682. *The Reactions of Hexachlorodisilane with Ammonium Halides and Trimethylamine Hydrohalides.*

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A somewhat complex reaction occurs between hexachlorodisilane and ammonium halides, leading to the formation, for example, of silicon tetrachloride and trichlorosilane in approximately equimolecular proportions and silicon–nitrogen condensation products of low volatility. The evidence indicates initiation by ammonia from thermal decomposition of the ammonium halide, and ammonia itself brings about a similar reaction. Trimethylamine hydrochloride decomposes hexachlorodisilane catalytically according to the equation $n\mathrm{Si_2Cl_6} \longrightarrow (\mathrm{SiCl_2})_n + n\mathrm{SiCl_4}$, this reaction likewise being initiated by the free base.

The corresponding decompositions of ethylpentachlorodisilane and diethyltetrachlorodisilane with ammonium chloride and trimethylamine hydrochloride have also been examined. The behaviour of samples of the diethyl derivative gave information about the isomeric composition of this material as obtained from the interaction of ethylmagnesium bromide and hexachlorodisilane.

In an attempt to fluorinate hexachlorodisilane with ammonium fluoride it was found that the ammonium salt did not effect a simple halogen exchange (compare Wilkins, *J.*, 1951, 2726) but caused cleavage of the Si–Si bond, giving trichlorosilane, trichlorofluorosilane, and silicon tetrachloride as the chief volatile products. This type of reaction also extends to the other ammonium halides, and from the disilane and ammonium halide, in each case trichlorosilane and the tetrachloride were recovered in approximately equimolecular proportions (see Table). The formation of trichlorosilane and silicon tetrachloride from the reaction with ammonium chloride, for example, may *in effect* be represented: $\mathrm{Si_2Cl_6} + \mathrm{HCl} \longrightarrow \mathrm{SiHCl_3} + \mathrm{SiCl_4}$, but these volatile products account for only about 60% of the silicon, the rest remaining in the involatile residue which contains silicon–nitrogen condensation products. Ammonium bromide and ammonium iodide also yield trichlorosilane and silicon tetrachloride with no trace of bromide or iodide in the volatile products.

The degradation of an unsymmetrical derivative of hexachlorodisilane is illustrated by the reaction of ammonium chloride with ethylpentachlorodisilane. The volatile products (see Table) are ethyltrichlorosilane and trichlorosilane, but no ethyldichlorosilane or silicon tetrachloride, so that the reaction is to be represented as following course (1) rather than (2).

$$\mathrm{EtSiCl_2{\cdot}SiCl_3} \xrightarrow{\mathrm{NH_4Cl}} \mathrm{EtSiCl_3} + \mathrm{SiHCl_3} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{EtSiCl_2{\cdot}SiCl_3} \xrightarrow{\mathrm{NH_4Cl}} \mathrm{EtSiHCl_2} + \mathrm{SiCl_4} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Further, in an application of the ammonium chloride reaction, described below, for determining the isomeric composition of a sample of diethyltetrachlorodisilane, diethyldichlorosilane and trichlorosilane, but no diethylchlorosilane or silcon tetrachloride, were found among the products. It was therefore inferred that the unsymmetrical isomer had reacted analogously to the monoethyl derivative according to (3) and not (4).

$$\mathrm{Et_2SiCl{\cdot}SiCl_3} \xrightarrow{\mathrm{NH_4Cl}} \mathrm{Et_2SiCl_2} + \mathrm{SiHCl_3} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\mathrm{Et_2SiCl{\cdot}SiCl_3} \xrightarrow{\mathrm{NH_4Cl}} \mathrm{Et_2SiHCl} + \mathrm{SiCl_4} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The order of reactivities of the ethyl derivatives towards ammonium chloride, $\mathrm{Si_2Cl_6} \approx \mathrm{EtSi_2Cl_5} > \mathrm{Et_2Si_2Cl_4} > \mathrm{Si_2Et_6}$, is also the order in which acceptor properties will decrease. The correlation may be indirect in its significance, or even fortuitous, but encouraged the working assumption that the reaction is initiated by a nucleophilic attack on silicon, to which this atom is prone. Possible attacking reagents are chloride ion, or hydrogen chloride or ammonia from thermal decomposition of the ammonium halide.

