) of IIa, 0.1 gm. (1.5%) of Ia, and 0.5 gm. (7%) of an unknown solid melting over the range 203-211°C.

<u>In tetrahydrofuran at -70°C</u> Fifteen ml. of 0.485 M phenyllithium-ether (0.0073 mole) was added to a mixture containing 75 ml. of tetrahydrofuran and 7.65 gm. (0.01 mole) of 1<u>H</u>,4-chlorooctaphenyltetrasilane at -70°C. A bright orange color appeared and slowly faded after stirring for 1.5 hours.

An additional 5 ml. of the phenyllithium-ether mixture (0.0024 mole) was then added and the color became a dark reddish-brown which did not fade after 45 minutes. The reaction mixture was then rapidly hydrolized and the products were isolated as described in the previous experiments. The crude yield included three fractions: 1.5 gm. (20%), melting over the range 195-205°C; 3.1 gm. (42.5%), melting over the range 187-193°C; and 0.5 gm. (7%), melting over the range 147-155°C. Several recrystallizations gave 0.3 gm. of a solid which had a constant m.p. (199-201°C). A mixture m.p. of this compound with an authentic sample of 1,1,2,2,3,3,4,4-nonaphenyltetrasilane, m.p. 200-202°C, was depressed. Another fraction, 1.2 gm., had a constant m.p. of 218-220°C. Based on the ultraviolet spectrum in cyclohexane ($\lambda_{max.}$ 313.5 mμ), the infrared spectrum (which showed a strong SiH bond absorption at 4.76 μ (in CS_2) and the molecular weight determinations, the latter compound is believed to contain seven silicon atoms in the chain (86) and is probably 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7-pentadecaphenylheptasilane.

<u>Anal</u>. Calcd. for $C_{90}H_{76}Si_7$: mol. wt. 1352. Found: mol. wt. 1342, 1318, 1337, 1263.

<u>1H,4-Chlorooctaphenyltetrasilane and phenylmagnesium bromide (attempted)</u>

A mixture containing 7.65 gm. (0.01 mole) of 1<u>H</u>,4-chlorooctaphenyltetrasilane, 75 ml. of tetrahydrofuran and 25 ml. of 0.5 M phenylmagnesium bromide-tetrahydrofuran (0.0125 mole) was refluxed for 4 days. The mixture was then hydrolyzed with a 1% hydrochloric acid solution, extracted with ether, evaporated to dryness and the residue recrystallized in a benzene-petroleum ether (b.p. 60-70°C) mixture. An 88% recovery (6.7 gm.) of starting material was the only isolable product, m.p. and mixture m.p. 161-163°C.

1H,4-Chlorooctaphenyltetrasilane and phenylmagnesium iodide (attempted)

Phenylmagnesium iodide-ether, 18 ml. of 0.81 M (0.0146 mole), 1*H*,4-chlorooctaphenyltetrasilane, 7.65 gm. (0.01 mole), and 75 ml. of tetrahydrofuran were stirred at reflux temperature for 3 days. Color Test I was positive. Hydrolysis and work-up as in the previous experiment gave 6.4 gm. (84%) of starting material, m.p. 160-163°C, and 0.1 gm. (1.3%) of solids melting over the range 210-214°C.

Reactions of Decaphenylcyclopentasilane

Decaphenylcyclopentasilane with phosphorus pentachloride

In benzene in a 1:2 molar ratio (attempted) Decaphenylcyclopentasilane, 10.0 gm. (0.011 mole), phosphorus pentachloride, 4.2 gm. (0.022 mole), and 150 ml. of benzene were refluxed together for 2.5 hours. The solvent was then removed by distillation under reduced pressure. The residue, dissolved in 30 ml. of benzene, was then poured into 200 ml. of petroleum ether (b.p. 60-70°C). Filtration after 2 hours yielded

8.4 gm. (84%) of starting material, m.p. and mixture m.p. 456-464°C. Concentration of the filtrate yielded an additional 1.2 gm. (12%) of impure starting material, m.p. 432-440°C.

A duplicate reaction using xylene as solvent was carried out with a reaction time of 8 hours at 138°C. A quantitative recovery of the starting material (97%) resulted.

<u>In benzene in a 1:5 molar ratio</u> Decaphenylcyclopentasilane, 5.0 gm. (0.007 mole), phosphorus pentachloride, 7.1 gm. (0.034 mole), and 100 ml. of benzene were refluxed for 16 hours with stirring. Approximately 70 ml. of the solvent was then removed by distillation under reduced pressure. The remaining solution was then poured into 500 ml. of petroleum ether (b.p. 60-70°C) and filtered after 2-3 minutes. A light brown solid, 1.7 gm. (34%), melting over the range 380-420°C was obtained and identified, upon recrystallization, as unreacted starting material, m.p. 456-464°C. The filtrate, after standing overnight, yielded 2.5 gm. (68%) of 1,5-dichlorodecaphenylpentasilane, m.p. and mixture m.p. 180-184°C (see below).

<u>In 1,1,2,2-tetrachloroethane</u> Decaphenylcyclopentasilane, 20.0 gm. (0.022 mole), and phosphorus pentachloride, 5.0 gm. (0.024 mole), were added to 100 ml. of 1,1,2,2-tetrachloroethane. The suspension, soluble at 80°C, was refluxed for 15 minutes. The solvent (b.p. 65-70°C/20 mm.) was then removed by distillation under reduced pressure over a steam bath. The residue, dissolved in 20 ml. of benzene, was poured

into 200 ml. of rapidly stirred petroleum ether (b.p. 60-70°C). After stirring for 1 hour, 18.6 gm. (86%) of solid melting at 180-182°C was obtained. Recrystallization gave the constant m.p., 179-180°C. An infrared spectrum using KBr cells and carbon disulfide as solvent showed Si-Cl absorptions at 519 and 550 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane gave $\lambda_{max.}$ 292.5, 265 (sh) mμ.

Anal. Calcd. for $C_{60}H_{50}Cl_2Si_5$: Si, 14.30. Found: Si, 14.40, 14.37%.

Three similar reactions were carried out using 10.0 gm. (0.011 mole) of IIa and 2.5 gm. (0.012 mole) of phosphorus pentachloride in 100 ml. of 1,1,2,2-tetrachloroethane. The reaction mixtures were refluxed for six minutes, two hours and four hours. The results are given in Table 4. It was observed that maximum yields were obtained in 15 minutes or less with decreasing yields, probably due to secondary cleavages, of 1,5-dichlorodecaphenylpentasilane occurring with longer reaction times. All of the reactions of IIa with phosphorus pentachloride are summarized in Table 4.

In carbon tetrachloride Decaphenylcyclopentasilane, 10.0 gm. (0.011 mole), phosphorus pentachloride, 4.2 gm. (0.02 mole), and 100 ml. of carbon tetrachloride were refluxed together for 5 hours. Approximately 80 ml. of the solvent was then removed by distillation under reduced pressure. The reaction mixture was then poured into 400 ml. of petroleum ether (b.p. 60-70°C) and filtered after 2-3 minutes. Unreacted

Table 4. Decaphenylcyclopentasilane with phosphorus pentachloride

Molar ratio	Solvent	Time hours	Temp. °C	Products IIa[a]	(%) 1,5-[b]	Others[c]
1:2	benzene	2.5	80	92	--	--
1:5	benzene	16	80	34	46	--
1:1	xylene	8	138	96	--	--
1:2	CCl_4	5	78	73	23	--
1:1	CCl_4	24	78	78	13	trace
1:1	$C_2H_2Cl_4$	0.1	142	10	69	"
1:1	"	0.25	142	--	86	"
1:1	"	2	142	--	50	13
1:1	"	24	142	--	30	15

[a] Unreacted starting material.

[b] 1,5-Dichlorodecaphenylpentasilane.

[c] Low melting solids melting over the range 150-165°C. The remainder of the reaction residue consisted of unidentified viscous oils.

starting material, 7.3 gm. (73%), was obtained, m.p. and mixture m.p. 454-464°C. Concentration of the filtrate yielded an additional 2.5 gm. (23%) of a solid melting at 173-176°C. This material was recrystallized and identified by mixed m.p. (178-180°C) as 1,5-dichlorodecaphenylpentasilane.

A second reaction mixture using 10.0 gm. (0.011 mole) of

IIa and 2.5 gm. (0.012 mole) of phosphorus pentachloride in 100 ml. of carbon tetrachloride was refluxed for 24 hours. Work-up gave 7.8 gm. (78%) of IIa and 1.4 gm. (13%) of 1,5-dichlorodecaphenylpentasilane.

Decaphenylcyclopentasilane and 1,1,2,2-tetrachloroethane

Decaphenylcyclopentasilane, 20.0 gm. (0.022 mole), and 100 ml. of 1,1,2,2-tetrachloroethane were refluxed at 140°C for 50 hours. The solvent was then removed by distillation under reduced pressure. The residue, dissolved in 60 ml. of benzene, was added to 600 ml. of rapidly stirred petroleum ether (b.p. 60-70°C). The crude yield of product, m.p. 176-179°C, was 15.2 gm. (70.5%). Recrystallization gave a m.p. and mixture m.p. of 179-180°C. No attempt was made to identify small amounts of lower melting solids.

A similar reaction run for 36 hours gave 2.7 gm. (13.5%) of unreacted decaphenylcyclopentasilane and 13.6 gm. (63%) of 1,5-dichlorodecaphenylpentasilane. A third reaction with a reaction time of 24 hours gave 8.0 gm. (40%) of unreacted starting material and 6.5 gm. (30%) of 1,5-dichlorodecaphenylpentasilane.

Decaphenylcyclopentasilane with chlorine

A series of reactions was carried out in which decaphenylcyclopentasilane, 10.0 gm. (0.011 mole), was dissolved in 100 ml. of benzene or carbon tetrachloride. Chlorine gas was then introduced into the rapidly stirred solution through a sintered glass gas diffusion tube at a constant rate (approximately 200 ml./min.) for a specified time. The reaction was then quenched by the rapid removal of excess chlorine under reduced pressure. The products were isolated by fractional crystallization from benzene-petroleum ether (b.p. 60-70°C) mixtures.

A typical example using benzene as solvent involved the addition of chlorine at 200 ml./min. for 15 minutes. The excess chlorine and all but 30-35 ml. of the solvent was then quickly removed using a water aspirator and steam bath. The mixture was then added to 400 ml. of petroleum ether (b.p. 60-70°C), stirred for 1 hour and filtered. 1,5-Dichlorodecaphenylpentasilane, 3.25 gm. (30%), was obtained, m.p. and mixture m.p. 178-179°C. Evaporation of the filtrate to 20 ml. and addition of 50 ml. of petroleum ether (b.p. 60-70°C) gave, after standing overnight, 2.0 gm. (29%) of solid, m.p. 125-130°C. Recrystallization gave a m.p. of 126-128°C which was not depressed by a mixture m.p. with an authentic sample of 1,3-dichlorohexaphenyltrisilane. The filtrate was then evaporated to dryness and 25-30 ml. of petroleum ether (b.p. 60-70°C) added hot. Upon standing overnight, 1.0 gm. (19%) of material, m.p. 115-120°C, was obtained. Recrystallization of this material gave a m.p. of 116-117°C which was not depressed upon admixture with an authentic sample of 1,2-dichlorotetraphenyldisilane. The results of this series of reactions are summarized in Table 5.

Table 5. Decaphenylcyclopentasilane with chlorine

Solvent	Time min.	Temp. $^{\circ}C$	Starting material (%)	Dichloro derivatives (%)[a,b]		
				1,5-	1,3-	1,2-
benzene	10	18 - 20[c]	32	61	--	--
"	15	"	trace	76	--	--
"	30[d]	"	--	33	--	10
"	60	"	--	--	--	--
"	5	25 - 39	30	55	--	--
"	8	25 - 39	trace	78	--	--
"	10	25 - 44	--	53	--	--
"	15	25 - 46	--	30	30	19
"	20	25 - 46	--	trace	33	29
"	5	76 - 80	25	68	--	--
CCl_4	10	18 - 19[c]	73	70	--	--
"	30	21 - 25[c]	8.5	50	--	--
"	60[e]	25 - 35	--	--	trace	75
"	240	25 - 35	--	--	--	--

[a] Based on unrecovered starting material.

[b] The remainder of the reaction residue was an unidentified viscous oil.

[c] The temperature was regulated by a cooling bath.

[d] With reactions over 20 min. mixtures of hexachlorocyclohexane isomers were isolated when using benzene.

[e] The chlorine gas flow rate was not constant.

In ether Decaphenylcyclopentasilane, 10.0 gm. (0.011 mole), suspended in 90 ml. of ether was treated with chlorine at 200 ml./min. for 1 hour. Work-up yielded 8.6 gm. (86%) of starting material, m.p. and mixture m.p. 446-456°C. Evaporation of the filtrate yielded 1.2 gm. (11%) of 1,5-dichlorodecaphenylpentasilane, m.p. and mixture m.p. 178-180°C.

A similar reaction using petroleum ether (b.p. 60-70°C) or *n*-pentane as solvents with 10.0 gm. (0.011 mole) of IIa and addition of chlorine for 10 to 20 minutes gave a quantitative recovery of the starting material. Increasing the addition time of the chlorine to more than 30 minutes resulted in less recovered starting material. However, multiple cleavage occurred which made the products difficult to separate. Distillation of the solvents gave a mixture of high boiling liquids. The hydrocarbons were probably being chlorinated thus changing the solvent system and causing faster multiple cleavages of the polysilanes (see above). Addition of chlorine to *n*-pentane for 30 minutes at 200 ml./min. gave the same chlorinated products in the same ratio as found in reactions with IIa. The results were determined by gas phase chromatography.

Decaphenylcyclopentasilane with hydrogen halides (attempted)

Hydrohalogenation of IIa was attempted with various hydrogen halides using a variety of conditions with regard to solvent, temperature and time. In only two instances was there any appreciable reaction and in these cases secondary cleavage of the polysilane occurred to give intractable products. The attempted reactions, the conditions used and their results are tabulated in Table 6.

Decaphenylcyclopentasilane with organic halides (attempted)

Attempted reactions of IIa were carried out with _t_-butyl chloride, _t_-butyl bromide, 1,2,3,4,5,6-hexachlorocyclohexane and β,β'-dichlorodiethyl ether under conditions for which Ia reacted readily. A high recovery of starting material resulted with small amounts of viscous oils being isolated in each instance. The results are given in Table 7.

Decaphenylcyclopentasilane with hydrogen chloride at high pressure

A 68 gm. sample of IIa (0.0745 mole) was placed in a stainless steel autoclave and hydrogen chloride gas was added to a pressure of 300 p.s.i. (0.83 mole, a 11-fold excess) at 27°C. Over a period of 4 hours the autoclave was slowly heated to 143°C (320 p.s.i. pressure). At 85°C the pressure was 380 p.s.i. Upon cooling and release of the excess gas from the autoclave through a trap immersed in a dry ice-acetone bath, a mixture of liquids and solids was obtained. Distillation provided 32 gm. of benzene, b.p. 79-80°C, n_D^{20} 1,5085 (ref. sample n_D^{20} 1.5090). This accounts for 54.7% of the available phenyl groups. No further attempt to isolate or identify the products was made.

Table 6. Decaphenylcyclopentasilane with hydrogen chloride and hydrogen bromide (attempted)

IIa (mole)	Solvent (ml.)	Gas used	Temp. (°C)	Time hours	IIa recovered (%)
0.018	o-Dichlorobenzene (250)	HCl	170	10	84
0.019	o-Dichlorobenzene (200)	HCl	175	45	83
0.016	o-Dichlorobenzene (200)	HBr	170	7	37.5
0.022	Xylene (200)	HBr	138	48	91
0.022	Bromobenzene (200)	HBr	153	31	92.5
0.011	m-Dibromobenzene (70)	HBr	210	16	---
0.022	Triethylbenzene (150)	HBr	205	19	71

Decaphenylcyclopentasilane and nitrobenzene

A 10 gm. (0.011 mole) sample of IIa and 75 ml. of nitrobenzene were refluxed for 24 hours. Removal of the solvents by distillation under reduced pressure and addition of 50 ml. of acetone to the residue gave 2.1 gm. (21%) of IIa, m.p. 468-474°C. The tarry black filtrate was partly decolorized with activated charcoal and approximately 0.1 gm. of crystalline solids were removed with a spatula from the sides of the flask as the acetone evaporated. Recrystallization of these crystals gave impure solids having melting ranges of 178-180°

Table 7. Decaphenylcyclopentasilane with organic halides

IIa (mole)	Solvent (ml.)	Halide used	Temp. (°C)	Time hours	IIa recovered (%)
0.011	"neat" (100)	$(ClEt)_2O$[a]	170	11	86
0.036	Decalin (80)	$C_6H_6Cl_6$	150-160	24	95
0.0296	Decalin (100)	t-BuCl[b]	150	22	98
0.066	o-Dichlorobenzene (100)	t-BuCl	158	70	77[c]
0.066	Decalin (75)	t-BuBr[d]	153-166	48	91

[a] β,β'-Dichlorodiethyl ether.

[b] t-Butyl chloride.

[c] An infrared spectrum of vapors from a cold-trap connected to the condenser indicated that a small amount of olefin had been formed.

[d] t-Butyl bromide.

C, 160-164°C and 166-184°C. Ultraviolet, spectrum of the solids gave $\lambda_{max.}$ 253.5 mμ, 259, 264, 270.5 showing that the solid contained no polysilanes. An infrared spectrum showed Si-phenyl absorptions at 8.88, 8.92, and 9.68 and Si-O-Si bond absorptions at 9.25 (w) and 9.88 μ. These absorptions were identical to those in the spectrum of a mixture of octaphenylcyclotetrasiloxane and hexaphenylcyclotrisiloxane. No other crystalline solids were obtained upon treatment of the tarry residues with ethanol or petroleum ether (b.p. 60-70°C).

Dodecaphenylcyclohexasilane and nitrobenzene (attempted)

Dodecaphenylcyclohexasilane, 2.0 gm. (0.0018 mole) was heated in 50 ml. of refluxing nitrobenzene for 24 hours. The mixture was then cooled and filtered to give a quantitative recovery (2.0 gm.) of starting material, m.p. 492-500°C.

Hexaphenyldisilane and nitrobenzene (attempted)

A 10.4 gm. sample of hexaphenyldisilane (0.02 mole) was heated at 180-200°C for 24 hours in 75 ml. of nitrobenzene. The reaction mixture was then cooled and filtered to give 9.95 gm. (96%) of starting material, m.p. and mixture m.p. 368-370°C. The filtrate was concentrated to give an additional 0.1 gm. (1%) melting over the range 340-380°C.

1,5-Dihydroxydecaphenylpentasilane

1,5-Dichlorodecaphenylpentasilane, 5.0 gm. (0.005 mole), in 75 ml. of tetrahydrofuran was added to 20 ml. of 0.1 N hydrochloric acid and allowed to stand two days. The solvent was then removed by distillation under reduced pressure with a steam bath. The residue was dissolved in 25 ml. of benzene to which was added 30 ml. of petroleum ether (b.p. 60-70°C). The product, 5.0 gm. (102%), melted at 169-176°C. After several similar recrystallizations, 2.5 gm. (51%) of pure 1,5-dihydroxydecaphenylpentasilane, m.p. 174-176°C, was obtained. Identification was made by mixture m.p. (174-176°C) with an authentic sample obtained from the hydrolysis of 1.5-dibromodecaphenylpentasilane (9).

1,5-Di-n-Propoxydecaphenylpentasilane

1,5-Dichlorodecaphenylpentasilane, 3.0 gm. (0.003 mole), was added to 100 ml. of n-propanol and refluxed for 3-4 hours. The reaction was then cooled and filtered. The product, 2.8 gm. (91.7%), melted at 190-192°C. Recrystallization from benzene gave 1.6 gm. (52.5%) of pure material, m.p. 196-197°C.

An NMR spectrum of the product showed a triplet centered at 9.41 τ, a quartet centered at 8.82 τ and a triplet at 6.89 τ, indicative of the methyl, methylene, and methylene adjacent to oxygen protons, respectively. The aryl multiplet was centered at 3.13 τ. An average aryl to aliphatic proton ratio of 49.9:14 was found (3 determinations). Calculated ratio: 50:14. The ultraviolet spectrum in cyclohexane gave $\lambda_{max.}$ 294.5 mμ.

Anal. Calcd. for $C_{66}H_{64}O_2Si_5$: Si, 13.64. Found: Si, 13.71, 13.61, 13.62%.

1,5-Diallyloxydecaphenylcyclopentasilane

Allyl alcohol was purified by boiling with anhydrous potassium carbonate for 1 to 2 hours and then decanting off the liquid. This procedure was repeated four times. The alcohol was then distilled through a 12 in. by 11 mm. glass packed column from a flask containing 50 gm. of anhydrous potassium carbonate.

