100. *Organosilicon Compounds. Part V.* The Reaction between Organofluorosilanes and Aluminium Halides.*

By C. EABORN.

Organosilicon fluorides have been converted into the corresponding chlorides, bromides, and iodides by reaction with the appropriate aluminium halide, and diethyl- and diisopropyl-difluorosilane have also been converted into the dialkylchlorofluorosilanes. The rate-determining stage of this type of reaction probably involves nucleophilic attack on silicon as well as electrophilic attack on halogen.

Disproportionation of some organosilicon halides in the presence of aluminium halides has been demonstrated.

IN Part I (*J.*, 1949, 2755) the author described the reaction of trialkylfluorosilanes and of one dialkyldifluorosilane with aluminium iodide to give the corresponding alkyliodo-silanes. Fluorotri-*n*-propylsilane and solid aluminium chloride gave only impure chlorotri-*n*-propyl silane, but freshly purified aluminium chloride or bromide and triethyl-fluorosilane readily afforded chloro- or bromo-triethylsilane (preliminary report in Part II, *J.*, 1950, 3077). The wider applicability of the method has now been demonstrated by the success of the following conversions : $Et_3SiF \longrightarrow Et_3SiCl$ and Et_3SiBr; $Pr^i_3SiF \longrightarrow Pr^i_3SiCl$; $EtMe_2SiF \longrightarrow EtMe_2SiCl$ and $EtMe_2SiBr$; $Me_2PhSiF \longrightarrow Me_2PhSiCl$; $Ph_3SiF \longrightarrow Ph_3SiCl$; $Bu^i_3SiF \longrightarrow Bu^i_3SiBr$; $Et_2SiF_2 \longrightarrow Et_2SiFCl$, Et_2SiCl_2, and Et_2SiBr_2; $Pr^i_2SiF_2 \longrightarrow Pr^i_2SiFCl$ and $Pr^i_2SiBr_2$.

Reaction Conditions.—Although aluminium chloride was successfully used in some cases in absence of solvent, yet use of diethyl ether as solvent was more satisfactory for the preparation of the organochlorosilanes. Aluminium bromide disperses quickly and reacts when shaken with an alkylfluorosilane, and the reaction in absence of solvent was satisfactory in, *e.g.*, the conversions $Et_3SiF \longrightarrow Et_3SiBr$, and $Et_2SiF_2 \longrightarrow Et_2SiBr_2$, but where there is danger of disproportionation it is desirable to minimize the reaction temperature by use of a solvent, and ether and benzene proved satisfactory. Comparatively few common solvents are completely unaffected by boiling with aluminium halides, and care must be taken that no products from the solvent boil in the region of the organosilicon compounds under investigation. When decahydronaphthalene was used as a solvent for the conversion of diethyldifluoro- into dibromodiethyl-silane the latter compound was formed, but it could not be separated from a rearrangement product of the solvent which boiled in the same region (the formation of this product has been described by, *e.g.*, Jones and Linstead, *J.*, 1936, 616).

In spite of the presumably lower solubilities of the aluminium fluoro-chlorides, -bromides, and -iodides, it is clear that all three halogen atoms of the aluminium halides may react according to $3R_3SiF + AlX_3 \longrightarrow 3R_3SiX + AlF_3$. With aluminium chloride, however, the results indicate that all the chlorine atoms are utilized only with difficulty, and excess of this halide (when calculated according to $3R_3SiF + AlCl_3 \longrightarrow 3R_3SiCl$) is usually required to give good yields with reasonable speed. It is significant that in the reaction between triethylfluorosilane (2 mols.) and aluminium chloride (1 mol.) in ether, 72—78% of the fluoride reacted in 20 minutes and only 77—82% in 3 hours under comparable conditions. The decreasing availability of the chlorine atoms is probably mainly a solubility effect, for aluminium chlorofluorides are formed.

Preparative Value.—The method may be of value in the preparation of the silyl chlorides when the corresponding fluorides are easily prepared; *e.g.*, the excellent yield in the conversion of triethylsilyl fluoride into the chloride renders it more satisfactory than the method involving preparation of the ethoxide and reaction of this with acetyl chloride. For the preparation of organosilyl bromides and iodides, this method from fluorides is at least as convenient as that from chlorides *via* the anilides (Anderson, Seaton, and Rudnicki, *J. Amer. Chem. Soc.*, 1951, **73**, 2144; Anderson, *ibid.*, p. 5802). Perhaps the greatest value lies, however, in the formation in good yield of dialkylchlorofluorosilanes from difluoro-compounds, which are now readily available in several cases (see Parts III and IV, *J.*, 1952, 2840, 2846).

