

The Fluorination of Organochlorodisiloxanes.

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The reactions of dimethyl- and diphenyl-tetrachlorodisiloxanes and a series of ethylchlorodisiloxanes with ammonium fluoride are described.

MONOETHYL-, diethyl-, triethyl-, and dimethyl-chlorodisiloxanes react with ammonium fluoride yielding, by fission of the Si-O-Si linkage, polymeric material together with monosilane derivatives. The tetraethyl- and pentaethyl-chlorodisiloxanes under similar conditions yield only the corresponding ethylfluorodisiloxanes and diphenyltetrachlorodisiloxane gives a non-volatile resin.

The mild exchange of chlorine for fluorine in covalent halides is readily achieved by ammonium fluoride (Wilkins, *J.*, 1951, 2726). With hexachlorodisiloxane and with hexachlorodisilane under these conditions the Si-O-Si and Si-Si bonds break to yield monosilane derivatives. Hexachlorodisilane undergoes a similar fission with ammonium chloride or trimethylamine hydrochloride. Diethyltetrachlorodisilane reacts with ammonium chloride to yield a mixture of monoethyl- and diethyl-chlorosilanes; the analogous fission of diethyltetrachlorodisiloxane with ammonium fluoride, however, gives exclusively (in up to 90% yield) monoethyltrifluorosilane but no diethyldifluorosilane. These results served to identify the diethyltetrachlorodisiloxane obtained by the reaction of ethylmagnesium bromide with hexachlorodisiloxane as the symmetrical 1:2-isomer (Emeléus and Payne, *J.*, 1947, 1590). Triethyltrichlorodisiloxane similarly gives no triethylfluorosilane but yields a mixture of monoethyl- and diethyl-fluorosilanes, and is thus the 1:1:2-compound rather than the 1:1:1. The existence of only one of the possible isomers of the diethyl, triethyl, and tetraethyl derivatives is supported by the sharp boiling points of these compounds found during their preparation. Reaction in ether solution between ethylmagnesium bromide and hexachlorodisiloxane or its alkyl derivatives thus occurs exclusively at the chlorine atom attached to the least alkylated (*i.e.*, the least electronegative) silicon atom. Hexachlorodisilane under the same conditions gives a mixture

of isomers indicating that reaction occurs at both silicon atoms, although even in this case reaction at the less electronegative silicon atom is the more likely (Wilkins, *loc. cit.*).

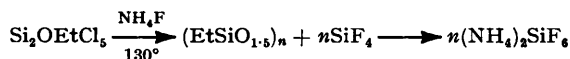
The fission reaction with ammonium fluoride is highly exothermic and does not appear to occur below a threshold temperature characteristic of the type of compound, which is 130° for ethylchlorodisiloxanes, and below room temperature for dimethyltetrachlorodisiloxane. Anhydrous hydrogen fluoride attacks the alkylchlorodisiloxanes similarly giving monosilane derivatives and a small amount of polymeric material. Here the attack on the Si-O-Si linkage is extended to the polymeric material which is one of the products of the reaction with ammonium fluoride, leading to almost complete conversion into fluorosilane derivatives.

It seems likely that the fission reaction proceeds by the attack of hydrogen fluoride derived from the ammonium fluoride by thermal dissociation on the Si-O-Si linkage, leading to the formation of Si-F and Si-OH groups, the latter undergoing further condensation with unchanged material and with fluoro-derivatives to yield polymers. Similarly, the ammonia freed during this reaction is absorbed by the halides to give condensation products of high molecular weight. Ammonia has no effect on the Si-O-Si bond in the alkylchlorodisiloxanes, reaction leading solely to the replacement of chlorine by an amino-group and further condensation. Wilkins (*J.*, 1953, 3409) has shown that the Si-Si linkage is attacked by the ammonia obtained by dissociation of the ammonium salt, which mechanism does not appear to occur with the disiloxane linkage.

EXPERIMENTAL

Ammonium fluoride was dried (CaCl₂, CaO), and before use, in a vacuum desiccator over phosphoric oxide. Anhydrous hydrogen fluoride was obtained from a cylinder and contained *ca.* 0.5% of impurities, chiefly sulphur dioxide. The organo-chlorodisiloxanes were freshly distilled and degassed before use. Each reaction was carried out in a Pyrex flask fitted with reflux condenser and attached directly to an all-glass vacuum system for the collection and examination of the volatile products. A plug of glass wool served to retain solid materials in the flask.

