the flask and irradiated with ultraviolet light, while chlorine was passed over the disulfide VI in intervals or continuously. At the end of the reaction the contents of the flask and the Dry Ice trap were fractionated through a small Raschig column. By variation of the chlorine stream, the reaction time, and the temperature the yield of II could be improved to 67.8% as illustrated by the following table.

Run	$(C_3F_7S)_2$, g. charged	Temp., °C.	Reaction time days	C_3F_7SCl		
				Yield		B.p. (760 mm.), °C.
				G.	%	
1[a]	54.3	125	1.25	3.14	4.9	50.5–55
2[a]	26.3	25–30	6	8.13	26.3	51.5–53.8
3[a]	69.0	25–30	16	42.85	53.0	50.5–54
4[b]	90.0	115–130	2	58.16	67.8[c]	49–56

[a] Chlorine charged in intervals of 3–8 hours. [b] Continuous slow stream of chlorine. [c] 17.1 g. of $(C_3F_7S)_2$ was recovered; conversion 81%.

The perfluoro-*n*-propanesulfenyl chloride (II) is an orange-colored liquid with a pungent odor, b.p. 51–51.5°, $n^{23}D$ 1.3239.

Anal. Calcd. for C_3ClF_7S: C, 15.23; Cl, 14.99; F, 56.23; S, 13.55. Found: C, 14.91; Cl, 14.93; F, 56.29; S, 13.34.

Since the separation of the disulfide VI from the other polysulfides by fractional distillation involves considerable loss, the crude mixture of the perfluorinated *n*-propyl sulfides was subjected to the above chlorination. This resulted in a very good yield of the sulfenyl chloride II, thus further improving the efficiency of the process. Sulfur dichloride was formed as a by-product in the latter experiment.

Heptafluoro-*n*-propanesulfenyl Fluoride (V).—The sulfenyl chloride II was refluxed over mercuric fluoride or silver fluoride for several hours, but only traces of a lower boiling material were collected in a Dry Ice cooled trap connected with the outlet of the reflux condenser; II was recovered in both experiments nearly quantitatively. Therefore, the experiment was carried out in a 300-ml. stainless steel autoclave by shaking a mixture of 33 g. of II and 29.5 g. of silver fluoride between 125 and 160° for six hours. After the autoclave had been cooled to −30°, it was unsealed and connected with a Dry Ice cooled trap. The autoclave was then slowly heated to 50–60° and kept at this temperature for 8 hours. About 1.5 g. (4.8% of the theory) of crude heptafluoro-*n*-propanesulfenyl fluoride (V) was collected in the trap. The crude V was purified by fractionation. The sulfenyl fluoride V distilled between −15 and 0°. This gas has a very pungent odor. Because of its high volatility, only carbon, hydrogen and sulfur could be determined.

Anal. Calcd. for C_3F_8S: C, 16.37; H, 0.00; S, 14.56. Found: C, 16.45; H, 0.00; S, 14.30.

The remainder of the reaction mixture was distilled *in vacuo* to give the principal product, bis-(heptafluoro-*n*-propyl) disulfide (VI) (24.4 g. or 87% yield), b.p. 118–122° (lit.[17] 120–123°), $n^{26.5}D$ 1.3226 (lit.[16] nD 1.3222).

Benzenesulfenyl Chloride and Mercuric Fluoride in Dichloromethane.—Mercuric fluoride (60 g.) was added to 40 g. of benzenesulfenyl chloride in 250 ml. of dichloromethane and the reaction mixture refluxed for 5 hours. After cooling, the solids were removed by filtration. Removal of the dichloromethane from the filtrate resulted in the precipitation of a solid which was filtered and identified as C_6H_5SHgCl, m.p. 190–192° (from benzene), lit.[18] 191.5°.

The oily filtrate was distilled yielding diphenyl disulfide which crystallized in the receiver; m.p. 57–59° (lit.[19] 60°). Another higher boiling compound was not identified, but was probably bis-(phenyl) trisulfide.

