583. *Organosilicon Compounds. Part I. The Formation of Alkyliodosilanes.*

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Iodine in the presence of aluminium iodide has been found to break silicon–carbon bonds in tetra-alkylsilanes, with formation of alkyliodosilanes. In the compounds examined, the ease of displacement of the various alkyl groups is in the order, phenyl $\gg$ methyl $>$ ethyl $>$ *n*- and *iso*-propyl. Triethyliodosilane reacts further with iodine in the presence of aluminium iodide to give diethyldi-iodosilane. Alkyliodosilanes have also been prepared by reaction of the corresponding alkylfluorosilanes with aluminium iodide. Alkyliodosilanes react with solid silver cyanide to give the corresponding *alkyl*(iso)*cyanosilanes.*

Only one alkyliodosilane has previously been reported : trimethyliodosilane, prepared by prolonged boiling of phenyltrimethylsilane with iodine under reflux (Pray, Sommer, Goldberg, Kerr, Di Giorgio, and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 433). Two other organosilicon iodides have previously been described : octaphenyl-1 : 4-di-iodotetrasilane and octa-*p*-tolyl-1 : 4-di-iodotetrasilane, solids prepared by the action of iodine in benzene on compounds of formula Si_4Ph_8 and $Si_4(C_6H_4Me\text{-}p)_8$, respectively (Kipping and Sands, *J.*, 1921, 830; Steele and Kipping, *J.*, 1929, 2545). The properties of the compounds were not investigated in any of these cases. The use of aluminium chloride to produce phenyltrichlorosilane from diphenyldichlorosilane, and silicon tetrachloride from both tetraphenylsilane and tetrabenzylsilane (Evison and Kipping, *J.*, 1931, 2774), has recently been extended to the preparation of silicon tetrachloride from tetraethylsilane in chloroform solution (Manulkin, *J. Gen. Chem. Russia*, 1948, **18**, 299). It was thus in the hope of preparing ethyliodosilanes that the reaction between aluminium iodide and tetraethylsilane was examined.

Originally the aluminium iodide was prepared directly in boiling benzene solution from iodine and aluminium powder. Added tetraethylsilane was converted on boiling with this solution, followed by hydrolysis, into hexaethyldisiloxane in 90% yield, indicating that the expected reaction, $Et_4Si + AlI_3 \longrightarrow Et_3SiI + EtAlI_2$ had occurred. When, however, the solvent was omitted, and tetraethylsilane was boiled directly with the appropriate quantities of iodine and aluminium, the iodine was fairly quickly used up without the disappearance of appreciable amounts of the aluminium. Ethyl iodide and *triethyliodosilane* were formed according to the equation $Et_4Si + I_2 \longrightarrow Et_3SiI + EtI$. Since iodine alone reacts only very slowly with tetraethylsilane the aluminium was evidently acting as a catalyst, probably by initial formation of a small amount of aluminium iodide. It was later found that iodine in the presence of aluminium or aluminium iodide may be generally effective in the breaking of silicon–alkyl and silicon–aryl bonds.

Breaking of Si–Alkyl Bonds by Iodine + Aluminium (or Aluminium Iodide).—When aluminium alone is used as catalyst for the reaction between iodine and tetraethylsilane there is an initial period in which iodine is removed only slowly, presumably while aluminium iodide is being formed. This " induction period " is absent when aluminium iodide is used as catalyst, either alone or with aluminium. Yields of ethyl iodide are in the region of 90% of the theoretical, and yields of triethyliodosilane rather lower. Triethyliodosilane reacts with further iodine to give *diethyldi-iodosilane*, though in this case no ethyl iodide is obtained, even if opportunity is offered for this compound to distil off continuously during the reaction. Instead, a gas is evolved, and although this has not been analysed it is suggested that it may be a mixture of hydrocarbons, probably formed by a secondary reaction of the ethyl iodide. The quantity of iodine required to produce the diethyldi-iodosilane, and the volume of gas evolved, are approximately those required by an overall reaction of the type $2Et_3SiI + I_2 \longrightarrow 2Et_2SiI_2 + C_4H_{10}$. The displacement of an ethyl group from triethyliodosilane is slower than from tetraethylsilane, in spite of the higher temperature of reaction, and requires the presence of rather larger amounts of aluminium iodide, though the action of the latter is still catalytic. Diethyldi-iodosilane reacts very slowly with further quantities of iodine, and the fact that, in early experiments, iodine in twice the quantity actually required was employed in the reaction with triethyliodosilane and was removed during several hours by conversion into aluminium iodide without appreciably lowering the yield of diethyldi-iodosilane, suggests that the displacement of a third ethyl group by iodine is more difficult than that of the first two such groups.

Dimethyldiethylsilane and methyltriethylsilane react with iodine (1 molar equivalent) to give mainly ethyl and methyl iodide, with little gas formation. *Methyltri-*n*-propylsilane*, on the other hand, gives only a small amount of alkyl iodides, and the iodine needed is only a little greater than that required by a reaction of the type $2SiMePr_3 + I_2 \longrightarrow 2Pr_3SiI + C_2H_6$, and the volume of gas evolved a little less than that required. (The fact that a mixture of *n*-propyl iodide, methyltri-*n*-propylsilane, and aluminium iodide gives off a similar gas on heating suggests that the gas formed during the reation of the tetra-alkylsilane with iodine comes from secondary reactions of the alkyl iodides formed. With more than one kind of alkyl group present, as in the reactions involving methyltri-*n*-propylsilane, and with the high probability of rearrangements under the conditions employed, the gas is likely to be a complex mixture of hydrocarbons.) *Dimethyldi*iso*propylsilane* is intermediate in behaviour, *ca.* 0·8 mol. of iodine being required to give 1 mol. of trialkyliodosilane, and some gas being evolved. Whether a particular tetra-alkylsilane will require 1 mol., 0·5 mol., or some intermediate amount of iodine probably depends on the temperature of the refluxing liquid as well as on the nature of the alkyl groups involved.

When the four alkyl groups attached to the silicon atom are not identical, separation of either the alkyl iodides or the trialkyliodosilanes formed gives an indication of the relative ease of displacement of the groups concerned. If the alkyliodosilanes could not be conveniently separated they were hydrolysed and converted into the corresponding alkylfluorosilanes. From dimethyldiethylsilane, methyl iodide and ethyl iodide were obtained in the mol. ratio of *ca.* 2 : 1, and from methyltriethylsilane they were obtained in the molecular ratio of 2 : 3. Since there are three times as many ethyl as methyl groups available for reaction in the case of methyltriethylsilane, methyl groups in both tetra-alkylsilanes are displaced roughly twice as readily as ethyl groups. From dimethyldi*iso*propylsilane, *methyldi*iso*propyliodosilane* was obtained in 80% yield, so that methyl and *iso*propyl groups in this compound are displaced in the ratio of at least 4 : 1. The iodide mixture from methyltri-*n*-propylsilane was shown, by conversion into tri-*n*-propyl- and *methyldi-*n*-propyl-fluorosilane*, to consist of tri-*n*-propyliodosilane and methyl-*n*-propyliodosilane in the mol. ratio of *ca.* 2 : 1. Phenyltrimethylsilane gave an almost quantitative yield of iodobenzene. In the compounds examined, then, the ease of removal of the various alkyl groups from the silicon is in the order, phenyl $\gg$ methyl $>$ ethyl $>$ *n*-propyl, and methyl $>$ ethyl $>$ *iso*propyl. (No comparison of *n*- and *iso*-propyl is possible on the available results.) The series may be compared with the order of the ease of removal of various groups from tin by halogens, *viz.*, phenyl $>$ benzyl $>$ methyl $>$ ethyl $>$ *n*-propyl (Bullard, *J. Amer. Chem. Soc.*, 1929, **51**, 3065; cf. Manulkin, *J. Gen. Chem. Russia*, 1941, **11**, 386).

