Systematic Synthesis in the Polysilane Series

GRANT URRY

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The congeneric relationship of silicon to carbon has stimulated a considerable volume of scientific effort exploring for reactions in silicon chemistry analogous to previously demonstrated organic reactions. The preparation of tetraethylsilane by the reaction of silicon tetrachloride with diethylzinc, reported over a century ago by Friedel and Crafts,[1] was a harbinger of the productive investigations in the field of organosilicon chemistry dominated during much of this century by Kipping and Gilman. The work of Kipping and his coworkers led directly to a healthy growth of knowledge culminating in the robust industrial field of silicone chemistry.[2] The work of Gilman continues to inspire new efforts among the present generation of chemists.

In spite of these and other heartening successes, the carbon–silicon analogy often serves to retard progress in the field of polysilane chemistry, the chemistry of compounds possessing silicon to silicon bonds. The profusion of organic compounds found in nature includes many important homologous series useful in advancing the knowledge of organic chemistry while naturally occurring silicon compounds, in every sense as abundant and diverse, afford access to knowledge of compounds possessing silicon–oxygen bonds not analogous to and quite different from organic chemistry. While mineralogy is undeniably an interesting and challenging discipline, these silicon resources have so far proved less susceptible to chemical modification by silicon chemists than have petroleum resources for the organic chemist.[3] On the other hand, it should be commented that the current state of polysilane chemistry is no worse than the hypothetical state of organic chemistry were the only naturally occurring sources for the element carbon the carbonates and carbon dioxide.

Another disadvantage borne by the chemist sufficiently adventurous to maintain an interest in polysilanes is the absence of silicon analogs of unsaturated organic compounds. While this deficiency can be rationalized by differences in electronic composition or configuration, small comfort accrues to the polysilane chemist upon reading long and often labored discussions explaining why the "low-lying 3d orbitals," readily accessible in most silicon compounds, forestall admission to chemistry parallel with the elegant organic chemistry of alkenes, alkynes, and polyenes.

It is perhaps appropriate to chide the polysilane enthusiast for milking the horse and riding the cow in attempting to adapt the successes of organic chemistry in the study of polysilanes. A valid argument can be made for the point of view that the most effective chemistry of silicon arises from the differences with the chemistry of carbon compounds rather than the similarities.

One such difference is the behavior of these two classes of compounds toward nucleophiles. For example, the hydrocarbons are little affected by most nucleophiles while "saturated polysilanes," Si_2H_{2n+2}, react in diverse fashions, some productive and others more frustrating. Thus it is possible to prepare higher homologs in the hydrocarbon series in a systematic fashion by the venerable reaction of an alkyl halide with a metal alkyl without hazarding the destruction of the newly formed homolog by further reaction with the metal alkyl. The reactivity of the silicon–silicon bond toward such nucleophiles is emphasized by the rarity of simple metal silyls. Potassium silyl, $KSiH_3$, was first observed by Isenberg[4] and Johnson as a white crystalline solid which precipitated when a potassium solution in liquid ammonia was treated with silane. They demonstrated the nature of this solid by reactions with methyl chloride and ammonium chloride but were unable to isolate it from the ammonia, probably as a result of extensive ammonolysis. Ring and Ritter in more recent work[5] were able to isolate and characterize this silyl anion by carrying out the same reaction in 1,2-dimethyoxyethane as a solvent, thus avoiding the solvolysis of the product.

Attempts to prepare potassium disilanyl, KSi_2H_5, by a similar reaction between potassium and disilane have failed. The reaction is complex and yields only products expected from silane itself and polymeric solids of depressing familiarity to polysilane chemists. These solids often arise when the higher silanes are treated with nucleophiles or are pyrolyzed. They have their analog in organic chemistry in the residual tars which often signal an unfortunately low yield of desired product from an organic reaction.

When potassium silyl is treated with bromosilane, only a trace of the hoped-for disilane is obtained, the major volatile product being silane.[5] The remainder of the silicon is accounted for in the previously mentioned "solids." This again illustrates the susceptibility of the silicon–silicon bond to reaction with nucleophiles.

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(1) C. Friedel and J. Crafts, *Justus Liebig's Ann. Chem.*, **127**, 31 (1863).

(2) For an excellent summary of this field and an account of its healthy growth see E. G. Rochow, "An Introduction to the Chemistry of the Silicones," Wiley, New York, N. Y., 1951.

(3) This is not to belittle the work of M. E. Kenney and others whose current studies of the chemical modification of various silicate minerals might force amendment of this dogmatic statement.

(4) S. Isenberg, Ph.D. Dissertation, University of Chicago, 1937.

(5) M. A. Ring and D. M. Ritter, *J. Amer. Chem. Soc.*, **83**, 802 (1961).

