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On the Reaction of Alkylsilicon Fluorides with Primary Amines

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Trialkylfluorosilanes and dialkyldifluorosilanes did not react with primary amines but alkyltrifluorosilanes gave strongly exothermic reactions. A new type of organosilicon salts, containing the pentafluoro(alkyl)silicate ion, $[SiF_5R]^{2-}$ analogous to the hexafluorosilicate ion, SiF_6^{2-}, could be isolated from the reaction mixtures.

The most important method of obtaining silylamines involves treatment of a halosilane with ammonia or a protic amine; the hydrogen halide released during the course of the reaction being precipitated as the ammonium or amine salt.[1-2]

$$R_{4-n}SiX_n + 2nR'NH_2 \rightarrow R_{4-n}Si(NHR')_n + nR'NH_3X \quad (1)$$

Of the different halides, the chlorosilanes are most frequently employed owing to their availability and reactivity. When both the halosilane and the amine contain bulky groups, bromo- and iodosilanes have been found to react more readily than the corresponding chlorosilanes.[3] Only in a few cases has reaction (1) been carried out with fluorosilanes. 1-Naphthyltrifluorosilane and di-1-naphthyldifluorosilane could be converted into the corresponding amino- and anilino compounds according to reaction (1) but tri-1-naphthylfluorosilane and triphenylfluorosilane reacted only with the alkali-metal amides,[4-5] and trialkylfluorosilanes failed to react with sodium in liquid ammonia.[6] Silicon tetrafluoride, on the other hand, has been reported to give no exchange reaction but forms complexes, $SiF_4 \cdot 2H_3N$ and $SiF_4 \cdot H_2NCH_2CH_2NH_2$, with ammonia [7-8] and ethylenediamine [9] in which silicon uses two of its vacant d-orbitals for bonding. This work is a report of some experiments which demonstrate the difference between various types of alkylsilicon fluorides in their reactions with primary aliphatic amines. It was found that the expected silylamines generally are not obtained under conditions at which the corresponding chlorosilanes react according to eqn. (1). During the course of the work observations were made on the ability of the various types of alkylsilicon fluorides to coordinate fluoride ions.

It is well known that the reactivity upon hydrolysis of organosilicon fluorides is distinctly governed by the number of fluorine atoms.[10] Alkyl- and aryltrifluorosilanes fume slightly in moist air and are immediately hydrolysed by water, but the corresponding difluorosilanes are unaffected on exposure to the atmosphere and are slowly hydrolysed by water. Monofluorosilanes are still more resistant to the action of water. As could be expected from that general behaviour upon hydrolysis, alkyltrifluorosilanes were now found to be much more reactive also towards primary amines than were the other types of alkylsilicon fluorides.

In fact, no exchange reaction at all with protic amines was observed in the case of dialkyldifluorosilanes or trialkylfluorosilanes when perfectly dry reagents and solvents were used. The mixtures were poor conductors in acetonitrile and no solids — indicating reaction — formed even on cooling to −80°. On the contrary, N-substituted dialkyldiaminosilanes and trialkylaminosilanes dissolved two, respectively, one molar equivalents of alkylammonium fluoride to give mixtures of the corresponding fluorosilanes and amines, which could be separated by distillation, demonstrating that the equilibrium of reaction (1) in the case of these types of fluorosilanes is quite unfavourable for their conversion into aminosilanes. The fact that no solids formed when the reaction mixtures were cooled to −80° indicates that these fluorosilanes also fail to give complexes of the type which has been reported to form between silicon tetrafluoride and various amines (Ref.,[1] p. 92). If such complexes existed in the mixtures they must certainly be highly dissociated at room temperature since, for example, a mixture of dimethyldifluorosilane (b.p. 2.7°) and methylamine (b.p. −6.5°) distils below room temperature. When anhydrous hydrogen fluoride was added to the mixtures in ether the only solid product was alkylammonium fluoride which revealed no tendency to combine with the fluorosilanes. But the fluoride ion is generally more effective than amines in bringing out the higher covalencies of second-row elements, and if — according to these experiments — the fluoride ions fail to combine with dialkyl- and trialkylfluorosilanes, it can be stated with some certainty that no bond formation at all occurs between these types of fluorosilanes and amines.