Mechanism of the Catalysis.—The effectiveness of the aluminium iodide catalyst is shown by the fact that in the presence of aluminium the theoretical amount of iodine, added in small portions, reacted completely with boiling phenyltrimethylsilane in less than 20 minutes, whereas Pray *et al.* (*loc. cit.*) boiled this organosilicon compound with iodine alone for 12 hours without effecting complete reaction. Surprisingly, in view of the reaction which occurs in benzene, aluminium iodide itself does not react with tetraethylsilane in the absence of solvent.

An obvious suggestion to explain the action of the aluminium iodide is that the ions I^+ and AlI_4^- are formed, and that one or other of these is the attacking agent (the silicon atom in organosilicon compounds is normally susceptible to attack by nucleophilic groups, but the initial attack could conceivably be by I^+ on carbon). However, Calingaert and Beatty (*J. Amer. Chem. Soc.*, 1939, **61**, 2748) have shown that catalysts of the aluminium iodide type, *e.g.*, aluminium chloride, ferric chloride, boron trifluoride, etc. (aluminium iodide itself was not employed), are effective in causing random redistribution of the alkyl groups in boiling mixtures of two R_4M compounds (R = alkyl, M = Pb, Sn, Si, or Hg). These catalysts thus have the ability in themselves to cause fission of the M–R bond, and the action of aluminium iodide in facilitating the breaking of Si–C bonds may be directly dependent on this property. The initial step could be, for example, $AlI_3 + SiR_4 \longrightarrow R_3Si^+ + [AlRI_3]^-$, followed by $R_3Si^+ + I_2 \longrightarrow R_3SiI + I^+$, $[AlRI_3]^- + I^+ \longrightarrow AlI_3 + RI$, and similar reactions.

Reactions of Alkylfluorosilanes with Aluminium Iodide.—In the expectation of preparing an organo-iodofluorosilane, triethylfluorosilane was boiled with iodine in the presence of aluminium. The iodine disappeared much more slowly than in the reaction with tetraethylsilane, and considerably more aluminium was required. Triethyliodosilane was the only volatile product isolated. Tri-*n*-propylfluorosilane similarly gave *tri*-n-*propyliodosilane.* It seemed likely that aluminium iodide was the effective reactant in these cases, and triethylfluorosilane, tri-*n*-propylfluorosilane, and *methyldi*-n-*propylfluorosilane* were found to react with aluminium iodide (3 : 1 molecular ratio) to give triethyliodosilane, *tri*-n-*propyliodosilane,* and *methyldi*-n-*propyliodosilane* in good yield, according to the reaction, $3R_3SiF + AlI_3 \longrightarrow 3R_3SiI + AlF_3$. Moreover, *di*iso*propyldifluorosilane* reacts with aluminium iodide (3 : 2 molecular ratio) to give *di*iso*propyldi-iodosilane.* This method of preparing alkyliodosilanes is probably capable of wide application, although *dimethylethylfluorosilane* is not satisfactorily converted into the corresponding iodide in this way, possibly because of the low boiling point of this fluoride.

The method recalls the observation of Sommer, Bailey, and Whitmore (*J. Amer. Chem. Soc.*, 1948, **70**, 2869) that diethyl-2-chloroethylfluorosilane and aluminium chloride react to give diethyldichlorosilane, replacement of the fluorine having accompanied the usual removal of the 2-chloroethyl group. In the present work it was found that tri-*n*-propylfluorosilane reacts with aluminium chloride to give a product which is probably mainly *tri*-n-*propylchlorosilane.* Lithium iodide does not react with triethylfluorosilane, indicating that the difference in solubility of the aluminium fluoride and of aluminium iodide and chloride may not be the essential cause of the reaction of the last two substances with organofluorosilanes, and that the reactions are not simple " ion-exchange " reactions. Probably steps of the type $R_3SiF + AlI_3 \longrightarrow R_3Si^+ + AlI_3F^-$ are all-important.

Properties of Alkyliodosilanes.—Triethyliodosilane, tri-*n*-propyliodosilane, methyldi-*n*-propyliodosilane, methyldi*iso*propyliodosilane, diethyldi-iodosilane, and di*iso*propyldi-iodosilane were prepared. (Other alkyliodosilanes were undoubtedly formed, but were not obtained in a pure state.) All the iodides are strongly-fuming liquids of high density, colourless when first distilled but acquiring an iodine colour on storage, particularly in the light. The formation of free iodine is accelerated by surfaces, and addition of glass wool causes immediate blackening. The kinetics of the decomposition of triethyliodosilane in carbon tetrachloride, and of its formation from triethylsilane in this solvent, are being studied. Distillation of the iodides was usually carried out in a nitrogen atmosphere, although there appears to be no marked decomposition when this precaution is neglected. A sample of triethyliodosilane boiled at a remarkably constant temperature even on prolonged fractionation (with protection from light) in a column packed with glass helices. The trialkyliodosilanes are hydrolysed readily to the corresponding hexa-alkylsiloxanes. Diethyldi-iodosilane reacts very vigorously with water, to give a " silicone " gel; di*iso*propyldi-iodosilane is attacked more slowly. The iodides appear to react readily with Grignard reagents to give the normal products.

Since monoiodosilane reacts with magnesium under the conditions of a Grignard reaction, with possible formation of a " Grignard compound," $MgI{\cdot}SiH_3$ (Emeléus, Maddock, and Reid, *J.*, 1941, 353), the action of magnesium on triethyliodosilane in ether was examined. No general reaction occurred, and the bulk of the triethyliodosilane was recovered after prolonged refluxing. Triethyliodosilane catalyses markedly the reaction of magnesium and iodine in ether; whilst this may indicate the transient formation of a " Grignard " compound by the organoiodosilane, there is the possibility of the formation of small amounts of ethyl iodide (and, say, diethyldi-iodosilane) which would form ethylmagnesium iodide and so catalyse the main reaction and also re-form triethyliodosilane. Triethyliodosilane also reacted with magnesium in the absence of a solvent, but no evidence of the expected Si–Si bonds was found.

Triethyliodosilane reacts immediately in the cold with mercuric oxide, forming mercuric iodide, and after boiling of the mixture a good yield of hexaethyldisiloxane is obtained (Shaw, B.P. 606,301, has recently described the preparation of polysilicones by heating alkylchlorosilanes under reflux with metallic oxides). The alkyliodosilanes react with solid silver cyanide to give corresponding alkyl(*iso*)cyanosilanes as described below. Emeléus, Maddock, and Reid (*loc. cit.*) obtained " silyl cyanide " from the reaction between gaseous monoiodosilane and solid silver cyanide, and Anderson has prepared organosilicon *iso*cyanates and *iso*thiocyanates by interaction of the appropriate silver salt with alkylchlorosilanes in benzene (*J. Amer. Chem. Soc.*, 1949, **71**, 1801; Forbes and Anderson, *ibid.*, 1948, **70**, 1222, and refs.). In the present work tri-*n*-propylchlorosilane was found not to react appreciably with solid silver cyanide. The action of other salts on alkyliodosilanes is being investigated.

Alkyl(iso)*cyanosilanes.*—Triethyliodosilane, tri-*n*-propyliodosilane, and diethyldi-iodosilane react with solid silver cyanide to give compounds believed to be the corresponding alkyl*iso*cyanosilanes. The chemical evidence available does not indicate whether these substances are organosilicon cyanides or organosilicon *iso*cyanides, since both Si–CN and Si–NC bonds would presumably give cyanide ion on hydrolysis. On the basis of the fact that the compounds obtained boil a few degrees below the corresponding iodides, it is tentatively suggested (by analogy with organic cyanides, *iso*cyanides and iodides) that they are actually *iso*cyanides. Emeléus, Maddock, and Reid (*loc. cit.*), however describe the solid product from the reaction of gaseous monoiodosilane and silver cyanide as silyl cyanide, $SiH_3{\cdot}CN$.