This kind of reactivity is notably reduced for organopolysilanes. Hexamethyldisilane and hexaphenyldisilane can be prepared in good yield by a Würtz-type coupling using sodium and the appropriate chlorosilane. Structurally more interesting compounds such as octaphenyltetrasilane were reported by Kipping[6] as products of the reaction between sodium and diphenyldichlorosilane in boiling toluene or xylene. He found two products of this reaction which he identified as octaphenyltetrasilanes. One he thought to be an open-chain structure terminated at both ends by tervalent carbon and the other octaphenylcyclotetrasilane. A very careful recent reexamination of these products by Gilman and coworkers has shown that Kipping's supposed biradical is probably octaphenylcyclotetrasilane[7] and that the supposed octaphenylcyclotetrasilane is probably decaphenylcyclopentasilane.[8]

This same deactivating effect of the phenyl substituent on the nucleophilic susceptibility of the silicon–silicon bond allowed the first published example of a specific isomeric synthesis.[9] The reaction of lithium triphenylsilyl with trichlorosilane resulted in the formation of tris(triphenylsilyl)silane, or nonaphenylisotetrasilane. While the 4% yield of this product indicates serious problems in this synthesis, the work represents the first successful attempt at a systematic approach to the synthesis of polysilanes.

A more satisfying synthesis which illustrates the deactivating effect of the methyl group is the preparation of tetrakis(trimethylsilyl)silane, or dodecamethylneopentasilane, by the treatment of a mixture of trimethylchlorosilane and silicon tetrachloride dissolved in tetrahydrofuran with lithium wire.[10] The yield from this reaction is reported to be 40%, making this a respectable isomeric synthesis indeed.

Another reaction which produces a structure of interest, as well as illustrating deactivation by methyl substituents, is that of dimethyldichlorosilane with molten sodium which results in mainly polymeric materials, but respectable yields of dodecamethylcyclohexasilane also are obtained.[11]

Unfortunately, it is the very inertness of these permethylpolysilanes that makes extension of this structural chemistry difficult.

The hydrides display no such inertness, but structural chemistry among the hydrides is virtually nonexistent. The existence of the homologous series Si_nH_{2n+2} was demonstrated by Stock.[12] Using vacuum manipulation techniques which he developed, the mixture of polysilanes, resulting from the treatment of magnesium silicide with mineral acids, was separated into various fractions. He was able adequately to characterize Si_2H_6 and Si_3H_8. The higher silanes, Si_4H_{10}, Si_5H_{12}, and Si_6H_{14}, he isolated as mixtures of isomers but was able to prove their molecular formulas. Using the more effective methods of vapor phase chromatography, Borer and Phillips separated a mixture of polysilanes, obtained in a reaction similar to Stock's, into 21 components.[13] By means of nuclear magnetic resonance spectroscopy they identified n-Si_4H_{10}, n-Si_5H_{12}, and i-Si_5H_{12}. They tentatively identified n-Si_6H_{14}, n-Si_7H_{16}, and n-Si_8H_{18}. As yet no specific isomeric synthesis of a polysilane has been reported.

The higher polysilanes readily lose hydrogen at elevated temperatures.[12] While this reaction is analogous to the cracking of saturated hydrocarbons, the products in the case of the polysilanes are refractory solids of variable composition, SiH_n, where $2 > n > 1$, instead of the useful olefins and polyenes obtained from saturated hydrocarbons. The temperatures required for this "cracking" of polysilanes can be quite low in some cases. Losses of hydrogen from some solid polysilanes can occur slowly even at room temperature. It is most probable that these solid polysilanes are polycyclic structures. While they are reactive toward air, chlorine, and anhydrous hydrogen halides, no work has been reported where partial chemical reaction of these solids is used to prepare compounds more amenable to chemical study. It is possible that the solid hydrides could serve in this fashion as readily obtained starting material useful in preparing smaller molecules of structural interest.

Halogen substitution apparently enhances nucleophilic susceptibility of the polysilanes. Although hexamethyldisilane can be prepared by the reaction of methyl Grignard with hexachlorodisilane, as first reported by Bygdén,[14] the yields are low and tetramethylsilane is a major product of this reaction. Similarly the conversion of hexachlorodisilane to disilane using lithium aluminum hydride results in the formation of silane with a subsequent loss in yield of the disilane.[15] Conversion of octachlorotrisilane to trisilane has been reported recently using dibutyl ether as a solvent with rapid removal of the product while maintaining a low concentration of lithium aluminum hydride.[16]

Against this discouraging background even small successes are hardly won. With considerable effort on the part of some of the author's graduate students and appropriately less effort on the part of the author over the past 10 years some modest gains have been made.

Summary of Research

Our interest in polysilane chemistry began with a concept, probably erroneous, which nevertheless prompted experiments with significant results. Similar

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(6) F. S. Kipping and J. Sands, *J. Chem. Soc.*, **119**, 830 (1921); F. S. Kipping, *ibid.*, **123**, 2590 (1923); **125**, 2291 (1924); **129**, 2719 (1927).

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

(8) H. Gilman and G. L. Schwebke, *ibid.*, **86**, 2693 (1964).

(9) D. Wittenberg, M. V. George, and H. Gilman, *ibid.*, **81**, 4812 (1959).

(10) H. Gilman and C. L. Smith, *ibid.*, **86**, 1454 (1964).

(11) C. A. Burkhard, *ibid.*, **71**, 963 (1949).

(12) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(13) K. Borer and C. S. G. Phillips, *Proc. Chem. Soc., London*, 189 (1959).

(14) A. Bygdén, *Ber.*, **45**, 707 (1912).

(15) A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

(16) P. P. Gaspar, C. A. Levy, and G. M. Adair, *Inorg. Chem.*, **9**, 1272 (1970).

situations were typical for several of the useful developments discussed in this section.