Disproportionation.—In the presence of the highly active aluminium halide catalysts, disproportionation of organosilicon halides might be expected to become serious. That it was not often encountered in this work may be due to the fact that the aluminium halide was never used in more than two-fold excess [*e.g.*, ⫶SiF (2 mol.) + AlCl₃ (1 mol.)], so that little, if any, aluminium trichloride would remain unconverted into the less active chloro-fluorides. However, pure bromodiethylfluorosilane could not be isolated by the method used for the corresponding chlorofluoride, and it appeared that if any of the first compound was formed it disproportionated, on fractionation, into diethyldifluoro- and dibromodi-ethyl-silane, and this could have been catalysed by aluminium halide. An attempt to make bromofluorodi*iso*propylsilane also failed. Organic compounds containing Me–Si links also disproportionate; *e.g.*, the conversion $EtMe_2SiF \longrightarrow EtMe_2SiBr$ yielded also bromotrimethylsilane; and bromoethyldimethylsilane was shown to disproportionate when boiled with aluminium bromide. The decomposition involved in the interaction of fluorodimethylphenylsilane and aluminium bromide was more complex, and benzene was identified in the products in addition to bromotrimethylsilane. [Phenyl groups are known to be split off from silcon by aluminium chloride (Evison and Kipping, *J.*, 1931, 2774) and the success of the conversion of triphenylsilyl fluoride into the chloride in ether must indicate that the aluminium halide reacts preferentially at the Si–F bond.] Catalytic effects of the aluminium chloride probably account also for the failure to convert tri*iso*-butylfluorosilane satisfactorily into the chlorosilane, but chlorotriethylsilane is not decomposed by boiling with aluminium chloride.

The possibility of serious catalytic effects of the aluminium halides, particularly when

high distillation temperatures are involved, limits the preparative use of organosilicon fluorides and aluminium halides. The danger is reduced if dissolved aluminium halides are removed from a product before fractionation by adding a reactive alkylfluorosilane of suitable boiling point, as was done in the preparation of alkyliodosilanes (Part I, *loc. cit.*). This disproportionation itself, may, however, be of preparative value, and is being further investigated.

Mechanism of the Reaction.—In discussing the interaction of aluminium iodide and organofluorosilanes (Part I, *loc. cit.*) the author pointed out that lithium iodide was ineffective in the conversion, which probably was not a simple " halogen-exchange " reaction involving nucleophilic attack of iodide ion on silicon, but involved as the essential step a reaction of the type $R_3SiF + AlI_3 \longrightarrow R_3Si^+ + AlFI_3^-$. The failure of calcium chloride in acetonitrile to react with organofluorosilanes, although the solubility relations would favour the formation of calcium fluoride, confirms that the reaction is not of the " halogen-exchange " type, and it appears that the aluminium halides react in virtue of their electrophilic nature. That electrophilic attack on halogen is not the only rate-determining factor is suggested, however, by the observation that tri*iso*propylsilyl fluoride is converted into the chloride much less readily than are triethyl- and triphenyl-silyl fluorides. Under comparable conditions, with trialkylfluorosilane (2 mols.) and aluminium chloride (1 mol.) in ether, at least 72% of the triethyl compound reacts in 20 minutes whereas at most 10% of the tri*iso*propyl compound reacts in 3 hours. Even on the assumption of only a second-order reaction, with a second chlorine atom of the aluminium halide being as readily available as the first, this corresponds to a rate ratio of 200 : 1, and this is certainly a minimum value since the rate falls markedly as reaction proceeds. This low reactivity of the tri*iso*propylsilyl system accords with its comparative lack of reactivity in reactions such as hydrolysis and attack of Grignard reagents, which is to be attributed to the steric hindrance of the three large alkyl groups to nucleophilic attack on silicon. No appreciable steric hindrance would be expected to electrophilic attack on fluorine by aluminium halides, and it seems necessary to postulate that such electrophilic attack is also accompanied by a nucleophilic attack (of free or incipient halide ion) on silicon. The view that the reaction does not proceed through a siliconium ion is supported by the following facts : (i) siliconium ions, if formed at all, are much less stable than carbonium ions (Gilman and Dunn, *J. Amer. Chem. Soc.*, 1950, **72**, 2178; Hughes, *Quart. Reviews*, 1951, **5**, 245); (ii) the lower reactivity of triphenylsilyl fluoride when compared with triethylsilyl fluoride, although the triphenylsilyl system might be expected to give siliconium ions more readily than the trialkylsilyl system; (iii) the recent demonstration (Schumb and Breck, *J. Amer. Chem. Soc.*, 1952, **74**, 1754) that the reaction $SiF_4 + AlX_3$ (X = Cl or I) $\longrightarrow F_{4-y}SiX_y$ ($y = 0 \longrightarrow 4$) occurs also between the vapours, where siliconium ions would be even less likely than in solution.

EXPERIMENTAL

M. p.s and b. p.s are corrected.

General.—Dichloro-diethyl- and -dimethyl-silane were of " technical " grade, supplied by Midland Silicones Ltd. The aqueous hydrofluoric acid used was the 40% w/w " AnalaR " solution. Aluminium chloride was purified by sublimation, and aluminium bromide by distillation; molar quantities of these compounds are referred to the monomeric formula AlX_3.