***p*-Nitrobenzenesulfenyl Chloride and Mercuric Fluoride in Dichloromethane.**—Mercuric fluoride (31.5 g.) was added to 20 g. of *p*-nitrobenzenesulfenyl chloride in 100 ml. of dichloromethane. Upon addition of the mercuric fluoride, the reaction mixture warmed and became deep violet. After refluxing for four hours, the mixture was cooled, filtered and the dichloromethane removed from the filtrate. The resulting residue was distilled *in vacuo*. An oil distilled between 96–101.5° (2 mm.). This compound (5.8 g.) solidified in the condenser and was recrystallized from Skellysolve C to give mixed crystals of *p*-nitrobenzenesulfonyl fluoride and *p*-nitrobenzenesulfonyl chloride (XII), colorless needles, m.p. 69–71°.

Anal. Calcd. for $C_{12}H_8ClFN_2S_2O_8$: C, 33.77; H, 1.89; Cl, 8.32; F, 4.45; N, 6.56; S, 15.02. Found: C, 34.03; H, 1.71; Cl, 10.94; F, 4.48; N, 6.43; S, 15.02.

Bis-(*p*-nitrophenyl)-disulfide, m.p. 177–179° (lit.[20] 181°), was isolated from the distillation residue as well as from the filtered mercuric salts.

***p*-Nitrobenzenesulfenyl Chloride and Silver Fluoride.**—When *p*-nitrobenzenesulfenyl chloride and silver fluoride were heated between 100 and 110° without a solvent for three hours, the only product identified was bis-(*p*-nitrophenyl)-disulfide.

---

(18) H. Lecher, *Ber.*, **53**, 571 (1920).

(19) C. Vogt, *Ann.*, **119**, 150 (1861).

(20) Th. Zincke and S. Leonhardt, *ibid.*, **400**, 7 (1913).

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Cleavage Reactions of Some Organopolysilanes

BY DIETMAR WITTENBERG, M. V. GEORGE AND HENRY GILMAN

RECEIVED JANUARY 19, 1959

Lithium cleavage of octaphenyltrisilane in tetrahydrofuran gave a mixture of triphenylsilyllithium and pentaphenyldisilanyllithium. The latter reagent, along with triphenylsilyllithium and heptaphenyltrisilanyllithium, was also obtained when decaphenyltetrasilane was cleaved by lithium in tetrahydrofuran. Hexaphenyldisilane was isolated from the reactions of triphenylsilyllithium with silicon tetrachloride, ethyl silicate, dichlorodiphenylsilane, pentaphenyldisilane, chloropentaphenyldisilane and diphenyl-(diphenylmethoxy)-silane. Reaction of trichlorosilane with triphenylsilyllithium gave a small yield of tris-(triphenylsilyl)-silane, which is apparently the first branched chain organosilane of this type. The formation of diphenylsilyllithium and related reactive intermediates is discussed.

The silicon–silicon bond in hexaaryldisilanes has been cleaved by sodium–potassium alloy in ether[1,2]; by potassium in *n*-butyl ether[2]; by lithium, sodium and sodium–potassium alloy in 1,2-dimethoxyethane[3]; by lithium in tetrahydrofuran,[4] tetrahydropyran,[5] dioxane[5] and pyridine[6]; as well as by sodium in liquid ammonia.[7] Similarly, alkyldiarylsilyllithium and dialkylarylsilyllithium compounds were prepared by lithium cleavage of the corresponding disilanes in tetrahydrofuran.[4]

---

(1) R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

(2) H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951); *J. Org. Chem.*, **18**, 753 (1953).

(3) A. G. Brook and H. Gilman, *ibid.*, **76**, 278 (1954).

(4) H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 608 (1958).

(5) D. Wittenberg, D. Aoki and H. Gilman, *ibid.*, **80**, 5933 (1958).

(6) D. Wittenberg and H. Gilman, *Chemistry & Industry*, 390 (1958).

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

However, no silylmetallic compound containing more than one silicon atom has so far been isolated.