A 10.0 gm. (0.01 mole) sample of 1,5-dichlorodecaphenylpentasilane was heated in 100 ml. of the purified allyl alcohol for 10 hours. The dichloro compound slowly dissolved and after two hours of heating a white solid was slowly precipitated. Upon cooling and filtering the mixture, 5.9 gm. of a white crystalline solid was obtained, m.p. 175-177°C. Recrystallization from benzene-petroleum ether (b.p. 60-70°C) mixtures gave 4.9 gm. (47%) having a constant m.p. (175-176°C). A mixture m.p. with 1,5-dihydroxydecaphenylpentasilane, m.p. 176-177°C, was depressed (167-176°C). The infrared spectrum (in CS_2) of the compound, believed to be 1,5-diallyloxydecaphenylpentasilane, showed absorptions at 3.51, 9.45 and 10.88 μ assignable to the aliphatic CH, COSi and CH_2=CH vibrations, respectively (102, 103). The ultraviolet absorption spectrum in cyclohexane gave $\lambda_{max.}$ 294.5, 253 (sh) mμ.

Anal. Calcd. for $C_{66}H_{60}O_2Si_5$: Si, 13.68. Found: Si, 13.73, 13.76%.

Concentration of the filtrate gave an additional 1.9 gm. (20%) of a solid, m.p. 174-176°C. A mixture m.p. of this sample and 1,5-dihydroxydecaphenylpentasilane was not depressed. An infrared spectrum of this material showed absorptions at 2.7 and 12.3 μ assigned to the SiOH group (102).

Dodecaphenylpentasilane

Bromine, 3.3 gm. (0.021 mole), was added to 18.2 gm. of IIa dissolved in 100 ml. of benzene. The mixture was stirred at room temperature for 3 to 4 hours. The solvent was then removed under reduced pressure with a steam bath and the residue dissolved in 30 ml. of benzene. Petroleum ether (b.p. 60-70°C) was added and after standing two days 17.3 gm. (81%) of 1,5-dibromodecaphenylpentasilane, m.p. and mixture m.p. 205-207°C, was precipitated.

A 5.4 gm. (0.005 mole) sample of the above dibromide was dissolved in 47 ml. of benzene and 100 ml. of ether was added. Twenty ml. of a 0.65 M phenyllithium-ether solution (0.012 mole) was added and after 8 hours of stirring Color Test I remained positive. Upon work-up and fractional crystallization in benzene-petroleum ether (b.p. 60-70°C), only two pure samples were isolated. A 0.2 gm. (4%) sample of 1,5-dihydroxydecaphenylpentasilane was isolated, m.p. and mixture m.p. 174-176°C. A 0.15 gm. (3%) sample having a constant m.p. (231-232°C) was obtained and is believed to be dodecaphenylpentasilane. An infrared spectrum of the compound (in CS_2) was superimposable on the spectrum of IIa. The ultraviolet spectrum in cyclohexane gave $\lambda_{max.}$ 297 mμ.

Anal. Calcd. for $C_{72}H_{60}Si_5$: mol. wt. 1065. Found: mol. wt., 1067.

1,5-Dibromodecaphenylpentasilane with phenylmagnesium bromide

A 5.4 gm. (0.005 mole) sample of the previously prepared 1,5-dibromodecaphenylpentasilane in 30 ml. of tetrahydrofuran was treated with 120 ml. of a 0.8 M phenylmagnesium bromide-tetrahydrofuran solution (0.1 mole). The mixture was heated at the reflux temperature for 5 days. During the last day solvent was removed until the temperature reached 90°C. After hydrolysis, all attempts to obtain crystalline solids from benzene-petroleum ether mixtures failed. However, after removal of the solvents and allowing the oily residues to stand for several weeks, a few well formed clear crystals were handpicked with tweezers to yield 0.1 gm. of tetraphenylsilane, m.p. and mixture m.p. 234-236°C. Identification was confirmed by comparison of infrared and ultraviolet spectra.

Reactions of Dodecamethylcyclohexasilane

Dodecamethylcyclohexasilane with hydrogen chloride

In benzene (attempted)   A 21 gm. (0.06 mole) sample of IIIa dissolved in 300 ml. of benzene was treated with a continuous slow addition of hydrogen chloride at 80°C. Every 4 to 8 hours a small sample of the reaction mixture was removed for a vapor phase chromatographic analysis. After 48 hours there was no indication of any reaction products having been formed. Removal of the solvents under reduced pressure left 21.7 gm. (103%) of solid, crystalline starting material, identified by VPC.

In petroleum ether (b.p. 60-70°C) (attempted)   A 21.0 gm. (0.06 mole) sample of IIIa dissolved in 100 ml. of petroleum ether (b.p. 60-70°C) was treated as above with hydrogen chloride at 67°C. A vapor phase chromatographic analysis indicated that no trace of a reaction had occurred after 48 hours. The solvent was removed under reduced pressure and the residue washed with acetone to give an 86% (18.1 gm.) recovery of pure starting material, identified by VPC.

In chloroform (attempted) Compound IIIa, 21.0 gm. (0.06 mole) was dissolved in 150 ml. of chloroform and the mixture heated to the reflux temperature, 62°C. Hydrogen chloride gas was added continuously for 120 hours.

Vapor phase chromatographic analysis indicated that no reaction had occurred. Evaporation of the solvents under reduced pressure with a rotary evaporator left 21.0 gm. (100%) of solid crystalline residue. The residue was washed with ca. 20 ml. of acetone to give an 18.1 gm. (86%) recovery of pure starting material, identified by VPC.

In carbon tetrachloride (attempted) Compound IIIa, 21.0 gm. (0.06 mole) was dissolved in 300 ml. of carbon tetrachloride and the mixture heated to 78°C. Hydrogen chloride gas was added continuously for 30 hours. Vapor phase chromatographic analysis indicated that no reaction had occurred. Removal of the solvent gave a 65% (13.6 gm.) recovery of starting material.

In o-dichlorobenzene Hydrogen chloride was added to a mixture containing 21.0 gm. (0.06 mole) of IIIa and 300 ml. of o-dichlorobenzene in the manner described above. The gas was added continuously for 36 hours at 175-178°C. A sample was taken for a vapor phase chromatographic analysis every 4 to 8 hours. A sample taken after the addition of hydrogen chloride for 4 hours showed five components to be present in the reaction mixture. Later comparisons of VPC retention times with those of pure samples indicated the major products at this stage to be 1*H*,6-chlorododecamethylhexasilane and 1*H*,-5-chlorodecamethylpentasilane. Gas phase chromatography showed that the relative concentration of these two compounds remained approximately equal and reached a maximum concentration at 10 to 12 hours. After this time the concentrations of IIIa, 1*H*,6-chlorododecamethylhexasilane and 1*H*,5-chlorodecamethylpentasilane were about equal and an increase in the proportion of lower boiling products was evident. A sample taken after a 24 hour reaction time showed only traces of IIIa, and the 1*H*,6-chloro and 1*H*,5-chloro compounds to be present.

Distillation of the product mixture through a 12 mm. x 20 cm. glass packed column gave no pure products. The major products appeared to have boiling point ranges too near that of the solvent for easy separation. Gas phase chromatography indicated that 1,2-dichlorotetramethyldisilane and 1,3-dichlorohexamethyltrisilane were present in the crude fractions.

A second reaction was carried out in which a mixture containing 87 gm. (0.25 mole) of IIIa in 200 ml. of *o*-dichlorobenzene was heated to 184°C and hydrogen chloride added continuously for 29 hours. In an attempt to remove low boiling products as they were formed, a 12 mm. by 25 cm. glass packed column and distillation head were attached to the reaction flask.

The hydrogen chloride gas used was passed through concentrated sulfuric acid before entering the reaction vessel.

A vapor phase chromatogram, after 29 hours of reaction, indicated very little decrease in the concentration of the starting material. The distillate collected, ca. 50 ml., showed the major component to be solvent. No further work-up or identification was attempted.

In xylene A 21.0 gm. (0.06 mole) sample of IIIa dissolved in 300 ml. of xylene was treated continuously with hydrogen chloride for 70 hours at 139°C. Periodic vapor phase chromatographic analysis showed the reaction to be quite slow, with a multitude of products slowly being formed. The rate of reaction of the higher polysilanes appeared to be about equal to that of the cyclic compound IIIa.

The solvent was removed by distillation and 3.6 gm. (17%) of crystalline starting material was obtained by filtration of the reaction mixture. The filtrate, 12.0 gm. (57% based on starting material), was distilled through a 12 mm. by 20 cm. glass packed column under reduced pressure. No pure fractions were obtained but comparison of gas chromatograms of known dichloro compounds and later identified αH,ω-chloro compounds showed the following compounds to be present: 1H,-chlorohexamethyltrisilane, 1,3-dichlorohexamethyltrisilane, 1H,4-chlorooctamethyltetrasilane, 1,4-dichlorooctamethyltetrasilane, 1<u>H</u>,5-chlorodecamethylpentasilane, 1<u>H</u>,6-chlorododecamethylhexasilane, IIIa and 1,6-dichlorododecamethylhexasilane.

Comparison of the chromatogram peak areas indicated dichloro compounds to be in excess (<u>ca</u>. 2:1) except for the hexa- and pentasilanes. The ratio was reversed for the hexasilanes. It was later found that, at the temperature used for the gas chromatogram, any 1,5-dichlorodecamethylpentasilane present would have had the same retention time as the starting material.

In a second reaction 105 gm. (0.3 mole) of IIIa, dissolved in 200 ml. of xylene, was heated to 143°C and hydrogen chloride added at a slow continuous rate for four days. The solvent was removed by distillation under reduced pressure. Distillation of the product mixture under reduced pressure through a 12 mm. by 20 cm. glass packed column gave 14 liquid fractions having a total weight of 27.1 gm. (25.7% based on starting material). The residue was then cooled and crystalline IIIa precipitated upon standing. The liquid was decanted into a 250 ml. flask attached to a Widmer spiral and an additional 8 fractions (17.0 gm., 16.2% based on starting material) were collected by distillation under reduced pressure. Table 8 lists the products identified and their approximate yield, as determined by vapor phase chromatography using known or later identified compounds.

Redistillation of the above fractions gave 1.5 gm. (1.2%) of 1<u>H</u>,3-chlorohexamethyltrisilane, b.p. 89-90°C/35 mm. (extra-

Table 8. Dodecamethylcyclohexasilane with hydrogen chloride in xylene

Product	$Cl-(SiMe_2)_n-X$	Yield ± 2%	
n	X	gm.	%
3	H	5.0	4
3	Cl	6.0	4
4	H	4.5	3.7
4	Cl	4.6	3.3
5	H	5.4	4.5
6	H, Cl	10.5	9

polated b.p. 183°C/760 mm., calcd. b.p. 183°C) (27,104) n_D^{23} 1.4740. The ultraviolet absorption spectrum in cyclohexane gave $\lambda_{max.}$ 217 mμ.

Anal. Calcd. for $C_6H_{19}ClSi_3$: Cl, 16.81; mol. wt. 210.8. Found: Cl, 16.17%; mol. wt., 245, 250. (Difficulties in determining mol. wt. values have been experienced with similar known methylsilanes[1]).

Also obtained pure was 1.8 gm. (1.2%) of 1,3-dichlorohexamethyltrisilane, b.p. 92-95°C/11 mm., n_D^{20} 1.4850. The ultra-

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[1] J. M. Holmes. Iowa State University of Science and Technology, Ames, Iowa. Information on mol. wt. determinations of polysilanes. Private communication. 1965.

violet absorption spectrum in cyclohexane gave $\lambda_{max.}$ 217 mu. (lit. b.p. 89-92°C/15 mm., n_D^{20} 1.4852 UV spectrum cyclohexane gave $\lambda_{max.}$ 218.5 mμ.) (19, 87).

A third component obtained was 1<u>H</u>,4-chlorooctamethyltetrasilane, 1.5 gm. (1.2%), b.p. 66-70°C/1.5-2.0 mm. (extrapolated b.p. 243°C/760 mm., calcd. b.p. 239°C), n_D^{23} 1.4983. The ultraviolet absorption spectrum in cyclohexane gave $\lambda_{max.}$ 234.5 mμ.

<u>Anal.</u> Calcd. for $C_8H_{25}ClSi_4$: Cl, 13.2; mol. wt., 269.0. Found: Cl, 14.4, 14.0%; mol. wt. 277, 284.

<u>In dichloromethane</u> Hydrogen chloride gas was added at a slow rate for 8 days to 21.0 gm. of IIIa (0.06 mole) dissolved in 50 ml. of dichloromethane. Solvent was lost from the heated reaction mixture (40-55°C) <u>via</u> the gas stream and it was necessary to add additional solvent periodically. Vapor phase chromatographic analysis of samples removed daily indicated that the reaction rate was very slow with the product distribution being about the same as in the previous reaction. Removal of the solvent left 21.0 gm. of liquid which was distilled under reduced pressure to give 13 fractions totalling 18 gm. (86% based on starting material). A vapor phase chromatogram of the fractions showed no pure products, but comparison with retention times, boiling points and refractive indices of samples obtained pure in later reactions showed the compounds in the series $H-(SiMe_2)_n-Cl$, where n = 3 to 6, and compounds in the series $Cl-(SiMe_2)_n-Cl$, where n = 3, 4

and 6. The yields of the products could not be determined.

A second reaction was carried out in which 105 gm. (0.3 mole) of IIIa, dissolved in 250 ml. of dichloromethane, was heated to 42°C and treated with hydrogen chloride gas for approximately three days. The gas was dried by bubbling it through two bottles of concentrated sulfuric acid before it entered the reaction flask. Analysis of a sample of the reaction mixture by vapor phase chromatography indicated that no reaction had occurred. Removal of the solvent with a rotary evaporator gave 99.8 gm. (95%) of starting material, m.p. and mixed m.p. 255-258°C. Other than the drying of the gas, there was no apparent reason for the lack of reaction.

Dodecamethylcyclohexasilane and hydrogen chloride at high pressures

In a 1:3 molar ratio   A 175.5 gm. sample (0.5 mole) of IIIa was placed in a 1 l. stainless steel autoclave. The autoclave was purged with a rapid stream of nitrogen for 45 minutes and then hydrogen chloride gas was added to a pressure of 510 p.s.i. at 25°C (1.4 moles). A pressure drop of 70 p.s.i. was observed after 30 minutes. Sixty p.s.i. of gas was added and there was a pressure drop of 10 p.s.i. in 30 minutes. The pressure was brought up to 500 p.s.i. with hydrogen chloride (total HCl 1.6 moles, 58 gm.). The autoclave was then slowly heated to 80°C over 65 minutes (pressure 560 p.s.i.). After 70 minutes the temperature was 113°C and then quickly rose to 175°C in the next 5 minutes. After

80 minutes the temperature had dropped to 170°C and the pressure was 380 p.s.i. Upon cooling to 35°C, the pressure was 210 p.s.i. (0.56 mole gas). The gas was released through a dry ice-acetone trap. The volatile materials condensed in the trap and the contents of the autoclave weighed 230 gm., an increase of 55 gm. over the weight of starting material.

A second reaction was carried out in the same manner as above. As before the reaction slowly became exothermic above 70°C (heating time 70 min.) with a very fast rise in temperature above 115°C to a maximum of 177°C. Upon cooling to 11°C, the pressure was 290 p.s.i. (0.85 mole gas). The products, 235 gm., showed a weight gain of 60 gm. over the starting material.

The two reaction mixtures were combined and distilled through a Todd Stedmann, 12 mm. by 90 cm., glass packed column with an automatic distillation head set at a reflux ratio of 10:1. The over-all yield of products obtained from these reactions is included in Table 17. The yields are based on the sum of the pure fractions obtained plus estimated yields of intermediate fractions by comparison of peak areas of their vapor phase chromatograms. Pure fractions of all compounds of the series $Cl-(SiMe_2)_n-Y$, where n = 1-4 and Y = hydrogen or chlorine, were obtained from this reaction. Higher boiling fractions were combined with comparable fractions in the next reaction for final purification.

A 11.0 gm. (3%) recovery of starting material, identified by VPC, was made. However, VPC analysis of the high boiling fractions mentioned showed considerable quantities of IIIa to be present.

<u>In a 1:2 molar ratio</u> One-half mole, 175 gm., of IIIa was added to the Parr stainless steel autoclave and the system was purged with nitrogen. Hydrogen chloride, 360 p.s.i. at 25°C (1.0 mole), and nitrogen (280 p.s.i., 0.89 mole at 27°C) were added. The autoclave was heated for 8 hours at 40°C. Release of the gas and removal of the solids gave a 175 gm. (100%) recovery of starting material, shown to be pure by VPC.

The reaction was repeated and the autoclave was heated at 56°C for 20 hours. The reaction mixture was then cooled (pressure 410 p.s.i. at 27°C) and the gas was removed through a dry ice-acetone trap. The contents of the autoclave were poured through a Büchner funnel, without filter paper, to obtain 56.8 gm. of wet solid which, when washed with cold acetone, gave 38.6 gm. (22%) of pure starting material, m.p. and mixture m.p. 252-254°C.

A third reaction was carried out in the autoclave with 175 gm. (0.5 mole) of IIIa, 360 p.s.i. of hydrogen chloride at 27°C (1.0 mole, 36 gm.) and 240 p.s.i. of nitrogen at 27°C. The mixture was heated at 60°C for 48 hours (pressure 590 p.s.i. at 57°C) and then cooled to room temperature. Work-up as above provided a 15.7 gm. recovery of starting material, m.p. and mixture m.p. 253-257°C. The product mixture weighed

207 gm., a weight gain of 32 gm.

The latter two reaction products were combined and distilled, as described in the 1:3 molar ratio reaction, to give the product distribution and yields reported in Table 17. Pure fractions, as indicated by VPC analysis, of all compounds in the series Cl-$(SiMe_2)_n$-Y, where n = 3-6 and Y = hydrogen or chlorine, were obtained. Over-all yields were determined as in the 1:3 molar ratio reaction. The purity of all major fractions was estimated to be in excess of 95%. An additional 21 gm. (6%) of crystalline starting material was recovered during the distillation. IIIa co-distils with the compound 1,5-dichlorodecamethylpentasilane and a redistillation was made several times to provide as pure a sample as possible. However, a mass spectrum analysis which showed mass 360 for the molecular ion (calcd. 360) also showed a small peak at 348 due to trace impurities of IIIa not detectable by VPC. A mass spectrum of IIIa was used for comparison. IIIa is only partly soluble in all of the penta-and hexasilane homologs and most of it can be removed by decanting or filtration. Distillation of the higher molecular weight fractions was found to be more successful using a Nestar/Faust spinning spiral 18 inch by 6 mm. distillation column.

<u>In a 1:4 molar ratio</u> A 1 l. Parr autoclave containing 122 gm. (0.35 mole) of IIIa and 525 p.s.i. of hydrogen chloride at 30°C (1.4 moles) was heated at 68°C for 4.5 hours.

The reaction mixture was cooled to 26°C (275 p.s.i., 0.75 mole gas) and part of the gas was released through a double dry ice-acetone trap into a 5 l. evacuated flask. A later attempt was made to derivatize the gas (see below). A sample of the gas was used for a qualitative mass spectrum analysis after being passed through the cold trap and bubbled through distilled water. The mass spectrum analysis indicated the presence of hydrogen, methane and higher mass fragments up to 127 mass units. A sample of the gas collected in a test tube was heavier than air and burned rapidly upon ignition with a flame. The product mixture weighed 172 gm. giving a weight increase of 50 gm. or 1.37 moles of hydrogen chloride.

A second reaction was carried out in which 175 gm. (0.5 mole) of IIIa and 600 p.s.i. of hydrogen chloride at 30°C (1.65 mole) were heated at 70°C for 4.5 hours (pressure 400 p.s.i.). An additional 140 p.s.i. at 70°C (0.33 mole) of hydrogen chloride (1:4 molar ratio) was added and heating continued for three hours. The mixture was cooled (pressure 250 p.s.i. at 24°C, 0.7 mole gas) and the gas was released through a dry ice-acetone trap.

Distillation of the lower boiling fractions from these two reactions gave essentially the same products and yields. The higher boiling fractions were combined for distillation. The over-all yields are listed in Table 17 for all of the compounds in the series $Cl-(SiMe_2)_n-Y$, where $n = 1-6$ and $Y =$ hydrogen or chlorine. In addition, 23 gm. (12%) of impure IIIa was obtained, identified by VPC.

Table 9. Properties of $Cl-(SiMe_2)_n-Cl$ compounds

Compound n	b.p. °C/mm.	$n_D^{20°}$	Reference
1	70°/760	1.4060	105
2	60°/40	1.4540	19, 106
3	97°/18	1.4848	19, 107
4	72°/0.06; 89°/1.1	1.5127	19
5	86-87°/0.1	1.5225	--
6	112-114°/0.06	m.p. 45-47°	19

Table 9 lists the compounds and physical properties of the series $Cl-(SiMe_2)_n-Cl$, where n = 1-6, obtained in the series of reactions described. Identification was made by comparison of vapor phase chromatograms of authentic samples, by comparison of published physical properties and by a chlorine analysis. A variance in the boiling point of a compound was sometimes found using the Todd or the Nestar/Faust spinning spiral column, with the same pressure gauge.