The Reaction between Ammonium Fluoride and Monoethylpentachlorodisiloxane.—Monoethylpentachlorodisiloxane (0.04 mole) reacted vigorously at 130° with an excess of solid ammonium fluoride (0.4 mole). No volatile silicon compound was formed, and the residue consisted of a water-soluble mixture of ammonium chloride, fluoride, and fluorosilicate, and a water-insoluble portion which was dried at 130° (3.2 g.) [Found: C, 23.4; H, 5.9. Calc. for (EtSiO_{1.5})_n: C, 29.6; H, 6.2%]. The reaction being assumed to proceed according to the equation:



the yield of polymer was 100%.

The Reaction between Ammonium Fluoride and Diethyltetrachlorodisiloxane.—Diethyltetrachlorodisiloxane reacted with ammonium fluoride as shown in the following table:

Si ₂ OCl ₄ Et ₂ used, mole	0.0175	0.0330	0.0165	0.0120
NH ₄ F used, mole	0.070	0.135	0.066	0.077
Mole ratio, Si ₂ OCl ₄ Et ₂ : NH ₄ F	1:4	1:4	1:4	1:6.5
EtSiF ₃ , mole	0.011	0.025	0.009	0.011
Mole ratio, EtSiF ₃ : Si ₂ OCl ₄ Et ₂	0.65:1	0.75:1	0.55:1	0.90:1

The silicon-containing volatile product was ethyltrifluorosilane, together with a very small amount of a material, insufficient of which was available even after pooling the products of several experiments for complete identification, but which was possibly a partially fluorinated diethyltetrachlorodisiloxane. The residue was a white insoluble polymer and excess of ammonium fluoride. No diethyldifluorosilane or fluorochlorosilane derivative was obtained. At 120° the reaction was very slow but at 130° it proceeded vigorously, and the variation of yield was considered to be due to the difficulty of controlling it.

The Reaction between Ammonium Fluoride and Triethyltrifluorodisiloxane.—Reaction of triethyltrifluorodisiloxane (0.075 mole) and ammonium fluoride (0.4 mole) gave: a volatile mixture of ethyltrifluorosilane (0.006 mole) and diethyldifluorosilane (0.04 mole), a residue

consisting of a water-soluble portion, ammonium fluoride and chloride, and an ether-soluble fluorine-containing oil, which did not distil below $250^{\circ}/10^{-3}$ mm. No trifluorotriethylidisiloxane or triethylfluorosilane was obtained.

The Reaction between Ammonium Fluoride and Tetraethyldichlorodisiloxane.—Tetraethyldichlorodisiloxane (0.035 mole) reacted vigorously with ammonium fluoride (0.175 mole) at 136° , a very small quantity of a volatile product being obtained, b. p. ca. 60° (cf. diethyldifluorosilane, b. p. 62°). *Tetraethyldifluorodisiloxane* (5.35 g., 70% yield) was obtained from the residue as a liquid, b. p. 175° (Found: C, 42.2; H, 9.1; Cl, 0. $\text{Si}_2\text{OEt}_4\text{F}_2$ requires C, 42.5; H, 8.9%). It is hydrolysed only slowly by water but more rapidly by alkalis.

The Reaction between Ammonium Fluoride and Pentaethylchlorodisiloxane.—When pentaethylchlorodisiloxane (0.05 mole) reacted with ammonium fluoride (0.135 mole) no readily volatile material was collected. *Pentaethylfluorodisiloxane* (10 g., 85% yield) was obtained from the residue as a liquid, b. p. $114\text{--}116^{\circ}/43$ mm. (Found: C, 49.25; H, 10.9; Cl, 0. $\text{Si}_2\text{OEt}_5\text{F}$ requires C, 50.8; H, 10.6%). This compound is not hydrolysed by water, or cold *n*-sodium hydroxide, but is hydrolysed by boiling 10*N*-sodium hydroxide to yield the corresponding pentaethylidisiloxanol.

The Reaction between Ammonium Fluoride and Dimethyltetrachlorodisiloxane.—Dimethyltetrachlorodisiloxane (0.0575 mole) reacted with ammonium fluoride (0.3 mole) giving a large volume of volatile product, consisting of methyltrifluorosilane (0.051 mole, 90% yield) and a very small quantity of an unidentified liquid containing fluorine and chlorine. The solid residue yielded a white polymeric material (2.1 g.) [Found: C, 17.9; H, 4.2. Calc. for $(\text{MeSiO}_{1.5})_n$: C, 18.0; H, 4.5%]. No evidence for the formation of dimethyldifluorosilane was obtained.

The Reaction of Ammonium Fluoride and Diphenyltetrachlorodisiloxane.—Several attempts were made to carry out this reaction, but no volatile material containing silicon was obtained and all the products were brown resins. In one experiment a small amount of benzene was collected.