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}_D 1.4105, and 10 g. (0.040 mole) of hexaethyldisiloxane, b. p. 137° (29 mm.), n^{20}_D 1.4332.

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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]

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

(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.

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

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}_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}_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. (0.060 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}_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}_D 1.4563, d^{20} 1.1403, a yield of 70%.

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(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).

Anal. Calcd. for $C_6H_{15}SiBr$: Br, 40.95; neut. equiv., 195. Found: Br, 40.93; neut. equiv., 196.

An ether solution of α-chloroethyldiethylaminosilane, 24 g. (0.145 mole) was treated with dry hydrogen bromide to give 12 g. (0.052 mole) of α-chloroethyldiethylbromosilane, b. p. 194–196°, n^{20}_{D} 1.4762, a yield of 26%. A product of higher purity was obtained in the reaction with hydrobromic–sulfuric acid mixture.

Anal. Calcd. for $C_6H_{14}SiClBr$: Br, 34.81; neut. equiv., 230. Found: Br, 33.99; neut. equiv., 234.

E. With Hydrobromic–Sulfuric Acid Mixture.—In a one-liter three-necked flask equipped with reflux condenser, mercury-sealed stirrer, and dropping funnel, there was placed 300 cc. of 48% hydrobromic acid. This was cooled in an ice-bath and 200 cc. of concentrated sulfuric acid was added. To the mixture there was then added through the dropping funnel 41 g. (0.31 mole) of triethylaminosilane. After stirring the reaction mixture for twenty minutes, the resulting two layers were separated and the organic layer dried over sodium sulfate. Fractionation gave 33.5 g. (0.17 mole) of triethylbromosilane, b. p. 78–79° (45 mm.), n^{20}_{D} 1.4561, Br, 40.8% (calcd. 40.95%), a yield of 55%.

α-Chloroethyldiethylaminosilane, 52 g. (0.31 mole), was treated with hydrobromic–sulfuric acid by a procedure similar to that used for triethylaminosilane. Distillation of the product gave 58.5 g. (0.255 mole) of α-chloroethyldiethylbromosilane, b. p. 105–106° (46 mm.), n^{20}_{D} 1.4784, d^{20} 1.2661, Br, 34.8% (calcd. 34.81%), a yield of 81%.

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Conductivities of Aqueous Solutions of Dodecylammonium Chloride

BY A. W. RALSTON AND D. N. EGGENBERGER

We are currently engaged in a study of the effects of inorganic electrolytes and of various organic compounds upon the electrical behavior of solutions of cationic colloidal electrolytes. During the course of this investigation we have redetermined the equivalent conductivities of aqueous solutions of dodecylammonium chloride at various temperatures and have found that the values are somewhat lower than those which we have previously reported.[1,2] We are of the opinion that the dodecylammonium chloride which was used in our earlier work contained traces of impurities, since our present values have been reproduced with several quite pure samples of this amine salt prepared by different investigators. The values herein reported, when plotted against the square root of the volume normality, $\sqrt{N_v}$, show a decidedly less steep slope within the first range, although the concentrations of amine salt at the critical points for micelle formation are in agreement with those reported previously.

The values of the equivalent conductivities of aqueous solutions of dodecylammonium chloride at various temperatures are shown in Table I.

TABLE I

EQUIVALENT CONDUCTIVITIES OF AQUEOUS SOLUTIONS OF DODECYLAMMONIUM CHLORIDE

N_v 20°	Λ	N_v 25°	Λ	N_v 30°	Λ	N_v 40°	Λ	N_v 50°	Λ	N_v 60°	Λ
0.000507	87.6	0.000777	96.0	0.000985	106.4	0.000801	127.7	0.000968	148.6	0.000905	172.1
.00127	86.5	.00177	95.2	.00179	105.7	.00186	126.0	.00212	147.4	.00194	169.5
.00284	85.0	.00398	93.1	.00335	104.8	.00405	124.0	.00445	145.5	.00466	166.7
.00402	84.4	.01003	91.3	.00384	104.4	.00728	123.0	.00820	142.4	.01433	160.6
.00635	83.0	.01025	90.9	.00608	103.5	.00806	121.5	.00933	141.8	.0180	155.0
.00934	81.7	.0156	86.6	.00842	102.4	.01455	119.7	.01417	140.7	.0248	130.0
.01025	81.4	.0168	83.1	.01137	101.5	.0177	107.2	.0181	128.6	.0439	96.0
.0170	74.1	.0172	80.7	.01354	100.7	.0207	96.5	.0223	112.5	.0729	79.7
.0181	70.3	.0196	73.5	.0150	98.9	.0480	61.8	.0240	109.0	.1345	70.8
.0208	64.1	.0223	68.4	.0173	90.5	.0796	52.1	.0423	80.5		
.0265	54.3	.0437	45.7	.0226	75.4	.1353	47.2	.0682	67.0		
.0484	38.1	.0769	36.3	.0235	72.9			.1383	58.4		
.0782	31.1	.1371	31.7	.0384	54.9						
.1397	26.8			.0622	43.7						
				.1008	38.7						
				.1493	36.4						

Experimental

Preparation of Dodecylammonium Chloride.—Commercially distilled dodecylamine was fractionated through a Stedman packed column and the fraction boiling at 111.5° at 4 mm. retained. This fraction melted at 28.30°. The amine (200 g.) was dissolved in benzene (2 liters) and treated with dry hydrogen chloride. Upon cooling, crystals of dodecylammonium chloride precipitated. The crystals were removed by filtration and crystallized three times from benzene. The sample was analyzed by a previously described procedure.[3] (*Anal.* Calcd. for $C_{12}H_{25}NH_2$, 83.54; Cl, 16.00. Found: $C_{12}H_{25}NH_2$, 83.84; Cl, 16.06).

Conductivity Determinations.—Conductivities were determined in the manner and with the equipment previously described.[1]

(1) Ralston, Hoerr and Hoffman, THIS JOURNAL, **64**, 97 (1942).

(2) Ralston and Hoerr, *ibid.*, **64**, 772 (1942).

(3) Ralston and Hoerr, *Ind. Eng. Chem., Anal. Ed.*, **16**, 459 (1944).

RESEARCH LABORATORY OF ARMOUR AND COMPANY
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Trimethylgermanium Chloride

BY EUGENE G. ROCHOW[1]

The preparation of methylgermanium trichloride and dimethylgermanium dichloride by the

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(1) Research Laboratory, General Electric Company.