438. *Dimethylaminochlorosilanes.*

By R. Cass and G. E. Coates.

Dimethylaminotrichlorosilane and bisdimethylaminodichlorosilane have been prepared from dimethylamine and silicon tetrachloride. Both compounds give silane instead of the expected dimethylaminosilanes on reduction with lithium aluminium hydride. They are sufficiently basic to form several hydrochlorides, but no quaternary salts are formed with methyl iodide.

In an attempt to prepare dimethylaminosilanes by the reduction of the corresponding chloro-silanes with lithium aluminium hydride, the reaction between dimethylamine and silicon tetrachloride was studied, since the required aminochlorosilanes have not been reported. Several other similar amino-derivatives of silicon have been described however; diethylamino-, b. p. 104°/80 mm., and *iso*butylamino-trichlorosilane, b. p. 120—124°/30 mm., were obtained by Michaelis and Luxembourg (*Ber.*, 1896, **29**, 714) from silicon tetrachloride and the corresponding amine. Several alkyl- (Johannson, U.S.P. 2,429,883/1947; Mjörne, *Svensk Kem. Tidsk.*, 1950, **62**, 120) and alkoxy- (Rosnati, *Gazzetta*, 1948, **78**, 516) derivatives have also been obtained from secondary amines and alkyl- and alkoxy-chlorosilanes, respectively. No silanes containing more than two amino-groups have resulted from condensation reactions of this type, but tetrakisdibenzylaminosilane is formed from dibenzylamine and silicon disulphide (Malatesta, *ibid.*, p. 753).

Emeléus and Miller (*J.*, 1939, 819) attempted to prepare dimethylaminosilane from chlorosilane and dimethylamine, but the product immediately underwent further reaction with chlorosilane with the formation of an unstable quaternary ammonium salt which decomposed into silane, chlorosilane, and dichlorosilane.

When dimethylamine reacts with silicon tetrachloride, dimethylaminotrichlorosilane and bisdimethylaminodichlorosilane can be isolated in small yield. The ratio $NHMe_2 : SiCl_4$ affects the proportion of the two compounds obtained, *e.g.* a 2 : 1 ratio gives a product containing the trichloro- and the dichloro-silane in a 3 : 1 ratio, whereas a 4 : 1 ratio of the reactants gives a 2 : 7 ratio in the product together with a small proportion of less volatile material. When the ratio is increased to 8 : 1 the greatest part of the product (80%) consists of the dichloro-compound, the remainder possibly containing more highly substituted derivatives. The low yields are due to the formation of much solid salt containing silicon (in addition, of course, to dimethylamine hydrochloride) from which it has not been possible to separate any free base except dimethylamine; treatment with anhydrous bases, such as pyridine and triethylamine, did not succeed and both aqueous and alcoholic solutions cause immediate hydrolysis of the required products. A similar difficulty arises in the preparation of the dimethylaminochloroborines (Wiberg and Schuster, *Z. anorg. Chem.*, 1933, **213**, 77, 89; Coates, *J.*, 1950, 3481).

Dimethylaminotrichloro- and bisdimethylaminodichloro-silane are colourless fuming liquids which are rapidly hydrolysed by water with the deposition of silica; their physical properties are given in the table.

	A *	*B* *	B. p. (extrapolated)	M. p.	L_v	Trouton constant
$Me_2N\cdot SiCl_3$	1639·4	6·984	123°	−81°	7·51	19·0
$(Me_2N)_2SiCl_2$	2142·0	7·985	166	−48	9·84	21·6

* $\log_{10}$ (v. p.)$_{mm.}$ = $-(A/T) + B$. L_v = latent heat of evaporation, kcal./mole.

Attempts to prepare more highly substituted derivatives in sufficient quantities for manipulation were unsuccessful. The dichloro-compound did not react further with dimethylamine even in a sealed tube at 100°. In spite of the inductive effect of the electronegative chlorine atoms bound to the silicon, both the dichloro- and the trichloro-compound readily form hydrochlorides, stable in a vacuum, when brought into contact with hydrogen chloride; the trichlorosilane gives a monohydrochloride which is a colourless deliquescent crystalline substance, while the dichloro-compound forms a liquid trihydrochloride, which loses hydrogen chloride above −60° *in vacuo* forming a colourless crystalline dihydrochloride. The dichlorosilane hydrochlorides are rapidly decomposed by water into silica, dimethylamine hydrochloride, and hydrochloric acid. Neither of the bases forms quaternary compounds with methyl iodide.