Hexachlorodisilane in one sense is a saturated compound. However, as a consequence of the presence, in the silicon valence shell, of unutilized orbitals with proper symmetry it should possibly exhibit properties as a π acid. In earlier work of this author, the π acidity of diboron tetrachloride was demonstrated by its reaction with olefins.[17] It was hoped that a similar reaction could be demonstrated as a consequence of the π acidity of hexachlorodisilane. Upon examination it was determined that a reaction between ethylene and hexachlorodisilane could be promoted photochemically, but the quantum yield of this reaction was discouragingly low and the rate of ethylene uptake distressingly slow. Indeed, the rate of ethylene addition was so slow that it appeared probable that Kaczmarczyk, who was working on this problem, would require several decades for the completion of this study. Such progress being incompatible with his aims to achieve a doctorate, it was decided that a more direct assessment of the acidity of this compound be made.

Initially, trimethylamine and hexachlorodisilane mixtures were studied to demonstrate the existence of amine complexes. The complex of one molecule of the disilane with two molecules of trimethylamine was shown to be stable in the presence of excess amine. The heat of dissociation for the equilibrium shown in eq 1 was determined to be approximately 10 kcal/mol.[18]

$$Si_2Cl_6 \cdot 2N(CH_3)_3 \rightleftharpoons Si_2Cl_6 \cdot N(CH_3)_3 + N(CH_3)_3 \qquad (1)$$

Attempts to determine dissociation constants for the second amine molecule were frustrated because of an irreversible reaction, as shown in eq 2.

$$0.83xSi_2Cl_6 \cdot N(CH_3)_3 \longrightarrow 0.66xSiCl_4 + 0.62xN(CH_3)_3 + [SiCl_{2.36} \cdot 0.21N(CH_3)_3]_x \qquad (2)$$

This reaction does not occur in the presence of amine over the stoichiometric amount for the 1:1 complex. At the other end of the scale it can be induced by very small traces of trimethylamine in pure hexachlorodisilane. The amount of amine required depends on the state of purity of the disilane. Commercially obtained hexachlorodisilane generally contains an impurity of titanium tetrachloride which reacts with trimethylamine. In these cases a slight excess of amine over that required to effect the reduction of the titanium tetrachloride is needed. For pure hexachlorodisilane 0.1 mol % of trimethylamine is sufficient to induce at a satisfactory rate the quantitative reaction shown in eq 3.[19]

$$5Si_2Cl_6 \xrightarrow[N(CH_3)_3]{} 4SiCl_4 + Si_6Cl_{14} \qquad (3)$$

The stoichiometry of this reaction clearly indicated the formation of tetradecachlorohexasilane. This result was confirmed by means of elemental analysis and molecular weight determinations. Since the reaction proceeds quantitatively as shown, this represents a considerable improvement in synthesis for this perchloropolysilane. The largest amount of any isomer of tetradecachlorohexasilane previously reported was 0.5 g, prepared by Martin;[20] this resulted from the treatment of 50 kg of ferrosilicon with 143 kg of chlorine at elevated temperatures. Needless to say, this synthesis failed to excite any experimental work during the intervening 50 years.

The hexasilane prepared in this amine-induced disproportionation differs in several respects from that prepared by Martin. Martin reported his product as a low-volatile liquid. This hexasilane is a beautiful white crystalline solid which sublimes *in vacuo* at temperatures around 100° and melts at approximately 320°. In larger scale preparations it was noted that a more volatile crystalline solid also was formed in this disproportionation. The amounts of this more volatile compound varied with each preparation. Isolation and characterization of this substance proved it to be one of the isomers of dodecachloropentasilane.[21a] While it is more volatile than the hexasilane, subliming *in vacuo* at 70°, it melts at a higher temperature, around 345°.

Both of these new solid perchloropolysilanes display an interesting chemical property. They form reversible complexes with silicon tetrachloride, as shown in eq 4 and 5.

$$Si_5Cl_{12} \cdot SiCl_4 \rightleftharpoons SiCl_4 + Si_5Cl_{12} \qquad (4)$$

$$Si_6Cl_{14} \cdot SiCl_4 \rightleftharpoons SiCl_4 + Si_6Cl_{14} \qquad (5)$$

Nuss determined that complexes could be formed with other chlorosilanes such as methyltrichlorosilane and dimethyldichlorosilane, but not with trimethylchlorosilane.[22] On the hypothesis that these complexes were donor complexes, utilizing the nonbonding pairs of the monosilane chlorines, the failure of trimethyltrichlorosilane to form a complex with either of these perchloropolysilanes suggests structural inhibition. In a careful study of the dissociation energies of these complexes it was determined that symmetry of the donor chlorosilane also was important. An examination of the vapor-phase infrared spectra of the two perchloropolysilanes, as well as their spectra in solvents such as silicon tetrachloride and methylene chloride, permitted the assignment of the neopentyl structure for Si_5Cl_{12} and the neohexyl structure for Si_6Cl_{14}.[22] Chemical support for this assignment of the neopentyl structure is obtained from its reaction with anhydrous hydrogen chloride, which proceeds according to eq 6 as shown.

$$Si_5Cl_{12} + 4HCl \longrightarrow 4SiHCl_3 + SiCl_4 \qquad (6)$$

An examination of the sequence of formation of the

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[17] G. Urry, J. Kerrigan, T. D. Parsons, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **76**, 5299 (1954).