The course of the degradation of the ethyl derivatives, however, does not suggest an initial attack by chloride ion for this would be likely to occur at the more highly charged and, probably too, more accessible silicon atom already linked to the larger number of chlorine atoms to yield products from reactions (2) and (4) rather than (1) and (3). It was found too that hydrogen chloride alone does not react with hexachlorodisilane (vapour) in a silica tube below 550°, or below 400° in the presence of potassium chloride. On the other hand direct evidence for ammonia as initiating reagent was obtained. Addition of ammonia to hexachlorodisilane causes the separation of solid, but a subsequent reaction which occurs at 60—70° gives trichlorosilane and silicon tetrachloride in yields comparable with those obtained by the use of ammonium chloride. There is no possibility that this reaction with ammonia takes place through intermediate formation of ammonium chloride since the ammonium chloride reaction does not appear below 120—130°.

Reaction of hexachlorodisilane and its ethyl derivatives with ammonium halides.

Reactants	Time, hr.	Temp.	Yields, %, of			
			$SiHCl_3$	$SiFCl_3$	$SiCl_4$	
$Si_2Cl_6 + NH_4F$	60	125—130	33	22	8 *	
$Si_2Cl_6 + NH_4Cl$	36	130—140	30	—	28	
,, ...	15	145	28	—	32	
$Si_2Cl_6 + NH_4Br$	48	145	30	—	27	
$Si_2Cl_6 + NH_4I$	90	145	12	—	10 †	
			$SiHCl_3$	$EtSiCl_3$	Et_2SiCl_2	$EtSiHCl_2$
$EtSi_2Cl_5 + NH_4Cl$	15	160	33	28	—	—
$Et_2Si_2Cl_4 + NH_4Cl$	72	200	5	19	5	16
$Si_2Et_6 + NH_4Cl$	—	250		No reaction		
$Si_2Et_6 + NH_4F$	—	200		Si_2Et_6 recovered		

* Also a mixture of more volatile fluorinated products. † Reaction was incomplete.

The formation of silicon–nitrogen condensation products cannot occur when trimethylamine or its hydrohalides are used in place of ammonia or ammonium salts. These reagents (apart from the hydrofluoride which was not examined) bring about, instead, a catalytic decomposition of hexachlorodisilane according to the ideal equation

$$n\mathrm{Si_2Cl_6} \longrightarrow (\mathrm{SiCl_2})_n + n\mathrm{SiCl_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The yield of silicon tetrachloride is almost quantitative and samples of the involatile polymer were of composition $SiCl_{2\cdot05}$—$SiCl_{2\cdot10}$. The material is thus of similar composition to the complex silicon chlorides $Si_{10}Cl_{22}$, $(SiCl_2)_n$, and $Si_{25}Cl_{52}$ (approx.) described by Schwarz and his co-workers (*Z. anorg. Chem.*, 1937, **232**, 241; 1937, **232**, 249; *Ber.*, 1947, **80**, 444).

As with ammonia and the ammonium halides, trimethylamine decomposes hexachlorodisilane at a lower temperature (room temperature) than does its hydrochloride (80°) so that the latter almost certainly reacts through thermal decomposition to the free base. The formation of trichlorosilane in the reactions with ammonium halides but not with trimethylamine hydrohalides is consistent with the view that attack by the free base is involved in both cases.

The decomposition of ethylpentachlorodisilane under the influence of trimethylamine hydrochloride gave ethyltrichlorosilane in 80—85% yield, so that essentially the reaction follows the course

$$n\mathrm{EtSiCl_2{\cdot}SiCl_3} \longrightarrow (\mathrm{SiCl_2})_n + n\mathrm{EtSiCl_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

No silicon tetrachloride or other volatile products could be detected. Hence the reaction steps leading to the formation of the polymer must include disruption of the Si–Si bond in all of the disilane molecules.