Analyses.—Alkylbromo- and alkylchloro-silanes were analysed for halogen by adding a weighed amount to aqueous alcohol containing excess of potassium hydroxide and diluting the solution to a standard volume by addition of ethanol and water in such proportions as were necessary to give a homogeneous system. The halide ion was then determined by Volhard's method. Thiocyanates were similarly hydrolysed, and the thiocyanate was determined by titration against silver nitrate. For fluoride analyses see Part I (*loc. cit.*).

Diethyldifluorosilane.—A mixture of dichlorodiethylsilane (157 g.), ethanol (600 ml.), water (20 ml.), and aqueous hydrofluoric acid (140 ml.) was warmed under reflux for 3 hours at a few degrees below its b. p. It was then poured into excess of water, and the upper layer, after being washed with water, was dried (Na_2SO_4) and fractionated to give diethyldifluorosilane, b. p. 62·5° (91 g., 75%).

Fluorodimethylphenylsilane.—(i) A mixture of pentamethylphenyldisiloxan (12·5 g.),

ethanol (120 ml.), and aqueous-alcoholic hydrogen fluoride (30 ml.), after 5 hours' treatment as above, finally gave *fluorodimethylphenylsilane*, b. p. 162·4°, n_D^{25} 1·4110 (7 g., 80%) (Found : F, 12·3. $C_8H_{11}SiF$ requires F, 12·3%). (ii) The Grignard reagent from bromobenzene (2·5 mole), magnesium (2·6 g.-atom), and ether (750 ml.) was added during 1½ hours to dichloro-dimethylsilane (240 g.) in ether (400 ml.) with vigorous stirring. The mixture was stirred for a further ½ hour, and then 10% sulphuric acid was added until two clear layers were formed. The ethereal layer was washed and dried, and liquid was distilled off until the b. p. reached 240°. The residue was added to ethanol (1 l.) containing hydrogen fluoride (350 ml.). The mixture was kept just below the b. p. for 8 hours. The fluorodimethylphenylsilane, b. p. 162·4° (200 g., 70%), was isolated as before.

The preparations illustrate the value of aqueous-alcoholic hydrofluoric acid (cf. Part IV, *loc. cit.*) in converting into fluorides siloxans containing Si–Ph bonds, which are cleaved by the ammonium fluoride–sulphuric acid reagent.

Ethylfluorodimethylsilane.—The Grignard reagent from ethyl bromide (2 moles), magnesium (2·1 g.-atom), and ether (750 ml.) was added to the dichlorodimethylsilane (1·5 moles) in ether (800 ml.) during 1 hour. The mixture was boiled under reflux for 1 hour, and 10% sulphuric acid added as above; the ethereal layer was washed, dried (Na_2SO_4), and fractionated. Diethyl-dimethylsilane, b. p. 93·5° (33 g., 20%), was isolated, and distillation was interrupted when the b. p. reached 145°. The residue (*ca.* 120 ml.) was warmed beneath a reflux condenser with ethanol (600 ml.) and hydrogen fluoride (200 ml.) for 5 hours just below the b. p. of the mixture; gas evolution ($SiMe_2F_2$?) was vigorous at first. The mixture was poured into excess of ice-cooled water, and the upper layer was washed, dried (Na_2SO_4), and fractionated, to give ethylfluorodimethylsilane, b. p. 50—50·5° (72 g., 45%).

Explanation of Table.—The Table lists the reactions between organofluorosilanes and aluminium chloride or bromide which do not require special description. Where a solvent was employed this was added (carefully in the case of ether) to the aluminium halide through a reflux condenser and the mixture was shaken or warmed, if necessary, until dissolution was complete. The fluoride was then added through the condenser and washed down with a little of the solvent, and the mixture was boiled under reflux for the time stated. In procedure A