[18] A. Kaczmarczyk and G. Urry, *J. Inorg. Nucl. Chem.*, **26**, 415 (1964).

[19] (a) A. Kaczmarczyk and G. Urry, *J. Amer. Chem. Soc.*, **82**, 751 (1960); (b) A. Kaczmarczyk, J. W. Nuss, and G. Urry, *J. Inorg. Nucl. Chem.*, **26**, 427 (1964).

[20] G. Martin, *J. Chem. Soc.*, **105**, 2836 (1914).

[21] (a) A. Kaczmarczyk, M. Millard, and G. Urry, *J. Inorg. Nucl. Chem.*, **17**, 186 (1961); (b) A. Kaczmarczyk, M. Millard, J. W. Nuss, and G. Urry, *ibid.*, **26**, 421 (1964).

[22] J. W. Nuss and G. Urry, *ibid.*, **26**, 435 (1964).

more volatile products of this reaction, silicon tetrachloride and trichlorosilane, suggests that it proceeds according to steps 7–10.[21b]

$$\mathrm{Si_5Cl_{12} + HCl \longrightarrow Si_4Cl_{10} + SiHCl_3} \qquad (7)$$

$$\mathrm{Si_4Cl_{10} + HCl \longrightarrow Si_3HCl_7 + SiCl_4} \qquad (8)$$

$$\mathrm{Si_3HCl_7 + HCl \longrightarrow Si_2HCl_5 + SiHCl_3} \qquad (9)$$

$$\mathrm{Si_2Cl_5H + HCl \longrightarrow 2SiHCl_3} \qquad (10)$$

In the study cited there was no attempt to isolate the decachlorotetrasilane, the heptachlorotrisilane, or the pentachlorodisilane. It is highly probable that the reaction conditions can be controlled in such a fashion that any of these compounds might be obtained in good yield from this degradation. Since the initial reactant is dodecachloroneopentasilane, it is likely that these degradation products structurally are decachloroisotetrasilane and 1,1,1,2,3,3,3-heptachlorotrisilane. The latter compound, as well as the pentachlorodisilane which exists only as one isomer, are of considerable interest to us in reactions to be described later. For these reasons we are currently examining this reaction to see if such control is feasible.

Simple control of the amino-induced disproportionation of hexachlorodisilane is possible. For example, if the reaction is effected in a fashion such that the silicon tetrachloride is removed as it is formed, dodecachloroneopentasilane is the sole crystalline product, as shown in eq 11.[21b]

$$\mathrm{4Si_2Cl_6 \xrightarrow[N(CH_3)_3]{} Si_5Cl_{12} + 3SiCl_4\uparrow} \qquad (11)$$

It is pertinent to note that the solvent phase during the entire course of this reaction is the reactant, hexachlorodisilane, in which the product is insoluble. If, however, the amine-induced reaction is allowed to proceed in a closed vessel of limited vapor volume, the reaction shown in eq 12 occurs.

$$\mathrm{5Si_2Cl_6 \xrightarrow[N(CH_3)_3]{} Si_6Cl_{14}\cdot SiCl_4\downarrow + 3SiCl_4} \qquad (12)$$

Large clear cubic crystals of the silicon tetrachloride adduct of tetradecachloroneohexasilane precipitate during the final stages of the reaction. In this case the solvent phase at the beginning is hexachlorodisilane, but as the reaction progresses silicon tetrachloride accumulates, so that at completion it is the solvent. The tetradecachloroneohexasilane is readily freed from its silicon tetrachloride complex *in vacuo* at room temperature. Thus, the simple solubility difference permits control of this reaction to give either product in an essentially quantitative reaction.

The disproportionation of hexachlorodisilane can be promoted by a variety of nucleophiles, including carefully dried potassium hydroxide. Volatile bases are more convenient since the product perchloropolysilanes undergo further disproportionation when heated in the presence of the catalyst and volatile bases are more easily removed after the reaction is complete. The dodecachloroneopentasilane appears to be less susceptible than the hexasilane to such nucleophilic attack.

There also is a difference among the lower members of the perchloropolysilanes in this catalyzed disproportionation. Thus, with octachlorotrisilane, 0.01 mol % is sufficient to promote rapid reaction, as shown in eq 13, without causing measurable disproportionation of

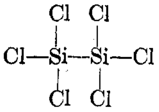
$$\mathrm{3Si_3Cl_8 \xrightarrow[N(CH_3)_3]{} Si_5Cl_{12} + 2Si_2Cl_6} \qquad (13)$$

the product hexachlorodisilane.[21b]

The catalyzed disproportionation of octachlorotrisilane can be modified so that the product is tetradecachloroneohexasilane. If the reaction is carried out in silicon tetrachloride as a solvent, it proceeds as in eq 14.[19b] These reactions of octachlorotrisilane also illustrate the solvent control of product since both reactions proceed quantitatively, as shown in eq 13 and 14.

