model does not include Sternheimer corrections.[53] Furthermore, the asymmetry values assume that the Mulliken population analysis is appropriate for the interaction of the rather diffuse metal 4p wave function with the halogen. Nevertheless, we present these values in the hope of encouraging nqr studies on these species.

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The Synthesis of Novel Chlorosilyl and Chlorogermyl Mercurials with Some of Their Chemical Reactions[1a]

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When a mercury alkyl is irradiated in the presence of trichlorosilane, bis(trichlorosilyl)mercury, a white crystalline solid, and the alkane are formed. In a similar reaction with methyldichlorosilane, bis(methyldichlorosilyl)mercury is a product. With trichlorogermane as a reactant a similar light-induced reaction produces bis(trichlorogermyl)mercury. These novel mercurials react with compounds possessing a silicon–hydrogen bond to form disilanes. Preparations are described for methylpentachlorodisilane, 1,1-dimethyltetrachlorodisilane, 1,2-dimethyltetrachlorodisilane, 1,1,1,-trimethyltrichlorodisilane, 1,1,2-trimethyltrichlorodisilane, 1,1,1,2-tetramethyldichlorodisilane, 1,1,2,2-tetramethyldichlorodisilane, pentamethylchlorodisilane, trichlorosilyltrichlorogermane, and trimethylsilylmethyltrichlorogermane using various modifications of this reaction. Syntheses have been devised for the mercurials, bis(trichlorosilyl)mercury, bis(methyldichlorosilyl)mercury, bis(trichlorogermyl)mercury, and (trimethylsilylmethyl)trichlorogermylmercury. Bis(dimethylchlorosilyl)mercury is formed at low temperatures but decomposes at temperatures above −79°. Bis(trichlorosilyl)mercury also reacts with dimanganese decacarbonyl to form trichlorosilylmanganese pentacarbonyl.

Introduction

Since Wiberg and his coworkers first reported the preparation and characterization of bis(trimethylsilyl)mercury,[2] there has been a steady increase in the attention devoted to the chemistry of this most interesting compound. The photolysis and pyrolysis yield reactions readily interpreted as reactions of the trimethylsilyl radical.[3–5] Other reactions more readily can be described as four-center reactions.[6,7] The reaction of bis(trimethylsilyl)mercury with dichlorobromomethyl mercurial results in the formation of the most interesting bis(trimethylsilyldichloromethyl)mercury,[8] presumably as a consequence of the insertion of dichlorocarbene into the Hg–Si bond in bis(trimethylsilyl)mercury.

Bis(trialkylgermyl)mercury compounds first were reported by Vyazankin,[9] who with his several colleagues has reported the preparation and several chemical reactions of these germyl mercury compounds. Also various different trialkylsilyl mercury compounds have been examined.[10]

Until the present work no chlorosilyl or chlorogermyl mercurials have been reported.

Results and Discussion

When bis(trimethylsilylmethyl)mercury is irradiated in the presence of the approximate stoichiometric amount of trichlorosilane, a reaction occurs as described in eq 1.

$$(CH_3)_3SiCH_2HgCH_2Si(CH_3)_3 + 2SiHCl_3 \longrightarrow 2Si(CH_3)_4 + Cl_3SiHgSiCl_3 \quad (1)$$

The reaction shown is essentially quantitative and it is possible to obtain highly pure bis(trichlorosilyl)mercury from the product mixture by removing the very volatile tetramethylsilane and extracting the grayish white crystalline solid residue with dry methylene chloride. Removal of the solvent from the extracted material leaves beautiful white platelike crystals of the mercurial. The new compound, bis-

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(trichlorosilyl)mercury, is stable for long periods if stored in the dark at room temperature. At elevated temperatures or in the light it decomposes mainly according to eq 2.

$$Cl_3SiHgSiCl_3 \longrightarrow Hg + Si_2Cl_6 \qquad (2)$$

When the beautiful white crystals are exposed to air, decomposition also occurs with the crystals turning to gray, then black. The products of this decomposition have not been identified.

The mode of the photochemical and thermal decomposition for this mercurial are apparently unlike the decomposition of chloroalkyl mercury compounds which Seyferth has used in such an elegant fashion as a source of carbenes.[11] It should be noted, however, that the decomposition of bis(trichlorosilyl)mercury has not yet been studied in a variety of solvents. It is possible that in the appropriate solvent this mercurial could act as a source of the dichlorosilylene moiety.

In a reaction similar to (1), bis(methyldichlorosilyl)mercury can be prepared. Thus with methyldichlorosilane the reaction in eq 3 results, and eq 4 describes the

$$(CH_3)_3SiCH_2HgCH_2Si(CH_3)_3 + 2CH_3SiHCl_2 \longrightarrow 2Si(CH_3)_4 + CH_3Cl_2SiHgSiCl_2CH_3 \qquad (3)$$

reaction which might be expected when bis(trimethylsilylmethyl)mercury is irradiated in the presence of dimethylchlorosilane at temperatures below −79°.

$$(CH_3)_3SiCH_2HgCH_2Si(CH_3)_3 + 2(CH_3)_3SiClH \longrightarrow 2Si(CH_3)_4 + (CH_3)_2ClSiHgSiCl(CH_3)_2 \qquad (4)$$

When the product mercurial, bis(dimethylchlorosilyl)mercury, is allowed to warm to −79° or higher, then reaction 5 occurs spontaneously

$$(CH_3)_2ClSiHgSiCl(CH_3)_2 \longrightarrow Hg + (CH_3)_2ClSiSiCl(CH_3)_2 \qquad (5)$$

In this latter case the characterization of bis(dimethylchlorosilyl)mercury has been limited to the decomposition reaction. It is possible to use the unstable mercurial as a reactant in subsequent reactions if they are carried out at low temperatures (below −79°).

