130 g. (0.85 mole) of trimethylbromosilane,[9] b. p. 79° (744 mm.), a yield of 85%, and 130 g. (0.84 mole) of bromobenzene. The bromosilane was analyzed for bromine content.

Anal. Calcd. for C_3H_9SiBr: Br, 52.3. Found: Br, 52.3, 52.3.

Trimethyliodosilane.—In a 500-cc. round-bottomed flask there were placed 75 g. (0.5 mole) of phenyltrimethylsilane and 127 g. (0.5 mole) of iodine crystals. After refluxing the reaction mixture for twelve hours, unreacted iodine was removed by adding 15 g. of powdered antimony. Fractional distillation gave 56 g. (0.28 mole) of trimethyliodosilane, b. p. 106.5° (734 mm.), d^{20} 1.47, a yield of 56%.

Anal. Calcd. for C_3H_9SiI: I, 63.5. Found: I, 63.0, 62.8.

DEPARTMENT OF CHEMISTRY
SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.

RECEIVED MAY 17, 1947

Competitive Reactions between Trialkylchlorosilanes and Alkylmagnesium Bromides[1]

BY LEO H. SOMMER, GEORGE T. KERR AND FRANK C. WHITMORE

In connection with studies in the chemistry of trialkylsilyl compounds, it was of interest to determine the effect of structural variations on the reactivity of trialkylchlorosilanes with alkylmagnesium bromides. Three studies of this type are reported in the present paper.

In one experiment, methyl- and ethylmagnesium bromides, 0.42 mole of each, were allowed to compete for 0.42 mole of triethylchlorosilane. The latter reacted exclusively with the methylmagnesium bromide.

$$CH_3MgBr + C_2H_5MgBr + (C_2H_5)_3SiCl \longrightarrow (C_2H_5)_3SiCH_3 \quad (1)$$

This result is in line with the generally observed greater reactivity of the shorter-chain aliphatic Grignard reagents with purely organic compounds.[2]

Treatment of a mixture of trimethylchlorosilane and triethylchlorosilane, 0.5 mole of each, with ethylmagnesium bromide, 0.5 mole, gave ethyltrimethylsilane and tetraethylsilane in a mole ratio of approximately 2 to 1.

$$2(CH_3)_3SiCl + (C_2H_5)_3SiCl + 3C_2H_5MgBr \longrightarrow 2(CH_3)_3SiC_2H_5 + (C_2H_5)_4Si \quad (2)$$

n-Propylmagnesium bromide, which is generally less reactive than ethylmagnesium bromide, gave stronger emphasis to the difference in the reactivity of trimethyl- and triethylchlorosilane. No appreciable amount of *n*-propyltriethylsilane was found.

$$(CH_3)_3SiCl + (C_2H_5)SiCl + C_3H_7MgBr \longrightarrow (CH_3)_3SiC_3H_7 \quad (3)$$

In general, the decreased activity toward Grignard reagents with increased size of the alkyl groups on silicon, as in reactions 2 and 3, is paralleled by a similar change in reactivity with structure of other trialkylsilyl compounds toward other reagents. For example, trimethylsilanol is far more susceptible toward intermolecular dehydration to the disiloxane than is triethylsilanol.[3]

