601. *Organosilicon Compounds. Part II. A "Conversion Series" for Organosilicon Halides, Pseudohalides, and Sulphides.*

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Interactions of triethylsilicon and trimethylsilicon halides, pseudohalides, and sulphides with silver salts have been examined, and the "conversion series," $R_3SiI \longrightarrow (R_3Si)_2S \longrightarrow R_3SiBr \longrightarrow R_3SiNC \longrightarrow R_3SiCl \longrightarrow R_3SiNCS \longrightarrow R_3SiNCO$, has been established. A compound may be converted into any other on its right in good yield by boiling it with the appropriate silver salt, but cannot be appreciably converted in this way into a compound on its left (except that some conversion $R_3SiCl \longrightarrow R_3SiNC$ occurs). Possible extensions of these series are discussed, and it is suggested that the "conversion series," $\equiv SiI \longrightarrow (\equiv Si)_2S \longrightarrow \equiv SiBr$ ($\longrightarrow \equiv SiH$) $\longrightarrow \equiv Si{\cdot}NC$ and $\equiv SiCl \longrightarrow \equiv Si{\cdot}NCS \longrightarrow \equiv Si{\cdot}NCO \longrightarrow (\equiv Si)_2O$ and $\equiv SiF$, may be general for interactions of silicon and organosilicon compounds with metallic salts. The series is discussed in terms of the solubilities of the salts and of "ionic bond energies." A "stability series" based on these "ionic bond energies." is proposed for silicon compounds. The first organosilicon sulphides are reported.

In the past few years the interaction of silver pseudohalides and organosilicon chlorides, usually in benzene, has been used to prepare organosilicon pseudohalides, R_xSiX_{4-x}, where $X = {}^-NCO$ or ${}^-NCS$, and R = alkyl or phenyl (Forbes and Anderson, *J. Amer. Chem. Soc.*, 1948, **70**, 1043, 1222; Anderson, *ibid.*, 1947, **69**, 3049; 1948, **70**, 1220; 1949, **71**, 1801; 1950, **72**, 196). Recently the range of organosilicon pseudohalides has been extended to include (*iso*)cyanides by utilizing the interaction of organosilicon iodides and silver cyanide in the absence of solvent (Part I of this series, *J.*, 1949, 2755). The present investigation began when hexaethyldisilthian,*

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* For the nomenclature disilthian for $H_3Si{\cdot}S{\cdot}SiH_3$ see *Compt. rend.* XV*th Conference, Internat. Union Pure Appl. Chem.* (Amsterdam), 1949, p. 127.

$(Et_3Si)_2S$, prepared by interaction of silver sulphide and triethyliodosilane in the absence of a solvent, was found to be almost quantitatively converted into triethylchlorosilane by silver, lead, or cadmium chloride. The reactions of hexaethyldisilthian and of all the known triethylsilyl halides and pseudohalides with silver salts were examined, to see which conversions were possible and which impracticable.

Conversion Series for Triethylsilicon Derivatives.—As has been briefly reported (*Nature*, 1950, **165**, 685), it was found that conversions take place either almost completely or inappreciably (with the exception noted below), and that the compounds fall into a well-defined series :

$$Et_3SiI \longrightarrow (Et_3Si)_2S \longrightarrow Et_3SiBr \longrightarrow Et_3Si{\cdot}NC \longrightarrow Et_3SiCl \longrightarrow Et_3Si{\cdot}NCS \longrightarrow Et_3Si{\cdot}NCO$$

Any compound in this series may be converted into any other on its right by heating it with the appropriate silver salt. The yields, in the main, exceed 90%, exceptions being the preparation of hexaethyldisilthian from triethyliodosilane and of (*iso*)cyanotriethylsilane from chlorotriethylsilane. All the conversions except the last are probably almost quantitative, since no appreciable amounts of the original silicon compounds are recovered. A compound does not react with the appropriate silver salt to give detectable amounts of any compound on its left, except that the chloride is converted in small yield into the (*iso*)cyanide. Only in the case of the (*iso*)cyanotriethylsilane–chlorotriethylsilane conversion is there an equilibrium falling within the limits of detection on a preparative scale, and with these compounds it probably lies at >80% conversion into the chloride. Although the series has been investigated fully only for silver salts, it seems that in some cases other heavy metal salts may be employed. The conversions $(Et_3Si)_2S + PbCl_2$ or $CdCl_2 \longrightarrow Et_3SiCl$, $Et_3SiBr + CuCNS \longrightarrow Et_3Si{\cdot}NCS$, $Et_3Si{\cdot}NC + CuCNS \longrightarrow Et_3Si{\cdot}NCS$, for example, were successful. Mercuric salts are effective, but their volatility leads to contamination of the organosilicon product. Silver salts are undoubtedly the most generally satisfactory of those examined.

Generality of the Conversion Series.—A similar series $Me_3SiI \longrightarrow (Me_3Si)_2S \longrightarrow Me_3SiBr \longrightarrow Me_3Si{\cdot}NC \longrightarrow Me_3SiCl \longrightarrow Me_3Si{\cdot}NCS \longrightarrow Me_3Si{\cdot}NCO$ has been satisfactorily established for trimethylsilicon derivatives, although in this case not all the possible conversions of a compound to any other on its right were attempted, for it seemed sufficient to establish that a compound could be converted into the one immediately on its right. In the few additional cases examined, " forward " conversions were confirmed, and " backward " conversions found not to occur. [In this series, the equilibrium mixture of the (*iso*)cyanide and chloride over the silver salts appears to contain rather more of the (*iso*)cyanide than is the case in the triethylsilicon series.]

It is reasonable to expect similar series to apply to trialkylsilicon derivatives other than the triethyl and the trimethyl compounds, and it seems worth while to consider whether the order of the conversions may not apply generally to interactions of silicon and organosilicon derivatives with metallic halides in non-polar environments. Anderson has effectively demonstrated the generality of the reaction of R_xSiCl_{4-x} compounds ($x = 0$—3) with silver thiocyanate and silver cyanate (usually in benzene or a similar solvent, but often also in absence of solvent) to give high yields of the $R_xSi(NCS)_{4-x}$ and $R_xSi(NCO)_{4-x}$ compounds, where R may be not only an alkyl group, Me, Et, Pr^n, Pr^i, Bu^n, or benzyl, but also phenyl, methoxy, or ethoxy (*J. Amer. Chem. Soc.*, 1947, **69**, 3049; also *locc. cit.* and references therein). The conversions $Si_2OCl_6 + AgNCO \longrightarrow Si_2OSi(NCO)_6$, $Si_2OCl_6 + AgNCS \longrightarrow Si_2O(NCS)_6$, and $Si_3O_2Cl_8 + AgNCO \longrightarrow Si_3O_2(NCO)_8$ also take place (Forbes and Anderson, *ibid.*, 1947, **69**, 3048). Furthermore, the reactions $Et_2SiI_2 + AgCN \longrightarrow Et_2Si(NC)_2$ (Part I) and $Me_2Si(NCS)_2 + AgNCO \longrightarrow Me_2Si(NCO)_2$ take place, and di-iododimethylsilane reacts readily with silver sulphide and silver cyanide to give solid products which have not been fully investigated, but which are probably dimethylsilicon sulphide, $(Me_2SiS)_x$, and di(*iso*)cyanodimethylsilane respectively.

As for the inorganic silicon compounds, Mellor (" A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, 1940, pp. 967, 984, 986), records the following conversions : $Si_2I_6 + HgCl_2 \longrightarrow Si_2Cl_6$; $SiS_2 + HgCl_2 \longrightarrow SiCl_4$; $SiS_2 + Hg(CN)_2 \longrightarrow$ " silicon cyanide "; $SiCl_4 + Pb(CNS) \longrightarrow$ " silicon tetrathiocyanate "; and he records no reaction of a silicon compound with a metallic salt which contradicts the " conversion series " found for triethyl- and trimethyl-silicon derivatives. The interaction of iodosilane with silver cyanide to give " silyl cyanide, $SiH_3{\cdot}CN$," has been described by Emeléus, Maddock, and Reid, (*J.*, 1941, **353**), and the production of bromochlorosilanes by interaction of tetrabromosilane and the appropriate quantity of antimony trichloride has been described by Schumb and Anderson (*J. Amer. Chem. Soc.*, 1937, **59**, 651). Anderson has recently shown that the conversions $SiCl_3{\cdot}SH + AgNCO \longrightarrow Si(NCO)_4$, and $SiCl_2Br_2 + AgNCO \longrightarrow Si(NCO)_4$, take place in benzene (*ibid.*, 1950, **72**, 193).

As far as evidence is available, then, the nature of the other groups on the silicon atom appears not to affect the positions of the various halides, pseudohalides, and sulphides in the "conversion series," and it seems reasonable to regard the series $\equiv\text{SiI} \longrightarrow (\equiv\text{Si})_2\text{S} \longrightarrow \equiv\text{SiBr} \longrightarrow =\text{Si·NC}$ and $\equiv\text{SiCl} \longrightarrow \equiv\text{Si·NCS} \longrightarrow \equiv\text{Si·NCO}$ as of very wide applicability, if not, indeed, as a general one. The series would be contradicted, of course, only by evidence of transformations proceeding against the direction of the series; failure of an expected "forward" transformation cannot be regarded as particularly significant in view of physical factors (*e.g.*, low solubility or low rate of dissolution of the salt, and coating of the salt with an inactive compound) which might make the conversion very slow. In some cases special causes of the failure of expected transformations to take place may be suggested; for example, although lead chloride added to triethyliodosilane immediately becomes yellow, no further reaction occurs, possibly because of the formation of a coating of lead iodide on the chloride. Again, the fact that tetra*iso*thiocyanatosilane does not react with silver cyanate (Anderson, *J. Amer. Chem. Soc.*, 1950, **72**, 193), although successful transformation does occur with triethyl*iso*thiocyanatosilane, trimethyl*iso*thiocyanatosilane, or dimethyldi*iso*thiocyanosilane, may be attributable to steric hindrance, the case being analogous to the failure of tetrabromosilane to react with Grignard reagents (Wilkins, Brown, and Stevens, *J.*, 1950, 163).