The preparation of bis(trichlorogermyl)mercury is simply accomplished by reaction 6. The reaction

$$Hg[CH_2Si(CH_3)_3]_2 + 2HGeCl_3 \longrightarrow 2Si(CH_3)_4 + Cl_3GeHgGeCl_3 \qquad (6)$$

shown occurs when the reactants with trichlorogermane in excess are irradiated at −45°. With equimolar quantities of reactants the reaction shown in eq 7 occurs without irradiation at ambient temperatures.

$$Hg[CH_2Si(CH_3)_3]_2 + HGeCl_3 \longrightarrow Si(CH_3)_4 + (CH_3)_3SiCH_2HgGeCl_3 \qquad (7)$$

We have not examined any reactions of this unsymmetrical mercurial beyond studying its decomposition. Upon pyrolysis at 120° this mercurial decomposes smoothly and apparently quantitatively into mercury and trimethylsilylmethyltrichlorogermane as in eq 8.

$$(CH_3)_3SiCH_2HgGeCl_3 \longrightarrow Hg + (CH_3)_3SiCH_2GeCl_3 \qquad (8)$$

The utility of these new mercurials as reactants in further synthesis is considerably enhanced by a reaction also discovered recently in this laboratory. A silyl mercurial reacts with any silane possessing a Si–H bond to form mercury and a disilane. Thus, the reaction of bis(trimethylsilyl)mercury with trichlorosilane produces 1,1,1-trimethyltrichlorodisilane, mercury, and trimethylsilane as in (9).

$$Hg[Si(CH_3)_3]_2 + SiHCl_3 \longrightarrow Hg + HSi(CH_3)_3 + (CH_3)_3SiSiCl_3 \qquad (9)$$

Any specifically substituted methylchlorodisilane in the series $(CH_3)_nSi_2Cl_{6-n}$ can be prepared in a similar reaction with a suitable choice of mercurial or silane. Thus 1,1,2-trimethyltrichlorodisilane is prepared in the reaction of bis(dimethylchlorosilyl)mercury with methyldichlorosilane or in the reaction of bis(methyldichlorosilyl)mercury with dimethylchlorosilane. The latter is the preferred synthesis in this case because of the previously described instability of bis(dimethylchlorosilyl)mercury.

In addition to the preparation of disilanes, the mercurials can be used to prepare compounds with silicon–metal bonds. Thus with trichlorogermane, bis(trichlorosilyl)mercury reacts to form (trichlorosilyl)trichlorogermane as in eq 10.

$$Hg(SiCl_3)_2 + HGeCl_3 \longrightarrow Hg + HSiCl_3 + Cl_3SiGeCl_3 \qquad (10)$$

The new silyl mercurials also react with transition metal compounds possessing M–M bonds. Thus, bis(trichlorosilyl)mercury reacts in an essentially quantitative fashion with dimanganese decacarbonyl to form trichlorosilylmanganese pentacarbonyl.

Experimental Section

Apparatus and Methods.—Except where otherwise noted, the reactions described were effected in an all-glass vacuum apparatus with the exclusion of air and moisture. Irradiation of reaction mixtures generally used the visible portion of the spectrum from a General Electric uv lamp (G.E. H-100 A 4/T). Vapor phase chromatography was carried out using an Aerograph Model A-700 "Autoprep" unit equipped with a 20 ft × $^3/_8$ in. column packed with 30% QF-1 (FS-1265) fluorosilicone on 60/80 Chromosorb P. The conditions used are given in each case where appropriate. Nuclear magnetic resonance spectra were obtained using a Varian A-60 A spectrometer. Unless otherwise noted, the nmr samples examined were dilute tetramethylsilane solutions. Refractive indices were determined with a Bausch & Lomb Abbe refractometer. Mass spectra were obtained using Hitachi RMU-G and Consolidated Electrodynamics Corporation 21-104 spectrometers. Infrared spectra were measured on a Perkin-Elmer Model 621 spectrophotometer. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., or by Dr. C. S. Yeh of the Purdue University Microanalytical Service.

Reagents.—**Bis(trimethylsilylmethyl)mercury** was prepared by the method of Seyferth and Freyer[12] with the reaction of the trimethylsilylmethyl Grignard with mercuric chloride modified by the addition of hydrazine hydrate after the procedure of Gilman and Barnett.[13]

Chloromethyltrimethylsilane was used as received from Peninsular ChemResearch, Gainesville, Fla., without further purification since it was shown to be pure by gas chromatographic analysis in our laboratory.

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Dimanganese decarbonyl obtained from Alfa Inorganics, Beverly, Mass., was purified by sublimation *in vacuo* at 60° before use.

Dimethylchlorosilane was obtained from Peninsular Chem-Research, Gainesville, Fla., and further purified by a fractional condensation through a series of U-tube traps maintained at −79, −95, and −196°, respectively. The fraction retained at −95° exhibited a vapor tension of 191 mm at 0.2°. This vapor tension was independent of vapor volume and thus was assumed to be pure.