Reactants (quantities, in mole)	Solvent (ml.)	Time (hr.)	Products	Notes (see p. 498)
Et_3SiF (0·33), $AlCl_3$ (0·12)	—	3½	R.F, b. p. 104—115° (5 g.); Et_3SiCl, b. p. 145° (0·22 mole)	B
Et_3SiF (0·25), $AlCl_3$ (0·10)	Et_2O (100)	1½	R.F, b. p. 108—110° (3 g.); Et_3SiCl, b. p. 145° (25 g., 65%)	A
Et_3SiF (0·25), $AlCl_3$ (0·12)	Et_2O (100)	4	Et_3SiCl, b. p. 145° (30 g., 80%) (Found : Cl, 23·6. Calc. : Cl, 23·5%)	A
Et_3SiF (0·33), $AlCl_3$ (0·13)	C_6H_6 (50)	4	R.F, b. p. 110° (16 g.); Et_3SiCl, b. p. 145° (0·14 mole)	(1)
$EtMe_2SiF$ (0·19), $AlCl_3$ (0·071) ...	Et_2O (30)	2	$EtMe_2SiCl$, b. p. 88—88·5° (14 g., 60%) (Found : Cl, 28·9. Calc. : Cl, 28·9%)	A (2)
Me_2PhSiF (0·152), $AlCl_3$ (0·0495)	Et_2O (40)	4½	$Me_2PhSiCl$, b. p. 195°, n_D^{25} 1·5065 (11 g., 45%) (Found : Cl, 20·9. Calc. : Cl, 20·9%)	B (3) (4)
Pr^i_3SiF (0·1), $AlCl_3$ (0·033)	Et_2O (60)	48	R.F, b. p. 169° (0·0225 mole); Pr^i_3SiCl, b. p. 202°, n_D^{20} 1·4518 (9 g., 0·047 mole) (Found : Cl, 18·4. Calc. : Cl, 18·4%)	B (5) (7)
Pr^i_3SiF (0·174), $AlCl_3$ (0·0592) ...	Et_2O (45)	48	R.F, b. p. 169° (0·051 mole); Pr^i_3SiCl, b. p. 202° (15 g., 0·078 mole)	B (6) (7)
Pr^i_3SiF (0·174), $AlCl_3$ (0·068) ...	Et_2O (40)	48	Pr^i_3SiCl, b. p. 202° (27 g., 80%) (Found : Cl, 18·4. Calc. : Cl, 18·4%)	B (7) (8)
Et_2SiF_2 (0·15), $AlCl_3$ (0·064)	Et_2O (50)	1	R.F, b. p. 61—63° (3·5 g.); Et_2SiFCl, b. p. 96° (7 g., 33%) (Found : Cl, 25·2. Calc. : Cl, 25·2%); Et_2SiCl_2, b. p. 128—130° (5 g.)	B
Et_2SiF_2 (0·15), $AlCl_3$ (0·119)	Et_2O (60)	2	R.F, b. p. 61—63° (2·5 g.); Et_2SiFCl, b. p. 96·5° (5 g., 25%; Et_2SiCl_2, b. p. 130° (9 g., 40%) (Found : Cl, 44·8. Calc. : Cl, 45·1%)	B
Et_3SiF (0·17), $AlBr_3$ (0·056)	C_6H_6 (40)	2	R.F, b. p. 109—110° (3 g.); Et_3SiBr, b. p. 164° (27 g., 80%) (Found : Br, 40·9. Calc. : Br, 40·9%)	B
Et_3SiF (0·25), $AlBr_3$ (0·11)	Et_2O (100)	4	R.F, b. p. 109—110° (2 g.); Et_3SiBr, b. p. 164° (35 g., 70%)	A
Bu^i_3SiF (0·1), $AlBr_3$ (0·33)	—	½	Bu^i_3SiBr, b. p. 240—243° (20 g., 70%) (Found : Br, 28·4. Calc. : Br, 28·6%)	B (9)

(see Notes) the liquid was decanted from the reaction mixture after the reflux period, combined with the ethereal washings of the residual solid, and fractionated. In B all the liquid was distilled quickly from the reaction mixture and the distillate was fractionated. " R.F " in the products column denotes the fluoride recovered.

Notes to Table. (1) Much of the aluminium chloride became coated and remained undissolved in the benzene even on boiling. (2) Chlorobenzene was used as a " chaser " in the fractionation. (3) A precipitate was formed immediately the fluoride was added to the aluminium chloride solution. The initial distillation gave (after removal of ether) 15 ml. of a slightly-fuming liquid, b. p. 50—80°, smelling of ether, and then 26 ml. at 180—196°. The latter was fractionated to give 1 ml. of a strongly-fuming liquid at 58—62° (Me_3SiCl by disproportionation ?), 5 ml. at 160—190°, and then the chlorodimethylphenylsilane. (4) Daudt and Hyde (*J. Amer. Chem. Soc.*, 1952, **74**, 386) describe this chloride as having b. p. 191°, n_D^{25} 1·5082, but Lewis and Newkirk (*ibid.*, 1947, **69**, 701) report b. p. 195°. (5) As very little solid had separated after 24 hours' refluxing, ether was distilled off until the total volume was *ca.* 30 ml. and the boiling was continued for a further 24 hours. (6) After the mixing of the reactants, ether was distilled off until the reflux temperature rose to *ca.* 50°. (7) A column of efficiency >40 plates was used in the fractionation. Gilman and Clark (*ibid.*, p. 1499) describe this chloride as having b. p. 198°/739 mm., n_D^{20} 1·4518. (8) The yield of the chlorotri*iso*propylsilane was improved by using a greater proportion of aluminium chloride; further, ether was distilled off until the reflux temperature was *ca.* 70° both after the mixing of the reactants and after 24 hours when the reflux temperature had fallen considerably. (9) The product from the initial distillation boiled over the range 205—245°, with the bulk constant at 241°; the latter was redistilled to give the yield shown. Taurke (*Ber.*, 1905, **38**, 1661) describes this bromide as being " yellowish," and having b. p. 245°, but our product was colourless.