Extension of the Series.—The possible extension of the "conversion series" on the right to include fluorides and oxides may be considered in view of the numerous examples of conversions of silicon and organosilicon chlorides into oxides and fluorides by metallic oxides and fluorides [*e.g.*, (oxides) Shaw, Smith, and Emblem, B.P., 606,301; Vyle and Kipping, *J.*, 1924, **125**, 2616; (fluorides) Emeléus and Wilkins, *J.*, 1944, 454; Schumb and Gamble, *J. Amer. Chem. Soc.*, 1932, **54**, 583; Booth *et al.*, *ibid.*, 1946, **68**, 2650 *et seq.*]. Furthermore, (*iso*)cyanotriethylsilane and triethyliodosilane are converted into hexaethyldisiloxan by mercuric oxide (Part I), hexaethyldisilthian and bromotriethylsilane are converted into hexaethyldisiloxan by zinc oxide. Triethyl*iso*thiocyanatosilane appears to give some hexaethyldisiloxan with zinc oxide; triethyl*iso*cyanatosilane is unaffected by zinc oxide, but probably gives hexaethyldisiloxan with mercuric oxide. Hexaethyldisiloxan is unaffected by silver cyanate.

Silicon bromides and iodides may be converted into fluorides by metallic fluorides (Schumb and Anderson, *ibid.*, 1936, **58**, 994; Anderson, *ibid.*, 1950, **72**, 193). Tetra*iso*cyanatosilane with antimony trifluoride gives tetrafluorosilane and *iso*cyanatofluorosilanes (Forbes and Anderson, *ibid.*, 1947, **69**, 1241). While in the present work *iso*cyanatotriethylsilane was not found to react with silver fluoride or zinc fluoride, triethylfluorosilane was found to be unaffected by silver cyanate, and it seems probable that, with appropriate metallic fluorides, all the other silicon halides, pseudohalides, and sulphides would be converted into the fluorides. The evidence available does not allow siloxans and fluorides to be separated in the "conversion series." In the present work triethylfluorosilane was unaffected by prolonged boiling with silver, mercury, or zinc oxides, and fluorotriphenylsilane (chosen for its high boiling point in an attempt to hasten any reaction) was unaffected by prolonged boiling with zinc oxide, whereas hexaethyldisiloxan was apparently slowly converted into a mixture of triethylfluorosilane and diethyldifluorosilane by mercurous, mercuric, zinc, and antimony fluorides, but it is not certain that the essential reactions were between the siloxan and the metallic salts (see Experimental section). Difluorodiphenylsilane is reported to give a trimer of diphenylsilanone ("diphenyl silicone") when boiled with zinc oxide (Shaw, Smith, and Emblem, F.P. 946,003), and gaseous silicon tetrafluoride is converted into silica or silicates by various metallic oxides (see Mellor, *op. cit.*, p. 939). It is probably advisable to group fluorides and siloxans together on the extreme right of the series.

The interaction of triethylsilane with silver salts was examined, and the interactions giving (*iso*)cyanotriethylsilane, triethyl*iso*thiocyanatosilane, and *iso*cyanatotriethylsilane were found to take place (with evolution of hydrogen), whereas no reaction takes place with silver sulphide or bromide. Very little reaction occurs with silver chloride, but reaction does occur with mercuric chloride, to give chlorotriethylsilane (the gas evolved in this case being apparently hydrogen chloride). Mellor (*op. cit.*, pp. 221, 939, 970) reports the reactions $\text{SiH}_4 + \text{SbCl}_5$ or $\text{SnCl}_4 \longrightarrow \text{Si}_2\text{Cl}_6$, $\text{SiHCl}_3 + \text{SbF}_3 \longrightarrow \text{SiF}_4$ (but $\text{SiHCl}_3 + \text{SnF}_4$ or $\text{TiF}_4 \longrightarrow \text{HSiF}_3$). It seems clear that in the conversion series the $\equiv$SiH group must be placed to the right of the $\equiv$SiBr and to the left of the $\equiv$Si·NC group, it being remembered, of course, that conversions of $\equiv$SiBr, $\equiv$SiI, and $(\equiv\text{Si})_2\text{S}$ compounds into $\equiv$SiH compounds by heavy-metal hydrides are not possible because of the instability of these hydrides. The extended conversion series may, then, be written:

$$\equiv\text{SiI} \longrightarrow (\equiv\text{Si})_2\text{S} \longrightarrow \equiv\text{SiBr} \longrightarrow (\equiv\text{SiH} \longrightarrow)$$

$$\overbrace{\equiv\text{Si·NC},\quad \equiv\text{SiCl}} \longrightarrow \equiv\text{Si·NCS} \longrightarrow \equiv\text{Si·NCO} \longrightarrow \overbrace{(\equiv\text{Si})_2\text{O},\quad \equiv\text{SiF}},$$

where $\equiv$Si·NC and $\equiv$SiCl have been written together because they form an equilibrium mixture over silver salts.

The Nature of the Interactions.—The experimental evidence allows no decision to be made with regard to the mechanism of the interactions. The silicon atom is particularly susceptible to nucleophilic attack, and it is probable that the reactions bear some analogy to the " halogen-exchange " reactions of organic chemistry, *i.e.*, that the determinant step in the interaction of a silicon compound, $\equiv$SiX, with a metal salt, MY, is the nucleophilic attack of the Y^- ion on the silicon atom. However, the fact that silver salts (and, as far as they have been examined, mercuric salts) are outstandingly effective suggests, by analogy with organic chemistry, that the metal ions play some significant part in the reactions, possibly assisting the separation of anions from silicon. The solid metallic salt may have a catalytic effect, but the fact that a particular interaction sometimes takes place more effectively in one solvent than another (Anderson, *locc. cit.*) suggests that the reaction is mainly between entities in solution. Support for this view is found in the fact that when a silicon *iso*cyanide and chloride form an equilibrium mixture over silver chloride and cyanide, the composition of this mixture is not affected by excess of either salt—as is to be expected if the solubilities of the salts govern their effective concentrations.

Factors governing the Order of the " Conversion Series."—Without any particular mechanism for the interactions being specified, it seems that the two factors most likely to govern the direction of a $\equiv\text{SiX} \longrightarrow \equiv\text{SiY}$ conversion are, first, the relative solubilities of the silver salts MX and MY, which determine the effective concentrations of the X^- and Y^- ions and, secondly, the relative affinities of silicon for X and Y.

Evidence that the solubilities of the salts, while they must be important, may not be the major factor determining the order of the " conversion series " is found in the following facts. (*a*) While silver salts are the most generally effective, salts of several metals (mercury, lead, cadmium, zinc, copper, and antimony) have been employed in particular conversions. It is to be expected that the relative solubilities of the various salts do not have the same values for all the metals concerned, and that if solubilities were the determinant factor the series established mainly for silver salts would be contradicted with salts of some other metals. (*b*) Only for the $\equiv\text{Si·NC} \longrightarrow \equiv\text{SiCl}$ interconversion is there a detectable equilibrium. More examples of such equilibria would be expected if salt solubilities determined the completeness of reactions. (*c*) If the solubilities of the silver salts in the organosilicon liquids retain the order found for water, *viz.*, $Ag_2S \ll AgI < AgBr < AgSCN < AgNC < AgCl < AgNCO$, then sulphides and thiocyanates fall markedly out of their expected places in a conversion series determined by solubilities. (*d*) Metal oxides, sulphides, and fluorides are normally highly insoluble, and yet are effective in conversions. (*e*) While triethylsilane is converted into triethylsilicon (*iso*)cyanide, *iso*thiocyanate, and *iso*cyanate by the appropriate silver salts, no reaction occurs with silver bromide, chloride, or sulphide, although it seems unlikely that the instability of silver hydride allows even a very small concentration of hydride ions to be maintained.

The affinity of silicon for the negative groups might be expected to be related to the various Si–X bond strengths, and the order of increasing Si–X bond energy (Sidgwick, " Chemical Elements and their Compounds," 1950, p. xxxi) shows a striking similarity to the " conversion series," *viz.*: Si–I, 51·1; Si–S, 60·9; Si–Br, 69·3; Si–H, 75·1; Si–Cl, 85·8; Si–O, 89·3; Si–F, 127·9 kcals. It was, in fact, from consideration of this order that the interactions of triethylsilane with silver salts were examined, and the compound was found to fall into the expected place in the conversion series. It is significant that tetraethylsilane, however, is not affected by silver salts and the Si–C bond (bond energy, 69·1 kcals.) does not fall into its place [Emeléus, Maddock, and Reid, (*J.*, 1941, 353) derived other values for some of these bond energies, mainly as a result of using a different value for the heat of atomization of silicon. Use of their values would necessitate little modification of the discussion below if all the bond energies were adapted to the alternative heat of atomization].