Alkyltrifluorosilanes, however, gave strongly exothermic reactions with primary amines and solids formed at decreased temperatures far above the melting points of the components, but no precipitation occurred in ether or benzene at room temperature. Obviously, reaction between alkyltrifluorosilanes and primary amines does not take place according to eqn. (1). The reversal of (1) has been carried out by Anderson [11]

$$C_2H_5Si(NHC_6H_5)_3 + 3\ C_6H_5NH_3F \rightarrow C_2H_5SiF_3 + 6\ C_6H_5NH_2$$

the volatile ethyltrifluorosilane being continuously distilled from the mixture. In this work it was found that N-substituted alkyltriaminosilanes generally react with three molar equivalents of alkylammonium fluoride to give a liquid system. However, the volatile alkyltrifluorosilane which should form according to the reversal of eqn. (1) could only be removed by distillation from mixtures containing a relatively high-boiling amine (amylamine). From mixtures contain-

ing propylamine or more volatile amines, even the most volatile trifluorosilanes did not escape. The amine distilled first at its ordinary boiling point until the distillation temperature rapidly rose and a distillate was obtained at constant temperature containing trifluorosilane and amine in a mole ratio which was always somewhat less than 1:2 (Table 1). These products lost more amine at reduced pressure and temperature and gave residues with a mole ratio near 1:2. Authentic propyltrifluorosilane and excess of amine behaved in the same way upon distillation. And since a mixture of ethylamine (b.p. 17°) and excess of propyltrifluorosilane (b.p. 25°) on distillation gave propyltrifluorosilane at its ordinary boiling point, and after a rapid rise of distillation temperature to 44° a product containing trifluorosilane and amine in a mole ratio of 1:1.7, it is rather clear that alkyltrifluorosilanes react reversibly with primary amines in a 1:2 mole ratio.

Table 1. Alkyltrifluorosilanes and primary amines.

No.	Alkyltrifluorosilane	Amine	B.p. °C of mixture	E_1[a]	$RSiF_3/R'NH_2$
1	CH_3SiF_3; b.p. −30.2°	CH_3NH_2; b.p. −6.5°	30	77.6	1:2.15
2	CH_3SiF_3	n-$C_3H_7NH_2$; b.p. 49°	51	—	$\ll$1:2
3	$C_2H_5SiF_3$; b.p. −4.2°	$C_2H_5NH_2$; b.p. 17°	39	95.1	1:2.28
4	$C_2H_5SiF_3$	n-$C_3H_7NH_2$	54.5	88.0	1:3.94
5	n-$C_3H_7SiF_3$; b.p. 24.9°	CH_3NH_2	38	92.8	1:2.07
6	n-$C_3H_7SiF_3$	$C_2H_5NH_2$	44	108.3	1:2.02
7	n-$C_3H_7SiF_3$	n-$C_3H_7NH_2$	58	101.5	1:3.02
8	n-$C_3H_7SiF_3$	i-$C_3H_7NH_2$	45	114.1	1:2.33

[a] Amine content.

The products referred to in Table 1 were mobile liquids fuming vigorously in contact with the atmosphere. They solidified at low temperatures far above the melting points of the trifluorosilane and the amine and were soluble in ether and benzene. So far it would be reasonable to interpret them as unstable molecular addition compounds, $RSiF_3 \cdot 2R'NH_2$ of the type which silicon tetrafluoride is reported to give with various donor molecules.[1-2] They were, however, fair conductors in acetonitrile which indicates that, at least to some extent, ion formation is involved, and this could be directly demonstrated in the following way. In petroleum ether two liquid layers formed on reaction between alkyltrifluorosilanes and primary amines when excess of amine was omitted, and after repeated washing of the bottom layer with small portions of the solvent, alkylammonium pentafluoro(alkyl)silicate precipitated. This means that replacement of fluorine by amino group is to some extent involved, the released fluoride ion being co-ordinated to unreacted trifluorosilane with formation of the complex pentafluoro(alkyl)silicate ion according to the scheme