Dimethylmercury prepared by the method of Gilman and Brown[14] was purified by vacuum distillation through traps maintained at −30, −63, and −196°. The material retained by fractional condensation at −63° was identified as tensiometrically pure dimethylmercury by its 0° vapor tension of 19 mm.[15]

Mercuric Chloride.—Fisher Reagent Grade was used without further purification.

Methyldichlorosilane, obtained from Dow-Corning Corp., Midland, Mich., was purified by vacuum distillation through U traps maintained at −79, −84, and −196°, respectively. The material fractionally condensed at −84° was determined to be tensiometrically pure methyldichlorosilane since it exhibited a 0° vapor tension of 146.5 mm in satisfactory agreement with reported values.[16]

Methylene chloride was used as obtained from Matheson Coleman and Bell, East Rutherford, N. J., after drying by distillation over phosphorus pentoxide.

Methyl iodide was obtained in a sufficiently pure state from Columbia Organic Chemicals Co., Columbia, S. C., and was used without further treatment.

Trichlorosilane, obtained in an impure state from Dow-Corning Corp., Midland, Mich., required purification by distillation through a fractional condensation train with traps maintained at −84, −95, and −196°. Essentially pure trichlorosilane retained in the −95° trap exhibited a vapor tension of 218 mm at 0°.[17]

Preparation of Bis(trichlorosilyl)mercury.—In a typical preparation a mixture of bis(trimethylsilylmethyl)mercury (9.19 mmol) and trichlorosilane (18.25 mmol) was sealed in an evacuated reaction vessel and the vessel and its contents were irradiated for 2 hr at room temperature with an ultraviolet lamp (GE H-100 A-4/T). Since the vessel was constructed of Pyrex, only the visible wavelengths of the lamp were effective. During the period of irradiation the temperature of the reaction vessel was raised to about 50° as a consequence of the heat generated by the lamp. After the irradiation, the initially clear liquid mixture had been converted to a slightly gray solid in the presence of a clear liquid.

The reaction vessel then was attached to the vacuum apparatus and cooled to −84°, and the material volatile *in vacuo* at this temperature was removed. This material was identified as tetramethylsilane (18.05 mmol). The previously described gray solid remained in the reaction vessel. Approximately 15 ml of liquid methylene chloride was distilled onto this solid and the mixture was allowed to stir until the solid dissolved. The solution was then filtered, leaving a small trace of mercury behind in the reaction vessel.

The methylene chloride was vacuum distilled from the filtrate. During this distillation beautiful white platelike crystals formed which upon analysis gave the following results. *Anal.* Calcd for $Hg(SiCl_3)_2$: Si, 12.1; Cl, 46.0; Hg, 42.3. Found: Si, 11.9; Cl, 45.4; Hg, 42.8.

The new bis(trichlorosilyl)mercury sublimes *in vacuo* at approximately 135° with slight decomposition to disilicon hexachloride and mercury. It melts with considerable decomposition at 173° and decomposes quantitatively to mercury, disilicon hexachloride, and higher perchloropolysilanes if held at high temperatures for extended periods. It is also decomposed by light and oxidized on exposure to air.

Thermal Decomposition of Bis(trichlorosilyl)mercury.—A sample of bis(trichlorosilyl)mercury (2.62 mmol) was sealed into an ampoule fitted with a break-off seal and the ampoule with its contents were heated in an oil bath at 110° for 2 days. At the end of this period the ampoule was cooled to room temperature. At this point the ampoule contained mercury, a clear liquid, and a white solid. The contents of the ampoule were removed and separated and found to consist of silicon tetrachloride (0.832 mmol), disilicon hexachloride (1.63 mmol), a small amount (0.0821 g) of a mixture of disilicon hexachloride and trisilicon octachloride, tetrasilicon decachloride (approximately 0.27 mmol), and mercury (2.57 mmol). The yield of disilicon hexachloride is 62% of that expected from the reaction in eq 2.

Preparation of Bis(trichlorogermyl)mercury.—A clear liquid mixture of trichlorogermane (10.7 mmol) and bis(trimethylsilylmethyl)mercury (2.48 mmol) was cooled to −45° and irradiated at that temperature with visible light from a General Electric H-100-A4/T lamp for a period of 1.5 hr. During this irradiation a white solid was formed. The irradiation vessel and its contents, still at −45°, were opened to the vacuum apparatus and the material volatile at that temperature was removed. This was a mixture of tetramethylsilane (4.77 mmol) and unchanged trichlorogermane (5.38 mmol).

The residual white solid was allowed to warm to room temperature, dissolved in methylene chloride, and filtered. Removal of the solvent from the filtrate resulted in the recrystallization of the white solid (1.3033 g). This white crystalline solid was identified as bis(trichlorogermyl)mercury by its decomposition into mercury and digermanium hexachloride. Photolysis of a 0.4906-g sample of this solid (0.879 mmol as $Hg(GeCl_3)_2$) gave 0.1733 g of mercury (0.867 mg-atom) and a white crystalline solid characterized as Ge_2Cl_6 by hydrolysis. Hydrolysis of a 0.0098-g sample (0.0274 mmol as Ge_2Cl_6) produced 0.0259 mmol of hydrogen.

The 1.3033 g of $Hg(GeCl_3)_2$ recovered after filtration in the preparation corresponds to an overall yield of 96.5% for this synthesis, based upon the 4.87 mmol of trichlorogermane consumed.