A careful analysis by vapor phase chromatography of all the fractions obtained and of authentic samples indicated that only traces of the compounds in the series $H-(SiMe_2)_n-H$, where n = 1-6, were present.

Table 10 lists the retentions in cm., from a typical vapor phase chromatogram analysis of the compounds prepared in

Table 10. Vapor phase chromatographic analysis[a,b] of the $Cl-(SiMe_2)_n-Y$ series compounds

		Retentions in cm.												
Compound	n	1	1	2	2	3	3	4	4	5	IIIa	5	6	6
	y	H	Cl	H	Cl	H	Cl	H	Cl	H	---	Cl	H	Cl
temp. °C		0.7	0.8	1.6	2.7	7.2	---	---	---	---	---	---	---	---
75°		---	0.75	1.1	1.6	3.4	6.9	---	---	---	---	---	---	---
100°		---	---	---	---	1.9	3.0	6.3	---	---	---	---	---	---
125°		---	---	---	---	---	1.8	3.0	5.1	---	5.5	6.3	---	---
150°		---	---	---	---	---	---	1.7	2.7	4.1	6.1	7.1	11	15
175°		---	---	---	---	---	---	---	1.1	2.3	3.3	3.6	5.5	8.7

[a] Silicone gum rubber SE30 on chromosorb W (1:20) column.

[b] F and M model 500 gas chromatograph.

this study.

Dodecamethylcyclohexasilane and t-butyl chloride

A 1:4 molar ratio pressure reaction   To a 1 l. Parr autoclave was added 140 gm. (0.4 mole) of IIIa and 76 gm. (0.8 mole) of *t*-butyl chloride. The autoclave was sealed and heated at 145 to 158°C for 19 hours (pressure 120 p.s.i. after 10 hours at 158°C). An infrared spectrum of the gas removed after cooling showed strong absorptions in the SiH and CH stretching region but none attributable to isobutylene (103). An additional 76 gm. (0.8 mole) of *t*-butyl chloride was added and the autoclave was sealed and heated to 149°C for 11 hours (120 p.s.i. at 149°C). The reaction mixture weighed 275 gm., a weight loss of 17 gm. The distillation of the mixture gave the polysilanes and yields listed in Table 17. All the compounds in the series $Cl-(SiMe_2)_n-Y$, where $n = 1-6$ and Y = hydrogen or chlorine, were obtained. Also obtained were the following products: 5.4 gm. of 2,2,-4-trimethylpentane, identified by comparison with the b.p. (98°C), refractive index (n_D^{20} 1.3928), infrared spectrum and VPC retention time of an authentic sample; 4.0 gm. of another hydrocarbon, as indicated by its infrared spectrum, b.p. 111-112°C, believed to be 2,5-dimethylhexane, b.p. 111°C; and a small amount, 2.0 gm., b.p. 99°-109°C which was not pure (VPC) but was probably 2,2,3,3-tetramethylbutane, b.p. 107°C. Smaller, nonisolable amounts of higher boiling components were evident in the vapor phase chromatographic analysis of intermediate fractions.

At atmospheric pressure A 500 ml. round-bottomed flask containing 52 gm. (0.15 mole) of IIIa was immersed in an oil bath heated from 144 to 190°C. Every 2 to 4 hours 4 ml. of t-butyl chloride was added. The internal flask temperature varied from 95 to 163°C. A vapor phase chromatogram of the reaction mixture indicated that no reaction had occurred after 21 hours of heating.

In o-dichlorobenzene To the above reaction mixture was added 50 ml. of o-dichlorobenzene. The mixture was then heated over the range of 173 to 183°C for 24 hours with 2 ml. of t-butyl chloride added every hour for the first 12 hours. Ten ml. was then added and heating continued between 154 to 178°C for 23 hours. A vapor phase chromatogram of a sample indicated only trace amounts of components other than starting materials. Therefore, heating was discontinued.

α,ω-Substituted Polydimethylsilanes

1,4-Dichlorooctamethyltetrasilane with t-butyl chloride

1,4-Dichlorooctamethyltetrasilane, 30.3 gm. (0.1 mole), t-butyl chloride, 9.3 gm. (0.1 mole), and nitrogen (100 p.s.i. at 27°C) were heated at 100°C in an autoclave for 5 hours (pressure 140 p.s.i.). A vapor phase chromatogram of the mixture indicated that no reaction had occurred. An additional

5 ml. of t-butyl chloride was added and the autoclave heated at 170°C for 6 hours. An increase of 20 p.s.i. over the initial pressure was noted upon cooling to 27°C.

Distillation of the reaction mixture gave the products and yields listed in Table 19. Also obtained were 0.7 gm. of 2,2,4-trimethylpentane and 0.3 gm. of 2,5-dimethylhexane.

The characterization of new compounds in the Cl-$(SiMe_2)_n$-Y series

The observed boiling points, refractive indices and densities of compounds of the series H-$(SiMe_2)_n$-Cl prepared in this study are given in Table 18. The ultraviolet absorption spectraldata are given in Table 20 and the NMR proton resonance spectral data are given in Table 24.

1-Chloro-1,1,2,2-tetramethyldisilane

Anal. Calcd. for $C_4H_{13}ClSi_2$: Cl, 23.20; MR, 46.49; B.P.N. 23.85, b.p. 119°C. Found: Cl, 22.7, 22.7%; MR, 46.77; B.P.N. 23.82, b.p. 118°C. The infrared spectrum (in CS_2) contained absorptions in μ at: 3.37, 3.45 (m doublet), 4.74 (s), 7.20 (m), 8.03 (s), 11.37, 12.03, 12.58, 12.95 (s), 13.23 (w), 15.30 (s).

1-Chloro-1,1,2,2,3,3-hexamethyltrisilane

Anal. Calcd. for $C_6H_{19}ClSi_3$: Cl, 16.8; MR, 67.54; B.P.N. 31.55, b.p. 184°C. Found: Cl, 17.3, 17.2%; MR, 66.73; B.P.N. 31.41, b.p. 183°C. The infrared spectrum (in CS_2) contained absorptions in μ at: 3.37, 3.45 (m doublet), 4.77 (s), 7.20 (m), 8.03 (s), 11.37, 12.05, 12.58, 12.95 (s), 13.70, 14.25 (w), 15.30 (m).

1-Chloro-1,1,2,2,3,3,4,4-octamethyltetrasilane

Anal. Calcd. for $C_8H_{25}ClSi_4$: Cl, 13.2; MR, 88.6; B.P.N. 39.25, b.p. 239°C. Found: Cl, 13.3, 13.35%; MR, 87.54; B.P.N. 38.19, b.p. 232°C. The infrared spectrum (in CS_2) gave absorptions in μ at: 3.38, 3.46 (m doublet), 4.78 (s), 7.15 (m), 8.03, 11.40, 12.05 (s), 12.50 (m), 12.87 (s), 13.70 (m), 14.50 (w), 15.07 (m).

1-Chloro-1,1,2,2,3,3,4,4,5,5-decamethylpentasilane

Anal. Calcd. for $C_{10}H_{31}ClSi_5$: Cl, 10.85; MR, 109.6; B.P.N. 46.95, b.p. 287°C. Found: Cl, 10.37, 10.97%; MR, 109.6; B.P.N. 48.79, b.p. 298°C. The infrared spectrum (in CS_2) gave absorptions in μ at: 3.40, 3.47 (m doublet), 4.77 (m), 7.20 (w), 8.05 (s), 11.45 (s), 12.05 (s), 12.60 (m), 13.00 (s), 13.70 (s), 14.5 (w), 15.07 (m).

1-Chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecamethylhexasilane

Anal. Calcd. for $C_{12}H_{37}ClSi_6$: Cl, 9.2; MR, 130.7; B.P.N. 54.65, b.p. 330°C. Found: Cl, 9.25, 9.32%; MR, 131.6; B.P.N. 55.90, b.p. 337°C. The infrared spectrum (in CS_2) gave absorptions in μ at: 3.37, 3.46 (m doublet), 4.77 (m), 7.35 (m), 8.04 (s), 11.42 (s), 12.03 (s), 13.15 (s), 13.70 (m), 14.50 (m), 15.05 (m).

1,5-Dichloro-1,1,2,2,3,3,4,4,5,5-decamethylpentasilane

Anal. Calcd. for $C_{10}H_{30}Cl_2Si$: Cl, 19.45; MR, 113.6; B.P.N. 50.18, b.p. 309°C; mol. wt. 261. Found: Cl, 16.92, 17.0% (see experimental section); MR, 115.2; B.P.N. 50.92; b.p. 310°C; mol. wt. 260 (mass spectrum). The infrared spectrum (in CS_2) gave absorptions in μ at: 3.40, 3.46 (m doublet), 7.20 (m), 8.04 (s), 12.00 (s), 12.55 (s), 13.0 (s), 13.70 (s), 14.5 (m), 15.0 (m). The ultraviolet absorption spectrum gave $\lambda_{max.}$ 250.0, 214 $m\mu$ (ϵ 19,532, 9,906) in 4.27×10^{-5} M cyclohexane solutions.

Diphenyl derivatives

The α,ω-diphenyl derivatives of the new compounds in this study were prepared by the addition of a 0.5 molar solution of phenyllithium-ether to a sample of the compound dissolved in ether. A 100% excess of phenyllithium was used. The yields and properties of the diphenyl derivatives obtained are listed in Table 11. An ultraviolet spectrum identical to that of an authentic specimen was found for each derivative.

1,1,2,2,3,3,4,4-Octamethyltetrasilane

In a manner previously described (58), 21.0 gm. (0.07 mole) of 1,4-dichlorooctamethyltetrasilane, dissolved in 60 ml. of ether, was added over 20 minutes to a flask containing 6.1 gm. (0.16 mole) of lithium aluminum hydride and 200 ml. of ether. The mixture was refluxed for 12 hours. The excess

Table 11. Diphenyl derivatives[a] of the Cl-(SiMe$_2$)$_n$-Y compounds

Cl-(SiMe$_2$)$_n$-X			PhLi	Ph-(SiMe$_2$)$_n$-Ph	
n	X	moles	moles	Yield (%)	b.p. or m.p. (°C)
2	H	0.02	0.05	54	106/0.6mm.
3	H	0.03	0.06	97	121/0.45mm.
4	H	0.02	0.055	63.5	61-62
5	H	0.01	0.02	82	61-62
5	Cl	0.005	0.011	5[b]	62-64
6	H	0.005	0.011	73	85-86.5

[a] Identification was made by comparison of b.p., mixture, m.p. and ultraviolet spectra (86) of authentic samples.[1]

[b] A crude yield of 68% of the compound, m.p. 51-53°C, was obtained whose UV spectrum was identical with that of an authentic sample.

lithium aluminum hydride was removed by pouring the mixture through an oven-dried Soxhlet extraction thimble. The filtrate was distilled to yield 12.9 gm. (78%) of 1,1,2,2,3,3,-4,4-octamethyltetrasilane, b.p. 98°C/14 mm., n_D^{20} 1.4930 (lit. b.p. 74°C/19 mm., n_D^{20} 1.4922) (58). The compound was shown to be pure by VPC. The ultraviolet spectrum gave $\lambda_{max.}$ 235.5 (ϵ

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[1] G. Schwebke and W. H. Atwell, Iowa State University of Science and Technology, Ames, Iowa. Samples kindly provided. 1965.

12,250) in 6.0 x 10^{-5} M cyclohexane solution.

1,1,2,2,3,3,4,4,5,5-Decamethylpentasilane

Following the described synthesis, 8.2 gm. (0.025 mole) of 1H,5-chlorodecamethylpentasilane and 1.2 gm. (0.032 mole) of lithium aluminum hydride gave 4.5 gm. (62%) of 1,1,2,2,3,3,4,4,5,5-decamethylpentasilane, b.p. 142°C/19 mm., n_D^{20} 1.5074, d^{20} 0.8256. The ultraviolet spectrum gave $\lambda_{max.}$ 249.0, 214 (sh) (ϵ 13,590, 9,440) in 4.29 x 10^{-5} M cyclohexane solution. An infrared spectrum was superimposable on the spectrum of the starting material. MR calcd. 105.7. Found 105.5.

Preparations and Reactions of Heterocyclic Polysilanes

Octaphenyloxatetrasilacyclopentane

1,4-Dichlorooctaphenyltetrasilane, 24.0 gm. (0.03 mole), was heated at reflux in 150 ml. of propyl alcohol for 4 hours. The reaction mixture was then cooled and filtered to give 22.1 gm. (99%) of octaphenyloxatetrasilacyclopentane. Recrystallization and infrared spectra comparisons indicated that the compound was pure but it was found that the melting point varied as reported earlier.[1] As with VIII (see below), the

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[1] Kipping reported (4): "The melting of such preparations were most indefinite and irregular; some samples sintered from 205-210°C and melted complete at about 220°C; others did not sinter until about 220°C and melted gradually up to 245°C or occasionally as high as 250-260°C."

melting point was dependent upon the temperature at which the sample was placed in the melting point block. However, with IV it was observed that introduction of a fresh sample at temperatures between 240-270°C caused sintering and gave melting points approximately 6°C above the temperature at which the sample was introduced. A sharp distinct melting point was obtained at 282-283°C with addition of the sample to the block at 280°C at a temperature increase of 1.5°C/min. The ultraviolet absorption in cyclohexane gave a $\lambda_{max.}$ 253 mμ (sh). The infrared spectrum (in CS_2) showed the following absorptions in μ: 3.27 (m), 5.13, 5.31, 5.52, 7.30, 7.52, 7.72, 7.95 (w), 8.42 (m), 9.08 (s), 9.42 (w), 9.75, 10.03 (m), 10.45, 13.64, 14.44 (s), and 15.05 (m). The strong absorption of the silicon-oxygen band at 10.45 μ is characteristic of this cyclic oxide and provided identification (26).

Octaphenyloxatetrasilacyclopentane with phosphorus pentachloride

In 1,1,2,2-tetrachloroethane   A mixture containing 75 ml. of 1,1,2,2-tetrachloroethane, 7.45 gm. (0.01 mole) of octaphenyloxatetrasilacyclopentane and 2.1 gm. (0.01 mole) of phosphorus pentachloride was heated at 140°C for 10 minutes. The reaction mixture was then cooled and the solvent removed by distillation under reduced pressure. The residue was dissolved in benzene and 50 ml. of petroleum ether (b.p. 60-70°C) added. Upon allowing the solution to stand overnight 1.8 gm. (22%) of solid, m.p. 162-163°C, was obtained. Repeated recrystallizations provided 0.9 gm. (11%) of a pure compound, m.p. 169-170°C, identified by its hydrolysis product as 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane (XII) (see below). The ultraviolet spectrum in cyclohexane gave a $\lambda_{max.}$ 245 mμ (sh). The infrared spectrum (in CS_2) showed absorptions in μ at: 3.27 (m), 5.13, 5.30, 5.50, 7.31, 7.51, 7.70, 7.95 (w), 8.42 (m), 8.67 (w), 8.92, 9.01, 9.07 (s triplet), 9.50 (s), 9.76, 10.04 (m), 13.64, 13.97, 14.45 (s).

Anal. Calcd. for $C_{48}H_{40}Cl_2OSi_4$: Si, 13.76; mol. wt., 816; Found: Si, 13.68, 13.61%; mol. wt., 807.

In benzene Octaphenyloxatetrasilacyclopentane, 14.9 gm. (0.02 mole), phosphorus pentachloride, 4.5 gm. (0.022 mole), and 100 ml. of benzene were heated at 81°C for 10 minutes. The reaction was then cooled and the solvent removed by distillation under reduced pressure. Recrystallization of the residue from benzene-petroleum ether (b.p. 60-70°C) provided 13.3 gm. (81.5%) of solid, m.p. 125-182°C. Repeated fractional recrystallizations gave two pure compounds: 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane (XII), 1.5 gm. (9%), m.p. and mixture m.p. with an authentic sample (see above) 169-170°C and 1,3-bis(chlorodiphenylsilyl)-1,1,3,3-tetraphenyldisiloxane (XI), 1.3 gm. (8%), m.p. 114-116°C, identified by its hydrolysis product (see below). The latter compound gave an ultraviolet spectrum maximum as a weak shoulder at 240 mμ in cyclohexane. The infrared spectrum contained absorptions (in CS_2) in μ at: 3.27 (m), 5.13, 5.30, 7.31, 7.51, 7.70, 7.94 (w), 8.42 (m), 8.68 (w), 9.06, 9.47 (s), 9.78, 10.04 (m), 13.59 (s), 14.27 (sh), 14.40 (s).

Anal. Calcd. for $C_{48}H_{40}Cl_2OSi_4$: Si, 13.76; mol. wt., 816. Found: Si, 13.77, 13.67%; mol. wt., 803, 796.

Octaphenyloxatetrasilacyclopentane with chlorine

Chlorine was added at approximately 200 ml./min. to a suspension of 22.4 gm. (0.03 mole) of octaphenyloxatetrasilacyclopentane in 150 ml. of petroleum ether (b.p. 60-70°C) for 10 minutes (2 l., 0.082 mole) between 10-20°C. The excess of chlorine and part of the solvent were removed under reduced pressure. The solid was then filtered off and 21.1 gm. (86%) of crystalline material was obtained, melting over the range 140-145°C. The solvent was concentrated to give an additional 2.6 gm. (11%), m.p. 127-128°C. The overall yield of solid was 97%. The reaction was repeated several times with the yield of the mixture of products being between 94-98% (based on a 1:1 mole ratio addition of chlorine). A 40 gm. mixture, m.p. 137-163°C, of the reaction products was fractionally crystallized in benzene-petroleum ether (b.p. 60-70°C) mixtures. A 3.55 gm. (9%) sample of 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane, m.p. 169-170°C, was the only pure product isolated. The separation of the hydrolysis products showed that the reaction was nearly quantitative and that there were only two products, 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane (XII) and 1,3-bis-(chlorodiphenylsiloxy)-1,1,3,3-tetraphenyldisiloxane (XI) (see below).

Hydrolysis of 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane (XII)

Three gm. (0.0037 mole) of XII was heated at reflux temperature in 80 ml. of propyl alcohol for 16 hours. Upon cooling, 2.4 gm. (86%) of solid melting at 246-249°C was obtained. Concentration of the filtrate provided only trace amounts of solid. The product was then recrystallized in a benzene-petroleum ether (b.p. 60-70°C) mixture to provide 0.8 gm. (29.6%) of a pure compound, m.p. 257-257.5°C. If a sample of the compound was placed in the melting point block at temperatures lower than 250°C the melting point was lowered *e.g.*, a sample introduced at 150°C melted at 242-244°C and another introduced at 240°C melted at 254-255°C. The maximum melting point obtained was 257-257.5°C. A mixture m.p. with a compound, m.p. 245-246°C, prepared from the reaction of octaphenylcyclotetrasilane and nitrobenzene, as described by Kipping and tentatively identified (26) as octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane (VIII), melted mid-way between the two. X-ray powder pattern photographs of the two compounds indicated that they were identical. Repeated recrystallizations in petroleum ether (b.p. 80-115°C) of the product obtained from nitrobenzene and (Ia) gave fractions that had a m.p. and mixture m.p. of 255-257°C (see below). The ultraviolet absorption spectrum in cyclohexane showed $\lambda_{max.}$ 256 mμ. The infrared spectrum gave absorptions (in CS_2) in μ at: 3.25 (m), 5.12, 5.30, 5.50, 6.1, 7.3, 7.55, 7.72, 7.94 (w), 8.43 (m), 8.92, 8.99, 9.07 (s triplet), 9.65, 9.80, 9.97 (s), 10.07 (m), 13.63, 14.00, 14.40 (s), 14.83 (m).

Anal. Calcd. for $C_{48}H_{40}O_2Si_4$: Si, 14.76; mol. wt., 761; hydrogen value (46, 47), 58.8 ml./gm. Found: Si, 14.64, 14.71%; mol. wt., 746, 745, 748; hydrogen value, 54.1 ml./gm.