Experimental

Reaction of Triethylchlorosilane with Methyl- and Ethylmagnesium Bromides.—In a 3-liter, three-necked flask, fitted with a mercury-sealed stirrer, a reflux condenser and a separatory funnel, were placed 139 cc. (0.42 mole) of methylmagnesium bromide and 165 cc. (0.42 mole) of ethylmagnesium bromide. To a mixture of Grignard reagents in ether solution was added, during fifteen minutes, with stirring and cooling, 63.0 g. (0.42 mole) of triethylchlorosilane. The mixture was refluxed for four hours, and then the reaction flask was fitted with a condenser for distillation of material volatile at steam-bath temperature. Completion of the distillation after four hours was followed by heating of the residue on the steam-bath for eight hours. The distillate was then returned to the flask, and 500 cc. of water was slowly added with stirring in order to decompose unreacted Grignard reagent. The resulting product was steam-distilled, the organic layer was separated and the aqueous layer extracted with 65 cc. of ether. Ether was removed from the product by distillation and the residue was refluxed with dilute hydrochloric acid for eight hours in order to convert any triethylsilanol (from the hydrolysis of unreacted triethylchlorosilane) to hexaethyldisiloxane. The organic layer was separated, washed free of acid, and dried over anhydrous magnesium sulfate. Fractionation in a glass-helix packed column of about 20 theoretical plates gave 36.1 g. (0.28 mole) of methyltriethylsilane,[4] b. p. 126° (729 mm.), n^{20}D 1.4160, and no tetraethylsilane.

Reaction of Ethylmagnesium Bromide with Trimethyl- and Triethylchlorosilanes.—Addition of a mixture of trimethyl- and triethylchlorosilane (0.5 mole of each) to ethylmagnesium bromide (0.5 mole) was followed by a treatment similar to that employed above. Fractionation gave: 18.3 g. (0.18 mole) of ethyltrimethylsilane,[4] b. p. 62° (734 mm.), n^{20}D 1.3819–1.3821, and 13.6 g. (0.095 mole) of somewhat impure tetraethylsilane,[4] b. p. 152–156° (734 mm.), n^{20}D 1.4259–1.4245. In addition, there were obtained 18.5 g. (0.091 mole) of 1,1,1-trimethyl-3,3,3-triethyldisiloxane,[5] b. p. 172° (724 mm.), n^{20}D 1.4104 and 25.1 g. (0.101 mole) of hexaethyldisiloxane,[6] b. p. 128° (30 mm.), n^{20}D 1.4335.

Reaction of *n*-Propylmagnesium Bromide with Trimethyl- and Triethylchlorosilanes.—Addition of a mixture of trimethyl- and triethylchlorosilane (0.5 mole of each) to *n*-propylmagnesium bromide (0.5 mole) was followed by treatment of the reaction mixture in a manner similar to that above, except that the crude reaction product was treated with 50 cc. of cold concentrated sulfuric acid prior to fractionation in an attempt to separate tetraalkylsilane, which is known to be insoluble in concentrated sulfuric acid, from the disiloxanes which are soluble. The upper layer, containing tetraalkylsilane, was washed free of acid with water and sodium bicarbonate solution, and was then dried with anhydrous sodium sulfate. Fractionation of the product gave 33.3 g. (0.287 mole) of *n*-propyltrimethylsilane,[4] b. p. 89° (729 mm.), n^{20}D 1.3930, and no appreciable quantity of *n*-propyltriethylsilane. In addition, there was obtained 22.1 g., (0.090 mole) of hexaethyldisiloxane, b. p. 129° (30 mm.), n^{20}D 1.4340.

---

(1) Paper XII in a series on organosilicon compounds; for Paper XI see THIS JOURNAL, **69**, 433 (1947).

(2) Gilman, St. John, St. John and Lichtenwalter, *Rec. trav. chim.*, **55**, 577, 588 (1936).

(3) Sauer, THIS JOURNAL, **66**, 1707 (1944); Sommer, Pietrusza and Whitmore, *ibid.*, **68**, 2282 (1946).

(4) Whitmore, Sommer, Di Giorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, THIS JOURNAL, **68**, 475 (1946).

(5) Sauer, *ibid.*, **68**, 954 (1946).

(6) Di Giorgio, Strong, Sommer and Whitmore, *ibid.*, **68**, 1380 (1946).

The lower sulfuric acid layer from treatment of the original crude product (see above) was treated with ice-water, the organic layer was separated, washed free of acid, dried over anhydrous sodium sulfate and fractionated. There was obtained 9.5 g. (0.045 mole) of 1,1,1-trimethyl-3,3,3-triethyldisiloxane, b. p. 80° (30 mm.), $n^{20}\mathrm{D}$ 1.4105, and 10 g. (0.040 mole) of hexaethyldisiloxane, b. p. 137° (29 mm.), $n^{20}\mathrm{D}$ 1.4332.