Preparation of (Trimethylsilylmethyl)trichlorogermylmercury, $(CH_3)_3SiCH_2HgGeCl_3$.—A liquid mixture of bis(trimethylsilylmethyl)mercury (3.85 mmol) and trichlorogermane (6.70 mmol) was held at −45° for 12 hr. At the end of this period there had formed a white crystalline solid and some liquid remained. The liquid was distilled away at −45°, the white solid dissolved in methylene chloride, and the solution, thus obtained, filtered. Removal of the solvent from the filtrate gave the white crystals, presumably in a pure form. The yield of this reaction calculated from the amount of tetramethylsilane collected was 98%. Analysis of this solid is consistent with the formula $(CH_3)_3SiCH_2HgGeCl_3$. *Anal.* Calcd for $(CH_3)_3SiCH_2HgGeCl_3$: C, 10.30; H, 2.36; Cl, 22.5; Si, 6.0; Hg, 42.8. Found: C, 10.50; H, 2.33; Cl, 22.7; Si, 6.1; Hg, 42.6.

Pyrolysis of (Trimethylsilylmethyl)trichlorogermylmercury.—A sample of (trimethylsilylmethyl)trichlorogermylmercury (2.035 mmol) was sealed in an evacuated ampoule and heated at 120° for 24 hr. During this treatment the mercurial had been converted to a clear liquid and mercury. The ampoule was attached to the vacuum apparatus and opened, and the liquid was removed. The liquid was tentatively identified as trimethylsilylmethyltrichlorogermane. *Anal.* Calcd for $(CH_3)_3SiCH_2GeCl_3$: C, 17.9; H, 4.10; Cl, 39.9; Si, 10.4. Found: C, 18.1; H, 4.23, Cl, 40.10 Si, 10.6.

The proton nmr spectrum consisted of 2 peaks at τ 9.880 and 8.739 in a ratio of 4.5:1 as expected, adding further support to the identification. The yield of this reaction is 99%.

Preparation of Trichlorosilyl(trichlorogermyl)mercury.—A mixture containing 3.597 g (7.67 mmol) of bis(trichlorosilyl)mercury and 2.77 g (15.3 mmol) of trichlorogermane in a sealed evacuated vessel was irradiated for 4 days at ambient temperatures. The reaction vessel then was attached to the vacuum

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(14) H. Gilman and R. E. Brown, *J. Amer. Chem. Soc.*, **52**, 3314 (1930).

(15) A 0° vapor tension of 17.2 mm was reported by M. E. Russell and R. B. Bernstein, *J. Chem. Phys.*, **30**, 607 (1959).

(16) H. S. Booth and R. L. Jarry, *J. Amer. Chem. Soc.*, **71**, 971 (1949).

(17) An identical value for the 0° vapor tension of trichlorosilane is reported by A. Stock, *Z. Elektrochem.*, **32**, 341 (1926).

apparatus, cooled to −196°, and opened. A trace (0.01 mmol) of hydrogen had been formed during the irradiation. The reaction mixture was warmed to −45° and the material volatile at that temperature allowed to distil away. This material was separated by fractional condensation in traps at −78 and −196° into 1.367 g (7.60 mmol) of unchanged trichlorogermane and 8.27 mmol of trichlorosilane. Remaining in the reaction vessel was a grayish white solid. This solid was mainly dissolved in methylene chloride and the mixture filtered. Removal of solvent from the filtrate gave 3.2448 g of a white crystalline solid. Partial analysis of this white solid gave the following data. *Anal.* Calcd for $Cl_3SiHgGeCl_3$: Cl, 41.4; Hg, 39.0. Found: Cl, 39.6; Hg, 38.7.

The white solid, thus characterized as (trichlorosilyl)trichlorogermyl)mercury, melts with some decomposition at 90°. If the volatile decomposition product is removed by evacuation during decomposition, the solid decomposes completely to mercury and a low volatile liquid which is tentatively identified as trichlorosilyltrichlorogermane on the basis of its chloride content.

Preparation of Bis(methyldichlorosilyl)mercury.—A mixture of methyldichlorosilane (14.12 mmol) and bis(trimethylsilylmethyl)mercury (7.04 mmol) was prepared in the vacuum apparatus and sealed into a reaction vessel. The reaction vessel then was irradiated for nearly 2 hr in the fashion already described. Following the same procedure as with the preparations of the other mercurials, a white crystalline solid weighing 1.8835 g was obtained. Elemental analysis of this white solid identified it as bis(methyldichlorosilyl)mercury. *Anal.* Calcd for $Hg(SiCl_2CH_3)_2$: C, 5.60; H, 1.41; Cl, 33.1; Hg, 46.8; Si, 13.1. Found: C, 5.89; H, 1.44; Cl, 32.8; Hg, 46.5, Si, 13.0.

The proton nmr spectrum obtained for a methylene chloride solution of the white solid consisted of a singlet at τ 8.99 relative to tetramethylsilane. The infrared spectrum (CsBr) showed the absorptions (cm^{-1}): 1260 (w), 773 (s), 720 (s), 485 (s), 320–300 (w) (in Nujol mull).

The bis(methyldichlorosilyl)mercury appears to be somewhat more stable than bis(trichlorosilyl)mercury since it sublimes *in vacuo* at 105° to form beautiful clear plates without noticeable decomposition. It does, however, melt under autogenous pressure at 175° and decomposes slowly if heated for extended periods above 135°.