Whereas chloropentaphenyldisilane did not react with lithium in ether,[8] sodium in refluxing xylene gave a 57% yield of decaphenyltetrasilane.[8,9] Lithium cleavage of octaphenyltrisilane in tetrahydrofuran has now been found to give a mixture of triphenylsilyllithium and pentaphenyldisilanyllithium. Subsequent to acid hydrolysis, triphenylsilane and pentaphenyldisilane were obtained in almost equimolar amounts. When decaphenyltetrasilane was treated in the same manner, pentaphenyldisilane was obtained in a 45.2% yield. In addition, 30.8% of triphenylsilane and 17.1% of heptaphenyltrisilane were isolated.

$$\mathrm{(C_6H_5)_3SiSi(C_6H_5)_2Si(C_6H_5)_3 \xrightarrow{Li} (C_6H_5)_3SiLi + (C_6H_5)_3SiSi(C_6H_5)_2Li}$$

$$\mathrm{(C_6H_5)_3SiSi(C_6H_5)_2Si(C_6H_5)_2Si(C_6H_5)_3 \xrightarrow{Li} (C_6H_5)_3SiSi(C_6H_5)_2Li + (C_6H_5)_3SiSi(C_6H_5)_2Si(C_6H_5)_2\,Li + (C_6H_5)_3SiLi}$$

When diphenyl-(diphenylmethoxy)-silane, obtained from diphenylsilane and benzophenone,[10] was allowed to react with triphenylsilyllithium, benzhydrol was formed in an 81% yield. However, only 9.6% of pentaphenyldisilane was isolated, the main product being hexaphenyldisilane. The products suggested as the possible course of reaction a cleavage of the silicon–silicon bond in pentaphenyldisilane by the silyllithium reagent with the formation of hexaphenyldisilane and diphenylsilyllithium.

$$\mathrm{(C_6H_5)_2SiH[OCH(C_6H_5)_2] + (C_6H_5)_3SiLi \longrightarrow (C_6H_5)_2CHOLi + (C_6H_5)_3SiSiH(C_6H_5)_2}$$

$$\mathrm{(C_6H_5)_3SiSiH(C_6H_5)_2 + (C_6H_5)_3SiLi \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + (C_6H_5)_2SiHLi}$$

In order to investigate further the possible value of such a reaction for the synthesis of reactive silylmetallic intermediates, triphenylsilyllithium was allowed to react with pentaphenyldisilane. Hexaphenyldisilane was formed in high yield. Upon acid hydrolysis of the reaction mixture, hydrogen was evolved, indicating the presence of lithium hydride. No diphenylsilane was isolated, the reaction product being a resin-like polymer. Apparently diphenylsilyllithium is not stable under the experimental conditions employed, possibly decomposing to lithium hydride and a diphenylsilylene polymer.

$$n\ \mathrm{(C_6H_5)_2SiHLi \longrightarrow}\ n\ \mathrm{LiH + [(C_6H_5)_2Si]}_n$$

Cleavages of disilanes by organometallic compounds have been known since 1869, when Friedel and Ladenburg[11] investigated the reaction of diethylzinc with hexaiododisilane and obtained tetraethylsilane, in addition to hexaethyldisilane. Similarly, tetraphenylsilane was the only product formed from hexachlorodisilane, chlorobenzene and sodium.[12] Schwarz and Sexauer[13] isolated dichlorodiphenylsilane together with other products from the reaction of phenylmagnesium bromide with hexachlorodisilane. When octachlorotrisilane was treated with phenylmagnesium bromide, the products obtained were hexaphenyldisilane and tetraphenyldisilane.[14]

It has been reported[15] that triphenylsilylpotassium forms 1,1,1-trichloro-2,2,2-triphenyldisilane and 1,1 - dichloro - 1,2,2,2 - tetraphenyldisilane on treatment with silicon tetrachloride or trichlorophenylsilane, respectively. In both reactions, hexaphenyldisilane was isolated as a by-product, possibly formed by cleavage of the primary reaction products by the silylpotassium reagent.

$$\mathrm{(C_6H_5)_3SiK + (C_6H_5)_3SiSiCl_3 \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + [SiCl_2] + KCl}$$

When silicon tetrachloride was allowed to react with four equivalents of triphenylsilyllithium in tetrahydrofuran, a 72.5% yield of hexaphenyldisilane was isolated, rather than the expected tetrakis-(triphenylsilyl)-silane. Similar results were obtained in the reaction of triphenylsilyllithium with ethyl silicate.