All three alkyl(*iso*)cyanosilanes prepared, *viz.*, *triethyl*(iso)*cyanosilane*, *tri-*n*-propyl*(iso)-*cyanosilane*, and *diethyldi*(iso)*cyanosilane*, are obtained as colourless, non-fuming liquids, which set to white solids; only the last named, however, is solid at room temperature. They are rapidly hydrolysed by aqueous alkalis to give cyanide ion; solid diethyldi(*iso*)cyanosilane reacts with water with a sharp crack. With methylmagnesium iodide, diethyldi(*iso*)cyanosilane gives dimethyldiethylsilane, *i.e.*, the Grignard reagent displaces the (*iso*)cyanide groups as it does halogens and does not add to the carbon–nitrogen multiple bond as it does with organic cyanides and *iso*cyanides. Triethyl(*iso*)cyanosilane reacts with mercuric oxide to give hexaethyldisiloxane. When first obtained the alkyl(*iso*)cyanosilanes have an odour resembling that of acetonitrile, but on storage an odour of organic *iso*cyanides develops; in both cases the smell probably arises from impurities.

Preparative Methods.—Some interesting observations were made during preparations incidental to this investigation.

Alkylfluorosilanes were prepared by passing silicon tetrafluoride into a Grignard reagent in ether (cf. Gierut, Sowa, and Nieuwland, *J. Amer. Chem. Soc.*, 1936, 58, 897; Medox, *J. Gen. Chem. Russia*, 1938, **8**, 291; Medox and Kotelkov, *ibid.*, 1937, **7**, 2007; Gaeger and Dykstra, *Z. anorg. Chem.*, 1925, **143**, 233). Whereas (Gierut, Sowa, and Nieuwland, *loc. cit.*) ethyl-, *n*-propyl-, *n*-butyl-, and *n*-amyl-magnesium chloride yield almost exclusively the corresponding trialkylfluorosilanes (with the exception of the first named, which gives also tetraethylsilane), it was found in the present work that *iso*propylmagnesium chloride gives mainly di*iso*propyldifluorosilane (the first dialkyldifluorosilane prepared from silicon tetrafluoride), along with some *tri*iso*propylfluorosilane*. Gilman and Clarke (*J. Amer. Chem. Soc.*, 1947, **69**, 1499) have recently reported that *iso*propylmagnesium chloride will cause replacement of only two of the chlorine atoms of trichlorosilane, and that *iso*propyl-lithium will cause replacement of only three chlorine atoms of silicon tetrachloride, and have ascribed these effects to steric hindrance. The action of silicon tetrafluoride on Grignard reagents containing other groups which might cause steric hindrance is being examined.

Sodium ethoxide in absolute alcohol was used to convert di*iso*propyldifluorosilane and tri-*n*-propylfluorosilane into *diethoxydi*iso*propylsilane* and *ethoxytri-*n*-propylsilane* respectively, and this method (which has been applied to the preparation of other alkylethoxysilanes which will be described in a later communication) appears to be of general application. Emeléus and Robinson (*J.*, 1947, 1592) prepared organoethoxysilanes by the action of dry sodium ethoxide on organochlorosilanes.

The method of Flood (*J. Amer. Chem. Soc.*, 1933, **55**, 1735; cf. Di Giorgio, Strong, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 1380) has been applied to the preparation of *dimethylethylfluorosilane* from s-*tetramethyldiethyldisiloxane*, and of methyldi-*n*-propylfluorosilane and *methyldi*iso*propylfluorosilane*.

Tetra-alkylsilanes have been obtained in good yield from alkylfluorosilanes and methylmagnesium iodide.

EXPERIMENTAL.

(All b. p.s are corrected.)

Analyses.—Alkyliodosilanes were analysed for iodine by adding a weighed sample to aqueous potassium hydroxide in a closed flask, setting the mixture aside for ¼ hour, then adding small volumes of alcohol cautiously, and finally making up to a standard volume with alcohol. Aliquots were taken from a burette calibrated for alcohol solutions, and run into excess of water. Iodide ion was titrated against potassium iodate by the positive halogen method.

Alkyl(*iso*)cyanosilanes were hydrolysed in the same way, and cyanide ion was titrated against silver nitrate by the turbidimetry method. (After an aliquot of the alcoholic solution had been run into water, time was allowed for the organosilicon material thrown out of solution to form into drops.)

Alkylfluorosilanes were not analysed directly for fluorine, but aliquot volumes of an alcoholic solution were added (as soon as possible after the solution was made up, to avoid any reaction of hydrofluoric acid with the glass of the container) to excess of standardized alcoholic potash, and the excess of alkali was determined by dilution with water and titration against standard potassium hydrogen phthalate solution (phenolphthalein). A layer of light petroleum was used to exclude atmospheric carbon dioxide during titration. The error is probably $< 1\%$.

Microanalyses.—Carbon and hydrogen were determined by Drs. Weiler and Strauss, Oxford.

Molecular Weights.—These were determined by the Victor Meyer method.

Densities.—These were very roughly determined by measuring approximately the volume occupied by samples weighed for analysis.

General.—Atmospheric moisture was excluded in all reactions involving organosilicon iodides, (*iso*)cyanides, and chlorides, and aluminium iodide and chloride by means of sulphuric acid bubblers, unless otherwise specified.

All fractionations were carried out in a column 30″ in length, packed with glass helices, lagged, and fitted with an electrically-heated jacket. At the reflux ratios used the total efficiency was probably $>$ 12 theoretical plates.

Reactions were carried out in all-glass apparatus, with the exception of those involving Grignard reagents. The latter were made and employed in the conventional three-neck flask fitted with dropping funnel, mercury-seal stirrer, and reflux condenser.

Aluminium Iodide.—This was prepared from iodine and aluminium in a stream of nitrogen. Excess of aluminium was usually added to the fused material to remove any free iodine. Unless otherwise specified, the aluminium iodide thus contained a little ($<1\%$) free aluminium.

Silicon Tetrafluoride.—This was prepared by warming a mixture of sodium fluosilicate, silica, and concentrated sulphuric acid.

Triethylsilane.—This was prepared (cf. Kraus and Nelson, *J. Amer. Chem. Soc.*, 1934, **56**, 195) by the addition of silicochloroform (0·67 mol.) in ether (200 ml.) to ethylmagnesium bromide (slightly >2 mols.). The mixture was heated under reflux for 1 hour, and diluted sulphuric acid was added until two clear layers formed. The ethereal layer was washed, dried, and fractionated, to give triethylsilane (40—50 g., *ca.* 52—65%), b. p. 107°.

Triethylfluorosilane and Tetraethylsilane.—The method of Gierut, Sowa, and Nieuwland (*loc. cit.*) was employed, except that after the reaction had been completed diluted sulphuric acid was added until two clear layers formed. The ethereal layer was washed, dried, and fractionated. Typical yields were : triethylfluorosilane, b. p. 109·0—109·5°, 30 g. (0·22 mol.), and tetraethylsilane, b. p. 153·0°, 42 g. (0·29 mol.), from 218 g. (2 mols.) of ethyl bromide.

Tri-n-*propylfluorosilane.*—This was prepared by the method described for triethylfluorosilane. A typical yield was 50 g. (43%) of tri-*n*-propylfluorosilane, b. p. 174·0°/760 mm., from 2 mols. of *n*-propylmagnesium bromide.

*Di*iso*propyldifluorosilane and Tri*iso*propylfluorosilane.*—Silicon tetrafluoride was passed into *iso*propylmagnesium chloride (from 2 mols. of *iso*propyl chloride) in ether (500 ml.) for 6 hours (*i.e.*, for 1 hour after the ether had ceased to reflux). The mixture was heated under reflux for 1 hour, and 10% sulphuric acid was added until two clear layers formed. The ethereal layer was washed, dried, and fractionated, to give *di*iso*propyldifluorosilane* (42 g., 0·27 mol.), b. p. 100·7—100·8°/742 mm., $n_D^{22\cdot2}$ 1·3662 (Found : F, 24·8, 24·7; *M*, 158, 154. $C_6H_{14}SiF_2$ requires F, 24·95%; *M*, 152), and *tri*iso*propylfluorosilane* (13 g.), b. p. 169·0°/742 mm., $n_D^{14\cdot5}$ 1·4200 (Found: F, 10·9, 10·9%; *M*, 177, 182. $C_9H_{21}SiF$ requires F, 10·8%; *M*, 176).