Such a simple relationship between bond energy and the direction of conversion must, however, be regarded as somewhat fortuitous, for in these reactions, involving ions, it seems highly probable that the Si–X bond breaks heterolytically and not to give atoms. A measure of the energy necessary to break the various Si–X bonds into Si^+ and X^- (called by Remick the " ionic bond energy ") is obtained by adding to the bond energy the ionization potential of silicon (187·1 kcals./g.-mol.) and subtracting the electron affinity of the group X (cf. Remick, " Electronic Interpretation of Organic Chemistry," 1943, p. 223). The results are shown in the Table.

In utilizing the " ionic bond energies " it has to be assumed that they are not greatly affected by the nature of the other groups on the silicon atom, or by ion-solvation in weakly polar media. The figures for the Si–S and Si–O bonds apply strictly to compounds of the type $\equiv$Si·SH, $\equiv$Si·OH. They can be extended to Si·SAlkyl, and Si·OAlkyl compounds, and to the breaking of one bond in $\equiv$Si·S·Si$\equiv$ and $\equiv$Si·O·Si$\equiv$ compounds by assuming that the electron affinities concerned are not greatly changed. To apply the figures to the complete breakdown of silthians and siloxans the further assumption must be made that the second Si–O or Si–S bond breaks more readily than the first; in the reactions with silver salts this may require no more than that the compounds $AgS{\cdot}SiR_3$, $AgO{\cdot}SiR_3$ are unstable, as are the compounds AgSH and AgOH.

Bond.	Bond energy.[1]	Electron affinity [2] (kcals.).	" Ionic bond energy."
Si–I	51·1	76	162·2
Si–Br	69·3	84	172·4
Si–Cl	85·8	86	186·9
Si–S–	60·9	61	187·0
Si–F	127·9	95	220·0
Si–O–	89·3	48	228·4
Si–C$\equiv$	69·1	21	235·2
Si–H	75·1	16·4	245·8

[1] Bond energies are from Sidgwick, *op. cit.* [2] Electron affinities are from Syrkin and Dyatkina, " Structure of Molecules and the Chemical Bond," 1950, except that for the values for S– and O– the figures of West (*J. Physical Chem.*, 1935, **39**, 493) for the electron affinity of SH, and of Goubeau and Klemm (*Z. physikal. Chem.*, 1937, 36, *B*, 362) for OH have been employed in preference to the values for the sulphur and oxygen atoms.

The order of increasing " ionic bond energy " is seen to differ from the order of the " conversion series " in the two cases (*viz.*, in the positions of $\equiv Si_2S$ and $\equiv$SiH compounds) in which the greatest divergence would be expected, for the very low solubility of silver sulphide, and the instability of silver hydride, allow no appreciable concentrations of sulphide and hydride ions to be maintained during the interaction of the organosilicon compounds with silver salts. The resistance of $\equiv$Si·C compounds to metallic salts is much better suggested by the " ionic bond energies " than by the simple bond energies. It seems reasonable provisionally to regard the order of the " conversion series " as governed mainly by the affinity of the silicon atom for the various groups, as indicated by the " ionic bond energies," though salt concentration effects (governed by the solubility or stability of the salt) may be great enough in some cases to cause " displacements " from the expected order.

The energy required to break the Si–X bond into Si^+ and X^- is, of course, lower in all cases in solvating media, and, if the heats of hydration of the ions I^-, Br^-, Cl^-, F^-, and H^- are taken as 46, 58, 64, 96, and 96 kcals./g.-mol. respectively (Eley and Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093; the H^- ion, having a radius close to that of the F^- ion is assumed to have a similar heat of solvation), the endothermicity of the processes $SiX \xrightarrow{\text{Aq.}} \equiv Si^+ + X^-_{aq.}$ are : for SiI, 116; for SiBr, 114; for SiCl, 123; for SiF, 124; and for SiH, 150 kcals./g.-mol. [There can be little doubt that solvation of the separating ion considerably facilitates nucleophilic attack on silicon, particularly the attack of a neutral molecule such as water, and the importance of the solvation of the separating ion has been emphasised in the hydrolysis of triarylfluorosilanes in aqueous acetone (Swain, Esteve, and Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 965), and kinetically demonstrated in the hydrolysis of trialkylsilanes in aqueous-alcoholic alkali (Price, *ibid.*, 1947, **69**, 2600) It is, thus, not surprising to find that interaction between silicon chlorides and water, which is so very vigorous in the liquid state, does not occur at all in the gas phase (Hudson, XIV*th. International Congress Pure Appl. Chem.*, London, 1947).]

Solvation of the halogen ions tends to counteract the differences in the energies required to split the various bonds to give ions, and transformations seemingly contradicting the " conversion series " may appear in solvating media. Thus, the hypothetical reaction $I^-_{aq.} + \equiv SiCl \longrightarrow \equiv SiI + Cl^-_{aq.}$, in water, is seen to involve a heat absorption of only 7 kcals., whereas the process $I^- + \equiv SiCl \longrightarrow \equiv SiI + Cl^-$ involves a heat absorption of 25 kcals. It is not, of course, possible to examine this reaction in aqueous solvents, but it was found that in acetonitrile, a solvent of medium solvating power, chlorotriethylsilane is converted into triethyliodosilane by sodium iodide, the conversion being facilitated by the lower solubility of the sodium chloride.

A " Stability Series " for Organosilicon Compounds.—The order of " ionic bond energies " should provide a guide to the relative reactivities of the various types of $\equiv$SiX compounds in those cases which involve ionic fission of the Si–X bond, *i.e.*, presumably in the vast majority of reactions in solution. It is certainly clear that the " ionic bond energies " give a more accurate indication of the relative reactivities of the various compounds than do the simple bond energies, and this is particularly evident for the Si–F, Si–H, and Si–C bonds, the first of which is more reactive, and the other two considerably less reactive, than would be expected from the simple bond energies. That the reactivity of the Si–S bond is also more accurately indicated by the " ionic bond energy " than by the simple bond energy is suggested by the fact that triethoxysilanethiol is formed by interaction of trichlorosilanethiol with three moles of alcohol, the Si–Cl bands being broken more readily than the Si–SH bond (Friedel and Ladenburg, *Annalen*, 1867, **145**, 179). The " ionic bond energies " divide the various types of compound fairly sharply into two classes, the $\equiv$SiI, $\equiv$SiBr, $\equiv$SiCl, and $\equiv\mathrm{SiS}^-$ compounds, and the $\equiv$SiF, $\equiv\mathrm{SiO}^-$, $\equiv\mathrm{Si{\cdot}C}\equiv$, and $\equiv$SiH compounds, the second class being considerably less reactive than the first in, for example, hydrolysis and attack by acetone.

The " ionic bond energies " of the Si–N bond in the silicon pseudohalides cannot be estimated because the required electron affinities are not available, but in view of the fair agreement between the " conversion series " and the order of " ionic bond energies " it seems reasonable provisionally to write a " stability series " in which the silicon pseudohalides fall into the position they occupy in the " conversion series." The order of decreasing reactivity of the various types of compounds would then be $\equiv\mathrm{SiI}$, $\equiv\mathrm{SiBr}$, $\overbrace{\equiv\mathrm{SiCl}, \equiv\mathrm{Si{\cdot}NC}, \equiv\mathrm{Si{\cdot}S}^-}$, $\equiv\mathrm{Si{\cdot}NCS}$, $\equiv\mathrm{Si{\cdot}NCO}$, $\equiv\mathrm{SiF}$, $\equiv\mathrm{Si{\cdot}O}^-$, $\equiv\mathrm{Si{\cdot}C}\equiv$, $\equiv\mathrm{SiH}$.

Ease of hydrolysis is in general agreement with the proposed series. Silicon iodides, bromides, chlorides, (*iso*)cyanides, and sulphides hydrolyse very readily, fluorides less readily, and silicon esters, siloxans, and silanes ($\equiv$SiH) require alkali for hydrolysis. (The series is in error in indicating that Si–Alkyl bonds should be more reactive than Si–H bonds, and this may be because solvation of the small hydride ion is likely to make $\equiv$SiH compounds more reactive.) These generalisations have been supplemented by examination of the hydrolysis of triethylsilicon derivatives. Triethylsilyl iodide and bromide are very readily hydrolysed by water alone, in spite of their low solubility. The hydrolyses of triethylsilyl sulphide, chloride, *iso*cyanide, *iso*thiocyanate, *iso*cyanate, and fluoride, and of triethylsilane were compared in dioxan solution. Under comparable conditions, the first three compounds were probably completely hydrolysed, triethylsilyl *iso*thiocyanate was approximately 50% hydrolysed, triethylsilyl *iso*cyanate was less than 20% hydrolysed, and triethylsilyl fluoride and triethylsilane were not appreciably affected. The agreement with the proposed " stability series " is apparent.

Attack by Grignard reagents is generally easier with compounds on the left of the series than with those on the right, but there are anomalies. Iodides, bromides, chlorides, and (*iso*)cyanides are readily attacked (except when there is steric hindrance—cf., *e.g.*, Wilkins, Brown, and Stevens, *J.*, 1950, 163; Nebergall and Johnson, *J. Amer. Chem. Soc.*, 1949, **71**, 4022), but methyl groups may not be attached to silicon by interaction of silicon tetra*iso*cyanate and Grignard reagents (Forbes and Anderson, *ibid.*, 1948, **70**, 1222), and in the present work it was found that (*iso*)cyanatotriethylsilane was not attacked by methylmagnesium iodide. From the position of the Si–S– bond in the " stability series " it was thought that it would be attacked by Grignard reagents; the failure of hexaethyldisilthian to react with methylmagnesium iodide may be steric in origin, and analogous to the failure of alkoxytrialkylsilanes and hexa-alkyldisiloxans to react with Grignard reagents, although the Si–O bond in $\mathrm{R}_x\mathrm{Si(OR)}_{4-x}$ (x = 0—2) and in $(\mathrm{R_2SiO})_n$ compounds is broken by these reagents (Di Giorgio, Strong, Sommer, and Whitmore, *ibid.*, 1946, **68**, 1380; Kipping and Hackford, *J.*, 1911, **99**, 138; Sauer, *J. Amer. Chem. Soc.*, 1944, **66**, 1707). Lithium alkyls in ether attack even the Si–H bond (Gilman and Clark, *J. Amer. Chem. Soc.*, 1946, **68**, 1675), and in the absence of steric effects it seems likely that all the bonds listed will be susceptible to attack by these reagents.