Whereas the reaction of triphenylsilylpotassium with dichlorodiphenylsilane[16] gave good yields of chloropentaphenyldisilane, free of secondary products, the corresponding reaction with triphenyl silyllithium followed by reduction of the reaction mixture by lithium aluminum hydride gave a 45% yield of hexaphenyldisilane, in addition to 24.5% of pentaphenyldisilane and 9.6% of octaphenyltrisilane.

Similarly, the reaction of triphenylsilyllithium with chloropentaphenyldisilane resulted in the formation of 43.3% of hexaphenyldisilane, in addition to 25.7% of octaphenyltrisilane.

$$\begin{array}{r}\mathrm{(C_6H_5)_3SiSi(C_6H_5)_2Cl + (C_6H_5)_3SiLi \longrightarrow} \\ \mathrm{(C_6H_5)_3SiSi(C_6H_5)_3 +} \\ \mathrm{(C_6H_5)_3SiSi(C_6H_5)_2Si(C_6H_5)_3 + LiSi(C_6H_5)_2Cl} \\ \downarrow \\ \mathrm{LiCl + [(C_6H_5)_2Si]}_n \end{array}$$

The formation of hexaphenyldisilane in the above-mentioned reactions might possibly be explained also on the basis of a halogen–metal reaction between the silyllithium reagent and the appropriate chlorosilane, followed by a coupling reaction.[4]

Milligan and Kraus have obtained tris-(triphenylgermyl)-silane from the reaction of triphenylgermylsodium with trichlorosilane[17a]; when triphenylsilyllithium was allowed to react with trichlorosilane, tris-(triphenylsilyl)-silane[17b] was isolated in a 4.4% yield, in addition to hexaphenyldisilane. To our knowledge this is the first reported preparation of a branched chain organopolysilane.

---

(8) T. C. Wu, unpublished studies.

(9) H. A. Hartzfeld, unpublished studies.

(10) H. Gilman and D. Wittenberg, *J. Org. Chem.*, **23**, 501 (1958).

(11) C. Friedel and A. Ladenburg, *Compt. rend.*, **68**, 923 (1869); *Ann. chim. phys.*, [5] **19**, 401 (1880); *Ann.*, **203**, 251 (1880).

(12) L. G. Gattermann and K. Weinlig, *Ber.*, **27**, 1946 (1894).

(13) R. Schwarz and W. Sexauer, *ibid.*, **59B**, 333 (1926); see also W. C. Schumb, J. Ackerman and C. M. Saffer, THIS JOURNAL, **60**, 2486 (1938); W. C. Schumb and C. M. Saffer, *ibid.*, **63**, 93 (1941).

(14) W. C. Schumb and C. M. Saffer, *ibid.*, **61**, 363 (1939).

(15) H. Gilman and T. C. Wu, *ibid.*, **75**, 3762 (1953).

(16) H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, *ibid.*, **74**, 561 (1952); see also, H. Gilman and J. J. Goodman, *ibid.*, **75**, 1250 (1953).

(17) (a) J. G. Milligan and C. A. Kraus, *ibid.*, **72**, 5297 (1950); (b) an alternate name for this compound is 2-triphenylsilyl-1,1,1-3,3,3-hexaphenyltrisilane.