*Diethoxydi*iso*propylsilane.*—Di*iso*propyldifluorosilane (10 g.) was added to a solution prepared by dissolving sodium (2 g.) in absolute alcohol (40 ml.). The mixture was poured slowly through a layer of light petroleum (b. p. $<40°$) into water. The light petroleum layer was washed, dried, and distilled, to give *diethoxydi*iso*propylsilane* (6 g., 45%), b. p. 186—187°/760 mm., $n_D^{25\cdot8}$ 1·4130 (Found : C, 59·2; H, 11·7. $C_{10}H_{24}SiO_2$ requires C, 58·8; H, 11·8%). The yield of impure material (b. p. 184—189°) was *ca.* 85%.

Methyltri-n-*propylsilane.*—(*a*) Tri-*n*-propylfluorosilane (17·6 g., 0·1 mol.) in ether (30 ml.) was added to methylmagnesium iodide (*ca.* 0·14 mol.) in ether (40 ml.). Heating under reflux on a bath for 1 hour was followed by the addition of sulphuric acid (10%). The ethereal layer was repeatedly washed with aqueous potassium hydroxide and then with water, dried, and fractionated, to give *methyltri*-n-*propylsilane* (14 g., 83%), b. p. 183·0°/760 mm., $n_D^{16\cdot5}$ 1·4290 (Found : C, 69·5; H, 14·1. $C_{10}H_{24}Si$ requires C, 69·7; H, 14·05%).

(*b*) Silicon tetrafluoride was passed into *n*-propylmagnesium bromide (2 mols.) in ether (500 ml.) until two layers separated. After 1 hour's stirring, methylmagnesium iodide (0·67 mol.) in ether (350 ml.) was added. The mixture was heated under reflux for 4 hours, and after the addition of excess of dilute sulphuric acid the ethereal layer was repeatedly washed with aqueous potassium hydroxide and then with water. After drying, fractionation gave methyltri-*n*-propylsilane (58 g., 50%), b. p. 182·7°/747 mm.

*Dimethyldi*iso*propylsilane.*—Di*iso*propyldifluorosilane (36 g.) in ether (50 ml.) was added to methylmagnesium iodide (0·75 mol.) in ether (180 ml.) during ½ hour. Vigorous stirring for a further ½ hour was followed by ½ hour's heating under reflux. Dilute sulphuric acid was added, and the ethereal layer was washed with aqueous potassium hydroxide and with water, dried, and fractionated, to give *dimethyldi*iso*propylsilane* (27 g., 80%), b. p. 141·0—141·3°/760 mm. n_D^{26} 1·4198 (Found : C, 67·0; H, 14·4. $C_8H_{20}Si$ requires C, 66·6; H, 14·0%).

Dimethyldiethylsilane and s-*Tetramethyldiethyldisiloxane.*—Dimethyldichlorosilane (110 g.) in ether (100 ml.) was added to ethylmagnesium bromide (2 mol.) in ether (500 ml.) during ½ hour. After 1 hour's vigorous stirring of the mixture, dilute sulphuric acid was added, and the ethereal layer was dried and fractionated, to give dimethyldiethylsilane (41 g.), b. p. 94·8—95·0°/752 mm., and s-*tetramethyldiethyldisiloxane* (34 g.), b. p. 150·5°/750 mm., n_D^{15} 1·4028 (Found : C, 50·75; H, 11·7. $C_8H_{22}Si_2O$ requires C, 50·5; H, 11·6%).

In a second experiment, in which addition of the dimethyldichlorosilane was followed by boiling under reflux for 1 hour, 46 g. of dimethyldiethylsilane and 30 g. of *s*-tetramethyldiethyldisiloxane were obtained.

Methyltriethylsilane.—Triethylfluorosilane (25 g.) in ether (20 ml.) was run into methylmagnesium iodide (*ca.* 0·25 mol.) in ether (60 ml.) at such a rate as to maintain gentle reflux. The addition took ½ hour, and stirring for a further ½ hour was followed by addition of 10% sulphuric acid. The ethereal layer was washed with aqueous potassium hydroxide, dried, and fractionated. Methyltriethylsilane (21 g., 88%), b. p. 126·8°/760 mm. was obtained.

Phenyltrimethylsilane.—Phenylmagnesium bromide (0·34 mol.) in ether (150 ml.) was added to silicon tetrachloride (60 g.) in ether (100 ml.) during ½ hour. The mixture was heated under reflux for 1 hour, and then methylmagnesium iodide (1·5 mols.) in ether (450 ml.) was run in during ½ hour. The mixture was boiled under reflux for 6 hours. Sulphuric acid (10%) was added to give two clear layers, and the ethereal layer was dried and fractionated, to give trimethylphenylsilane (13 g., 25%), b. p. 171·5°/752 mm.

Dimethylethylfluorosilane.—*s*-Tetramethyldiethyldisiloxane (42 g.) was dissolved in concentrated sulphuric acid (100 ml.) with cooling, and ammonium fluoride (50 g.) was added, with cooling and vigorous stirring, at such a rate that the temperature was kept below 15°. Addition took ¾ hour, and stirring was continued for a further ¼ hour. The mixture was added to ice, and the upper layer was washed, dried (Na_2SO_4), and fractionated. *Dimethylethylfluorosilane* (35 g., 75%) boiled at 49·8°/742 mm., n_D^{15} 1·3568 (Found : F, 17·6, 18·0%; *M*, 108, 110. $C_4H_{11}SiF$ requires F, 17·9%; *M*, 106). The fluoride has a pleasant, sweet odour.

Methyldi-n-*propylfluorosilane.*—Tetraethoxysilane (104 g., 0·5 mol.) was added quickly to a solution of *n*-propylmagnesium bromide (*ca.* 1·3 mols.) in ether (500 ml.). The mixture was stirred for ¾ hour and boiled under reflux for 8 hours. Methylmagnesium iodide (1 mol.) in ether (250 ml.) was added during ¼ hour, and the mixture was boiled under reflux for 4 hours. Sulphuric acid (*ca.* 15%) was added until two clear layers formed, and vigorous stirring was maintained for ½ hour (to hydrolyse any Si–OEt bonds present). The ethereal layer was washed, dried, and distilled. The liquid boiling at 240—255° (*ca.* 55 ml.) was dissolved, with cooling, in concentrated sulphuric acid (200 ml.), and ammonium fluoride (70 g.) was added, with cooling and vigorous stirring, at such a rate that the temperature was kept below 35°. The addition took ½ hour, and stirring was continued for a further ½ hour. The mixture was poured on ice, and the upper layer was washed, dried (Na_2SO_4), and fractionated, to give *methyldi*-n-*propylfluorosilane* (44 g., 60% on tetraethoxysilane taken), b. p. 130·2°/760 mm., n_D^{19} 1·3942 (Found : F, 13·0, 13·0%; *M*, 146, 142. $C_7H_{17}SiF$ requires F, 12·8%; *M*, 148). The fluoride has a pleasant, sweet odour.

Ethoxytri-n-*propylsilane.*—Sodium (3 g.) was dissolved in dried ethyl alcohol (70 ml.), and tri-*n*-propylfluorosilane (21 g.) was added. After 10 minutes, light petroleum (b. p. <40°; 50 ml.) was added, and the precipitate was allowed to settle. Water (400 ml.) was added, and the light petroleum layer was shaken several times with water, dried, and distilled. After removal of the solvent almost all the residue distilled at 201—205°, with the bulk at 203°. Redistillation of the middle fraction (15 g.) gave *ethoxytri*-n-*propylsilane* (10 g., 42%), b. p. 203·0°, $n_D^{13·6}$ 1·4288 (Found : C, 65·6; H, 12·8. $C_{11}H_{26}SiO$ requires C, 65·3; H, 12·9%). The yield of unpurified material (b. p. 201—205°) was almost theoretical.

Tri-n-*propylchlorosilane.*—Tri-*n*-propylethoxysilane (7 g.) was added to acetyl chloride (16 ml.). No visible reaction took place on mixing. After 10 minutes' gentle boiling, excess of acetyl chloride was distilled off. The residue boiled at 200—204°. Redistillation gave *tri*-n-*propylchlorosilane* (6·5 g., 85%) b. p. 202·0°, $n_D^{16·5}$ 1·442 (Found : C, 56·5; H, 11·2; Cl, 18·6. $C_9H_{21}SiCl$ requires C, 56·1; H, 11·0; Cl, 18·4%). The liquid does not fume in the air, but fumes are detectable when aqueous ammonia is brought near; it reacts relatively slowly with water, and rapidly with alcohol.