$$\begin{array}{ccc} \mathrm{Si{-}F} + \mathrm{R'NH_2} & \xrightarrow{A} & \mathrm{Si{-}\overset{+}{N}H_2R'} + \mathrm{F^-} \\ & C \downarrow \ \mathrm{R'NH_2} \quad B \downarrow \ \tfrac{1}{2}\ \mathrm{RSiF_3} & \\ \mathrm{Si{-}NHR'} + \mathrm{R'\overset{+}{N}H_3} & & \tfrac{1}{2}\ [\mathrm{SiF_5R}]^{2-} \end{array}$$

On extraction with petroleum ether the complex ion could be isolated as the alkylammonium-salt; *i.e.* proton transfer according to *C* took place. It should be noted that this route of reaction is similar to that of the hydrolysis of silicon tetrafluoride which occurs according to the equation [12]

$$3\ \mathrm{SiF_4} + 2\ \mathrm{H_2O} \rightarrow \mathrm{SiO_2} + 2\ \mathrm{H_2SiF_6}$$

i.e. the fluoride ions released combine with unreacted SiF_4 forming the stable hexafluorosilicate ion.

The qualitative experiments so far performed give of course no information about the identity of the ions in solution nor the extent to which ion formation is involved in the vigorous reaction between an alkyltrifluorosilane and a primary amine, but they certainly show that the possibility of ion formation should always be considered in discussing the structure of molecular addition compounds between silicon halides and donor molecules.

Alkylammonium pentafluoro(alkyl)silicates were also obtained when anhydrous hydrogen fluoride was added to the reaction mixtures of alkyltrifluorosilane and amine in ether. They were all white, non-hygroscopic powders insoluble in common organic solvents. They dissolved in water to give acidic solutions which soon became turbid due to hydrolysis and alkyltrifluorosilane was immediately liberated when the salts were added to 40 % hydrofluoric acid. All of them, except those obtained from methyltrifluorosilane,

Table 2. Physical constants and analyses of alkylammonium pentafluoro(alkyl)silicates.

Compound	M.p. °C[a]	E_1[b]		E_2[c]		Wave number cm^{-1}
		found	calc.	found	calc.	
$(CH_3NH_3)_2[SiF_5(CH_3)]$	>300	100.5	101.2	40.2	40.4	740
$(n\text{-}C_3H_7NH_3)_2[SiF_5(CH_3)]$	>300	127.9	129.2	50.5	51.7	742
$(C_2H_5NH_3)_2[SiF_5(C_2H_5)]$	126–27	120.6	122.2	47.6	48.9	730
$(n\text{-}C_3H_7NH_3)_2[SiF_5(C_2H_5)]$	137–38	135.2	136.2	54.4	54.5	730
$(C_2H_5NH_3)_2[SiF_5(n\text{-}C_3H_7)]$	116–17	128.8	129.2	51.4	51.7	752
$(n\text{-}C_3H_7NH_3)_2[SiF_5(n\text{-}C_3H_7)]$	129–30	140.5	143.2	56.7	57.3	752
$(i\text{-}C_3H_7NH_3)_2[SiF_5(n\text{-}C_3H_7)]$	82–83	142.5	143.2	57.0	57.3	752
$(n\text{-}C_4H_9NH_3)_2[SiF_5(n\text{-}C_3H_7)]$	126–27	155.4	157.2	62.0	62.9	752
$(n\text{-}C_3H_7NH_3)_2[SiF_5(C_6H_{11})]$	120–22	163.5	163.2	66.5	65.3	736

[a] In sealed capillary.
[b] Amine content.
[c] Fluorine content.