Experimental

All melting points are uncorrected. In general, reactions were carried out under an atmosphere of dry, oxygen-free[18] nitrogen. Tetrahydrofuran, boiling at 65–66°, was freed from peroxides and moisture before use by refluxing over sodium and then distillation from lithium aluminum hydride. Silicon analyses were carried out by a reported procedure.[19] Triphenylsilyllithium solutions in tetrahydrofuran were prepared by cleavage of hexaphenyldisilane with lithium.[20]

Lithium Cleavage of Octaphenyltrisilane in Tetrahydrofuran.—To a stirred mixture of 3.5 g. (0.005 mole) of octaphenyltrisilane[21] and 0.7 g. (0.1 g. atom) of finely cut lithium ribbon, 20 ml. of anhydrous tetrahydrofuran was added. After a few minutes a yellow color developed. Color Test I[22] was positive. After 3 hr. of stirring at room temperature, the brown solution was filtered through glass wool and hydrolyzed with dilute sulfuric acid. Subsequent to the addition of some ether, the organic layer was extracted with water, dried with sodium sulfate and the solvent removed. Fractional distillation under reduced pressure yielded 1.2 g. (92%) of triphenylsilane, b.p. 130–135° (0.05 mm.). Recrystallization from methanol gave 1.0 g. (77%) of pure product, m.p. 45–46°. The distillation residue was recrystallized from petroleum ether (b.p. 60–70°) to yield 1.7 g. (77%) of pentaphenyldisilane, m.p. 126–128°, identified by a mixed melting point.

Cleavage of Decaphenyltetrasilane in Tetrahydrofuran.—A mixture of 3.3 g. (0.00375 mole) of decaphenyltetrasilane,[8,9] 0.7 g. of lithium and 25 ml. of tetrahydrofuran was stirred at room temperature for one hour, and the resulting red-brown solution was hydrolyzed by dilute sulfuric acid. The solution was extracted with ether, and removal of the solvent under reduced pressure gave a viscous liquid which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60–70°) gave 0.3 g. (30.8%) of triphenylsilane which melted at 45–46° after crystallization from the same solvent. The identity was established by a mixture melting point (45–46°) and also by a comparison of the infrared spectra.

Repeated elution of the alumina column with petroleum ether (b.p. 60–70°) gave 1.5 g., 45.2%, of pentaphenyldisilane. It melted at 126–127° on crystallization from petroleum ether (b.p. 60–70°) and did not depress the melting point of an authentic sample.

Elution of the column with benzene gave 0.4 g. (17.1%) of heptaphenyltrisilane, m.p. 157.5–158°, after crystallization from hot petroleum ether (b.p. 60–70°). The infrared spectrum of this substance in carbon tetrachloride showed a strong absorption band at 4.78 μ characteristic of Si–H compounds.

Anal. Calcd. for $C_{42}H_{36}Si_2$: Si, 13.50. Found: Si, 13.59, 13.71.

Reaction of Triphenylsilyllithium with Diphenyl-(diphenylmethoxy)-silane.—A solution of 0.01 mole of triphenylsilyllithium was added to 3.66 g. (0.01 mole) of diphenyl-(diphenylmethoxy)-silane. Color Test I was negative immediately after the additon. Subsequent to hydrolysis, 1.1 g. (42%) of hexaphenyldisilane, m.p. 353–355° (mixed m.p.), was removed by filtration. The organic layer of the filtrate was dried and the solvent removed by distillation. The residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave a colorless oil, which crystallized partially on treatment with petroleum ether. One recrystallization from the same solvent yielded 0.40 g. (9.6%) of pentaphenyldisilane, m.p. 126–127°. Elution with benzene gave 1.48 g. (81%) of benzhydrol, m.p. 66–67°

Reaction of Triphenylsilyllithium with Pentaphenyldisilane.—A solution of 0.015 mole of triphenylsilyllithium was added to 6.6 g. (0.015 mole) of pentaphenyldisilane in 20 ml. of tetrahydrofuran. The reaction was slightly exothermic, and a precipitate was formed. The mixture was stirred for 3 hr. at room temperature and subsequently hydrolyzed with dilute acid. Gas evolution indicated the presence of lithium hydride in the mixture; after the addition of some ether, filtration gave 6.0 g. (78%) of hexaphenyldisilane, m.p. 354–357° (mixed m.p.). The organic layer of the filtrate was dried and distilled at reduced pressure, subsequent to the removal of the solvent. No low boiling fraction was collected, indicating the absence of diphenylsilane. There was obtained 0.8 g. (10%) of triphenylsilane, b.p. 130–135° (0.01 mm.), m.p. 42–45°. No crystalline compound was isolated from the resin-like distillation residue.