Octaphenyl-1,3- and 1,4-dioxaoctaphenyltetrasilacyclohexane

Octaphenyloxatetrasilacyclopentane, 22.0 gm. (0.0296 mole), was added to 180 ml. of petroleum ether (b.p. 60-70°C). Chlorine was added to the suspension at 200 ml./min. for 25 minutes (5 l., 0.2 mole) between 15-25°C. The temperature was held at 25°C with an ice-bath. The excess chlorine was removed and the solid filtered off to give 23.0 gm. (95.5%) of crystalline material, m.p. 134-146°C. This material (0.0282 mole) was then added to 180 ml. of propyl alcohol and the mixture was refluxed for 20 hours. Upon filtering, cooling and concentration of the solution, two fractions of crystalline material were obtained, 16.7 gm. (78%), melting over the range 227-236°C and 4.1 gm. (19%) m.p. 253-256°C. Separation of the two cyclic oxides was easily effected by boiling the crude fractions in acetone. This procedure gave 12.5 gm. (58.5%) of octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (VIIa), m.p. 225-227°C, insoluble in hot acetone, and 8.15 gm. (38%) of octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane, (VIII), m.p. and mixture m.p. with the previously prepared compound 255-256°C. In three reactions the percent of 1,4- and 1,3-dioxa derivatives was 54 and 40, 54 and 42 and 62 and 36%, respectively, with over-all yields ranging from 94-98%. The 1,4-dioxa compound was identified by a mixture m.p. with an authentic sample prepared by the hydrolysis of 1,2-dibromotetraphenyldisilane.[1] Since a mixture m.p. depression is not observed by some similar silanes[2] the following additional properties are given. The ultraviolet absorption spectrum in cyclohexane gave a $\lambda_{max.}$ as a shoulder at 245 mμ. The infrared spectrum gave absorptions (in CS_2) in μ at: 3.27 (m), 5.13, 5.30, 5.50, 7.0, 7.31, 7.6, 7.72, 7.94 (w), 8.42 (m), 9.01, 9.06 (s doublet), 9.67, 9.81 (s), 10.05 (m), 13.57 (s), 14.24 (sh), 14.36 (s).

Anal. Calcd. for $C_{48}H_{40}O_2Si_4$: mol. wt., 761; hydrogen value (46, 47), 58.8 ml./gm. Found: mol. wt., 741; hydrogen value, 60.4.

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[1] G. L. Schwebke. Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Sample kindly provided. 1964.

[2] 1,1,2,2,3,3,4,4-Octaphenyltetrasilane, m.p. 161-162°C, 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 160-162°C, and 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 162-164°C, show no depression in a mixture m.p. with each other.

1-Chloro-5-(chlorodiphenylsilyl)-1,1,3,3,5,5-hexaphenyltrisiloxane

Chlorine was added at 200 ml./min. for 25 minutes (5 l., 0.02 mole) to a suspension of 13.0 gm. (0.017 mole) of octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane (VIII) in 170 ml. of petroleum ether (b.p. 60-70°C). The temperature was maintained between 18-32°C by means of an ice-bath. The bright yellow color imparted to the suspension by the chlorine rapidly disappeared at 32°C. The excess of chlorine was removed under reduced pressure and the solid was removed by filtration to give 12.0 gm. (85%) of 1-chloro-5-(chlorodiphenylsilyl)-1,1,3,3,5,5-hexaphenyltrisiloxane (XIII), m.p. 106-107°C. Recrystallization from petroleum ether (b.p. 60-70°C) caused no change in the melting point. Concentration of the filtrate provided an additional 1.3 gm. (9%), m.p. 103-106°C, and 0.3 gm. (2%) of crude product, m.p. 100-102°C. The ultraviolet spectrum of the pure compound gave a $\lambda_{max.}$ 240.5 mμ (sh) in cyclohexane. The infrared spectrum (in CS_2) gave the following absorptions in μ: 3.27 (m), 5.13, 5.31, 5.50, 7.31, 7.52, 7.70, 7.95 (w), 8.47 (m), 8.92 (s), 9.07 (sh), 9.49 (s), 9.75, 10.05 (m), 13.58, 13.95, 14.43 (s), 14.90 (m).

Anal. Calcd. for $C_{48}H_{40}Cl_2O_2Si_4$: Si, 13.63; mol. wt., 832. Found: Si, 13.63, 13.65%; mol. wt., 813.5, 801.

1,6-Dichloro-1,1,3,3,4,4,6,6-octaphenyl-2,5-dioxa-1,3,4,6-tetrasilahexane

In petroleum ether A suspension of 3.8 gm. (0.005 mole) of octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane

(VIIa) in 100 ml. of petroleum ether (b.p. 60-70°C) was treated with chlorine gas added at 190 ml./min. for a period of 32 minutes (6.1 l., 0.25 mole). The temperature rose from 28 to 35°C during the first 10 minutes, rose to 50°C in the next 5 minutes and was held at 53°C with an ice-bath. The bright yellow color imparted by the chlorine rapidly disappeared above 40°C. Removal of the solids by filtration gave an 89.5% (3.4 gm.) recovery of the starting material, m.p. 227-228°C. Distillation of the filtrate under reduced pressure provided 15.2 gm. of liquid having a boiling point above that of the solvent. A vapor phase chromatographic analysis of the petroleum ether showed that it contained 4 major components. A similar chromatogram of the high boiling liquid obtained above indicated the presence of 8 major components. The residue from the distillation was dissolved in 10 ml. of petroleum ether (b.p. 60-70°C) and after standing several hours 0.3 gm. (8%) of a crystalline white solid was precipitated, m.p. 149-151°C.

<u>In n-pentane</u> Chlorine gas was added at 200 ml./min. for 30 minutes (6 l., 0.25 mole) to a suspension containing 7.6 gm. (0.01 mole) of octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane in 100 ml. of *n*-pentane. The temperature was maintained between 17-30°C with an ice-bath. Filtration of the reaction mixture gave a 7.45 gm. (98%) recovery of the starting material. A vapor phase chromatogram indicated that the filtrate contained two major components with greater re-

tention times than that of the n-pentane used. A treatment of n-pentane with chlorine under comparable conditions with comparisons by vapor phase chromatography showed that the solvent was chlorinated at about the same rate with or without the cyclosilane being present.

In carbon tetrachloride-petroleum ether Octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane, 7.6 gm. (0.01 mole), suspended in 80 ml. of carbon tetrachloride and 50 ml. of petroleum ether (b.p. 60-70°C) was treated with chlorine at 200 ml./min. for 25 minutes (5 l., 0.2 mole) between 16-34°C. Excess chlorine was removed under reduced pressure and 3.4 gm. of solid (41%), m.p. 149-151°C, was obtained by filtration. Concentration of the solvents to 20 ml. and addition of 30 ml. of petroleum ether (b.p. 60-70°C) gave an additional 4.15 gm. (51%) of crystalline material, m.p. 148-150°C. Recrystallization gave a constant melting point of 149-150°C. The ultraviolet spectrum in cyclohexane gave $\lambda_{max.}$ 244 mμ (sh). The infrared spectrum (in CS_2) gave the following absorptions in μ: 3.27 (m), 5.13, 5.30, 5.50, 7.30, 7.54, 7.70, 7.95 (w), 8.43 (m), 8.92, 9.00, 9.07 (s triplet), 9.47 (s), 9.76, 10.03 (m), 13.59, 13.95, 14.20 (sh), 14.39 (s), 14.80 (w).

Anal. Calcd. for $C_{48}H_{40}Cl_2O_2Si_4$: Si, 13.50; mol. wt., 832. Found: Si, 13.57, 13.53%; mol. wt., 817, 823.

Hydrolysis of 1-chloro-5-(chlorodiphenylsilyl)-1,1,3,3,5,5-hexaphenyltrisiloxane (XIII)

At 30-40°C Propyl alcohol, 50 ml., was added to 10.8 gm. (0.013 mole) of (XIII), the resulting suspension allowed to stand for 2 hours at 30-40°C and then filtered. The solid obtained, 10.1 gm. (89%), m.p. 77-80°C was recrystallized from propyl alcohol to a constant melting point, 79-80°C. Concentration of the filtrate gave an additional 0.8 gm. (8%) of solid, m.p. 182-190°C. Recrystallization from petroleum ether (b.p. 80-115°C) provided 0.5 gm. (5%) of a pure compound, m.p. 223-226°C, identified in a later experiment as octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane. The low melting material, m.p. 79-80°C, believed to be 1-(diphenylpropoxysilyl)-1,1,3,3,5,5-hexaphenyl-5-propoxytrisiloxane, gave a $\lambda_{max.}$ 245 mμ (sh), in an ultraviolet spectrum in cyclohexane. The infrared spectrum (in CS_2) contained absorptions in μ at: 3.27, 3.38, 3.44, 3.50 (m), 5.12, 5.30, 5.49, 7.20, 7.28, 7.53, 7.68, 7.94 (w), 8.44 (m), 8.95, 9.07 (s), 9.24-9.54 (s broad), 9.75 (m), 9.86 (sh), 10.03 (m), 12.15 (m), 13.60, 13.97, 14.36 (s), 14.72 (w).

Anal. Calcd. for $C_{54}H_{54}O_4Si_4$: Si, 12.77; mol. wt., 879. Found: Si, 12.95, 12.92%; mol. wt., 895, 900.

At 98°C Compound XIII, 4.1 gm. (0.005 mole), was heated at reflux in 100 ml. of propyl alcohol for 3-4 hours. The suspension was allowed to stand for several hours and then filtered to yield 2.5 gm. (65.5%) of crystalline solid, m.p.

226-228°C. Concentration of the filtrate gave an additional 0.1 gm. (1.5%), m.p. 218-221°C. Repeated recrystallizations from petroleum ether (b.p. 80-115°C) gave a variety of fractions melting at 220-221°C, 231-232°C or at temperatures intermediate between these limits. The first fractions from a recrystallization always melted at 230-231°C with subsequent fractions at lower melting points. It was determined by analysis, ultraviolet, infrared, X-ray powder pattern photograph and chemical reaction that the compound existed in at least two isomorphic forms, one melting at 221-222°C and the other at 231-232°C with mixtures of the two melting at intermediate ranges. The ultraviolet spectrum in cyclohexane gave $\lambda_{max.}$ 239.5 mμ. The infrared spectrum (in CS_2) gave the following absorption in μ: 3.27 (m), 5.13, 5.30, 5.50, 7.30, 7.55, 7.72, 7.95 (w), 8.43 (m), 8.9, 8.97, 9.06 (s triplet), 9.47 (s), 9.76 (s), 10.04 (m), 13.59, 13.96, 14.38 (s), 14.80 (w), 15.47 (m).

Anal. Calcd. for $C_{48}H_{40}O_3Si_4$: Si, 14.44; mol. wt., 777. Found: Si, 14.54, 14.53%; mol. wt., 752, 760.

A second reaction was carried out with 10.0 gm. (0.012 mole) of XIII in 300 ml. of propyl alcohol. The yield of the octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane, m.p. 222-224°C, was 43.5% (4.0 gm.). Also obtained was 4.5 gm. (42.5%) of solid melting over the range 58-70°C. Recrystallization from propyl alcohol gave 1.9 gm. of 1-(diphenylpropoxysilyl)-1,1,3,3,5,5-hexaphenyl-5-propoxytrisiloxane, m.p.

79-80°C, identified by a mixture m.p. and infrared spectrum comparison with the previously prepared sample.

Hydrolysis of 1-(diphenylpropoxysilyl)-1,1,3,3,5,5-hexaphenyl-5-propoxytrisiloxane (XVI)

Refluxing 10.0 gm. (0.013 mole) of XVI in 100 ml. of propyl alcohol for 15 hours resulted in a 95% (9.5 gm.) recovery of the starting material, m.p. 78-80°C. No other isolable crystalline products were found.

A second reaction was carried out with 8.7 gm. (0.01 mole) of XVI in 150 ml. of propyl alcohol which was saturated with anhydrous hydrogen chloride. After refluxing for 24 hours, the reaction mixture was cooled to 5°C for 2 hours and then filtered to give 0.35 gm. (4%) of solid melting over the range 74-125°C. Concentration of the filtrate gave an additional 7.1 gm. (78.5%) of solid melting over the range 76-118°C. The solids were extracted several hours with 20 ml. of cold petroleum ether (b.p. 60-70°C) leaving 0.65 gm. (8.5%) of octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane, m.p. 222-223°C. Evaporation of the filtrate and recrystallization of the residue in propyl alcohol yielded 5.9 gm. (68%) of starting material, m.p. 79-81°C.

In a third reaction, anhydrous hydrogen chloride was bubbled at a slow constant rate through 100 ml. of refluxing propyl alcohol containing 4.7 gm. (0.0054 mole) of XVI for 6 to 7 hours. The reaction was then cooled and the mixture filtered to give 2.3 gm. (55.5%) of octaphenyl-1,3,5-trioxa-

2,4,6,7-tetrasilacycloheptane, m.p. 223-224°C. Concentration of the filtrate gave 0.4 gm. (9.5%) of crude material, m.p. 176-180°C. No attempt was made to purify this fraction.

The pyrolysis of 1-(diphenylpropoxysilyl)-1,1,3,3,5,5-hexaphenyl-5-propoxytrisiloxane (XVI)

A 1.76 gm. (0.001 mole) sample of XVI, placed in a long open tube, was put in a furnace in such a way that the top of the tube protruding from the furnace remained cool. The tube was then heated at 160°C for 2 hours, at 200°C for 12 hours and at 300°C for 9 hours. During the last 7 hours the liquid in the tube turned to a light straw color and several drops of a liquid condensed on the upper portion of the tube. The weight loss of the pyrolized material was 0.06 gm. Upon cooling the reaction mixture a viscous liquid remained which was soluble in petroleum ether (b.p. 60-70°C) and propyl alcohol. IXa is insoluble in the former solvent and the latter precipitates XVI. Organic solvents were removed from the resin with a heating pistol at 58°C and 1 mm. pressure. An infrared spectrum of the residue was similar to that of the starting material.

Hydrolysis of 1,6-dichloro-1,1,3,3,4,4-6,6-octaphenyl-2,5-dioxa-1,3,4,6-tetrasilahexane (XIV)

A 4.2 gm. (0.005 mole) sample of XIV was heated in propyl alcohol, 150 ml., at 97°C for 4 to 5 hours. Cooling and filtering provided 0.2 gm. of solid, m.p. 217-219°C. Concentration of the filtrate gave the following fractions: 1.2 gm., melting over the range 104-144°C; 2.0 gm., melting over the range 97-137°C; and 0.1 gm., m.p. 218-219°C. Recrystallization from petroleum ether (b.p. 60-70°C) yielded 0.4 gm. (10%) of octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane, m.p. 223-224°C, identified by infrared spectra comparison and mixture m.p. A second pure fraction weighed 1.4 gm. (34%), m.p. 106-107°C, and was identified as 5,5,7,7,8,8,10,10-octaphenyl-4,6,9,11-tetraoxa-5,7,8,10-tetrasilatetradecane (XVII). The compound showed a $\lambda_{max.}$ 243 mμ in cyclohexane in the ultraviolet region. An infrared spectrum (in CS_2) gave absorptions in μ at: 3.27, 3.37, 3.47 (m), 5.12, 5.30, 5.48, 7.20, 7.28, 7.68, 7.93 (w), 8.42 (m), 8.75, 8.92, 9.04 (s triplet), 9.53, 9.75 (s), 9.85 (sh), 10.03, 12.07 (m), 13.58, 13.96, 14.35 (s), 14.67 (m).

Anal. Calcd. for $C_{54}H_{54}O_4Si_4$: Si, 12.77; mol. wt., 879. Found: Si, 12.87, 12.82%; mol. wt., 833, 875, 882, 909.

With hydrogen chloride Hydrogen chloride gas was added to 150 ml. of propyl alcohol at a slow steady rate for 10 minutes. The temperature was then 45°C. Compound XIV, 7.0 gm. (0.008 mole), was added and the mixture refluxed for 7 hours with slow addition of the hydrogen chloride. Upon cooling and standing two days, 4.9 gm. (79%) of octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane, m.p. 223-224°C was obtained by filtration. No other crystalline materials were isolated.

1,7-Dichloro-1,1,3,3,5,5,7,7-octaphenyltetrasiloxane

In carbon tetrachloride-petroleum ether Chlorine was added at 190 ml./min. for 20 minutes (3.8 l., 0.015 mole) to a mixture containing 1.9 gm. (0.0024 mole) of IXa in 60 ml. of carbon tetrachloride and 50 ml. of petroleum ether (b.p. 60-70°C). Work-up as previously described gave 1.75 gm. (85%) of crude product, melting over the range 96-104°C. Partial hydrolysis occurred during recrystallization to give impure fractions melting above 200°C. Only a small amount, 0.5 gm. (25%), m.p. 96-97°C, of 1,7-dichloro-1,1,3,3,5,5,7,7-octaphenyltetrasiloxane was obtained. The ultraviolet spectrum of the dichloride in cyclohexane showed $\lambda_{max.}$ 271 mμ, 264, 259, 254. The infrared spectrum (in CS_2) contained absorptions in μ at: 3.27 (m), 5.13, 5.30, 5.50, 7.30, 7.53, 7.70, 7.94 (w), 8.44 (m), 8.90 (s), 9.22 (m), 9.50 (s), 9.75, 10.03 (m), 13.57, 13.95, 14.41 (s).

Anal. Calcd. for: $C_{48}H_{40}Cl_2O_3Si_4$: Si, 13.23; mol. wt., 848. Found: Si, 13.36, 13.41%; mol. wt., 827, 816, 824.

In petroleum ether Chlorine was added at 200 ml./min. for 21 minutes (4.2 l., 0.017 mole) to a suspension of octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane (IXa), 3.9 gm. (0.005 mole), in 100 ml. of petroleum ether (b.p. 60-70°C). After treatment with chlorine for 9 minutes the temperature rose rapidly to 45°C and an ice-bath was used to hold the temperature at 26-29°C. The excess of chlorine was removed under reduced pressure and the mixture filtered to obtain 1.2 gm.

(28%) of crude product, m.p. 98-101°C. Concentration of the filtrate afforded three additional fractions: 1.2 gm. (28%), m.p. 98-100°C; 0.9 gm. (22%), m.p. 96-98°C; and 0.4 gm. of solid of which the major portion melted at 97-100°C with the balance at 170°C. The total crude yield was 3.7 gm. (87%) with a 3.3 gm. (78%) yield of pure 1,7-dichloro-1,1,3,3,5,5-7,7-octaphenyltetrasiloxane, m.p. 98-100°C.

Octaphenylcyclotetrasiloxane

Hydrogen chloride was added for 45 minutes at a slow constant rate to 140 ml. of propyl alcohol. At 50°C a total of 3.9 gm. (0.0046 mole) of 1,7-dichloro-1,1,3,3,4,4,7,7-octaphenyltetrasiloxane (XVIII) was added: 2.2 gm. (0.026 mole) of XVIII from the chlorination of the cyclic trioxide IXa obtained by hydrolysis of 1-(chlorodiphenylsilyl)-3-(chlorodiphenylsiloxy)-1,1,3,3-tetraphenyldisiloxane (XIII) and 1.7 gm. (0.02 mole) of XVIII from the chlorination of the cyclic trioxide IXa obtained by hydrolysis of 1,6-dichloro-1,1,3,3,4,4-6,6-octaphenyl-2,5-dioxa-1,3,4,6-tetrasilahexane (XIV). The mixture was then heated at 90°C for 6 hours, cooled, allowed to stand several days and the solid filtered off to obtain 3.0 gm. (82%) of crude octaphenylcyclotetrasiloxane, m.p. 196-200°C. Concentration of the filtrate provided only a trace of additional solid material. Recrystallization of 2.0 gm. in petroleum ether (b.p. 80-115°C) gave 1.8 gm. of pure octaphenylcyclotetrasiloxane identified by mixture m.p. (200-202°C) with an anthentic sample.

In a separate experiment 0.5 gm. of XVIII was refluxed in 15 ml. of propyl alcohol for 2-3 hours. Cooling precipitated 0.1 gm. of solid, m.p. 203-210°C. Concentration of the solution gave, after several days, a few large clear crystals (approximately 0.1 gm.) melting at 59-60°C. The ultraviolet spectrum in cyclohexane showed $\lambda_{max.}$ 270 mu, 264, 258, 252, 246. The infrared spectrum indicated that the compound is probably 1,1,3,3,5,5,7,7-octaphenyl-1,7-dipropoxytetrasiloxane and (in CS_2) showed absorptions in μ at: 3.28, 3.38, 3.50 (m), 5.13, 5.31, 5.50, 7.22, 7.31, 7.54, 7.71, 7.95 (w), 8.46 (m), 8.92, 9.22, 9.54 (s), 9.75, 10.03, 12.03 (m), 13.57, 13.98, 14.37 (s), 14.65 (m).

Octaphenyloxatetrasilacyclopentane (IVa) with nitrobenzene

A mixture of 7.5 gm. (0.01 mole) of IV 50 ml. of nitrobenzene was heated to the boiling point over a period of 40 minutes. After refluxing for 10 minutes, the mixture was allowed to cool and the solvents were removed by distillation under reduced pressure. Treatment of the black tarry residue with acetone and acetone-ethanol mixtures gave three fractions of solid: 1.5 gm., m.p. 270-274°C; 3.6 gm., m.p. 224-228°C and 0.7 gm. melting over the range 208-222°C. The over yield of solid obtained, based on starting material, was 5.8 gm. (78%). Recrystallization from acetone gave 0.5 gm. of pure octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane (VIII) identified by a mixture m.p. (256-257°C) and infrared spectrum comparison with an authentic sample. Several other fractions gave constant sharp melting points at the same and at lower temperatures but infrared spectra comparisons indicated that they were mixtures of five-, six-, and seven-membered ring compounds (see Table 14).

