538. *Organosilicon Compounds. Part IV.* The Preparation of Organofluorosilanes.*

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The use of aqueous-alcoholic hydrogen fluoride to convert a wide variety of organosilicon compounds into organofluorosilanes is described.

Organofluorosilanes have been prepared by the following methods : (1) interaction of tetrafluorosilane and Grignard reagents (Gierut, Sowa, and Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 897; Medox and Kotelkov, *J. Gen. Chem. U.S.S.R.*, 1937, **7**, 207; 1938, **8**, 291; Eaborn, preceding paper); (2) the action of anhydrous hydrogen fluoride (Pearlson, Brice, and Simons, *J. Amer. Chem. Soc.*, 1945, **67**, 1769), zinc fluoride and antimony trifluoride (Emeléus and Wilkins, *J.*, 1944, 454; Newkirk, *J. Amer. Chem. Soc.*, 1946, **68**, 2736; Booth and Carnell, *ibid.*, p. 2650; McKusker and Green, *ibid.*, 1948, **70**, 2807; Booth and Jarry, *ibid.*, 1949, **71**, 971) or ammonium fluoride (Wilkins, *J.*, 1951, 2736) on the corresponding organochlorosilanes; and (3) the interaction of organosiloxans and ammonium fluoride or calcium fluoride in sulphuric acid (Flood, *J. Amer. Chem. Soc.*, 1933, **55**, 1735; Emeléus and Wilkins, *loc. cit.*). Marans, Sommer, and Whitmore (*J. Amer. Chem. Soc.*,

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* Part III, preceeding paper.

1951, **73**, 5127) reported a very convenient method of obtaining organofluorosilanes involving the reaction of alkoxysilanes or trialkylchlorosilanes with aqueous hydrofluoric acid at 0°. The present author has for some years prepared organofluorosilanes by a rather similar method, *viz.*, by treating aqueous-alcoholic hydrogen fluoride not only with dialkyldiethoxysilanes, trialkylethoxysilanes, and trialkylchlorosilanes, but alternatively with trialkylsilyl hydroxides and bromides, triarylsilyl hydroxides, ethoxides, chlorides, or bromides, dialkyldichlorosilanes, or hexa-alkyldisiloxans. Under the reaction conditions the chlorides and bromides are undoubtedly hydrolysed more rapidly than the fluorides are formed, and it seems likely that any organosilicon compounds which undergo ready hydrolysis (*e.g.*, silyl sulphides, iodides, cyanides, and thiocyanates) will be converted into the corresponding fluorides in the reaction medium. Although hexaethyldisiloxan and *s*-diethyltetramethyldisiloxan are satisfactorily converted, hexaphenyldisiloxan does not react appreciably under the conditions employed, possibly because of its insolubility.

Apart from being applicable to a wider range of compounds, the method has the advantage over that employed by Marans, Sommer, and Whitmore of involving a homogeneous system, and it is likely to be the more effective even for ethoxides and trialkylsilyl chlorides when fluorides are to be made from less soluble, and particularly solid, organosilicon compounds (Marans *et al.* employed only liquids). Furthermore, the method described here has the advantage of employing more dilute hydrofluoric acid solutions, so that hard glass apparatus may be used. Of importance is the satisfactory conversion of the readily available dichlorodiethylsilane into the difluoro-compound, because in contact with an exclusively aqueous system this dichloride is likely to give insoluble siloxans. With alkylsiloxans the method is likely to prove particularly useful where the presence of a reactive group (*e.g.*, Si–H, Si–Ph) precludes the use of the sulphuric acid–ammonium fluoride method. It is of interest that the sterically hindered tri*cyclo*hexyl- and tri-*o*-tolyl-silyl hydroxides are converted into the fluorides under these conditions, since they are sometimes unreactive in " general" hydroxysilane reactions (cf. *e.g.*, Gilman and Miller, *ibid.*, p. 2367 ; Gilman and Brannan, *ibid.*, p. 4640).