Fluorotriphenylsilane and Aluminium Chloride.—(i) The fluoride (7 g., 0·025 mole) in ether (20 ml.) was added to aluminium chloride (0·012 mole) in ether (10 ml.). Ether was distilled off until the volume of the residue was *ca.* 15 ml., and the latter was boiled under reflux for 5 hours. The liquid was decanted and combined with the ethereal washings of the residual gel. The ether was boiled off with continuous addition of light petroleum (b. p. 40—60°) and the light petroleum solution was filtered hot. The filtrate was concentrated to *ca.* 12 ml., and on cooling and seeding it deposited colourless crystals (4·0 g., 55%), m. p. 87—92°, raised to 94·5—95·5° by recrystallization from light petroleum. The mixed m. p. with authentic chlorotriphenylsilane was undepressed. The solvent was removed from the mother-liquor, and addition of ethanol gave crystals of fluorotriphenylsilane (0·5 g.), m. p. 60—63°, raised to 63—64° by recrystallization from ethanol. A mixed m. p. with authentic fluorotriphenylsilane was undepressed, but a mixture of the product with ethoxytriphenylsilane (m. p. 66°) was completely liquid below 40°. (ii) A similar procedure, but involving 0·010 mole of aluminium chloride and 3½ hours' refluxing, gave chlorotriphenylsilane (2·5 g., 33%) and fluorotriphenylsilane (3·0 g.).

Diethyldifluorosilane and Aluminium Bromide.—(i) The fluoride (0·11 mole) was added to aluminium bromide (0·073 mole, *i.e.*, exact equivalent on basis of all bromine atoms reacting) in the form of small lumps. The mixture became hot on being shaken for a few minutes and a gel-like bulky solid formed. After ¼ hour's refluxing, the liquid was distilled off, and all boiled in the range 167—172°. Redistillation from a small amount of copper powder and with protection from light gave *dibromodiethylsilane*, b. p. 168·5—169·5° (20 g., 75%) (Found : Br, 65·0. $C_4H_{10}Br_2Si$ requires Br, 65·0%). (ii) Diethyldifluorosilane (0·13 mole) was boiled under reflux with aluminium bromide (0·13 mole) in decalin (100 ml.) for 2 hours. Fractionation gave little liquid boiling below 160°, and *ca.* 60 ml. in the range 165—173°. This was refractionated, and the 30 ml. of liquid distilling in the range 163—169° (a sample of b. p. 167° contained Br, 43%. Calc. for $C_4H_{10}Br_2Si$: Br, 65%) were boiled with silver chloride (35 g.) under a fractionating column; dichlorodiethylsilane, b. p. 131° (14 g., 70%), was obtained, along with *ca.* 18 ml. of liquid, b. p. *ca.* 165—169°. This liquid, which had a strong peppermint odour, was washed with water, dried (Na_2SO_4), and redistilled; it then all boiled in the range 165—168° and had n_D^{18} 1·4548—1·4555.

Attempted Preparation of Bromodiethylfluorosilane.—(i) Diethyldifluorosilane (0·12 mole) was boiled under reflux with a solution of aluminium bromide (0·056 mole) in *o*-dichlorobenzene (40 ml.) for 1½ hours. When the liquid was distilled off, only 1 ml. boiled below 115°, and after a few ml. at 115—120°, the remainder distilled over the range 120—176°. When the distillate was fractionated, however, diethyldifluorosilane, b. p. 62° (4 g.), was obtained, followed by 0·8 g. of liquid at 115—117° (Found : Br, 37·6. Calc. for $C_4H_{10}BrFSi$: Br, 43·2%),

and then little liquid below 166°. It seems possible that Et_3SiFBr was obtained in the original distillation but underwent disproportionation on fractionation. (ii) Dibromodiethylsilane (0·07 mol.) was added to dried ammonium fluoride (0·1 mol.), and the reaction vessel connected to a fractionating column of low hold-up. When the mixture was warmed, liquid refluxed at 62°. Fractionation gave diethyldifluorosilane, b. p. 62·5° (5·2 g., 85% based on NH_4F taken), and no bromodiethylfluorosilane.

Difluorodiisopropylsilane and Aluminium Bromide.—When the fluoride (24 g., 0·158 mole) was shaken with solid aluminium bromide (17·5 g., 0·0656 mole) the mixture became only warm and the bromide dispersed only slowly. The mixture was boiled under reflux for ½ hour with occasional shaking, and the liquid was then distilled off to give *ca.* 10 ml. of liquid of b. p. 100—120°, 5 ml. of b. p. 120—160°, and 10 ml. of b. p. 200—208°. Fractionation gave : 0·75 ml., b. p. 85—102° ; 10·5 g., b. p. 103° ($Pr^i_2SiF_2$) ; 0·75 ml., b. p. 190—202° ; 15 g., b. p. 203·5—204·5°. The last fraction was *dibromodi*isopropylsilane (Found : Br, 58·0. $C_6H_{14}Br_2Si$ requires Br, 58·3%) in a yield of 62% based on unrecovered difluoride.