Reaction of Triphenylsilyllithium with Silicon Tetrachloride.—A solution of 0.080 mole of triphenylsilyllithium was added slowly, with continuous stirring, to 3.4 g. (0.020 mole) of silicon tetrachloride. After the addition of the third equivalent of the lithium reagent, Color Test I was negative; however, a positive Color Test was obtained after the addition of the fourth equivalent. Stirring was continued for one hour and the mixture subsequently hydrolyzed with dilute acid. Fifteen grams (72.5%) of hexaphenyldisilane, m.p. 357–360°, was removed by filtration. The layers of the filtrate were separated, the organic layer dried, and the solvent removed. The viscous residue was extracted with five 50-ml. portions of hot petroleum ether (b.p. 60–70°), the solution chromatographed on alumina and eluted with the same solvent to give 1.55 g. (7.5%) of triphenylsilane, m.p. 42–45°.

The resin-like residue was insoluble in ethanol, but soluble in benzene and ethyl acetate. Its acetone solution evolved hydrogen upon addition of one drop of aqueous sodium hydroxide, indicative of Si–Si bonds. The spectrum indicated the absence of any Si–H bonds, and the presence of Si–O and O–H linkages. Analyses of the resin gave 15.73 and 15.96% Si.

Reaction of Triphenylsilyllithium with Ethyl Silicate.—A solution of 0.030 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 2.08 g. (0.01 mole) of ethyl silicate. Color Test I was strongly positive immediately after the addition and after 15 hr. of stirring at room temperature. Subsequent to hydrolysis with dilute acid and addition of some ether, 4.1 g. (53%) of hexaphenyldisilane, m.p. 355–358°, was removed by filtration. The organic layer of the filtrate was dried and the solvent removed. The residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°), yielded 1.6 g. (21%) of triphenylsilane. Carbon tetrachloride and benzene eluted resin-like materials which could not be crystallized or otherwise purified.

Reaction of Triphenylsilyllithium with Dichlorodiphenylsilane, followed by Lithium Aluminum Hydride.—A solution of 0.1 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 25.3 g. (0.1 mole) of dichlorodiphenylsilane. Color Test I was negative immediately after the addition. Three and eight-tenths grams (0.1 mole) of lithium aluminum hydride then was added and the reaction mixture refluxed for one hour. Excess of hydride was destroyed by slow addition of ethyl acetate, followed by distilled water and dilute sulfuric acid. A colorless precipitate was separated by filtration and washed with hot benzene to give 11.5 g. (45%) of hexaphenyldisilane, m.p. 352–356° (mixed m.p.). The organic layer of the combined filtrates was dried and the solvent removed. The residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave a product, which was subsequently recrystallized twice from petroleum ether. There was obtained 10.8 g. (24.5%) of impure pentaphenyldisilane, m.p. 117–123°. Two further recrystallizations from the same solvent raised the melting point to 127–128°. The product eluted with carbon tetrachloride and benzene was recrystallized from a mixture of benzene and petroleum ether to give 3.5 g. (9.6%) of octaphenyltrisilane, m.p. 248–255°. An additional recrystallization from the same solvent pair raised the melting point to 260–262°.

Reaction of Triphenylsilyllithium with Chloropentaphenyldisilane.—A solution of 0.02 mole of triphenylsilyllithium in 36 ml. of tetrahydrofuran was added to 9.6 g. (0.02 mole) of chloropentaphenyldisilane dissolved in 25 ml. of tetrahydrofuran, during 30 minutes. The mixture was hydrolyzed with water and extracted with ether. The insoluble residue was removed by filtration and treated with cold benzene. The benzene-insoluble portion contained 4.5 g. of hexaphenyldisilane, m.p. and mixed m.p. 365–366°. The benzene-soluble portion was chromatographed on alumina. Elution of the column with benzene gave 2.1 g. of octaphenyltrisilane, m.p. and mixed m.p. 260–262°.

