537. *Organosilicon Compounds. Part III.* Some Sterically Hindered Compounds.*

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It has been shown that Grignard reagents may be conveniently used to attach three *iso*propyl, *cyclo*hexyl, or *o*-tolyl groups to silicon if fluorosilanes, as distinct from chlorosilanes, are employed in the preparations. This result is explicable in terms of steric effects, as is the fact that difluorodi*iso*propylsilane reacts more readily with *iso*propylmagnesium chloride than with the bromide. The greater ease of replacement of the chlorine atom in chlorofluorodi*iso*propylsilane than in chlorodi*iso*propylsilane may be polar in origin.

Three stable dialkylsilanediols, *viz.*, di*iso*propyl-, di*iso*butyl-, and di*cyclo*hexyl-silanediol, are described.

The effects of steric hindrance have been clearly demonstrated in attempts to attach three or four large alkyl or aryl groups to silicon. Thus, Cusa and Kipping (*J.*, 1933, 1040) found that only two chlorine atoms of phenyltrichlorosilane could be replaced by *cyclo*hexyl groups in the reaction with *cyclo*hexylmagnesium bromide, and Jenkins and Post (*J. Org. Chem.*, 1950, **15**, 522) obtained tri*cyclo*hexylsilane in only 4·4% yield from the prolonged interaction of trichlorosilane and excess of *cyclo*hexylmagnesium chloride. Nebergall and Johnson (*J. Amer. Chem. Soc.*, 1949, **71**, 4022), by employing an excess of *cyclo*hexyl-lithium, obtained chlorotri*cyclo*hexylsilane from tetrachlorosilane, but the presence of the three large alkyl groups prevented further reaction of the chloride even with methyl-, ethyl-, or phenyl-lithium under forcing conditions. Similar effects were observed with the *iso*propyl group, so that Gilman and Clark (*ibid.*, 1947, **69**, 1499) were unable to replace more than two chlorine atoms of trichlorosilane in interaction with *iso*propylmagnesium chloride, but by reaction of *iso*propyl-lithium with trichlorosilane and with tetrachlorosilane they obtained tri*iso*propylsilane and chlorotri*iso*propylsilane, respectively. These compounds would not react further with *iso*propyl-lithium, but gave phenyltri*iso*propylsilane with phenyl-lithium. More recently, Gilman and Smart (*J. Org. Chem.*, 1950, **15**, 720) have shown that identifiable products are not obtained when tetrachlorosilane reacts with excess of *o*-tolylmagnesium bromide, confirming an earlier result of Schumb and Saffer (*J. Amer. Chem. Soc.*, 1939, **61**, 363). They found, however, that trichlorosilane does yield tri-*o*-tolylsilane with excess of the Grignard reagent, and that the tri-*o*-tolylsilyl derivatives resemble the corresponding *iso*propyl compounds in reacting with unhindered lithium aryls. Important steric effects of *tert.*-butyl groups (Tyler, Sommer, and Whitmore, *ibid.*, 1948, **70**, 2876: in this case no more than two alkyl groups can be attached to silicon even with *tert.*-butyl-lithium at high temperature) and α-naphthyl groups (Gilman and Brannen, *ibid.*, 1951, **73**, 4640) in organosilicon compounds have also been demonstrated.

The overall impression gained from the literature is that attachment of three sterically-hindering alkyl or aryl groups to silicon calls for the use of lithium alkyls. It might be expected that the presence of small fluorine atoms as substituents on the silicon would reduce the steric hindrance in the replacements. The work described below indicates that if tetrafluorosilane is taken as the starting point, three *iso*propyl, *cyclo*hexyl, or *o*-tolyl groups can be attached to silicon by means of Grignard reagents without great difficulty.

Interaction of Silyl Fluorides with iso*Propyl-*, cyclo*Hexyl-*, o-*Tolyl-, and* iso*Butyl-magnesium Halides.*—Passage of tetrafluorosilane into an ethereal solution of *iso*propylmagnesium halide, followed by heating, yields a mixture of difluorodi*iso*propylsilane and fluorotri*iso*propylsilane (Eaborn, *J.*, 1949, 2755); the relative proportions of the products will clearly depend on the amount of gas passed, and on the rate of its passage. It has now been found that difluorodi*iso*propylsilane reacts readily, as expected, with *iso*propylmagnesium chloride to give the trialkylsilyl fluoride, but markedly less readily with

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* Part II, *J.*, 1950, 3077.

