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ORGANOSILICON COMPOUNDS OF FLUORINE

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I. INTRODUCTION

The first compound of silicon and fluorine, silicon tetrafluoride, was prepared by Scheele in 1771.[1] However, organic derivatives of silicon fluorides were prepared only recently. In the last 10 to 15 years, owing to advances in the chemistry of organosilicon and organofluorine compounds, a great deal of research has been devoted to organosilicon compounds containing fluorine, in connection with attempts to combine the valuable properties of organosilicon and organofluorine materials and to obtain new polymers. A critical review of research in this field is therefore needed.

II. PHYSICAL PROPERTIES OF ORGANOSILICON FLUORINE COMPOUNDS

Fluorine is the most electronegative element of the Periodic System, and has the smallest covalent radius of the halogens. It forms a very stable bond with silicon. The difference between the Si–F and the C–F bond is a result of the properties of the silicon atom (Table 1). The electronegativity of silicon is considerably lower than that of carbon, and its covalent radius considerably larger. In contrast to carbon, silicon is able to use its $3d$ orbital to form bonds. Its co-ordination number is six.

The energy of the Si–F bond is, on average, 134 kcal × × mole^{-1}, considerably higher than the energies of bonds of silicon with other elements[2–5]. The average Si–F bond length is 1.56 Å,[6–20] similar only to silicon-hydrogen (1.49 Å) and silicon-oxygen (1.61 Å) bond lengths. The bonds with chlorine, bromine, and iodine are considerably longer, 2.02, 2.19, and 2.49 Å respectively. The Si–F bond length depends on the other atoms and groups linked to the silicon. Usually, the higher their electronegativity, the shorter is the Si–F bond.

Electron diffraction[6,9] and microwave spectroscopy[10–21], which is more precise, are used to determine the internal rotation barrier[19] and dipole moments of organosilicon

TABLE 1.

Element	Physical properties of atoms				Bond energy, kcal mole^{-1}		Bond length, Å		Bond refraction, ml mole^{-1}	
	nuclear charge	electronic configuration	relative electronegativity	co-ordination number	C	Si	C	Si	C	Si
C	6	$1s^2 2s^2 2p^2$	2.5	4	84.9	75.0	1.54	1.93	1.25	2.56
Si	14	$1s^2 2s^2 2p^6$ $3s^2 3p^2$	1.8	6	75.0	51.0	1.93	2.34	2.56	5.65
F	9	$1s^2 2s^2 2p^5$	4.0	—	102.0	134.0	1.36	1.54	1.72	1.50

compounds [11,19,20]. From microwave spectra Laurie [20] obtained the following Si–F bond lengths for a series of fluorosilanes:

	H_2SiF	H_2SiF_2	$HSiF_3$	SiF_4
Si–F bond length (Å)	1.595	1.577	1.565	1.54

Others have noted a similar change of Si–F bond length [16,19]. As the number of fluorine atoms attached to silicon increases, the bond lengths for other atoms attached to silicon change considerably, as a rule, becoming shorter. For the Si–F bond this shortening is illustrated by the following [21]:

	$(CH_3)_2SiHF$	CH_3SiHF_2	H_2SiF_2	$HSiF_3$
Si–F bond length (Å)	1.473	1.474	1.471	1.455

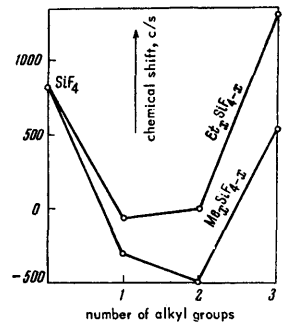
Vibration frequencies of the Si–F bond. The valency vibrations of the Si–F bond in fluorosilanes are in the 850–920 cm^{-1} region of the infra-red [22-24] and Raman spectra [22-28]. The frequency obviously depends on the radicals attached to silicon. According to Ebsworth *et al.* [22], it is 858 cm^{-1} in CH_3SiH_2F, and 916 cm^{-1} in $(CH_3)_3SiF$. The fluorine atoms, therefore, affect the vibration frequencies of the other bonds considerably, generally increasing them. Thus, the vibration frequency of the Si–H bond increases as more fluorine atoms are attached to silicon [21]. Moreover, the introduction of fluorine atoms into organic radicals, increasing their electronegativity, also increases the vibration frequency of the Si–H bond. Ponomarenko *et al.* [29,30] suggested a simple empirical relationship between the vibration frequencies (ν) of the Si–H and Si–D bonds and the effective electronegativity of silyl groups containing fluorine and other halogens:

$$\nu = AX_c,$$

where A is a constant, equal to 1011 for hydrides and 734 for deuterides of silicon, and X_C is the effective electronegativity of the silyl group. This relationship is obeyed by many silicon and germanium hydrides and deuterides.

Chemical shift in nuclear magnetic resonance spectra. This effect of an atom or radical bound to silicon on the properties of the Si–F bond is also exhibited in nuclear magnetic resonance spectra. The atoms or groups attached to silicon may strengthen or weaken the shielding of the fluorine atom by changing the character of the electron shell of silicon. This is manifested in nuclear magnetic resonance as the ^{19}F chemical shift. The Figure shows the change of chemical shift in methyl- and ethyl--silyl fluorides on gradual replacement of fluorine in SiF_4 by methyl or ethyl radicals [31,32]. The similar changes of chemical shift are explained by the superposition of two effects, namely shielding of ^{19}F owing to d_π-p_π bonding, and the inductive effect of the methyl and ethyl groups. Gradual replacement of methyl or ethyl groups by fluorine causes the chemical shift of the hydrogen atoms in the remaining groups to decrease [32].

Refraction of the Si–F bond. Warrick's value of 1.50 ml mole^{-1} for the refraction of the Si–F bond is now generally adopted [33,34], though some workers accept the higher value, 1.95 ml mole^{-1}. [35] This discrepancy possibly arises because the refraction of the Si–F bond depends on the atoms and groups bound to silicon. Ponomarenko and Snegova [36] noticed that the discrepancy between the calculated and experimental values for molecular refraction increases with the number of fluorine atoms attached to silicon. Group refractions have been proposed for certain fluorine-containing organic radicals bound to silicon [37].



Dependence of the ^{19}F chemical shift on the number of fluorine atoms and alkyl groups attached to silicon.

The above properties of the Si–F bond have a considerable effect on the physical and chemical properties of organosilicon fluorine compounds.

Dipole moments of organosilicon fluorine compounds. Because of the large difference in the electronegativities between silicon and fluorine, the Si–F bond is polar, producing dipole moments in silicon fluorides (Table 2).

TABLE 2.

Compound	Dipole moment, D	Ref.	Compound	Dipole moment, D	Ref.
H_3SiF	1.27	20	$(C_2H_5)_2SiF_2$	2,23	38
H_2SiF_2	1.54	20	$C_2H_5SiF_3$	2 77	38
$HSiF_3$	1.268	2,20	$(C_6H_5)_2SiF_2$	2.57	38
CH_3SiHF_2	2.11	19	$(C_6H_5)_3SiF$	1.84	38
$(C_2H_5)_3SiF$	1.72	38			

Silicon fluoride complexes. The basic difference between silicon and carbon is in the ability of the former to use its 3*d* orbital to form complexes in which it is penta- or hexa-co-ordinated. Owing to the small covalent radius and high electronegativity of fluorine, silicon fluorides form complexes with amines, amides, alcohols, and other electron donors more readily than other silicon halides. The complexes known include: $SiF_4.2NH_3$, [39,40] $SiF_4.N(CH_3)_2CHO$, [40] $SiF_4.2[N(CH_3)_2CHO]$, [40] $SiF_4.[H_2NCH_2.CH_2NH_2]$, [41] $SiF_4.(CH_3OH)_6$, [42] $SiF_4.(CH_3OH)_8$, [42] and $SiF_2.(OR)_4$. [42] Inorganic complexes known are H_2SiF_6 and its salts [1,2,43]. This pronounced capacity for complex-formation will later be shown to reveal itself in their chemical properties.

Compounds of fluorine with bivalent silicon are also known [44].

III. PREPARATION AND CHEMICAL PROPERTIES OF ORGANOSILICON FLUORINE COMPOUNDS IN WHICH FLUORINE IS BOUND TO SILICON

1. Methods of Preparation

Methods at present known for preparing organosilicon fluorine compounds with a fluorine atom bound to silicon are: a) replacement of halogen in the Si–X bond by F (where X = Cl, Br, I); b) replacement of oxygen in the Si–O bond by F; c) replacement of nitrogen in the Si–N bond by F; d) rupture of a Si–C bond, with formation of a Si–F bond; e) replacement of hydrogen in the Si–H bond by F; f) rupture of a Si–Si bond, with formation of a Si–F bond.

Replacement of halogen in the Si–X bond by F. Of these methods for forming a Si–F bond the first has been most studied. In 1905 Ruff and Albert[45] found that the reaction of trichlorosilane with SbF_3 or AsF_3 yields exclusively SiF_4, but with SnF_4 and TiF_4 partially fluorinated products are produced. The applicability of the Swarts reaction to organosilicon compounds was thus established. It was shown later that stepwise fluorination may yield mono-, di-, and tri-substituted derivatives of $HSiCl_3$ in good yield[46]. $HSiF_3$ was found to decompose even at low temperatures according to the equation:

$$4HSiF_3 \longrightarrow SiH_4 + 3SiF_4.$$

Booth *et al.*[47,48] applied the Swarts reaction to $SiCl_4$, and prepared all the products of stepwise replacement of chlorine in $SiCl_4$ by fluorine. The Swarts reaction proceeds readily at low temperatures with such compounds as $SiCl_4$, $HSiCl_3$, and $GeCl_4$, which can form co-ordination compounds with antimony fluorides:

$$SiCl_4 + SbCl_2F_3 \longrightarrow Cl_4Si\langle{}^{F}_{F}\rangle SbCl_2F \longrightarrow SiCl_3F + SbCl_3F_2.$$

Replacement of the chlorine atoms attached to silicon by fluorine renders such co-ordination easier and favours complete fluorination. Polyhalogen compounds of carbon behave quite differently in this respect:

$$CCl_4 + SbCl_2F_3 \longrightarrow Cl_2C\langle{}^{Cl}_{Cl}\rangle SbCl_2F_3 \longrightarrow CCl_3F + SbCl_3F_2.$$

The Swarts reaction can be successfully used to prepare various mixed fluorochlorobromosilanes[49], fluorosilanes[50,51], fluorodisiloxanes, and fluorodisilanes[53]. In contrast to SiH_2I_2 and $SiHI_3$, monoiodosilane does not form the corresponding fluorosilane H_3SiF in the reaction with HgF_2 or AgF.

Various compounds can be used as fluorinating agents. Hill and coworkers[54,55] obtained mixed fluorochlorosilanes by passing a mixture of SiF_4 and $SiCl_4$ through a glass tube packed with small pieces of porous material and heated to 600°. Anderson[56], with different reaction conditions (empty glass tube, 700°), obtained mixtures of silicon fluorobromides, fluoroiodides, and fluoroisocyanates. Replacement of halogens by fluorine proceeds readily with silicon halides containing organic radicals. In 1946 Booth and coworkers[57–62] found that fluorination of alkyltrichlorosilanes by the Swarts method gave mono-, di-, and tri-fluoro derivatives. Ethoxychlorosilanes are also readily fluorinated[63]. The resulting trifluoro- and difluoro-ethoxysilanes, in contrast to triethoxyfluorosilane, have a tendency to disproportionation. The Swarts reaction is convenient for the fluorination of phenylchlorosilanes[64–66], mixed alkylarylchlorosilanes[36,67,68], and alkylsilicon hydrides[38,69,70]. In the last case the Si–H bond could not be disrupted by antimony fluoride. Trichlorosilane is an exception in this respect[45].

In 1944 Emeléus and Wilkins used zinc fluoride for the first time to fluorinate alkyl- and phenyl-chlorosilanes[71]. It proved to be a very efficient fluorinating agent, which could be used to separate the azeotropic mixture of trimethylchlorosilane and tetrachlorosilane, since it fluorinates almost exclusively trimethylchlorosilane[72,73]. Zinc fluoride has subsequently been widely used for fluorinating various alkyl(aryl)chlorosilanes[74,75] and alkylalkoxychlorosilanes[76]. The yield of alkylalkoxyfluorosilanes did not exceed 22% owing to side reactions. Schnell[77] used a mixture of metallic zinc and zinc fluoride to prepare vinyltrifluorosilane from vinyltrichlorosilane, in 75% yield. Ammonium fluoride is a milder fluorinating agent for alkylchlorosilanes than zinc fluoride[78,70]. In fluorination of alkoxychlorosilanes with ammonium fluoride, the alkoxy group is not replaced[78]. Payne[80] showed that in fluorination of monomethyl-, diethyl-, triethyl-, and dimethyl-chlorodisiloxanes with ammonium fluoride the silicon–oxygen bond is broken, while under similar conditions tetraethyl- and pentaethyl-chlorodisiloxanes are fluorinated without this side reaction, forming tetraethyldifluorodisiloxane and pentaethylfluorodisiloxane, respectively.

Pearson and Brice[81] suggested an interesting method for fluorinating alkyl(aryl)chlorosilanes using anhydrous HF at low or room temperatures. It is a good fluorinating agent[82,83] which does not disrupt the Si–C bond under these conditions.

Boron trifluoride can also be used as a fluorinating agent. In the high-temperature condensation of benzene with trichlorosilane in the presence of boron trifluoride at high pressure, small amounts of phenylfluorodichlorosilane and phenyldifluorochlorosilane were obtained in addition to phenyltrichlorosilane[84,85].

Replacement of oxygen in the Si–O bond by F. In 1933 Flood[86] developed a convenient method for the preparation of triethylfluoro(chloro, bromo)silane in almost quantitative yield by the reaction of hexaethyldisiloxane with sodium or ammonium fluorides (chlorides, bromides) in the presence of concentrated sulphuric acid at low temperatures. Sommer and coworkers[87–89] used this reaction for the preparation of other trialkylfluorosilanes, in particular trimethylfluorosilane and trimethylchlorosilane of high purity. It was later shown that calcium fluoride can also be used[90].

In a patent[91] alkylalkoxysilanes were fluorinated with alkali metal bifluorides. For instance, on boiling pentyltriethoxysilane for 15 min with sodium bifluoride pentyltrifluorosilane was obtained in 89% yield. To fluorinate hexa-alkyldisiloxanes Voronkov[92] used potassium and ammonium bifluorides in the presence of concentrated sulphuric acid:

$$R_3Si{-}O{-}SiR_3 + KHF_2 + H_2SO_4 \longrightarrow 2R_3SiF + KHSO_4 + H_2O$$

The yield of fluorination products reached 88%.

Since 1944[71] hydrogen fluoride has been extensively used in the preparation of fluorinated organosilicon compounds

from alkylsiloxanes and alkylalkoxysilanes. To avoid side reactions, all reactions with hydrogen fluoride are carried out at about 0°. In spite of the low temperature, the rate of reaction is sufficiently high and the reaction is practically complete in 15 to 45 min. For the preparation of alkylfluorosilanes from alkylsiloxanes, anhydrous hydrogen fluoride is usually used in the presence of concentrated sulphuric acid[82,93,94], which is not, however, indispensable[80,95]. Booth and Freedman[95] used HF in their study of the structure of siloxanes. The reaction of siloxanes with HF results in cleavage of the Si–O bond only, giving a quantitative yield of alkylsilyl fluorides:

$$\equiv Si{-}O{-}Si\equiv + 3HF \longrightarrow 2\equiv SiF + HF\cdot H_2O.$$

Anhydrous hydrogen fluoride reacts with alkylalkoxysilanes[75,91,96,97] forming alkylsilyl fluorides. To separate phenyltrichlorosilane from phenylmethyldichlorosilane, they are fluorinated by an alcoholic HF solution[75,97], or by passing HF through their solution in absolute alcohol[96]. The resulting fluorides are easily separated by rectification.