---

[18] L. J. Brady, *Ind. Eng. Chem., Anal. Ed.*, **20**, 1034 (1948).

[19] H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950).

[20] H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 608 (1958).

[21] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, *ibid.*, **74**, 561 (1952).

[22] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

The ether extract was dried over sodium sulfate, and removal of the solvent under reduced pressure gave a viscous solid. It was treated with a mixture of 50 ml. of petroleum ether (b.p. 60–70°) and 10 ml. of benzene. The soluble portion gave 5.1 g. of a polymeric substance from which no crystalline product could be isolated. The insoluble portion gave 1.5 g. of octaphenyltrisilane which melted at 260–262°, after crystallization from benzene. The combined yield of octaphenyltrisilane was 3.6 g., 25.7%.

Reaction of Triphenylsilyllithium with Trichlorosilane.—A solution of 0.060 mole of triphenylsilyllithium was added slowly to 2.71 g. (0.020 mole) of trichlorosilane. During the addition, the flask was cooled in a Dry Ice–acetone-bath. The reaction mixture was allowed to warm to room temperature. Color Test I was then negative. Subsequent to hydrolysis and addition of some ether, 3.2 g. (20.6%) of hexaphenyldisilane, m.p. 354–357°, was removed by filtration. The organic layer of the filtrate was dried and the solvent removed. The residue was chromatographed on alumina. Petroleum ether (b.p. 60–70°) eluted 4.6 g. (29.5%) of triphenylsilane, m.p. 45–47°. The product eluted with cyclohexane melted over the range 182–198°. Fractional crystallization from the same solvent yielded a trace of a compound, m.p. 185–187°, the structure of which has not yet been determined. The product eluted with carbon tetrachloride was recrystallized three times from a mixture of ethyl acetate and methanol to give 0.7 g. (4.4%) of tris-(triphenylsilyl)-silane,[17b] m.p. 206–209°. The infrared spectrum of the compound had characteristic absorption bands at 3.3, 4.8 and 9.08 μ, indicative of aromatic C–H, of the Si–H and of the silicon–phenyl linkages, respectively.

Anal. Calcd. for $C_{54}H_{46}Si_4$: Si, 13.92. Found: Si, 13.67, 13.80.

Acknowledgment.—This research was supported by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright–Patterson AFB, Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to Dr. V. Fassel and Mr. R. Kniseley for the spectra.

AMES, IOWA

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Catalysis by Metal Halides. I. Mechanism of the Disproportionation of Ethyltrimethylsilane

BY GLEN A. RUSSELL[1]

RECEIVED JANUARY 29, 1959

The catalyzed disproportionation of ethyltrimethylsilane has been investigated in regard to the catalytic effects of various metal halides, the effects of co-catalysts on the rate of the aluminum bromide-catalyzed reaction, the effects of solvent and temperature upon the rate and equilibrium, the kinetics of the reaction, and the possible occurrence of reaction intermediates. It is concluded that catalysis involves the ability of the metal halide to function as a Lewis acid. Evidence is presented against the formation of ions or of organometallic intermediates in the reaction. It is concluded that the reaction occurs *via* the interaction of two silane molecules, one containing a polarized silicon–carbon bond formed by the interaction of the metal halide with the tetraalkylsilane.

Introduction

The catalyzed disproportionation of substituted silanes was first recognized by Friedel and Ladenburg who found that triethoxysilane could be disproportionated in the presence of sodium (a reaction undoubtedly catalyzed by ethoxide ion).[2a]

$$4SiH(OC_2H_5)_3 \overset{C_2H_5O^-}{\rightleftarrows} SiH_4 + 3Si(OC_2H_5)_4$$

Numerous other examples of base-catalyzed disproportionations of alkoxysilanes are now known.[3] Ladenburg later discovered that certain tetraalkylsilanes would disproportionate spontaneously at elevated temperatures in the range of 300°,[2b] a reaction investigated in more detail by Ipatieff and Dolgov.[4] Numerous other thermal disproportionations have been realized, particularly when disproportionation involves the exchange of two negative groups,[5] or the migration of a hydrogen atom.[6] These reactions often have been observed as unexpected side reactions.[6b]

The first disproportionation with unquestioned catalysis by a metal halide was reported by Stock and Somieski who found that aluminum chloride would catalyze the reaction between silane and dichlorosilane to yield monochlorosilane.[7] The metal halide-catalyzed disproportionation has subsequently been investigated from a synthetic,[8] equilibrium[9] and mechanistic[10] point of view.