The Si–Cl bond has been shown to be attacked slowly by lithium hydride in boiling dioxan and very readily by lithium aluminium hydride in ether (Finholt, Bond, Wilzbach, and Schlesinger, *ibid.*, 1947, **69**, 2692). Reaction with lithium hydride in dioxan is of particular interest, in that the susceptibilities of various types of compound to attack by a (presumably) very small but definite concentration of hydride ions may be compared. In the present work triethylsilyl bromide, iodide, chloride, and (*iso*)cyanide were found to be attacked by lithium hydride in dioxan; hexaethyldisilthian was very slightly attacked, and triethylsilyl *iso*thiocyanate and fluoride gave no evidence of attack under comparable conditions. This behaviour is in accord with what would be expected from the " stability series." The effectiveness of lithium hydride is apparently limited by its very low solubility; lithium aluminium hydride which behaves as a potential source of hydride ions (Trevoy and Brown, *ibid.*, 1949, **71**, 1675) has been found to reduce triethylfluorosilane to triethylsilane very readily, giving a high yield.

It may be concluded that, while the evidence for the proposed " stability series " is far from complete, this series, based mainly on " ionic bond energies," does give a general indication of the relative reactivities of the various types of silicon compounds concerned.

Preparative Methods and New Compounds.—The possible value of the " conversion series " in the preparation of new compounds is apparent. In the present work all the conversions were carried out in absence of solvent to avoid losses, but in view of Anderson's work there seems little reason to doubt that the majority of the conversions reported would take place in weakly polar solvents. The disadvantage of using no solvent is that high temperatures are necessary to force the last traces of organosilicon compound from the solid; this does not appear to lead to any serious decomposition of the product, which, however, is contaminated in some cases (particularly on distillation from silver pseudohalides) by gases from the decomposition of the silver salt. This difficulty does not arise, of course, in purely preparative work when the last few drops of product may be neglected. An important advantage of omitting the solvent is that the reflux temperature indicates the progress of the reaction, and by this means several conversions were found to be complete in a few minutes of heating. It is of interest that Anderson (*ibid.*, 1950, **72**, 196) found the conversion of chlorotriethylsilane into *iso*cyanatotriethylsilane to be unsatisfactory in benzene (and added nitromethane to the solvent to improve the yield), whereas in the present work the reaction was found to be complete after *ca.* 5 minutes' heating in absence of solvent.

It has become clear that alkyl(*iso*)cyanosilanes may be prepared pure more conveniently from alkylbromosilanes than from the iodosilanes previously employed (Part I, *J.*, 1949, 2755). (*iso*)Cyanotrimethylsilane boils rather higher than was expected, but there seems no reason at present to amend the original suggestion that the compounds are silicon *iso*cyanides rather than cyanides. That the (*iso*)cyanide group is replaced by Grignard reagents has been confirmed by interaction of (*iso*)cyanotrimethylsilane and phenylmagnesium bromide.

Hexaethyl- and hexamethyl-disilthian are the first organosilicon sulphides to be reported, presumably because the preparation of such sulphides depends on the availability of alkyliodosilanes, which have only recently been investigated (*see* Part I). The silthians are of particular interest as the analogues of the siloxans, which are of such importance at the present time, but the sulphur compounds lack the stability of the siloxans. Hexaethyldisilthian is readily and completely hydrolysed when brought into solution, although it is surprisingly resistant to water and aqueous alkali, apparently because of its insolubility; it has an unpleasant, quite characteristic odour; hexamethyldisilthian smells more strongly of hydrogen sulphide. It is of interest that the hydrolyses of (*iso*)cyanotriethylsilane, triethyl*iso*thiocyanatosilane, and hexaethyldisilthian give good yield of triethylsilanol, unlike the hydrolyses of triethylhalogenosilanes which give hexaethyldisiloxan unless special precautions are taken (cf. Sommer, Pietrusza, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 2282). The stability of the triethylsilanol in the three cases referred to is probably a result of the absence of formation of strong acid in the hydrolyses.

The bromotriethylsilane and chlorotriethylsilane employed were mainly prepared by interaction of triethylfluorosilane with aluminium bromide and chloride respectively. The production of alkyliodo-, alkylbromo- and alkylchloro-silanes by interaction of alkylfluorosilanes with aluminium halides appears to be a useful method of wide applicability; details will be given in a separate communication.

Interaction of dimethyldiphenylsilane and iodine in presence of aluminium iodide gives di-iododimethylsilane in good yield, extending the series of alkyliodosilanes reported in Part I. The first phenyl group appears to be replaced considerably more readily than the second. The use of aluminium iodide as catalyst has increased the yield of iodotrimethylsilane in the interaction of iodine and trimethylphenylsilane from 56% after 12 hours' boiling (Pray *et al.*, *ibid.*, 1948, **70**, 433) to 90% after 2 hours' boiling.

In attempts to replace the iodine atom by the nitro-, nitrate and carbonate groups, the interaction of triethyliodosilane with silver nitrite, nitrate, and carbonate was examined. In each case gas was evolved and hexaethyldisiloxan was formed.

EXPERIMENTAL.

(All b. p.s are corrected.)

Analyses.—Alkyliodo-, alkylbromo-, and alkylchloro-silanes were analysed for halogen by adding weighed samples to aqueous dioxan containing a small excess of potassium hydroxide and diluting the solutions to a standard volume with such proportions of water and dioxan as were necessary to maintain a clear solution. Aliquots were run into excess of water, and halogen ion was determined by the Volhard method. Alkyl*iso*thiocyanatosilanes were hydrolysed in the same way, and thiocyanate ion was titrated against silver nitrate. Alkyl*iso*cyanatosilanes were hydrolysed in the same way, and aliquots of the resulting solution were made just acid to phenolphthalein with dilute acetic acid, excess of standard silver nitrate solution was added, and the silver ion present after filtration was determined, allowance being made in the calculation for the solubility of silver cyanate in the measured volume of water used for washing (the necessity for this correction introduces a possible error of at least 1%). Sulphur in hexa-alkyldisilthians was determined by adding a known weight of the substance (*ca.* 1 g.) to a slight excess of silver nitrate in aqueous dioxan (*ca.* 10 ml. of water +20 ml. of dioxan); the precipitated silver sulphide, after being washed with dioxan and much water, was dissolved in boiling dilute nitric acid, and ionic silver was determined by titration.

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

General.—Atmospheric moisture was excluded from all reactions by means of sulphuric acid bubblers.

Triethyliodosilane.—This was variously prepared from triethylsilane, tetraethylsilane, or triethylfluorosilane, as described in Part I.

Triethylpseudohalogenosilanes.—These were prepared mainly from bromotriethylsilane by interaction with the appropriate silver salt, but samples prepared incidentally in other experiments were, of course, also employed.

Trimethylsilyl Derivatives.—These were prepared from iodotrimethylsilane or bromotrimethylsilane by interaction with the appropriate silver salts.

Trimethylphenylsilane and Dimethyldiphenylsilane.—A few drops of bromobenzene were added to a solution of dichlorodimethylsilane (258 g., 2 mols.) in ether (250 ml.), containing magnesium turnings (55 g., 2·25 mols.). When reaction began, bromobenzene (354 g., 2·25 mols.) in ether (1·5 l.) was added during 5 hours, with vigorous stirring. Further magnesium (55 g., 2·25 mols.) was added, followed by methyl iodide (319 g., 2·25 mols.) in ether (500 ml.), added during 2 hours. Much solid separated. The mixture was boiled under reflux for 10 hours, and then treated with dilute sulphuric acid. The ethereal layer, after being dried (Na_2SO_4), was fractionated to give trimethylphenylsilane (144 g., 0·96 mol., 48%), b. p. 171°. The residue from the fractionation was combined with a similar residue from a second preparation, and distillation gave 90 ml. of impure dimethyldiphenylsilane, b. p. 275—284° (Found: C, 77·9; H, 7·4. Calc. for $C_{14}H_{16}Si$: C, 79·2; H, 7·6%).

Iodotrimethylsilane.—The method of Pray *et al.* (*loc. cit.*) was modified by using aluminium iodide as catalyst. Iodine (124 g., 0·49 mol.) was added in *ca.* 20-g. portions to trimethylphenylsilane (75 g., 0·5 mol.), containing aluminium iodide (1 g.), and the liquid was boiled under reflux after each addition until the iodine had been largely consumed. Further aluminium iodide (1 g.) was added when *ca.* 60 g. of iodine had been used. All the iodine had reacted in a total of 2 hours' boiling. The product was fractionated, after the addition of a little antimony powder, to give iodotrimethylsilane (94 g., 94%), b. p. 106·8°/742 mm. (Found: I, 63·5. Calc. for C_3H_9ISi: I, 63·4%). In a similar experiment iodotrimethylsilane was obtained in 92% yield, and iodobenzene in 90% yield.