Marans, Sommer, and Whitmore[98] found a 48% aqueous solution of hydrogen fluoride to be a good fluorinating agent for alkylalkoxysilanes. This was corroborated by Anderson[35] and Sommer[99]. To prepare alkylsilyl fluorides from various organosilicon compounds Eaborn[100] used aqueous–alcoholic HF solution. The importance of this is that dilute HF solutions can be used without reducing the yield of fluorinated products, and the reaction can be carried out in glass apparatus.

Peppard, Brown, and Johnson[101] investigated the possibility of preparing alkylsilyl fluorides from alkylalkoxysilanes by the action of SbF_3 on them in the presence of $SbCl_5$. They found the course of the reaction to depend considerably on the alkyl and alkoxy groups bound to silicon. For instance, while $(C_2H_5O)_4Si$ is readily fluorinated giving $(C_2H_5O)_3SiF$ and $(C_2H_5O)_2SiF_2$, tetra-allyloxysilane and triallyloxysilane do not react with SbF_3 at all, even in the presence of $SbCl_5$. Heal[63] showed that SbF_3 does not remove the ethoxy group in the absence of $SbCl_5$, but instead vigorously substitutes fluorine for chlorine in ethoxysilanes, the most stable of the three ethoxyfluorosilanes being $(C_2H_5O)_3SiF$. Trifluoroethoxy- and difluoroethoxy-silanes formed in the reaction undergo disproportionation even at low temperatures according to:

$$2C_2H_5OSiF_3 \longrightarrow SiF_4 + (C_2H_5O)_2SiF_2,$$
$$3(C_2H_5O)_2SiF_2 \longrightarrow SiF_4 + 2(C_2H_5O)_3SiF.$$

BF_3 is also a good fluorinating agent[102]. It reacts vigorously with methylmethoxysilanes, completely or partially replacing methoxy groups by fluorine to give methylfluorosilanes. Hexamethyldisiloxane reacts with excess BF_3 giving trimethylfluorosilane and B_2O_3. Sommer and Ansul[103,104] extended these studies using alcoholic BF_3 solution as fluorinating agent at 50° to 60°. The yields of fluorinated products reached 95%.

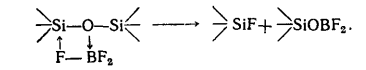
Emeléus and Onyszchuk[105] found that the reaction of 1,3-dimethyldisiloxane and 1,3,3,3-tetramethyldisiloxane with BF_3 proceeds in two stages:

$$2(CH_3SiH_2)_2O + BF_3 \longrightarrow CH_3SiH_2OBF_2 + CH_3SiH_2F.$$

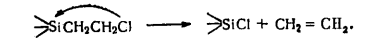
The resulting $CH_3SiH_2OBF_2$ begins to decompose even at -78°. At room temperature this process is quickly completed:

$$3CH_3SiH_2OBF_2 \longrightarrow 3CH_3SiH_2F + BF_3 + B_2O_3.$$

The authors suggested the following mechanism for this reaction:



This is the most probable mechanism, if one considers the complex-forming capabilities of boron and silicon atoms. The decomposition of the intermediate complex and the intermediate products recalls the well-known β-decomposition of β-halogenoalkylsilanes:



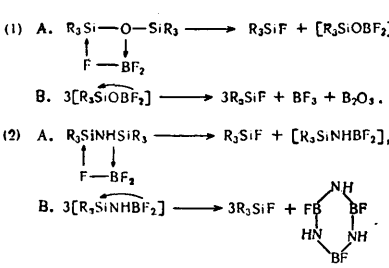
This will be discussed later.

Fluorosulphonic acid[106] and acetyl fluoride[107] can also be used to replace the alkoxy group in alkylalkoxysilanes by fluorine.

Replacement of nitrogen in the Si–N bond by F. According to Burg and Kuljian[108] trisilylamine and boron trifluoride, in a 1:1 ratio, react at -78° to -40° to form unstable adducts which decompose irreversibly at a higher temperature to form H_2SiF_2, $HSiF_3$, and other compounds. A detailed study of the reactions of BF_3 with $(H_3Si)_3N$, $(H_3Si)_2NCH_3$, and $H_3SiN(CH_3)_2$ showed[109] that the white solid adducts formed at -80° decompose slowly forming H_3SiF and $(H_3Si)_2NBF_2$, $H_3SiN(CH_3)BF_2$ and $(CH_3)_2NBF_2$ respectively. The silyldifluoroaminoboranes are in their turn unstable and on increasing the temperature decompose further to derivatives of borazole and H_3SiF. Thus, $H_3SiN(CH_3)BF_2$ gives *N,N′,N″*-trimethyl-*B,B′,B″*-trifluoroborazole and H_3SiF, and $(H_3Si)_2NBF_2$ gives *N,N′,N″*-trisilyl-*B,B′,B″*-trifluoroborazole and H_3SiF.

Tris(methylsilyl)amine, dimethyl(methylsilyl)amine, and dimethyl(trimethylsilyl)amine[110] react with BF_3 at -78° forming crystalline adducts, which decompose in the presence of BF_3 to give respectively methylfluorosilane and *N,N*-bis(methylsilyl)-*B,B*-difluoroaminoborane, methylfluorosilane and *N,N*-dimethyl-*B,B*-difluoroaminoborane, and trimethylfluorosilane and *N,N*-dimethyl-*B,B*-difluoroaminoborane. Like silylamines, hexamethyldisilazane forms with BF_3 a complex $[(CH_3)_3Si]_2NH.BF_3$ which decomposes on heating into $(CH_3)_3SiF$ and $(CH_3)_3SiNHBF_2$[102].

A thorough study of the reactions of silylamines and siloxanes with BF_3 reveals similarities between their mechanisms:



Bailey, Sommer, and Whitmore[111] found that by the action of concentrated HF on trialkylaminosilane the nitrogen in the Si–N bond can be replaced by fluorine, to form trialkylfluorosilanes in up to 89% yield. Nitrogen in the Si–N bond of tetraisocyanosilane is easily replaced by fluorine by using SbF_3.[112] SiF_4 can also cause isocyanate groups to be replaced by fluorine. For example, all three possible fluoroisocyanosilanes are formed[56] by passing an equimolar mixture of SiF_4 and $Si(NCO)_4$ through a glass tube at 700°.

Rupture of a Si–C bond with formation of a Si–F bond. Several cases are known of replacement of carbon in the Si–C bond by fluorine. Eaborn and Jeffery[113] found that the reactions of p-$ClC_6H_4(CH_3)_2SiCH_2OC_2H_5$ and p-$CH_3C_6H_4(CH_3)_2SiCH_2OC_2H_5$ with aqueous-alcoholic solutions of HF proceeded as follows:

$$ArMe_2SiCH_2OEt + H_3O^+ \overset{\text{fast}}{\rightleftharpoons} ArMe_2SiCH_2\overset{+}{O}(H)Et + H_2O,$$

$$ArMe_2SiCH_2\overset{+}{O}(H)Et \longrightarrow ArMe_2SiCH_2^+ + EtOH,$$

$$ArMe_2SiCH_2^+ \longrightarrow ArCH_2Me_2Si^+,$$

$$ArCH_2Me_2Si^+ \xrightarrow[\text{or } F^-]{EtOH} ArCH_2Me_2SiOEt \text{ or } ArCH_2Me_2SiF.$$

Under these conditions only the Si–C(arom.) bond in p-$CH_3OC_6H_4(CH_3)_2SiCH_2OC_2H_5$ is broken, anisole and $(CH_3)_2 \cdot (C_2H_5OCH_2)SiF$ being formed.

In his study of the action of various reagents on triethylsilane Anderson[114] discovered that silver fluoride was capable of fluorinating not only the Si–H bond, but also one of the Si–C bonds forming triethylfluorosilane and diethylfluorosilane. Eaborn[5] discovered a number of transformations of the Si–C bond in studying transformations of various organosilicon compounds under the action of silver and other metal halides.

Alkylfluorosilanes can be obtained by the reaction between R_4Si and SiF_4.[115] For instance, heating $(C_2H_5)_4Si$ and SiF_4 in a 1:1 ratio for three hours in an autoclave at 300° to 350° and 13 to 14 atm gave 22% $C_2H_5SiF_3$, 46.6% $(C_2H_5)_2 \cdot SiF_2$, 23.7% $(C_2H_5)_3SiF$ and 7.5% unreacted $(C_2H_5)_4Si$.

None of these methods for replacing the Si–C bond by Si–F have as yet more than limited preparative value.

Replacement of hydrogen in the Si–H bond by F. In 1905, in an effort to prepare mixed fluorides from trichlorosilane and SbF_3 or AsF_3, Ruff and Albert[45] found SiF_4 to be the only reaction product. They established that $HSiF_3$ is very unstable decomposing at high temperatures according to:

$$4HSiF_3 \longrightarrow 2H_2 + 3SiF_4 + Si.$$

This was in fact the first observation of disproportionation in fluorosilanes.

Disproportionation of halogenosilanes[116] presumably depends on their ability to use the 3d orbital of silicon to form activated complexes, which decompose into new products according to the scheme:

$$2H_3SiF \rightleftharpoons \left[H_3Si\overset{F}{\underset{H}{\diagup\diagdown}}SiH_2F \right] \longrightarrow SiH_4 + H_2SiF_2, \text{ etc.}$$

Since the tendency to form activated complexes increases with the electronegativity of the halogen atoms bound to silicon, the tendency to disproportionation also increases on passing from iodosilanes to fluorosilanes.

Replacement of the Si–H bond by Si–F occurs not only by the action of SbF_3, AsF_3, or by disproportionation, but also, as mentioned above, by the action of silver fluoride[114].

Rupture of a Si–Si bond with formation of a Si–F bond. We conclude this survey by quoting two preparative methods using compounds containing a Si–Si bond. In one, mixed fluorochlorosilanes were prepared by Schumb and coworkers[117,118] by the action of chlorine or bromine on hexafluorodisilane. The main reaction products were SiF_4, $SiClF_3$, $SiCl_2F_2$, and $SiBrF_3$, $SiBr_2F_2$, and $SiBr_3F$.

In the other method[80] fluorochlorosilanes can be obtained by boiling hexachlorodisilane with NH_4F.

2. Chemical Properties

All known reactions of silicon fluorides may be divided into the following principal types: replacement of fluorine in the Si–F bond by (a) group IV elements; (b) group V elements; (c) group VI elements; (d) group VII elements and hydrogen; and (e) reactions in which the Si–F bond remains intact.

Replacement of fluorine in the Si–F bond by group IV elements. This type of substitution covers all reactions of organic and inorganic silicon fluorides with organic compounds of magnesium, sodium, lithium, and aluminium, and other alkylating agents.

In 1936, in their study of the reaction of ethylmagnesium chloride and bromide with silicon tetrafluoride, Gierut, Sowa, and Nieuwland observed that fluorine can be replaced by organic radicals giving triethylfluorosilane[39]. The same results were obtained with propyl-, butyl-, and pentylmagnesium halides. Ethylmagnesium bromide also gave 5% tetraethylsilane. Compared with alkylmagnesium bromides, alkylmagnesium chlorides give better yields of trialkylfluorosilanes.

The formation of trialkylfluorosilanes in these reactions is connected mainly with steric effects of organic radicals. In tributyl- and tripentyl-fluorosilanes the Si–F bond is so protected that it can react neither with the Grignard reagent, nor even with sodium in liquid ammonia. The same results were obtained by Medoks and Kotelkov[120] in the reaction of phenylmagnesium bromide with SiF_4 in ether solution at room temperature, where triphenylfluorosilane was the main product. From a thorough investigation Medoks[121] suggested this scheme for the reaction of the Grignard reagent with SiF_4 in ether solution:

$$RMgX\cdot 2(C_2H_5)_2O + SiF_4 \longrightarrow RMgX(SiF_3)F + 2(C_2H_5)_2O,$$

$$RMgX(SiF_3)F \longrightarrow RMgX(SiF_3)F \longrightarrow XMgF + RSiF_3,$$

$$XMgF + 2(C_2H_5)_2O \longrightarrow XMgF\cdot 2(C_2H_5)_2O \text{ etc.}$$

The $RSiF_3$ produced reacts with another molecule of RMgX in like manner. Given the strongly pronounced tendency of SiF_4 to form complexes, the author assumes that reaction of SiF_4 with XMgF etherate takes place simultaneously with the above reaction, according to:

$$2MgClF\cdot[(C_2H_5)_2O]_2 + SiF_4 \longrightarrow MgSiF_6 + MgX_2\cdot[(C_2H_5)_2O]_2 + 2(C_2H_5)_2O.$$

This assumption is fully justified since $MgSiF_6$ is in fact found among the reaction products. Soschestvenskaya [122,123] found incidentally that even salts of fluorosilicic acid (*e.g.* Na_2SiF_6) can react with Grignard reagents at 160° to 170° to give tetra-alkyl(aryl)silanes. Under these conditions $MgSiF_6$ decomposes to SiF_4.

As already remarked, steric hindrance has a considerable effect on the course of the reaction of SiF_4 with RMgX. In his study of the reaction of isopropylmagnesium chloride with SiF_4 Eaborn [124,125] obtained mainly di-isopropyldifluorosilane. Even greater steric hindrance was found with the α-naphthyl radical. According to Petrov and Chernysheva [126-129], the reaction of α-naphthylmagnesium bromide with SiF_4 results in two products, α-naphthyltrifluorosilane and di-α-naphthyldifluorosilane. Tri-α-naphthylfluorosilane is formed only on heating. The authors showed that in the synthesis of tetrasubstituted silanes, by using RLi instead of RMgX and SiF_4 instead of SiX_4 considerable steric hindrance could be overcome, since the R–Li and Si–F bonds are more ionic than the R–MgX and Si–X bonds (where X = Cl, Br, I). These conclusions were subsequently confirmed by the synthesis of triphenyl(vinylethynyl)silane [130] and triphenylvinylsilane [131].

Steric hindrance can also be overcome by using excess of the Grignard reagent, increasing the reaction temperature, using solvents other than ether [132,133], and in a number of other ways. When the reaction is not limited by steric hindrance, in order to obtain silicon fluorides R_2SiF_2 (R = phenyl, benzyl) the temperature should be kept below 0°, and the addition of SiF_4 to the Grignard reagent speeded up [134-136]. SiF_4 and Na_2SiF_6 can also be alkylated by other than organolithium or organomagnesium reagents. Several patents appeared recently on the use of the etherate of $(C_2H_5)_3Al$ [137-139] at 200°–250° and a mixture of CH_3AlCl_2 with $(CH_3)_2AlCl$ [140] at 200°–220° as alkylating agents. Ethylfluorosilanes [115] can also be obtained by the reaction of equimolar quantities of $(C_2H_5)_4Si$ and SiF_4 in an autoclave at 300°–350°, and methyltrifluorosilane [141] by passing a mixture of CH_3Cl and SiF_4 through a mixture of silicon and reduced copper heated to 300°.

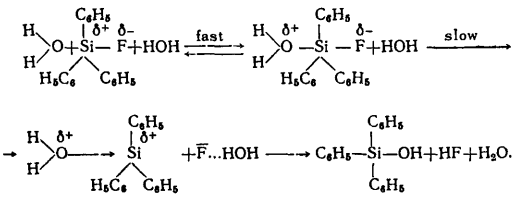
Since SiF_4 and Na_2SiF_6 are manufactured industrially, all these methods for the replacement of fluorine in them are of commercial as well as preparative importance.

Replacement of fluorine in the Si–F bond by group V elements. Only two short papers have appeared [56,142] dealing with replacement of fluorine in the Si–F bond by nitrogen or nitrogen-containing groups. We have already discussed one of them [56]. In the other, Chugunov used the reaction of triphenylfluorosilane with diphenylamine in boiling toluene solution in the presence of lithium. A 20% yield of triphenylsilyldiphenylamine, a crystalline product, m.p. 224°–225°, was obtained.