*iso*propylmagnesium bromide under similar conditions. This result is of interest in that the reactivity of *iso*propylmagnesium chloride and bromide have been shown to be in the reverse order in interaction with benzonitrile (Gilman, St. John, St. John, and Lictenwalter, *Rec. Trav. chim.*, 1936, **55**, 577). It suggests that the additional size of the bromine atom of the Grignard reagent is further reducing the stability of a transition state in which steric hindrance must be considerable.

Since difluorodi*iso*propylsilane reacts readily with *iso*propylmagnesium chloride whereas chlorodi*iso*propylsilane (Gilman and Clark, *loc. cit.*) does not, it was thought of interest to examine the behaviour of chlorofluorodi*iso*propylsilane. This compound was found to react fairly readily with *iso*propylmagnesium chloride in ether, the replacement being exclusively of the chlorine atom as far as could be ascertained. It is interesting to speculate whether the greater reactivity of the chlorofluoro-compound than of the chlorohydrogeno-compound could possibly arise from a fluorine atom causing less steric hindrance to reaction than a hydrogen atom. The van der Waals radius of hydrogen (1·2 Å) is rather less than that of fluorine (1·35 Å) but its covalent radius (0·30 Å) is markedly less than that of fluorine (0·64 Å), and it is possible to imagine a critically-compressed transition state in which the fact that the fluorine atom stands further out from the silicon would tend to counteract the difference in van der Waals radii in determining the atomic compressions. More important than this, however, is likely to be the large amount of ionic character in the Si–F bond, which can presumably lead to relatively low directional rigidity of the bond, and thus reduce the compression in the critically compressed transition state (the effect being analogous to the lack of rigidity of Si–O bonds in siloxan chains (cf. Rochow, " The Chemistry of the Silicones," 1951, p. 115). However, the greater reactivity of chlorofluorodi*iso*propylsilane could be polar in origin, for in spite of any counteracting mesomeric effect (" back-co-ordination "), the overall effect of replacing hydrogen attached to silicon by the strongly electronegative fluorine must be to increase the amount of positive charge on the silicon atom, and consequently to render it more susceptible to nucleophilic attack. Examination of the relative reactivities of R_2SiHCl and R_2SiFCl structures in which steric effects are not of such great significance as in the compounds under consideration is being undertaken in these laboratories.

Interaction of tetrafluorosilane with *cyclo*hexylmagnesium chloride gives difluorodi*cyclo*hexylsilane (not obtained pure) and higher-boiling substances which could not be identified but may contain tri*cyclo*hexylsilyl compounds. Interaction of the difluoride with further *cyclo*hexylmagnesium chloride gave, after hydrolysis, good yields of tri*cyclo*hexylsilanol and tri*cyclo*hexyl*cyclo*hexyloxysilane. The latter compound presented some difficulties in identification until it was recalled that the analogous compound di*cyclo*hexyl*cyclo*hexyloxyphenylsilane was obtained by Cusa and Kipping (*loc. cit.*) in the interaction of trichlorophenylsilane with *cyclo*hexylmagnesium bromide. The highly hindered tri*cyclo*hexyl*cyclo*hexyloxysilane is remarkably stable towards alkaline hydrolysis but readily hydrolysed by acid. Fluorotri*cyclo*hexylsilane was prepared by interaction of tri*cyclo*hexylsilanol and aqueous-ethanolic hydrogen fluoride, an example of a general method which is commonly employed in this laboratory (details will be published later).

Tetrafluorosilane reacts with *o*-tolylmagnesium bromide to give a satisfactory yield of difluorodi-*o*-tolylsilane. This difluoride reacts with more *o*-tolylmagnesium bromide under more severe conditions to give products from which tri-*o*-tolylsilanol may be obtained in reasonable yield. With *iso*butylmagnesium chloride, tetrafluorosilane gives mainly tri*iso*butylfluorosilane, but some di*iso*butyldifluorosilane is also usually obtained, indicating that the steric effect of the *iso*butyl groups is, as expected, intermediate between those of *iso*propyl and of *n*-alkyl groups, which under these conditions give tetra-alkylsilanes or trialkylfluorosilanes and no dialkyldifluorosilanes (cf. Gierut, Sowa, and Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 897). Furthermore, tri*iso*butylsilyl fluoride resembles the triethylsilyl and the tri-*n*-propylsilyl compound in reacting with methylmagnesium iodide with replacement of the fluorine, under conditions in which the tri*iso*propylsilyl compound is not attacked.