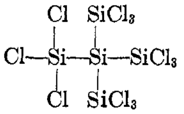
$$\mathrm{5Si_3Cl_8 \xrightarrow[N(CH_3)_3]{} SiCl_4 + 2Si_6Cl_{14}\cdot SiCl_4} \qquad (14)$$

It is natural to speculate concerning the mechanism of such a simple, easily controlled isomeric synthesis. In effect, hexachlorodisilane with structure I is converted to dodecachloroneopentasilane, structure II, in one case, and to structure III for tetradecachloroneohexasilane in the other. There is a possibility of trimethylamine causing the decomposition of hexachlorodisilane to silicon tetrachloride and a reactive carbene-like dichlorosilene which subsequently inserts in a silicon–chlorine bond, resulting in the net effect of substituting a trichlorosilyl moiety for chlorine.



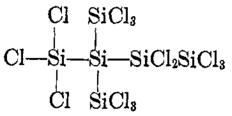
$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{Si}}{-}\overset{Cl}{\underset{Cl}{Si}}{-}Cl}$$

I



$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{Si}}{-}\overset{SiCl_3}{\underset{SiCl_3}{Si}}{-}SiCl_3}$$

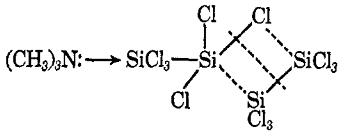
II



$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{Si}}{-}\overset{SiCl_3}{\underset{SiCl_3}{Si}}{-}SiCl_2SiCl_3}$$

III

Another possibility is a four-center reaction where the trimethylamine–hexachlorodisilane complex reacts with an uncomplexed hexachlorodisilane molecule



The four-center reaction is shown as occurring at the silicon not involved in the amine complex. This is most appealing as the sterically favored arrangement, but not essential, since silicon forms many six-coordinate complexes as would be required by the reaction occurring at the amine-complexed silicon.

It is difficult to conceive a simple experimental method of distinguishing even between these two mechanisms, let alone among all of the possible mechanisms for this reaction. It was thought to be more profitable to expend our efforts in studying modifications of this reaction in order to gain further insight into its mode of behavior.

Accordingly, the effect of catalytic amounts of trimethylamine upon various methylchlorodisilanes was examined.[23] In this study it was found that the disproportionation of methylpentachlorodisilane was effected by trimethylamine less readily than the dispro-

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(23) R. F. Trandell, Ph.D. Dissertation, Purdue University, 1970.

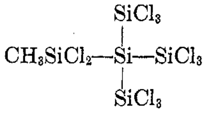
portionation of hexachlorodisilane. The symmetrically substituted 1,2-dimethyltetrachlorodisilane was even less reactive, requiring temperatures of 65° for 2 weeks in the presence of an amount of trimethylamine sufficient to promote complete reaction of hexachlorodisilane in hours at room temperature. Similar amounts of amine failed to promote reaction of 1,1,2,2-tetramethyldichlorodisilane even after 2 months at 100°. These results can be rationalized by the assumption that increased methyl substitution reduces the ability of the chlorodisilanes to form trimethylamine complexes. This assumption is consistent with the reported behavior of silicon tetrachloride and the methylchlorosilanes as studied by Beattie and Leigh.[24] Whatever the mechanism of the trimethylamine-catalyzed disproportionation of chlorodisilanes, Trandell's work improved our understanding.

The product of the disproportionation of methylpentachlorodisilane is a white crystalline solid, less volatile than either dodecachloroneopentasilane or tetradecachloroneohexasilane, which did not melt even at temperatures as high as 310° but showed evidence of slow decomposition at around 200°. This decomposition is evidenced by a yellowing of the white solid. Analysis and its molecular weight in benzene identified this white crystalline solid as a methylundecachloropentasilane. Its proton magnetic resonance spectrum consisted of a sharp singlet at τ 8.80, relative to internal tetramethylsilane. This, in conjunction with the fragmentation pattern displayed in its mass spectrum, allowed a structural assignment as methylundecachloroneopentasilane (IV). The yield of this product is approximately 60% that expected from eq 15.

$$4CH_3Si_2Cl_5 \xrightarrow[N(CH_3)_3]{} 3CH_3SiCl_3 + CH_3Si_5Cl_{11} \tag{15}$$

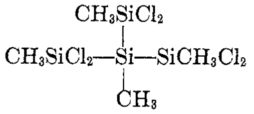
This chloropentasilane undergoes further reaction, producing a mixture of silicon tetrachloride and methyltrichlorosilane along with a nonvolatile yellow crystalline solid, accounting for the less than quantitative yield from eq 14. Clearly the solubility relationships of the various possible products of this reaction also are important in determining the product. This system is more complex than the case of hexachlorodisilane and requires more study.