A duplicate reaction mixture was heated at reflux temperature for 2 hours prior to the usual work-up, and gave 3.4 gm. (45% based on starting material) of crystalline solids. Recrystallizations gave 2.7 gm. (34.5%) of octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane (IXa), m.p. 221-222°C. The ultraviolet spectrum showed a $\lambda_{max.}$ 239 mμ in cyclohexane. The infrared spectrum (in CS_2) gave the following absorptions in μ: 3.27 (m), 5.12, 5.30, 5.50, 7.30, 7.54, 7.68, 7.94, 8.43 (w), 8.91, 8.97 (s doublet), 9.06 (w sh), 9.44, 9.76 (s), 10.02 (m), 13.58, 13.96, 14.37 (s), 15.45 (m).

Anal. Calcd. for $C_{48}H_{40}O_3Si_4$: Si, 14.44; mol. wt., 777. Found: Si, 14.51, 14.56%; mol. wt., 791.

Since this compound, previously prepared by the hydrolysis of XIII, gave a m.p. of 231-232°C X-ray powder photographs were taken of the two compounds. The X-ray powder photographs were not identical. Fractions of IIa, m.p. 221-222°C, were later obtained from the hydrolysis of XIV, and the mixture m.p. of this sample with the above product was not depressed. No chemical, analytical or spectral evidence was found to indicate the compound was not IXa.

Octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane with nitrobenzene

A 3.8 gm. sample of octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane (VIII) (0.005 mole) was heated at reflux for 2 hours in 50 ml. of nitrobenzene. The mixture was then cooled and filtered to obtain 3.1 gm. (82%) of solid material, m.p. 242-244°C. Concentration of the filtrate provided 0.35 gm. (9%) of solid material melting over the range 220-240°C. Recrystallization yielded 2.9 gm. (76%) of pure VIII, m.p. 253-255°C, and a trace of solid melting at 214-226°C.

A second treatment of VIII, 3.8 gm. (0.005 mole), with 50 ml. of refluxing nitrobenzene for 24 hours gave no insoluble material upon cooling and standing for several hours. Distillation of the solvent under reduced pressure and addition of acetone to the black residue also gave no precipitate upon standing. Evaporation of the acetone and addition of 40 ml. of ethyl alcohol provided two crops of crystalline dark brown solids, 1.6 gm. (42% based on starting material), m.p. 174-180°C, and 0.3 gm. (8%) melting over the range 162-172°C. The solids were dissolved in acetone and decolorized with activated charcoal. The acetone was then evaporated and the residue recrystallized from petroleum ether (b.p. 80-115°C). A 0.2 gm. sample of a white crystalline solid was obtained, m.p. 189-193°C. A mixture m.p. with an authentic sample of hexaphenylcyclotrisiloxane, m.p. 192-193°C, melted at 191-193°C. The ultraviolet spectrum of this and all fractions obtained showed $\lambda_{max.}$ in cyclohexane at 254 mμ, 259, 264.5, 270 indicating that no polysilane compounds were present. From a 0.45 gm. fraction, m.p. 193-195°C, pure crystals of octaphenylcyclotetrasiloxane were handpicked with tweezers and the mixture m.p. with an authentic sample, m.p. 204-205°C, was not depressed. An infrared spectrum was also used to identify these two products. Since these two compounds are known to form eutectic mixtures and exhibit polymorphism (108, 109) no further attempts to separate the products were made.

Octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane with nitrobenzene

A mixture containing 75 ml. of nitrobenzene and 6.85 gm. (0.009 mole) of octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (VIIa) was heated at 205°C for 4 hours. The reaction mixture was then cooled and upon standing overnight, 6.55 gm. (96%) of the starting material was recovered, m.p. and mixture m.p. 227-229°C. Concentration of the filtrate gave 0.1 gm. (1.5%) of a black crystalline solid, m.p. 216-220°C.

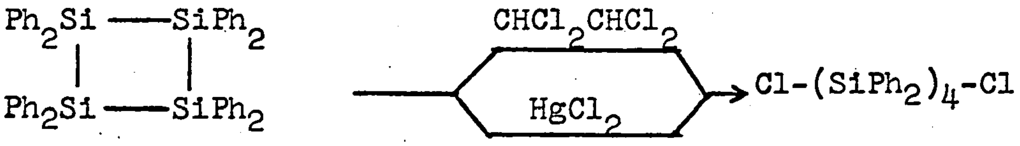
In a second reaction 5.35 gm. (0.007 mole) of VIIa was heated at reflux for 24 hours in 50 ml. of nitrobenzene. Upon cooling and standing no precipitate was formed. Distillation of the solvent under reduced pressure and addition of 50 ml. of acetone also provided no precipitate upon standing. Most of the acetone was allowed to evaporate and 40-50 ml. of ethyl alcohol was added. A 2.15 gm. (40% based on starting material) sample of brown crystals was obtained melting over the range 165-178°C. Evaporation of the filtrate to 10 ml. and addition of 50 ml. of ethyl alcohol yielded no more crystalline solids upon standing several weeks. The residue obtained by removal of the solvent from the filtrate consisted of a black tar. This was soluble in acetone but formed an insoluble oil in petroleum ether (b.p. 60-70°C). Recrystallization of the solids from acetone and petroleum ether (b.p. 80-115°C) gave 0.4 gm. of pure octaphenylcyclotetrasiloxane m.p. 204-205°C. It was identified by mixture m.p., comparison of the infrared spectra, and by an ultraviolet spectrum in cyclohexane, $\lambda_{max.}$ 253 mμ, 259, 269.5, 270.5. Also obtained was 0.6 gm. of hexaphenylcyclotrisiloxane which was identified by a mixture m.p., infrared spectrum and by the ultraviolet spectrum in cyclohexane, $\lambda_{max.}$ 253.5 mμ, 259.5, 264.5, 270. Other fractions obtained, 0.65 gm. melting over the range 160-175°C and 0.6 gm. melting over the range 179-188°C, appeared to be eutectic mixtures of these two compounds as indicated by comparison of the infrared spectra.

DISCUSSION

The Chlorination of Perphenylated Cyclosilanes

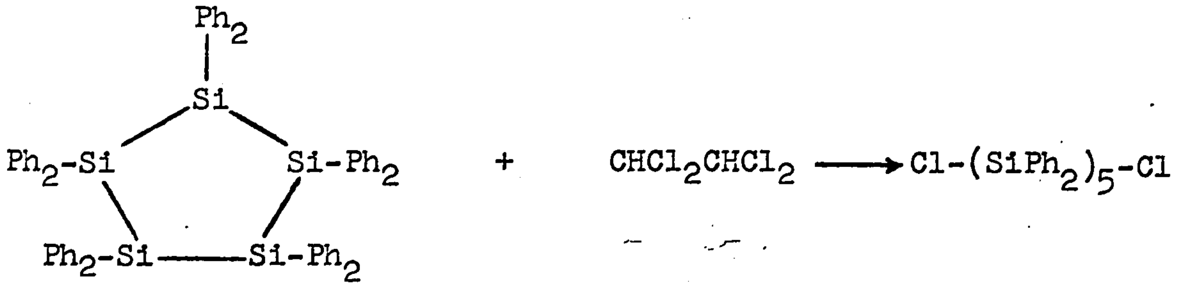
Recent advances in the preparation of organic substituted cyclosilanes, such as octaphenylcyclotetrasilane (Ia) (9), decaphenylcyclopentasilane (IIa) (9) and dodecamethylcyclohexasilane (IIIa) in high yields,have provided a means of preparation of a large variety of heretofore unavailable polysilanes.

1,4-Dichlorooctaphenyltetrasilane has been prepared by the halogenation of Ia with a variety of reagents. These include organic and inorganic halides of which some typical reactions are illustrated below (17).



Our interest centered about the determination of suitable methods for obtaining maximum yields of 1,4-dichlorooctaphenyltetrasilane and of the previously unprepared 1,5-dichlorodecaphenylpentasilane in large scale laboratory preparations. This report is concerned with the reaction of Ia and IIa with chlorinating agents such as chlorine, phosphorus pentachloride and 1,1,2,2-tetrachloroethane.

Ia is known to react readily with refluxing 1,1,2,2-tetrachloroethane to give 1,4-dichlorooctaphenyltetrasilane (4). A recent small scale preparation (2.0 gm.) afforded a 94% yield of the 1,4-dichloro compound after 30 minutes at 140°C.[1] Kipping, who was the first to prepare Ia and IIa and to report on the facile reactivity of Ia toward halogen-containing hydrocarbons, also reported that no reaction occurred with IIa in refluxing tetrachloroethane (110). We have found, however, that IIa does react slowly with 1,1,2,2-tetrachloroethane and provides good yields of 1,5-dichlorodecaphenylpentasilane after prolonged refluxing. Compound IIa gave a 30% yield (based on the starting material) of the 1,5-dichloro compound after 24 hours at 142°C in 1,1,2,2-tetrachloroethane with 42% of the starting material being recovered. A similar reaction for 36 hours gave 61% of 1,5-dichlorodecaphenylpentasilane and 13.5% of recovered starting material. After 50 hours in refluxing 1,1,2,2-tetrachloroethane, no starting material was recovered and the yield of the 1,5-dichloro compound was 70.5%. It was noted that prolonged reaction gave increasing quantities of intractable tars as the only other reaction products.



IIa

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[1] J. M. Kraemer, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of IIa with 1,1,2,2-tetrachloroethane. Private communication. 1960.

Phosphorus pentachloride has been reported to react rapidly with Ia in refluxing benzene to provide good yields of 1,4-dichlorooctaphenyltetrasilane (17). We have found that utilization of this procedure, as described in the experimental section, on a larger scale (44.0 gm.), gave excellent yields (93%) of the 1,4-dichloro compound. The reaction was found to proceed equally well using refluxing benzene or xylene as solvent. Phosphorus trichloride was obtained from the reaction of Ia with phosphorus pentachloride. Phosphorus trichloride did not react with Ia after 24 hours at 80°C using benzene as the solvent.

$$\text{Ia} + \text{PCl}_5 \longrightarrow \text{Cl-(SiPh}_2)_4\text{-Cl} + \text{PCl}_3$$

We have found that 1,5-dichlorodecaphenylpentasilane can be prepared by the cleavage of IIa with phosphorus pentachloride in good yields. However, the reaction is dependent upon the solvent used, the temperature and the reaction time. Compound IIa did not react with phosphorus pentachloride in refluxing benzene or xylene unless a large excess of the chlorinating agent was used. However, with the use of carbon tetrachloride or 1,1,2,2-tetrachloroethane as solvent, equal molar quantities of phosphorus pentachloride did react with IIa to provide the 1,5-dichloropolysilane in yields of 86%. Carbon tetrachloride was found to be a less effective solvent than 1,1,2,2-tetrachloroethane and provided only 23% of 1,5-dichlorodecaphenylpentasilane after refluxing IIa and phosphorus pentachloride (mole ratio 1:2) in this solvent for 5 hours. Prolonged heating with either carbon tetrachloride or 1,1,2,2-tetrachloroethane caused a decrease in the yield of 1,5-dichlorodecaphenylpentasilane with the production of an unidentified low-melting fraction (up to 15%), m.p. 150-165°C, and a non-isolable viscous oil. Repeated recrystallization of the low melting fraction provided no pure products. Using 10% excess phosphorus pentachloride, 1,5-dichlorodecaphenylpentasilane in 86% yields was obtained after 15 minutes at 140°C with 1,1,2,2-tetrachloroethane as solvent.

No reaction occurred between IIa and 1,1,2,2-tetrachloroethane or IIa and phosphorus trichloride in 1,1,2,2-tetrachloroethane after 1 hour at 140°C. The increased yields resulting from the use of 1,1,2,2-tetrachloroethane as solvent, as opposed to xylene, may be due to the increased solubility of chlorine in the former solvent. The reaction probably proceeds via the dissociation of phosphorus pentachloride to form phosphorus trichloride and chlorine with subsequent attack on the cyclosilane by chlorine. The influence of solvent, time and temperature on the reaction of IIa with phosphorus pentachloride is summarized in Table 4 (see Experimental section).

Compound Ia is known to be cleaved by iodine and bromine, while IIa is slowly cleaved by bromine (4, 9). Good yields of the corresponding α,ω-dihalopolysilanes have been obtained using these reagents. If a 2:1 molar ratio of bromine and Ia are used, further cleavage of the silicon chain occurs and an 85% yield of 1,2-dibromotetraphenyldisilane has been reported (9). No previous reports on the reaction of cyclosilanes with chlorine have been made.

We have found the reaction of Ia and IIa with chlorine to be an extremely interesting and useful reaction, not only for the preparation of the 1,4-dichloro- and 1,5-dichloro- compounds, but for other shorter chain α,ω-dichloro polysilanes as well. When Ia is suspended in ether and chlorine is added at a constant rate (approximately 200 ml./min.) the reaction is complete in less than 10 minutes and provides near quantitative yields (98%) of 1,4-dichlorooctaphenyltetrasilane. After addition of chlorine at the same rate for one hour no additional cleavage occurred and a 98% yield of the 1,4-dichloro compound was again obtained. The reaction of Ia with chlorine in ether or hydrocarbon solvents was unique in providing a means of obtaining a quantitative reaction of a cyclosilane with no cleavage of the resulting linear 1,4-dichloro compound. Attempts to retard this facile ring-opening with chlorine by excluding all light had no effect. However, the addition of a small amount of hydroquinone to the mixture essentially stopped the reaction and a 92% recovery of Ia was observed in a reaction involving the addition of chlorine for 10 minutes. The addition of chlorine at the same rate for less than two minutes, without the presence of hydroquinone, gave a quantitative yield of 1,4-dichlorooctaphenyltetrasilane.

Hence, there is some indication that silicon-silicon cleavage with chlorine involves a free radical mechanism, although the evidence is not definitive.

It was found that with the use of carbon tetrachloride as solvent the reaction of chlorine with Ia was very fast and further cleavage of the silicon chain was observed. However, initial ring-opening of the cyclosilane proceeds at a much

$$\text{Ia} + \text{Cl}_2 \longrightarrow \text{Cl-(SiPh}_2\text{)}_n\text{-Cl} \qquad n = 2, 4$$

faster rate than cleavage of the resulting polysilane and good product control was obtained by the addition of chlorine at a constant rate for a specified time. A series of reactions was carried out with carbon tetrachloride as solvent and the results are given in Table 2.

A good example of the difference in reactivity of Ia and IIa is found in the reaction of chlorine and IIa in ether. Addition of chlorine for 20 minutes (200 ml./min.) gave no reaction with IIa. After one hour under the same conditions, only 11% of 1,5-dichlorodecaphenylpentasilane was obtained with 86% of IIa being recovered. With the use of benzene or carbon tetrachloride as solvents in the reaction of IIa and chlorine, a mixture of 1,5-dichlorodecaphenylpentasilane, 1,3-dichlorohexaphenyltrisilane and 1,2-dichlorotetraphenyldisilane is obtained.

$$\text{IIa} + Cl_2 \longrightarrow Cl\text{-}(SiPh_2)_n\text{-}Cl \qquad n = 5, 3, 2$$

This cleavage reaction is particularly facile; however, by careful control of the reaction time and temperature and with constant addition of the chlorine gas the desired product can be obtained as the major component. The results of a series of reactions with IIa and chlorine are shown in Table 5.

It appears that cleavage of the silicon chain, subsequent to initial ring-opening, occurs at a position $\underline{\beta}$ to the terminal chlorine atom. Thus, addition of chlorine to Ia gave no 1,3-dichlorohexaphenyltrisilane and addition of chlorine to IIa provided no 1,4-dichlorooctaphenyltetrasilane. Prolonged addition of chlorine to Ia or IIa in carbon tetrachloride yielded only trace amounts of dichlorodiphenylsilane and an unidentified, clear, viscous resin.

Identification of 1,5-dichlorodecaphenylpentasilane was made by infrared analysis and by preparation of the 1,5-di-n-propoxydecaphenylpentasilane, 1,5-dihydroxydecaphenylpentasilane and 1,5-diallyloxydecaphenylpentasilane derivatives.

$$Cl\text{-}(SiPh_2)_5\text{-}Cl \xrightarrow{H_3O^+} HO\text{-}(SiPh_2)_5\text{-}OH$$

$$Cl\text{-}(SiPh_2)_5\text{-}Cl \xrightarrow{CH_3CH_2CH_2OH} CH_3CH_2CH_2O\text{-}(SiPh_2)_5\text{-}OCH_2CH_2CH_3$$

$$Cl\text{-}(SiPh_2)_5\text{-}Cl \xrightarrow{CH_2=CHCH_2OH} CH_2=CHCH_2O\text{-}(SiPh_2)_5\text{-}OCH_2CH=CH_2$$

1,5-Dichlorodecaphenylpentasilane has also recently been prepared by the following reactions.[1]

$$\begin{tikzcd}
\text{IIa} \arrow[r, "\text{Li}"] & \text{Li-}(\text{SiPh}_2)_5\text{-Li} \arrow[d, "\text{H}_3\text{O}^+"] \\
\text{Cl-}(\text{SiPh}_2)_5\text{-Cl} & \text{H-}(\text{SiPh}_2)_5\text{-H} \arrow[l, "\text{PCl}_5"']
\end{tikzcd}$$

Infrared spectral studies in the 400-700 cm.$^{-1}$ region show that the introduction of two or more chlorine atoms onto an organic substituted silane causes absorption of the silicon-chlorine bond to vary in a regular manner (102). This phenomenon is illustrated in Table 12. These absorptions are useful for quantitative as well as qualitative analysis (102). Our studies on the preparation of compounds in the series Cl-$(\text{SiPh}_2)_n$-Cl, where n = 2-5, gave us the opportunity of studying the silicon-chlorine stretching frequencies of α,ω-dichloro polysilanes of increasing chain length. The observed absorptions are recorded in Table 13. Also included are the silicon-chlorine absorptions of the later prepared 1<u>H</u>,4-chlorooctaphenyltetrasilane. As a help in assigning the silicon-chlorine absorptions, a spectrum of 1,1,2,2,3,3,4,4-octaphenyltetrasilane was found to contain no absorption in the assigned re-

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[1] S. Cooper, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the chlorination of H-$(\text{SiPh}_2)_5$-H. Private communication. 1962.

gions.

Table 12. Silicon-chlorine infrared absorptions of Ph_n-$SiCl_{4-n}$ compounds

Compound	Characteristic band position (cm.$^{-1}$)
Ph_3SiCl	560
Ph_2SiCl_2	540,580
$PhSiCl_3$	515,595
$SiCl_4$	424,612

Table 13. Silicon-chlorine infrared absorptions of α,ω-disubstituted polydiphenylsilanes[a]

Compound	Characteristic band position (cm.$^{-1}$)
$Cl-SiPh_2-Cl$	540, 577
$Cl-(SiPh_2)_2-Cl$	531, 584
$Cl-(SiPh_2)_3-Cl$	524, 560
$Cl-(SiPh_2)_4-Cl$	520, 544, 561
$Cl-(SiPh_2)_5-Cl$	519, 527 (sh), 550
$H-(SiPh_2)_4-Cl$	520, 560

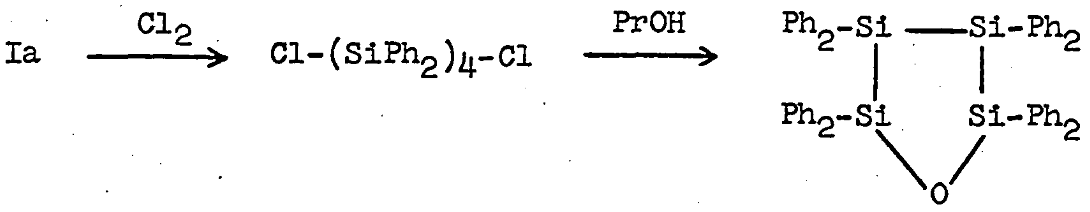
[a] Infrared spectra were made with a Beckman IR-7 spectrophotometer with sodium chloride optics using KBr cells with carbon disulfide as solvent.

The Chlorination of Heterocyclic Polysilanes

Our interest in the preparation of polysilanes containing terminal substituted, stable functional groups by the cleavage reactions of cyclosilanes, was directed toward the use of a heterocyclic polysilane, octaphenyloxatetrasilacyclopentane (IV). In an attempt to prepare the 1,4-dipropoxy derivative of 1,4-dichlorooctaphenyltetrasilane, it was found that a quantitative yield of the five-membered cyclic oxide was obtained. A study of the directive effects of a heteroatom upon cleavage of cyclosilanes with chlorine and observation of the reactivity of the silicon-silicon bond in cyclic compounds of increasing ring-size was particularly rewarding.