Replacement of fluorine in the Si–F bond by group VI elements. These reactions include alcoholysis, hydrolysis, and certain others. The rate of alcoholysis depends to a considerable extent on the structure of the silicon fluoride and the alcohol. The first investigation in this field [39] had already shown that while methyl and ethyl alcohols reacted quantitatively with SiF_4, propyl, isopropyl, and isobutyl alcohols underwent only 20 to 60% reaction. Moreover, compounds containing both fluorine and ethoxy groups not only undergo disproportionation readily [63,78], but also enter into exchange reactions with alcohols of higher molecular weight (*e.g.* $CH_2{=}CHCH_2OH$, $n\text{-}C_4H_9OH$) to form, in all cases, trialkoxyfluorosilanes [101].

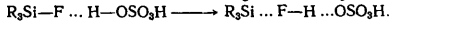
The reaction of phenyltrifluorosilane with ethanol also yields only phenyldiethoxyfluorosilane, the third fluorine atom being completely inactive [64]. The same is true of the reaction of water with phenyltrifluorosilane [143] at 70°, when also one Si–F bond remains intact. On boiling in anhydrous ethanol, triphenylfluorosilane undergoes only 80% alcoholysis [100].

The reaction of alkyl(alkoxy)fluorosilanes and SiF_4 with alcohols, phenols, and *o*-, *m*-, and *p*-cresol can sometimes be accelerated by the addition of aluminium ethoxide [144] or ammonia [145]. Under the action of alkali all alkyl(aryl, alkoxy)fluorosilanes readily undergo hydrolysis [76,87,88,136]. In 1949 Swain and coworkers [146] made a thorough study of the kinetics of triphenylfluorosilane hydrolysis and suggested the following reaction mechanism:



This hydrolysis mechanism is also valid† for other organic and inorganic silicon halides. It is based on the assumption that silicon is capable of forming stable or unstable bonds involving its 3*d* orbitals.

The action of sulphuric acid upon alkyl-, aryl-, and benzyl-fluorosilanes is more complex, since rupture of the Si–C bond often occurs as well as hydrolysis [147]. Szmant and coworkers maintain that in this case there is nucleophilic attack of the sulphate anion on the silicon. However, one cannot exclude the possibility of the reaction also proceeding according to the scheme:



The nature of the radicals bound to silicon has a substantial effect on the behaviour of silicon fluorides in chemical reactions. Sommer and coworkers [87,148] studied the stability of organosilicon compounds containing α- and β-halogen atoms towards various reagents; they found that those containing a β-halogen are unstable, decomposing with rupture of the Si–C bond under the action of alkalis, water, potassium acetate, CH_3MgBr, etc. The compound $(CH_2ClCH_2)\cdot(C_2H_5)_2SiF$ decomposes more rapidly than the compound $(CH_2ClCH_2)(C_2H_5)_3Si$.

Replacement of fluorine in the Si–F bond by oxygen-containing groups is possible in reactions other than alcoholysis or hydrolysis. Anderson [149] observed that hexaethyldistannoxane reacts with diphenyldifluorosilane in the following way:



Replacement of fluorine in the Si–F bond by group VII elements and hydrogen. Schumb and coworkers [150] studied the action of anhydrous aluminium, magnesium, iron, calcium, boron, and barium chlorides

† Compare, however, Eaborn, "Organosilicon Compounds", 1st Edn., pp. 103–113 and 177–183 (Ed. of Translation).

on various fluorine-containing compounds, including SiF_4 and alkylfluorosilanes. They showed SiF_4 to react at atmospheric pressure with all these chlorides except $BaCl_2$ to form $SiCl_4$ (as main product) and all the intermediate fluorochlorosilanes. Chlorination of SiF_4 with aluminium chloride at 8–9 atm and 195°–250° gave only $SiCl_4$, which was explained by disproportionation of the intermediate fluorochlorosilanes into $SiCl_4$ and SiF_4 under these conditions.

Alkylfluorosilanes are also readily chlorinated by anhydrous aluminium chloride. This reaction was extended by Eaborn[124,151] who established that anhydrous aluminium bromide, chloride, and iodide are efficient reagents for replacement of fluorine in alkyl-, aryl-, and alkylaryl-fluorosilanes. Simultaneous replacement of the fluorine in the Si–F bond by chlorine and hydrogen is achieved by passing a 1 : 1 or 3 : 1 $HCl–SiF_4$ mixture through ground silicon or silicon-containing material at 385°–525°.[152] $HSiClF_2$ and $HSiCl_2F$ are the main reaction products. Alkylsilicon hydrides containing more than one Si–H bond are obtained by heating a mixture of 80% diethylaluminium hydride and 20% triethylaluminium with SiF_4 in an autoclave at 260°.[153] Besides SiF_4, $SiCl_4$, and $Si(OR)_4$ can be used in this reaction.

Reactions in which the Si–F bond remains intact. The extraordinary stability of the Si–F bond is the reason why, in contrast to bonds of silicon with other halogens or other atoms, it can remain intact in a number of chemical reactions. In 1933 Flood and coworkers[86,154] found that the Si–F bond in triethylfluorosilane is not hydrolysed in the presence of water nor is fluorine exchanged for bromine or iodine when this compound is acted upon by these halogens. In the latter cases one ethyl group is easily lost, diethylbromo(iodo)fluorosilane and ethyl bromide (iodide) being formed:

$$R_3SiF+X_2 \longrightarrow R_2SiXF+RX.$$

It was further shown that in phenylfluoro-, phenylchlorofluoro-, alkylphenylfluoro-, and alkylchlorofluoro-silanes[64] one Si–F bond is very stable and does not react with water or alcohol. The high stability of this Si–F bond has permitted the preparation of alkyl- and phenyl-polysiloxanes containing an Si–F bond[143,155].

Reference has been made[156] to the very high stability of the Si–F bond in diethyldifluorosilane to the action of 100% H_2O_2 in ether solution at -20° to -35°. Only the Si–C bond was oxidised to a small extent (21–23%) to form $C_2H_5.(C_2H_5O)SiF_2$ and $(C_2H_5O)_2SiF_2$. In the action of n-butyl and allyl alcohols on triethoxyfluorosilane only the ethoxy groups are replaced by n-butoxy and alloxy[101], the fluorine atoms remaining:

$$(C_2H_5O)_3SiF+3n\text{-}C_4H_9OH \longrightarrow (n\text{-}C_4H_9O)_3SiF+3C_2H_5OH.$$

In mixed fluorobromo- and fluoroiodo-silanes also chlorine replaces only bromine and iodine, and not fluorine[49], while in alkyl(aryl)fluorosilanes only the alkyl and aryl radicals are replaced[83]. Ponomarenko and Snegova found recently[65] that in chlorination, and more so in bromination, of phenyltrifluorosilane in the presence of powdered iron, rupture of the Si–C bond took place, but the Si–F bond remained intact. The behaviour of $C_6H_5SiF_3$ in these reactions differs sharply from the behaviour of $C_6H_5.SiCl_3$. This is explained by the greater electrophilic character of the Si atom in $C_6H_5SiF_3$ and the smaller size of fluorine compared with chlorine. From a systematic study of the orienting capacity of fluorosilyl groups in radical or electrophilic chlorination and bromination of ethyl- and phenyl-silyl chlorides, Ponomarenko and Snegova[36,65] were able to show that stepwise replacement of alkyl radicals by fluorine results in a sharp increase of the orienting capacity of these groups. In the photochemical chlorination of ethylsilyl fluorides this is evident from the formation of a larger proportion of β-isomers than in chlorination of the corresponding ethylsilyl chlorides. The $-SiF_3$ group in $C_6H_5SiF_3$ has a strong meta-orienting tendency. Fluorosilyl groups also have a considerable stabilising effect on the C–Cl bonds in alkyl radicals in dehydrochlorination by means of quinoline, so that α- and β-chlorides behave differently.

Alkali metal mercaptides, organomagnesium compounds, and alcohols react at -78° with dichlorodifluorosilane, replacing selectively the chlorine atoms only[157,158]. These reactions are often the most suitable for the preparation of compounds of type R_2SiF_2, $(RS)_2SiF_2$, and $(RO)_2SiF_2$.

According to Yakubovich and Ginsburg[159], $SiCl_4$, and $SiBr_4$ react vigorously with 2.5–3% solutions of diazomethane in ether at -45° to -55°:

$$SiCl_4+CH_2N_2 \longrightarrow ClCH_2SiCl_3+N_2,$$

$$ClCH_2SiCl_3+CH_2N_2 \longrightarrow (ClCH_2)_2SiCl_2+N_2, \text{ etc.}$$

SiF_4, on the other hand, does not react with diazomethane to form organosilicon fluorine compounds. In the authors' opinion this is because of the high activation energy for methylation of the Si–F bond.

It follows from the chemical reactions of organic and inorganic silicon fluorides that fluorine bound to silicon has a number of specific features, compared to the other halogens, which are consistent with the physical properties of the Si–F bond discussed in section II.

Although a considerable number of organosilicon compounds containing fluorine attached to silicon have so far been obtained, and their physical and chemical properties studied to some extent, very little is known about their application in industry. Organosilicon compounds containing fluorine in an organic radical are more promising in this respect.

IV. PREPARATION AND CHEMICAL PROPERTIES OF FLUORO-ORGANOSILICON COMPOUNDS WHERE FLUORINE IS IN THE ORGANIC RADICAL

1. Methods of Preparation

At present the following methods are known for the preparation of fluoro-organosilicon compounds with fluorine in the organic radical: (a) organometallic method; (b) replacement of hydrogen in the Si–H bond by organic radicals; (c) the Swarts reaction; (d) direct synthesis; (e) reactions of alkenylsilanes; (f) other reactions.

Organometallic method. The first fluoro-organosilicon compound was prepared by this method in 1949 by Roberts and coworkers[160] from $p\text{-}FC_6H_4MgBr$ and $(CH_3)_3SiCl$. This method is interesting because it can be used to prepare relatively easily fluorine-containing organosilicon monomers which are very important for research. $(m\text{-}CF_3C_6H_4)_3SiF$ and $(m\text{-}CF_3C_6H_4)_4Si$ were thus prepared from $m\text{-}CF_3C_6H_4MgBr$ and SiF_4,[161] $(p\text{-}CF_3C_6H_4)_3SiH$ from $p\text{-}CF_3C_6H_4MgBr$ and $HSiCl_3$,[162] and $p\text{-}FC_6H_4SiCl_3$ and

$(p\text{-}FC_6H_4)_2SiCl_2$ from $p\text{-}FC_6H_4MgBr$ and $SiCl_4$.[163,164] An especially large number of derivatives was prepared from trifluoromethylphenylmagnesium bromide and $SiCl_4$,[165-168] CH_3SiCl_3,[169-171] $ClCH_2SiCl_3$,[171] $CH_2=CHSiCl_3$,[172] or $(C_2H_5O)_4Si$.[66] Gilman, Brook, and Miller[173] obtained $(C_6H_5)_3(m\text{-}CF_3C_6H_4)Si$ from $(C_6H_5)_3SiCl$ and $m\text{-}CF_3C_6H_4Li$. Mindlin and Andrianov[174] prepared $m\text{-}CF_3C_6H_4(CH_3)Si.(OC_2H_5)_2$ and $m\text{-}CF_3C_6H_4Si(OC_2H_5)_3$, in one stage, in 30% yield, from $m\text{-}CF_3C_6H_4MgBr$ with $CH_3Si(OC_2H_5)_3$ and $(C_2H_5O)_4Si$, respectively.

Reactions of tetrachlorosilane and alkylchlorosilanes with more complex Grignard reagents, namely $3,5\text{-}(CF_3)_2.C_6H_3MgBr$, $2,5\text{-}(CF_3)_2C_6H_3MgBr$,[166,167] and $4\text{-}Cl\text{-}3\text{-}CF_3C_6H_3.MgBr$[175] have also been used. They all give good yields of the corresponding organosilicon fluorine compounds.

Lithium can also be used in the reaction of aromatic fluorine-containing compounds with chlorosilanes. Fluorinated organolithium compounds react with $SiCl_4$[176] and alkyl-(aryl)chlorosilanes[177,178], to form $(m\text{-}CF_3C_6H_4)_4Si$, $(CF_3)_2.C_6H_3Si(Cl_2)CH_3$, $(C_6H_5)_2Si(C_6H_3CF_3\text{-}m)_2$, and other fluorine-containing arylsilanes. Although by using lithium instead of magnesium the reaction can be carried out at lower temperatures and higher yields of the products are obtained, organolithium compounds are still not widely used for the synthesis of organosilicon fluorine compounds.

Organosilicon monomers have also been prepared from aliphatic fluoro-compounds capable of forming Grignard reagents. In 1951 Henne and Francis[179] described the preparation of a Grignard reagent from heptafluoroiodopropane in ether solution at -80° in a dry nitrogen atmosphere. Haszeldine subsequently published[180-182] the preparation of perfluoromethylchlorosilanes from CF_3MgI and $SiCl_4$. McBee and coworkers[183-185] and others[186,187] extended this to the preparation of various organosilicon fluorine compounds, *e.g.* $[(C_3F_7)CH_2CH_2]_4Si$, $[(C_3F_7)CH_2CH_2]_3SiCl$, $[(C_3F_7)CH_2CH_2]_2Si(OC_2H_5)_2$, $[(C_3F_7)CH_2CH_2](CH_3)Si(OC_2H_5)_2$, $(C_3F_7)Si(C_2H_2)_2$, $(CF_3CH_2CH_2)_2Si(OCH_3)_2$, from Grignard reagents or from fluoro-organolithium compounds.

Not only aromatic and aliphatic fluoro-organosilicon compounds may be obtained from organomagnesium compounds. Unsaturated polyfluorides can also react with chlorosilanes under Grignard conditions. Knunyants and coworkers found recently[188] that $CF_2=CFMgI$ reacts with tetrachlorosilane to form $(CF_2=CF)_4Si$ as the only reaction product. They were not, however, successful in causing perfluorovinylmagnesium iodide to react with CH_3SiCl_3, $CH_3(C_6H_5)SiCl_2$, and $C_6H_5SiCl_3$. They explained this by a change in the electron density of the silicon atom under the influence of the atoms or groups bound to it. In their opinion the reaction proceeds most readily with those compounds in which the central atom has the lowest electron density. Of the silicon halides, therefore, only $SiCl_4$ reacts with $CF_2=CFMgI$. Replacement of one chlorine atom in $SiCl_4$ by a perfluorovinyl group lowers the electron density of the silicon even more, rendering the subsequent substitution easier.

Replacement of hydrogen in the Si–H bond by organic radicals. The possibility of addition of silicon hydrides to unsaturated fluorine-containing compounds using heterogeneous catalysts was first discovered by Wagner[189], and by Mackenzie, Spialter, and Schoffmann[190] in 1954. $HSiCl_3$ was added to $CH_2=CF_2$ and $CF_2=CF_2$, admittedly with very low yields. In 1956 Ponomarenko, Sokolov, and Petrov[191] described the preparation of a series of organosilicon fluorine compounds from CH_3SiHCl_2 and $C_2H_5SiHCl_2$, $CF_2=CFCl$, and $CF_2=CF_2$ in the presence of 1% platinised charcoal, yields up to 23% being obtained. Under these conditions CH_3SiHCl_2 and $C_2H_5SiHCl_2$ gave both α- and β-chlorides in the reaction with $CF_2=CFCl$. The above silicon hydrides gave with $CF_2=CFCl$ and $CF_2=CF_2$ not only addition products but also telomerisation products[192].