Di-iododimethylsilane.—Iodine was added in *ca.* 10-g. portions to dimethyldiphenylsilane (71 g., 0·33 mol.) containing aluminium iodide (2 g.), and the liquid was boiled under reflux after each addition until the iodine colour was removed. After 85 g. (*i.e.*, *ca.* 0·33 mol.) of iodine had been used in 1 hour (and presumably one phenyl group per molecule had been replaced), further removal of iodine was slow in spite of further additions (total *ca.* 4 g.) of aluminium iodide. After a total of 15 hours' boiling, when *ca.* 162 g. of iodine had been used, fluorotri-*n*-propylsilane (*ca.* 10 ml.) was added and the liquid was boiled for ¼ hour to destroy the aluminium iodide. The product was fractionated after the addition of a little antimony powder, to give *di-iododimethylsilane* (76 g., 74%), b. p. 170·0°/760 mm. (Found: I, 81·2. $C_2H_6I_2Si$ requires I, 81·3%). The colourless, strongly-fuming liquid has a high density (*ca.* 2·2). It reacts with silver cyanide and with silver sulphide to give white solids (m. p.s *ca.* 85 and 110°, respectively) which are under investigation.

Bromotrimethylsilane.—This was prepared from bromine and trimethylphenylsilane (Pray *et al.*, *loc. cit.*). A 10% excess of trimethylphenylsilane was employed. The yield (based on Br used) was 95%, and the b. p. 79·5°/760 mm.

(iso)*Cyanotrimethylsilane.*—Bromotrimethylsilane (15·3 g., 0·1 mol.) was added to silver cyanide (18 g., 0·133 mol.); considerable heat was developed on mixing, and the solid immediately became bright yellow. When heat was applied, the reflux temperature rose to 115° in 5 minutes. After ¼ hour's boiling, the liquid was slowly distilled from the solid, and redistilled to give (iso)*cyanotrimethylsilane* (9·0 g., 90%), b. p. 114—117°. The bulk had b. p. of 116°/750 mm., m. p. 11·5° ± 0·5° (Found: C, 48·4; H, 9·1; CN, 26·2. C_4H_9NSi requires C, 48·45; H, 9·15; CN, 26·2%). The liquid is colourless, and smells strongly of hydrogen cyanide.

Interaction of (iso)*Cyanotrimethylsilane and Phenylmagnesium Bromide.*—(*iso*)Cyanotrimethylsilane (9·9 g., 0·1 mol.) in an equal volume of ether was added dropwise during ¼ hour to a solution of phenylmagnesium bromide (*ca.* 0·125 mol.) in ether (50 ml.), vigorous stirring being maintained. Reaction took place with refluxing of the ether and separation of a viscous lower layer. After the addition, the mixture was boiled under reflux for ½ hour, and then water was added, followed by very dilute sulphuric acid until two clear layers separated. The ethereal layer was dried (Na_2SO_4) and distilled to give trimethylphenylsilane (10·5 g., 70%), b. p. 170—173°, n_D^{25} 1·4880.

Hexaethyldisilthian.—In a typical preparation, triethyliodosilane (48·4 g., 0·2 mol.) was added to dried, finely-powdered silver sulphide (30 g., 0·12 mol.) without visible evidence of reaction. The liquid was boiled gently under reflux for 2 hours, during which the solid became yellow and increased considerably in bulk. After cooling, the organosilicon liquid was extracted with light petroleum (b. p. <40°). After removal of the solvent, the liquid distilled as follows: 1 ml. 140—200°; 3 ml. 200—268°; 6 ml. 268—275°; 16 ml. 275—279°; 1 ml. 279—284°, with little residue. Redistillation of the main fraction in an atmosphere of dry nitrogen gave 12 g. of *hexaethyldisilthian*, b. p. 276—279°, with the bulk boiling at 277—279° (Found: C, 55·1; H, 11·6; S, 12·2. $C_{12}H_{30}SSi_2$ requires C, 54·9; H, 11·5; S, 12·2%). The yield of pure material was *ca.* 46%, and of material of b. p. 268—280°, *ca.* 75%. The colourless liquid obtained (*d ca.* 0·9 ; n_D^{12} 1·492) set to a white solid at the temperature of solid carbon dioxide. It deposited a bright yellow solid, presumably sulphur, on storage for several days in tubes closed with rubber bungs.

Hexaethyldisilthian (10·5 g., 0·04 mol.) in ether (10 ml.) was added rapidly to a solution of methylmagnesium iodide (*ca.* 0·1 mol.) in ether (30 ml.) which was just not boiling. There was no visible evidence of reaction. The mixture was boiled under reflux for 7 hours without evidence of reaction, and the system remained homogeneous on cooling. Dilute sulphuric acid was added to destroy the unchanged Grignard reagent, and the ethereal layer was dried (Na_2SO_4) and fractionated to give (after removal of the ether) only 0·5 ml. of liquid boiling below 150°, indicating that little, or no triethylmethylsilane was present. The residue was not investigated.

Hexamethyldisilthian.—Iodotrimethylsilane (40 g., 0·2 mol.) was warmed with silver sulphide (37 g., 0·15 mol.). After 14 hours' boiling, the reflux temperature had risen to 150°. The liquid was distilled off from the solid, and redistilled to give *hexamethyldisilthian* (13 g., 0·073 mol., 73%), b. p. 162—164°/750 mm. with the bulk boiling at 162·5—163·5° (Found : C, 40·8 ; H, 10·2 ; S, 17·8. $C_6H_{18}SSi_2$ requires C, 40·4 ; H, 10·2 ; S, 18·0%). In other experiments the necessary time of boiling was found to depend on the sample of silver sulphide taken.

(iso)*Cyanatotriethylsilane.*—Chlorotriethylsilane (15 g., 0·1 mol.) was added to silver cyanate (20 g., 0·133 mol.), considerable heat being generated on mixing. When heat was applied, the liquid began to reflux at 161° (*i.e.*, conversion was almost complete) and the reflux temperature rose to 163° in 10 minutes. After this time the liquid was distilled very slowly from the solid (prolonged gentle heating was employed to prevent decomposition of unchanged silver cyanate), and redistilled to give *iso*cyanatotriethylsilane (14·5 g., 90%) boiling at 164—167°, with the bulk having b. p. 165·5°/750 mm., n_D^{15} 1·4329 (Found : C, 53·3 ; H, 9·7 ; CNO, 26·6. Calc. for $C_7H_{15}ONSi$: C, 53·45 ; H, 9·6 ; CNO, 26·7%). Anderson (*J. Amer. Chem. Soc.*, 1950, **72**, 196) has since described this material as having b. p. 165·1°, n_D^{20} 1·4295.

Interaction of Organosilicon Compounds with Metallic Salts.—Most of the interactions were examined in a small distillation flask (*ca.* 25 ml. capacity) having a water-cooled side-arm, fitted with an adapter which carried the test-tube receiver and had a side tube connected to a sulphuric acid bubbler. By tilting the flask, the condenser could be used for refluxing or distilling, losses thus being kept to a minimum. In most interactions 4—10 ml. of liquid were employed. All the metal salts were thoroughly dried, and powdered where possible before use. Usually about a 20% excess of the salt was employed, but sometimes a further quantity was necessary to effect complete reaction. Silver chloride was sometimes obtained in the form of fairly large, malleable particles, and a large excess of the solid had then to be employed. Distillations of the liquids from the solid residues were carried out slowly in an attempt to avoid decomposition of the solids ; silver cyanate, described in the literature as " explosive," sometimes decomposed with evolution of gas, the decomposition being rapid once initiated.

After some analyses had indicated the general nature of the interactions, products were identified by their b. p.s and refractive indices and by qualitative tests on the solutions obtained by hydrolysis of samples in aqueous dioxan containing some alkali.

The table on p. 3086 lists the *successful* interactions not described elsewhere. Parentheses enclosing a reaction time indicate that the reflux temperature was not followed, so that reaction may have been complete in considerably less time than was allowed. The yields within definite b. p. limits are given in the fifth column. A positive sign in the last column indicates that easily detectable heat was generated on mixing the reactants.

Interaction of (iso)*Cyanotriethylsilane and Silver Chloride.*—(*iso*)Cyanotriethylsilane (7 g., 0·05 mol.) was added to silver chloride (10 g., 0·07 mol.) ; no detectable reaction took place. When heat was applied the liquid began to reflux at 155°. The reflux temperature fell to 153° in 1½ hours, and was not changed by addition of more silver chloride (8 g.) (followed by an additional ½ hour's boiling), and further silver chloride (16 g.) (followed by an additional 1 hour's boiling). The organosilicon material was distilled off, to give *ca.* 7·5 ml. of liquid, which redistilled at 152—162°. Fractionation with hexaethyldisiloxan as " chaser " gave chlorotriethylsilane (5 g., *ca.* 70%), b. p. 143—144° (Found : Cl, 23·4. Calc. for $C_6H_{15}ClSi$: Cl, 23·5%).

Interaction of Chlorotriethylsilane and Silver Cyanide.—Chlorotriethylsilane (5 ml.) was added to silver cyanide (6 g.). The reflux temperature was 156° after 1½ hours, and was unaltered by addition of more silver cyanide (3 g.) followed by a further 1 hour's boiling. Distillation, followed by redistillation, gave 3 ml. of liquid of b. p. 148—158°, and 2 ml. of b. p. 158—165°. All the fractions gave some cyanide ion as well as chloride ion on hydrolysis.

