cury with an immersed capillary to serve as a manometer. The remaining air was displaced by mercury. The tube was heated at 49° for about 20 hr. The rising Hg in the long capillary indicated a pressure of about 2 atm. Then the reaction mixture was cooled to 0°, transferred into a beaker and immediately treated with an excess of 3 *N* HCl to dissolve the resulting $N(CH_3)_3$ and the unused reactants. The oil was shaken with dilute HCl several times, washed with water, separated and dried with anhydrous Na_2CO_3. A small amount of material was recovered from the aqueous layers by extracting with hexane. In a number of experiments yields in the range of 50 to 56% of $(iso\text{-}C_3H_7O)_3PBH_3$ were obtained, the average being 53%.

Reactivity of Trialkyl Phosphite Borines Toward I_2. Method.—A weighed amount of the substance was dissolved in 2 ml. of CH_3OH and added to a mixture of 50 ml. of 0.1 *N* I_2 and 100 ml. of CH_3OH at 23°. After 70 hr. the unreacted I_2 was titrated with 0.1 *N* arsenite solution in the presence of $NaHCO_3$. The I_2 consumed is calculated in milliequivalents and shown in the table below. The last column contains the number of equivalents of I_2 consumed per mole of substance. According to the equation $(RO)_3PBH_3 + 4I_2 + 4H_2O = H_3BO_3 + 8HI + OP(OR)_3$ one mole of trialkyl phosphite borine should consume 8 equivalents of I_2.

$H_3BP(OR)_3$	Substance used, mmole	I_2 consumed, meq.	Eq. I_2 consumed per mole substance
$R = CH_3$	0.71	0.35	0.49
$R = C_2H_5$	0.92	1.11	1.20
$R = iso\text{-}C_3H_7$	0.66	1.61	2.45

Because of a possible side reaction, the results obtained may not represent the actual extent of the over-all reaction. However, qualitatively these attempts indicate that the order of reactivity of the trialkyl phosphite borines toward I_2 is

$$(CH_3O)_3PBH_3 < (C_2H_5O)_3PBH_3 < (iso\text{-}C_3H_7O)_3PBH_3$$

The ratio of reactivities of $(CH_3O)_3PBH_3$, $(C_2H_5O)_3PBH_3$ and $(i\text{-}C_3H_7O)_3PBH_3$ is 1:2.45:5.0.

Reactivity of Trialkyl Phosphite Borines toward I_2 in the Presence of Pyridine.—The same conditions (23°, 70 hr.) were applied as described above; however, 5 ml. of pyridine was added to the reaction mixture to suppress the side reaction of $(RO)_3PBH_3$ with HI which would be formed by the main reaction. Since I_2 reacts with CH_3OH in the presence of pyridine (1.5 ml. of 0.1 *N* I_2 was consumed in the blank test), this number of milliliters of I_2 was subtracted from the amount of 0.1 *N* I_2 consumed in the tests.

$(RO)_3PBH_3$	Mmoles used	Meq. I_2 consumed	Eq. I_2 consumed per mole substance
$R = CH_3$	1.05	0.32	0.31
$R = C_2H_5$	1.30	0.86	0.66
$R = iso\text{-}C_3H_7$	0.92	1.23	1.34

The results show that the numbers of equivalents of I_2 consumed per mole of substance are smaller than in the previous experiments (in the absence of pyridine). However, the ratio of the reactivities of $(CH_3O)_3PBH_3$, $(C_2H_5O)_3PBH_3$ and $(iso\text{-}C_3H_7O)_3PBH_3$ is 1:2.13:4.3 which is close to the previous results found in the absence of pyridine.