Triethyliodosilane.—Triethylsilane (22 g.) was added dropwise to iodine (48 g.) contained in a 250-ml. three-neck flask fitted with dropping funnel, nitrogen inlet, and a reflux condenser with a calcium chloride tube at its exit. Gentle reflux was maintained by the heat of reaction during the addition (¼ hour), and much hydrogen iodide was evolved. When addition was complete the mixture was boiled under reflux for a further ¼ hour, with carefully-dried nitrogen bubbling through the liquid to carry off hydrogen iodide. Further triethylsilane (*ca.* 1 g.) was added to remove the remaining iodine, and refluxing, with passage of nitrogen, was continued for ¼ hour. After the addition of a little magnesium powder, the liquid was fractionated in a column pre-flushed with nitrogen, with protection from light. Triethyliodosilane (41 g., 85%) boiled (constantly) at 190·5°/744 mm. (Found : C, 30·0; H, 6·4; I, 52·8. $C_6H_{15}SiI$ requires C, 29·75; H, 6·2; I, 52·4%). The density of the liquid is *ca* 1·4.

Action of Aluminium Iodide on Tetraethylsilane.—(*a*) Aluminium iodide (30 g., 0·073 mol.) was boiled with anhydrous benzene (90 ml.). Tetraethylsilane (10 g., 0·07 mol.) was added, and the mixture was boiled under reflux for 2 hours. Water was carefully added, with ice-cooling, and the benzene layer was washed, dried, and distilled. Hexaethyldisiloxane (8·0 g., *ca.* 90%), b. p. 230—234°, n_D^{19} 1·4345, was obtained.

(*b*) Aluminium iodide (22 g., 0·054 mol.) was boiled under reflux with tetraethylsilane (7·2 g., 0·05 mol.) for 3 hours. On distillation of the mixture in nitrogen, tetraethylsilane (6·4 g.), b. p. 152—154°, was recovered, no liquid of higher boiling point being obtained.

Action of Iodine with Aluminium or Aluminium Iodide on Tetraethylsilane.—These reactions were carried out in a nitrogen atmosphere. (*a*) In a typical experiment, aluminium powder (0·2 g.) and iodine (2 g.) were added to tetraethylsilane (14·4 g.). The iodine was used in 20 minutes' boiling under reflux. Further 2-g. portions of iodine were used in a few minutes' boiling. When the calculated amount of iodine (25·4 g.) had been used up (total time, 1½ hours), the mixture was distilled, to give ethyl iodide (14·5 g., 95%), b. p. 70—74°, and triethyliodosilane (16 g., 65%), b. p. 186—191°. A little triethylfluorosilane was added to the triethyliodosilane (to remove aluminium iodide), and redistillation gave 14 g., b. p. 187—191° (Found : I, 52·8. Calc. for $C_6H_{15}SiI$: I, 52·4%). Hydrolysis by aqueous potassium hydroxide, followed by the usual treatment with ammonium fluoride in concentrated sulphuric acid, gave triethylfluorosilane (6 g.), b. p. 107—110°, $n_D^{19·5}$ 1·3915.

(*b*) In a similar experiment with aluminium iodide (0·2 g.) along with the aluminium, the first 2 g. of iodine were used in *ca.* 5 minutes' boiling, and the reaction proceeded as before.

(*c*) In an experiment with aluminium iodide alone as catalyst, iodine (2 g.) and aluminium iodide (0·4 g., containing a small amount of free iodine) were added to tetraethylsilane (7·2 g.). The iodine was used in a few minutes' boiling. The remaining iodine (10·7 g.) was added in 2-g. portions as it was used, ethyl iodide being distilled off continuously from the top of the reflux air-condenser. Reaction was complete in ¾ hour. Ethyl iodide (7·2 g., *ca.* 90%) and triethyliodosilane (9·6 g., 77%), b. p. 187—191° were obtained. Hydrolysis followed by fluorination gave triethylfluorosilane (*ca.* 3·5 g.), b. p. 107—110°.

Action of Iodine with Aluminium Iodide on Triethyliodosilane.—(*a*) In an early experiment, tetraethylsilane (14·4 g., 0·1 mol.) was boiled under reflux with aluminium powder (0·2 g.) and iodine was added in 2-g. portions, as used. After 15 g. of iodine had been used, and again after 25 g. had been used, ethyl iodide was distilled off (total ethyl iodide, *ca.* 7·5 ml.). Further additions of iodine were made, and, with additions of aluminium powder from time to time, 37 g. (*ca.* 0·15 mol.) of iodine had been used in a total of 5 hours. After 50·8 g. (0·2 mol.) of iodine had been used (9 hours, a total of *ca.* 1·4 g. of aluminium having been added) the liquid was distilled off, all distilling at 98—102°/17 mm. On redistillation, the bulk (25 g.) distilled at 217—224°/760 mm., with 12 g. at 220—221°. The 220—221° fraction was redistilled, to give *diethyldi-iodosilane*, b. p. 85°/15 mm., 220—221°/760 mm. (*d ca.* 1·9). (Found : C, 13·9 ; H, 3·0 ; I, 75·2. $C_4H_{10}SiI_2$ requires C, 14·1 ; H, 3·0 ; I, 74·7%). Yield of unrefined material, 70%. Some of the material of b. p. 217—224° (20 g.) was added slowly to a solution of methylmagnesium iodide (0·2 mol.) in ether (50 ml.). Reaction was vigorous, and two layers formed quickly. After ¼ hour's vigorous stirring, 10% sulphuric acid was added, and the ethereal layer was washed, shaken with mercury to remove iodine, dried, and distilled, to give dimethyldiethylsilane (6·1 g., 87%), b. p. 93—97°.

(*b*) Triethyliodosilane (42 g., 0·174 mol.) was boiled under reflux with iodine (22 g., 0·087 mol.) and aluminium iodide (*ca.* 0·5 g.). Aluminium iodide (total, *ca.* 1·5 g.) was added from time to time as the reaction slowed down, as indicated by decrease in the rate of gas evolution. After 2½ hours, gas evolution ceased and the liquid became colourless. Distillation in nitrogen gave 54 g. (90%) of material boiling at 216—223°. Redistillation in nitrogen, after the addition of a little triethylfluorosilane, gave diethyldi-iodosilane (40 g.), b. p. 219—222° (Found : I, 75·1%).

(*c*) The exit from the reflux condenser was connected through a sulphuric acid bubbler to a cylinder in which gas could be collected over water. Triethyliodosilane (12 g., 0·05 mol.) was boiled with aluminium iodide (0·4 g.) until escape of gas caused by expansion had ceased, and iodine (6·3 g., 0·025 mol.) was added. The iodine was used in 1½ hours' boiling, and 590 ml. (N.T.P.) of gas were collected. (0·025 Mol. of hydrocarbons would occupy 560 ml. The gas was heavier than air, and burned with a quiet, blue flame, depositing no silica or iodine.) Distillation gave diethyldi-iodosilane (14·5 g., 85%), b. p. 217—224°.