Dialkylsilanediols.—Although silanediols containing aryl groups have long been known, *e.g.*, diphenylsilanediol (Kipping, *J.*, 1912, **101**, 2108), ethylphenylsilanediol, and dibenzylsilanediol (Robison and Kipping, *J.*, 1912, **101**, 2142, 2156), only one silanediol free from aromatic groups was known until recently. This compound, di*cyclo*hexylsilanediol, was obtained by Cusa and Kipping (*J.*, 1932, 2205) in small yield as an unexpected by-product, and possibly because its identity was not very soundly based its existence has been overlooked in reviews of the subject (Burkhard, Rochow, Booth, and Hartt, *Chem. Reviews*, 1947, **41**, 97; Digiorgio, Sommers, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 346); its identity is confirmed, however, by the work described below.

That dialkylsilanediols containing smaller alkyl groups are also stable was demonstrated by the preparation of diethyl-, di-*n*-propyl-, and di-*n*-butyl-silanediol by the carefully controlled hydrolysis of the corresponding dichlorosilanes (Digiorgio, Sommers, and Whitmore, *loc. cit.*; Digiorgio, Abstract of paper, Atlantic City Meeting, Amer. Chem. Soc., April 1946). In the present work di*iso*propyl- and di*iso*butyl-silanediol have been prepared by hydrolysis of the corresponding difluorosilanes, and found to be stable solids. Both compounds resemble diethylsilanediol in being soluble in water, but furthermore they may actually be recrystallized from water as well as from light petroleum. The compounds are not decomposed when their aqueous solutions are briefly boiled, and di*iso*propylsilanediol was not decomposed when heated at 130° for some hours and was recovered unchanged when its aqueous solution was allowed to evaporate to dryness during several days. Both compounds are more soluble in aqueous alkali than in water and are precipitated unchanged when the solution is acidified. The stability of these silanediols is presumably to be attributed to the steric effects of the particular alkyl groups involved.

EXPERIMENTAL.

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

Analyses.—Hydrolysable fluorine was determined by adding a measured volume of an approximately 0·1N-alcoholic solution of the fluoride to excess of alcoholic alkali, keeping the mixture for a few minutes, adding water, and back-titrating the excess of alkali.

Microanalyses are by Drs. Weiler and Strauss, Oxford, or (marked *) by Dr. Elek, of Los Angeles.

General.—Unless otherwise stated, the reaction mixtures from Grignard reagents were hydrolysed by adding 10% sulphuric acid until two clear layers were formed. Ethereal extracts were dried over sodium sulphate. Yields from reactions involving Grignard reagents are based on the silicon compound taken, except when tetrafluorosilane was involved; the yield is then based on the alkyl halide. Tetrafluorosilane was generated by heating a mixture of sodium fluorosilicate, silica, and sulphuric acid, and the ethereal Grignard reagent was well-stirred throughout the passage of the gas. Fractionations, unless otherwise specified, were carried out through columns of efficiency of *ca.* 10 theoretical plates.

*Difluorodi*iso*propylsilane.*—This compound was prepared from tetrafluorosilane as described in Part I (*J.*, 1949, 2755).

*Interaction of Difluorodi*iso*propylsilane and* iso*Propylmagnesium Chloride.*—Difluorodi*iso*propylsilane (0·2 mol.) in an equal volume of ether was added to the Grignard reagent from *iso*propyl chloride (0·33 mol.) and magnesium (0·34 mol.) in ether (130 ml.), and the mixture was boiled under reflux for 20 hours. After the hydrolysis of the mixture, the ethereal layer was separated, dried, and fractionated. No unchanged difluoride was present, and fluorotri*iso*propylsilane (27 g., 80%), b. p. 170°/760 mm., n_D^{20} 1·4185, was obtained.