Tarrant and coworkers[193] used 5% platinised charcoal in the synthesis of fluorinated organosilicon monomers. The structure of the fluoro-olefine was found to affect the yield of the addition product considerably. While, for example, $CF_3CH=CH_2$ and $C_2F_5CH=CH_2$ give a good product yield (up to 72%) with $HSiCl_3$ and CH_3SiHCl_2 in the presence of 5% platinised charcoal at 250°, other olefines, *e.g.* $CF_2=CFCl$, react much less with these silicon hydrides (up to 25%). Under these conditions the reaction with $CF_3CF=CF_2$ is very explosive. CH_3SiHCl_2 and $HSiCl_3$ react with fluoro-olefines of type $CH_2=CHR_F$ according to:

$$CH_3SiHCl_2+CH_2=CHR_F \longrightarrow (CH_3)Cl_2SiCH_2CH_2R_F,$$

where $R_F = CF_3$, C_2F_5, C_3H_7, etc. $(CH_3)Cl_2SiCH_2CHF_2$, $(CH_3)Cl_2SiCH_2CH_2C_2F_5$, $(CH_3)Cl_2SiCH_2CH_2CF_3$, and many similar compounds have been prepared using platinised charcoal[194-196].

The most active initiator of addition based on platinum is chloroplatinic acid, whose catalytic properties were first discovered by Speier *et al.*[197] Ponomarenko *et al.*[198] first used H_2PtCl_6 for the synthesis of fluorinated organosilicon monomers. In the presence of 10% Pt/SiO_2 after heating CH_3SiHCl_2 with $CH_2=CF_2$ at 160° for 11 h only an 11% yield of product is obtained, while in the presence of a 0.1 M $H_2PtCl_6.6H_2O$ solution in iso-propanol heating for one hour under the same conditions gives a 34% yield. The yield obtained in the presence of H_2PtCl_6 also depends to a considerable extent on the structure of the fluoro-olefine. The rate of addition of silicon hydrides to fluoro-olefines decreases as the number of fluorine atoms at the double bond increases:

$$CH_2=CH_2>CH_2=CF_2>CF_2=CClF>CF_2=CF_2.$$

Telomerisation products are also obtained in additions of silicon hydrides to olefines which are initiated by chloroplatinic acid. The high catalytic activity of H_2PtCl_6 has been confirmed for a number of cases[199].

Petrov *et al.*[200-204] showed that the rate of addition in the presence of platinised charcoal and chloroplatinic acid is affected by the structure of the silicon hydride. For instance, the yields obtained from the fluoroethylallyl ethers $CH_2=CHCH_2OCF_2CFClH$ and $CH_2=CHCH_2OCF_2CF_2H$ in the presence of 1% platinised charcoal at 160° decrease in the following order:

$$RSiHCl_2>Cl_3SiH\gg R_2SiHCl\gg R_3SiH.$$

With simultaneous addition of pairs of silicon hydrides to the same ethers a different order of decreasing relative activity is found,

$$\underset{(1.9-2.5)}{R_3SiH} > \underset{(1.2-1.4)}{R_2SiHCl} > \underset{(1)}{RSiHCl_2} > \underset{(0.8-1)}{Cl_3SiH},$$

which corresponds to the order of increasing electronegativity of the silyl groups.

These peculiarities of the addition of silicon hydrides to unsaturated compounds in the presence of platinised charcoal led Petrov *et al.* to conclude, despite wide acceptance of the heterolytic character of these reactions[197,205-207],

that they are specific homolytic reactions [208]. Their specificity arises from their proceeding on the surface of a heterogeneous catalyst. Differences in the rates of normal and simultaneous addition are caused by the adsorbability of the silicon hydrides on the catalyst surface, and by the rate of formation and activity of the silyl radicals. The latter depends on inductive and steric effects of the substituents bound to silicon. Proof of the homolytic nature of the process lies in the fact that at the temperature at which the reaction starts platinised charcoal considerably facilitates the homolytic hydrogenation of diphenylpicrylhydrazyl:

$$(1)\ \rangle Si{-}H \xrightarrow{Pt/C} \rangle \dot{S}i + \dot{H},$$

$$(2)\ \dot{H} + (C_6H_5)_2N\dot{N}[C_6H_2(NO_2)_3] \longrightarrow (C_6H_5)NNH[C_6H_2(NO_2)_3].$$

Deuterium exchange at the reaction temperature in the presence of platinised charcoal provides further evidence for this reaction scheme:

$$C_2H_5SiHCl_2 + CH_3(C_2H_5)_2SiD \xrightarrow{Pt/C} C_2H_5SiDCl_2 + CH_3(C_2H_5)_2SiH.$$

Petrov *et al.* synthesised a series of fluorinated organosilicon monomers, *e.g.* $C_6H_5SiCl_2CH_2CH_2CF_3$, *p*-$FC_6H_4SiCl_2.CH_2CH_2CF_3$, $(CH_3)Cl_2SiCH_2CH_2CH_2OCF_2CFClH$, $(CH_3)Cl_2.SiCH_2CH_2CH_2OCF_2CF_2H$, $C_6H_5SiCl_2CH_2CH_2CH_2OCF_2CF_2H$, $Cl_2Si(CH_2CH_2CF_3)_2$.

Addition in the presence of H_2PtCl_6 is complicated because, during the reaction, H_2PtCl_6 may be reduced to Pt. Even in this case, however, the homolytic mechanism provides a better explanation for the experimental facts than the heterolytic.

Besides platinum, ultra-violet light is widely used to initiate addition of silicon hydrides to fluoro-olefines. Haszeldine and coworkers [209-211] found that under ultra-violet irradiation $HSiCl_3$ and CH_3SiHCl_2 combined almost quantitatively with $CF_2{=}CF_2$ in 60 to 110 h. Haszeldine considers the reaction to proceed by a radical-chain mechanism:

$$HSiCl_3 \xrightarrow{h\nu} Cl_3\dot{S}i + \dot{H}$$

$$Cl_3\dot{S}i + CF_2{=}CF_2 \longrightarrow Cl_3SiCF_2\dot{C}F_2$$

$$Cl_3SiCF_2\dot{C}F_2 + CF_2{=}CF_2 \longrightarrow Cl_3SiCF_2CF_2CF_2\dot{C}F_2 \text{ etc.}$$

$$Cl_3Si(CF_2CF_2)_n + HSiCl_3 \longrightarrow Cl_3Si(CF_2CF_2)_nH + Cl_3\dot{S}i \text{ etc.}$$

The chain length n can be regulated by altering the reagent proportions. The absence of even traces of hydrogen from the reaction products can be explained by the following parallel reactions:

$$\dot{H} + CF_2{=}CF_2 \longrightarrow CF_2H\dot{C}F_2,$$

$$CF_2H\dot{C}F + HSiCl_3 \longrightarrow CF_2HCF_2H + Cl_3\dot{S}i \text{ etc.}$$

With silicon hydrides R_2SiH_2 and $RSiH_3$ the reaction proceeds in stages, one hydrogen atom reacting at a time [211,212].

Under the action of ultra-violet light $CF_3CH{=}CH_2$, $CF_3.CF_2CH_2CH{=}CH_2$, and $CF_3(CH_3)C{=}CH_2$ react in high yield with $HSiCl_3$ and H_2SiCl_2 without forming telomers [213]. Dichlorosilane gave good yields for replacement of either one or both hydrogen atoms.

In a number of cases peroxides are good initiators for addition of silicon hydrides to fluoro-olefines. In their study of the comparative activity of t-butyl peroxide and ultra-violet light in initiating addition of silicon hydrides to unsaturated fluorine derivatives, McBee *et al.* [214] observed that often the peroxide was the more active initiator. For example, the reaction of methyldichlorosilane with $CF_3CH{=}CH_2$ yields, on irradiation for 90 h, only 3.6% $CH_3Cl_2.SiCH_2CH_2CF_3$, but in the presence of t-butyl peroxide 69.5% is obtained in a shorter time.

5% and 10% solutions of ozone in CCl_3F are also good initiators for addition of $HSiCl_3$ to $CF_2{=}CF_2$ and $CF_2{=}CFCl$. [215,216] The yields reached 40%, whereas using platinised charcoal the maximum yield of the same products did not exceed 23%. [191]

In 1958 El-Abbady and Anderson [217] showed that γ-rays could be used as initiators for addition of silicon hydrides to fluoro-olefines: 3 kcurie of ^{60}Co was used as source. The yield of addition product depended on the structure of the fluoro-olefine and often reached 52%. $C_2F_5CH_2CH_2SiCl_3$, $C_3F_7CH_2CH_2SiCl_3$, $C_2F_5(CH_3)CHCH_2SiCl_2(CH_3)$, and $C_3F_7CH_2.CH_2SiCl_2(CH_3)$ were prepared in this way.

Under the action of γ-rays, ultra-violet light, peroxides, and ozone, addition proceeds by a free-radical mechanism, according to the above scheme [209-217]. The similarity of the addition mechanisms is confirmed by the reaction order being the same for all the initiators (the Farmer rule is applicable), the identical effect of the silicon hydride structure on yields of addition product (Cl_3SiH gives better yields than CH_3SiHCl_2), and other analogies.

Addition of silicon hydrides to fluoro-olefines is one of the most convenient methods for the preparation of fluoro-organosilicon compounds in the laboratory and on an industrial scale.

Another method for replacement of hydrogen in the Si–H bond by organic radicals containing fluorine is high-temperature condensation. CH_3SiHCl_2 reacts with C_6H_5F in the presence of H_3BO_3 or B_2O_3 in an autoclave at 232°–260° to form a mixture of isomeric (fluorophenyl)methyldichlorosilanes in yields up to 18%. [218,219] This reaction can also proceed without catalysts. For example, on prolonged heating of $HSiCl_3$ and CH_3SiHCl_2 with $CF_2{=}CF_2$, $CF_2{=}CFCl$, $CF_2{=}CFCF{=}CF_2$, and other fluoro-olefines at 200°–250° without any catalyst [220,221] substitution takes place to give $CF_2{=}CFSiCl_3$, $CFCl{=}CFSiCl_3$, $(CF_2{=}CF)(CH_3)SiCl_2$, etc. Addition also occurs, yielding $HCF_2CF_2SiCl_3$ and $HCF(Cl).CF_2SiCl_3$.

High-temperature condensation of silicon hydrides with fluoro-olefines containing chlorine atoms at the double bond, at atmospheric pressure, is of considerable theoretical and practical interest. This reaction proceeds at 350°–600°. Mironov *et al.* [222] carried out such a reaction using CH_3SiHCl_2 and $CF_2{=}CFCl$ in an empty tube at 500° and obtained a small yield of $(CH_3)Cl_2SiCF{=}CF_2$. Other more complex unsaturated fluorine-containing compounds can react in the same way [223] at 350°–600°, for example:

$$\begin{matrix} CF_2{-}CH \\ | \quad \diagdown \\ CF_2{-}CF_2 \end{matrix} CCl + CH_3SiHCl_2 \xrightarrow{-HCl} \begin{matrix} CF_2{-}CH \\ | \quad \diagdown \\ CF_2{-}CF_2 \end{matrix} C{-}Si(CH_3)Cl_2.$$

This method for the preparation of fluorinated organosilicon monomers has not yet been fully developed.

The Swarts reaction is a convenient method for the synthesis of organosilicon compounds containing fluorine bound to silicon. It can, however, also be used to prepare such compounds containing fluorine in the organic

radical. In 1954 Frost[66] showed that good yields of *m*- and *p*-$CF_3C_6H_4SiF_3$ can be obtained by the reaction of *m*- and *p*-$CCl_3C_6H_4SiCl_3$ with a mixture of SbF_3 and $SbCl_5$. Subsequently, with a view to reducing the consumption of SbF_3 and $SbCl_5$, he suggested the following general scheme for the synthesis of *o*-, *m*-, and *p*-(trifluoromethylphenyl)trifluorosilanes[83]:

$$CH_3C_6H_4MgBr+SiCl_4 \longrightarrow CH_3C_6H_4SiCl_3+MgClBr,$$

$$CH_3C_6H_4SiCl_3 \xrightarrow{+HF} CH_3C_6H_4SiF_3 \xrightarrow{+Cl_2} CCl_3C_6H_4SiF_3,$$

$$CCl_3C_6H_4SiF_3 \xrightarrow{SbF_3+SbCl_5} CF_3C_6H_4SiF_3.$$

Motsarev and Yakubovich[224] later prepared *p*-$CF_3C_6H_4SiF_3$ by this method. The Swarts reaction has also been applied to halogenated aliphatic organosilicon compounds. In the reaction of a SbF_3–$SbCl_5$ mixture with $CCl_3CH_2CHBrSiCl_2.(CH_3)$ and $CBr_3CBr_2CH_2CHBrSiCl_2(C_6H_5)$ at 120°–130°, in both compounds all the halogen atoms, except the α-bromine atoms, are replaced by fluorine[67,68].

The potentialities of the Swarts reaction for the preparation of fluorinated organosilicon compounds have not yet been sufficiently studied.

Direct synthesis. In 1951 Izard and Kwolek[226] attempted to obtain fluoro-organosilicon compounds directly from CF_3Cl and silicon–copper alloy or pure silicon at 360°–700° by the Rochow method[225], but failed. In the same year Haszeldine[181] obtained the first fluorinated organosilicon monomers to be prepared by this method, using CF_3I instead of CF_3Cl.

The direct synthesis was later carried out using the perfluoroalkyl bromides CF_3Br and C_2F_5Br[227,228] and the perfluoroalkyl chlorides CF_3Cl, C_2F_5Cl, and C_3F_7Cl.[229] It is interesting that, in spite of the assertions of Izard and Kwolek[226] that fluoro-organosilicon compounds could not be obtained by direct synthesis starting from CF_3Cl, the authors of a patent[229] succeeded in obtaining a series of perfluoroalkylsilicon compounds, *e.g.* $(CF_3)_2Si_2Cl_2$, $(C_2F_5)_2SiCl_2$, and $(C_3F_7)_2SiCl_2$, by passing these perfluoroalkyl chlorides over silicon–copper alloy (in a ratio between 90 : 10 and 99 : 1) at 400°–500°. One of the most serious shortcomings of the direct method for the preparation of fluoro-organosilicon compounds is the low yield of the desired products.

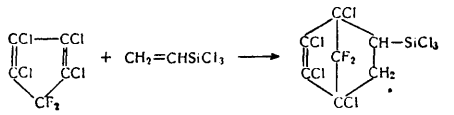
Reactions of alkenylsilanes. Reactions of alkenylsilanes yielding fluorine-containing organosilicon compounds which are known at present are: copolymerisation of alkenylsilanes with perfluoro-olefines, the Diels–Alder reaction, and addition of perfluorobromo(iodo)alkanes.

In 1953 Frost[230] showed that alkenylsilanes react with perfluoro- and perfluorochloro-olefines when heated in an autoclave at 100° either in the presence of organic peroxides and ozonides or in their absence.

$$CF_2{=}CF_2+CH_2{=}CHCH_2Si(CH_3)(OC_2H_5)_2 \longrightarrow \begin{matrix} CF_2 \\ CF_2 \\ CH_2 \end{matrix}\!\!>\!CHCH_2Si(CH_3)(OC_2H_5)_2$$

This reaction has been studied using $(CH_2{=}CHCH_2)_2Si(OC_2H_5)_2$, $CH_2{=}CHSiCl_3$, $CH_2{=}CHSiCl_2(CH_3)$, and other alkenylsilanes, and the following perfluoro-olefines: $CF_2{=}CFCl$, $CF_2{=}CF_2$, $CF_3CF{=}CF_2$, and $C_2F_5CF{=}CF_2$.[230-232]

A logical extension of this work is the synthesis of fluoro-organosilicon compounds by the Diels–Alder reaction[37,233]. Ponomarenko and Snegova[37] showed 5,5-difluorotetrachlorocyclopentadiene to enter more readily than hexachlorocyclopentadiene into diene synthesis with vinyl- and allyl-silanes:



Fairly high yields (up to 60%) and experimental simplicity render the Diels–Alder reaction a convenient method for the preparation of fluoro-organosilicon compounds.