Action of Iodine with Aluminium Iodide (*or Aluminium*) *on Other Tetra-alkylsilanes.*—(Iodine was usually added in several portions to a reaction mixture, a further amount being added only after the disappearance of the colour of the previous portion.) (a) *On methyltri-*n*-propylsilane.* Connection was made from the top of the reflux air-condenser to a water-cooled condenser and a receiver, and then, through a sulphuric acid bubbler, to a gas-collecting cylinder (collection over water). Iodine was added in approx. 6-g. lots to boiling methyltri-*n*-propylsilane (34·5 g., 0·2 mol.) containing aluminium iodide (0·2 g.). After 20 minutes, aluminium powder (0·3 g.) was added, because the reaction had slowed down, as indicated by the decrease in the rate of gas evolution. After 1¼ hours 25·5 g. (0·1 mol.) of iodine had been used, and 3·5 g. of *n*-propyl iodide and 1·4 l. of gas (of properties similar to those described for the gas from the diethyldi-iodosilane preparation above) had been collected. Further iodine (3 g.) was added to replace that used by the propyl iodide, and that lost by reaction with the aluminium. All the iodine had been used in a total reaction time of 1½ hours, and *ca.* 4·5 g. of propyl iodide and 1700 (± 150) ml. of gas had been collected. On distillation in nitrogen, all the liquid boiled between 190° and 237°, with *ca.* 9 ml. at 190—220° (methyldi-*n*-propyliodosilane boils at 200—204°) and *ca.* 25 ml. at 225—236° (tri-*n*-propyliodosilane boils at 235°). The distillate was shaken with concentrated aqueous potassium hydroxide until free iodine had been removed, and the upper layer was washed, separated, and added to concentrated sulphuric acid (100 ml.), with cooling. Ammonium fluoride (35 g.) was added, with cooling and vigorous stirring during ½ hour (temperature kept <35°) and the mixture was stirred for a further ½ hour. It was then poured on ice, and the upper layer was washed, dried (Na_2SO_4) and fractionated. Hexa-*n*-propyldisiloxane (*ca.* 6 ml.), which had been used to wash the sodium sulphate, was employed as a "chaser." Methyldi-*n*-propylfluorosilane (8·5 g., 0·0574 mol.) distilled at 130—132°, $n_D^{18\cdot5}$ 1·3936 (slightly impure), and tri-*n*-propylfluorosilane (20 g., 0·114 mol.) distilled at 175·0°, n_D^{20} 1·4118, with 3 g. of liquid at 132—174°. Mol. ratio, $Pr_2MeSiF : Pr_3SiF = 1 : 2\cdot0$.

(b) *On dimethyldiethylsilane.* (*i*) Iodine (60 g., 0·236 mol.) was added in 10-g. portions to boiling dimethyldiethylsilane (33 g., *i.e.*, excess) containing aluminium (0·2 g.) and aluminium iodide (0·2 g.). Liquid of b. p. <70° was allowed to distil off from the top of the reflux condenser from time to time. In 3 hours all the iodine had been used up, *ca.* 18 ml. of low-boiling liquid had distilled off, and a little gas (<200 ml.) had been evolved. The residue (*ca.* 45 g.) was distilled in nitrogen from 130—190°. Fractionation of the low-boiling liquid gave 0·5 ml. of b. p. 26—28° (tetramethylsilane formed by redistribution ?), methyl iodide (20 g.), b. p. 40—41°, and ethyl iodide (10·2 g.), b. p. 71—73°, with *ca.* 2 g. of liquid at 41—55°, and *ca.* 2 g. at 50—68°. If the 41—55° fraction is assumed to be mainly methyl iodide, and the 55—68° fraction ethyl iodide, MeI : EtI = 22 : 12 g. = 0·155 : 0·077 mol. = 2 : 1 mol. The 130—190° distillate was fractionated; the only constant-boiling product distilled at 169° (6 g.) and had an iodine content of 58·8% (Calc. for Et_2MeSiI : 55·6%). The whole of the distillate of b. p. 130—190° was hydrolysed with aqueous potassium hydroxide, and the product was fluorinated in concentrated sulphuric acid in the usual way. The sulphuric acid solution was poured on ice, the organosilicon material was extracted with toluene, and the toluene layer was dried and fractionated. Dimethylethylfluorosilane (2 g.) boiled at 50—51°/574 mm. and had n_D^{17} 1·3582 (impure). Liquid (4·5 g.) boiling at 80—82°/754 mm. and having n_D^{17} 1·3820, was probably methyldiethylfluorosilane. The low yield of alkylfluorosilanes is attributed to the solubility of the corresponding siloxanes (or silanols) in the strong alkali used for hydrolysis. (*ii*) In a similar experiment involving dimethyldiethylsilane (22 g.), iodine (48 g.), and aluminium (0·3 g.), methyl iodide (16·0 g.) and ethyl iodide (9·5 g.) were obtained (mol. ratio, 1·85 : 1). A fraction (5 g.), b. p. 136—144°, contained 58·4% of iodine (Calc. for

EtMe$_2$SiI : 59·3%), and a fraction, b. p. 161—166° (8 g.) contained 56·8% of iodine (Calc. for Et$_2$MeSiI : 55·6%).

(c) *On methyltriethylsilane.* (*i*) Iodine (52 g.) was added in *ca.* 5-g. portions to boiling methyltriethylsilane (30 g. ; excess) containing aluminium iodide (*ca.* 1 g.). Liquid was allowed to distil off from the top of the reflux condenser from time to time. There was no gas evolution during refluxing. All the iodine had been used in 2½ hours, and liquid was then allowed to distil off from the top of the condenser up to 105° (total wt. of low-boiling liquid, 29 g.). This liquid was fractionated, with bromobenzene as " chaser," to give methyl iodide (10·2 g., 0·072 mol.) and ethyl iodide (16·5 g., 0·105 mol.). The main residue of alkyliodosilanes was shaken with excess of aqueous potassium hydroxide, and the hydrolysis product was dried, added to concentrated sulphuric acid (100 ml.), and fluorinated in the usual way, the temperature being kept below 20°. Fractionation of the product gave 5 g. of liquid, b. p. 81—83°, n_D^{21} 1·3738 (probably impure methyldiethylfluorosilane), and triethylfluorosilane (9 g.), b. p. 109°, n_D^{19} 1·3915. The yield of triethylfluorosilane agrees with that expected from the amount of methyl iodide formed. The low yield of methyldiethylfluorosilane probably arises from the solubility of the hydrolysis product of methyldiethyliodosilane in the strong alkali used to effect hydrolysis. (*ii*) In a separate experiment, in which iodine (34 g.) was added to methyltriethylsilane (18 g.) containing aluminium powder (0·2 g.) and aluminium iodide (0·2 g.), the iodine was used in 2 hours, and distillation gave 16 g. of liquid boiling below 80°, 18 g. at 125—180°, and 12 g. at 184—195°. Hydrolysis and fluorination of the liquid boiling above 125° gave, on distillation, 3·5 g. of liquid, b. p. 79—85°, and triethylfluorosilane (6·5 g.), b. p. 107—109°.

(d) *On dimethyldi*iso*propylsilane.* Iodine was added in *ca.* 4-g. portions to boiling dimethyldi*iso*propylsilane (21 g.) containing aluminium iodide (1 g.). There was a definite gas evolution, but this could not be conveniently measured because liquid (b. p. 45°) was allowed to distil off from the top of the reflux condenser from time to time. After 28 g. of iodine had been used (1½ hours), a further 3 g. did not disappear completely on ½ hour's boiling, but further dimethyldi*iso*propylsilane (1 g.) removed the colour in a few minutes. [If it is assumed that the slowing of the reaction coincided with the formation of the maximum amount of trialkyliodosilanes, then *ca.* 31 g. (0·122 mol.) of iodine were required to displace 0·153 mol. of alkyl group from 22 g. (0·153 mol.) of dimethyldi*iso*propylsilane; thus, 0·056 mol. of the tetra-alkylsilane has reacted to give gas, and the yield of alkyl iodides should be *ca.* 0·091 mol.] All the liquid removed from the top of the condenser boiled, on redistillation, at 43—44°, and was methyl iodide (12·5 g., 0·088 mol.). The residue from the reaction was distilled to give 6 g. of a liquid, boiling at 140—194°, and 32 g. at 194—201°, with the bulk (20 g.) at 198—201°. The 198—201° fraction was boiled for ¼ hour with tri-*n*-propylfluorosilane (1 g.) to remove any aluminium iodide, and redistilled to give *methyldi*iso*propyliodosilane* (18 g.), b. p. 200—201° (Found : I, 49·8. C$_7$H$_{17}$SiI requires I, 49·6%). Most (25 g.) of the product of the main reaction boiling between 194° and 201° was hydrolysed with aqueous potassium hydroxide; the hydrolysis product was dissolved in concentrated sulphuric acid (100 ml.) and fluorinated with ammonium fluoride (35 g.), the temperature being kept below 35°. The product was separated in the usual way, and on fractionation, with tri-*n*-propylfluorosilane as " chaser ", gave *methyldi*iso*propylfluorosilane* (10 g., 68%), b. p. 124·5°/760 mm., n_D^{21} 1·3958 (Found : F, 12·9, 12·7%; *M*, 144. C$_7$H$_{17}$SiF requires F, 12·9%; *M*, 148). The liquid, as obtained, had a slight pink colour, but this was removed by shaking it with antimony powder, followed by redistillation, without appreciable change in b. p. or refractive index.

