175. *Derivatives of Monosilane. Part I. The Reactions of Chlorosilane with Aliphatic Amines.*

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Chlorosilane, SiH_3Cl, reacts with methylamine to form methyldisilylamine, $CH_3\cdot N(SiH_3)_2$, b. p. 32·3°. This is quantitatively decomposed by aqueous sodium hydroxide and with hydrogen chloride regenerates chlorosilane. With dimethylamine there is a comparable reaction, which leads to the formation of a compound $N(CH_3)_2\cdot SiH_3$; but this cannot be isolated owing to secondary reactions. Trimethylamine reacts in equimolecular proportion with chlorosilane to form a solid quaternary compound, $N(CH_3)_3(SiH_3)Cl$, which dissociates irreversibly on heating owing to disproportionation of the chlorosilane formed into silane and dichlorosilane. The quaternary chloride reacts with water to form disilyl ether, $(SiH_3)_2O$, and undergoes a comparable reaction with ethyl alcohol.

The investigation of the volatile and monomeric compounds of silicon has hitherto been restricted chiefly to those of the types prepared by Kipping, and to the hydrides SiH_4, Si_2H_6, Si_3H_8, and Si_4H_{10}, and a relatively small number of their simpler derivatives, such as disilyl ether (Stock *et al.*, *Ber.*, 1917, **50**, 1754), trisilylamine, $N(SiH_3)_3$ (*Ber.*, 1921, **54**, 740), and the chloro-, bromo-, and iodo-derivatives. This has been largely due to the difficulty of handling many of these substances save by the vacuum-technique. Now those compounds which contain the silyl radical, $SiH_3\cdot$, are of special interest on account of their tendency to remain monomeric where their congeners containing such radicals as $SiH_2\colon$ polymerise; and our first object in reopening this field was to prepare and characterise some of the numerous silyl derivatives which are at present unknown and should be accessible through the halogenated silanes. A further aim was to prepare compounds which might serve later as a means of characterising free radicals containing silicon.

The new silyl derivatives, methyl- and ethyl-disilylamine, dimethylsilylamine, and trimethylsilylammonium chloride, have been obtained by the action of silyl chloride on methylamine, ethylamine, dimethylamine, and trimethylamine respectively; their properties, compared with those of the corresponding amines, illustrate the persistence of the reactivity of the silyl radical in its derivatives. The stability of quaternary compounds of the type $N(CH_3)_x(SiH_3)_{4-x}Cl$ appears to decrease with increase in the number of silyl radicals present: and of these, trimethylsilylammonium chloride provides a ready means of preparing yet other compounds containing the silyl radical, *e.g.*, disilyl ether by the action of water, and there are strong indications that further syntheses may be effected by means of the same reagent.

EXPERIMENTAL.

Monosilane was prepared by the liquid-ammonia method of Johnson and Isenberg (*J. Amer. Chem. Soc.*, 1935, **57**, 1349). The magnesium silicide employed was produced by heating the finely powdered elements together at 700° for 24 hours in a current of hydrogen. The yield of hydride was greatly improved by carrying out the reaction under a reflux condenser packed with solid carbon dioxide, which had the effect of keeping the liquid ammonia largely in the reaction vessel. The hydride was obtained tensimetrically pure in a vacuum-apparatus of the type used by Stock, his method of purification being improved and expedited by carrying out the distillation of the hydride from a bath of pentane cooled by liquid nitrogen at −150°, instead of at −125°. A mixture of mono- and di-chlorosilane was prepared by heating monosilane and hydrogen chloride at 110° in presence of aluminium chloride, which acts as a catalyst (Stock, *Ber.*, 1919, **52**, 695). It was found unnecessary to seal off the reaction vessel containing the catalyst, and successive preparations could be carried out in a vessel connected with the apparatus by a mercury valve, without renewing the catalyst. Chlorosilane was obtained tensimetrically pure by fractionation.