Proof of the Constitution of $(RO)_3PBH_3$.—

$$(C_6H_5O)_3PBH_3 + P[N(CH_3)_2]_3 \longrightarrow [(CH_3)_2N]_3PBH_3 + P(OC_6H_5)_3 \quad (a)$$

A mixture of 2.4 g. of $(C_6H_5O)_3PBH_3$ and 3.6 g. of $P[N(CH_3)_2]_3$ was heated at 100° for 30 minutes. The reaction mixture was steam distilled. The distillate was acidified with HCl, the crystalline product filtered, washed with H_2O and dried in air to a constant weight, producing 0.985 g. = 75.0% of $[(CH_3)_2N]_3PBH_3$; m.p. 32.0°. The constitution of $[(CH_3)_2N]_3PBH_3$ has been established.[2]

$$(iso\text{-}OC_3H_7)_3PBH_3 + P[N(CH_3)_2]_3 \longrightarrow [(CH_3)_2N]_3PBH_3 + (iso\text{-}C_3H_7O)_3P \quad (b)$$

A mixture of 2.22 g. of $(iso\text{-}C_3H_7O)_3PBH_3$ and 4.89 g. of $P[N(CH_3)_2]_3$ was heated at 110° for 45 minutes. The reaction mixture was worked up as in the foregoing experiment; obtained 1.25 g. of $[(CH_3)_2N]_3PBH_3$, 70.5%.

$$(CH_3O)_3PBH_3 + (iso\text{-}C_3H_7O)_3P \longrightarrow (iso\text{-}C_3H_7O)_3PBH_3 + P(OCH_3)_3\uparrow \quad (c)$$

A mixture of 13.78 g. of $(CH_3O)_3PBH_3$ and 40.0 g. of $(iso\text{-}C_3H_7)_3P$ was subjected to distillation at atmospheric pressure. One fraction was taken, the vapor temperature being 110 to 120°. The distillation was interrupted because of fear of a sudden decomposition of the residue. The distillate was redistilled. Obtained 6.5 g. of $P(OCH_3)_3$, b.p. 111–113°. Thus, the phosphite borine contains the unchanged $P(OCH_3)_3$ moiety.

Acknowledgments.—I wish to express my appreciation to Messrs. John L. O'Sullivan and James W. Buckley for carrying out the analyses of the substances.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, N. Y.]

Cleavage and Disproportionation of Polychlorodisilanes, Trichloromethylchlorosilanes and Hexachlorodisiloxane by Amines and Ammonium Salts

BY GLENN D. COOPER AND ALFRED R. GILBERT

RECEIVED FEBRUARY 25, 1960

The cleavage and disproportionation reactions of polychlorodisilanes with amines and ammonium salts had been briefly examined and a mechanism is advanced for these reactions. Trichloromethyl-substituted chlorosilanes were found to undergo similar reactions; trichloromethyltrichlorosilane yields silicon tetrachloride with tri-*n*-butylamine, and a mixture of chloroform and silicon tetrachloride with the amine hydrochloride. Hexachlorodisiloxane disproportionates in the presence of tri-*n*-butylamine to silicon tetrachloride and perchloropolysiloxanes.

The cleavage and disproportionation of polychlorodisilanes by ammonium halides and amines was reported by Wilkins.[1] Hexachlorodisilane reacted with ammonium chloride at 120–130° to form trichlorosilane and silicon tetrachloride, and with ammonium fluoride to yield trichlorosilane, trichlorofluorosilane and silicon tetrachloride. Non-volatile residues which contained nitrogen, presumably in the form of silazanes, also were obtained.

$$Cl_3SiSiCl_3 + NH_4Cl \longrightarrow SiCl_4 + HSiCl_3 \quad (1)$$

Trimethylamine brought about the disproportionation of hexachlorodisilane to silicon tetrachloride and poly-(dichlorosilane).

$$nCl_3SiSiCl_3 \longrightarrow nSiCl_4 + (SiCl_2)_n \quad (2)$$

Recently Kaczmarczyk and Urry[2] found that in the

---

[1] C. J. Wilkins, *J. Chem. Soc.*, 3409 (1953).

[2] A. Kaczmarczyk and G. Urry, THIS JOURNAL, **82**, 751 (1960).

presence of traces of trimethylamine hexachlorodisilane disproportionates quantitatively to silicon tetrachloride and hexasilicon tetradecachloride, Si_6Cl_{14}.