The Degradation of Diethyltetrachlorodisilane and Determination of its Isomeric Composition.—This compound may exist as the symmetrical $(EtSiCl_2)_2$ or the unsymmetrical isomer $Et_2SiCl{\cdot}SiCl_3$. There was no evidence from its distillation behaviour of the presence of two isomers in the substance, as obtained from the reaction between hexachlorodisilane and ethylmagnesium bromide. Degradation of the material with ammonium chloride and trimethylamine hydrochloride indicated, nevertheless, that both isomers were present. The products from the ammonium chloride reaction (see Table) were diethyldichlorosilane and trichlorosilane in almost equimolecular amounts from reaction (3), and ethyldichlorosilane and ethyltrichlorosilane, also in an almost equimolecular ratio, from degradation of the symmetrical isomer :

$$\mathrm{EtSiCl_2{\cdot}EtSiCl_2} \xrightarrow{\mathrm{NH_4Cl}} \mathrm{EtSiHCl_2} + \mathrm{EtSiCl_3} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

The proportions in which the two pairs of degradation products were recovered corresponds to a three- or four-fold predominance of the symmetrical isomer. While this result must be treated with some reserve in view of the rather low total yield of volatile products, the behaviour of a sample of diethyltetrachlorodisilane with trimethylamine hydrochloride was in substantial accord. A small proportion of the disilane decomposed to give diethyldichlorosilane, but the remainder was resistant to decomposition either by the hydrochloride or by the free base. If the dichlorosilane arose from the decomposition of the unsymmetrical isomer :

$$n\mathrm{Et_2Si_2Cl_4} \longrightarrow (\mathrm{SiCl_2})_n + n\mathrm{Et_2SiCl_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

analogous to equation (6), the yield corresponded to the presence of 15—25% of this isomer. The resistance of the symmetrical isomer to decomposition may be attributable to reduction in the susceptibility of *both* silicon atoms to nucleophilic attack, but this is not the only explanation possible.

The diethyltetrachlorodisilane isomers must be considered as produced by further ethylation of ethylpentachlorodisilane formed as an intermediate. Hence the presence of the isomers in the above proportions means that the probability that replacement of chlorine in the molecule $\mathrm{EtSi^{(i)}Cl_2{\cdot}Si^{(ii)}Cl_3}$ by the use of ethylmagnesium bromide will occur at atom (ii) is about four times as great as at atom (i).

EXPERIMENTAL

Reagents.—Ammonium halides were dried and pulverised before use. Hexachlorodisilane of technical grade was fractionally distilled (b. p. 146—147°); some was also prepared by controlled chlorination of calcium disilicide ("Inorganic Syntheses," Vol. I, H. S. Booth, ed., McGraw-Hill, New York, p. 42).

Reactions with Ammonium Halides.—About 0·08 mole of hexachlorodisilane, or its ethyl derivatives, and an excess (0·3—0·4 mole) of ammonium salt were used in each experiment. Reactions were carried out in a 40-ml. flask fitted through ground joints with a distillation head leading to a trap at $-78°$. The flask was heated in an oil-bath so long as volatile products passed over. The crude condensate was fractionated through an 18-in. column of glass helices, toluene or *p*-cymene being used as "chasers." Re-distillation of small intermediate fractions was sometimes necessary to give sufficiently complete separation. Each compound distilled within 1—2° of the accepted boiling point, and the identities of the degradation products from diethyltetrachlorodisilane were confirmed by chloride analysis.

The non-volatile products comprise material which could not be pumped from the reaction vessel under the vacuum from a mechanical pump. The residue from the reaction between ammonium chloride and hexachlorodisilane was partly recovered by ether extraction as an oil in which the ratio Si : N was 1·74 : 1.