The identity of the dibromide was confirmed by shaking a solution of it (13 g.) in ether (60 ml.) with excess of aqueous ammonia for 10 minutes, separating and drying (Na_2SO_4) the ethereal layer, then evaporating off the ether and adding light petroleum to give needles of di*iso*propylsilanediol (6·3 g., 90%), m. p. 113—114°, undepressed by admixture with an authentic sample. This yield of the diol is distinctly superior to that obtained when the fluoride is hydrolysed (Part III, *loc. cit.*).

Comparative Interactions of Triethyl-, Triisopropyl-, and Triphenyl-silyl Fluorides with Aluminium Chloride in Ether.—In these experiments the relative amounts and the initial concentrations of the reactants were the same in all cases. The aluminium chloride taken would be equivalent to the fluoride in each case if two of the chlorine atoms were available.

(i) Triethyl- or tri*iso*propyl-silyl fluoride (0·1 mole) was added through a reflux condenser to the aluminium chloride (0·05 mole) dissolved in ether, and was washed down with a small amount of ether (total vol., 25 ml.). The mixture was boiled under reflux for the time stated, and then quickly cooled. Excess of water was added carefully through the condenser, with cooling of the reaction vessel in ice–water. The ethereal layer was dried (Na_2SO_4), and most of the ether was taken off through a column packed with glass helices. The residue was fractionated through a centre-rod column with an efficiency of *ca.* 10 theoretical plates and a hold-up of 1 ml. A blank experiment confirmed that triethylfluorosilane was not appreciably decomposed during the hydrolysis of the excess of aluminium chloride. The results are summarized in the following table.

	SiR_3F	Time, min.	Fluoride recovered	Other products	Residue	Reaction, %
I	Et_3SiF (13·4 g.)	20	2·9 g., b. p. 110°	$Et_3Si\cdot OH$, b. p. 155—157°, 9·0 g.	0·7 g.	72—78
II	,, ,,	180	2·5 g., b. p. 110	$Et_3Si\cdot OH$, b. p. 155—157°, 9·5 g.	0·9 g.	77—82
III	Pr^i_3SiF (17·6 g.)	180	15·8 g., b. p. 169—171°	0·2 g., b. p. 173—180°	0·7 g.	4—10
IV	,, ,,	360	14·5 g., b. p. 169—171°	1·0 g., b. p. 172—190°	1·2 g.	8—20

(ii) Fluorotriphenylsilane (11·2 g., 0·042 mole) was added to a solution of aluminium chloride (2·7 g., 0·022 mole) in ether (10 ml.), and the mixture boiled under reflux for 2 hours. Water was then added, the ethereal layer separated, and the ether distilled off. The residue was separated into triphenylsilanol (7·3 g.), m. p. 155—156°, and fluorotriphenylsilane (3·0 g.), m. p. 62—64°, by making use of the low solubility of the former in light petroleum and of the latter in ethanol. The recovery of 3·0 g. of fluoride means that not more than 73% had reacted, and probably rather less.

In a similar procedure involving 7 g. (0·025 mole) of the fluoride, 1·7 g. (0·0127 mole) of aluminium chloride, and ether (7 ml.) and 20 minutes' refluxing, 3·1 g. of triphenylsilanol were obtained, and 2·8 g. of the fluoride recovered. Not more than 4·2 g. (60%) of the fluoride had reacted.

In a procedure modified to allow chlorotriphenylsilane to be isolated, fluorotriphenylsilane (7 g., 0·025 mole) was boiled under reflux with a solution of aluminium chloride (1·7 g., 0·0127 mole) in ether (7 ml.) for 20 minutes. The mixture was then cooled, light petroleum (b. p. 40—60°) added, and solvent distilled off (with further addition of light petroleum) during 15 minutes to remove ether and precipitate aluminium salts. The solution was filtered hot, and the filtrate concentrated to *ca.* 10 ml. and cooled. The solid which separated was recrystallized from light petroleum to give chlorotriphenylsilane (3·6 g.), m. p. 94—95°,

unchanged by admixture with authentic sample. From the mother-liquors, triphenylsilanol (1·7 g.) and fluorotriphenylsilane (0·9 g.) were isolated in the usual way. The yield of chloride corresponds to a minimum reaction of 50%, but part of this may have taken place during the boiling with light petroleum.