Preparation and Properties of Methyldisilylamine.—306·0 C.c. of chlorosilane and 331·1 c.c. of methylamine were measured out successively in a calibrated bulb in the vacuum-apparatus, distilled into traps on opposite sides of a 2-l. globe, and allowed to vaporise and mix in the bulb. A fog of methylamine hydrochloride formed immediately, and the volatile products were distilled into the vacuum-apparatus and analysed. When the residual solid was treated with water, the greater part dissolved, leaving only a small residue of silicon-containing polymers which were decomposed by alkali with evolution of hydrogen. The solution was filtered and examined quantitatively for chlorine (Found, 218·0 c.c. of Cl′). A preliminary fractionation of the volatile product was carried out at −115°, and the material volatile at this temperature was tensimetrically pure chlorosilane (95·5 c.c.; v. p. 195 mm. at − 58·0°). There was no residual methylamine. The ratios, $CH_3{\cdot}NH_2,HCl$ found/$CH_3{\cdot}NH_2$ taken, and SiH_3Cl reacting/$CH_3{\cdot}NH_2$ reacting, were thus evaluated as 0·654 and 0·632 respectively, showing that the reaction may be represented approximately by the equation

$$2SiH_3Cl + 3CH_3{\cdot}NH_2 = CH_3{\cdot}N(SiH_3)_2 + 2CH_3{\cdot}NH_2,HCl$$

The substance which was not volatile at −115° and, from the equation, should have the formula $CH_3{\cdot}N(SiH_3)_2$ was next isolated by fractional distillation at −95°, followed by fractional condensation at −85°. The condensate at this temperature was divided into three parts by fractional distillation; these had identical vapour-pressure curves, showing that the substance was homogeneous. The vapour density was measured in a Stock **V**-tube [Found: *M*, 91·6. Calc. for $CH_3{\cdot}N(SiH_3)_2$: *M*, 91·7]. 11·46 C.c. of the substance, decomposed by 40% aqueous alkali, evolved 68·80 c.c. of hydrogen, indicating the reaction

$$CH_3{\cdot}N(SiH_3)_2 + 4NaOH + 2H_2O = CH_3{\cdot}NH_2 + 2Na_2SiO_3 + 6H_2$$

The vapour-pressure data for methyldisilylamine were as follows:

Temp.	−72·1°	−62·3°	−52·1°	−44·4°	−38·9°	−27·2°	−21·5°
V. p. (mm.)	2	6	8	16	23	47	64
Temp.	−14·2°	− 3·6°	0·0°	5·2°	9·1°	13·4°	17·9°
V. p. (mm.)	96	162	192	243	286	346	413

The log p–$1/T$ curve gave an extrapolated b. p. of 32·3°, and a latent heat of vaporisation of 74·1 cals./g., as compared with 65·0 cals./g. for trisilylamine, calculated from the work of Stock (*loc. cit.*), and 101·3 cals./g. for trimethylamine.

The reaction of methyldisilylamine with hydrogen chloride was investigated by condensing 6·71 c.c. of the amine on 31·44 c.c. of hydrogen chloride held in liquid air, and allowing the two substances to volatilise and react. The volatile products were pumped off and hydrolysed by sodium hydroxide solution, whereby 38·97 c.c. of hydrogen were evolved, indicating the presence of 12·66 c.c. of chlorosilane in a total volume of 24·74 c.c. of chlorosilane–hydrogen chloride (calc., 24·73 c.c. from the equation below). The chlorine in the solid deposits was estimated gravimetrically (Found, 6·59 c.c.). These values are close to those required by the equation:

$$CH_3{\cdot}N(SiH_3)_2 + 3HCl = CH_3{\cdot}NH_2,HCl + 2SiH_3Cl$$

A mixture of the amine (pressure, 26 mm. in a vessel of 150 c.c. capacity) and oxygen (327 mm.), introduced while the amine was held at −78°, was heated gradually. There was no visible reaction below 140°, but at this temperature an explosion took place resembling in violence that obtained when silane itself is mixed with oxygen and heated.