Starting with compound Ia, compounds IV, octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (VIIa), octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane (VIII), octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane (IXa) and octaphenylcyclotetrasiloxane (X) can be made in essentially quantitative yields by the insertion of one oxygen atom at a time into the ring using a procedure involving hydrolysis subsequent to chlorination of the appropriate smaller ring compound. Parallel to the above syntheses was the preparation and study of α,ω-dichloro polydiphenylsilanes containing one, two, three or four oxygen atoms in the organic substituted silicon compound.

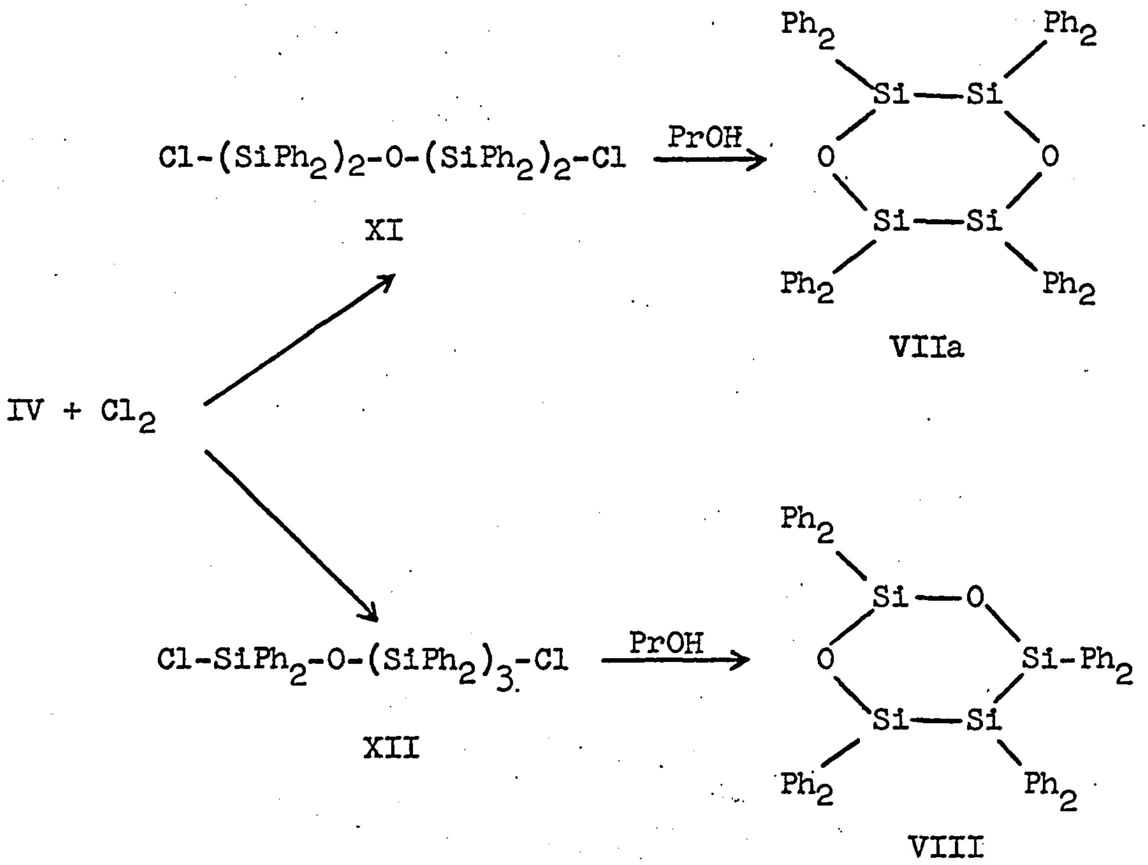
The addition of chlorine to Ia in ether, pentane or petroleum ether (b.p. 60-70°C) provides a quantitative preparation of 1,4-dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane. The hydrolysis of the dichloride with hot propyl alcohol gave octaphenyloxatetrasilacyclopentane (IV) quantitatively. Cyclization to the five-membered ring monoxide was so facile that attempts to prepare a 1,4-dipropoxy derivative by hydrolysis at lower temperatures resulted only in recovery of starting material and a lower yield of the cyclic oxide. This is quite different from 1,5-dichlorodecaphenylpentasilane which gave only the 1,5-dipropoxy derivative in good yield when treated with hot propyl alcohol. Also the 1,6-dichloropolysilane (XIII) (see below) gave the dipropoxy derivative in high yield when treated with propyl alcohol at 30°C.



IV

$$\text{IIa} \xrightarrow{Cl_2} Cl-(SiPh_2)_5-Cl \xrightarrow{PrOH} PrO-(SiPh_2)_5-OPr$$

Octaphenyloxatetrasilacyclopentane (IV) reacts readily with chlorine in petroleum ether (b.p. 60-70°C) or with phosphorus pentachloride in refluxing 1,1,2,2-tetrachloroethane or benzene to form two 1,5-dichlorooxatetrasilapentanes: 1-chloro-3(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane (XII) and 1,3-bis(chlorodiphenylsilyl)-1,1,3,3-tetraphenyldisiloxane (XI). The two isomeric products were difficult to separate by fractional recrystallization and only small quantities of each were obtained pure for analysis. Identification was achieved by hydrolysis of XI to the known octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (VIIa) (26).



VIIa was found to be insoluble in hot acetone and nearly insoluble in hot benzene while VIII was readily soluble in hot acetone and cold benzene. It is interesting to note that the symmetrical products in both the chlorination and hydrolysis had the lower melting points with XI melting at 114-116°C while XII melted at 169-170°C, VIIa at 227-228°C and VIII at 256-257°C.

After isolation of the hydrolysis products it was ascertained that the chlorination of the monoxide was quantitative. The cleavage reaction, rather than being random, favored by a factor of 3:1 the cleavage of the 3,4-silicon-silicon bond. This is to be expected, as the electronegative oxygen atom would make adjacent silicon atoms less susceptible to oxidation (111). Delocalization of unshared electron pairs from the oxygen atom to free d orbitals of the adjacent silicon atoms, retarding possible formation of a pentacovalent intermediate, would also be a factor contributing to the observed ratio (27, 111). Possibly due to ring conformation, these effects appear to be decreased in a heterocyclic polysilane. This can best be demonstrated by the rapid cleavage of IXa with chlorine as compared to no observed cleavage of the linear compounds, XI, XIII or XIV with chlorine under comparable conditions.

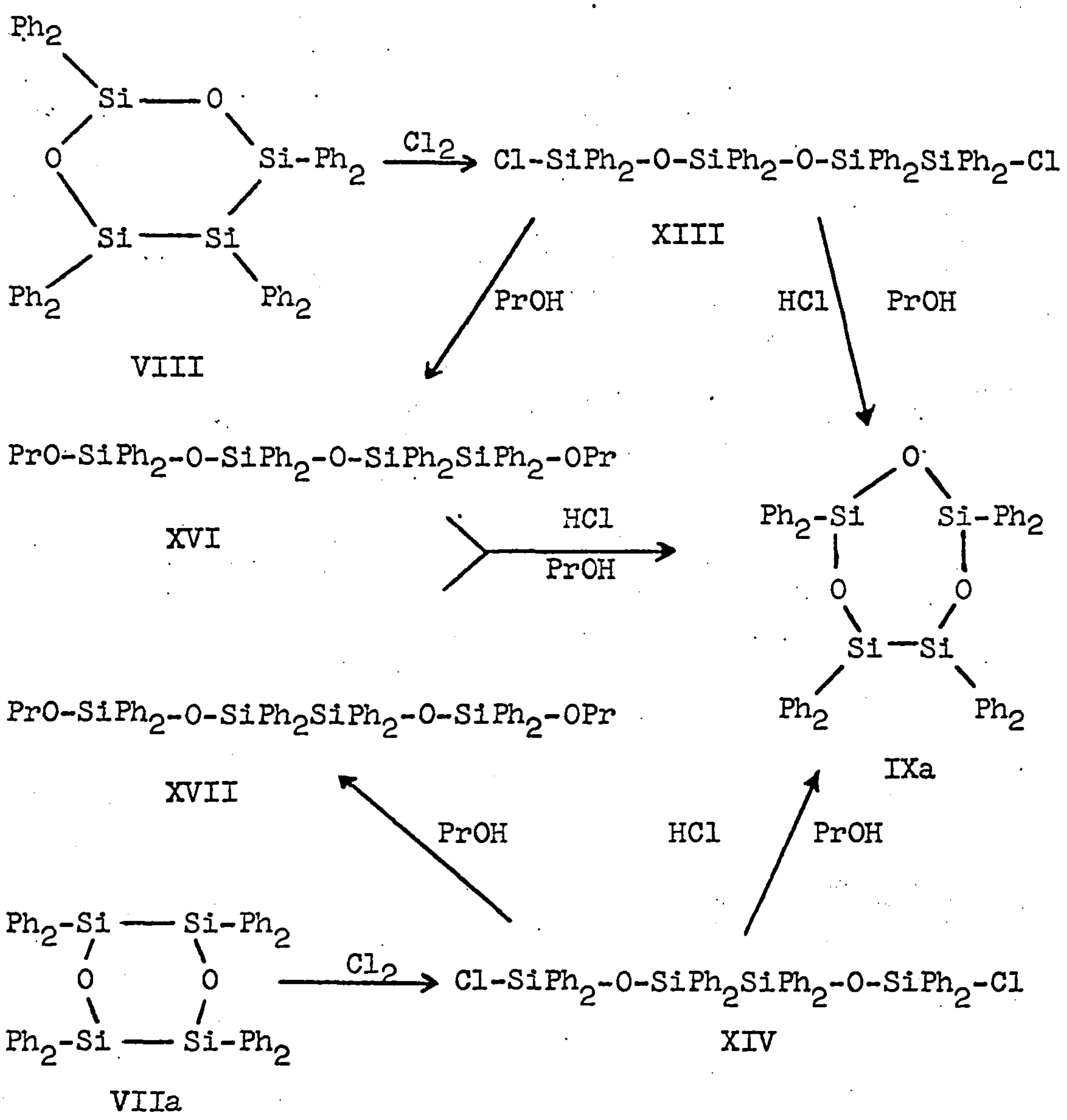
The reaction of IV with chlorine appears to be nearly as fast as the reaction of Ia with chlorine. Again, this is in contrast to the reactions of the five-membered ring, IIa, which reacts very slowly with chlorine in petroleum ether (b.p. 60-70°C) and not at all with equimolar quantities of phosphorus pentachloride in benzene. Steric factors are believed to play an important part in the latter reaction (2). However, this rapid decrease in reactivity, with increasing ring size, has also been noted in comparisons of nucleophilic cleavage of 1,1,2-triphenyl-1-silacyclobutane and 1,1,2-triphenyl-1-silacyclopentane (78). The decrease in reactivity with increasing ring size was attributed to differences in ground and transition state energies caused by ring strain, steric factors and molecular geometry in the formation of a pentacovalent intermediate (see Historical section). These same properties may in part account for the reactions observed in this thesis. This can best be demonstrated by a comparison of the effect of adding chlorine to IXa and XIV. The adjacent electronegative or electron donor properties of oxygen may decrease the ground state energy of XIV more than that of IXa due to conformational effects as well as ring strain. The same electron delocalization of the oxygen atom would cause a decrease in the transition state energy of IXa as compared to that of XIV. This does not, however, account for the inability of chlorine to cleave compounds such as 1,4-dichlorooctaphenyltetrasilane under the conditions used. The addition of chlorine to a heterogeneous suspension of a solid in petroleum ether to give an insoluble product is in itself a somewhat unusual process. Solubility and solvent effects, difficult to interpret, are undoubtedly involved. As shown above, chlorine adds rapidly to linear α,ω-dichloro- polydiphenylsilanes as well as to cyclic polysilanes in solution.

Compound VIII reacted rapidly with chlorine in petroleum ether (b.p. 60-70°C). Ring cleavage of the trisilane at either silicon-silicon bond provides the same product, 1-chloro-5-(chlorodiphenylsilyl)-1,1,3,3,5,5-hexaphenyltrisilane (XIII), and the yield was essentially quantitative. The product was easily hydrolyzed unless some care was taken to prevent exposure to moist air while recrystallizing.

Treatment of XIII with propyl alcohol at room temperature provided a high yield of a dipropoxy derivative, 1-(diphenylpropoxysilyl)-1,1,3,3,5,5-hexaphenyl-5-propoxytrisiloxane (XVI) and a small amount of the cyclic trioxide, octaphenyl-1-3,5-trioxa-2,4,6,7-tetrasilacycloheptane (IXa). Repeating the reaction with refluxing propyl alcohol increased the yield of the cyclic trioxide (IXa) to 43-65% with only small amounts of XVI being isolated. However, the treatment of XVI with hot propyl alcohol resulted only in recovered XVI. A continuous slow addition of anhydrous hydrogen chloride to hot propyl alcohol containing XVI did cause cyclization and a 55% yield of IXa was obtained.

The pyrolysis of a small amount of XVI at 300°C left only a light straw colored viscous polymer. No evidence for the formation of IXa was found. The infrared spectrum of the resin was similar to the spectrum of XVI. Telomerization appeared to occur rather than cyclization or decomposition.

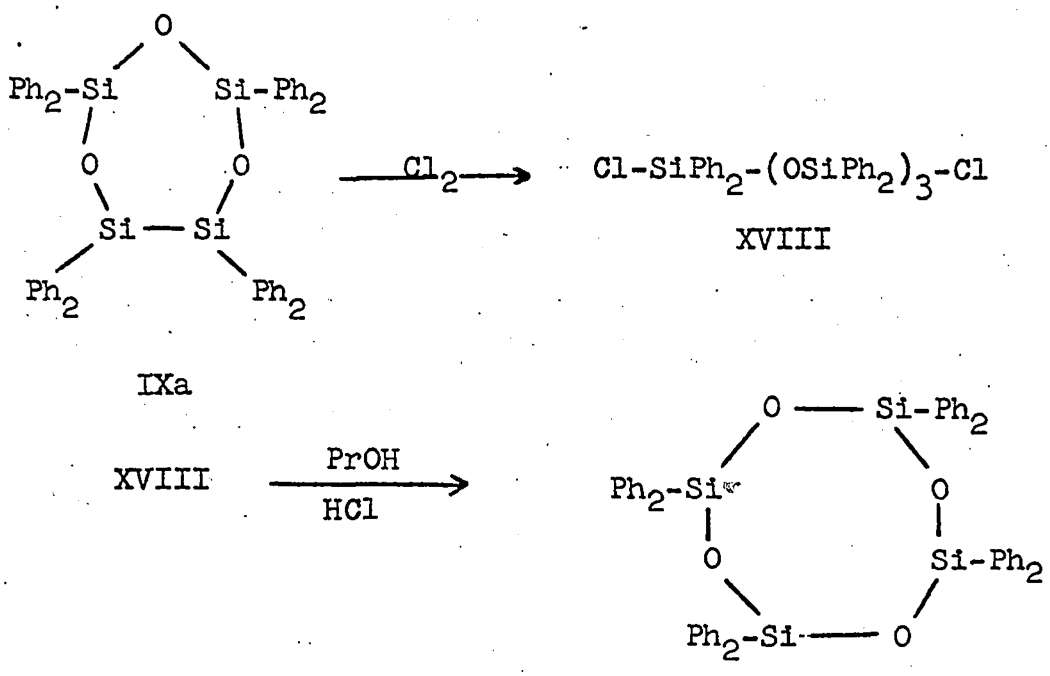
Compound VIIa was found to be nearly as insoluble as Ia in most solvents and it resisted all attempts to cleave the silicon-silicon bonds with chlorine in petroleum ether (b.p. 60-70°C) or *n*-pentane. However, it was found that the reac-



tion proceeded smoothly with a suspension of VIIa in a mixture of carbon tetrachloride and ether or carbon tetrachloride and petroleum ether (b.p. 60-70°C). The product, 1,6-dichloro-1,1,3,3,4,4,6,6-octaphenyl-2,5-dioxa-1,3,4,6-tetrasilahexane (XIV), which was obtained in high yield, was hydrolyzed in hot propyl alcohol to yield the same cyclic trioxide (IXa) as obtained by hydrolysis of XIII. The hydrolysis in hot propyl alcohol gave a mixture of IXa and the dipropoxy derivative, 5,5,7,7,8,8,10,10-octaphenyl-4,6,9,11-tetraoxa-5,7,8,10-tetrasilatetradecane (XVII). Continuous slow addition of anhydrous hydrogen chloride to hot propyl alcohol and then addition of XIV to the hot mixture gave IXa (79%) as the only isolable product.

Compound IXa, which was also prepared by the reaction of nitrobenzene on Ia and on IV (see below), gave constant melting fractions at 221-222°C, 231-232°C and at intermediate ranges. The X-ray powder pattern photographs of IXa, obtained from the hydrolysis of XIII, m.p. 231-232°C, and from the reaction of nitrobenzene on IV, m.p. 221-222°C, were not identical indicating that the compound existed in at least two isomorphic forms. No spectral, analytical or chemical evidence was found to indicate that they were not the same compound.

The crude product obtained from the cleavage of IXa in a carbon tetrachloride-petroleum ether (b.p. 60-70°C) mixture was identified as 1,7-dichloro-1,1,3,3,5,5,7,7-octaphenyltetrasiloxane. The 84% yield was slightly less than that of the smaller ring homologs. None of the starting material was recovered. The hydrolysis of the dichloro derivative occurred readily during recrystallization and only small fractions of the compound were isolated pure. It was found, surprisingly, in contrast to VIIa, that IXa reacted readily with chlorine in petroleum ether (b.p. 60-70°C) to provide XVIII in good yield.



IXa $\xrightarrow{Cl_2}$ $Cl\text{-}SiPh_2\text{-}(OSiPh_2)_3\text{-}Cl$

XVIII

XVIII $\xrightarrow[HCl]{PrOH}$ X

All of the cyclosilanes investigated reacted readily with chlorine in petroleum ether (b.p. 60-70°C) regardless of ring size, with the exception of VIIa. No evidence was found for any silicon-silicon bond cleavage of any straight chain polysilane under the conditions specified.

Attempts to prepare X by the treatment of XVIII with hot propyl alcohol gave only mixtures from which no pure fractions were obtained. As an additional proof of structure of IXa, XVIII was prepared by chlorination of IXa obtained from the hydrolysis of XIII and of XIV. This sample was hydrolyzed in hot propyl alcohol continuously saturated with anhydrous hydrogen chloride. An 82% yield of X was obtained. Although attempts to prepare and isolate XVIII and to hydrolyze it to X have been made (112), this is the first reported, unambiguous synthesis of XVIII and of X.

The Oxidation of Polysilanes with Nitrobenzene

A difference of 11°C was found in the melting point of VIII, prepared by the hydrolysis of XII, and the compound believed to have the same structure (26), prepared by Kipping from the reaction of nitrobenzene with Ia (4). The reaction was repeated in the manner described by Kipping using a much larger quantity of starting material than was available to Kipping. Our studies were extended to include the reaction of nitrobenzene on IV, VIIa, VIII, IIIa, IIa and hexaphenyldisilane.

Below 140°C very little reaction occurred between nitrobenzene and Ia. However, at 165°C the reaction became rapidly exothermic and was complete in a few minutes. The products obtained consisted of unidentified black tars and approximately 50%, based on starting material, of crystalline solids. Recrystallization to a constant melting point yielded a product presumably the same as that reported by Kipping, m.p. 245-246°C (4).

An infrared spectrum of the compound showed an Si-O-Si bond absorption at 9.77 μ and a shoulder at 9.43 μ. After repeated recrystallizations the melting point of the major fraction remained constant, but small fractions melted at 255-257°C and gave Si-O-Si absorptions in the infrared region only at 9.81 μ (see Table 14). Also obtained were fractions melting at 219-220°C and 231-232°C. These last fractions gave only strong Si-O-Si absorptions in the infrared region at 9.44 μ identical to that of IXa. It appears that Kipping's compound may well have been an eutectic mixture of VIII and IXa.

X-ray powder pattern photographs of a fraction having a constant m.p. 245-246°C and of VIII, m.p. 256-257°C, obtained from the hydrolysis of XII, were identical. This would indicate that the two compounds were identical and not different isomorphic forms of the same compound. The quantity of IXa in the eutectic is evidently too small to be observed in the X-ray pattern photograph. An infrared spectrum of a mixture of VIII and IXa gave an identical spectrum to that of the eutectic.

Infrared studies of lower melting trace fractions from the reaction of Ia and nitrobenzene indicated the presence of X and of hexaphenylcyclotrisiloxane.

No evidence for the presence of IV was found from the reaction of Ia and nitrobenzene. However, it was found that IV reacted only slowly with hot nitrobenzene. The major crystalline product was IXa. With incomplete reaction of IV, small fractions of VIII were found to be present.