*Interaction of Difluorodi*iso*propylsilane and* iso*Propylmagnesium Bromide.*—A procedure similar to the foregoing, but involving difluorodi*iso*propylsilane (0·55 mol.), *iso*propyl bromide (1·0 mol.), and magnesium (1·05 mol.) in ether (450 ml.), and 48 hours' boiling under reflux, gave unchanged difluoride (33 g., 40%), b. p. 101°/760 mm., and fluorotri*iso*propylsilane (30·5 g., 30%), b. p. 170°/760 mm., n_D^{20} 1·4183. (Grignard reagent was still present at the end of the reflux period.)

*Interaction of Chlorofluorodi*iso*propylsilane and* iso*Propylmagnesium Chloride.*—Chlorofluorodi*iso*propylsilane (0·1 mol.) was boiled under reflux for 30 hours with the Grignard reagent from *iso*propyl chloride (0·2 mol.) and magnesium (0·21 mol.) in ether (70 ml.). Grignard reagent was still present at the end of this period, and was destroyed by filtering off the magnesium salts from the ethereal solution and adding a dilute ethereal solution of iodine to the filtrate until the yellow colour persisted. Filtration, followed by fractionation of the filtrate, gave fluorotri*iso*propylsilane (12 g., 70%), b. p. 169—171°, n_D^{15} 1·4200, with no recovery of chlorofluorodi*iso*propylsilane and leaving a residue (hold-up) of 3 ml. Tests on the precipitated magnesium salts showed no appreciable amount of fluoride to be present.

*Di*iso*propylsilanediol.*—A solution of potassium hydroxide (0·036 mol.—a slight deficiency) in water (8 ml.) was added to a solution of difluorodi*iso*propylsilane (0·02 mol.) in dioxan (25 ml.) with stirring. After 2 minutes, excess of water was added and the organosilicon material was extracted with ether. The ethereal extract was dried, the ether evaporated until about 5 ml. of liquid remained, and light petroleum then added. The solid which separated was recrystallized from light petroleum, giving long needles of *di*iso*propylsilanediol* (1·5 g., 50%), m. p. 114° (Found: C, 48·8; H, 10·7. $C_6H_{16}O_2Si$ requires C, 48·6; H, 10·9%).

A sample of the solid was kept in a m. p. tube at 130° for 3 hours, during which most of it sublimed to the cooler parts of the tube. The condensed material had m. p. 112—114°. A sample of the pure solid was recrystallized from water (the water being boiled for a short while in the process) to give material, m. p. 113—114°. The mother-liquor was allowed to evaporate to dryness during several days, during which long needles, m. p. 112—114°, were deposited. The solid dissolved more readily in 2N-aqueous sodium hydroxide than in water, and was precipitated when the solution was acidified with concentrated hydrochloric acid; the precipitate after being washed and dried had m. p. 112—114°.

*Tri*iso*propylsilanol.*—Fluorotri*iso*propylsilane (0·07 mol.) was added to a solution of potassium hydroxide (0·065 mol.) in sufficient aqueous alcohol to give a homogeneous system. After a few minutes excess of water was added, the organosilicon material was extracted with light petroleum, and the extract dried. The solvent was distilled off, and the residue was fractionated through a centre-rod column (efficiency >40 plates) to give *tri*iso*propylsilanol* (8 g., 65%), b. p. 196°/750 mm., n_D^{21} 1·4532 (Found *: C, 61·9; H, 12·6. $C_9H_{22}O$ requires C, 62·0; H, 12·7%).

*Ethoxytri*iso*propylsilane.*—Sodium (0·1 mol.) was dissolved in ethanol (40 ml.), and fluorotri*iso*propylsilane (0·07 mol.) was added with stirring. After 5 minutes, the mixture was added to an equal volume of light petroleum, and the petroleum solution was washed with water and dried ($CaSO_4$). After removal of the solvent, the residue was fractionated through a centre-rod column (efficiency >40 plates) to give ethoxytri*iso*propylsilane (7 g., 50%), b. p. 204°/750 mm., n_D^{20} 1·4347 (Found *: C, 65·3; H, 12·6. Calc. for $C_{11}H_{26}OSi$: C, 65·3; H, 12·95). Gilman and Clark (*loc. cit.*) describe this substance as having b. p. 200°/738 mm., n_D^{20} 1·4560.