In the presence of radical initiators alkenylsilanes react with perfluoroalkyl bromides and iodides[213,234]. Haszeldine and coworkers[213] carried out addition of CF_3I, CF_3Br, $CF_2ClCFClI$, and CCl_3Br to $CH_2{=}CHSiCl_3$ and $CH_2{=}CHSiCl_2(CH_3)$. The reaction mechanism is:

$$CF_3I \xrightarrow{h\nu} \dot{C}F_3+\dot{I}$$

$$\dot{C}F_3+CH_2{=}CHSiCl_3 \longrightarrow CF_3CH_2\dot{C}HSiCl_3$$

$$CF_3CH_2\dot{C}HSiCl_3+CF_3I \longrightarrow CF_3CH_2CHISiCl_3+\dot{C}F_3 \text{ etc.}$$

The methods of synthesis discussed in this section may also have practical importance.

Other reactions. Anderson and coworkers[235,236] developed a convenient method for the preparation of various complex fluoro-organosilicon esters starting from alkyl(aryl)chlorosilanes and the silver salts of perfluoro-organic acids:

$$R_{4-n}SiCl_n+nR'COOAg \longrightarrow R_{4-n}Si(OCOR')_n+nAgCl,$$

where n = 1, 2, 3; R = CH_3, C_2H_5, C_6H_5, etc.; R′ = CHF_2, CF_3, C_2F_5, C_3F_7.

Fluoro-organosilicon ethers are formed in the reaction of halogenosilanes with fluorine-containing alcohols or salts[237,238]. For example, the reaction of $CF_3CF_2CH_2OH$ with $(Cl_3Si)_2O$ yields $(CF_3CF_2CH_2O)_4Si$, $[(CF_3CF_2CH_2O)_3Si]_2O$ and $[(CF_3CF_2CH_2O)_3SiO]_2Si(CH_2CF_2CF_3)_2$. The formation of the last compound is rather difficult to explain. According to Voronkov and Dolgov[238] β-fluoroethoxysilanes can easily be prepared by the exchange reaction:

$$\equiv SiOCH_3+HOCH_2CH_2F \longrightarrow \equiv SiOCH_2CH_2F+CH_3OH,$$

or by the reaction of silicon hydrides with $HOCH_2CH_2F$:

$$R_3SiH+HOCH_2CH_2F \xrightarrow{CH_3FCH_2OK} R_3SiOCH_2CH_2F+H_2.$$

Finally, according to a patent[228] fluoro-organosilicon compounds can be prepared by passing a F_2–SiF_4 mixture over CaC_2 at high temperatures. $C_4F_9SiF_3$ and other fluoro-organosilicon compounds were isolated from the resulting complex mixture of perfluoroalkylsilicon fluorides.

Petrov *et al.*[201,204] found that organosilicon alcohols, just like ordinary alcohols, react easily with tetrafluoroethylene under the influence of sodium alcoholates:

$$(CH_3)_3Si(CH_2)_nOH+CF_2{=}CF_2 \xrightarrow{Na} (CH_3)_3Si(CH_2)_nOCF_2CF_2H,$$

where n = 1, 2, or 3.

Silicon-containing ethers do not rearrange in the presence of 96% H_2SO_4; *cf.* ethers of the type $ROCF_2CF_2H$:

$$ROCF_2CF_2H + H_2O \xrightarrow{H_2SO_4} ROCCF_2H + 2HF.$$

2. Chemical Properties

The known reactions of fluoro-organosilicon compounds may be divided into: (a) reactions involving rupture of the Si–C bond; (b) the action of acids or alkalis on fluoropolysiloxanes; (c) reactions of fluoro-organosilicon hydrides; and (d) reactions of fluoro-organosilicon halides.

Reactions involving rupture of the Si–C bond. In the presence of various electrophilic or nucleophilic reagents or on heating, a number of β-halogenated organosilicon compounds containing Si–F bonds decompose with rupture of the Si–C bond according to[87,148]:

$$OH^- + \gtrless SiCH_2CH_2Cl \longrightarrow \gtrless SiOH + CH_2{=}CH_2 + Cl^-.$$

Fluoro-organosilicon compounds containing β-chlorine atoms also decompose in the presence of nucleophilic reagents. Haszeldine and coworkers showed[209,211], however, that the decomposition products are different in this case:

$$OH^- + \gtrless SiCF_2CF_2Cl \longrightarrow \gtrless SiOH + -CF_2CF_2Cl.$$

The fluorine atoms have a stabilising effect on the chlorine atoms, preventing formation of a chloride anion in aqueous solution. At the same time the perfluoroalkyl group, which behaves like a pseudohalogen, increases the susceptibility of the silicon atom to nucleophilic attack. According to Knunyants and coworkers[188], under the action of aqueous alkali solutions, all the Si–C bonds in tetraperfluorovinylsilane $Si(CF{=}CF_2)_4$ are broken, $CF_2{=}CFH$ being formed quantitatively. Although ordinary β-chloro-derivatives are unstable towards nucleophilic attack, *e.g.* to a Grignard reagent, these β-fluorine atoms in $CF_3CF_2CF_2CH_2SiCl_3$ do not react even with an excess of Grignard reagent[214].

At temperatures above 200° perfluoroalkylchlorosilanes such as $Cl_3SiCF_2CF_2H$, $Cl_3SiCF_2CF_2Cl$, and $(CH_3)Cl_2SiCF_2.CF_2H$ begin to decompose according to:

$$Cl_3SiCF_2CF_2H \longrightarrow Cl_3SiF + CF_2{=}CFH,$$

i.e. they undergo β-decomposition. Polysiloxanes obtained from these monomers, *e.g.* $[CF_2HCF_2SiO_{1.5}]_n$, are more stable[209,211].

Ponomarenko *et al.*[198] found that in the catalytic addition of CH_3SiHCl_2 to $CH_2{=}CF_2$ in the presence of 10% Pt/SiO_2 at 160°, in addition to the main reaction

$$CH_3SiHCl_2 + CH_2{=}CF_2 \longrightarrow (CH_3)Cl_2SiCH_2CF_2H,$$

the by-products CH_3SiCl_2F, CH_3SiCl_3, $(CH_3)Cl_2SiCH_2CH_3$, and a complex mixture of telomers are also formed. These products (especially CH_3SiCl_2F) can be explained only by β-decomposition of the addition product.

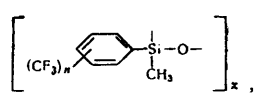
The stability of fluoro-organosilicon compounds towards aqueous alkali solutions is higher the further away the fluorine atoms are from the silicon atoms. Alkylsilicon fluorides, such as $CF_3CH_2CH_2SiCl_3$ and $CF_3CH_2CH_2SiCl_2.(CH_3)$, which contain fluorine atoms in the γ-position and beyond, are stable in the presence of alkali[214]. Polysiloxanes obtained from alkylsilicon fluorides, such as $(CF_3CH_2.CH_2SiO_{1.5})_n$, $[(CF_3CH_2CH_2)(CH_3)SiO]_n$, and $[(CF_3CH_2CH_2)_2.SiO]_n$, are very resistant to heat; they do not decompose on prolonged heating at 250°.[213]

In arylsilicon fluorides containing a fluorine atom in the *para*-position, *e.g.* p-$FC_6H_4Si(CH_3)_3$, the $Si-C_{arom}$ bond is ruptured under the action of an aqueous-methanol solution of HOCl much slower than in other substituted arylsilanes, except for the chloro and bromo derivatives[239]. Under the action of nitric acid p-(fluorophenyl)alkylchlorosilanes undergo quantitative rupture of the $Si-C_{arom}$ bond[163,164].

According to Motsarev and Yakubovich[224], the trifluoromethyl group in the *para*-position strongly inactivates the aromatic ring and stabilises the $Si-C_{arom}$ bond. This is shown by the fact that, on prolonged action of chlorine in the presence of $FeCl_3$, p-$CF_3C_6H_4SiF_3$ is not chlorinated nor is the $Si-C_{arom}$ bond ruptured, while under the same conditions p-$CH_3C_6H_4SiCl_3$ and p-$CCl_3C_6H_4SiCl_3$ are not only chlorinated but also undergo partial rupture of the $Si-C_{arom}$ bond.

Action of acids and alkalis on fluorine-containing polysiloxanes. The action of acids and alkalis on fluorine-containing polysiloxanes has already been discussed. Their stability to acids, alkalis, and other reagents depends to a great extent on the structure of the fluoroalkyl and fluoroaryl radicals bound to silicon. For example, polysiloxanes obtained from $CF_3CH_2CH_2SiCl_3$, $(CF_3CH_2CH_2)_2SiCl_2$, and $(CF_3CH_2CH_2)_3SiCl$ are resistant to heat and acids, and do not decompose on prolonged heating with 10% KOH.[187] On the other hand, polysiloxanes obtained from $HCF_2CF_2SiCl_3$ and $ClCF_2CF_2SiCl_3$ are decomposed readily by alkali solutions, even without heating[209].

The most resistant to heat and chemical reagents are polysiloxanes derived from arylsilicon fluorides with the general formula:



where n is not higher than 3, and $x = 3-10$. These polysiloxanes do not decompose even on prolonged boiling with fuming sulphuric or nitric acids[167,170].

In fluorine-containing cyclic polysiloxanes $[R_FCH_2CH_2.(CH_3)SiO]_{3-4}$, where $R_F = CF_3$, C_2F_5, or C_3F_7, the ring is opened on heating with solid alkali and there is further polymerisation to form polyfluoroalkylsiloxanes $[R_FCH_2CH_2.(CH_3)SiO]_n$, where $n = 5000-6000$.[240]

Reactions of fluoro-organosilicon hydrides. It is obvious from the above that the trifluoromethyl group has a considerable effect on the properties of fluoro-organosilicon compounds in which it occurs, its position in the molecule with respect to silicon being of decisive importance. Steward and Pierce[186] proved this especially clearly in their comparative study of hydrolysis of the Si–H bond in a series of fluoro-organosilicon hydrides. They established that the relative rate of hydrolysis of the Si–H bond in $CF_3CH_2CH_2(CH_3)_2SiH$ is 59 times higher, and in $CF_3CH_2CH_2CH_2(CH_3)_2SiH$ 8.3 times higher, than in $CH_3.CH_2CH_2(CH_3)_2SiH$. The rate of hydrolysis increases several times if the silicon atom is bound to two organic

radicals containing CF_3 groups. For instance, it is 2100 times higher in $(CF_3CH_2CH_2)_2(CH_3)SiH$ than in $CH_3CH_2CH_2.(CH_3)_2SiH$.[186] The increased hydrolysis rate is connected with the higher susceptibility of the silicon atom to nucleophilic attack under the influence of the CF_3 group.

It may be that it is owing to the inductive, rather than the steric, effect of the CF_3 group that the compound $(m\text{-}CF_3C_6H_4)_3SiH$ does not react with organolithium compounds[178].

Reactions of fluoro-organosilicon halides. Like the ordinary alkyl(aryl)halogenosilanes, fluoroalkyl-(aryl)halogenosilanes yield polysiloxanes on hydrolysis. The most widely used method for the preparation of polyfluoro-organosiloxanes is by aqueous or acid hydrolysis of fluoro-organosilicon monomers containing chlorine attached to silicon and by subsequent polycondensation of the hydrolysis products. The Si–Cl bond in the fluoroalkylsilicon chlorides $HCF_2CF_2SiCl_3$, $CF_3CH_2CH_2SiCl_3$, and $CF_3.CH_2CH_2(CH_3)SiCl_2$[181,187,195,209,211,213,221], in the fluoroarylsilicon chlorides $CF_3C_6H_4SiCl_3$, $CF_3C_6H_4(CH_3)SiCl_2$, $(CF_3C_6H_4)_2SiCl_2$, and $[3,5\text{-}(CF_3)_2C_6H_3]_2SiCl_2$,[165,166,170,175] and in other fluoro-organosilicon monomers[231-233,241] readily undergoes hydrolysis. Although hydrolysis of these monomers proceeds relatively easily, the polycondensation of the products of hydrolysis, even unifunctional ones, containing simple fluoroalkyl radicals, is more difficult. For example, even at high temperatures $[3,5\text{-}(CF_3)_2C_6H_3]_3SiOH$ does not dimerise, but melts instead[167].

Polyfluoro-organosiloxanes can also be obtained by hydrolysis of the ethoxy derivatives of fluoro-organosilicon compounds, *e.g.* $\overline{CF_2CF_2CH_2}CHCH_2Si(CH_3)(OC_2H_5)_2$, $(\overline{CF_2CF_2CH_2}CHCH_2)_2Si(OC_2H_5)_2$.[230] This method, however, has no advantages over those discussed above.

Fluoro-organosilicon monomers can be converted to polysiloxanes without resorting to hydrolysis. One patent[242] claims the preparation of polyfluoro-organosiloxanes by boiling fluoro-organosilicon compounds containing Si–Cl bonds with metal oxides (Pb, Ca, Mg, or Zn) in the presence of organic nitriles. This reaction is considerably accelerated by addition of $CaCl_2$ or $HgCl_2$.

V. APPLICATIONS OF FLUORO-ORGANOSILICON COMPOUNDS

The development of the chemistry of fluoro-organosilicon compounds in the last decade has been mainly determined by practical demands of attempting to combine the invaluable properties of fluorocarbon polymers with those of organosilicon polymers in order to obtain polymers with new properties such as greater resistance to oils and fuels, thermal stability, lubricating properties, adhesion, etc. This is evident from the existence of innumerable patents on this subject, and the commercial availability of new fluoro-organosilicon polymers.

The use of fluoropolyorganosiloxanes has been recommended for the preparation of heat-resistant rubbers and resins[187,195,232,243-246], heat-resistant lubricants and hydraulic fluids[91,143,165,230-234,247,248] and dielectrics and insulating materials[133,175,224,242]. An example[244] is the new fluorosilicone rubber "Silastic LS-53" which the American firm "Dow-Corning" put on the market in 1957. The properties of the resin based on this new rubber are given in Table 3, together with the properties of the resin obtained from ordinary polydimethylsilicone rubber. This fluorosilicone rubber has brittle point -68°, glass point -61°, and remains practically unchanged on aging for 16 weeks at 200°, and is resistant to fuels, oils, and hydraulic fluids. The resin from it is used in the manufacture of aeroplane gaskets. "Silastic LS-53" is a copolymer of dimethyldichlorosilane with methyl(trifluoropropyl)dichlorosilane[249].

Fluorosilicone oils obtained from $\overline{CF_2CF_2CH_2}CHCH_2Si.(OC_2H_5)_2CH_3$ have a high heat-resistance, and are good lubricants, their friction coefficient being (steel on steel) 0.167.[230] Good lubricating properties are also exhibited by fluorosilicone oils of the general formula:

$$[m\text{-}CF_3C_6H_4Si(CH_3)O]_n$$[247] and $$[[3,5\text{-}(CF_3)_2C_6H_3]_2SiO]_n$$[165].

Non-hydrolysable trialkyl(aryl)fluorosilanes containing fluorine attached to silicon have been suggested as additives for high-temperature oils[91] and resins[250,251].

Compounds R_3SiF, where R is an alkyl radical with 4 to 18 carbon atoms a cyclic radical with 5 to 8 carbon atoms, or a phenyl, phenylethyl, or benzyl radical, are recommended as lubricants or hydraulic fluids. They are chemically inert, have a high viscosity index, low friction coefficient, and satisfactory lubricating properties[252,253]. Tripentylfluorosilane $(C_5H_{11})_3SiF$ is recommended for filling gun recoil shock absorbers[253].

Monomers such as $C_2H_5SiCl_2F$, $CH_3(C_6H_5)SiF_2$, $C_6H_5Si.Cl_2F$, $(C_6H_5)_2SiClF$, whose one Si–F bond remains intact on hydrolysis, have been proposed as insecticides[64].

Complex organosilicon fluorine compounds of the type $[(C_6H_5)_2NH]_2SiF_6$ can be used to prepare certain herbicides[254].

The physical properties (b.p., m.p., density, and refractive index) of all organosilicon fluorine compounds at present known are collected in Table 4.