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.
RECEIVED MAY 17, 1947

Some Reactions of Trialkylaminosilanes[1]

BY D. L. BAILEY,[2] L. H. SOMMER AND F. C. WHITMORE

In continuation of previous studies on the chemistry of trialkylsilyl compounds, the present paper reports reactions of triethylaminosilane (I)[3] and α-chloroethyldiethylaminosilane (II).

Compounds I and II were prepared from the corresponding chlorosilanes[4,5] by treatment with liquid ammonia, a method previously used by Sauer.[3]

$$\mathrm{R(C_2H_5)_2SiCl + 2NH_3 \longrightarrow R(C_2H_5)_2SiNH_2 + NH_4Cl}$$

(R is C_2H_5— in compound I, and CH_3CHCl— in compound II)

Conversion of compounds I and II to halosilanes[6] was achieved with hydrogen chloride, hydrogen bromide, concentrated hydrochloric acid, concentrated hydrofluoric acid, and hydrobromic–sulfuric acid mixture.

$$\mathrm{R(C_2H_5)_2SiNH_2 + 2HX \longrightarrow R(C_2H_5)_2SiX + NH_4X}$$

These reactions indicate possible use of trialkylaminosilanes as intermediates for the preparation of other halosilanes from chlorosilanes. They further emphasize the great differences in the reactions of the silicon–amino and carbon–amino bonds.

Experimental

Triethylaminosilane.[3]—A description of our procedure may be useful in view of the low yield (26%) originally reported for this compound.

In a 200-cc., three-necked flask equipped with dropping funnel, mercury-sealed stirrer and reflux condenser there was placed 100 cc. of liquid ammonia. The flask was then immersed in a Dry Ice and acetone-bath and 75 g. (0.5 mole) of triethylchlorosilane was added from the dropping funnel during one-half hour. After stirring for one hour, the excess ammonia was evaporated and the contents of the flask were diluted with ether and filtered to remove ammonium chloride. The ether was then removed from the product which was fractionally distilled in a glass-helix packed column of about 20 theoretical plates. There was obtained 46 g. (0.35 mole) of triethylaminosilane, b. p. 134°, $n^{20}\mathrm{D}$ 1.4267, a yield of 70%. Weighed samples added to a mixture of methanol and excess standard acid followed by back-titration with standard alkali gave a neutral equivalent of 132. Calcd. neutral equivalent for complete hydrolysis of the silicon–amino bond, 131. The compound was also analyzed by the Kjeldahl method.

Anal. Calcd. for $C_6H_{17}SiN$: N, 10.69. Found: N, 10.69, 10.70.

α-Chloroethyldiethylaminosilane.—Addition of 93 g. (0.5 mole) of α-chloroethyldiethylchlorosilane[5] to 100 cc. of liquid ammonia and use of a procedure similar to that employed for the triethylaminosilane gave 72 g. (0.44 mole) of α-chloroethyldiethylaminosilane, b. p. 93° (38 mm.), $n^{20}\mathrm{D}$ 1.4570, d^{20} 0.9604, a yield of 88%.

Anal. Calcd. for $C_6H_{16}SiClN$: Cl, 21.40; neut. equiv., 166. Found: Cl, 21.36; neut. equiv., 166.

Reactions

A. With Concentrated Hydrochloric Acid.—In a 200-cc., three-necked flask equipped with a reflux condenser, dropping funnel, and mercury-sealed stirrer, there was placed 160 cc. of concentrated hydrochloric acid. This was cooled in an ice-bath and 13 g. (0.1 mole) of triethylaminosilane was added by means of the dropping funnel. After stirring for thirty minutes, the reaction mixture was placed in a separatory funnel and the two layers were separated. Upon drying with sodium sulfate, the undistilled triethylchlorosilane, 14.5 g. (0.09 mole), analyzed for 23.3% Cl (calcd. for triethylchlorosilane, 23.5%). Distillation of this material gave 12 g. (0.08 mole) of triethylchlorosilane, b. p. 144–145°, d^{20} 0.8977, a yield of 80%.