*Attempt to prepare Ethoxyfluorodi*iso*propylsilane.*—In a single experiment, sodium (0·08 mol.) was dissolved in anhydrous ethanol (25 ml.), and the solution was added with stirring to a solution of difluorodi*iso*propylsilane (0·1 mol.) in anhydrous ethanol (10 ml.). The mixture was kept for 2½ hours, and then poured into excess of water. Extraction with ether, followed by drying and fractionation of the extract, gave unchanged difluorodi*iso*propylsilane (6 g.) and diethoxydi*iso*propylsilane (5 g.), b. p. 186—187°/760 mm. Only 2 ml. of liquid distilled between 110° and 180°. (Presumably under these conditions the reversibility of the reaction $\equiv Si{\cdot}OEt + HF \rightleftharpoons \equiv Si{\cdot}F + HOEt$ leads to destruction of any ethoxyfluorosilane formed.)

*Interaction of Fluorotri*iso*propylsilane and Methylmagnesium Iodide.*—A mixture of fluorotri*iso*propylsilane (0·07 mol.) and methylmagnesium iodide (0·1 mol.) in ether (50 ml.) was boiled under reflux for 5 hours. No solid separated during this time. Addition of sulphuric acid, followed by separation, drying, and fractionation of the ethereal layer, gave recovered fluorotri*iso*propylsilane (10 g., 80%), b. p. 170°/760 mm., n_D^{21} 1·419. The small residue (hold-up) all boiled below 175°.

*Preparation of Chlorotri*cyclo*hexylsilane, Tri*cyclo*hexylsilanol, and Di*cyclo*hexylsilanediol* (cf. Nebergall and Johnson, *loc. cit.*, who obtained only chlorotri*cyclo*hexylsilane from this reaction, but in much better yield than is reported below).—*cyclo*Hexyl-lithium was prepared during 6 hours from chloro*cyclo*hexane (1·5 mol.) and lithium ribbon (3·5 g.-atom) in olefin-free light petroleum. Tetrachlorosilane (0·15 mol.) was added during ½ hour, and the mixture was stirred, and boiled under reflux for ½ hour. Further tetrachlorosilane (0·15 mol.) was then added, and the mixture was boiled under reflux for 5 hours, and kept overnight at room temperature. The liquid was siphoned off, and combined with the light petroleum washings of the solid residue. The solvent was removed, and distillation of the residue gave 10 ml. of liquid of b. p. 220—250° and 8 ml. of b. p. 250—310° (*A*), and left a residue (*B*) of b. p. >310°. On cooling, (*B*) deposited a solid, which was removed from the residual oil (*C*), recrystallized from ether, and found to be chlorotri*cyclo*hexylsilane (15 g., 16%), m. p. 101°. The oil (*C*) was hydrolysed by warming it with excess of aqueous-ethanolic potassium hydroxide, and the mixture was poured into water. Ether-extraction, followed by removal of the solvent, gave a solid, which, after recrystallization from light petroleum containing a little ether, was found to be tri*cyclo*hexylsilanol (11 g., 13%), m. p. 177—178° [Nebergall and Johnson, *loc. cit.*, report m. p. 176—177° (uncorr.) for this compound. The product, m. p. 176—178°, obtained by Jenkins and Post (*J. Org. Chem.*, 1950, **15**, 556) from the hydrolysis of bromotri*cyclo*hexylsilane, and described by them as 'probably hexa*cyclo*hexyldisiloxane' would also appear to be tri*cyclo*hexylsilanol]. The liquid (*B*), which it was believed would contain dichlorodi*cyclo*hexylsilane, was hydrolysed as described for (*C*), and the product worked up in the same way to give di*cyclo*hexylsilanediol (4 g., 6%), m. p. 164—165° (Found *: C, 63·0; H, 10·6. Calc. for $C_{12}H_{24}O_2Si$: C, 63·1; H, 10·6%). The pure compound showed no evidence of decomposition at 180°, but samples containing impurities gave off gas bubbles above the m. p. Cusa and Kipping (*J.*, 1932, 2205) describe the compound as effervescing above its m. p. of 164—165°.