TABLE 3.

Physical and mechanical indices		Polydimethylsilicone resin	Polyfluorosilicone resin
Tensile strength, kg cm^{-2}		49	56
Tear-resistance		moderate	satisfactory
Permanent set at 150°, %		20	7
Brittle point, °C		– 60	– 65
Swelling after 4 days, %, in			
	kerosene	> 100 (at 100°)	18 (at 150°)
	ether lubricant	10 (at 100°)	7 (at 150°)
	mineral oil	5 (at 100°)	0 (at 150°)

TABLE 4. Physical properties of organosilicon fluorine compounds.

Empirical formula	Structural formula	B.p., °C	M.p., °C	d_4^{20}	n_D^{20}	Reference
$HSiClF_2$	$HSiClF_2$	—50	—144	—	—	46
$HSiCl_2F$	$HSiCl_2F$	—18.4	—149.5	—	—	46
$HSiF_3$	$HSiF_3$	—97.5	—131.2	—	—	45,46,51
H_2SiF_2	H_2SiF_2	—77.5	—119.1	—	—	50,51
H_3SiF	H_3SiF	—88.1	—	—	—	109,51
$SiClBr_2F$	$SiClBr_2F$	59.5	—99.3	—	—	49
$SiClF_3$	$SiClF_3$	—70	—142	—	—	48,55,117
$SiCl_2BrF$	$SiCl_2BrF$	35.4	—112.3	—	—	49
$SiCl_2F_2$	$SiCl_2F_2$	—32.2	—139.7	—	—	48,55,117
$SiCl_3F$	$SiCl_3F$	12.2	—120.8	—	—	47,48,55,79
SiF_4	SiF_4	—95.7	—	—	—	1,2,45,48
$SiBrF_3$	$SiBrF_3$	—41.7	—70.5	—	—	118
$SiBr_2F_2$	$SiBr_2F_2$	—13.7	66.9	—	—	118
$SiBr_3F$	$SiBr_3F$	83.8	—82.5	—	—	118
$SiFI_3$	$SiFI_3$	188(752)	—	3.164^{30}	—	56
SiF_2I_2	SiF_2I_2	84—85(756)	—	2.41^{25}	—	56
SiF_3I	SiF_3I	—24	—	—	—	56
$CSiF_3NO$	$SiF_3(NCO)$	—6	—	—	—	112
$CSiBrF_5$	CF_3SiBrF_2	12—13	—	—	—	227
$CSiF_6$	CF_3SiF_3	—42	—	—	—	227
CH_3SiClF_2	CH_3SiClF_2	— 0.5	—110	—	—	59
CH_3SiCl_2F	CH_3SiCl_2F	29.5	—98.7	—	—	59,198
CH_3SiF_3	CH_3SiF_3	—30.2	—72.8	—	—	59, 72,74,81,95
CH_4SiClF	$CH_3SiHClF$	1.2	—	—	—	170
CH_4SiF_2	CH_3SiHF_2	—35.6	—	—	—	69
CH_6SiF	CH_3SiH_2F	—44	—	—	—	105
$C_2SiCl_3F_3$	$CF_2=CFSiCl_3$	74—76(746)	—	—	—	221
$C_2SiCl_4F_2$	$CFCl=CFSiCl_3$	116—117(746)	—	—	—	221
$C_2SiCl_4F_4$	$CF_2ClCF_2SiCl_3$	102	—	—	—	209
$C_2SiF_2N_2O_2$	$(OCN)_2SiF_2$	68.6	—75	1.437	1.3536	112
$C_2HSiCl_3F_4$	$CF_2HCF_2SiCl_3$	84.2	—	—	1.367	209,215,216,220
$C_2HSiCl_4F_3$	$C_2HClF_3SiCl_3$	123	—	—	—	214,215,216
$C_2H_3SiCl_3F_2$	$C_2H_3Cl_2SiF_3$	91.7—92(749)	—	1.5007	1.3750	36
$C_2H_3SiCl_3F_2$	$CF_2HCH_2SiCl_3$	104—105.5	—	1.43	1.4050	189
$C_2H_3SiF_3$	$CH_2=CHSiF_3$	—25	—	—	—	77
$C_2H_4SiClF_3$	$CH_2CHClSiF_3$	39—39.5(749)	—	1.2806	1.3180	36
$C_2H_4SiClF_3$	$CH_2ClCH_2SiF_3$	68.5(749)	—	1.3661	1.3418	36
$C_2H_5SiClF_2$	$C_2H_5SiClF_2$	27.2	—	1.103	—	57,64
$C_2H_5SiCl_2F$	$C_2H_5SiCl_2F$	62.2	—	1.151	—	57,64
$C_2H_5SiF_3$	$C_2H_5SiF_3$	— 4.4	—105	—	—	36,57,64,71,107
$C_2H_5SiF_3O$	$C_2H_5OSiF_3$	— 7	—122	—	—	63,78
C_2H_6SiClF	$(CH_3)_2SiClF$	36.4	—85.1	—	—	60
$C_2H_6SiF_2$	$(CH_3)_2SiF_2$	2.7	—87.5	—	—	60,72,74,81
C_2H_7SiF	$(CH_3)_2SiHF$	— 9	—115	—	—	105
$C_3SiCl_8F_2$	$CCl_2=C(CF_3)SiCl_3$	77.5—78.5(35)	—	—	—	214
$C_3SiCl_7F_3$	$CCl_3CCl(CF_3)SiCl_3$	118—120(8.5)	—	—	—	214
$C_3SiFN_3O_3$	$(OCN)_3SiF$	134.3	—29.2	1.456	1.4161	112
$C_3HSiCl_6F_3$	$CHCl_2CCl(CF_3)SiCl_3$	78—78.5(3.8)	—	—	—	214
$C_3H_3SiCl_2F_3$	$CH_3(CF_2=CF)SiCl_2$	97—100	—	1.3311	1.3904	221,222
$C_3H_3SiCl_2F_3$	$CH_3(CClF=CF)SiClF$	94(740)	—	—	—	221
$C_3H_3SiCl_3F_2$	$CH_3(CClF=CF)SiCl_2$	121(741)	—	—	—	221
$C_3H_3SiCl_3F_3I$	$CF_3CH_2CHISiCl_3$	79(25)	—	—	—	213
$C_3H_4SiCl_2F_4$	$CH_3(CHF_2CF_2)SiCl_2$	96	—	1.3879	1.3689	191,211
$C_3H_4SiCl_3F_3$	$CH_3(CHF_2CClF)SiCl_2$	124.5(734)	—	1.4211	1.4000	191,193
$C_3H_4SiCl_3F_3$	$CF_3CH_2CH_2SiCl_3$	114	—	1.3951^{28}	1.3845^{28}	187,193,213,214
$C_3H_5SiCl_2F_3$	$CF_3CH_2CH_2SiHCl_2$	90—91	—	—	—	213
$C_3H_6SiCl_2F_2$	$CH_3(CHF_2CH_2)SiCl_2$	113—113.5(743)	—	1.2790	1.3941	198
$C_3H_6SiCl_3F$	$CH_3CHFCH_2SiCl_3$	123—124	—	$1.1924^{21.5}$	$1.4348^{21.5}$	193
$C_3H_7SiClF_2$	$n\text{-}C_3H_7SiClF_2$	55—57(745)	—	—	—	58
$C_3H_7SiClF_2$	$iso\text{-}C_3H_7SiClF_2$	48.8	—	—	—	61
$C_3H_7SiCl_2F$	$iso\text{-}C_3H_7SiCl_2F$	84	—	—	—	61
$C_3H_7SiF_3$	$n\text{-}C_3H_7SiF_3$	24.9	—	—	—	58
$C_3H_7SiF_3$	$iso\text{-}C_3H_7SiF_3$	24.9	—127.6	—	—	61
C_3H_9SiF	$(CH_3)_3SiF$	16,4	—74.3	—	—	60,72,74,89,92,95,98,99
$C_4HSiCl_3F_5$	$CF_2=CFCHFCF_2SiCl_3$	146	—	—	—	221
$C_4HSiCl_3F_6$	$CHF_2CF_2CF_2CF_2SiCl_3$	90(195)	—	—	—	209
$C_4H_3SiCl_3F_6$	$CF_3CF_2CHF\ CH_2SiCl_3$	127—127.8(758)	—	—	—	214
$C_4H_3SiCl_4F_3$	$CH_3(CCl_2=C(CF_3))SiCl_3$	76—76.5(32)	—	—	—	214
$C_4H_3SiCl_6F_3I$	$CClF_2GClFCH_2CHISiCl_3$	124(1)	—	—	—	213
$C_4H_4SiCl_3F_6$	$CF_3CF_2CH_2CH_2SiCl_3$	120	—	—	1.3705^{25}	217
$C_4H_6SiClBrF_4$	$CH_3(CClF_2CH_2CHBr)SiF_2$	67.5—68(50)	—	1.631^{25}	1.4000^{25}	67,68
$C_4H_6SiCl_2F_4$	$C_2H_5(CHF_2CF_2)SiCl_2$	119.7(748)	—	1.3527	1.3819	191
$C_4H_6SiCl_3F_3$	$C_2H_5(CHF_2CClF)SiCl_2$	154(754)	—	1.4170	1.4120	191
$C_4H_6SiBrF_5$	$CH_3(CF_3CH_2CHBr)SiF_2$	114—115(736)	—	1.579^{25}	1.3680^{25}	67,68
$C_4H_7SiCl_2F_3$	$CH_3(CF_3CH_2CH_2)SiCl_2$	122	—	1.2611	1.3946	186,193,195,213,214
$C_4H_8SiClF_3$	$CH_3(CF_3CH_2CH_2)SiHCl$	96.5(746)	—	1.1565	1.3651	203
$C_4H_8SiCl_2F_2$	$C_2H_5(C_2H_3Cl_2)SiF_2$	148.2(751)	—	1.3099	1.4207	36
$C_4H_8SiF_2$	$C_2H_5(CH_2=CH)SiF_2$	56(742)	—	0.9578	1.3346	36
$C_4H_8SiF_4$	$(CH_3)_2(CHF_2CF_2)SiH$	62,3	—	—	—	212
$C_4H_9SiClF_2$	$n\text{-}C_4H_9SiClF_2$	84,5	—	—	—	62
$C_4H_9SiClF_2$	$C_2H_5(CH_3CHCl)SiF_2$	103.2(753)	—	1.1155	1.3790	36
$C_4H_9SiClF_2$	$C_2H_5(CH_2ClCH_2)SiF_2$	125.5(751)	—	1.1467	1.3900	36
$C_4H_9SiCl_2F$	$n\text{-}C_4H_9SiCl_2F$	116.1	—	—	—	62
$C_4H_9SiF_3$	$n\text{-}C_4H_9SiF_3$	52.4	—96.9	$1.006^{26.5}$	—	63,81,106
$C_4H_9SiF_3$	$CH_3(CF_3CH_2CH_2)SiH_2$	58.2(759)	—	0.9802	1.3408	30
$C_4H_{10}SiClF$	$(C_2H_5)SiClF$	96—97(758)	—	—	—	79
$C_4H_{10}SiF_2$	$(C_2H_5)_2SiF_2$	61—62	—	0.9289^{27}	1.3393^{23}	5,36,38,71,79,94,100,93, 106,107
$C_4H_{10}SiF_2O_2$	$(C_2H_5O)_2SiF_2$	83—83.5	—	—	—	101
$C_4H_{10}SiF_2S_2$	$(C_2H_5S)_2SiF_2$	163—164	—	—	—	157,158
$C_4H_{11}SiF$	$(CH_3)_2(C_2H_5)SiF$	51	—	—	1.3570^{15}	100,124
$C_5H_4SiCl_2F_6$	$CH_3(CHF_2CF_2CF_2CF_2)SiCl_2$	138(753)	—	1.5119	1.3570	192,211
$C_5H_4SiCl_3F_7$	$CF_3CF_2CF_2CH_2CH_2SiCl_3$	62—64(49)	—	—	1.3626^{25}	217
$C_5H_6SiCl_2F_6$	$CH_3(CF_3CF_2CHFCH_2)SiCl_2$	128—129.1(746)	—	—	—	214
$C_5H_6SiCl_3F_5$	$CF_3CF_2CH(CH_3)CH_2SiCl_3$	64—65(28)	—	—	1.3812^{25}	217
$C_5H_6SiCl_4F_3I$	$CH_3(CClF_2CClFCH_2CHI)SiCl_2$	116.5(33)	—	1.846^{25}	1.4895^{25}	68,213,234
$C_5H_7SiCl_2F_5$	$CH_3(CF_3CF_2CH_2CH_2)SiCl_2$	131	—	1.3136^{26}	1.3691^{25}	193,195
$C_5H_7SiCl_3F_4O$	$CHF_2CF_2OCH_2CH_2CH_2SiCl_3$	186(751)	—	1.4335	1.3994	201
$C_5H_7SiCl_4F_3O$	$CHClFCF_2OCH_2CH_2CH_2SiCl_3$	213(753)	—	1.4563	1.4230	200
$C_5H_8SiCl_3F_4O$	$CHF_2CF_2OCH_2CH_2CH\ SiHCl_2$	165.2(742)	—	1.3693	1.4001	204
$C_5H_8SiCl_3F_3O$	$CHClFCF_2OCH_2CH_2CH_2SiHCl_2$	188(746)	—	1.3886	1.4171	202

TABLE 4 (contd.)