It was necessary to heat a reaction mixture of 1,2-dimethyltetrachlorodisilane and the usual catalytic amount of trimethylamine for over 2 weeks at 65° to effect disproportionation of the disilane. The main product of this reaction, in approximately 50% yield, was a white crystalline solid which melts at 109–110° and is more volatile than dodecachloroneopentasilane, subliming readily at 60° *in vacuo*. This solid was characterized as a tetramethylhexachlorotetrasilane by means of its analysis and molecular weight. The proton magnetic resonance spectrum, consisting of two singlets, one at τ 9.16 (relative intensity 3.0) and one at τ 9.60 (relative intensity 1.0) with benzene as internal standard at τ 2.73, unequivocally identifies this as the isotetrasilane, 1,2,3-trimethyl-2-(methyldichlorosilyl)tetrachlorotrisilane (V).



$$\begin{array}{c} SiCl_3 \\ | \\ CH_3SiCl_2{-}Si{-}SiCl_3 \\ | \\ SiCl_3 \end{array}$$

IV



$$\begin{array}{c} CH_3SiCl_2 \\ | \\ CH_3SiCl_2{-}Si{-}SiCH_3Cl_2 \\ | \\ CH_3 \end{array}$$

V

From these results it appears probable that, whatever the mechanism, substitution of a silyl group for a methyl substituent is forbidden and the substitution of a silyl for a chlorine occurs at the silicon involved in the triethylamine complex. This possibility also is consistent with the observed behavior of octachlorotrisilane. The monosilane produced in the reaction as a favored product is the most highly methylated possibility from the disilane undergoing reaction.

It should be noted that this work also furnishes the second example of a specific synthesis of an isotetrasilane. The tetrasilane prepared here, 1,2,3-trimethyl-2-(methyldichlorosilyl)hexachlorotrisilane, enjoys an advantage over the isotetrasilane prepared by Wittenberg, George, and Gilman[9] in possessing chloro substituents, allowing further chemistry. Furthermore, the rules suggested by this work permit predictions concerning the major products to be expected from disproportionations of other chlorodisilanes, for example, as shown in eq 16–20.

$$4HSi_2Cl_5 \xrightarrow[N(CH_3)_3]{} 3SiCl_4 + (HCl_2Si)Si(SiCl_3)_3 \tag{16}$$

$$4(CH_3)_2ClSiSiCl_3 \xrightarrow[N(CH_3)_3]{} 3(CH_3)_2SiCl_2 + (CH_3)_2ClSiSi(SiCl_3)_3 \tag{17}$$

$$4(CH_3)_3SiSiCl_3 \xrightarrow[N(CH_3)_3]{} 3(CH_3)_3SiCl + (CH_3)_3SiSi(SiCl_3)_3 \tag{18}$$

$$3(CH_3)_2ClSiSi(CH_3)Cl_2 \xrightarrow[N(CH_3)_3]{} 2(CH_3)_2SiCl_2 + (CH_3)_2ClSiSi(CH_3)[Si(CH_3)Cl_2]_2 \tag{19}$$

$$3(CH_3)_3SiSi(CH_3)Cl_2 \xrightarrow[N(CH_3)_3]{} 2(CH_3)_3SiCl + (CH_3)_3SiSi(CH_3)[Si(CH_3)Cl_2]_2 \tag{20}$$

Returning to a consideration of the possible mechanism of this reaction, the involvement of an intermediate carbene-like silene seems less likely than a four-center mechanism. This is a matter of vague suspicion rather than conviction. The unusual specificity of products would require a highly fortuitous selectivity of reaction for the silene species. Such a selectivity, however, cannot be ruled out. For this reason, the synthesis of compounds likely to generate silenes, similar to those postulated as intermediates in the catalyzed disproportionation reaction, was undertaken.

In this, the impressive work of Seyferth and his colleagues on the decomposition of chloromethyl mercurials as a convenient source of a variety of carbenes served as a model.[25] Accordingly, the preparation of

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[24] I. R. Beattie and G. J. Leigh, *J. Inorg. Nucl. Chem.*, **23**, 55 (1961).

[25] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. P. Mui, H. D. Simmons, A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

chlorosilyl mercurials was undertaken. In the first attempt Bettler examined the reaction between trichlorosilane and bis(trimethylsilyl)mercury, one of only two previously reported silyl mercurials.[26] This reaction did not yield the desired product but instead proceeded as shown in eq 21.

$$HSiCl_3 + Hg[Si(CH_3)_3]_2 \longrightarrow Hg + HSi(CH_3)_3 + (CH_3)_3SiSiCl_3 \qquad (21)$$

This unanticipated result is most useful since it is a synthesis of a polysilane and occurs in excellent yield (98%). Good syntheses for specific substitutional isomers of the methylchlorodisilanes are rare. Of the eight possible isomers for the series, $Si_2(CH_3)_nCl_{6-n}$ ($n = 1$–5), only three have been reported in any state of purity. Kumada has prepared two of these, 1,1-dimethyltetrachlorodisilane and 1,1,2,2-tetramethyldichlorodisilane, by reaction of hexamethyldisilane with ammonium chloride in the presence of concentrated sulfuric acid.[27] The methylpentachlorodisilane in a reasonable state of purity was reported by Barry and Gilkey.[28]

The so-called "disilane fraction" from the direct synthesis of dimethyldichlorosilane in the silicone industry probably contains a mixture of all of these substitutional isomers, but no means of separating all of them has been described.

The only previously reported synthesis of the 1,1,1-trimethyltrichlorodisilane, the product of the reaction in eq 21, was a mercury-sensitized photochemical reaction of trimethylsilane with silicon tetrachloride induced by ultraviolet radiation.[29] This is an unsatisfactory method with respect to yield and purity.