Preparation and Properties of Ethyldisilylamine.—390·2 C.c. of chlorosilane were allowed to react with 516·6 c.c. of pure ethylamine as described above, and the products examined as in the case of methyldisilylamine. The reacting volume ratios $C_2H_5{\cdot}NH_2/C_2H_5{\cdot}NH_2,HCl$ and $SiH_3Cl/C_2H_5{\cdot}NH_2$ were 1·474 and 0·679 respectively, in accordance with the equation

$$2SiH_3Cl + 3C_2H_5{\cdot}NH_2 = C_2H_5{\cdot}N(SiH_3)_2 + 2C_2H_5NH_2,HCl$$

The vapour pressures of freshly fractionated ethyldisilylamine were as follows:

Temp.	−45·4°	−35·6°	−26·7°	−20·6°	−11·7°	−10·6°	1·5°	4·5°	9·1°	16·0°	20·0°
V. p. (mm.)	2	7	14	20	34	40	68	83	103	135	153

The b. p. extrapolated from the log p–$1/T$ curve was 65·9°, the latent heat of evaporation being 67·6 cals./g. The m. p. was −127°. On standing, slight decomposition occurred: after 10 days, for example, the vapour pressure was 144 mm. at 13·1°, 100 mm. at 1·6°, and 67 mm. at −13·3°. The increase in pressure was due in part to silane, which could be pumped off at −130°, and in part to a substance of medium volatility, which was not identified. Ethyldisilylamine could, however, be freed from this less volatile decomposition product by distillation at −65°, at which temperature the ethyldisilylamine alone was volatile. The vapour density of a sample of ethyldisilylamine which had been standing for some days gave a molecular weight of 103·4 [Calc. for $C_2H_5{\cdot}N(SiH_3)_2$: *M*, 106·9], and evolved 5·8 times its volume of hydrogen on hydrolysis with sodium hydroxide solution.

4·27 C.c. of the amine, when treated with 25·57 c.c. of hydrogen chloride, gave a gaseous mixture of volume 20·82 c.c. (calc., 21·30 c.c.), which gave 26·84 c.c. of hydrogen on treatment with 40% alkali solution, indicating the presence of 8·71 c.c. of chlorosilane after reaction, and confirming the equation

$$C_2H_5{\cdot}N(SiH_3)_2 + 3HCl = C_2H_5{\cdot}NH_2{,}HCl + 2SiH_3Cl$$

Preparation of Dimethylsilylamine.—168·0 C.c. of dimethylamine were allowed to react with 95·0 c.c. of chlorosilane at room temperature as already described. The reacting ratios $NH(CH_3)_2{,}HCl/NH(CH_3)_2$ and $SiH_3Cl/NH(CH_3)_2$ were 0·46 and 0·54 respectively, in approximate agreement with the equation

$$SiH_3Cl + 2NH(CH_3)_2 = N(CH_3)_2{\cdot}SiH_3 + NH(CH_3)_2{,}HCl$$

This is almost certainly the primary reaction, but it is complicated by secondary processes, which render the isolation of the pure amine impossible by fractionation. Thus in the above experiment, the total volatile product was distilled away from the dimethylamine hydrochloride, and the excess of chlorosilane was taken off at −110°; but the residue could not be further separated, as at −85° it was completely involatile, and at −75° the whole mass distilled in the course of 5 hours. It evolved monosilane slowly (25·0 c.c. in 10 days). After removal of this at −130° there remained a liquid at room temperature, from which, on cooling to −10°, a crystalline solid separated. The vapour density of the mixture gave a molecular weight of 84·47 [Calc. for $N(CH_3)_2{\cdot}SiH_3$: *M*, 75·37]. Another experiment, in which an excess of dimethylamine (241·3 c.c. of dimethylamine : 109·2 c.c. of chlorosilane) was used, gave a similar mixture.

It was considered, by comparison with the reaction with trimethylamine to be described later, that, during the fractionations at low temperatures, a certain percentage of the dimethylsilylamine had formed a quaternary salt, $N(CH_3)_2(SiH_3)_2Cl$, with the excess of chlorosilane. This had then dissociated in part into its components on warming to room temperature; and the chlorosilane thus formed had undergone disproportionation, thus :

$$2SiH_3Cl = SiH_4 + SiH_2Cl_2$$

a process catalysed by the double compound. This conjecture was supported by the identical discrepancies (8%) in both the reaction ratios given above, and by the high vapour density of the mixture, which would all be accounted for on this theory.