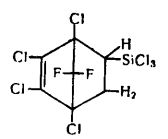
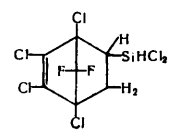
Empirical formula	Structural formula	B.p., °C	M.p., °C	d_4^{20}	n_D^{20}	Reference
$C_6H_9SiCl_2F_3$	$CH_3[CH_2CH(CF_3)CH_2]SiCl_2$	139	—	1.2322[26]	1.3936	193,213,248
$C_6H_9SiF_3O_2$	$(CH_3)_3SiOCOCF_3$	90.2	—	1.077	1.338	235
$C_6H_{10}SiClF_3$	$(CH_3)_2(CF_3CH_2CH_2)SiCl$	118	—	1.113[25]	1.3727[25]	186
$C_6H_{10}SiClF_3$	$(CH_3)_2(C_2HClF_3)Si$	43—44(43)	—	1.134	1.3887[22]	214
$C_6H_{12}SiF_4O_3$	$CHF_2CF_2Si(OCH_3)_3$	98(190)	—	—	—	209
$C_5H_{11}SiF_3$	$n\text{-}C_5H_{11}SiF_3$	77	—	1.0023[26,5]	—	81,91,106
$C_5H_{11}SiF_3$	$(CH_3)_2(CF_3CH_2CH_2)SiH$	80(748)	—	0.954[25]	1.3485[25]	186
$C_5H_{12}SiF$	$CH_3(C_2H_5)_2SiF$	80—82(754)	—	—	1.3820[17]	124
$C_5H_{13}SiFO$	$(CH_3)_2(C_2H_5OCH_2)SiF$	88—89	—	—	1.3710	113
$C_6HSiCl_3F_{12}$	$CHF_2CF_2CF_2CF_2CF_2CF_2SiCl_3$	128(205)	—	—	—	209
$C_6H_3SiCl_3F_6$	$CH_3(CF_2CF_2CF_2CCl{=}C)SiCl_2$	161(740)	—	—	—	221
$C_6H_4SiClF_3$	$o\text{-}ClC_6H_4SiF_3$	150—150.5(747)	—	1.3856	1.4460	65
$C_6H_4SiClF_3$	$m\text{-}ClC_6H_4SiF_3$	139.5—140.4(759)	—	1.3684	1.4430	65
$C_6H_4SiCl_3F_5$	$CH_3(CF_2CF_2CF_2CH{=}C)SiCl_2$	144(740)	—	1.481[25]	—	221
$C_6H_4SiCl_3F$	$p\text{-}FC_6H_4SiCl_3$	194.5(738)	—	—	—	163,164
$C_6H_4SiF_4$	$CF_3C_6H_4SiF_3$	116.5—117(747)	—	1.400[25]	1.3778	67
$C_6H_5SiClF_2$	$C_6H_5SiClF_2$	130—135	—	1.200[27]	—	64,85
$C_6H_5SiCl_2F$	$C_6H_5SiCl_2F$	163—166	—	1.274[26]	—	64,85
$C_6H_5SiCl_2F$	$p\text{-}FC_6H_4SiHCl_2$	177(747)	—	1.2936	1.5030	202
$C_6H_5SiCl_2F_7$	$CH_3(CF_2CF_2CF_2CH{=}CH)SiCl_2$	144	—	1.481	—	223
$C_6H_6SiF_3$	$C_6H_5SiF_3$	102	—18	1.2169	1.4110	38,64,65,71,75,81,91
$C_6H_6SiCl_3F_7$	$CF_3CF_2CF_2CH(CH_3)CH_2SiCl_3$	53—54(24)	—	—	1.3722[25]	217
$C_6H_6SiF_6O_4$	$(CH_3)_2Si(OCOCF_3)_2$	128.2	—	1.361	1.331	235
$C_6H_7SiCl_2F_7$	$CH_3(CF_2CF_2CF_2CH_2CH_2)SiCl_2$	147	—	1.3707	1.3136	193,195,213,217
$C_6H_8SiCl_2F_6$	$(CF_3CH_2CH_2)_2SiCl_2$	162—163	—	1.3843	1.3810	187,202,213
$C_6H_8SiF_8$	$(CH_3)_2(CHF_2CF_2)_2Si$	120	—	—	—	212
$C_6H_9SiCl_2F_3$	$(CH_3)_3[CCl_2{=}C(CF_3)]Si$	157(756)	—	1.243	1.4322	214
$C_6H_9SiCl_3F_5$	$CH_3[CF_2CF_2CH(CH_3)CH_2]SiCl_2$	65(52)	—	—	1.3884[25]	217
$C_6H_{10}SiClF_5$	$(CH_3)_2(CF_2CF_2CH_2CH_2)SiCl$	129(750)	—	1.199[25]	1.3608[25]	186
$C_6H_{10}SiCl_2F_4O$	$CH_3(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	190.1(750)	—	1.3140	1.3960	201
$C_6H_{10}SiCl_3F_3O$	$CH_3(CHClFCF_2OCH_2CH_2CH_2)SiCl_2$	215(753)	—	1.3395	1.4160	200
$C_6H_{10}SiF_2$	$(CH_2{=}CHCH_2)_2SiF_2$	46.5(20)	—	—	—	134
$C_6H_{10}SiF_6$	$(CF_3CH_2CH_2)_2SiH_2$	45.5(33)	—	1.1928	1.3446	30
$C_6H_{11}SiBrF_2$	$(CH_3)_3(CBrF_2CH{=}CH)Si$	66—68(52)	—	—	—	213
$C_6H_{11}SiF_3$	$C_6H_{11}SiF_3$	105.3	—	1.113	1.3717	35,106
$C_6H_{11}SiF_5$	$(CH_3)_2(CF_3CF_2CH_2CH_2)SiH$	94(743)	—	1.078[25]	1.3387[25]	186
$C_6H_{12}SiClF_3$	$CH_3(C_2H_5)(CF_3CH_2CH_2)SiCl$	140(758)	—	1.1044	1.3871	203
$C_6H_{12}SiClF_3O$	$(CH_3)_3(CHClFCF_2OCH_2)St$	141(751)	—	1.0966	1.3810	204
$C_6H_{12}SiBr_2F_2$	$(CH_3)_3(CBrF_2CH_2CHBr)Si$	95(25)	—	—	—	213
$C_6H_{12}SiF_3I$	$(CH_3)_3(CF_2CH_2CHI)Si$	72(20)	—	—	—	213
$C_6H_{13}SiF$	$C_6H_{11}SiH_2F$	118.1	—	0.925	1.4207	35
$C_6H_{13}SiF_3$	$(CH_3)_2(CF_3CH_2CH_2CH_2)SiH$	105(756)	—	0.950[25]	1.3612[25]	186
$C_6H_{13}SiF_3$	$(CH_3)_3(CF_3CH_2CH_2)Si$	94.3—95.1(750)	—	0.896	1.3576	214
$C_6H_{13}SiF_3O_3$	$CH_3(CF_3CH_2CH_2)Si(OCH_3)_2$	96.5—96.8(751)	—	1.0954	1.3576	185,213
$C_6H_{13}SiF_3O_3$	$CF_3CH_2CH_2Si(OCH_3)_3$	144	—	1.137	1.3547	185,213,214
$C_6H_{14}SiClF$	$(n\text{-}C_3H_7)_2SiClF$	140—144	—	—	—	158
$C_6H_{14}SiClF$	$(C_6H_5)_2(CH_3CHCl)SiF$	152	—	0.9955	1.4208	87,111
$C_6H_{14}SiClF$	$(C_2H_5)_2(CH_2ClCH_2)SiF$	171	—	1.0100	1.4277	87
$C_6H_{14}SiF_2$	$(n\text{-}C_3H_7)_2SiF_2$	111—113	—	0.9113	—	98,158
$C_6H_{14}SiF_2$	$(iso\text{-}C_3H_7)_2SiF_2$	102	—	—	1.3663	100,124
$C_6H_{14}SiF_2O_2$	$(CH_3CH_2CH_2O)_2SiF_2$	35(16)	—	0.8692	1.3830	42
$C_6H_{15}SiF$	$(C_2H_5)_3SiF$	109—110	—	0.8360	1.3900	5,27,38,86,92,98,100,111, 119,124,238
$C_6H_{15}SiFO_2$	$(C_2H_5)_3SiF$	133—133.5	—	—	—	63,78,101
$C_6H_{15}SiFS_2$	$(C_2H_5S)_2SiF$	114—115(10)	—	—	—	157,158
$C_7H_3SiCl_7F_2$		130(10)	—	1.7010	1.5141	37
$C_7H_4SiCl_3F_3$	$o\text{-}CCl_3C_6H_4SiF_3$	229	—9	1.562[25]	1.4997[25]	83
$C_7H_4SiCl_3F_3$	$m\text{-}CF_3C_6H_4SiCl_3$	108(47.4)	—	—	1.4678[25]	66,166,167
$C_7H_4SiCl_3F_3$	$p\text{-}CCl_3C_6H_4SiF_3$	212.2	5—5.5	1.510[25]	1.4833[25]	83
$C_7H_4SiCl_6F_2$		88(16)	—	1.4474	1.4326	37
$C_7H_4SiF_6$	$o\text{-}CF_3C_6H_4SiF_3$	138	—36	1.435[25]	1.3876[25]	83
$C_7H_4SiF_6$	$m\text{-}CF_3C_6H_4SiF_3$	118.2	—34	1.3985[25]	1.3783[25]	66
$C_7H_4SiF_6$	$p\text{-}CF_3C_6H_4SiF_3$	118.6	—3	1.399[25]	1.3783[25]	66,83,224
$C_7H_7SiF_3$	$o\text{-}CH_3C_6H_4SiF_3$	130.8	—78	1.190[25]	1.4278[25]	83
$C_7H_8SiF_2$	$CH_3(C_6H_5)SiF_2$	141—142	—	1.0993	—	64,75,96—99
$C_7H_8SiCl_3F_7$	$CH_3[CF_2CF_2CF_2CH(CH_3)CH_2]SiCl_2$	65(26)	—	—	1.3748[25]	217
$C_7H_{11}SiClF_6$	$CH_3(CF_2CH_2CH_2)_2SiCl$	45.5—47(6)	—	1.2791	1.3699	186,203
$C_7H_{11}SiCl_4F_3$	$(CH_3)_2(CClF_2CClFCH{=}CH)Si$	57—59(15)	—	—	—	213
$C_7H_{11}SiF_3$	$(CH_3)_2(CF_2{=}CFCH{=}CH)Si$	25(25)	—	—	—	213
$C_7H_{12}SiCl_2F_4O$	$C_2H_5(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	207.2(749)	—	1.2837	1.4033	201
$C_7H_{12}SiCl_3F_3I$	$(CH_3)_3(CClF_2CClFCH_2CHI)Si$	99—100(9)	—	—	—	213
$C_7H_{12}SiCl_3F_3O$	$C_2H_5(CHClFCF_2OCH_2CH_2CH_2)SiCl_2$	231.5(751)	—	1.3155	1.4249	200
$C_7H_{12}SiF_6$	$(CH_3)_2(CF_2CF_2CHFCH_2)Si$	109.8—111.5(747)	—	1.133	1.3441	214
$C_7H_{12}SiF_6$	$CH_3(CF_2CH_2CH_2)_2SiH$	64(40)	—	1.163[25]	1.3500[25]	186
$C_7H_{13}SiF_5$	$(CH_3)_2(CF_2CF_2CH_2CH_2)Si$	100—101	—	—	1.3000	217

TABLE 4 (contd.)

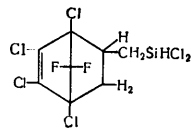
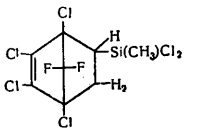
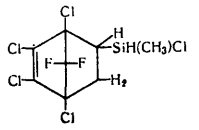
Empirical formula	Structural formula	B.p., °C	M.p., °C	d_4^{20}	n_D^{20}	Reference
$C_7H_{14}SiF_4O$	$(CH_3)_3(CHF_2CF_2OCH_2CH_2)Si$	137(746)	—	1,0550	1.3670	204
$C_7H_{15}SiF_3$	n-$C_7H_{15}SiF_3$	127	—	0,983	1.3606	70
$C_7H_{16}SiF_2$	n-$C_7H_{15}SiHF_2$	132.6	—	0.916	1.3759	70
$C_7H_{17}SiF$	n-$C_7H_{15}SiH_2F$	138.1	—	0.828	1.3997	70
$C_7H_{17}SiF$	$CH_3(n$-$C_6H_{13})_2SiF$	130.2	—	—	1.3942^{19}	124
$C_7H_{17}SiF$	$CH_3(iso$-$C_3H_7)_2SiF$	124.5	—	—	1.3958^{21}	124
$C_7H_{17}SiFO$	$(C_2H_5)_2(CH_3CH(CH_3)O)SiF$	127(750)	—	0.8745	1.3803	76
C_9SiF_{12}	$(CF_2{=}CF)_4Si$	119—120	—	1.6182	1.3621	188
$C_8H_3SiCl_3F_6$	2,5-$(CF_3)_2C_6H_3SiCl_3$	80(25)	—	—	—	166,167
$C_8H_3SiCl_3F_6$	3,5-$(CF_3)_2C_6H_3SiCl_3$	55—57.2(1.7)	—	1.532^{20}	1.4322	166,167
$C_8H_6SiCl_3F_3$	$CH_3Cl(CF_3C_6H_4)SiCl_2$	86(3.6)	—	1.4663^{25}	1.4839^{25}	171
$C_8H_6SiCl_6F_2$		102—103(2.5)	—	1.5483	1.5110	37
$C_8H_6SiCl_6F_2$		130(8)	—	1.6041	1.5121	37
$C_8H_7SiCl_2F_3$	$CH_3(m$-$CF_3C_6H_4)SiCl_2$	115.5(50)	—	1.3436^{25}	1.4639^{25}	166,169,170
$C_8H_7SiCl_5F_2$		122(8)	—	1.5355	1.5066	37
$C_8H_8SiF_{12}O_4$	$(CF_3CH_2O_2)_4Si$	165—166(750)	—	—	—	237
$C_8H_9SiF_3$	$CH_3(m$-$CF_3C_6H_4)SiH_2$	43(15)	—	1.1042	1.4460	30
$C_8H_{10}SiClF$	$(CH_3)_2(p$-$ClC_6H_4)SiF$	198	—	—	1.4930^{25}	113
$C_8H_{10}SiF_2$	$C_2H_5(C_6H_5)SiF_2$	163—164	—	—	—	96,97
$C_8H_{11}SiF$	$(CH_3)_2(C_6H_5)SiF$	161—162	—	—	1.4712^{25}	113
$C_6H_{12}SiClF_3$	$(CH_3)_2(CH_2{=}CH)(CH_2CF_2CClFCH)Si$	82(30)	—	1.144^{25}	1.4220^{25}	196
$C_8H_{13}SiF_3$	$CH_3(CH_3{=}CH)_2(CF_3CH_2CH_2)Si$	134	—	—	1.395^{25}	196
$C_8H_{13}SiF_7$	$(CH_3)_2(CF_3CF_2CF_2CH_2CH_2)Si$	36(30)	—	—	1.3390^{25}	217
$C_8H_{14}SiCl_2F_4O$	n-$C_3H_7(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	101(11)	—	1.2484	1.4062	201
$C_8H_{14}SiCl_2F_3O$	n-$C_3H_7(CHClFCF_2OCH_2CH_2CH_2)SiCl_2$	115,5(8)	—	1.2763	1.4270	200
$C_8H_{15}SiF_9O_2$	$(CF_3CH_2CH_2)_2Si(OCH_3)_2$	175—176	—	1.256	1.3531	185,213
$C_8H_{15}SiClF_4O$	$CH_3(C_2H_5)(CHF_2CF_2OCH_2CH_2CH_2)SiCl$	199(749)	—	1.1681	1.3956	201
$C_8H_{15}SiCl_2F_3O$	$CH_3(C_2H_5)(CHClFCF_2OCH_2CH_2CH_2)SiCl$	223(746)	—	1.1918	1.4175	200
$C_8H_{16}SiClF_3O$	$(CH_3)_2(CHClFCF_2OCH_2CH_2CH_2)Si$	182(742)	—	1.0866	1.3985	200
$C_8H_{16}SiF_4O$	$(CH_3)_2(CHF_2CF_2OCH_2CH_2CH_2)Si$	156(746)	—	1.0453	1.3732	201
$C_8H_{16}SiF_4O_4$	$(CH_2FCH_2O)_4Si$	258(766)	—	1.2750	1.3891	238
$C_8H_{17}SiF_3$	$CH_3(CH_2)_4CH(CH_3)CH_2SiF_3$	50—54(24)	—	—	—	106
$C_8H_{18}SiF_2$	$(n$-$C_4H_9)_2SiF_2$	156(733)	—	0.8999	1.4049^{25}	81,98,99,106
$C_8H_{18}SiF_2$		145	—	—	—	125
$C_8H_{18}SiF_2O_2$	$(n$-$C_4H_9O)_2SiF_2$	58—59(13)	—	—	—	157,158
$C_8H_{19}SiFO$	$(C_2H_5)_2SiOCH_2CH_2F$	173.5—(764)	—	0.9062	1.4129	238
$C_9H_7SiCl_2F_3$	m-$CF_3C_6H_4(CH_2{=}CH)SiCl_2$	91—92(10)	—	—	1.4755	172
$C_9H_7SiF_9O_6$	n-$C_3H_7Si(OCOCF_3)_3$	157	—	1.434	1.3277	236
$C_9H_8SiCl_2F_4$	p-$FC_6H_4(CF_3CH_2CH_2)SiCl_2$	101—103(10)	—	1.3641	1.4645	202
$C_9H_9SiCl_2F_3$	$C_6H_5(CF_3CH_2CH_2)SiCl_2$	99—100(10)	—	1.3048	1.4737	202
$C_9H_9SiCl_2F_3$	$CH_3(CH_2Cl)(CF_3C_6H_4)SiCl$	130.8(25)	—	1.3411	1.4796^{25}	171
$C_9H_{10}SiClF_3$	$(CH_3)_2(o$-$CF_3C_6H_4)SiCl$	78(12)	—	—	—	66
$C_9H_{10}SiF_6O_6$	n-$C_3H_7Si(OCOCHF_2)_3$	230	—	1.440	1.3771	236
$C_9H_{12}SiClF$	$(CH_3)_2(p$-$ClC_6H_4CH_2)SiF$	247	—	—	1.4955^{25}	113
$C_9H_{13}SiF$	$(CH_3)_2(p$-$FC_6H_4)Si$	170.1(745)	—	0.9656	1.4751	160,163,164
$C_9H_{15}SiCl_2F_3$	$(C_2H_5)_3(CCl_2{=}C)(CF_3)Si$	119(28)	—	1.193	1.4532	214
$C_9H_{15}SiF$	$(CH_2{=}CHCH_2)_3SiF$	67(20)	—	—	—	134
$C_9H_{15}SiFO_3$	$(CH_2{=}CHCH_2O)_3SiF$	99—99.5(32)	—	—	—	101
$C_9H_{16}SiCl_3F_2O$	$(CH_3)_2(C_2Cl_3F_2CH_2CHCH_2)SiOC_2H_5$	220	<—75	—	1.159^{25}	230
$C_9H_{16}SiF_6$	$CH_3(C_2H_5)_2(CF_3CF_2CHFCH_2)Si$	154—155(747)	—	1.115	1.3687	214
$C_9H_{16}SiF_4O$	$(CH_3)_2(CF_3CF_2CH_2CHCH_2)SiOC_2H_5$	176	<—75	1.092^{25}	—	230
$C_9H_{18}SiClF_3O$	$(CH_3)_2(C_2H_5)(CHClFCF_2OCH_2CH_2CH_2)Si$	204(740)	—	1.0771	1.4073	200
$C_9H_{18}SiF_4O$	$(CH_3)_2(C_2H_5)(CHF_2CF_2OCH_2CH_2CH_2)Si$	176(739)	—	1.0402	1.3830	201
$C_9H_{19}SiF_3$	$(C_2H_5)_3(CF_3CH_2CH_2)Si$	166.1—167.8(753)	—	0.961	1.3962	214
$C_9H_{21}SiF$	$(n$-$C_3H_7)_3SiF$	174.5	—	0.8384	1.4117	92,98,99,119,124
$C_9H_{21}SiF$	$(iso$-$C_3H_7)_3SiF$	170	—	—	1.4185	124,125
$C_{10}H_3SiF_{15}O_6$	$CH_3Si(OCOC_2F_5)_3$	159	—	1.589	1.3033	236
$C_{10}H_8SiCl_3F_3$	$C_6H_5(CClFCF_2CH_2CH)SiCl_2$	135(21)	—	1.385^{25}	1.5002^{25}	231
$C_{10}H_{10}SiF_{14}$	$(C_2H_5)_2(CF_3CF_2CF_2)_2Si$	79(12)	—	—	1.3380	184
$C_{10}H_{10}SiF_{14}O_2$	$(CF_3CF_2CF_2CH_2CH_2)_2Si(OH)_2$	—	64.5—65	—	—	183
$C_{10}H_{12}SiClF_3$	$(CH_3)_2[4$-$Cl-5-(CF_3)C_6H_3]Si$	213.9	—34.1	1.166^{25}	1.4663^{25}	83,175
$C_{10}H_{13}SiF_3$	$(CH_3)_2(o$-$CF_3C_6H_4)Si$	185.5	<—78	1.089^{25}	1.4561^{25}	83
$C_{10}H_{13}SiF_3$	$(CH_3)_2(m$-$CF_3C_6H_4)Si$	175.1	<—78	1.053^{25}	1.4413^{25}	83
$C_{10}H_{13}SiF_3$	$(CH_3)_2(p$-$CF_3C_6H_4)Si$	180.7	—23	1.052^{25}	1.4403^{25}	83
$C_{10}H_{14}SiCl_2F_6O_2$	$(CHF_2CF_2OCH_2CH_2CH_2)_2SiCl_2$	122(3)	—	1.4222	1.3960	204
$C_{10}H_{14}SiCl_4F_4O_2$	$(CHClFCF_2OCH_2CH_2CH_2)_2SiCl_2$	151—152(6)	—	1.4296	1.4240	202
$C_{10}H_{15}SiF$	$(CH_3)_2(p$-$CH_3C_6H_4CH_2)SiF$	201	—	—	1.4775^{25}	113
$C_{10}H_{18}SiFO_2$	$C_6H_5(C_2H_5O)_2SiF$	64—75(200)	—	1.038^{25}	—	64
$C_{10}H_{17}SiF_7O_2$	$CH_3(CF_3CF_2CF_2CH_2CH_2)Si(OC_2H_5)_2$	82—83(28)	—	—	1.3502	185,213
$C_{10}H_{18}SiF_6$	$(C_2H_5)_3(CF_3CF_2CHFCH_2)Si$	173.1(753)	—	1.110	1.3800	214