Treatment of the dichloro- and the trichloro-silane with lithium aluminium hydride, alone or in ethereal solution, did not afford either dimethylamino- or bisdimethylaminosilane; instead there was a nearly quantitative formation of silane together with a trace of hydrogen. In this connection, Burg and Kuljian (*J. Amer. Chem. Soc.*, 1950, **72**, 3103) have shown that Si–N bonds are very readily broken, since trisilylamine combines with boron trichloride even at −78° giving chlorosilane and disilylaminodichloroborine. It would appear from the present work that lithium aluminium hydride is able to reduce not only the chloro- but also the dimethylamino-substituent. This contrasts with the ready reduction of bisdimethylaminochloroborine to the corresponding hydride by means of lithium aluminium hydride (Coates, *loc. cit.*).

EXPERIMENTAL

All reactions, other than the initial preparation of dimethylaminotrichloro- and bisdimethylaminodichloro-silane, were carried out in a vacuum apparatus of the usual type (see, *e.g.*, Stock, "Hydrides of Boron and Silicon," Cornell, 1933; Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, 1948).

Dimethylaminotrichlorosilane.—Dimethylamine (54 g., 1·2 moles) at 0° in carefully dried *n*-pentane (300 c.c.) was added, during one hour, to a well stirred solution of silicon tetrachloride (100 g., 0·6 mole) in *n*-pentane (500 c.c.) at −20°. After the addition, the reaction mixture was allowed to warm to room temperature and was then filtered rapidly to remove insoluble hydrochlorides. The residue was washed free from aminochlorosilanes with pentane (200 c.c.). The filtrate and the washings were mixed, and the bulk of the pentane was distilled from the products. Distillation of the straw-coloured residual liquid at atmospheric pressure yielded pentane (4 c.c.) and silicon tetrachloride (12 c.c.), b. p. 56·6—57·9°/759 mm.; the pressure was then reduced and two further fractions were obtained: *dimethylaminotrichlorosilane* (12 c.c.), b. p. 69—70·2°/170 mm. (Found: Si, 15·5; Cl, 59·4. $C_2H_6NCl_3Si$ requires Si, 15·8; Cl, 59·6%); and *bisdimethylaminodichlorosilane* (4 c.c.), b. p. 79·1—80·5°/70 mm. (Found: Si, 14·9; Cl, 39·1; NMe_2, 46·4. $C_4H_{12}N_2Cl_2Si$ requires Si, 15·1; Cl, 37·9; NMe_2, 47·1%).

Bisdimethylaminodichlorosilane.—This was prepared by a similar method from dimethylamine (46·2 g., 1·03 mole) and silicon tetrachloride (50 g., 0·3 mole). Fractionation of the products at atmospheric pressure yielded pentane (5 c.c.) and no silicon tetrachloride. At reduced pressure two fractions were obtained, dimethylaminotrichlorosilane (6 c.c.), b. p. 29·8—30·1°/40 mm., and bisdimethylaminodichlorosilane (12 c.c.), b. p. 48—50·2°/21 mm. (Found: Si, 14·8; Cl, 39·0; NMe_2, 46·5%). A residue (about 2 c.c.) remained which could not be distilled without decomposition.

When the ratio $NHMe_2 : SiCl_4$ was 8 : 1, approximately 80% of the product was obtained as the dichloro-derivative, the remainder being a viscous liquid which could not be distilled above room temperature without decomposition. After pumping had been continued at room temperature for 3 days, about $\frac{1}{2}$ c.c. had condensed in a liquid-air trap as a colourless oil ($d < 1$), which did not fume in air and was only slowly hydrolysed by water (Found: Cl, 7·7. Calc. for $C_6H_{18}N_3ClSi$: Cl, 18·5%). This could possibly have been a mixture of the tris- and the tetrakis-substitution products; no separation into single substances was achieved.