As observed by Kipping, very little reaction was found to occur with VIIa and VIII on short contact with refluxing nitrobenzene (4). However, treatment with refluxing nitrobenzene for longer periods caused complete reaction, with unidentified black tars again the major product. A 40-42% yield, based on starting material, of crystalline solid was obtained from VIIa and VIII. From this solid was isolated X, hexaphenyltrisiloxane and eutectic mixtures of these two compounds.

The isomorphic forms and eutectic mixtures of these two compounds have been well characterized (108, 109, 112). Our investigations indicate that VIII and IXa exhibit similar properties. No VIIa was isolated as a product from any of the reactions with nitrobenzene. Compound VIIa was the only heterocyclic compound prepared which showed no isomorphic properties. As a result of its insolubility it was easily separated from VIII, the only other compound in reaction mixtures containing VIIa.

Ultraviolet and infrared spectra were particularly useful in the identification and characterization of the compounds. Characteristic infrared absorptions due to Si-O-Si groups have been found to shift significantly with increasing ring size. The five-membered ring IV gives a characteristic band at 10.45 μ (26). Characteristic cyclotrisiloxane bands are shifted to 9.8 μ while cyclic tetramers and pentamers have a band at 9.2 μ which gradually widens and splits as the ring size increases (102, 113). The seven-membered ring, IXa, gave absorptions at 9.45 μ.

Table 14 lists the Si-O-Si bond infrared absorptions found in several linear and cyclic siloxane compounds. Comparison of the six-membered rings, VIIa and VIII, (9.81 μ) with

Table 14. Si-phenyl and Si-O-Si bond infrared absorptions in the 8.5-11.0 μ region

Compound	Characteristic band position (μ)(in CS_2)	
	Si-phenyl	Si-O-Si[a]
$(Ph_2SiO)_3$	8.88, 8.97	9.87
$(Ph_2SiO)_4$	8.88, 8.96 (small)	9.25
Ph_8Si_4O (IV)	9.08	10.45
$Ph_{10}Si_5O$ (V)	9.08	9.80
$Ph_8Si_4O_2$ (VIIa)	9.02, 9.07 (small)	9.84
$Ph_8Si_4O_2$ (VIII)	8.90, 8.97, 9.07	9.81
$Ph_8Si_4O_3$ (IXa)	8.90, 8.97[b]	9.44
$Me_{12}Si_6O$ (VI)		9.60
$Cl\text{-}SiPh_2\text{-}O\text{-}(SiPh_2)_3\text{-}Cl$	8.92, 9.0, 9.07	9.50
$Cl\text{-}(SiPh_2)_2\text{-}O\text{-}(SiPh_2)_2\text{-}Cl$	9.06	9.47
$Cl\text{-}(SiPh_2)_2\text{-}(OSiPh_2)_2\text{-}Cl$	8.92, 9.07	9.50
$(Cl\text{-}SiPh_2\text{-}O\text{-}SiPh_2)_2$	8.92, 8.97[b]	9.47
$Cl\text{-}SiPh_2\text{-}(OSiPh_2)_3\text{-}Cl$	8.90	9.50

[a] All of the Si-O-Si absorptions were broad except those for the six-membered rings.

[b] These samples showed poorly resolved shoulders at 9.06 μ.

hexaphenylcyclotrisiloxane (9.88 μ) which is planar (114) would indicate a similar ring strain and one might expect a planar structure for these compounds. The absorption of IXa at 9.45 μ is identical to that of the straight chain α,ω-dichloro compounds and the bonding would appear to be strain-free. The cyclotetrasiloxane (X) is a non-planar structure (115).

The characteristic Si-phenyl absorption at 8.9 μ has been observed to split when two phenyl groups are present on the same atom but revert to a single absorption for the triphenylsilyl group (102). In our studies it was observed that the absorption for a diphenylsilylene group splits to give a doublet at 8.87 and 8.97 μ. A tetraphenyldisilanylene group (27) gave a single absorption at 9.06 μ or a poorly resolved doublet at 9.02 and 9.06 μ. A hexaphenyltrisilanylene group gives a single absorption at 9.07 μ. Consequently a compound having a mono- and a trisilane moiety (VIII, XII) gave a triplet at 8.92, 9.00 and 9.06 μ and a compound with a mono- and a disilane moiety (IXa, XIII) gave a doublet at 8.92 and 9.05 μ. Characteristic absorptions found are listed in Table 14 for the respective compounds.

Recent studies on ultraviolet absorptions of polysilanes (82 -89) have given ample evidence for the utility of this method for characterization and identification of polydiphenylsilanes. Table 15 lists the ultraviolet spectra $\lambda_{max.}$ values for the compounds prepared and $\lambda_{max.}$ for similar polysilanes.

Table 15. Ultraviolet spectral data of some polysilanes and siloxanes

Compound	Ref.	Band position, (cyclohexane) $\lambda_{max.}$, mμ. (ε)
$(Ph_2SiO)_4$		253, 259, 264.5, 270.5
Ph_8Si_4O (IV)		253 (50,300)
$Ph_{10}Si_5O$ (V)		250 (sh) (50,300)
$Ph_8Si_4O_2$ (VIIa)		245 (30,910)
$Ph_8Si_4O_2$ (VIII)		256 (22,035)
$Ph_8Si_4O_3$ (IXa)		239 (sh)
$Me_{12}Si_6$ (IIIc)	86	232, 255 (sh) (5,800, 2,000)
$Me_{12}Si_6O$ (VI)		239
$Cl\text{-}SiPh_2\text{-}O\text{-}(SiPh_2)_3\text{-}Cl$		245 (sh)
$Cl\text{-}(SiPh_2)_2\text{-}O\text{-}(SiPh_2)_2\text{-}Cl$		240 (sh)
$Cl\text{-}(SiPh_2)_2\text{-}(OSiPh_2)_2\text{-}Cl$		240.5 (sh)
$(Cl\text{-}SiPh_2\text{-}O\text{-}SiPh_2)_2$		----[a]
$Cl\text{-}SiPh_2\text{-}(OSiPh_2)_3\text{-}Cl$		254, 259, 264.5, 271
$PrO\text{-}(SiPh_2)_2\text{-}(OSiPh_2)_2\text{-}OPr$		245 (sh)
$(PrO\text{-}SiPh_2\text{-}O\text{-}SiPh_2)_2$		243
$PrO\text{-}SiPh_2\text{-}(OSiPh_2)_3\text{-}OPr$		252, 258, 263, 270
$PrO\text{-}SiPh_2SiPh_2\text{-}OPr$		243
$H\text{-}SiPh_2SiPh_2\text{-}H$		243
$Me\text{-}SiPh_2SiPh_2\text{-}Me$	83	240 (25,900)

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[a] A shoulder too weak to estimate was observed.

Table 15. (continued)

Compound	Ref.	Band position, (cyclohexane) $\lambda_{max.}$, mμ. (ϵ)
$Ph-SiPh_2SiPh_2-Ph$	81	246.5 (32,000)
$H(SiPh_2)_3H$		249.5
$Cl-(SiPh_2)_3-Cl$		245 (w sh)
$Ph-(SiPh_2)_3-Ph$	86	255 (32,200)

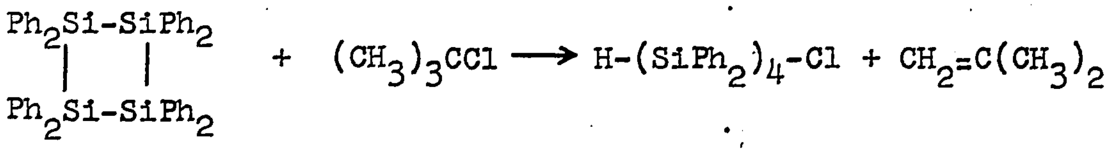
The Hydrohalogenation of Octaphenylcyclotetrasilane

Octaphenylcyclotetrasilane has been found to react with hydrogen bromide and hydrogen iodide to form the corresponding 1H,4-halooctaphenyltetrasilane (9). However, the stability of the silicon-halogen bond toward hydrolysis etc. decreases in the order Cl $>$ Br $>$ I. This decrease may be noted from the difficulty in isolating 1,4-diiodooctaphenyltetrasilane from the reaction of Ia with iodine (4). Also the compound 1H,4-iodooctaphenyltetrasilane, prepared from the reaction of hydrogen iodide with Ia, was not isolated but was hydrolyzed directly to 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol (9).

With hydrogen iodide and hydrogen bromide, one hour and four hours, respectively, were required to bring about the complete disappearance of Ia (9). Under similar conditions octaphenylcyclotetrasilane was found by this author to react only slowly with anhydrous hydrogen chloride. After a reaction time of twelve hours, 86% of the Ia was recovered. A 2% yield of 1*H*,4-chlorooctaphenyltetrasilane was obtained. Therefore, the order of reactivity of the hydrogen halides with Ia is HI $>$ HBr $>$ HCl.

Having obtained and characterized 1*H*,4-chlorooctaphenyltetrasilane, it appeared advisable to study conditions which might allow us to prepare the 1*H*,4-chloro compound in higher yields. Table 3 gives the various conditions used relative to time, temperature and solvents and the respective yields of 1*H*,4-chlorooctaphenyltetrasilane obtained. Treatment of Ia with hydrogen chloride for three hours in *o*-dichlorobenzene gave a 93% yield of 1*H*,4-chlorooctaphenyltetrasilane.

Also by token of its reactivity octaphenylcyclotetrasilane was found capable of dehydrohalogenating certain halogen-containing hydrocarbons. Thus, Ia reacts with β,β'-dichlorodiethyl ether, 1,2,3,4,5,6-hexachlorocyclohexane, *t*-butyl bromide and 2-chlorobutane to give the corresponding 1-halo-octaphenyltetrasilane. Table 16 gives the results obtained from the reaction of various organic halides with Ia.



$$\begin{array}{l} Ph_2Si{-}SiPh_2 \\ \quad | \qquad\quad | \\ Ph_2Si{-}SiPh_2 \end{array} + (CH_3)_3CCl \longrightarrow H{-}(SiPh_2)_4{-}Cl + CH_2{=}C(CH_3)_2$$

Table 16. The reaction of octaphenylcyclotetrasilane with organic halides

Halide (mole)	Solvent (ml.)	Ia (mole)	Time hours	Temp. (°C)	Recovered I (%)	Products	(%)
β,β'-Dichlorodiethyl ether (solvent)	(100)	0.02	1.5	Reflux	15	$Cl(SiPh_2)_4Cl$ $H(SiPh_2)_4Cl$	(29)
Hexachlorocyclohexane (0.04)	Decalin (100)	0.11	5	185	24	$H(SiPh_2)_4Cl$ $Cl(SiPh_2)_4Cl$	(55)
t-Butyl chloride (0.30)	Decalin (100)	0.03	72	83	99.1	------------	
t-Butyl chloride (0.092)	Decalin (100)	0.03	23	148	----	$H(SiPh_2)_4Cl$	(78)
t-Butyl chloride (0.092)	Xylene (200)	0.03	48	133	31	$H(SiPh_2)_4Cl$ Isobutylene	(57.3)
t-Butyl chloride (0.083)	o-Dichlorobenzene (150)	0.055	9	158	27.5	$H(SiPh_2)_4Cl$	(70)
2-Chlorobutane (0.133)	o-Dichlorobenzene (100)	0.01	17	147	85	$H(SiPh_2)_4Cl$	(6.8)
n-Butyl chloride (0.079)	Xylene (100)	0.01	70	129	99	-----------	
n-Butyl chloride (0.086)	o-Dichlorobenzene (100)	0.01	67	157	93	-----------	
t-Butyl bromide (0.062)	Decalin (100)	0.01	1.5	162	---	$H(SiPh_2)_4Br$ $Br(SiPh_2)_4Br$	(77)

The reaction of Ia with t-butyl chloride was very slow at temperatures below 140°C but good yields (57-78%) were obtained using xylene, decalin or o-dichlorobenzene as solvent. A secondary reaction occurred in the case of t-butyl bromide, 1,2,3,4,5,6-hexachlorocyclohexane and β,β'-dichlorodiethyl ether and the silicon hydride formed was converted to a silicon halide to give the corresponding 1,4-dihalooctaphenyltetrasilane. This conversion has already been noted to occur with other silicon hydrides (27). This reaction does not necessarily involve a dehydrohalogenation of the alkyl halide and evidently does not follow the same mechanistic route as that of the acid halide or t-butyl halide causing silicon-silicon cleavage (116). Ia has been halogenated with numerous alkyl polyhalo compounds (3) and the reaction of Ia with hexachlorocyclohexane is probably a competitive reaction between halogenation and hydrohalogenation to give a mixture of 1,4-dichloro and 1H,4-chlorooctaphenyltetrasilane.

$$\mathrm{RBr} + \equiv\mathrm{Si{-}H} \longrightarrow \mathrm{RH} + \equiv\mathrm{Si{-}Br}$$

Desilylation of arylsilanes is dependent on inductive, resonance and steric effects (27). Studies in this thesis and in other recent reports (86) have shown that 1,4-octaphenyltetrasilane derivatives are highly conjugated and also exhibit a great deal of steric hindrance to substitution reactions. These factors and others (117) probably account for the lack of any silicon-phenyl cleavage occurring under the conditions used.

The Hydrohalogenation of Decaphenylcyclopentasilane

In contrast to the high reactivity of octaphenylcyclotetrasilane, decaphenylcyclopentasilane resists cleavage by nearly all reagents which react rapidly and in high yield with Ia. However, we have found that IIa does react at a slower rate with chlorine, inorganic halides, 1,1,2,2-tetrachloroethane and nitrobenzene. However, reaction conditions suitable for ring-opening of IIa usually cause secondary cleavage of the resulting linear polysilane at an equal or faster rate than with the cyclosilane.

Hydrohalogenation of IIa was attempted with various hydrogen halides and organic halides using a variety of conditions with regard to solvent, temperature and time. In only two instances did any appreciable reaction occur and secondary cleavage of the polysilane occurred to give intractable products. No results from hydrohalogenation _via_ organic halides was observed. Tables 6 and 7 list the various attempts made to cleave IIa with a variety of hydrogen halides and organic halides.

A comparison of the decreasing reactivity with increasing ring size of 1,1,2-triphenyl-1-silacyclobutane and 1,1,2-triphenyl-1-silacyclopentane (17) has been made with respect to the ground state energy, the formation of a pentacovalent intermediate and the resultant transition or intermediate state energy. Similar comparisons have been made of the relative reactivities of Ia and IIa (9) (see Historical section). However, recent studies of dodecaphenylcyclohexasilane indicate that steric effects of the bulky phenyl groups may well be a major factor in protecting the silicon-silicon bond of IIa from cleavage. The facile reactivities of certain six- and seven-membered ring heterocyclic polysilanes studied in this thesis provide evidence for this observation.

The Hydrohalogenation of Dodecamethylcyclohexasilane

Only two cyclohexasilanes have been prepared and studied in relation to their reactivity to various cleavage reactions. Dodecaphenylcyclohexasilane (7) is formed in very low yield as a by-product from the general preparation of Ia and IIa (see Experimental section). Shielded by bulky phenyl groups, it is the most stable and unreactive cyclosilane known. Ring-opening occurs only under strong forcing conditions which cause multiple cleavages (7).

Dodecamethylcyclohexasilane can be obtained in good yield (72%) and appeared to be a valuable precursor for the preparation of a large number of otherwise unavailable α,ω-substituted polydimethylsilanes. New polysilane compounds have been prepared by the halogenation of IIIa with iodine (118), chlorine[1], phosphorus pentachloride (19) and 1,1,2,2-tetra-

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[1] P. K. Sen and R. A. Tomasi, op. cit., p.8.

chloroethane (19). However, cleavage reactions of the resulting linear polysilane, after initial ring-opening, become competitive and a number of compounds of varying chain length are obtained.

This thesis includes the reaction of anhydrous hydrogen chloride and t-butyl chloride with IIIa to give a series of highly synthetically valuable compounds having the general formula $Cl\text{-}(SiMe_2)_n\text{-}Y$, where Y is either hydrogen or chlorine and n = 1 to 6. The general illustrative reaction is:

$$\begin{array}{lcl} (Me_2Si)_6 \;+\; RCl & \longrightarrow & Cl\text{-}(SiMe_2)_n\text{-}Y \\ \qquad\quad R{=}H,\ Me_3C & & Y = H,\ Cl \\ & & n = 1 \text{ to } 6 \end{array}$$

IIIa is slowly cleaved by anhydrous hydrogen chloride in refluxing dichloromethane, xylene or o-dichlorobenzene. The rate of cleavage is increased at higher temperatures and the reaction mixture contains all the products where n = 1 to 6 and Y = hydrogen or chlorine. No significant reaction occurred in refluxing benzene, petroleum ether (b.p. 60-70°C), chloroform or carbon tetrachloride. The reaction of anhydrous hydrogen chloride with IIIa was rapid in a stainless steel autoclave at pressures of 400 to 600 p.s.i. and temperatures of 50 to 70°C. Above 70 to 100°C the reaction became exothermic and the temperature rose as high as 175°C. The yield of dichloro compounds and low molecular weight homologs in the series increased with increasing amounts of hydrogen chloride.

Table 17 lists the products and yields obtained using a 1:2, 1:3 and 1:4 molar ratio of dodecamethylcyclohexasilane to hydrogen chloride.

No apparent reaction occurred between IIIa and t-butyl chloride in o-dichlorobenzene at 155-180°C after 48 hours. A mixture of t-butyl chloride and IIIa reacted smoothly when placed in a stainless steel autoclave and heated at 140-150°C for several hours. The pressure rose from ambient to 140 p.s.i. The silane products obtained using a 4:1 molar ratio of halide to cyclosilane are included in Table 17. Table 18 lists the new compounds prepared in this study with some of their physical properties.

It was observed that in all the pressure reactions with hydrogen chloride the weight gain of the product mixture was equal to the hydrogen chloride used but that the pressure drop accounted for only part of the gas being used. A qualitative mass spectrum analysis of the gases removed from the autoclave through a trap cooled in dry ice-acetone showed the presence of some hydrogen and methane with higher molecular weight fragments up to 121 mass units. An attempt to derivatize the gas mixture by passing it through a solution of phenyllithium in ether gave a small amount of a low melting mixture of solids from which no definitive products were isolated.

The inability of t-butyl chloride to react with IIIa in o-dichlorobenzene and the much slower reaction of hydrogen

Table 17. The reactions of IIIa with hydrogen chloride and with *t*-butyl chloride

$\text{Cl-(SiMe}_2)_n\text{-Y}$		Molar ratio of reactants			
		HCl/IIIa	HCl/IIIa	HCl/IIIa	*t*-BuCl[a]/IIIa
n	Y	2:1	3:1	4:1	4:1
1	H	15 %[b]	16 %[b]	14 %[b]	1 %[b]
1	Cl	2	4	4	8
2[c]	H	1	4	3.5	1
2	Cl	2	8	9	16
3[c]	H	3	4	8	10
3	Cl	3	8	8	17
4[c]	H	4	2.5	5	6
4	Cl	2	5	11	12
5[c]	H	6	4	2.5	5
5[c]	Cl	-[d]	5.5[d]	2.5	3
6[c]	H	-[d]	5[d]	3.0	6
6	Cl	-[d]	3[d]	3.0	7

[a] *t*-Butyl chloride.

[b] Yields based on available dimethylsilylene.

[c] This is the first reported synthesis.

[d] Combined yield of 2 and 3:1 molar ratio reactions.

Table 18. Properties of Cl-$(SiMe_2)_n$-Y compounds

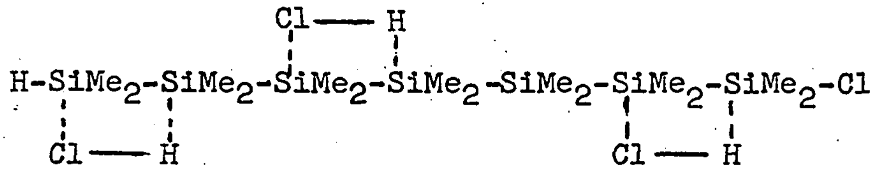
n	Y	b. p. °C/mm.	b.p. °C/ 760 mm.	$n_D^{20°}$	$d^{20°}$
1	H	-------	35	1.3838	
2	H	-------	119	1.4421	0.8664
3	H	77/14	183[a]	1.4735	0.8886
4	H	59/0.08-1.0	226-232[a]	1.4986	0.9018
5	H	79/0.1; 75/0.06	298-301[a]	1.5145	0.8983
6	H	105/0.1; 100/0.06	337-340[a]	1.5302	0.9042
5	Cl	87-89/0.1	310-312[a]	1.5220	0.9581

[a] Extrapolated from a chart similar to those originated in the laboratories of Standard Oil Company (104).

chloride with IIIa in this solvent is very different from the reactivity of Ia with these reagents under the same conditions. Again it may be noted that Ia, due to its molecular geometry and following the principle of "least motion" of non-reacting groups, (79) may be able to form a pentacoordinate intermediate or transition state of lower energy than the corresponding cyclohexasilane, IIIa. However, less ring strain and the resultant lower ground state energy for IIIa also contribute to its lower reactivity.