Preparation and Properties of Trimethylsilylammonium Chloride.—Several preparations of this compound were carried out by the interaction of chlorosilane and trimethylamine at room temperature. Trimethylamine was prepared by heating the hydrochloride in a vacuum with quicklime, the gas evolved being dried in succession with potassium hydroxide and phosphoric oxide. The reactants combined in strictly equal volumes, as the data in Table I show.

TABLE I.

The Combining Ratios of Trimethylamine and Chlorosilane.

Vol. $N(CH_3)_3$, c.c.	Vol. SiH_3Cl, c.c.	Excess gas, c.c., measured.	Excess gas, c.c., calculated.	Reaction ratio $N(CH_3)_3 : SiH_3Cl$.
22·32	18·70	3·68	3·62	1 : 1·004
6·07	5·94	0·15	0·13	1 : 1·005
19·95	9·80	9·70	10·15	1 : 0·975
104·2	123·5	21·0	19·3	1 : 0·984

The white solid product was not volatile at −78°, and could thus be held at this temperature while the excess of either reactant was pumped off and measured. In all cases the excess remaining, whether of chlorosilane or of trimethylamine, was tensimetrically pure. The solid could be sublimed into the apparatus in a high vacuum. It was analysed by forming it directly in the decomposition vessel from known volumes of the gases, the excess of either being pumped off at −78° and measured. A 40% solution of sodium hydroxide was then run on it, the evolved hydrogen measured, and chlorine in the resulting solution estimated gravimetrically. The results of two such experiments are below :

	C.c. at *N.T.P.*	
Vol. of $N(CH_3)_3$	22·32	6·07
Vol. of SiH_3Cl	18·70	5·94
Excess gas (measured)	3·68	0·15
,, (calculated)	3·62	0·13
Vol. of H_2	55·70	18·74
Vol. of Cl' in soln.	18·72	5·90

These data are in fairly close agreement with the equation

$$N(CH_3)_3(SiH_3)Cl + 3NaOH = Na_2SiO_3 + NaCl + N(CH_3)_3 + 3H_2$$

The dissociation pressures of the quaternary compound at a series of temperatures were measured by forming a quantity of the compound in a small bulb attached to a spring gauge, sealing off the bulb, and immersing the whole in a variable-temperature thermostat of 2 gallons capacity. Values of the dissociation pressure for a series of temperatures up to 86°, 45 minutes being allowed for equilibrium to be established at each temperature, were obtained, and are tabulated below. The values in the second line are for increasing temperatures, and those in the fourth line for decreasing temperatures.

TABLE II.

The Dissociation Pressures of Trimethylsilylammonium Chloride.

Temp.	18·6°	33·5°	45·7°	62·2°	75·6°	86·5°
Press. (mm.)	27	39	65	158	312	531
Temp.	80·9°	70·7°	57·5°	19·6°		
Press. (mm.)	420	283	173	83		

It is apparent from these data that the dissociation is not reversible. The contents of the vapour-pressure determination apparatus were returned to the vacuum-apparatus at the end of the experiment; it was then found that monosilane and a material of medium volatility had been formed in small amounts. This pointed to a disproportionation of the chlorosilane formed in the primary dissociation, thus :

$$(1)\ N(CH_3)_3(SiH_3)Cl = N(CH_3)_3 + SiH_3Cl$$
$$(2)\ 2SiH_3Cl = SiH_4 + SiH_2Cl_2$$

Chlorosilane was known from the work of Stock to disproportionate in this manner; and the process could well be catalysed by the presence of the undissociated quaternary compound. It will be seen that reaction (2) entails no volume change; and on this hypothesis, the data recorded in the second line of Table II would represent true dissociation pressures.