Ethylfluorodimethylsilane and Aluminium Bromide.—When ethylfluorodimethylsilane (23 g., 0·216 mole) was added to solid aluminium bromide (21 g., 0·0788 mole) beneath a reflux condenser the liquid boiled and the solid dispersed to a bulky gel. The mixture was warmed and shaken for 10 minutes, and then more ethylfluorodimethylsilane (1·5 g.) was added. The mixture was boiled under reflux for $\frac{1}{2}$ hour and distilled; 1 ml. boiled below 100°, 2 ml. at 100—113°, and the remainder at 113—118°, and some gas was evolved in the last stages. The distillate was fractionated to give : 3·2 ml., b. p. 38—92° (with *ca.* 1 ml. at 78—83°; ? Me_3SiBr); 2·5 ml., b. p. 92—99°; and *ca.* 17 ml., b. p. 100—142°, with the bulk at 106—116°. All the liquid boiling above 92° was refractionated, to give : (i) 1 ml., b. p. 78—82°; (ii) 2·5 ml., b. p. 82—110°; (iii) 16·5 g., b. p. 110—112°, with the bulk at 110·5—111·5°; residue, 4 ml. Fraction (i) was probably bromotrimethylsilane (b. p. 80°); when it was heated in a test-tube with silver thiocyanate the reflux temperature rose quickly to 140° and then remained steady (Me_3SiNCS has b. p. 141°). Fraction (iii) was bromoethyldimethylsilane (Found : Br, 48·0. Calc. for $C_4H_{11}BrSi$: Br, 47·8%), in 44% yield.

Disproportionation of Bromoethyldimethylsilane in Presence of Aluminium Bromide.—Bromoethyldimethylsilane (13·5 g.) was boiled with aluminium bromide (0·6 g.) beneath a centre-rod fractionating column (efficiency, *ca.* 10 plates; hold-up, 1 ml.). After 1 hour the temperature of the vapour at the top of the column had fallen to 80°, and a slow take-off was begun. The boil-up and take-off rates were adjusted so that the b. p. at the top of the column did not exceed 81°, and 5·5 g. of liquid (i) of b. p. 77—81° were obtained in 12 hours. After this the b. p. could not be brought down below 83° on further boiling, and normal take-off gave : (ii) 0·7 ml., b. p. 82—86°; (iii) 1·5 ml., b. p. 136—162°; (iv) 2·2 ml., b. p. 161—166°. Fraction (i) contained only 48·5% of Br, and was thus not pure bromotrimethylsilane (Calc. : Br, 52·2%), but when 4 ml. were boiled with excess of silver thiocyanate, and the product was distilled off and redistilled, trimethyl*iso*thiocyanatosilane (2·5 g.), b. p. 141—144°, n_D^{20} 1·4812, was obtained. It seems probable that fraction (i) was mainly bromotrimethylsilane (5·5 g., 62% of theoretical according to $3Me_2EtSiBr \longrightarrow 2Me_3SiBr + Et_3SiBr$). Fraction (iv), which probably contained bromotriethylsilane, was added to ammonium fluoride; the liquid was distilled off and redistilled to give 0·3 ml. of b. p. 80—108°, and 0·7 ml. of b. p. 109—111°, n_D^{25} 1·388 (triethyl-fluorosilane has b. p. 110°, n_D^{25} 1·3900).

Fluorodimethylphenylsilane and Aluminium Bromide.—Fluorodimethylphenylsilane (18 g., 0·117 mole) was added to four lumps of the solid bromide (9·8 g., 0·0367 mole). The mixture was shaken beneath a reflux condenser for 10 minutes, during which all the aluminium bromide dispersed, the flask became too hot to touch, and the mixture became a thick gel. The mixture was distilled, and after 5 ml. of liquid had been removed in the b. p. range 120—180° the vapour temperature began to fall and *ca.* 12 ml. of liquid distilled at 160—165°, but with continual variation, indicating decomposition. The last liquid distilled at 220°. The total distillate was fractionated to give 11·8 g. of liquid of b. p. 78—82°, 0·4 ml. in the range 83—208°, and 1·5 g. at 208—210°, with a residue (hold-up) of 1 ml. The 208—210° fraction was probably impure *bromodimethylphenylsilane* (Found : Br, 38·0. $C_8H_{11}SiBr$ requires Br, 37·2%). The 78—82° fraction, which fumed strongly and gave much bromide ion on hydrolysis, was boiled with excess of silver thiocyanate; the liquid was distilled from the solid and fractionated to give : (i) 3·4 g., b. p. 78—83°; (ii) 0·8 ml., b. p. 83—130°; (iii) 4·8 g., b. p. 141—143°, and a residue of 1 ml. (hold-up). Fraction (iii) had n_D^{20} 1·4810 and was trimethyl*iso*thiocyanatosilane (b. p. 143·1°, n_D^{20} 1·4820 ± 0·0005; Anderson, *J. Amer. Chem. Soc.*, 1947, **69**, 3049). Fraction (i), which smelled strongly of benzene, was shaken with water, dried (KOH), and distilled; it all boiled at 77—80° and had n_D^{20} 1·4998 (benzene has b. p. 80°, n_D^{20} 1·5016). Benzene was confirmed by preparation of *m*-dinitrobenzene, m. p. and mixed m. p. 90·5°. Fraction (ii) also gave *m*-dinitrobenzene.