Interaction of (iso)*Cyanotrimethylsilane and Silver Chloride.*—(*iso*)Cyanotrimethylsilane (5 ml.) was warmed with silver chloride (8 g.), and the liquid began to reflux at 72°. The reflux temperature did not change during ¼ hour of boiling. Further addition of silver chloride (4 g.), followed by an additional 1 hour's boiling, caused no change in the reflux temperature. Distillation followed by redistillation gave 2·5 ml. of liquid of b. p. 65—70° and 2·0 ml. of b. p. 70—85°. All the fractions collected gave cyanide and chloride ion on hydrolysis.

Interaction of Chlorotrimethylsilane and Silver Cyanide.—Chlorotrimethylsilane (4 g.) was added to silver cyanide (6 g.). When heated, the liquid refluxed at 75° and this reflux temperature was not changed by addition of more silver cyanide (3 g.) followed by further (1 hour) boiling. Distillation followed by redistillation gave 2·5 ml. of liquid of b. p. 67—80° and 1 ml. of b.p. 80—90°. Both fractions gave chloride and cyanide ion on hydrolysis.

Interactions of Triethylsilyl Compounds and Metallic Oxides.—In addition to the interactions described above and below the following interactions were observed which did not allow definite conclusions to be drawn. Probably some hexaethyldisiloxan was formed in all cases. (i) Triethyl*iso*thiocyanatosilane (4 ml.)

Reactants.		Product.	Reaction time (mins.).	Yield, % (with b.p.s).	Notes.
Et_3SiI	$AgBr$	Et_2SiBr	10	>85; 162—165°	(1)
,,	$AgCl$	Et_3SiCl	60	>90; 143—146	(2)
,,	$AgNCS$	Et_3SiNCS	(30)	>85; 209—211	+
,,	$AgNCO$	Et_3SiNCO	(15)	>85; 163—167	+
,,	Hg_2S	$(Et_3Si)_2S$	180	80; 260—280	
$(Et_3Si)_2S$	$AgCl$	Et_3SiCl	10	>85; 143—147	(2)
,,	$PbCl_2$	,,	(60)	90; 143—147	
,,	$CdCl_2$	,,	(120)	>75; 143—147	
,,	$AgBr$	Et_3SiBr	15	90; 162—165	
,,	$AgCN$	Et_3SiNC	15	85; 183—185	+
,,	$AgNCS$	Et_3SiNCS	(60)	>85; 209—213	
,,	$AgNCO$	Et_3SiNCO	(30)	85; 163—167	
,,	HgO	$(Et_3Si)_2O$	10	90; 230—236	
Et_3SiBr	$AgCl$	Et_3SiCl	(120)	90; 143—147	
,,	$AgCN$	Et_3SiNC	10	90; 181—184	+
,,	$AgNCS$	Et_3SiNCS	10	90; 209—211	+
,,	$AgNCO$	Et_3SiNCO	10	90; 165—166	+
,,	$CuNCS$	Et_3SiNCS	10	90; 208—211	
,,	HgO	$(Et_3Si)_2O$	10	85; 230—235	+
Et_3SiH	$AgCN$	Et_3SiNC	180	90; 180—185	(3)
,,	$HgCl_2$	Et_3SiCl	60	>85; 141—146	(4)
,,	$AgNCS$	Et_3SiNCS	(120)	90; 209—211·5	(5)
,,	$AgNCO$	Et_3SiNCO	30	90; 165—166	(6)
Et_3SiNC	$AgNCS$	Et_3SiNCS	(30)	>85; 209—211	
,,	$AgNCO$	Et_3SiNCO	(30)	90; 163—167	
,,	$CuNCS$	Et_3SiNCS	5	90; 209—211	
Et_3SiCl	$AgNCS$	Et_3SiNCS	30	90; 208—211	
Et_3SiNCS	$AgNCO$	Et_3SiNCO	10	75; 163—167	+; (7)
Me_3SiI	$AgCl$	Me_3SiCl	120	85; 58—62	(8)
,,	$AgBr$	Me_3SiBr	45	90; 79—81	
,,	$AgCN$	Me_3SiNC	(30)	90; 114—177	
$(Me_3Si)_2S$	$AgBr$	Me_3SiBr	90	90; 79—81	(2, 9)
,,	$AgCl$	Me_3SiCl	60	85; 57—60	(2)
,,	$PbCl_2$	Me_3SiCl	15	85; 57—60	
,,	$AgCN$	Me_3SiNC	10	90; 114—117	+
,,	$AgNCS$	Me_3SiNCS	10	90; 139—144	+
Me_3SiBr	$AgNCS$	Me_3SiNC	15	90; 143—144	+
,,	$AgNCO$	Me_3SiNCO	15	90; 90—92	(2)
Me_3SiNC	$AgNCS$	Me_3SiNCS	15	85; 141—144	
Me_3SiNCS	$AgNCO$	Me_3SiNCO	15	90; 90—92	
Me_2SiCl_2	$AgNCS$	$Me_2Si(NCS)_2$	25	85; 215—217	+
$Me_2Si(NCS)_2$	$AgNCO$	$Me_2Si(NCO)_2$	30	40; 138·5—139·5	(10)

Notes. (1) Throughout this work, and in separate preparations involving efficient fractionation, bromotriethylsilane gave the consistent b. p. of 163—164°, not 161° the value favoured by Lewis and Newkirk (*ibid.*, 1947, **69**, 701). (2) 100% excess of the silver salt was taken. (3) Reflux temperature rose to 135° in 1 hour, and 179° in 3 hours; throughout the first 2 hours there was marked evolution of gas, which seemed to be mainly hydrogen, and contained no hydrogen cyanide. (4) In an experiment in which triethylsilane and mercuric chloride were used in 2 : 1·1 mol. ratio considerably more mercuric chloride had to be added to maintain the rise in b. p.; with 1 : 1·1 mol. ratio reaction began on warming, and the reflux temperature rose to 134° after ½ hour and 142° after 1 hour; the gas evolved throughout was completely soluble in water, and appeared to be hydrogen chloride; the solid residue was a grey powder, not containing free mercury, and mainly insoluble in water (mercurous chloride ?). (5) Gas evolution occurred throughout. (6) No reaction was apparent on mixing of the reagents, but after gentle heating a vigorous reaction began, with gas evolution, and the liquid refluxed for 10 mins. without external heating; when heating was resumed, the reflux temperature was 130°, and rose to 164° in ¼ hour. (7) The reflux temperature fell to 164° after 5 minutes' heating, indicating complete interaction, but the yield was lowered by decomposition of the solid. (8) The last portion of the distillate gave some iodide ion on hydrolysis. (9) The product gave a little sulphide ion on hydrolysis. (10) The yield was low because the solid was not heated strongly to avoid danger of explosion; the reflux temperature fell to 140° in ½ hour, indicating that reaction was complete; the product had $n_D^{16.5}$ 1·4230.

was warmed with silver oxide (4 g.). A vigorous reaction began, red-hot particles appearing in the solid. After ¼ hour's heating, the liquid was distilled off, and redistilled from a little fresh silver oxide (the solid again igniting), to give 2·0 ml. of b. p. 190—220° and 1·0 ml. of b. p. 220—232°. (ii) *iso*Cyanatotriethylsilane (4·5 ml.) was boiled under reflux with silver oxide (3 g.) for 2 hours. Gas evolution took place throughout this period, and the reflux temperature rose to 174°. Distillation, followed by redistillation, gave 2 ml. of liquid of b. p. 158—170°, 1 ml. of b. p. 170—220°, and 1 ml. of b. p. 220—235° (n_D^{15} varied from 1·4285 to 1·4345). (iii) Triethyl*iso*thiocyanatosilane (6 ml.) was added to mercuric oxide (8 g.), heat being generated on mixing them. When the mixture was warmed, a vigorous reaction began.

After $\frac{1}{4}$ hour's boiling, more mercuric oxide (3 g.) was added, and the liquid was boiled for $\frac{3}{4}$ hour. The liquid was distilled off, and redistilled to give 1·5 ml. of b. p. 180—230° and 2·5 ml. of b.p. 230—234°. The latter fraction had n_{D}^{18} 1·436, and gave only a little thiocyanate ion on hydrolysis. (iv) Triethylsilane (5 ml.) was warmed with silver oxide (6 g.). After $\frac{3}{4}$ hour, when the reflux temperature had risen to 115°, more silver oxide (3 g.) was added, and the reflux temperature rose to 132° in a further 1 hour. Distillation gave 0·5 ml. of liquid of b. p. 130—220° and 4 ml. of b. p. $>220°$, with a little water in both fractions. Drying and redistillation gave 3 ml. of liquid of b. p. 232—235°, n_{D}^{23} 1·4330, which was completely soluble in concentrated sulphuric acid and was almost certainly hexaethyldisiloxan. The water may have come from interaction of the oxide with the triethylsilane, since no hydrogen evolution was detected, or it may have been present in the original silver oxide, which is extremely difficult to dry completely.