The purpose of this communication is to report some further observations on the cleavage and disproportionation of polychlorodisilanes and of some other classes of compounds. Tri-*n*-butylamine caused the decomposition of hexachlorodisilane according to (2), although higher temperatures were required than with trimethylamine. When silicon tetrachloride was removed by distillation as it was formed the yield varied between 74 and 79 wt. % of the original disilane, somewhat greater than the amount possible (61%) from (2) but less than the amount (95%) corresponding to complete decomposition to silicon tetrachloride and silicon. Tetramethylammonium chloride also brought about this disproportionation, but at a slower rate.

Bluestein[3] heated a mixture of methylchlorodisilanes having an average composition corresponding to $(CH_3)_2Si_2Cl_4$ with tertiary amine hydrochlorides or with hydrogen chloride and tertiary amines and obtained large amounts of dimethyldichlorosilane, methyltrichlorosilane, and methyldichlorosilane, CH_3SiHCl_2, along with smaller amounts of other chlorosilanes. This cleavage is obviously analogous to (1). We have found that these disilanes also react with tri-*n*-butylamine or tetramethylammonium chloride according to (2), yielding methyltrichlorosilane, dimethyldichlorosilane and trimethylchlorosilane, but none of the Si-H compounds obtained by Bluestein. Surprisingly, tetramethylammonium chloride was more effective than tri-*n*-butylamine in this case, as was tetraethylphosphonium iodide.[4]

Two other classes of compounds which were found to undergo reactions similar to those above are the trichloromethylchlorosilanes and the perchlorosiloxanes. Both trichloromethyltrichlorosilane, CCl_3SiCl_3, and trichloromethyl(methyl)dichlorosilane, $Cl_2Si(CH_3)CCl_3$, reacted with tri-*n*-butylamine at 130-150°. The former yielded silicon tetrachloride equal to 38% of the amount theoretically possible from complete disproportionation according to (3)

$$4CCl_3SiCl_3 \longrightarrow (CCl_3)_4Si + 3SiCl_4 \qquad (3)$$

and the latter gave essentially a quantitative yield of methyltrichlorosilane

$$3Cl_2Si(CH_3)CCl_3 \longrightarrow 2CH_3SiCl_3 + CH_3Si(CCl_3)_3 \qquad (4)$$

Reactions 3 and 4 are analogous to (2). Reaction corresponding to (1) occurred when hydrogen chloride was passed into a mixture of trichloromethyltrichlorosilane and the amine at 80-140°; the volatile product consisted of approximately equimolar amounts of chloroform and silicon tetrachloride. Hydrogen chloride alone did not react with trichloromethyltrichlorosilane at 150°.

Hexachlorodisiloxane disproportionated at 135° in the presence of tri-*n*-butylamine to produce a mixture of silicon tetrachloride, hexachlorodisiloxane, octachlorotrisiloxane and higher-boiling polysiloxanes. No reaction occurred at this temperature in the absence of the amine.

$$Cl_3SiOSiCl_3 \underset{}{\overset{Bu_3N}{\rightleftarrows}} SiCl_4 + Cl_3SiOSiCl_2OSiCl_3, \text{ etc.} \qquad (5)$$

Discussion.—The similarity in the cleavage and disproportionation reactions described above suggests that all may proceed by essentially the same mechanism. A possible mechanism for reactions 1 and 2 is outlined.

$$R_3N + Cl_3SiSiCl_3 \rightleftarrows R_3N^{\oplus}SiCl_3 + SiCl_3^{\ominus} \qquad (6)$$

$$SiCl_3^{\ominus} + HCl \longrightarrow HSiCl_3 + Cl^{\ominus} \qquad (7)$$

$$SiCl_3^{\ominus} + Cl_3SiSiCl_3 \longrightarrow Cl_3SiSiCl_2SiCl_3 + Cl^{\ominus} \qquad (8)$$

$$Cl^{\ominus} + R_3N^{\oplus}SiCl_3 \longrightarrow SiCl_4 + R_3N \qquad (9)$$

In the first step of this sequence ammonia or an amine attacks a silicon atom, displacing a trichlorosilyl anion[5] which reacts with hydrogen chloride or ammonium ion to produce trichlorosilane. When no proton source is present the trichlorosilyl anion displaces chloride ion from a molecule of hexachlorodisilane (or higher polysilane), increasing the number of silicon atoms in the molecule by one. The chloride ion formed in (7) or (8) reacts with the quaternary ion produced in the first step, forming silicon tetrachloride and regenerating the amine, which continues the reaction.[6]