---

(1) Department of Chemistry, Iowa State University, Ames, Iowa.

(2) (a) C. Friedel and A. Ladenburg, *Ann.*, **143**, 124 (1867); (b) A. Ladenburg, *Ber.*, **7**, 387 (1874).

(3) D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, **77** (1946); C. R. Hance and G. H. Wagner, U. S. Patent 2,530,367 (1950); D. L. Bailey, U. S. Patents, 2,723,983, 2,723,985 (1955), 2,745,860 (1956); E. W. Beck, W. H. Daudt, H. J. Fletcher, M. J. Hunter and A. J. Barry, THIS JOURNAL, **81**, 1256 (1959).

(4) V. I. Ipatieff and B. N. Dolgov, *Ber.*, **62B**, 1220 (1929); B. N. Dolgov and Y. N. Volnov, *J. Gen. Chem.* (*USSR*), **1**, 91 (1931).

(5) (a) C. Friedel and J. Crafts, *Ann.*, **127**, 28 (1863); A. Besson, *Compt. rend.*, **112**, 1314 (1891); Y. N. Volnov, *J. Gen. Chem.* (*USSR*), **17**, 1428 (1947); (b) G. S. Forbes and H. H. Anderson, THIS JOURNAL, **66**, 931 (1944); **67**, 1911 (1945); H. H. Anderson, *ibid.*, **66**, 934 (1944); **73**, 5804 (1951).

(6) (a) H. S. Booth and W. D. Stillwell, *ibid.*, **56**, 1531 (1934); H. J. Emeleus, A. G. Maddock and C. Reid, *J. Chem. Soc.*, 353 (1941); H. J. Emeleus and A. G. Maddock, *ibid.*, 293 (1944); (b) H. Gilman and D. H. Miles, *J. Org. Chem.*, **23**, 326 (1958); N. C. Goodspeed and R. T. Sanderson, *J. Inorg. Chem.*, **2**, 266 (1956); A. F. Reilly and H. W. Post, *J. Org. Chem.*, **16**, 387 (1951); (c) Dow Corning Ltd., British Patent 663,810 (1951).

(7) A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919); **56B**, 1087 (1923).

(8) R. O. Sauer, U. S. Patents 2,647,136 (1953), 2,730,540 (1956); A. J. Barry and J. W. Gilkey, British Patent 642,630 (1950), U. S. Patent 2,647,912 (1953); B. A. Bluestein, U. S. Patent 2,717,257 (1955); G. H. Wagner and M. M. Burnham, U. S. Patent 2,746,980–3 (1956); Baeyer Farbenfabriken, British Patent, 671,880 (1952); D. L. Bailey and G. H. Wagner, U. S. Patent 2,732,281 (1956); E. M. Soshestnenskaya, *J. Gen. Chem.* (*USSR*), **26**, 247 (1946); B. N. Dolgov, S. N. Borsov and M. G. Voronkov, *ibid.*, **27**, 709, 2062, 2692 (1957); *Doklady*, **114**, 93 (1957); J. L. Speier and R. E. Zimmerman, THIS JOURNAL, **77**, 6395 (1955); C. E. Erickson and G. H. Wagner, U. S. Patent 2,627,451 (1953).

(9) (a) G. Calingaert, H. Soroos and V. Hnizda, THIS JOURNAL, **62**, 1107 (1940); (b) R. O. Sauer and E. M. Hadsell, *ibid.*, **70**, 3590 (1948);