The Reaction between Ammonia and Hexachlorodisilane.—Ammonia (0·05 mole) was distilled into an ampoule containing hexachlorodisilane (0·04 mole). An exothermic reaction occurred at room temperature, and a crust of solid formed over the surface of the liquid. Further reaction, which commenced at about 60°, gave trichlorosilane (0·023 mole) and silicon tetrachloride (0·024 mole).

The Catalytic Decomposition of Hexachlorodisilane by Trimethylamine and its Hydrochloride.—These reactions were generally carried out with not more than 0·25 g. of catalyst. In a typical experiment, trimethylamine hydrochloride and hexachlorodisilane (8·5 g.) were warmed to 80—100°, giving 5·0 g. of silicon tetrachloride [theoretically obtainable from reaction (5) : 5·3 g.]. Trimethylamine reacted at ordinary temperature. Addition of 3 drops of the base to 10 g. of hexachlorodisilane at 15° caused a temperature rise of 20° accompanied by a slow separation of white solid; the residue was freed from volatile material at 100° [Found : Si, 27·0; Cl, 70·5. Calc. for $(\mathrm{SiCl_2})_n$: Si, 28·4; Cl, 71·6%]. The polymer dissolves very readily in dilute alkali with evolution of hydrogen; ammonia converts the material into silicic acid, again with evolution of hydrogen. It inflames in air below 100° and frequently ignites in contact with water.

The Action of Trimethylamine Hydrochloride on Diethyltetrachlorodisilane.—The disilane (14 g.) was heated with trimethylamine hydrochloride (0·25 g.), at first under reflux. A little solid quickly separated. Fractional distillation of the volatile products gave diethyldichlorosilane (1·5—2·0 g.), most of which distilled at 128—130°, and a small quantity of unidentified lower-boiling material. (*p*-Cymene was added as " chaser " since it was not expected that any sufficiently low-boiling material would remain.) By use of diphenyl as " chaser " some 9 g. of distillate were then obtained within the range 190—220°, and systematic redistillation gave about 6 g. of unchanged diethyltetrachlorodisilane, b. p. 203—209°, there being some loss of material in handling. This material was unchanged by further treatment with trimethylamine or its hydrochloride.

Preparation of Ethylpentachlorodisilane and Diethyltetrachlorodisilane.—These compounds were obtained by the interaction of hexachlorodisilane and ethylmagnesium bromide in appropriate proportions. Schumb and Saffer (*J. Amer. Chem. Soc.*, 1939, **61**, 363) have reported this reaction as suitable for the preparation of hexaethyldisilane, but its application to the preparation of intermediate products is new.

In the preparation of ethylpentachlorodisilane, a solution of ethylmagnesium bromide (from 0·13 g.-atom of Mg) was added dropwise during ½ hr. to a rapidly stirred solution of hexachlorodisilane (0·11 mole) in ether (200 ml.), cooled in ice water. After being stirred for a further ½ hr., the mixture was heated under reflux for 2 hr., filtered, and fractionally distilled. The *pentachloro*-compound (10 g.) had b. p. 182—184° (Found: by Mohr's titration, Cl, 67·1. Calc. for $EtSi_2Cl_5$: Cl, 67·5%).

Diethyltetrachlorodisilane was prepared similarly from hexachlorodisilane (0·22 mole) and ethylmagnesium bromide (from 0·50 g.-atom of Mg). The product (15 g.) had b. p. 206—209° (Found: gravimetrically, Cl, 55·7. $Et_2Si_2Cl_4$ requires Cl, 55·3%. The small fraction, b. p. 219—223°, was examined to determine whether it contained a concentration of one of the isomers. The chlorine content accorded closely, however, with that calculated for triethyltrichlorodisilane (Found: Cl, 47·9. Calc. for $Et_3Si_2Cl_3$: Cl, 48·0%). The close agreement between these values is probably fortuitous as the purity of this small fraction was not considered high.

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