This mechanism obviously can be applied also to the cleavage and disproportionation of alkylchlorodisilanes. The reactions of hexachlorodisiloxane and trichloromethylchlorosilanes can be explained on the same basis, except that a trichlorosiloxy or trichloromethyl anion is displaced in (6). The activity of the ammonium salts, including the quaternary ammonium chloride, presumably results from the amine produced by thermal decomposition.

Experimental

Materials.—Hexachlorodisilane and hexachlorodisiloxane were commercially available materials which were purified by distillation under nitrogen before use. The mixed methylchlorodisilanes were a fraction of the high-boiling residues obtained in the preparation of methylchlorosilanes from methyl chloride and silicon.[7] This fraction, which boiled at 155-155.5°, has the approximate composition $(CH_3)_2Cl_4Si_2$. Trichloromethyltrichlorosilane and trichloromethyl(methyl)dichlorosilane were prepared by chlorination of methyltrichlorosilane and dimethyldichlorosilane.[8]

Reactions of Hexachlorodisilane. (I) With Tri-*n*-butylamine.—Fifty grams of hexachlorodisilane was refluxed under nitrogen for 5 minutes to remove traces of hydrogen chloride and then cooled to room temperature; 1 ml. of tri-*n*-butylamine was added and the solution was again heated. Boiling began when the pot temperature reached 137°. The pot temperature dropped steadily and reached 80° after 1 hour. The mixture then was distilled slowly through a short Vigreux column to remove the silicon tetrachloride as it was formed. After 27 g. of silicon tetrachloride (>99% pure by mass spectrometric analysis) had been removed the reaction became very slow. A second 1-ml. portion of tri-*n*-butylamine was added and distillation was

---

[3] B. A. Bluestein, U. S. Patent 2,709,176 (1955).

[4] A. R. Gilbert and G. D. Cooper, U. S. Patent 2,842,580 (1955).

[5] This is analogous to the formation of the trichlorosilyl anion by the reaction of tertiary amines with trichlorosilane, which has been postulated as the initiating step in the amine-catalyzed addition of trichlorosilane to acrylonitrile [S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan*, **29**, 322 (1955)].

[6] Wilkins' report that silicon tetrachloride, but no trichlorosilane, was obtained from the reaction of hexachlorodisilane with trimethylamine hydrochloride is inconsistent with the suggested mechanism and with Bluestein's results on cleavage of methylchlorodisilanes. This reaction was reinvestigated and was found to produce substantial amounts of trichlorosilane. Wilkins' failure to observe this product presumably was due to the very small scale on which he carried out the reaction.

[7] E. G. Rochow, THIS JOURNAL, **67**, 963 (1945).

[8] R. H. Krieble and J. R. Elliott, *ibid.*, **67**, 1810 (1945).

continued until the pot temperature reached 120°, yielding 10 g. more silicon tetrachloride; total, 37 g. (74% of the original weight of hexachlorodisilane). In two other experiments the yields were 75 and 79%. The brown pyrophoric residue reacted vigorously with sodium hydroxide solution, giving off hydrogen. It is believed to be either a subchloride of silicon having the approximate composition $(SiCl)_x$ or a mixture of silicon and polydichlorosilane $(SiCl_2)_x$.