Interaction of Tetrafluorosilane and cyclo*Hexylmagnesium Bromide.*—The Grignard reagent was prepared from *cyclo*hexyl bromide (2 mol.) and magnesium (2·05 mol.) in ether (1 l.), and tetrafluorosilane was passed in for 6 hours (*i.e.*, for 1 hour after the ether had ceased to reflux). The mixture was boiled under reflux for 2 hours, and after hydrolysis the ethereal layer was separated, dried, and distilled up to 300° leaving a residue of oil from which crystalline products (other than a little di*cyclo*hexylsilanediol) could not be obtained even after alkaline hydrolysis. The liquid, b. p. 230—270°, was twice redistilled, to give 50 ml. of liquid, b. p. 248—260°, which was taken to be impure difluorodi*cyclo*hexylsilane. The liquid contained only 13·1% of hydrolysable fluorine, whereas $C_{12}H_{22}SiF_2$ requires 16·4%. Attempts to obtain a purer sample were unsuccessful. That the liquid contained a large proportion of the difluoride was confirmed by the fact that on hydrolysis of 4·6 g. of it with aqueous-alcoholic potassium hydroxide, followed by pouring of the product into water, extraction with ether, removal of the ether, and recrystallization of the solid residue from light petroleum (b. p. 40—60°) containing a little ether gave 3·0 g. of di*cyclo*hexylsilanediol, m. p. 164°, mixed m. p. with authentic sample, 164° (a yield of 70%, the liquid of b. p. 248—260° being assumed to be difluorodi*cyclo*hexylsilane).

*Interaction of Difluorodi*cyclo*hexylsilane and* cyclo*Hexylmagnesium Chloride.*—Difluorodi*cyclo*hexylsilane (0·1 mol.; impure material from preceding experiment) was added to the Grignard reagent from *cyclo*hexyl chloride (0·36 mol.) in ether (150 ml.). The ether was distilled off until a thermometer in the residue recorded 70°, and the mixture was kept at this temperature for 48 hours. Addition of ether was followed by addition of dilute sulphuric acid and separation and drying of the ethereal layer. The ether was removed to leave an oil, which on extraction with acetone left a white solid which proved, after recrystallization from light petroleum–acetone, to be *tri*cyclo*hexyl*cyclo*hexyloxysilane* (11 g., 30%), m. p. 204—205° [Found: C, 76·4; H, 11·8; Si, 7·4%; *M* (Rast), 384. $C_{24}H_{44}OSi$ requires C, 76·5; H, 11·8; Si, 7·45%; *M*, 376]. The solvent was removed from the acetone extracts, the residual oil was hydrolysed by boiling it with excess of aqueous alcoholic potassium hydroxide, and the mixture was poured into water. The solid which separated was dried and recrystallized from ether–light petroleum, to give tri*cyclo*hexylsilanol (17 g., 57%), m. p. 177—178°, mixed m. p. with an authentic sample 177—178°.

*Fluorotri*cyclo*hexysilane.*—Aqueous hydrofluoric acid (60 ml.; 40% acid) was added to a solution of tri*cyclo*hexylsilanol (0·017 mol.) in ethanol (350 ml.). The mixture was kept just below its b. p. for 2½ hours, and then poured into excess of water. Extraction with light petroleum followed by removal of the solvent gave *fluorotri*cyclo*hexylsilane* (4·6 g., 95%), m. p. 41—44° raised to 45—46° by recrystallization from ethanol–light petroleum (Found: F, 6·4. $C_{18}H_{33}SiF$ requires F, 6·4%).

*Tri*cyclo*hexyl*cyclo*hexyloxysilane.*—Sodium (0·05 g.-atom) was dissolved in warm anhydrous *cyclo*hexanol (30 ml.), and chlorotri*cyclo*hexylsilane (0·03 mol.) was added. The mixture was boiled under reflux for ½ hour, and light petroleum added. The mixture was poured into excess of water, and the petroleum layer was washed, separated, and evaporated to small volume. Addition of acetone gave tri*cyclo*hexyl*cyclo*hexyloxysilane (0·7 g., 44%), m. p. 203—204° after recrystallization (mixed m. p. with specimen prepared as described in an earlier experiment, 203—204°). Tri*cyclo*hexylsilanol (0·15 g.) was isolated from the acetone mother-liquors.

*Hydrolysis of Tri*cyclo*hexyl*cyclo*hexyloxysilane.*—The silane (1 g.) was warmed with concentrated hydrochloric acid (4 ml., *d* 1·12) in ethanol (35 ml.). All the solid dissolved in less than 10 minutes. The mixture was boiled under reflux for ¾ hour, and then cooled, and water was added. The solid which separated was filtered off, dried, and recrystallized from ether–light petroleum, to give tri*cyclo*hexylsilanol (0·55 g., 70%), m. p. 178—179°, mixed m. p. with authentic sample 178—179°. No tri*cyclo*hexyl*cyclo*hexyloxysilane could be recovered.