sublimed readily at 100°/10 mm. The ascribed structure was based on the way of formation, the analyses, and general behaviour, which suggested that the products were salts containing the pentafluoro(alkyl)silicate ion, $[SiF_5R]^{2-}$, analogous to the hexafluorosilicate ion, SiF_6^{2-}. This assignment was also supported by the fact that they all had a strong absorption band in the infrared near 750 cm^{-1}, which is considered to be due to the stretching of the silicon-fluorine bond in the octahedral position.[13] Analyses, melting points, and frequencies of the band around 750 cm^{-1} are given in Table 2, and some of the spectra in the region 1000—600 cm^{-1} are shown in Fig. 1.

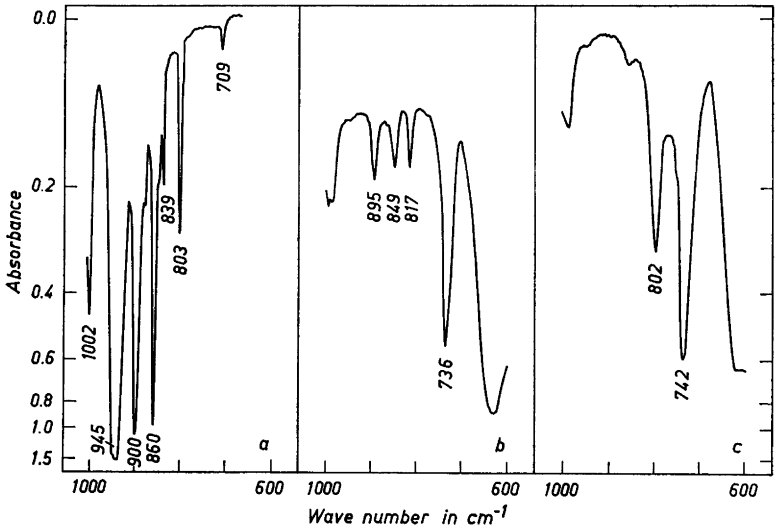

Fig. 1. IR-spectra of a) cyclohexyltrifluorosilane (71.5 mg/ml CS_2), b) propylammonium pentafluoro(cyclohexyl)silicate (in pressed KBr), c) propylammonium pentafluoro-(methyl)silicate (in pressed KBr) in the region 1000—600 cm^{-1}.

The pronounced differences observed between alkyltrifluorosilanes on one hand and dialkyldifluorosilanes or trialkylfluorosilanes on the other in their ability to co-ordinate fluoride ions can hardly be the result of steric effects only. It is rather an example of the general rule that second-row elements only appear with their highest covalency when combined with very electronegative atoms or groups. Craig *et al.*[14] suggested out from overlap integral calculations that the function of the electron attracting groups is to contract the diffuse 3d orbitals of the central atom. Without this perturbation by the peripheral ligands the sp^3d^2 hybridization would not be effective. According to this hypothesis the perturbing ability of the three highly electronegative fluorine atoms in alkyltrifluorosilanes would be said to be sufficient to permit the entrance of two fluoride ions and probably also other fair donor molecules while the presence of only two in dialkyldifluorosilanes or one in trialkyl-fluorosilanes are not.

EXPERIMENTAL

The acetonitrile used for conductometric measurements was treated successively with anhydrous potassium carbonate and phosphorus pentoxide before distillation (b.p. 82°). The measurements were performed at room temperature (22—24°) in a cell of constant 0.63 cm^{-1}.

Of the silylamines employed in the reactions, triamyl-(methylamino)-silane, I, and diethyldi-(ethylamino)-silane, II, have not been prepared before. They were prepared as described for N-substituted propyltriaminosilanes [15] from the appropriate organosilicon chloride and excess of amine, the yields lying between 80—90 %. Their physical constants and analyses are given in Table 3. In the table are also given the constants of dimethyldi-(methylamino)-silane, III, which has been previously described to have b.p. 66°/165 mm.[16]

The preparation of triethylfluorosilane, diethyldifluorosilane and cyclohexyltrifluorosilane was described in a previous paper.[17]

Table 3. Physical constants and analyses of $R_nSi(NHR')_{4-n}$.