(e) *On phenyltrimethylsilane.* Iodine (13·5 g.) was added in 2-g. portions to boiling phenyltrimethylsilane containing aluminium (0·2 g.) and aluminium iodide (0·1 g.). All the iodine was used in 30 minutes. Distillation in nitrogen gave 8·5 g. of liquid boiling at 106—120°, and 7 ml. at 180—190°. The latter fraction was washed with alkali, followed by water, dried, and redistilled. Iodobenzene (10 g., 92%) boiled at 184—188°, having n_D^{19} 1·6180. Of the 106—120° fraction, a sample of b. p. 106—110° contained only 58% of iodine, and a sample at 110—120° contained 63·0% of iodine (Calc. for Me$_3$SiI : 63·4%. Its b. p. is 106·5°; Pray *et al.*, *loc. cit.*). There was insufficient of the crude trimethyliodosilane to attempt purification. The samples obtained reacted with water much more vigorously than did triethyliodosilane.

Reaction of Alkylfluorosilanes with Aluminium + Iodine.—(*a*) *Triethylfluorosilane.* Iodine was added in 2-g. portions to boiling triethylfluorosilane (14 g.) containing aluminium powder (0·4 g.). After *ca.* 6 g. of iodine had been used, addition of a little more aluminium from time to time (total wt. *ca.* 1·2 g.) was necessary to remove the colour of more iodine. In 7 hours, 13 g. of iodine had been used. The liquid was distilled off from the grey solid which had formed; 21 g. distilled at 75—80°/17—20 mm. On redistillation, triethyliodosilane (18 g., 75%) distilled at 190—191°/755 mm. (Found: I, 53·1%). Treatment with methylmagnesium iodide (excess) in the usual way gave methyltriethylsilane, (5 g., 77%), b. p. 125°—128°/760 mm., n_D^{19} 1·4168.

(*b*) *Tri*-n-*propylfluorosilane.* Iodine (7 g.) was added in 3 portions to boiling tri-*n*-propylfluorosilane (10 g.) containing aluminium (0·5 g.). The iodine was used in 1 hour. The liquid was boiled for a further 1½ hours and then distilled. The bulk of the liquid (12 g.) boiled at 228—235°, with *tri*-n-*propyliodosilane* (7·5 g., 46%) (constant) at 235°, *d ca.* 1·2 (Found : I, 44·4. C$_9$H$_{21}$SiI requires I, 44·7%). The identity of the compound was confirmed by its reaction with silver cyanide (see below).

Reaction of Alkylfluorosilanes with Aluminium Iodide.—(a) *Triethylfluorosilane.* This (10 g.) was added to aluminium iodide (9·5 g.). Heat was developed during the addition. The liquid was heated under reflux for 1 hour and then distilled in nitrogen. No liquid boiled below 182°, and triethyliodosilane (10 g., 59%) boiled from 186 to 192°. A sample boiling at 189—191° contained 52·2% of iodine.

(b) *Tri*-n-*propylfluorosilane.* Tri-*n*-propylfluorosilane (10 g.) was boiled with aluminium iodide (7·5 g.) for ½ hour. The liquid was distilled off in nitrogen; all distilled at 226—234°. Redistillation, after addition of a little tri-*n*-propylfluorosilane, gave tri-*n*-propyliodosilane (11 g., 70%) at 231—234° (Found : I, 45·2%). The whole of the iodide available (b. p. 225—235°; 13·0 g.) was shaken several times with water, dried, and distilled, to give hexa-*n*-propyldisiloxane (6 g., 76%), b. p. 282—286°.

(c) *Methyldi*-n-*propylfluorosilane.* Methyldi-*n*-propylfluorosilane (14 g.) was boiled with coarsely-powdered aluminium iodide (13·6 g.). In the first few minutes' boiling a bulky finely-divided solid (aluminium fluoride) was formed. After ½ hour, further methyldi-*n*-propylfluorosilane (3 g.; excess) was added and boiling was continued for 20 minutes. Distillation gave 4 ml. of liquid, b. p. 130—145° (mainly the excess of methyldi-*n*-propylfluorosilane) and 13 g. of liquid, b. p. 195—205°. Redistillation of the latter fraction, after addition of a little methyldi-*n*-propylfluorosilane, gave *methyldi-*n*-propyliodosilane* (5 g., 25%), b. p. 200—204° (Found: I, 49·5. $C_7H_{17}SiI$ requires I, 49·6%). The yield of the impure iodide (b. p. 198—205°) was 12·5 g. (50%); this material was added to red mercuric oxide (8 g.), an immediate reaction occurring with development of heat and formation of mercuric iodide. The liquid was boiled under reflux for ¼ hour. Distillation gave *ca.* 2·5 g. of liquid, b. p. 245—255° (probably impure *s*-dimethyltetra-*n*-propyldisiloxane).

(d) *Di*iso*propyldifluorosilane.* Di*iso*propyldifluorosilane (8 g.) was boiled with aluminium iodide (17 g.) in a nitrogen atmosphere. After 1 hour, further di*iso*propyldifluorosilane (2 g.) was added, and boiling was continued for 1 hour. On distillation in nitrogen, all the liquid (18 g.) boiled at 235—256°, with the bulk (14 g.) at 246—254°. Redistillation, after the addition of a little di*iso*propyldifluorosilane, gave *di*iso*propyldi-iodosilane* (8 g., 33%), b. p. 252—254°, *d ca.* 1·8 (Found: I, 69·4. $C_6H_{14}SiI_2$ requires I, 69·0%). The liquid, b. p. 246—256° (14 g., 55%), was added to absolute alcohol (30 ml.) containing pyridine (10 ml.), with cooling in a solid dioxide–acetone bath. (Much heat was developed, although the reaction of this organosilicon iodide with alcohol alone is not particularly vigorous.) Pyridine hydriodide (*ca.* 14 g.; after drying) was filtered off, and the filtrate was added slowly to water through a layer of light petroleum (b. p. <40°). The light petroleum layer was washed with water, dried, and distilled, to give di*iso*propyldiethoxysilane (4 g., 53%), b. p. 185—188°, $n_D^{14\cdot5}$ 1·4162.

(e) *Dimethylethylfluorosilane.* Aluminium iodide (13·6 g.) was added to dimethylethylfluorosilane (11 g.). Heat was developed and the liquid refluxed for a short time without external heating. The mixture was heated under reflux for 6 hours in a nitrogen atmosphere. Distillation in nitrogen gave unchanged dimethylethylfluorosilane (4 g.), b. p. 49—52°, and 6 g. of liquid, b. p. 130—138°. The fraction, b. p. 134—136°, contained 59·3% of iodine (Calc. for Me_2EtSiI: 59·3%). When this experiment was repeated, however, with 18 hours' boiling in an attempt to effect the complete reaction, dimethylethylfluorosilane (3 g.) was recovered, and the residue (17 g.) distilled at 130—153°. The 136—138° fraction (3 g.) contained only 56·1% of iodine; a fraction (6 g.) boiling at 148—153° contained 59·3% of iodine.

Action of Lithium Iodide on Triethylfluorosilane.—Lithium iodide (10 g.; dried by fusion at 20 mm., with connection to a trap cooled to −80°) was coarsely powdered and added to triethylfluorosilane (10 g.). A thermometer in the liquid boiling under reflux showed no appreciable change in b. p. during 8 hours. After this time the solid was filtered off and found to be completely soluble in water (*i.e.*, no lithium fluoride was present). The filtrate (which did not fume) was washed with water, dried, and distilled, to give unchanged triethylfluorosilane (8 g.), b. p. 107—110°, n_D^{18} 1·3920.