Tri*cyclo*hexyl*cyclo*hexyloxysilane (0·5 g.) was added to a solution of potassium hydroxide (10 g.) in water (10 ml.) and ethanol (70 ml.), and the mixture was boiled under reflux for 2 hours. Water was added dropwise to the cooled mixture until precipitation was complete. The solid was filtered off, washed with water and a little alcohol, and recrystallized from light petroleum–(predominantly) acetone, to give the unchanged silane (0·45 g.), m. p. 203—204°.

*Interaction of Tri*cyclo*hexyl*cyclo*hexyloxysilane and Acetyl Chloride.*—Acetyl chloride (6 ml.) was boiled under reflux with the silane (0·3 g.). After 2 hours the acetyl chloride was rapidly distilled off and the cooled residue was dissolved in ether. The filtered ethereal solution was evaporated to a small volume, and light petroleum added. No solid separated. On concentration of the solution and addition of acetone, tri*cyclo*hexyl*cyclo*hexyloxysilane (0·22 g.), m. p. 201—203°, was recovered. Clearly, little, if any, conversion into the chloride had occurred.

Interaction of Tetrafluorosilane and o-*Tolylmagnesium Bromide.*—Tetrafluorosilane was passed through a solution of the Grignard reagent from *o*-bromotoluene (1 mol.) and magnesium (1·05 mol.) in ether (500 ml.) until refluxing of the ether had ceased (2 hours). Ether was added to replace that carried away in the gas stream, and the mixture was boiled under reflux for 4 hours, after which no *o*-tolylmagnesium bromide remained. The magnesium salts were filtered off and washed with ether, the ethereal filtrate and washings were combined, and the ether was removed by distillation. The residue on distillation gave 20 ml. of liquid boiling over the range 60—270°, 48 g. of liquid of b. p. 278—294°, 8 g. of b. p. 294—305°, and then little more below 360°, at which temperature distillation was stopped. No crystalline material could be isolated from the syrupy residue either before or after alkaline hydrolysis. The material of b. p. 278—294° was several times distilled, to give *difluorodi*-o-*tolylsilane* (30 g., 25%), b. p. 285—289° (Found: F, 15·1. $C_{14}H_{24}SiF_2$ requires F, 15·3%). The yield of crude product (b. p. 275—300°) was *ca.* 50 g. (40%).

Hydrolysis of Difluorodi-o-*tolylsilane.*—Difluorodi-*o*-tolylsilane (10 g., 0·04 mol.) was warmed for ¼ hour with excess of aqueous-alcoholic potassium hydroxide, sufficient alcohol being present to give a homogeneous system. The mixture was poured into water, and the organosilicon material was extracted with ether. The ether was removed, and light petroleum added to the residue to give a solid, which was recrystallized from light petroleum, giving di-*o*-tolylsilanediol (8 g., 80%), m. p. 137—138° [Gilman and Smart, *loc. cit.*, describe this compound as having m. p. 135·5—136·5° (uncorr.)].