No.	M	B.p. °C	Pressure mm Hg	n_D^{20}	d^{20}	MR_D	% Si		Equiv. wt.	
							found	calc.	found	calc.
I	271.55	128—29	0.5	1.4482	0.8195	88.74	10.3	10.3	271.0	271.6
II	174.36	66—67	10	1.4324	0.8280	54.66	16.1	16.1	87.4	87.2
III	118.26	62—63	155	1.4235	0.8357	36.07	23.9	23.8	59.7	59.1

Propyltrifluorosilane. 35.5 g (0.2 mole) of propyltrichlorosilane were warmed with a 50 % excess of zinc fluoride until the reaction began. When once the reaction had started no more heating was necessary, the heat of reaction being sufficient to distil off the lower-boiling product. This was redistilled from fresh zinc fluoride and then distilled again in a system which had been swept out with dry nitrogen. B.p. 25° (lit. value:[18] b.p. 24.9°). Yield 70 %. (Equiv.wt.: Found 42.3. Calc. 42.7).

Propyltrifluorosilane could also be obtained in the following way. 13.7 g (0.055 mole) of propyltriacetoxysilane [17] were added dropwise to 21.1 g (0.166 mole) of benzylammonium fluoride. Reaction occurred with evolution of heat. On heating the reaction mixture, 4.1 g distilled before the distillation temperature had reached 50°. This product was redistilled to give 3.0 g of propyltrifluorosilane.

The equivalent weights of fluorosilanes were determined by dissolving the compounds in excess of standard potassium methoxide. After a few minutes water was added and the excess of alkali back-titrated with standard hydrochloric acid using thymol-blue as the indicator.

Trialkylfluorosilanes and amines. 1.03 g (0.01 mole) of trimethyl-(methylamino)-silane and 0.51 g (0.01 mole) of methylammonium fluoride were mixed. Reaction occurred with the formation of methylamine. On gentle heating of the flask all but traces of the solid dissolved and the reaction mixture — methylamine, b.p. −6.5° and trimethylfluorosilane, b.p. 16.4° — distilled below room temperature. When the distillate was dissolved in 80 ml of acetonitrile the specific conductivity changed from 1.2×10^{-6} ohm^{-1} cm^{-1} of the pure solvent to 3.0×10^{-6} ohm^{-1} cm^{-1} of the solution, *i.e.* no appreciable increase. When anhydrous hydrogen fluoride was added to the ether solution of the distillate in another experiment the only solid product was methylammonium fluoride containing no silicon.

On fractionation of a mixture of 19.0 g (0.07 mole) of triamyl-(methylamino)-silane and 5.6 g (0.07 mole) of propylammonium fluoride, 15.1 g (83 %) of triamylfluorosilane were obtained at 135°/10 mm, n_D^{20} 1.4316 (lit. values:[6] b.p. 267° (745 mm), n_D^{25} 1.4305).

(Equiv. wt.: Found 258.1. Calc. 260.5). 1.4 g of this product was dissolved in 80 ml of acetonitrile, giving a solution with specific conductivity 3.5×10^{-6} ohm^{-1} cm^{-1}. When 1.2 g of propylamine was added by distillation over potassium hydroxide in an atmosphere of dry nitrogen, the specific conductivity increased to 6.2×10^{-6} ohm^{-1} cm^{-1}, *i.e.* no appreciable increase.

In the same way, triethylfluorosilane, b.p. 109°, was obtained from triethyl-(propylamino)-silane and propylammonium fluoride.

In no case did a mixture of a trialkylfluorosilane and a primary amine in ether form a solid phase, indicating reaction, when cooled to −80°C.