(II) With Tetramethylammonium Chloride.—Hexachlorodisilane (81 g., 0.3 mole) was heated under reflux for 16 hours with 2.9 g. (0.026 mole) of tetramethylammonium chloride, during which time the pot temperature dropped from 145 to 95°. The mixture then was distilled as in the preceding example, yielding 22.6 g. of silicon tetrachloride. The pot temperature increased gradually to 140° during the distillation. The mixture then stood at 20 mm. pressure giving 13.7 g. of liquid which on redistillation yielded 6.5 g. of silicon tetrachloride. Mass spectrometric analysis of the combined $SiCl_4$ fractions indicated the presence of approximately 0.015 g. (10^{-4} mole) of methyltrichlorosilane. This trace of methyltrichlorosilane is not believed to indicate any participation of the methyl groups of tetramethylammonium chloride in the reaction. The infrared spectrum of the hexachlorodisilane used indicated the presence of a very small amount of carbon bonded to silicon. No trichlorosilane could be detected either by infrared or mass spectrometric analysis.

(III) With Trimethylamine Hydrochloride.—Hexachlorodisilane (75.6 g., 0.28 mole) was heated under reflux with 4.9 g. (0.042 mole) of trimethylamine hydrochloride. Reflux started at a pot temperature of 89°. The pot temperature dropped rapidly, reaching 65° after 1 hour. The mixture was distilled, yielding 52.4 g. of material boiling at 50–56°. Mass spectrometric and infrared analysis of the product indicated that only $SiCl_4$ and $SiHCl_3$ were present; the amount of $SiHCl_3$ was 2.8 g., most of it in the first fraction of the distillation. When an attempt was made to continue the distillation the pot temperature increased rapidly to 150° and brown fumes began to appear in the flask. The mixture was cooled immediately and evaporated under vacuum, giving 4.1 g. of liquid, principally $SiCl_4$, and leaving 19 g. of brown solid residue. This residue reacted vigorously with 10% sodium hydroxide solution giving off hydrogen. Analysis of the residue showed 48.9% Cl, which is approximately that calculated for a mixture of 4 g. of trimethylamine hydrochloride and 14 g. of material having the average composition (SiCl). The infrared spectrum of the solid showed a weak band at 4.50 μ, indicating the presence of some silicon–hydrogen bonds.

(IV) With Other Compounds.—A very slow reaction occurred when hexachlorodisilane was heated under reflux with methyltrimethylsilylmethylsulfonium iodide, methyl trimethylsilylmethyl sulfide, or S-benzyl isothiouronium chloride, yielding 0.5–1.5 g. of low boiling material, principally silicon tetrachloride, from 100 g. of hexachlorodisilane and 5 g. of the sulfur compound in 5 days. No detectable reaction took place with hydrogen chloride, lithium chloride or cadmium bromide.

Reaction of Methylchlorodisilanes. (I) With Tetramethylammonium Chloride.—A mixture of 98 g. of the mixed methylchlorodisilanes and 4.5 g. of tetramethylammonium chloride was heated under reflux. The pot temperature decreased from its initial value of 153 to 118° in 4 hours. Distillation yielded 45 g. of a mixture of methylchlorosilanes boiling at 58–68°. Mass spectrometric analysis indicated approximately 40% each of methyltrichlorosilane and dimethyldichlorosilane and 20% trimethylchlorosilane.

(II) With Tetraethylphosphonium Iodide.—Distillation of a mixture of 100 g. of methylchlorodisilanes and 6 g. of tetraethylphosphonium iodide yielded 28 g. of methylchlorosilanes boiling at 58–68°.

Reaction of Hexachlorodisiloxane.—Hexachlorodisiloxane did not react with tetramethylammonium chloride even on prolonged heating at its reflux temperature (136°), but reacted slowly when heated with tri-*n*-butylamine. A mixture of 81 g. of hexachlorodisiloxane and 3.5 g. of tri-*n*-butylamine was heated under reflux for 94 hours, during which time the pot temperature, initially 136°, decreased to 95°. The mixture was evaporated at room temperature under vacuum, yielding 61 g. of volatile material, which on fractional distillation gave 31 g. of silicon tetrachloride, 38.3% of the original weight of hexachlorodisiloxane.