The work described here, considered along with accounts of the hydrolysis and alcoholysis of organofluorosilanes (Swain, Esteve, and Jones, *ibid.*, 1949, **71**, 965 ; Hughes, *Quart. Reviews*, 1951, **5**, 245), indicates the reversibility of the reactions $\equiv$Si·OR + HF $\rightleftharpoons$ $\equiv$SiF + ROH (R = H or Et) to which attention has not previously been drawn. Unpublished work by the author (under the direction of Professor E. D. Hughes) shows that fluorotriphenylsilane, for example, undergoes alcoholysis in 0·1M-solution in ethanol only to the extent of *ca.* 1%, and so may be satisfactorily recrystallized from this solvent, while tri-*n*-butylfluorosilane and difluorodi*iso*propylsilane undergo alcoholysis to about 2% and 20%, respectively, under the same conditions. Similarly, in aqueous acetone (1 : 3 by volume) triphenylfluorosilane (*ca.* 0·1M) is *ca.* 30% hydrolysed, and use of excess of hydrofluoric acid allows hydroxytriphenylsilane to be converted into the fluoride in this medium (see below). It should be noted, however, that Swain, Esteve, and Jones (*loc. cit.*) in their kinetic investigations of the hydrolysis of 0·01M-solutions of fluorotriphenylsilane in aqueous acetone did not observe indications of incomplete reaction.

EXPERIMENTAL

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

Analyses.—See Part III (*loc. cit.*).

Hydrofluoric Acid.—The 40% w/w " AnalaR " acid was employed.

Ethoxytriphenylsilane.—Sodium (3·5 g., 0·15 atom) was dissoved in anhydrous ethanol, and a solution of fluorotriphenylsilane (19·5 g., 0·7 mol.) in hot anhydrous ethanol was added with stirring. After a few minutes the mixture was poured into a large volume of water, and the solid which separated was filtered off, washed, and dried. Recrystallization from ethanol gave colourless plates, m. p. 61—64° (17 g., 80%). Recrystallization from nitromethane gave *ethoxytriphenylsilane*, m. p. 65° (Found : C, 78·6; H, 10·5. $C_{20}H_{20}OSi$ requires C, 78·9; H, 10·6%).

The same compound was obtained from triphenylsilane and sodium ethoxide in anhydrous ethanol, and from chlorotriphenylsilane and anhydrous ethanol.

Bromotriphenylsilane.—The material employed, m. p. 122—124°, was prepared by the action of bromine on triphenylsilane in carbon tetrachloride cooled in solid carbon dioxide–acetone, and was purified by non-ebullioscopic distillation at 1 mm. The same solid was obtained from ethoxytriphenylsilane and acetyl bromide.

Tri-n-*butylethoxysilane.*—Sodium (1 g.) was dissolved in anhydrous ethanol and tri-*n*-butylfluorosilane (9 g.) was added. The alcohol was removed on a boiling-water bath, and the residue was taken up in ether. The solution was filtered, and then fractionated, to give tri-*n*-butylethoxysilane (6 g., 60%), b. p. 143°/35 mm., n_D^{20} 1·4345 (Found: C, 68·9; H, 13·4. Calc. for $C_{14}H_{32}OSi$: C, 68·8; H, 13·2%). Marans, Sommer, and Whitmore (*loc. cit.*) describe this compound as having b. p. 145°/34 mm., n_D^{20} 1·4341.

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

*Tri*cyclo*hexylhydroxysilane and Hydroxytri*-o-*tolylsilane.*—These were prepared as described in Part III (*loc. cit.*).

Organofluorosilanes.—The Table lists all but one of the organofluorosilane preparations. It will be seen that the conditions were varied considerably without obvious serious effects. The organosilicon reactant was usually dissolved in ethanol, and hydrofluoric acid was added. If necessary, more alcohol was then added to ensure a homogeneous system at the reaction temperature (and it is this which largely accounts for the wide variations in the volume of the reaction medium). After the time stated, the mixture was poured into excess of water, whereupon the organosilicon material separated as a solid or as an upper liquid layer. Ether-extraction was sometimes employed (see Notes below). Liquid products were distilled or fractionated. The identity of solids was confirmed by mixed m. p.s or by analysis for hydrolysable fluorine.

A platinum basin was used for the reactions at room temperature, and a hard-glass flask and reflux condenser for those at higher temperatures. The glass was attacked, but not seriously.