Dialkyldifluorosilanes and amines. When 2.14 g (1.81×10^{-2} mole) of dimethyldi-(methylamino)-silane and 1.85 g (3.62×10^{-2} mole) of methylammonium fluoride were mixed the solid salt dissolved completely, and when the reaction flask was placed in a bath of 10° the liquid mixture (dimethyldifluorosilane, b.p. 2.7°, and methylamine, b.p. −6.5°) distilled rapidly. No precipitation, indicating reaction, occurred when the mixture was cooled to −80°C. When anhydrous hydrogen fluoride was passed into the mixture in ether the only solid product was methylammonium fluoride.

In the same way 8.65 g (0.05 mole) of diethyldi-(ethylamino)-silane and 6.5 g (0.1 mole) of ethylammonium fluoride reacted immediately but some of the solid (about 0.5 g) did not dissolve. It was removed by filtration and on fractionation of the filtrate, 4.0 g (64 %) of diethyldifluorosilane, b.p. 62°, were obtained.

In one experiment 0.85 g (0.0042 mole) of diethyldi-(propylamino)-silane and 0.665 g (0.0084 mole) of propylammonium fluoride were mixed in 85 ml of acetonitrile. 80 ml (diethyldifluorosilane, b.p. 62°, propylamine, b.p. 49°) were distilled from the flask in an atmosphere of dry nitrogen. The specific conductivity of the distillate was found to be 8.7×10^{-6} ohm^{-1} cm^{-1}, *i.e.* no appreciable increase compared with the specific conductivity of the solvent used (5.2×10^{-6} ohm^{-1} cm^{-1}).

Alkyltrifluorosilanes and amines. 4.7 g (2.3×10^{-2} mole) of propyltri-(ethylamino)-silane and 4.5 g (6.9×10^{-2} mole) of ethylammonium fluoride were mixed in a 50 ml flask. Reaction immediately occurred with loss of much heat and all but traces of solid material dissolved to give a liquid system which fumed vigorously in contact with the atmosphere. On fractionation of the reaction mixture, using a glass-helix packed column of a length of 15 cm 4.0 g (8.9×10^{-2} mole) of ethylamine were first obtained. Thereafter the distillation temperature rapidly rose to 43.5° and 4.3 g of a water-white liquid which fumed vigorously in contact with moist air to give a heavy white smoke, distilled at this temperature. A very small amount of a solid, which gave an acidic solution in water, was left in the distillation flask.

In the same way, a range of N-substituted alkyltriaminosilanes dissolved almost three molar equivalents of the appropriate alkylammonium fluoride and on distillation of the reaction mixtures, amine first distilled until the distillation temperature rapidly rose to a constant value and a fraction was obtained apparently consisting of a mixture of alkyltrifluorosilane and amine. The amine content of the products, which were mobile liquids at room temperature, was determined by back-titrating an acid fixed condensate from a boiling solution containing the substance in excess of standard base using methyl-red as the indicator. In Table 1 are given the boiling points (1 atm.), the amine content (E_1) and the mole ratio alkyltrifluorosilane: amine of the constant boiling mixtures obtained in these experiments. When ether solutions of these products were cooled to −80°C a solid always formed which disappeared on rise of temperature far below room temperature. Such a precipitation can be ascribed to hydrofluoride formation according to reaction (1) at low temperatures, but the fact that the solid dissolved on rise of temperature, even if most of the ether solution had been removed from the mixture when cooled indicates that the precipitation is due to complex formation. In the absence of solvent all the mixtures in Table 1 solidified when cooled to −40°C, far above the melting points of the components. The product $C_2H_5SiF_3 \cdot 2.28\ C_2H_5NH_2$ (No. 3 in Table 1) was cooled to −20°C and the pressure was reduced to 1 mm Hg. After one hour about half of it had distilled over into a trap cooled to −80°C, leaving a residue with $E_1 = 100.7$, corresponding to a 1:2.06 mole ratio. It solidified when cooled to −40°C but had no defined melting point. When the product $n\text{-}C_3H_7SiF_3 \cdot 2.33\ i\text{-}C_3H_7NH_2$ was treated in the same way the residue in the distillation flask had $E_1 = 120.6$, corresponding to a 1:2.08 mole ratio. This product too had ill-defined melting point. In one experiment, 7.0 g (0.155 mole) of anhydrous ethylamine were distilled into 18.6 g (0.145 mole) of freshly distilled propyl-