Reaction between Bisdimethylaminodichlorosilane and Dimethylamine.—Dimethylamine (223 c.c. at N.T.P., 10 mmoles) and the dichlorosilane (1·55 g., 8·3 mmoles) were condensed in a thick-walled glass ampoule, which was sealed off *in vacuo* and heated to 100° for 3 hours. The reactants were then frozen, the ampoule opened, and the contents introduced into the vacuum apparatus. No solid matter was formed during the reaction, and subsequent fractionation gave only starting materials.

Other Attempts at Further Dimethylamino-substitution.—Addition of silicon tetrachloride both to an ether suspension of dimethylaminolithium [from methyl-lithium and dimethylamine; Gilman and co-workers (*J. Amer. Chem. Soc.*, 1945, **67**, 2106)] and to the similar magnesium compound (from ethylmagnesium bromide and dimethylamine) gave no volatile products containing silicon, other than silicon tetrachloride.

Reaction of Dimethylaminotrichlorosilane and Lithium Aluminium Hydride.—Lithium aluminium hydride (1·096 g., 28 mmoles) was quickly powdered and transferred to a tube, which was connected by a ground-glass joint to the vacuum apparatus. Dimethylaminotrichlorosilane (1·8 g., 11 mmoles) was condensed *in vacuo* on to the lithium aluminium hydride, and the mixture allowed to warm to room temperature. The very slow reaction was complete after about 40 hours. A small quantity of hydrogen had been formed; the remaining volatile material consisted solely of silane (10·4 mmoles, 95%) (*M*, 32·3. Calc. for SiH_4: *M*, 32·1).

In a similar experiment in dry ether (25 c.c.) the reaction proceeded more rapidly (2 hours) to give silane and a trace of hydrogen.

Reaction of Bisdimethylaminodichlorosilane and Lithium Aluminium Hydride.—In a similar manner the dichlorosilane (1·13 g., 6 mmoles) was allowed to react with lithium aluminium hydride (1·35 g., 35·5 mmoles). The reaction was only complete (no further increase in pressure) after 3 days. A trace of hydrogen was obtained; the remaining volatile material consisted entirely of silane (5·4 mmoles, 90%) (*M*, 32·3).

In a similar reaction in ether the same volatile products, *i.e.* silane and a trace of hydrogen, were obtained.

Dimethylaminotrichlorosilane Hydrochloride.—Dimethylaminotrichlorosilane (0·224 g., 1·26 mmoles) and dry hydrogen cloride (0·0662 g., 1·82 mmoles) were condensed in an ampoule attached to the vacuum apparatus by means of a ground-glass joint. The ampoule was isolated from the rest of the apparatus and allowed to warm to room temperature, whereupon a white solid was formed. After some time, excess of hydrogen chloride (0·0202 g., 0·57 mmole) was pumped off, and the *hydrochloride* obtained as a white solid (Found: Cl, 65·8; NMe_2, 20·3. $C_2H_6NCl_3Si,HCl$ requires Cl, 66·0; NMe_2, 20·6%).

Bisdimethylaminodichlorosilane Trihydrochloride.—Bisdimethylaminodichlorosilane (0·2336 g., 1·25 mmoles) and dry hydrogen chloride (0·1968 g., 5·4 mmoles) similarly gave a white solid, but when the ampoule was cooled by means of a carbon dioxide–acetone bath this changed to a clear liquid. The excess of hydrogen chloride (0·046 g., 1·30 mmoles) pumped off at −78° showed that the liquid had the composition $SiCl_2(NMe_2)_2,(HCl)_{3\cdot28}$.

Bisdimethylaminodichlorosilane Dihydrochloride.—The liquid trihydrochloride was allowed to warm to room temperature whereupon hydrogen chloride was evolved and a white solid formed. After the hydrogen chloride had been removed, analysis showed the solid (m. p. 171—173°) to be the *dihydrochloride* (Found: Cl, 54·2. $C_4H_{12}N_2Cl_2Si,2HCl$ requires Cl, 54·6%).

UNIVERSITY OF BRISTOL.

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