In another experiment 3.4 ml. of hexachlorodisiloxane and 0.1 ml. of tri-*n*-butylamine were heated for 48 hours at 135° in a Pyrex glass tube sealed under vacuum. The tube was opened under dry nitrogen and a weighed sample was dissolved in *n*-nonane containing 1% *n*-heptane. Silicon tetrachloride and hexachlorodisiloxane were determined by gas phase chromatography on a 2M silicone oil column at 100° using *n*-heptane as the internal standard. The helium carrier gas was dried over Linde molecular sieve 5A. There was some indication of hydrolysis in the column, but the method gave good results with standard mixtures of silicon tetrachloride and hexachlorodisiloxane. The sample contained 35.9 wt. % silicon tetrachloride and 8.0% hexachlorodisiloxane; high boiling polychlorosiloxanes (by difference) were 56.1%. This appears to represent the equilibrium composition; in a similar experiment carried out for 96 hours, the composition was 36.3% silicon tetrachloride, 8.1% hexachlorodisiloxane and 55.6% high-boiling polysiloxanes.

Reaction of Trichloromethyltrichlorosilane. (I) With Tri-*n*-butylamine.—Trichloromethyltrichlorosilane (46.5 g.) was refluxed under nitrogen with 3 ml. of tri-*n*-butylamine. The pot temperature dropped from 150 to 115° in 3 hours. The mixture was then distilled under vacuum and the volatile fraction was redistilled, yielding 8.8 g. of material boiling at 50–60°. Mass spectrometric analysis showed this to be principally (90%) silicon tetrachloride, with small amounts of chloroform and carbon tetrachloride.[9]

(II) With Tri-*n*-butylamine and Hydrogen Chloride.—Dry hydrogen chloride was passed through refluxing trichloromethyltrichlorosilane (46.5 g.) for 10 minutes without effect (pot temperature 153°). Tri-*n*-butylamine (2 ml.) then was added and the hydrogen chloride was continued. The pot temperature decreased rapidly, reaching 100° within 15 minutes and 80° after 7 hours. The mixture was then distilled under vacuum and the volatile fraction was redistilled, yielding 23 g. of material boiling at 55–75°. Mass spectrometric analysis of this fraction showed it to be principally chloroform and silicon tetrachloride in approximately equal proportions, along with a small amount of carbon tetrachloride. The silicon tetrachloride, determined by analyses for hydrolyzable chlorine, was 54.4% of the total.

Reaction of Trichloromethyl(methyl)dichlorosilane with Tri-*n*-butylamine.—A mixture of 45.7 g. of trichloromethyl(methyl)dichlorosilane and 2 ml. of tri-*n*-butylamine was heated under nitrogen and the low boiling material was removed as it was formed by distillation through a 15-inch Vigreux column. There was obtained 24 g. of material boiling at 64–67°. Mass spectrometric analysis indicated that it was approximately 96% methyltrichlorosilane, the remainder being principally carbon tetrachloride, which was confirmed by analysis for hydrolyzable chlorine: found 67.2%, calcd. for CH_3SiCl_3 70.6%.

The dark brown residue reacted vigorously with 5% aqueous sodium hydroxide, producing chloroform and a gelatinous precipitate which had an infrared spectrum almost identical with that of methylsilsesquioxane, $CH_3SiO_{3/2}$, produced by hydrolysis of methyltrichlorosilane.

Acknowledgment.—The authors are indebted to Dr. F. J. Norton for the mass spectrometric analyses.

---

[9] Both trichloromethyltrichlorosilane and trichloromethyl(methyl)dichlorosilane were stable under the reaction conditions in the absence of the amine. The carbon tetrachloride and traces of other unidentified materials found in these reactions is probably due to thermal decomposition of poly-(trichloromethyl)-substituted silicon compounds formed in the reaction [L. W. Frost, Abstracts of papers presented at the 125th Meeting of the American Chemical Society, Kansas City, Mo., p. 14-N (March, 1954).]