Interaction of Difluorodi-o-*tolylsilane and* o-*Tolylmagnesium Bromide.*—Difluorodi-*o*-tolylsilane (0·1 mol.) was added to the Grignard reagent from *o*-bromotoluene (0·2 mol.) and magnesium (0·21 mol.) in ether (250 ml.). The ether was distilled off until a thermometer in the residue recorded 90°, and the mixture was kept at this temperature, with some ether refluxing, for 100 hours. Addition of ether and sulphuric acid was followed by separation and drying of the ethereal layer. Removal of the solvent left a syrupy liquid, from which liquid was distilled until the vapour temperature reached 360°. The residual oil cooled to a glassy solid which could not be crystallized. It was boiled with excess of aqueous-alcoholic potassium hydroxide for 1 hour, and the mixture was poured into water. Ether-extraction, followed by removal of the solvent, left a syrup which was soluble in all the common organic solvents and could not be crystallized. The syrup was boiled with aqueous-alcoholic hydrochloric acid for ½ hour, the mixture poured into water, and the oil recovered by ether-extraction followed by removal of the solvent. Recrystallization from aqueous acetone gave a little solid, and further amounts of this solid were obtained on recrystallization from aqueous methanol. After recrystallization from light petroleum the solid was found to be ethoxytri-*o*-tolylsilane (1·5 g.), m. p. 143—144° (Found: C, 79·2; H, 7·6. Calc. for $C_{23}H_{26}OSi$: C, 79·5; H, 7·6%) (Gilman and Smart, *loc. cit.*, give m. p. 144·5—145·0°). The remaining oil, after re-treatment with aqueous-alcoholic potassium hydroxide followed by recovery in the usual way, was crystallized by dissolving it in light petroleum and keeping the solution at 0° for some days. The solid separating was recrystallized from light petroleum, giving *tri*-o-*tolylsilanol* (13 g., 40%), m. p. 110—111° (Found: C, 79·0; H, 7·0. $C_{21}H_{22}OSi$ requires C, 79·2; H, 7·0%) (this compound has been referred to by Gilman and Smart, *loc. cit.*, but not described). The solid crystallizes remarkably slowly from its supersaturated solutions even when they are seeded and scratched, and it may have been failure to appreciate this which led to the difficulty of isolating the compound. The molten substance cools to a brittle glassy solid which usually takes some days to crystallize even when seeded.

Interaction of Tetrafluorosilane and iso*Butylmagnesium Chloride.*—In a typical experiment tetrafluorosilane was passed into the Grignard reagent from *iso*butyl chloride (4 mol.) and magnesium (4·0 mol.) in ether (2 l.) for 5 hours (*i.e.*, for 1 hour after the ether had stopped refluxing). The mixture was boiled under reflux for 1 hour, and after the addition of aqueous sulphuric acid the ethereal layer was separated, dried, and fractionated, to give *di*iso*butyldifluorosilane* (30 g., 8%), b. p. 145°/760 mm. (Found : F, 21·1. $C_8H_{18}SiF_2$ requires F, 21·1%), and *tri*iso*butylfluorosilane* (156 g., 53%), b. p. 205·5°/750 mm., n_D^{20} 1·14218 (Found : F, 8·75. $C_{12}H_{27}SiF$ requires F, 8·70%).

In one experiment under similar conditions a somewhat increased yield of tri*iso*butylfluorosilane was obtained, with no difluoride. The highest yield of difluoride obtained in any similar experiment was 25%.

*Interaction of Tri*iso*butylfluorosilane and Methylmagnesium Iodide.*—Tri*iso*butylfluorosilane (0·1 mol.) was added all at once to the Grignard reagent from methyl iodide (0·14 mol.) and magnesium (0·15 mol.) in ether (50 ml.), the solution being just below its b. p. Slow refluxing of the ether began and continued for 10 minutes with formation of two liquid layers. More ether (30 ml.) was added and the mixture was boiled under reflux for 3 hours. After addition of sulphuric acid the ethereal layer was separated, dried, and fractionated to give *tri*iso*butylmethylsilane* (18 g., 90%), b. p. 216·5°, n_D^{20} 1·4393 (Found: C, 72·4; H, 13·9. $C_{13}H_{30}Si$ requires C, 72·8; H, 14·1%).

*Di*iso*butylsilanediol.*—Di*iso*butyldifluorosilane (0·025 mol.) was added to a solution of sodium hydroxide (*ca.* 0·04 mol.) in aqueous ethanol (50 ml., including *ca.* 10 ml. of water). Concentrated aqueous sodium hydroxide solution was added dropwise with stirring until the mixture was alkaline to litmus. The mixture was poured into excess of water, and the organosilicon material was extracted with ether. The ethereal extract was dried, and the ether was removed, leaving a residue which set solid on cooling; recrystallization from light petroleum gave *di*iso*butylsilanediol* (2·8 g., 65%), which contracts to a semi-solid at 88—89° and collapses to liquid at 100—101° (Found : C, 54·5; H, 11·4. $C_8H_{20}SiO_2$ requires C, 54·5; H, 11·4%). The m. p. behaviour was unchanged by recrystallization from several solvents or by sublimation, and the possibility of a mesomorphic state is being investigated. The solid is recovered unchanged when its solution in boiling water is cooled or when its solution in aqueous sodium hydroxide is acidified with hydrochloric acid.

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