Bis(methyldichlorosilyl)mercury also can be prepared in the reaction of methyldichlorosilane with dimethylmercury and there is every reason to believe that any of the mercurials already described could be prepared using dimethylmercury as a substitute for the bis(trimethylsilylmethyl)mercury. This latter reactant enjoys some practical advantage, however, since the product alkane is a liquid at room temperature.

As a demonstration, a mixture of dimethylmercury (0.0116 mmol) and methyldichlorosilane was irradiated for 13 hr. During this time, methane was formed and the same white crystalline solid formed as before. *Anal.* Calcd for $Hg(SiCl_2CH_3)_2$: C, 5.60; H, 1.41; Cl, 33.1; Hg, 46.8; Si, 13.1. Found: C, 5.42; H, 1.39; Cl, 32.4; Hg, 47.0; Si, 13.3.

Preparation of Methylpentachlorodisilane.—To solid bis(trichlorosilyl)mercury (26.7 mmol), prepared as described previously, tensiometrically pure methyldichlorosilane (26.8 mmol) was added *in vacuo*. The mixture was irradiated at room temperature for 12 hr. During this treatment the solid bis(trichlorosilyl)mercury disappeared with the formation of a clear liquid and mercury. The reaction system was cooled to 0° and opened to the vacuum apparatus. The material volatile at that temperature was removed and fractionally condensed in the U-tube traps maintained at −45 and −196°. The −45° trap contained a solid which melted to a clear liquid at approximately 6°. The vapor pressure of this solid is 3 mm at 0° and the liquid at 22° exhibits a vapor pressure of 9 mm.

TABLE I

VAPOR TENSIONS OF METHYLPENTACHLORODISILANE

	Temp, °C						
	34.8	44.4	54.2	70.5	79.7	94.7	106.0
P(obsd), mm	10.1	16.0	25.3	50.5	73.0	127.1	187.8
P(calcd), mm	10.0	16.1	25.3	50.7	73.0	127.2	187.7

The proton nmr spectrum consisted of a single peak at τ 8.97 relative to external TMS. The sample was shown to be pure by vapor phase chromatography. The infrared spectrum (CsBr) showed the absorptions (cm^{-1}): 2975 (vw), 2930 (w), 2050 (vw), 1997 (w), 1408 (m), 1261 (s), 1100 (m, br), 791 (s), 740 (s), 580 (vs), 470 (s), 362 (s).

Calcd for $CH_3Si_2Cl_5$: C, 4.83; H, 1.22; Cl, 71.3; Si, 22.6. Found: C, 4.85; H, 1.28; Cl, 71.1; 22.7. The pure disilane gave vapor tensions shown in Table I.

The calculated values were obtained using the equation log $P_{mm} = 7.7743 - (2085.7/T)$. From this equation a boiling point of 153° can be extrapolated. This boiling point is not in good agreement with a previously reported value of 134–135°[18] but it is in agreement with the sequence with which the disilanes investigated in this work pass through a QF-1 column. This column is a boiling point column and methylpentachlorodisilane comes off the column well after hexachlorodisilane (bp 144°) and after 1,1,1-trimethyltrichlorodisilane (bp 147°) but before 1,1-dimethyltetrachlorodisilane (bp 154°). It would appear that the sample studied here could be of higher purity and that the extrapolated boiling point could be near to the actual value.

Methylpentachlorodisilane also can be prepared by the reaction of trichlorosilane with bis(methyldichlorosilyl)mercury. In this case, however, the product is contaminated by approximately 10% of a 1,2-dimethyltetrachlorodisilane identified by gas chromatography and nmr spectrum.

Preparation of 1,2-Dimethyltetrachlorodisilane.—A sample of bis(methyldichlorosilyl)mercury (7.01 mmol) was heated in a sealed tube for 3 days at temperatures between 120 and 135°. At the end of this time the initial white crystalline solid had been converted to a clear liquid and mercury. The reaction tube was attached to the vacuum apparatus and the material volatile at room temperature was removed by vacuum distillation through traps maintained at 0, −79, and −196°. All of the liquid was thus removed from the reaction vessel, leaving a residue of 1.3818 g of mercury (6.89 mg-atoms) or 98.3% of the theoretical amount.

The fractional condensation of the volatile liquid yielded methyltrichlorosilane (1.96 mmol) retained at −196° and 1,2-dimethyltetrachlorodisilane (3.14 mmol, 45% yield) retained in the −79° trap. *Anal.* Calcd for $(CH_3)_2Si_2Cl_4$: C, 10.53; H, 2.65; Cl, 62.18; Si, 24.63. Found: C, 10.80; H, 2.44; Cl, 62.55; Si, 24.25.

It was also identified by its proton nmr spectrum which consisted of a singlet at τ 9.067. The infrared spectrum (CsBr) showed the absorptions (cm^{-1}): 2975 (w), 2905 (w), 1403 (m), 1258 (s), 1070 (m, br), 778 (s), 770 (s), 730 (s, sh), 550 (s), 470 (s), 422 (m), 380 (m). The mass spectrum showed peaks at *m/e* 226 (M), 211 ($M - CH_3$), 191 ($M - Cl$), 113 ($M - SiCl_2CH_3$). (Note: in this and subsequent mass spectra, only those peaks are listed that serve to identify the parent species in an adequate fashion.)