Given the proper choice of mercurial and monosilane, the Bettler reaction can be applied to the synthesis of all of these substitutional isomers of the methylchlorodisilanes.[30] For example, the reaction between bis(trimethylsilyl)mercury and methyldichlorosilane, shown in eq 22, produces 1,1,1,2-tetramethyldichlorodisilane in excellent yield.

$$CH_3SiHCl_2 + Hg[Si(CH_3)_3]_2 \longrightarrow Hg + (CH_3)_3SiH + (CH_3)_3SiSi(CH_3)Cl_2 \qquad (22)$$

This reaction suggested itself as a useful way of attaching a trichlorosilyl group to any radical joined to mercury. In an attempt to prepare 2-methyl-1,1,1-trichloro-1,3-disilabutane, of interest in other work in the laboratory, Sendra treated bis(trimethylsilylmethyl)mercury with trichlorosilane.

Again we were frustrated in our immediate goal since the reaction shown in eq 23 was the consequence of this experiment.

$$2HSiCl_3 + Hg[CH_2Si(CH_3)_3]_2 \longrightarrow 2Si(CH_3)_4 + Hg(SiCl_3)_2 \qquad (23)$$

In this stumbling fashion we arrived at an excellent synthesis for the chlorosilyl mercurials, Bettler's original goal. The reaction shown proceeds with several alkyl mercurials and apparently any silane as long as a hydrogen and a chlorine substituent are present on the same silicon.[30] Dipentylmercury or bis(trimethylsilylmethyl)mercury are most convenient since the alkane produced is in the correct volatility range to avoid large pressure buildup in a closed vessel during the reaction, yet sufficiently volatile to allow easy removal from the product mercurial.

Reaction of trichlorogermane with a dialkylmercury compound in a reaction analogous to that shown in eq 23 forms bis(trichlorogermyl)mercury. By a reaction analogous to the Bettler reaction, compounds possessing metal to silicon bonds can be prepared as in eq 24.[31]

$$R_3SnH + Hg(SiCl_3)_2 \longrightarrow Hg + HSiCl_3 + R_3SnSiCl_3 \qquad (24)$$

The new chlorosilyl mercurials generally are useful in synthesis, but the present discussion is concerned mainly with polysilane syntheses. The Bettler reaction affords excellent means for the formation of silicon–silicon bonds while avoiding yield-reducing side reactions characteristic of other reactants.

An extension of this chemistry to more complex structures than the disilanes already mentioned is easily demonstrated. It is possible to prepare bis(pentachlorodisilanyl)mercury as in eq 25.

$$2HSi_2Cl_5 + HgR_2 \longrightarrow 2RH + Hg(Si_2Cl_5)_2 \qquad (25)$$

Photolysis of bis(pentachlorodisilanyl)mercury produces mercury and decachlorotetrasilane, with the normal structure, in a quantitative reaction.[32] Unfortunately, pentachlorodisilane required as a reactant in eq 25 is prepared with difficulty in the laboratory. The mercury-sensitized photolysis of trichlorosilane produces a mixture of hexachlorodisilane (85%) and pentachlorodisilane (15%).[29] The work with bis(pentachlorodisilanyl)mercury is severely restricted by this time-consuming synthesis. Pentachlorodisilane is a major component of the "disilane fraction" obtained as a by-product of the commercial preparation of trichlorosilane. As yet we have been unable to persuade any of our industrial friends to supply us with this possibly useful mixture.

In an attempt to overcome this impediment, a new synthesis for pentachlorodisilane is being sought. In eq 26 the reaction scheme proposed for this synthesis is shown. Even with a twofold excess of dichlorosilane

$$H_2SiCl_2 + Hg(SiCl_3)_2 \longrightarrow Hg + HSiCl_3 + HSi_2Cl_5 \qquad (26)$$

over that required by this equation, a different reaction, as shown in eq 27, dominates. While it is probable

$$H_2SiCl_2 + Hg(SiCl_3)_2 \longrightarrow Hg + 2HSiCl_3 + Si_3Cl_8 \qquad (27)$$

that reaction conditions can be found for the reaction in eq 26 to proceed as a good synthesis for pentachlorodisilane, the reaction already observed, as in eq 27, affords an excellent high-yield synthesis for the normal isomers

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(26) E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler, and E. Staude, *Angew. Chem., Int. Ed. Engl.*, **2**, 507 (1963).

(27) M. Kumada and K. Tamao, *Advan. Organometal. Chem.*, **6**, 19 (1968).

(28) A. J. Barry and J. W. Gilkey, U. S. Patent 2,681,355 (1954).

(29) J. D. Reedy, Doctoral Dissertation, Purdue University, 1968.

(30) C. R. Bettler, J. C. Sendra, and G. Urry, *Inorg. Chem.*, **9**, 1060 (1970).

(31) J. C. Sendra, Ph.D. Dissertation, Purdue University, 1970.