trifluorosilane, cooled to −80°. A solid product was obtained which melted and formed two liquid layers before room temperature. On distillation, propyltrifluorosilane distilled at its ordinary distillation temperature from the mixture. Thereafter the distillation temperature rapidly rose and 7.5 g of a distillate were obtained at 43.5−44° with E_1 = 119.0 corresponding to a mole ratio propyltrifluorosilane:amine of 1:1.74.

The products referred to in Table 1 were only slightly soluble in petroleum ether. For example, when 1.4 g of No. 3 were mixed with 8 ml of that solvent, two liquid layers resulted, and after the lower one had been washed with 5 portions of 4 ml of petroleum ether, a white solid precipitated which was further washed with petroleum ether on a filter and then with diethylether. The product, weighing 0.33 g was sublimed at 100°/10 mm to give 0.25 g of ethylammonium pentafluoro(ethyl)silicate, m.p. 126−28°. In the same way 1.32 g (0.008 mole) of cyclohexyltrifluorosilane and 0.77 g (0.013 mole) of propylamine gave a heterogeneous mixture with petroleum ether and after careful washing with this solvent, 0.20 g of propylammonium pentafluoro(cyclohexyl)silicate could be isolated.

Conductometric measurements indicated that alkyltrifluorosilanes react with primary amines with formation of ions. 1.40 g (0.0047 mole) of propyltri(propylamino)-silane and 1.35 g (0.0171 mole) of propylammonium fluoride were mixed in 85 ml of acetonitrile. 80 ml were distilled from the flask in an atmosphere of dry nitrogen. The specific conductivity of the distillate was found to be 1.5×10^{-3} ohm^{-1} cm^{-1}, *i.e.* an appreciable value compared with the specific conductivity of the solvent used (0.83×10^{-6} ohm^{-1} cm^{-1}).

1.0 g of propyltrifluorosilane distilled from the boiling reaction mixture of 3.0 g (0.0091 mole) of propyltri(amylamino)-silane and three molar equivalents of amylammonium fluoride before distillation temperature reached 30°C. Thereafter a fraction containing both the fluorosilane and the amine was obtained before pure amylamine distilled at its ordinary boiling point, 104°C. The reaction mixture of propyltri(butylamino)-silane and three molar equivalents of butylammonium fluoride distilled completely between 71 and 77°C (b.p. of butylamine 77°) and the distillate which was first obtained was found to contain more fluorosilane than the last fractions.

In one experiment, 4.08 g (0.02 mole) of propyltri(ethylamino)-silane were mixed with two molar equivalents of ethylammonium fluoride. On fractionation of the reaction mixture ethylamine first distilled and thereafter 1.1 g of a fraction roughly corresponding to $C_3H_7SiF_3 \cdot 2C_2H_5NH_2$ were obtained at 44−45°C. At 125−128°, 1.0 g of a product distilled, which fumed vigorously in contact with moist air, apparently propyl-(ethylamino)-difluorosilane [b.p. of dipropyldifluorosilane:[19] 111° (733 mm)]. Its amine and fluorine content were determined in the usual way to give E_1 155; E_2 79. Calc for $C_3H_7SiF_2(NHC_2H_5)$: E_1 153; E_2 77. A residue, which gave basic solution in water — probably containing some $C_3H_7Si(NHC_2H_5)_2F$ and $C_3H_7Si(NHC_2H_5)_3$ — remained in the distillation flask.