Vapor phase chromatographic analysis of the reaction mixture indicated that only traces of compounds in the series H-

$(SiMe_2)_n$-H were present. Relative to mechanisms involved, this observation indicates that addition of the hydrogen chloride at any point in the chain is markedly oriented in the manner shown.



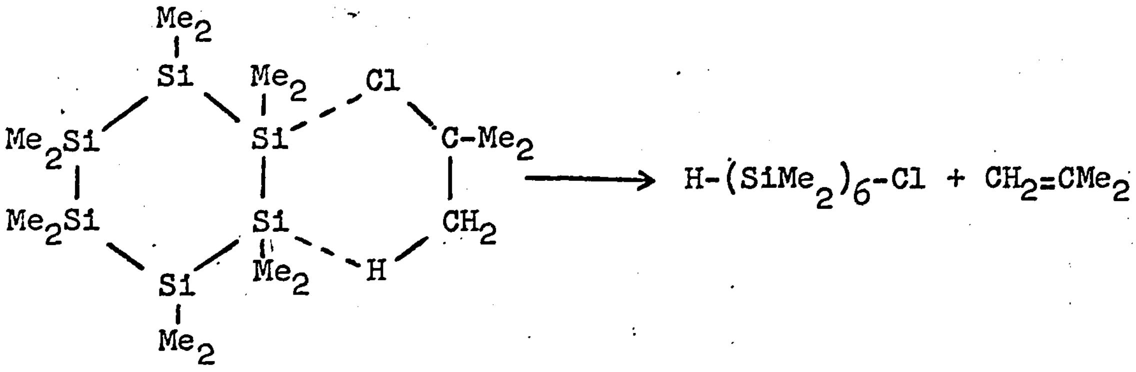
$$H\text{-}SiMe_2\text{-}SiMe_2\text{-}SiMe_2\text{-}SiMe_2\text{-}SiMe_2\text{-}SiMe_2\text{-}SiMe_2\text{-}Cl$$

Also concluded is that all of the dichloro compounds formed are due to reaction of the hydrogen chloride or t-butyl chloride with a silicon-hydrogen bond rather than by "symmetrical" cleavage of a linear polysilane.

$$Cl\text{-}(SiMe_2)_n\text{-}H \ + \ HCl \longrightarrow Cl\text{-}(SiMe_2)_n\text{-}Cl \ + \ H_2$$

$$H\text{-}(SiMe_2)_6\text{-}Cl \ + \ HCl \xrightarrow[\text{reaction}]{\text{no}} H\text{-}(SiMe_2)_n\text{-}H \ + \ Cl\text{-}(SiMe_2)_{6-n}\text{-}Cl$$

The specific orientation resulting in the products obtained is an indication that the mechanism involves a multi-centered reaction, i.e., four-center with hydrogen chloride as shown above and six-center with t-butyl chloride.



Other evidence for a multicenter reaction is the lack of any reaction with hydrogen chloride in solvents such as chloroform, carbon tetrachloride or petroleum ether (b.p. 60-70°C) which are used in the chlorination of Ia, IIa or IIIa. These reactions show evidence of following a free radical mechanism.

It will be noted here that if the rate determining step involved the nucleophilic attack of chlorine, cleavage would be on the silicon atom adjacent to the strongly electronegative chlorine atom. Dichlorodimethylsilane would be the expected product. This has been demonstrated by nucleophilic cleavage of α-chlorinated methylsilanes with bases in which the rate decreases in the order $CCl_3 \rangle CHCl_2 \rangle CH_2Cl$. Rather than this, the observed products require attack of the chlorine at a silicon atom adjacent to hydrogen or β to the chlorine atom. Again it appears that a multicentered mechanism is preferred.

The loss in reactivity of the silicon adjacent to a terminal chlorine was observed in the reaction of $Cl-(SiMe_2)_4-Cl$ with t-butyl chloride. At 100°C and 120 p.s.i. no apparent reaction occurred. At 170°C and 200 p.s.i. the reaction was slow and cleavage at the center of the chain was favored (3.5:1). The results are given in Table 19. Under comparable conditions IIIareacted rapidly with t-butyl chloride.

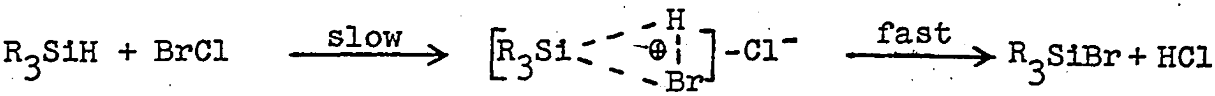
From the reaction of hydrogen chloride with silicon hydrides it is evident that the reaction is not an (S_Ni-S_Ei)-Si type three-center reaction, as proposed by Sommer for the halogenation of silicon hydrides (79).

Table 19. The reaction of t-butyl chloride and 1,4-dichlorooctamethyltetrasilane[a]

	Product $Cl\text{-}(SiMe_2)_n\text{-}X$	
n	X	Yield (%)
1	H	1.5
1	Cl	3.0
2	H	4.0
2	Cl	21.5
3	H	3.5
3	Cl	6.1
4	Cl	59.5[b]

[a] 0.1 mole, 6 hours at 170°C and 200 p.s.i. pressure.

[b] Recovered starting material.



$$R_3SiH + BrCl \xrightarrow{slow} \left[R_3Si \overset{H}{\underset{Br}{\cdots \oplus}}\right]\text{-}Cl^- \xrightarrow{fast} R_3SiBr + HCl$$

Formation of a pentacovalent transition state by electrophilic attack of a proton would result in internal return and no net reaction. Again a probable mechanism involves a 4-center transition state.

The observed formation of isooctane, 2,5-dimethylhexane and other hydrocarbons from the reaction of IIIa with t-butyl chloride provides a good argument against a possible multi-center reaction. However, comparison of the product distribution of the 4:1 molar ratio reactions of hydrogen chloride and t-butyl chloride with IIIa indicates that a much higher degree of reactivity exists between silicon hydrides and <u>t</u>-butyl chloride than with hydrogen chloride, <u>i.e.</u>, the ratio of the dichloro products is much higher with <u>t</u>-butyl chloride. The high yield of chlorodimethylsilane from the reaction of IIIa with hydrogen chloride indicates that this monomer is unreactive towards hydrogen chloride. However, the high yield of dichlorodimethylsilane, as compared to chlorodimethylsilane, from the reaction of IIIa with <u>t</u>-butylchloride is evidence that a different reaction following a mechanism unlike that of the reaction of hydrogen chloride occurs with <u>t</u>-butyl chloride (see Table 17).

Westermark reported the halogenation of triethylsilane with allyl bromide, β-bromomethylpropionate and <u>n</u>-propyl bromide giving yields of 97, 50 and 10%, respectively (116). The formation of the corresponding hydrocarbon with no olefinic products was observed.

Apparently this reaction, with possible free radical or carbonium ion formation, occurs also with <u>t</u>-butyl chloride.

$$\equiv\text{Si-H} + \text{RCl} \longrightarrow \text{RH} + \text{RR} + \equiv\text{Si-Cl}$$

The chromophoric, and particularly the ultraviolet, properties of polysilanes provide a useful means of identification and characterization in the field of organosilicon chemistry. Table 20 lists the ultraviolet spectral data for the α,<u>H</u>,ω-chloro polydimethylsilanes prepared in this study. Table 21 lists the ultraviolet spectral data for the corresponding

Table 20. UV spectral data of the H-$(SiMe_2)_n$-Cl series[a]

Compound n	Band position $\lambda_{max.}$, mμ	Molar absorptivity ε	Concentration $M \times 10^5$
2	194[b]	2,770	12.00
3	217.5	7,150	7.55
4	235.0	13,340	4.46
5	249.5, 215.0	16,380, 8,770	3.26
6	258.0, 225.0	21,807; 11,900	3.21

[a] Obtained with a Beckman DK-2A spectrophotometer using cyclohexane as solvent.

[b] Values are somewhat imprecise because of solvent cutoff.

Table 21. UV spectral data of the Cl-$(SiMe_2)_n$-Cl series[a]

Compound n	Band position $\lambda_{max.}$, mμ	Molar absorptivity ε	Concentration $M \times 10^5$
2	204.0[b]	3,228	28.0
3	219.0	8,610	4.31
4	235.0	17,426	3.68
5	250.0; 214	19,532, 9,906	4.27
6	259.0, 225	23,250, 11,091	3.20

[a] Obtained with a Beckman DK-2A spectrophotometer using cyclohexane as solvent.

[b] Values are somewhat imprecise because of solvent cutoff.

α,ω-dichloropolysilanes.

As reported earlier in a study of fully permethylated straight-chain polysilanes, the position of maximum absorption and the molar absorptivity increase regularly with increasing chain length (82). The conjugated system is also lengthened by replacement of a methyl group with substituents such as a phenyl or vinyl group which increase the $\lambda_{max.}$ and molar absorptivity. This apparently occurs through overlap with their π-electron systems and the d-orbitals of the polysilane (87). However, it was previously reported that replacing a methyl group with chlorine atoms had little effect on the ultraviolet spectra (87).

Comparison of our studies, shown in Tables 20 and 21, with the ultraviolet spectral data of the Me-$(SiMe_2)_n$-Me series (82) indicates that little or no change is observed in the $\lambda_{max.}$ of polydimethylsilanes substituted with a terminal methyl group, chlorine or hydrogen atom. However, differences of an apparently regular nature are observed in the molar absorptivity. The observed effects might well be expected, because differences in polarity of each of these homologous series, due to the inductive effects of the terminal atom or group, could effect electron transitions throughout the chain.

Several of the compounds in the series H-$(SiMe_2)_n$-H were available in These Laboratories. Using the available α,ω-dichloro- or αH,ω-chloro- polydimethylsilanes all of the compounds in the series H-$(SiMe_2)_n$-H, where n = 3 to 6, were purified or prepared. This includes the first reported synthesis of 1,1,2,2,3,3,4,4,5,5-decamethylpentasilane. The properties of this series are given in Table 22. The ultraviolet spectral properties are given in Table 23. Again comparison with Tables 20 and 21 demonstrates the utility of ultraviolet spectra in the characterization of polysilanes and in the measure of the relative inductive effect of the terminal substituent.

Further confirmation of the αH,ω-chloro polydimethylsilane series prepared was made with an NMR spectrum of each compound. Table 24 gives the NMR spectral data for the H-$(SiMe_2)_n$-Cl series. No obvious conclusions for the observed multiplicity of peaks for the 1H,6-chlorododecamethylhexasilane compound were apparent.

Some Observations on α,ω-Polydiphenylsilane Derivatives

In four instances unusual effects were noted in the reaction of some α,ω-disubstituted polydiphenylsilanes. 1H,4-Chlorooctaphenyltetrasilane was found to be unusually stable toward hydrolysis in an aqueous solution. A near quantitative recovery of the chlorosilane was made after stirring in a water-ether mixture for 8 hours at room temperature.

Condensation of hydroxysilanes to form siloxanes has been effectively carried out by heating the silanol in formic acid (47). Continuous heating of 1,1,2,2,3,3,4,4-octaphenyltetra-

Table 22. Properties of H-$(SiMe_2)_n$-H compounds

Compound n	Properties b.p.	n_D^{20}	D^{20}	Ref.
3	59°C/24 mm.			58[a]
4	98°C/24 mm.	1.4930		58
5	142°C/19 mm.	1.5074	0.8256	--
6	82°C/0.07 mm.	1.5256		--[a]

[a] J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Kindly provided sample. 1965.

Table 23. UV spectral data of the H-$(SiMe_2)_n$-H series[a]

Compound n	Band position $\lambda_{max.}$, mμ	Molar absorptivity ε	Concentration $M \times 10^5$
3	218.0	6,841	9.94
4	235.5	12,250	6.00
5	249, 214	13,590, 9,440	4.29
6	257.5, 225	19,456, 11,150	2.92

[a] Obtained with a Beckman DK-2A spectrophotometer using cyclohexane as solvent.

Table 24. NMR spectral data of the H-$(SiMe_2)_n$-Cl series[a]

n	$H^{b,c}$ τ	$SiMe_2{}^c$ τ	$(SiMe_2)_{n-2}$ τ	$SiMe_2Cl$ τ
2	6.2	9.77, 9.86		9.55
3	6.13	9.78, 9.86	9.82	9.53
4	6.13	9.79,[d] 9.87	9.79[d]	9.52
5	6.15	9.82,[d] 9.88	9.77, 9.82[d]	9.53
6	6.15	9.81, 9.88	9.76, 9.77, 9.79, 9.82	9.53

[a] Obtained with a Varian A-60 spectrometer.

[b] Center of a septet.

[c] $J = 4.5$ c.p.s.

[d] Relative intensities indicate two overlapping peaks.

silan-1-ol in a 98% formic acid solution for a prolonged period gave only a trace of nonisolable compounds possessing an Si-O-Si bond.

The reaction of 1H,4-chlorooctaphenyltetrasilane and 1,5-dibromodecaphenylpentasilane with phenylmagnesium bromide or with phenylmagnesium iodide gave no evidence of a reaction having occurred with the chlorosilane. At higher temperatures, unidentified tars and a trace of tetraphenylsilane were the only products obtained. However, silicon-silicon cleavage evidently occurred to give the tetraphenylsilane.

Grignard reagents have not been noted to be sufficiently strong nucleophiles to cause cleavage of a polysilane (27).

The reaction of phenyllithium with 1<u>H</u>,4-chlorooctaphenyltetrasilane and with 1,5-dibromodecaphenylpentasilane resulted in multiple cleavage of the polysilanes. Only a trace of the desired dodecaphenylpentasilane occurred in the latter reaction. At low temperatures a small amount of a heptasilane was isolated in the reaction of the tetrasilane with phenyllithium.

All of these reactions may be influenced by the electronic effects of the silane chain or the multiple of phenyl substituents on the chain. It would appear, in view of the other derivatives prepared by the formation of terminal alkoxy or alkyl substituents, that probably the greatest factors involved are due to the steric effects of the bulky phenyl groups.

While characterizing 1H,4-chlorooctaphenyltetrasilane, m.p. 161-162°C, it was observed that mixture melting points of this compound with 1H,4H-octaphenyltetrasilane, m.p. 160-162°C or with 1H,4-bromooctaphenyltetrasilane, m.p. 162-164°C were not depressed. Mixture melting points of the latter two compounds also gave no depression of the melting points. Care was taken with all of the compounds isolated to confirm the identity of the compound by other means as well as by a mixture m.p. This anomaly was not observed with any other compounds. The preparation of 1,5-diallyloxydecaphenylpentasilane; m.p. 172-174°C, also gave a small yield of 1,5-dihydroxydecaphenylpentasilane, m.p. 174-176°C. A mixture m.p. of these two compounds was depressed 6 to 8°C. All of the heterocyclic polysilanes studied exhibited polymorphism with the exception of VIIa. Some (VIII and IXa) appeared to form eutectic mixtures. This phenomena has been generally observed with cyclic siloxanes (108).

Suggestions for Further Research

In the present study a variety of heretofore unavailable linear, cyclic and heterocyclic polysilanes have been prepared. Many of these compounds contain functional terminal groups which may be useful in further synthetic work. The unsymmetrically disubstituted polysilanes are perhaps most useful in providing compounds which do not contain terminal substituents of equal reactivity. Kinetic studies or the use of erythro or threo isomers of organic halides in the hydrohalogenation of cyclosilanes would provide more valid interpretations of the mechanism and nature of this reaction. Heterocyclic polysilanes containing a variety of heteroatoms would undoubtedly provide useful studies. Cyclosilanes containing methylene groups would offer interesting comparisons to the present study. Using the ring closure methods demonstrated herein different hetero atoms may be introduced into a polysilane chain.

The recently observed ultraviolet absorption properties of polysilanes offer a variety of useful studies. The use of photochemistry in polysilane syntheses and reactions has been given very little attention. The preparation of aryl-substituted polysilanes and a study of their ultraviolet absorption properties will undoubtedly provide a means of measuring substituent effects on the aryl group. It was noted in this thesis that the introduction of an oxygen atom into a polysilane chain gave a $\lambda_{max.}$ value characteristic of the longest silicon chain present, *i.e.*, no transitions were observed through the heteroatom. Introduction of an element such as sulfur which has available *d*-orbitals similar to silicon may give transitions through the chain much like extending the polysilane chain. The introduction of a π-electron system, such as a phenyl group, into the silicon chain may also extend the conjugation effects.

The preparation of four- or five-membered rings containing substituents other than phenyl groups would provide a more suitable comparison of the reactivity of cyclosilanes. Physical studies of the conformation of cyclosilanes would be useful in interpreting ring strain effects.

SUMMARY

A review of the reported chemistry of known cyclosilane compounds is presented. All of the known cyclic or heterocyclic compounds containing at least one silicon-silicon bond are included.

A study of the preparation of α,ω-dichloro polydiphenylsilanes from octaphenylcyclotetrasilane and decaphenylcyclopentasilane with chlorinating reagents such as 1,1,2,2-tetrachloroethane, phosphorus pentachloride and chlorine is discussed. The study has led to the preparation of compounds of the general formula $Cl-(SiPh_2)_n-Cl$, where n equals 2 to 5. The conditions for chlorination of the cyclosilanes with or without silicon-silicon cleavage of the linear polysilane after initial ring-opening are described.

Conditions were found for the successful cleavage of octaphenylcyclotetrasilane with anhydrous hydrogen chloride. Organic halides such as β,β'-dichlorodiethyl ether, 1,2,3,4-5,6-hexachlorocyclohexane, _t_-butyl chloride, 2-chlorobutane and _t_-butyl bromide were found to be capable of hydrohalogenating octaphenylcyclotetrasilane to give the corresponding 1_H_,4-halooctaphenyltetrasilane. A variety of unsuccessful attempts to hydrohalogenate decaphenylcyclopentasilane was made.

Starting with octaphenylcyclotetrasilane, a number of heterocyclic polysilanes can be made by the insertion of one oxygen atom at a time into the ring, using a procedure in-

volving hydrolysis subsequent to chlorination of the appropriate smaller ring compound. The propyl alcohol hydrolysis of 1,4-dichlorooctaphenyltetrasilane gives octaphenyloxatetrasilacyclopentane which can be cleaved with chlorine and the products hydrolyzed to give the corresponding octaphenyl-1,3- and 1,4-dioxatetrasilacyclohexanes. The hydrolysis, subsequent to chlorination, of these two compounds gives a seven-membered ring cyclosilane, octaphenyl-2,3,5-trioxa-1,4,6,7-tetrasilacycloheptane. Chlorine added to this compound followed by cyclization gives the first unambiguous preparation of octaphenylcyclotetrasiloxane. The addition of chlorine to the above five-, six- and seven-membered ring compounds was rapid and quantitative. This is in contrast to the rate of addition of chlorine to perphenylated cyclosilanes which decreases rapidly with increasing ring size.

A study was made of the reaction of nitrobenzene on octaphenylcyclotetrasilane, decaphenylcyclopentasilane, dodecaphenylcyclohexasilane, hexaphenyldisilane and the above oxacyclosilanes. Octaphenylcyclotetrasilane and octaphenyloxatetrasilacyclopentane gave mixtures of the 1,3-dioxa and 2,3,5-trioxa cyclic compounds. These, the 1,4-dioxa compound and decaphenylcyclopentasilane reacted slowly to give hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane. Dodecaphenylcyclohexasilane and hexaphenyldisilane did not react under the conditions used.

Anhydrous hydrogen chloride and t-butyl chloride were used to hydrohalogenate dodecamethylcyclohexasilane to provide a series of very useful compounds of the general formula $Cl-(SiMe_2)_n-Y$, where $n = 1$ to 6 and Y = hydrogen or chlorine.

Derivatives were made of the various polysilanes with reagents such as alcohols, Grignard reagents and phenyllithium, or by hydrolysis with acids etc. Studies of the variety of polysilanes prepared included assignment of silicon-chlorine absorptions of α,ω-dichloro phenylpolysilanes with increasing chain length in the 400 to 700 cm.$^{-1}$ range. Infrared studies of the Si-O-Si absorption shifts in cyclic compounds of different ring-size and of the Si-phenyl absorptions observed in polydiphenylsilanes of varying chain length was useful in the characterization of the oxacyclosilane compounds prepared.

Ultraviolet absorption maxima were determined for all the compounds prepared. A study of the series $Y-(SiMe_2)_n-Y$, where $n = 2$ to 6 and Y = hydrogen or chlorine, showed the same $\lambda_{max.}$ for any given chain length. However, differences of a regular nature are observed in the molar absorptivity. Ample demonstration is given of the utility of ultraviolet absorption spectra in characterizing polysilanes and in measuring the relative electronic effects of varying terminal groups.

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