It thus seems probable that the 78—82° fraction (11·8 g.) in the first fractionation consisted of benzene (*ca.* 4·5 g., 50% of maximum possible) and bromotrimethylsilane (7·3 g., 61%). This amount of the bromide would theoretically give 6·2 g. of the *iso*thiocyanate, whereas 4·8 g. were obtained pure and a further 1 g. was probably contained in the hold-up and in fraction (ii).

*Tri*iso*butylfluorosilane and Aluminium Chloride.*—(i) The fluoride (0·1 mole) was added to aluminium chloride (0·0335 mole) in ether (30 ml.), and the mixture boiled under reflux for

$5\frac{1}{2}$ hours. The liquid was filtered through glass-wool, combined with the ethereal washings of the residue, and distilled. After the ether, there were obtained 4 ml. of liquid, b. p. 60—80°, 1 ml. of b. p. 206—222°, and 26 g. of b. p. 223—230°. The last fraction, which was cloudy and slightly green, was redistilled; it all boiled in the range 220—230°, with 10 ml. at 223—225° (i) and 7 ml. at 225—228° (ii). Since the product boiled in the region expected for tri*iso*butyl-chlorosilane, fractions (i) and (ii) were analysed, but contained only 8·7 and 10·4% of hydrolysable chlorine, respectively (Calc. for $C_{12}H_{27}ClSi$: Cl, 14·4%).

Evidently a complex reaction had occurred, and the 220—230° fraction was unstable to aluminium chloride, for when it (18 g.) was boiled with aluminium chloride (2 g.) for 2 hours, and the mixture fractionated, there were obtained : 1 ml., b. p. 108—139°; (A), 1·5 g., b. p. 139—141°; 1 ml., b. p. 180—204°; (B), 3·2 g., b. p. 205—207°; 9 ml., b. p. 220—223°. The b. p.s of fractions (A) and (B) suggest that disproportionation into Bu^iSiCl_3 and $Bu^i_2SiCl_2$ had occurred, but this must have been accompanied by more complex decomposition since fraction (A) contained only 31% of chlorine (Calc. for $C_4H_9Cl_3Si$: Cl, 54·9%). Hydrolysis of fraction (B), by the method used in the preparation of di*iso*propylsilanediol, gave di*iso*-butylsilanediol (0·9 g.).

(ii) When tri*iso*butylfluorosilane (0·1 mole) was added to excess of powdered aluminium chloride (0·037 mole), heat was developed and the bulk of solid increased. The mixture was boiled under reflux for 1 hour, then more aluminium chloride (0·5 g.) added, and boiling continued for 2 hours. Fractionation from the reaction mixture gave : 2·5 ml., b. p. 100—140°; 3·0 ml., b. p. 160—190°; 3 ml., b. p. 190—206°; and 8 ml., b. p. 206—210°. That some change was taking place during fractionation was indicated by the fact that when, during the take-off of the last fraction, the column was put under total reflux for 2 hours, the reflux temperature fell to 160°, and 1·5 ml. of liquid had to be taken off to restore the b. p. to 206°. Gas evolution occurred throughout the fractionation, and some liquid collected in the sulphuric acid traps used to exclude moisture.

Chlorotriethylsilane and Aluminium Chloride.—When chlorotriethylsilane (20 g.), b. p. 146°, was boiled with aluminium chloride (1·5 g.) beneath a centre-rod fractionating column, the reflux temperature at the top of the column remained at 146° during 4 hours. During an additional 4 hours, almost all the liquid distilled at 146°.

*Ethyldimethyl*iso*thiocyanatosilane.*—Chloroethyldimethylsilane (12 g.), prepared as shown in the Table, was boiled under reflux with excess of silver thiocyanate (22 g.) for $\frac{1}{4}$ hour and all the liquid was then distilled off. Fractionation gave *ethyldimethyl*iso*thiocyanatosilane*, b. p. 167·6°, n_D^{25} 1·484 (11 g., 75%) (Found : CNS, 40·1. $C_6H_{11}NSSi$ requires CNS, 40·0%).

*Dimethylphenyl*iso*thiocyanatosilane.*—Chlorodimethylphenylsilane (7 g.) was boiled under reflux with excess of silver thiocyanate for $\frac{1}{4}$ hour, during which the reflux temperature rose to 250°. The liquid was distilled off, and redistillation gave *dimethylphenyl*iso*thiocyanatosilane* (4 g., 50%) b. p. 257—259° (Found : CNS, 29·8. $C_9H_{11}NSSi$ requires CNS, 30·0%).