Preparation of pentafluoro(alkyl)silicates. Dry gaseous hydrogen fluoride was passed into the solution obtained from 6.7 g (0.04 mole) of cyclohexyltrifluorosilane and 2.4 g (0.04 mole) of propylamine in 75 ml of anhydrous ether, until no more precipitate was formed. After stirring for 30 min the mixture was filtered and left a white, non-hygroscopic solid on the filter, which, after drying at reduced pressure, weighed 6.5 g; calc. for the formation of $(C_3H_7NH_3)_2$ $[SiF_5(C_6H_{11})]$, 6.5 g.

When a solution of hydrogen fluoride in anhydrous ether was added to the ether solutions of the mixture of alkyltrifluorosilanes and amines referred to in Table 1, pentafluoro-(alkyl)silicates of the amines precipitated in almost quantitative yields, calculated on the added hydrogen fluoride.

The analyses, melting points, and frequencies for maximum absorption of the pentafluoro(alkyl)silicates are given in Table 2. Their amine content (E_1 in the table) was determined by back-titrating an acid fixed condensate from a boiling solution containing the compound in excess of standard base in methanol-water, using methyl-red as the indicator, and their fluorine content (E_2 in the table) was determined by back-titrating the excess of base with standard acid, using thymol blue as the indicator.

2.0 g (0.01 mole) of propyltri(ethylamino)-silane dissolved 3.9 g (0.015 mole) of ethylammonium pentafluoro(propyl)silicate. On distillation of the mixture, ethylamine first distilled at its ordinary boiling point and thereafter the distillation temperature rapidly rose to 44° and a fraction roughly corresponding to the composition n-$C_3H_7SiF_3 \cdot$

$2C_2H_5NH_2$ was obtained between 44 and 45°. Less than 0.5 g of solid material was left in the distillation flask.

The infra-red spectra were recorded with a Perkin-Elmer model 221 prism-grating instrument at the Infrared Laboratory of this Institute.

REFERENCES

1. Eaborn, C. *Organosilicon Compounds*, Butterworths, London 1960 (Chapter 11).
2. Fessenden, R. and Fessenden, J. S. *Chem. Rev.* **61** (1961) 361.
3. Tansjö, L. *Acta Chem. Scand.* **13** (1959) 35.
4. Chugunov, V. S. *Zh. Obshch. Khim.* **23** (1953) 777.
5. Chugunov, V. S. *Zh. Obshch. Khim.* **24** (1954) 868.
6. Gierut, J. A., Sowa, F. J. and Nieuwland, J. A. *J. Am. Chem. Soc.* **58** (1936) 897.
7. Gierut, J. A., Sowa, F. J. and Nieuwland, J. A. *J. Am. Chem. Soc.* **58** (1936) 786.
8. Miller, D. B. and Sisler, H. H. *J. Am. Chem. Soc.* **77** (1955) 4998.
9. Schumb, W. C. and Cook, P. S. *J. Am. Chem. Soc.* **75** (1953) 5133.
10. Emeleus, H. J. and Wilkins, C. J. *J. Chem. Soc.* **1944** 454.
11. Anderson, H. H. *J. Am. Chem. Soc.* **73** (1951) 5802.
12. Lange, W. in Simons, J. H. *Fluorine Chemistry I*, Academic Press, New York 1950, p. 128.
13. Piper, T. S. and Rochow, E. G. *J. Am. Chem. Soc.* **76** (1954) 4318.
14. Craig, D. P., Maccoll, A., Nyholm, R. S., Orgel, L. E. and Sutton, L. E. *J. Chem. Soc.* **1954** 332.
15. Tansjö, L. *Acta Chem. Scand.* **11** (1957) 1613.
16. Larsson, E. and Smith, B. *Acta Chem. Scand.* **3** (1949) 487.
17. Tansjö, L. *Acta Chem. Scand.* **15** (1961) 1583.
18. Booth, H. S. and Halbedel, H. S. *J. Am. Chem. Soc.* **68** (1946) 2652.
19. Marans, N. S., Sommer, L. H. and Whitmore, F. C. *J. Am. Chem. Soc.* **73** (1951) 5127.

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