In the 0° trap 0.544 g of a liquid was retained which apparently is 1,2,3-trimethylpentachlorotrisilane. Identification was made by elemental analysis. *Anal.* Calcd for $CH_3Cl_2SiSi(CH_3)ClSiCH_3Cl_2$: C, 11.64; H, 3.91; Cl, 57.2; Si, 27.2. Found: C, 12.45; H, 3.10; Cl, 56.6; Si, 26.5.

While these results are less satisfactory than those for the 1,2-dimethyltetrachlorodisilane, the proton nmr spectrum is consistent with the assigned formula consisting of two peaks at τ 9.084 and 9.170 with respective areas of 2:1. The infrared spectrum (CsBr) showed the absorptions (cm^{-1}): 2970 (w), 2900 (w), 1980 (w), 1395 (s), 1250 (s), 1060 (m, br), 760 (s), 720 (s), 540 (s), 415 (s), 350 (w). The mass spectrum showed peaks at *m/e* 304 (M), 289 ($M - CH_3$), 269 ($M - Cl$), 191 ($M - SiCl_2CH_3$).

It is possible to effect the photodecomposition of bis(methyldichlorosilyl)mercury in a fashion such that 1,2-dimethyltetrachlorodisilane is the only polysilane formed. Thus, in an experiment where bis(methyldichlorosilyl)mercury (10.6 mmol) is dissolved in a large excess of methyldichlorosilane and the solution

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

irradiated for 7 hr at ambient temperature, it is possible to obtain 10.3 mmol of pure 1,2-dimethyltetrachlorodisilane from the reaction mixture by fractional condensation techniques already described.

Preparation of 1,1-Dimethyltetrachlorodisilane.—A mixture of dimethylchlorosilane (6.84 mmol) and bis(trichlorosilyl)mercury (3.31 mmol) was irradiated at room temperature for 21 hr. At the end of this period the white crystalline solid mercurial had disappeared and mercury, along with a clear colorless liquid, remained in the reaction vessel. The reaction vessel was opened and the volatile liquid was distilled repetitively through traps maintained at 0, −79, and −196°. The liquid retained at −196° was shown to be a mixture of monosilanes by nuclear magnetic resonance. The −79° fraction consisted of a liquid whose proton nmr spectrum consisted of a singlet at τ 9.311. This liquid was examined by vapor phase chromatography on a 30% QF-1 column at 173° with a flow rate of 270 cm^3/min. A small peak at retention time of 2.42 min tailed off in a fashion suggesting disproportionation. The main peak at 7.15-min retention time was the liquid responsible for the nmr singlet. On the basis of these data the −79° fraction is identified as a mixture of 5–7% of hexachlorodisilane and 93–95% of a liquid which melted at 15° and was characterized as 1,1-dimethyltetrachlorodisilane on the basis of the following data. *Anal.* Calcd for $(CH_3)_2Si_2Cl_4$: C, 10.5; H, 2.65; Cl, 62.2; Si, 24.6. Found: C, 10.8; H, 2.87; Cl, 62.3; Si, 24.3.

The infrared spectrum (NaCl) showed the absorptions (cm^{-1}): 2965 (m), 2900 (w), 2024 (w), 1933 (w), 1403 (s), 1255 (s), 1070 (m, br), 846 (s, sh), 809 (s), 788 (s, sh), 680 (s). Vapor tensions for this disilane are shown in Table II.

TABLE II

VAPOR TENSIONS OF 1,1-DIMETHYLTETRACHLORODISILANE

	Temp, °C						
	27.1	36.2	53.7	66.0	83.2	94.5	102.6
P(obsd), mm	5.95	9.85	22.7	39.6	77.9	118.4	155.9
P(calcd), mm	6.11	9.83	22.8	39.1	78.1	118.8	158.0

The calculated values were obtained from the expression: $\log P_{\mathrm{mm}} = 7.8173 - (2111.2/T)$ from which a boiling point of 154° can be extrapolated. This is in good agreement with a previously reported value.[19]

Preparation of 1,1,1-Trimethyltrichlorodisilane.—Trichlorosilane (20.66 mmol) was condensed on bis(trimethylsilyl)mercury (3.74 mmol) held at −196° in a reaction vessel. The mixture thus obtained was allowed to warm to room temperature for 1 day. During this period the solution which initially was yellow due to the dissolved bis(trimethylsilyl)mercury changed to colorless. This change was accompanied by the precipitation of mercury. After 1 day the volatile material was removed from the reaction vessel, leaving a residue of mercury (3.66 mg-atoms) corresponding to 97.6% of the amount of mercury expected from the total reaction of the starting mercurial. A gas chromatogram on a 20 ft × $^3/_8$ in. column of 30% QF-1 at 151° with a helium flow rate of 270 cm^3/min gave peaks corresponding to the following compounds (retention time): $(CH_3)_3SiH$ (1.98 min), Cl_3SiH (2.6 min), $Si_2(CH_3)_6$ (4.2 min), $(CH_3)_3SiSiCl_3$ (12.2 min).

Only a trace of the hexamethyldisilane was obtained. The 1,1,1-trimethyltrichlorodisilane peak was collected for characterization. The yield of this disilane was 98%. Analysis gave these results: *Anal.* Calcd for $(CH_3)_3Si_2Cl_3$: C, 17.35; H, 4.35; Cl, 51.2; Si, 27.1. Found: C, 17.54; H, 4.62; Cl, 51.1; Si, 26.9.

The proton nmr spectrum of a TMS solution consisted of a singlet at τ 9.662 (TMS = τ 10). The melting point of this disilane is 21° and the refractive index is $n^{25}\mathrm{D}$ 1.4550.