Reactant	Wt., g.	EtOH, ml.	HF, ml.	Reaction time, hrs.	Temp.	Product	Yield, %	Notes
Et_2SiCl_2	25	90	30	1½	75°	Et_2SiF_2, b. p. 62°	70	1, 2
Et_3SiCl	18·5	90	20	2	75	Et_3SiF, b. p 109·5°, n_D^{20} 1·3910	85	2
Et_3SiBr	2·5	20	5	1½	75	Et_3SiF, b. p. 109°, n_D^{20} 1·3912	80	3
Et_3SiOH	6·0	50	2	1	50	Et_3SiF, b. p. 109—111°, n_D^{25} 1·3880	7	—
$(Et_3Si)_2O$	6·5	80	15	5½	75	Et_3SiF, b. p. 109—110°, n_D^{25} 1·3880	85	4
$(EtMe_2Si)_2O$	16	200	40	5	50	$EtMe_2SiF$, b. p. 51°, n_D^{15} 1·3570	60	2, 9
$Bu^n{}_3Si\cdot OEt$	3	30	5	5	75	$Bu^n{}_3SiF$, b. p. 221°, n_D^{20} 1·4236	75	3
$Pr^i{}_2Si(OEt)_2$	2	20	2	5	18	$Pr^i{}_2SiF_2$, b. p. 102°, n_D^{22} 1·3663	90	3
$(C_6H_{11})_3Si\cdot OH$ ...	5	350	60	2½	75	$(C_6H_{11})_3SiF$, m. p. 41—44°	95	5
$Ph_3Si\cdot OH$	2	30	2	24	18	Ph_3SiF, m. p. 61—63°	100	6
$Ph_3Si\cdot OEt$	2	30	3	24	18	Ph_3SiF, m. p. 61—63°	100	6
Ph_3SiCl	2	30	2	24	18	Ph_3SiF, m. p. 64°	50	7
Ph_3SiBr	2	30	2	24	18	Ph_3SiF, m. p. 64°	50	7
(*o*-Tolyl)$_3Si\cdot OH$...	4·8	100	20	2	75	(*o*-Tolyl)$_3SiF$, m. p. 86·5°	80	7, 8

Notes. B. p.s given are at *ca.* 760 mm.

1. The reaction mixture was homogeneous at first but a small upper layer was formed during warming.

2. The product was fractionated through a centre-rod column having an efficiency of ~10 theoretical plates and a small hold-up.

3. After the reaction mixture had been poured into water, the organosilicon material was extracted with ether, and the ethereal extract was washed and dried (Na_2SO_4). The ether was removed on a water-bath, and the residue was distilled non-ebullioscopically at <2 mm., the first and last portions of the distillate being rejected. This allows these small quantities to be handled without serious mechanical loss.

4. Some of the siloxan was undissolved at the start of the reaction, but disappeared during heating.

5. (Cf. Part III.) Ether-extraction was employed. The product, after recrystallization, had m. p. 45—46°.

6. The yield and m. p. refer to the solid obtained when the reaction mixture was poured into water. Recrystallization from nitromethane gave pure material of m. p. 64° but with some loss.

7. The yield is low because it refers to the pure, recrystallized material; no attempt was made to recover more solid from the mother-liquors.

8. After the reaction mixture had been poured into water the organosilicon material was extracted with ether. The ether was removed, and the resulting solid was recrystallized from methanol, to give *fluorotri-*o*-tolylsilane,* m. p. 86·5° (Found: F, 6·0. $C_{21}H_{21}SiF$ requires F, 5·9%). Further small quantities of less pure material were obtained by concentration of the methanolic mother-liquor.

9. The relatively low yield probably resulted from loss due to the volatility of this fluoride.

Interaction of Triphenylsilyl Hydroxide and Hydrofluoric Acid in Aqueous Acetone.—Triphenylsilyl hydroxide (0·7 g.) was dissolved in acetone (30 ml.), and hydrofluoric acid (10 ml.) was added. The solution, which remained clear, was set aside in a wax vessel for 18 hours, and then poured into excess of water. The solid which separated was dried and recrystallized from a little light petroleum, to give fluorotriphenylsilane (0·4 g., 60%), m. p. 63—65°, undepressed by admixture with an authentic sample.

Interaction of Hexaphenyldisiloxan and Aqueous-alcoholic Hydrogen Fluoride.—Hexaphenyldisiloxan (2·8 g.) was added to a mixture of ethanol (140 ml.) and hydrofluoric acid (20 ml.), and the mixture was kept just below its b. p. for 6½ hours, the bulk of the solid remaining undissolved. The mixture was set aside for 18 hours and then filtered. The precipitate (A) was extracted with small quantities of warm acetone, and the extracts were added to the aqueous-alcoholic filtrate. The combined solutions were poured into water, the organosilicon material was extracted with ether, and the ether was evaporated to dryness, to give *ca.* 0·2 g. of white solid of m. p. 200—215°, indicating the absence of appreciable quantities of fluorotriphenylsilane. The solid A was extracted with hot benzene and with warm ether, and the extracts were combined and concentrated to a small volume, unchanged hexaphenyldisiloxan (2·4 g., 85%), m. p. 222—224°, being obtained.

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