In order to test this view, 50·2 c.c. of trimethylamine were treated with a large excess (119·0 c.c.) of chlorosilane at room temperature, and the resulting mixture of the double compound with an excess (68·8 c.c. in theory) of chlorosilane was heated in a bulb at 50° for 48 hours in a water-bath. The products volatile at $-78°$ were returned to the fractionation apparatus, and had a total volume of 67·1 c.c. : they were found to consist of 27·74 c.c. of silane, which was separated quantitatively at $-135°$, and 39·40 c.c. of mixed chlorosilanes. Now, since 27·74 c.c. of silane had been evolved, if the equation $2SiH_3Cl = SiH_4 + SiH_2Cl_2$ had been followed, the mixture of chlorosilanes should consist in theory of 27·74 c.c. of dichlorosilane and $39{\cdot}40 - 27{\cdot}74 = 11{\cdot}66$ c.c. of monochlorosilane, and therefore have a mean content of 2·29 atoms H/mol. The chlorosilane mixture was in fact hydrolysed, the hydrogen evolved measured, and the chlorine in the resulting solution determined gravimetrically. The results (86·8 c.c. H_2 and 68·1 c.c. Cl′) indicated mean values of 2·22 and 2·27 atoms H/mol. respectively. As the excess of monochlorosilane had evidently disproportionated in this way, one could assume that any which had arisen in the first place from the dissociation of the double compound would also have disproportionated; and this theory of the decomposition of the quaternary salt appears, therefore, to be correct.

One can, indeed, draw up a series of such quaternary compounds, in which it appears that the stability decreases as the number of silyl radicals increases, thus :

$N(CH_3)_4Cl$	Stable
$N(CH_3)_3(SiH_3)Cl$	Moderately stable
$N(CH_3)_2(SiH_3)_2Cl$	Unstable
$N(CH_3)(SiH_3)_3Cl$	Not formed
$N(SiH_3)_4Cl$	Not formed

The fourth and the fifth compound, had they been formed, would have been detected in the preparation of methyldisilylamine and trisilylamine respectively, since these preparations were carried out in the presence of an excess of monochlorosilane.

Trimethylsilylammonium chloride inflamed spontaneously when pure oxygen was admitted on it at room temperature, but in moist air, being almost immediately hydrolysed, it fumed strongly without burning. Its behaviour with oxygen was complicated, however, by the monosilane produced on decomposition. Its reaction with water was studied by running out-gassed distilled water on a specimen prepared by the reaction between 9·80 c.c. of chlorosilane and 19·95 c.c. of trimethylamine, the 9·70 c.c. excess of trimethylamine being removed subsequently at −78°. A vigorous reaction took place, and a gas was evolved which was immediately pumped off through a line of liquid-nitrogen traps. It consisted of hydrogen and a condensable product, which was freed from water by fractionation at −78° and examined. This proved to be tensimetrically pure disilyl ether (3·38 c.c.); which showed that hydrolysis according to the equation

$$2N(CH_3)_3(SiH_3)Cl + H_2O = 2N(CH_3)_3,HCl + (SiH_3)_2O$$

had taken place to the extent of 69·0%, the remainder having reacted further with decomposition of the silyl radicals. This reaction is similar to the hydrolysis of chlorosilane itself (Stock, *Ber.*, 1923, **56**, 132), which takes place, however, to the extent of only 50%. On standing with water in a closed system overnight, the disilyl ether decomposed further, giving intermediate water-soluble hydrolysis products. These solutions reduced potassium permanganate, and were decomposed by alkali with evolution of hydrogen.

Some preliminary experiments were carried out on a small scale to discover the reactions of trimethylsilylammonium chloride. It reacted readily with an excess of ethyl alcohol, evolving hydrogen and a condensable gas, which was freed from alcohol by fractionation. This gas was stable, and is believed to be silyl ethyl ether, $SiH_3{\cdot}O{\cdot}C_2H_5$, mixed with di- and tri-ethoxysilane. The rather laborious fractionation of this mixture is being pursued. The quaternary compound also reacted with formaldehyde, the volatile products consisting of silane and a liquid of low volatility; no chlorosilanes were present. Further experiments are being carried out with the object of establishing fully the nature of the above compounds, and the reactions described are evidently likely to prove quite general. Experiments are also in progress to determine whether the quaternary compounds containing silicon yield conducting solutions in non-aqueous solvents.

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