The infrared spectrum (CsBr) showed the absorptions (cm^{-1}): 2993 (m), 2900 (s), 2000 (vw), 1950 (vw), 1883 (w), 1710 (w), 1445 (sh), 1410 (m), 1395 (sh), 1253 (s), 845 (s), 748 (m), 704 (m), 545 (s), 345 (m). The mass spectrum showed peaks at *m/e* 206 (M), 191 (M − CH_3), 171 (M − Cl), 73 (M − $SiCl_3$). The last peak is most abundant. The second most abundant peak is at *m/e* 93 ($Si(CH_3)_2Cl$). These are prominent peaks in this spectrum which indicate that the $Si(CH_3)_2Cl$ peak is due to rearrangement and fragmentation of species such as the *m/e* 191 (M − CH_3) ion. This rearrangement will be the subject of a separate paper since the discussion of the mass spectra of the disilanes is beyond the scope of this work. Vapor tensions for this disilane are shown in Table III.

TABLE III

VAPOR TENSION OF 1,1,1-TRIMETHYLTRICHLORODISILANE

	Temp, °C						
	20.8	29.6	52.8	64.2	80.4	88.0	97.6
P(obsd), mm	4.00	6.98	23.24	39.7	78.4	105.2	150.1
P(calcd), mm	4.27	7.06	23.31	39.5	78.7	106.5	153.3

The calculated values are from the equation $\log P_{\mathrm{mm}} = 8.1370 - (2206.5/T)$ from which an extrapolated boiling point of 147° can be obtained. This is good agreement with the reported value of 149–150.[19]

Preparation of 1,1,2-Trimethyltrichlorodisilane.—A large excess of dimethylchlorosilane (40.4 mmol) was condensed upon a sample of bis(methyldichlorosilyl)mercury (3.2 mmol). The mixture thus obtained was irradiated for 1 hr at room temperature. At this point, only mercury and a clear colorless liquid remained in the reaction tube. The tube was then opened and the liquid distilled through traps maintained at −63 and −196°. The −196° trap retained a mixture of mainly dimethylchlorosilane contaminated with methyldichlorosilane. The −63° trap maintained a liquid mixture which was separated by gas chromatography on a $^3/_8$ in. × 20 ft QF-1 column (30% on Chromosorb P) at 175° with a flow rate of 270 cm^3/min. This separation gave (in addition to the air peak at 1.4 min) two peaks at 6.2 and 6.8 min. These two peaks were not completely resolved. Collection of the major peak and examination of the proton nmr spectrum showed this to be mainly (66 mol %) 1,2-dimethyltetrachlorodisilane with a singlet at τ 9.067 and a compound which presented two peaks in the spectrum at τ 9.143 and 9.406 with a ratio 1:2.1. The latter compound is tentatively identified as 1,1,2-trimethyltrichlorodisilane on this basis.

The amount of mercury produced in this reaction was determined to be 0.6474 g (100.7% of the theoretical value).

Preparation of 1,1,2,2-Tetramethyldichlorodisilane.—An excess of dimethylchlorosilane (24.45 mmol) was condensed onto a sample of bis(trimethylsilylmethyl)mercury (7.27 mmol), the mixture warmed to room temperature, and irradiated for approximately 2 hr. During this time mercury precipitated from the clear solution. After irradiation the reaction tube was opened and the volatile liquids were distilled away, leaving 1.4429 g of mercury (7.20 mg-atoms) behind. The volatile liquid was separated into two components by fractional condensation with distillation through a −45° trap into a −196° trap. The liquid retained in the −45° trap was chromatogrammed on a $^3/_8$ in. × 20 ft 30% QF-1 column at a temperature of 150° and a helium flow rate of 270 cm^3/min.

A major peak with a retention time of 3.97 min was collected as well as a minor peak at 7.6 min. A trace of material (2% of total) with a retention time of 10.5 min also was observed but not identified. The major peak (94% of the total) was identified as 1,1,2,2-tetramethyldichlorodisilane by its analysis. *Anal.* Calcd for $(CH_3)_4Cl_2Si_2$: C, 25.66; H; 6.46; Cl, 37.82; Si, 30.01. Found: C, 25.86; H, 6.32; Cl, 38.00; Si, 29.80.

It was also identified as this by its nmr spectrum with a singlet at τ 9.479. The infrared spectrum (CsBr) showed the absorptions (cm^{-1}): 2960 (m), 2790 (s), 2540 (vw), 1400 (m), 1252 (s), 1210 (w), 1130 (w, sh), 1055 (m, br), 835 (s), 810 (m), 775 (s), 695 (vw, sh), 662 (m), 519 (m), 470 (s), 405 (vw, sh), 392 (w). The mass spectrum showed peaks at *m/e* 186 (M), 171 (M − CH_3), 151 (M − Cl), 93 (M − $SiCl(CH_3)_2$).

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

The minor peak (4% of the total) was tentatively characterized as 1,1,2,2,3,3-hexamethyldichlorotrisilane or one of its isomers by its partial analysis. *Anal.* Calcd for $(CH_3)_6Cl_2Si_3$: C, 29.37; H, 7.39. Found: C, 30.12; H, 7.51. The mass spectrum showed peaks at *m/e* 244 (M), 229 (M − CH_3), 209 (M − Cl), 151 (M − $SiCl(CH_3)_2$).