Interactions of Hexaethyldisiloxan and Metallic Fluorides.—In these interactions, while it seemed clear that triethylfluorosilane was formed, the complications detailed below make it somewhat uncertain that the effective reaction is between the organosilicon compound and the fluoride. (i) *With mercurous fluoride.* Hexaethyldisiloxan (9·5 g.) was heated with mercurous fluoride (20 g.), the vapour of any low-boiling liquid formed being bled off continuously. In 2 hours, 5 ml. of liquid of b. p. $<115°$ had been collected, and reaction appeared to have stopped. Further mercurous fluoride (20 g.) was added; on heating of the mixture, there was a marked gas evolution and more low-boiling liquid distilled off, so that in $\frac{1}{2}$ hour's heating the total volume of distillate (b. p. $<115°$) was brought up to 9 ml. Fractionation of the liquid, with tetraethylsilane as " chaser," gave 3 ml. of liquid having b. p. 61°, n_{D}^{12} 1·346 (probably diethyldifluorosilane) and 4 ml. of b. p. 109°, n_{D}^{12} 1·3928 (very probably triethylfluorosilane). The solid residue contained much mercury, and reaction may have been effected by fluorine evolved from the mercuric fluoride. (ii) *With mercuric fluoride.* A mixture of mercurous fluoride (14·7 g., 0·33 mol.), hexaethyldisiloxan (8·2 g., 0·033 mol.), and iodine (8·5 g., 0·33 mol.) was warmed under reflux until all the iodine had disappeared. Heating was continued, with the vapour of any low-boiling liquid being bled off continuously; steady evolution of an acid gas took place. After 2 hours, 2 ml. of liquid (b. p. $<115°$) had been collected and reaction appeared to have ceased. More iodine (8·5 g.) and mercurous fluoride (14·7 g.) were added; on heating of the mixture, gas evolution began again and 3 ml. of low-boiling liquid were collected in 1 hour. The solid residue was strongly heated but gave no further liquid, indicating a definite loss of organosilicon material, possibly in the evolved gases. The distillate was fractionated with tetraethylsilane as " chaser," to give 1 ml. of liquid of b. p. 61—62°, n_{D}^{12} 1·346 (probably diethyldifluorosilane) and 3 ml. of b. p. 109°, n_{D}^{12} 1·3930 (very probably triethylfluorosilane). (iii) *With zinc fluoride.* Hexaethyldisiloxan (6 ml.) was warmed with zinc fluoride (8 g.), the vapour of any low-boiling liquid formed being bled off continuously. Considerable gas evolution occurred throughout the reaction; in 6 hours, 4·5 ml. of liquid (b. p. $<115°$) were collected. The solid residue gave no further liquid on strong heating, and there was thus a definite loss of organosilicon material. The distillate was fractionated with tetraethylsilane as " chaser," to give 1·5 ml. of liquid of b. p. 61—62°, n_{D}^{15} 1·346, and 2 ml. of b. p. 109°, n_{D}^{15} 1·3925. (The gas evolved was acid to litmus, and fumed when mixed with ammonia. After collection over water a gas was obtained which burned with a quiet blue flame, depositing a little silica. This gas was insoluble in aqueous alkali, but readily soluble in alcohol and benzene. The glass of the reaction vessel was attacked, and some water droplets formed in the condenser in the later stages, although the zinc fluoride had been dried at 140° for several hours; this water may have been formed during the reaction. The possibility that the observed reaction was caused, at least in part, by hydrogen fluoride cannot be ignored.) (iv) *With antimony trifluoride.* Hexaethyldisiloxan (8 ml.) was warmed with antimony trifluoride (8 g.) containing a trace of bromine, the vapour of any low-boiling liquid formed being bled off continuously. The solid reactant, after initially becoming liquid, set to a hard inaccessible mass, and after 3 ml. of liquid (b. p. $<115°$) had been collected in 3 hours, no further reaction was apparent. The distillate was redistilled, and boiled at 70—115° (n_{D}^{12} 1·367—1·392), probably being a mixture of diethyldifluorosilane and triethylfluorosilane.

Trialkylsilyl Compounds and Metallic Salts not showing Interaction.—In the following cases no interaction was observed in the time (in hours) given in parentheses. In most cases absence of change in the reflux temperature was a good indication of the lack of detectable interaction; recovery of the organosilicon compound exceeded 90% except where otherwise indicated.

$Et_3SiI + PbCl_2$ (1); $(Et_3Si)_2S + AgI$ (1); $Et_3SiBr + AgI$ (1), Ag_2S (3), $CdCl_2$ (3); $Et_3Si{\cdot}NC + Ag_2S$ (3), AgBr (2); $Et_3SiCl + AgBr$ (2), Ag_2S (3); $Et_3Si{\cdot}NCS + AgCl$ (2), $PbCl_2$ (2), $CdCl_2$ (3), Ag_2S (4), AgCN (2); $Et_3Si{\cdot}NCO + Ag_2S$ (4), AgBr (2), AgCN (2), AgCl (2), AgNCS (2), HgO (2), ZnF_2 (2); $(Et_3Si)_2O + PbF_2$ (2); $Et_3SiF + PbO$ (2), HgO (2), Ag_2O (2), ZnO (2); $Et_3SiH + Ag_2S$ (3), AgBr (2), ZnO (2), $PbCl_2$ (2); $Et_3SiH + AgCl$ (2) (more than 90% of the Et_3SiH was recovered but the last portions of the distillate fumed slightly with ammonia and gave a little chloride ion on hydrolysis); $SiEt_4 + AgNCO$ (3) (only 70% of the $SiEt_4$ was recovered because of ignition of the solid during distillation, but the absence of change in the reflux temperature indicated that no reaction was occurring), $Me_3SiI + PbCl_2$ (2); $Me_3SiBr + Ag_2S$ (3), $PbCl_2$ (2), $TlCl_2$ (1), $CdCl_2$ (3); $Me_3Si{\cdot}NC + Ag_2S$ (3); $Me_3SiCl + AgBr$ (1). $Ph_3SiF + ZnO$ (3).

Interaction of Triethyliodosilane and Silver Nitrite.—Silver nitrite (9 g.) was added in small portions to triethyliodosilane (16 g.) through a reflux condenser, the container being cooled in ice. Vigorous reaction occurred, with considerable evolution of gas. (The gas, collected over water, was colourless but gave brown fumes on exposure to the air, and was probably, at least partly, nitric oxide.) After the reaction had subsided, gentle heat was applied for $\frac{1}{2}$ hour, gas evolution continuing throughout this time. The liquid was extracted from the solid with ether, and the extract was distilled; after removal of the ether, 1 ml. of liquid of b. p. 140—230° (mainly $>200°$), and 4 ml. of b. p. 230—236° were obtained. The latter fraction had n_{D}^{18} 1·4346, and was completely soluble in concentrated sulphuric acid, and was clearly hexaethyldisiloxan.

Interaction of Triethyliodosilane and Silver Carbonate.—Triethyliodosilane (14 g.) was added to silver carbonate (9 g.). Reaction began immediately, with generation of heat and evolution of much gas. When the gas evolution died away, the mixture was boiled gently under reflux for ½ hour. The liquid was distilled off; all of it (7 ml.) redistilled at 233—235° (n_D^{17} 1·4348). The liquid was soluble in concentrated sulphuric acid and was clearly hexaethyldisiloxan.

Interaction of Triethyliodosilane and Silver Nitrate.—Vigorous reaction occurred on addition of silver nitrate (*ca.* 2 g.) to triethyliodosilane (*ca.* 3 ml.); brown fumes were copiously evolved, and iodine was liberated. The b. p. of the liquid rose steadily to 230°. The liquid obtained on distillation boiled at 230—235° and was completely soluble in concentrated sulphuric acid and was clearly hexaethyldisiloxan.

Hydrolysis of Triethylsilyl Derivatives by Aqueous Dioxan.—In each case the triethylsilyl compound (0·1 mol., except for hexaethyldisilthian, of which 0·05 mol. was employed) was added to a mixture of dioxan (30 ml.) and water (4·5 ml.) at room temperature (*ca.* 15°). With chlorotriethylsilane, triethylfluorosilane, and *iso*cyanatotriethylsilane additional quantities of dioxan (10, 15, and 8 ml. respectively) had to be added to make the system homogeneous. After the mixture had been shaken, it was set aside for 5 minutes. At the end of this time more water (10 ml.) was added (which caused two layers to separate, roughly equal in volume), and, after a further 5 minutes, 200 ml. of water was added to liberate the organosilicon material, which separated as an upper layer. In the hydrolysis of hexaethyldisilthian and triethyl*iso*thiocyanatosilane the organosilicon material was extracted with light petroleum and the extract was dried (Na_2SO_4). In the other cases it was separated directly and dried (Na_2SO_4).

(i) *Hexaethyldisilthian.* The light petroleum extract was fractionated, with hexapropyldisiloxan as "chaser," to give triethylsilanol (12 g., 90%), b. p. 154°, n_D^{17} 1·4340. The residue was distilled; the distillate gave no sulphide ion on hydrolysis in alkaline aqueous acetone. (ii) *Chlorotriethylsilane* (heat was developed on addition of this compound to the aqueous dioxan). The product of hydrolysis distilled as follows: 7 g., 158—180°; 2 g., 180—230°; 3 g., 230—236° (n_D^{21} 1·4320). None of the fractions gave chloride ion on hydrolysis, so that no unchanged chlorotriethylsilane was present. The product was probably a mixture of triethylsilanol and hexaethyldisiloxan in *ca.* 90% yield. (iii) (iso)*Cyanotriethylsilane* (heat was developed on addition of this compound to the aqueous dioxan). The product of hydrolysis (all) distilled at 153—157° (11 g., *ca.* 80%, of triethylsilanol). No unchanged (*iso*)cyanotriethylsilane was present. (iv) *Triethyl*iso*thiocyanatosilane.* The light petroleum extract was fractionated, with hexaethyldisiloxan as "chaser," to give triethylsilanol (5 g.), b. p. 154°, n_D^{18} 1·4335, and unchanged triethyl*iso*thiocyanatosilane (8·5 g., 50%), b. p. 210·5°, n_D^{18} 1·4940. (v) iso*Cyanatotriethylsilane.* The hydrolysis product was fractionated, with hexaethyldisiloxan as "chaser," to give 0·5 ml. of liquid of b. p. 156—164°, and unchanged *iso*cyanatotriethylsilane (12·5 g., *ca.* 80%), b. p. 165·5°, n_D^{16} 1·4318 (Found: C, 53·6; H, 9·6; N, 8·6. Calc. for $C_7H_{15}ONSi$: C, 53·45; H, 9·6; N, 8·9%). (vi) *Triethylfluorosilane and triethylsilane.* Recovery of these compounds was *ca.* 90%, and there was no evidence of any hydrolysis.