α-Chloroethyldiethylaminosilane, 13 g. (0.08 mole), was treated with concentrated hydrochloric acid by a procedure similar to that used for triethylaminosilane. Distillation of the product gave 11.5 g. (0.062 mole) of α-chloroethyldiethylchlorosilane,[5] b. p. 178–179°, d^{20} 1.0399, a yield of 79%.

B. With Hydrofluoric Acid.—In a 200-cc. flask there was placed 60 cc. of 48% hydrofluoric acid. This was cooled in an ice-bath and 12 g. (0.09 mole) of triethylaminosilane was added from the dropping funnel during five minutes. After agitation of the reaction mixture for ten minutes, the resulting two layers were separated and the upper layer dried over sodium sulfate. Distillation gave 10.5 g. (0.08 mole) of triethylfluorosilane,[7] b. p. 109–110°, d^{20} 0.8380, F, 13.9% (calcd. 14.1%), a yield of 89%.

Treatment of α-chloroethyldiethylaminosilane, 11 g. (0.066 mole), with hydrofluoric acid (48%) gave 9 g. (0.053 mole) of α-chloroethyldiethylfluorosilane,[5] b. p. 149–150°, d^{20} 0.9961, F, 11.3% (calcd. 11.3%), in 82% yield.

C. With Hydrogen Chloride.—In a 200-cc. three-necked flask equipped with a reflux condenser, mercury-sealed stirrer, and gas delivery tube there were placed 150 cc. of dry ether and 20 g. (0.152 mole) of triethylaminosilane. Dry hydrogen chloride was passed into the reaction mixture until the solution was saturated. The ammonium chloride was filtered and the ether was evaporated on the steam-bath. Distillation of the residual liquid gave 16 g. (0.106 mole) of triethylchlorosilane, b. p. 143–145°, d^{20} 0.8974, Cl, 23.4% (calcd. 23.5%), a yield of 70%.

An ether solution of α-chloroethyldiethylaminosilane, 18 g. (0.11 mole) was treated with hydrogen chloride gas to give 15.5 g. (0.084 mole) of α-chloroethyldiethylchlorosilane,[5] b. p. 179–181°, d^{20} 1.0385, $n^{20}\mathrm{D}$ 1.4553, a yield of 76%.

D. With Hydrogen Bromide.—An ether solution of triethylaminosilane, 39 g. (0.30 mole) was treated with dry hydrogen bromide by a procedure similar to that used for the reaction of hydrogen chloride with this compound. There was obtained 41.5 g. (0.21 mole) of triethylbromosilane,[8] b. p. 162–163°, $n^{20}\mathrm{D}$ 1.4563, d^{20} 1.1403, a yield of 70%.

---

(1) Presented at the 109th Meeting of the American Chemical Society in Atlantic City, New Jersey, April 9, 1946. Paper XIII in a series on organosilicon compounds. For paper XII see THIS JOURNAL, **70**, 434 (1948).

(2) Gulf Oil Corporation Fellow, 1946–1947.

(3) Sauer and Hasek, THIS JOURNAL, **68**, 241 (1946).

(4) Triethylchlorosilane was prepared by the method of Di-Giorgio, Strong, Sommer and Whitmore, *ibid.*, **68**, 1380 (1946).

(5) α-Chloroethyldiethylchlorosilane was prepared by the method of Sommer, Bailey, Strong and Whitmore, *ibid.*, **68**, 1881 (1946).

(6) The conversion of hexamethyldisilazane to trimethylchlorosilane using hydrogen chloride has been reported in ref. 3.

(7) Flood, THIS JOURNAL, **55**, 1735 (1933).

(8) Grüttner and Cauer, *Ber.*, **51**, 1289 (1918).