Preparation of 1,1,1,2-Tetramethyldichlorodisilane.—A mixture of methyldichlorosilane (19 mmol) and bis(trimethylsilyl)mercury (5.13 mmol) in an evacuated sealed vessel was allowed to stand at room temperature. The solution in the reaction vessel, originally yellow, gradually bleached to a colorless solution and a precipitate of mercury during a 7-day period. The vessel then was attached to the vacuum apparatus and opened, and the materials volatile at room temperature were removed and separated by fractional condensation into a fraction retained at −79° and one retained at −196°. The −79° fraction was separated into its components by gas chromatography (on a 20 ft × $^3/_8$ in. column of QF-1 fluorosilicone, 30% on 60/80 Chromosorb P, at 151° with a flow rate of 270 cm^3/min). One component, 32% by volume, was identified as hexamethyldisilane by its 4.0-min retention time. The only other component, 68% by volume, had a retention time of 10.7 min. This was characterized as 1,1,1,2-tetramethyldichlorodisilane. *Anal.* Calcd for $(CH_3)_4Si_2Cl_2$: C, 25.9; H, 6.32; Cl, 29.8; Si, 38.0. Found: C, 25.7; H, 6.46; Cl, 30.0; Si, 37.9.

The proton nmr spectrum of a concentrated solution in tetramethylsilane consisted of two peaks at τ 9.24 and 9.76 with relative areas of 1:3 as expected. The molecular weight, by vapor density measurement, was found to be 195 (calculated 187).

Preparation of Pentamethylchlorodisilane.—A mixture of yellow crystalline bis(trimethylsilyl)mercury (7.896 mmol) and liquid dimethylchlorosilane (28.2 mmol) was irradiated for nearly 4 hr. During this time the yellow solid disappeared and mercury precipitated. At this point a clear colorless liquid was present in the reaction tube along with the mercury. This liquid was separated into its components by gas chromatography on a 30% QF-1 column at 151° with a helium flow of 270 cm^3/min. It consisted mainly of unreacted dimethylchlorosilane. Two peaks, one with a retention time of 4.2 min and one with a retention time of 8.35 min, were identified as disilanes. The former compound (retention time 4.2 min) was identified as hexamethyldisilane by comparison with an authentic sample. The latter compound (retention time 8.35 min) was identified as pentamethylchlorodisilane by analysis. *Anal.* Calcd for $(CH_3)_5ClSi_2$: C, 36.00; H, 9.06; Cl, 33.68; Si, 21.26. Found: C, 36.23; H, 8.95; Cl, 33.73; Si, 21.30.

Reaction of Bis(trichlorosilyl)mercury with Dimanganese Decarbonyl.—A mixture of bis(trichlorosilyl)mercury, 0.7426 g (1.582 mmol), and dimanganese decacarbonyl, 0.5829 g (1.496 mmol), was prepared in an inert-atmosphere box and placed in a reaction vessel without exposure to air or moisture. The reaction vessel then was evacuated, sealed off, and heated at 140° for nearly 60 hr. At the end of this treatment, as the reaction vessel cooled, a liquid present in the reaction vessel solidified. The reaction vessel was attached to the vacuum apparatus, opened, and heated to 60°. A crystalline white solid sublimed from the reaction vessel along with a trace of hexachlorodisilane and silicon tetrachloride (0.344 mmol). The white crystalline sublimate obtained in this fashion weighed 0.6746 g. This crystalline solid was characterized as trichlorosilylmanganese pentacarbonyl by the following data. *Anal.* Calcd for $Cl_3SiMn(CO)_5$: C, 18.3; Cl, 32.0; Si, 8.54; Mn, 13.7. Found: C, 17.9, Cl, 31.0; Si, 7.33; Mn, 14.8.

The molecular weight in benzene was found to be 342 (calculated 330). The infrared spectrum (CsBr, matched cell, cyclohexane solution) showed the absorptions (cm^{-1}): 2128 (s), 2037 (vs), 2005 (m), 660 (s), 650 (s), 555 (w), 533 (w), 503 (s), 467 (w).

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Mass Spectrometric Observations of Gaseous Boron Selenides

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The vapor species evaporating from a sample prepared to be B_2Se_3 were identified with a time-of-flight mass spectrometer. The sample was heated to progressively higher temperatures over the range from *ca.* 100 to *ca.* 700°. The sample was contained in a tungsten Knudsen cell. Parent gaseous species believed to be present were BSe_2(g) and B_2Se_3(g). In addition there were products from the hydrolysis reaction with the condensed B_2Se_3 phase. These results are compared with those for the B–S system by Gilles, *et al.* The B–S and B–Se systems show similar vaporization behavior; the principal difference observed was the absence of gaseous polymers of BSe_2 and B_2Se_3.

Introduction

Previous investigations of the B–Se system have been restricted to the condensed state. In two recent studies by Hutchinson and Eick[1] and Cueilleron and Hillel,[2] B_2Se_3(s) was prepared. Hutchinson and Eick[1] reported transformations at several temperatures, infrared spectra of B_2Se_3(s), and values of X-ray diffraction interplanar spacings. Cueilleron and Hillel[2] reported different infrared and X-ray diffraction data; in addition they noted the reaction of B_2Se_3 and silica. The latter

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(1) W. E. Hutchinson and H. A. Eick, *Inorg. Chem.*, **1**, 434 (1962).
(2) J. Cueilleron and R. Hillel, *Bull. Soc. Chim. France*, **8**, 2973 (1967).