Action of Lithium Hydride in Dioxan on Triethylsilyl Compounds.—The organosilicon compound (*ca.* 0·05 mol., except where stated) was added in small quantities to a mixture of dioxan (*ca.* 15 ml.) and finely-powdered lithium hydride (0·1 mol.), the mixture being boiled under reflux for a few minutes after each addition. When the addition had been completed, the mixture was boiled under reflux for the time stated, and all the liquid was distilled from the solid. Except where indicated, the distillate was poured into excess of water and the organosilicon material, after being washed with more water to remove any dioxan, was dried (Na_2SO_4) and either distilled directly or fractionated with tetraethylsilane as "chaser."

(i) *Triethyliodosilane.* When the iodide was added there was evolution of heat and a marked increase in the bulk of solid. After the addition (which took ½ hour), the mixture was boiled for 1 hour. The product, worked up as described above, was fractionated to give triethylsilane (4·5 g., *ca*, 80%), b. p. 107°, n_D^{19} 1·4120. (ii) *Bromotriethylsilane.* After the addition of the bromide, the mixture was boiled for 4 hours. The product, worked up as described, was distilled to give triethylsilane (4·5 g., *ca.* 80%), b. p. 106—110°, n_D^{18} 1·4130, with very little residue. (iii) *Chlorotriethylsilane.* A procedure identical with that employed with bromotriethylsilane gave triethylsilane (4 g., *ca.* 70%), with little residue. (iv) (iso)*Cyanotriethylsilane.* After the addition of the (*iso*)cyanide the mixture was boiled for 6 hours. The liquid was distilled off, and the first 15 ml. of the distillate (b. p. 100—170°, mainly 100—115°) were worked up in the way described above, and the product was fractionated to give triethylsilane (1·5 ml., *ca.* 20%), b. p. 107°, n_D^{18} 1·4130. The final 8 ml. of the distillate (b. p. >170°) were redistilled to give 2 ml. of liquid of b. p. 110—180°, and 3·5 ml. of b. p. 180—184° (presumably unchanged (*iso*cyanotriethylsilane). (v) *Hexaethyldisilthian.* In this case 0·025 mol. of the organosilicon compound was employed. The reaction mixture was boiled for 7 hours. All the liquid was distilled off, to give *ca.* 15 ml. at 101—120° (mainly 101—103°) and unchanged hexaethyldisilthian (6·0 g., *ca.* 90%), b. p. 275—281°. The 110—120° fraction was added to water, and *ca.* 0·3 ml. of organosilicon material separated. This liquid gave gas evolution with silver nitrate in aqueous acetone and with warm alcoholic alkali, and thus probably contained some triethylsilane. (vi) iso*Cyanatotriethylsilane.* The reaction mixture was boiled for 6 hours. The liquid was distilled from the solid, to give 16 ml. of b. p. 102—108°, and unchanged *iso*cyanatotriethylsilane (6 g., 80%) at 162—166°. The 102—108° fraction was added to water, and *ca.* 2 ml. of organosilicon material separated; this had b. p. 162—166°, n_D^{15} 1·4320, and was evidently mainly unchanged *iso*cyanatotriethylsilane. It gave no black precipitate or gas evolution with excess of silver nitrate in aqueous acetone, and thus contained no triethylsilane. (vii) *Triethylfluorosilane.* The reaction mixture was boiled for 8 hours, and the product was worked up in the usual way. All (6 g., *ca.* 90%) boiled at 108—110° (n_D^{18} 1·3930—1·3935). It gave no gas evolution with silver nitrate in aqueous acetone or with warm alcoholic alkali, and thus contained no triethylsilane and was evidently unchanged triethylfluorosilane.

Interaction of Lithium Hydride and Triethylsilyl Compounds in Anisole and in Absence of Solvent.—Anisole was tried as a solvent because of the nearness of the b. p.'s of dioxan and triethylsilane. It was not as satisfactory as dioxan. When triethyliodosilane (0·05 mol.) was boiled with lithium hydride

(0·1 mol.) in anhydrous anisole (10 ml.) for 2 hours, a white solid separated. On fractionation, impure triethylsilane (2·5 ml.), b. p. 107—110°, was obtained. No trace of triethylsilane was detected from hexaethyldisilthian and lithium hydride under these conditions, and the bulk of the organosilicon sulphide was recovered.

Bromotriethylsilane (0·03 mol.) and triethyliodosilane (0·03 mol.) were each boiled with lithium hydride (2 g., considerable excess) for 8 hours. A small amount (<0·3 ml.) of impure triethylsilane was obtained in each case on distillation.

Action of Lithium Aluminium Hydride on Triethylfluorosilane.—Lithium aluminium hydride (0·03 mol., excess) was stirred with anhydrous ether (30 ml.). To the warm solution, triethylfluorosilane (0·08 mol.) was added, with vigorous stirring. The ether boiled for a few minutes without external heating. The mixture was boiled under reflux for 2 hours, and a white solid separated during this time. Water was added, followed by dilute sulphuric acid. The ethereal layer was dried (Na_2SO_4) and fractionated, with methyltri-*n*-propylsilane as "chaser," to give triethylsilane (8 g., 85%), b. p. 107·0°/760 mm., n_D^{20} 1·4116. [With aqueous alcoholic alkali, 0·1785 g. of the product gave 35·0 ml. (N.T.P.) of hydrogen. Calc. for $C_6H_{16}Si$: 34·4 ml.] The physical properties agree well with recorded values for triethylsilane (Whitmore, Pietrusza, and Sommer, *J. Amer. Chem. Soc.*, 1947, **69**, 2108).

Action of Methylmagnesium Iodide on iso*Cyanatotriethylsilane.*—*iso*Cyanatotriethylsilane (8 g., *ca.* 0·05 mol.) was added to a solution of methylmagnesium iodide (0·1 mol.) in ether (30 ml.), vigorous stirring being maintained. There was no evidence of reaction. The mixture was boiled under reflux for 2 hours, during which there was no evidence of reaction and the system remained homogeneous. The excess of Grignard reagent was destroyed with dilute sulphuric acid, and the ethereal layer was dried (Na_2SO_4) and fractionated. Only 0·5 ml. of liquid distilled between 110° and 140°, indicating that little or no triethylmethylsilane was present. Liquid (3 ml.) distilling at 154° (n_D^{19} 1·4330) was probably triethylsilanol.

Interaction of Sodium Iodide and Chlorotriethylsilane in Acetonitrile.—Triethyliodosilane was not isolated from this interaction, but its formation was clearly indicated. A solution of sodium iodide (10 g., 0·066 mol.) in acetonitrile (60 ml.) was added to a solution of chlorotriethylsilane (7·5 g., 0·05 mol.) in acetonitrile (20 ml.). This mixture immediately became yellow and cloudy, and a fine solid began to separate. A clear upper liquid layer formed above the bulk. The mixture was boiled under reflux, and long flat plates of a white solid (*S*) formed in the reflux condenser. After ½ hour's boiling, the mixture was allowed to cool, and then filtered through sintered glass to give a white solid. This solid, after being washed with a little acetonitrile, benzene, alcohol, and light petroleum, weighed *ca.* 0·9 g., and was dissolved in water to give a solution containing sodium and chloride ions (but no iodide or cyanide ions), and was clearly sodium chloride. More of this solid separated when the filtrate was kept. The liquid in the filtrate was distilled off, and the distillate gave both iodide and chloride ion on hydrolysis.

Some of the solid *S* was washed from the reflux condenser with light petroleum. The material fumed and quickly became brown in the air, and then liquefied. A little of the solid, sealed in m. p. tubes as quickly as possible, began to decompose at *ca.* 60° and collapsed at 75—85°, the material being completely liquid (deep red) at the last temperature. The material did not solidify on cooling. The solid was immediately decomposed by water, to give a solution containing iodide ion. This solid seems to be an addition product of acetonitrile and triethyliodosilane, and closely resembled the product obtained by interaction of these compounds.

Interaction of Acetonitrile and Triethyliodosilane.—A mixture of acetonitrile (1 ml.) and triethyliodosilane (1 ml.) was deep red. When the mixture was boiled in a test-tube a white solid separated on the cooler parts of the tube. This solid had similar properties to the solid *S* obtained in the preceding experiment. On cooling, more of this solid separated from the liquid.

When acetonitrile (0·5 ml.) was added to a mixture of triethyliodosilane (1 ml.), light petroleum (2 ml.), and benzene (3 ml.), a fine white solid immediately separated. This solid was washed by decantation with a mixture of light petroleum and benzene, and was recrystallised from this mixed solvent to give long fine needles. The solid behaved similarly to the solid *S* (above), except that it began to decompose at 70° and collapsed at 90—98°, to give a deep-red liquid.

No solid was obtained when chlorotriethylsilane was boiled with acetonitrile under reflux, and when these compounds were mixed in benzene and light petroleum.

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