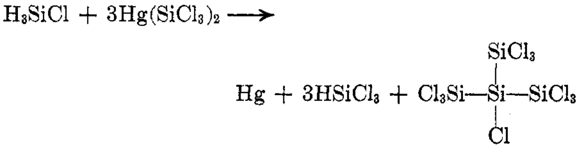
(32) J. Joiner and G. Urry, unpublished results.

of odd-numbered perchloropolysilanes. Thus, the normal isomer of dodecachloropentasilane should result from the reaction in eq 28.

$$\mathrm{H_2SiCl_2 + 2Hg(Si_2Cl_5)_2 \longrightarrow Hg + 2HSi_2Cl_5} + n\text{-}\mathrm{Si_5Cl_{12}} \qquad (28)$$

At the present time we have excellent syntheses for hexachlorodisilane, octachlorotrisilane, *n*-dodecachloropentasilane, dodecachloroneopentasilane, and tetradecachloroneohexasilane among the silane series. An encouragingly small number of experimental problems await solution before a complete synthesis system is possible. Perhaps the best way of illustrating this point is to outline some possible routes to as yet unreported isomers, stating the experimental problem presently obstructing the synthesis.

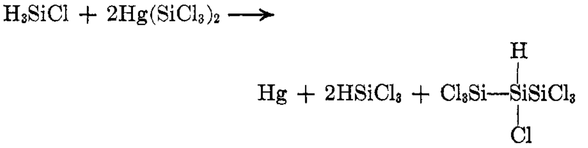
The simplest perchloropolysilane for which a synthesis has yet to be devised is decachloroisotetrasilane. A direct synthesis, as illustrated in eq 29, is being examined.



$$\mathrm{H_3SiCl + 3Hg(SiCl_3)_2 \longrightarrow Hg + 3HSiCl_3 + Cl_3Si{-}\overset{SiCl_3}{\underset{Cl}{Si}}{-}SiCl_3} \qquad (29)$$

We are presently unable to say whether the reaction proceeds as shown or if intermediate reactions, as in eq 30 and 31, are important.

$$\mathrm{H_3SiCl + Hg(SiCl_3)_2 \longrightarrow Hg + HSiCl_3 + H_2ClSiSiCl_3} \qquad (30)$$



$$\mathrm{H_3SiCl + 2Hg(SiCl_3)_2 \longrightarrow Hg + 2HSiCl_3 + Cl_3Si{-}\overset{H}{\underset{Cl}{Si}}SiCl_3} \qquad (31)$$

Whatever the result, we shall have a useful reaction since the 1,1,1,2,3,3,3-heptachlorotrisilane formed in eq 31 also is being sought. With this trisilane we hope to form the bis(heptachloroisotrisilanyl)mercury as in eq 32. If it is stable this mercurial should afford another route to decachloroisotetrasilane as shown in eq 33.

$$\mathrm{2HSi(SiCl_3)_2Cl + HgR_2 \longrightarrow 2RH + Hg[Si(SiCl_3)_2Cl]_2} \qquad (32)$$

$$\mathrm{HSiCl_3 + Hg[Si(SiCl_3)_2Cl]_2 \longrightarrow Hg + HSi(SiCl_3)_2Cl + ClSi(SiCl_3)_3} \qquad (33)$$

The bis(heptachloroisotrisilanyl)mercury also could be used to synthesize dodecachloroisopentasilane, the only perchloropentasilane for which a synthesis is not yet available, by means of a reaction with pentachlorodisilane as shown in eq 34.

$$\mathrm{HSi_2Cl_5 + Hg[Si(SiCl_3)_2Cl]_2 \longrightarrow Hg + HSi(SiCl_3)_2Cl + Cl_5Si_2Si(SiCl_3)_2Cl} \qquad (34)$$

Should bis(heptachloroisotrisilanyl)mercury prove to be unstable, it is likely to decompose in one of two fashions. The first, as shown in eq 35, would produce a new tetradecachlorohexasilane. The second would act as a possible source of a "silene" intermediate as in eq 36. Either result would be useful in our schemes.

$$\mathrm{Hg[Si(SiCl_3)_2Cl]_2 \longrightarrow Hg + Cl(Cl_3Si)_2SiSi(SiCl_3)_2Cl} \qquad (35)$$

$$\mathrm{Hg[Si(SiCl_3)_2Cl]_2 \longrightarrow HgCl + 2[:Si(SiCl_3)_2]} \qquad (36)$$

These speculations serve to emphasize our urgent interest in a plausible synthesis for 1,1,1,2,3,3,3-heptachlorotrisilane. In earlier discussion this compound was suggested as a likely intermediate in the reaction of anhydrous hydrogen chloride with dodecachloroneopentasilane as in eq 8.[21b] This reaction presently is being studied as a preparation for the desired trisilane as well as for pentachlorodisilane.

There is still interest in compounds capable of generating carbene-like species such as "dichlorosilene," in spite of the distractions that have intervened since Bettler's initial experiments.[30] Trichlorosilyltrimethylstannane prepared as in eq 24 may serve such a purpose. Upon standing at room temperature for several days this stannane decomposes extensively into trimethylchlorostannane and low-volatile perchloropolysilanes.[31] The availability of a "dichlorosilene generator" may allow other useful options valuable in specific isomeric syntheses among the members of this series.

As matters now stand we can confidently predict syntheses for any of the structural isomers in the series $\mathrm{Si}_n\mathrm{Cl}_{2n+2}$ up to $n = 6$. With little more knowledge than we now possess it will be possible to indulge in the luxury of alternate syntheses for members of this series.

The many contributions of my students, past and present, are noted in the text. Financial encouragement of this work by the Air Force Office of Scientific Research, the National Science Foundation and the Alfred P. Sloan Foundation is gratefully acknowledged.