*Action of Aluminium Chloride on Tri-*n*-propylfluorosilane.*—Tri-*n*-propylfluorosilane (9 g.) was added to coarsely-powdered aluminium chloride (2·2 g.). Heat was developed on mixing. The liquid was boiled gently under reflux, much gas being evolved. This gas fumed in the air and burned with a smoky, green-tipped flame. When gas evolution had ceased (¼ hour), the liquid was distilled. The bulk (6·5 g.) boiled at 199—204°/770 mm. The fraction, b. p. 202—204°, $n_D^{16\cdot5}$ 1·435, gave 17·0% of Cl′ on hydrolysis and was evidently impure tri-*n*-propylchlorosilane (b. p. 202°; $n_D^{16\cdot5}$ 1·442; Cl, 18·4%).

Action of Magnesium on Triethyliodosilane.—(a) *In ether.* A mixture of triethyliodosilane (14 g.), ethyl ether (30 ml.), and magnesium turnings (1 g.) was boiled under reflux for 18 hours, after addition of methyl iodide had produced a cloudiness but failed to induce general reaction. After a further 48 hours at room temperature, the liquid was decanted from the magnesium (which had become coated with a white powder), and the ether was distilled off. A white solid was left in the liquid residue. This residue boiled at 175—198°, with 11 g. at 186—194°. Hydrolysis, to give hexaethyldisiloxane, b. p. 230—236°, confirmed that the 186—194° fraction was mainly unchanged triethyliodosilane. The white solid residue from the distillation was soluble in water with evolution of heat, and did not burn or melt, but gave iodine when heated, and was probably magnesium iodide (which may result from reaction of the alkyiodosilane with the solvent).

In a second experiment, the same quantities of materials were employed, and after being heated for a similar length of time the whole of the liquid was decanted and treated with dilute sulphuric acid. The ethereal layer was quickly separated, dried, and distilled, to give 2 ml. of liquid, b. p. 160—225°, and 5 ml., b. p. 225—235°, n_D^{16} 1·4345 (impure hexaethyldisiloxane). None of the fractions gave gas with alcoholic alkali.

The initial bubbling which always occurred when triethyliodosilane was added to magnesium in ether was shown to arise from an impurity in the ether, by allowing the bubbling to die away and then adding a further volume of ether which caused bubbling to recommence. The ether (a commercial product, "Distilled from sodium") presumably contained small amounts of water or alcohol.

(b) Triethyliodosilane (13 g.) was boiled under reflux with magnesium (1·6 g.) for 25 hours, with no protection from the light. A white powder separated. On distillation, the b. p. rose steadily from 194—215°; the liquid of b. p. 194—197° (3 ml.) was of too low density (*ca.* 1·2) to be unchanged triethyliodosilane. After being shaken with water, none of the fractions gave gas with alcoholic alkali. The white powder (probably magnesium iodide) was dissolved in water, leaving unchanged magnesium (1·4 g.).

Action of Iodine on Triethyliodosilane and Magnesium in Ether.—When iodine was added to triethyliodosilane (11 g.) and magnesium in ether (35 ml.) a vigorous reaction began. Iodine and magnesium were added from time to time, with renewed reaction on each addition, but when 25 g. of iodine and 2·4 g. of magnesium had been consumed addition was discontinued. On cooling, much solid separated in transparent crystals, which were soluble in water with evolution of heat, leaving no residue. Water was added carefully to the reaction mixture, and the ethereal layer was washed with alkali, dried, and distilled, to give hexaethyldisiloxane (5 g., 90%), b. p. 231—233°, $n_D^{25\cdot5}$ 1·4325.

Triethyl(iso)*cyanosilane.*—Triethyliodosilane (18 g.) was added to silver cyanide (18 g.). Heat was developed, and the solid became bright yellow. The liquid was boiled under reflux gently in nitrogen for 1½ hours. Distillation in nitrogen gave 11 ml. of liquid, b. p. 179—184°. On redistillation from a little silver cyanide, *triethyl*(iso)*cyanosilane* (6 g., 57%), b. p. 181·0—182·0° (*d ca.* 0·9), was obtained (Found : C, 59·9; H, 10·7; CN, 18·2. $C_6H_{15}SiCN$ requires C, 59·5; H, 10·7; CN, 18·4%). Cooling in ice gave a solid, m. p. 4·5—5·5°. The liquid was vigorously attacked by aqueous alkali and, particularly, by alcohol.

Triethyl(*iso*)cyanosilane (5 g.) was added to mercuric oxide (7 g.). There was no visible reaction in the cold. The mixture was heated under gentle reflux for 3 hours, and the liquid distilled off. Hexaethyldisiloxane (2·5 g.), b. p. 230—234°, $n_{\rm D}^{20}$ 1·4345 (after redistillation), was obtained.

Tri-n-*propyl*(iso)*cyanosilane*.—Tri-*n*-propyliodosilane (6 g., from reaction of tri-*n*-propylfluorosilane with aluminium and iodine) was added to silver cyanide (10 g.). The solid quickly became bright yellow, but blackened on boiling of the liquid.

After 1 hour's gentle refluxing, distillation gave 5 ml. of liquid, all of b. p. 224—234°. Redistillation from a little silver cyanide gave *tri*-n-*propyl*(iso)*cyanosilane* (2 g., *ca.* 50%), b. p. 228—230°/755 mm., m. p. −10° to −8° (Found: C, 65·5; H, 12·0; CN, 14·4. $C_9H_{21}SiCN$ requires C, 65·5; H, 11·6; CN, 14·2%).

Diethyldi(iso)*cyanosilane*.—Diethyldi-iodosilane (34 g.) was boiled gently under reflux with silver cyanide (28 g.). Distillation from the bright yellow solid gave 16 ml. of liquid all boiling between 205° and 216°. The distillate, b. p. 209—216° (*ca.* 10 ml.), was boiled gently with a little silver cyanide (2 g.) for ¼ hour and then distilled. *Diethyldi*(iso)*cyanosilane*, b. p. 212—214°, m. p. 29—33° (3 g.), was obtained [Found : C, 52·7; H, 7·6; CN, 37·2. $C_4H_{10}Si(CN)_2$ requires C, 52·2; H, 7·3; CN, 37·6%]. This material reacts so violently with water that for analysis the solid was added to frozen aqueous potassium hydroxide in a closed flask, and melting was allowed to occur very slowly. The solid quickly liquefies when exposed to the atmosphere.

Action of Methylmagnesium Iodide on Diethyldi(iso)*cyanosilane*.—Diethyldi(*iso*)cyanosilane (8 g.) in ether (15 ml.) was added dropwise to methylmagnesium iodide (0·2 mol.) in ether (50 ml.). Vigorous reaction occurred. The addition was made during ½ hour, at such a rate that refluxing was maintained. The mixture became viscous, and so further ether (30 ml.) was added. After a further ½ hour's vigorous stirring, 10% sulphuric acid was added until two clear layers separated. The ethereal layer was dried and fractionated, with tetraethylsilane as " chaser ", to give dimethyldiethylsilane (3·5 g., 54%), b. p. 95·5°/760 mm., $n_{\rm D}^{18}$ 1·4020.

Action of Silver Cyanide on Tri-n-*propylchlorosilane*.—Tri-*n*-propylchlorosilane (10 g.; b. p. 200—203°) was added to silver cyanide (13 g.). After 1½ hours' refluxing the liquid distilled as follows : 7 g. at 199—203°; 1 g. at 203—206°. The last fraction gave a little cyanide ion on hydrolysis, but the other fractions did not; evidently the tri-*n*-propylchlorosilane was largely unchanged.

The author thanks Prof. E. D. Hughes, F.R.S., and Professor L. Hunter for their interest and advice. He is indebted to the Research Department of Wolsey Ltd. for a gift of dimethyldichlorosilane, and to the Chemical Society for a grant towards the purchase of chemicals.

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[*Received, July* 15*th*, 1949.]