TABLE 4 (contd.)

Empiral formula	Structural formula	B.p., °C	M.p., °C	d_4^{20}	n_D^{20}	Reference
$C_{10}H_{16}SiF_4O_2$	$CH_3(CF_2CF_2CH_2CHCH_2)Si(OC_2H_5)_2$	201	<—70	1.096[25]	—	230
$C_{10}H_{20}SiClF_3O$	$CH_3(C_2H_5)_2(CHClFCF_2OCH_2CH_2CH_2)Si$	94(7)	—	1.0776	1.4149	200
$C_{10}H_{20}SiF_4O$	$CH_3(C_2H_5)_2(CHF_2CF_2OCH_2CH_2CH_2)Si$	196.5(749)	—	1.0422	1.3930	201
$C_{10}H_{20}SiF_4O$	$(CH_3)_2(C_3H_7)(CHF_2CF_2OCH_2CH_2CH_2)Si$	193(751)	—	1.0267	1.3886	201
$C_{10}H_{22}SiF_2$	$(n\text{-}C_5H_{11})_2SiF_2$	193	—	0.8972[25.5]	—	81,91
$C_{11}H_9SiF_{15}O_6$	$C_2H_5Si(OCOC_3F_5)_3$	169	—	1.545	1.3091	236
$C_{11}H_{11}SiCl_2F_3O$	$p\text{-}FC_6H_4(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	137—137.5(8)	—	1.3695	1.4560	204
$C_{11}H_{11}SiF_9O_6$	$n\text{-}C_5H_{11}Si(OCOCF_3)_3$	181	—	1.363	1.3410	236
$C_{11}H_{12}SiCl_2F_4O$	$C_6H_5(CHF_2CF_2OCH_2CH_2CH_2)SiCl_2$	118.5(4)	—	1.3204	1.4650	204
$C_{11}H_{12}SiCl_3F_3O$	$C_6H_5(CHClFCF_2OCH_2CH_2CH_2)SiCl_2$	145(16)	—	1.3417	1.4825	204
$C_{11}H_{14}SiClF_3O$	$(CH_3)_2(4\text{-}Cl\text{-}5\text{-}CF_3C_6H_3)SiOC_2H_5$	65—67(1—2)	—	—	—	175
$C_{11}H_{15}SiF_3$	$(CH_3)_3(m\text{-}CF_3C_6H_4CH_2)Si$	195.6	<—78	1.034[25]	1.4451[25]	83
$C_{11}H_{16}SiF_6$	$CH_3(CH_2{=}CH)_2(CF_3CH_2CH_2CH)(CF_3)CH_2Si$	89(30)	—	—	1.3903[25]	196
$C_{11}H_{16}SiF_7O_3$	$CF_3CF_2CF_2CH_2CH_2Si(OC_2H_5)_3$	47(3)	—	—	—	183,185
$C_{11}H_{21}SiCl_2F_3O$	$(n\text{-}C_3H_7)_2(CHClFCF_2OCH_2CH_2CH_2)SiCl$	116.8—117.2(3)	—	1.1377	1.4286	204
$C_{11}H_{21}SiF_3O$	$(C_2H_5)_3\{CH_2{=}C[C(CH_2)(CF_3)(OH)]\}Si$	114—115(22)	—	1.0342	1.4291	199
$C_{12}H_5SiF_9O_6$	$C_6H_5Si(OCOCF_3)_3$	198	—	1.481	1.3784	236
$C_{12}H_7SiF_{15}O_6$	$n\text{-}C_3H_7Si(OCOC_2F_5)_3$	178	—	1.510	1.3156	236
$C_{12}H_8SiCl_2F_2$	$(p\text{-}FC_6H_4)_2SiCl_2$	293.4(738)	—	—	—	163,164
$C_{12}H_9SiF_9O_6$	$C_6H_5Si(OCOCHF_2)_3$	248	—	1.494	1.4290	236
$C_{12}H_8SiF_{20}O_4$	$(CF_3CF_2CH_2O)_4Si$	81—82(10)	—	—	—	237
$C_{12}H_{10}SiClF$	$(C_6H_5)_2SiClF$	123—125(5.5)	—	1.181[25.5]	—	64
$C_{12}H_{10}SiF_2$	$(C_6H_5)_2SiF_2$	247—248	—	1.151[25.5]	—	38,64,71,81 98,99,134,135
$C_{12}H_{11}SiF_9O_6$	$C_6H_{11}Si(OCOCF_3)_3$	200	—	1.418	1.3583	236
$C_{12}H_{16}SiClF_4O$	$CH_3(C_6H_5)(CHF_2CF_2OCH_2CH_2CH_2)SiCl$	118.5—119(3.5)	—	1.2286	1.4600	204
$C_{12}H_{17}SiF_3O_3$	$CH_3(m\text{-}CF_3C_6H_4)Si(OC_2H_5)_2$	105—108(13)	—	1.086	—	174
$C_{12}H_{20}SiF_4O_2$	$(CH_2{=}CHCH_2)(CF_2CF_2CH_2CHCH_2)Si(OC_2H_5)_2$	103(10)	<—75	1.096[25]	—	230
$C_{12}H_{23}SiF_3$	$C_{12}H_{23}SiF_3$	98—102(6—7)	—	0.9403[23]	1.3910[23]	91
$C_{12}H_{25}SiF_3$	$CH_3(CH_2)_{11}SiF_3$	101—110(3—4)	—	0.9376[23]	—	106
$C_{12}H_{27}SiF$	$(n\text{-}C_4H_9)_3SiF$	225.3	—	0.8404	1.4238	81,92,98,99,100,119
$C_{12}H_{27}SiF$	$(iso\text{-}C_4H_9)_3SiF$	205.5(750)	—	—	1.4218	125
$C_{12}H_{27}SiFO_3$	$(n\text{-}C_4H_9O)_3SiF$	133—134(32)	—	0.9383	—	101,107,158
$C_{13}H_{19}SiF_9O_3$	$m\text{-}CF_3C_6H_4Si(OC_2H_5)_3$	190	—	1.12	—	66,174
$C_{14}H_5SiF_{21}O_6$	$C_6H_5Si(OCOC_3F_7)_3$	199	—	1.624	1.3111	236
$C_{14}H_8SiCl_4F_6$	$(4\text{-}Cl\text{-}5\text{-}CF_3C_6H_3)_2SiCl_2$	112—115(1)	—	—	—	175
$C_{14}H_8SiCl_2F_6$	$(m\text{-}CF_3C_6H_4)_2SiCl_2$	124.7(3.4)	—	1.4274[25]	1.4884[25]	66,166,167
$C_{14}H_{10}SiF_6$	$(m\text{-}CF_3C_6H_4)_2SiH_2$	125—126(12)	—	1.2927	1.4806	30
$C_{14}H_{11}SiF_{15}O_6$	$C_6H_{11}Si(OCOC_2F_5)_3$	197	—	1.441	1.3267	236
$C_{14}H_{12}SiF_2$	$(o\text{-}CH_3C_6H_4)_2SiF_2$	285—289	—	—	—	125
$C_{14}H_{14}SiF_2$	$(CH_3)_2(p\text{-}FC_6H_4)_2Si$	184—185(60)	—	1.1121	1.5331	163,164
$C_{14}H_{14}SiF_2$	$(C_6H_4CH_2)_2SiF_2$	289—291(657)	—	—	—	134,136
$C_{14}H_{18}SiF_{14}O_2$	$(CF_2CF_2CF_2CH_2CH_2)_2Si(OC_2H_5)_2$	117.5—118(25)	—	—	—	183
$C_{14}H_{20}SiF_6O_2$	$(CF_2CF_2CH_2CHCH_2)_2Si(OC_2H_5)_2$	117(3)	<—75	1.259[25]	—	230
$C_{15}H_5SiF_{15}O_6$	$C_6H_5Si(OCOC_2F_5)_3$	215	—	1.546	1.3551	236
$C_{15}H_7SiF_{21}O_6$	$n\text{-}C_3H_7Si(OCOC_3F_7)_3$	208	—	1.584	1.3164	236
$C_{15}H_8SiCl_3F_6$	$CH_3(4\text{-}Cl\text{-}5\text{-}CF_3C_6H_3)_2SiCl$	128—129(1)	—	—	—	175
$C_{15}H_{10}SiCl_2F_6$	$(CH_2Cl)(CF_3C_6H_4)_2SiCl$	152(3.5)	—	1.4407[25]	1.4987[25]	171
$C_{15}H_{11}SiClF_6$	$CH_3(m\text{-}CF_3C_6H_4)_2SiCl$	123(4)	—	1.3535[25]	1.4841[25]	166,170
$C_{15}H_{11}SiF_{15}O_6$	$C_6H_{11}Si(OCOC_2F_5)_3$	216	46	—	—	236
$C_{16}H_{12}SiF_{21}Cl$	$(CF_3CF_2CF_2CH_2CH_2)_3SiCl$	133—134(15)	34—35	—	—	183
$C_{15}H_{13}SiF_{21}O$	$(CF_3CF_2CF_2CH_2CH_2)_3SiOH$	151—153	—	—	1.3378	183
$C_{16}H_{22}SiF$	$(n\text{-}C_5H_{11})_2SiF$	267(745)	—	0.8389[25]	1.4305[25]	81,119
$C_{16}H_6SiCl_2F_{12}$	$[2,5\text{-}(CF_3)_2C_6H_3]_2SiCl_2$	109.5—110(3)	—	—	1.4248[30]	166,167
$C_{16}H_6SiCl_2F_{12}$	$[3,5\text{-}(CF_3)_2C_6H_3]_2SiCl_2$	116.6(214)	—	1.567[30]	1.4424[30]	165,166,167
$C_{16}H_8SiF_{12}O_2$	$[3,5\text{-}(CF_3)_2C_6H_3]_2Si(OH)_2$	—	220	—	—	167
$C_{16}H_{12}SiCl_2F_6$	$(CH_3)_2(4\text{-}Cl\text{-}5\text{-}CF_3C_6H_3)_2Si$	326.2	45,4	—	—	83,175
$C_{16}H_{13}SiClF_6$	$CH_3(CH_2Cl)(CF_3C_6H_4)_2Si$	130.8—131.8(1.5)	—	1.3434[25]	1.4925[25]	171
$C_{16}H_{23}SiF_3$	$n\text{-}C_{16}H_{33}SiF_3$	171(45)	—	0.9221	—	98,99
$C_{16}H_5SiF_{21}O_6$	$C_6H_5Si(OCOC_3F_7)_3$	245	—	1.617	1.3495	236
$C_{18}H_{11}SiF_{21}O_6$	$C_6H_{11}Si(OCOC_3H_7)_3$	243	—	1.566	1.3370	236
$C_{18}H_{15}SiF$	$(C_6H_5)_3SiF$	200—210(10)	64	—	—	38,100,120,130,132,135,146
$C_{18}H_{16}SiF_6O_2$	$(m\text{-}CF_3C_6H_4)_2Si(OC_2H_5)_2$	104—115(1)	20	—	—	66
$C_{18}H_{33}SiF$	$(C_6H_{11})_3SiF$	160—170(5)	45—46	—	—	100,125,133
$C_{20}H_{14}SiF_2$	$(\alpha\text{-}C_{10}H_7)_2SiF_2$	210—213(3)	79—81	—	—	126
$C_{20}H_{16}SiF_{28}$	$(CF_3CF_2CF_2CH_2CH_2)_4Si$	71—72(25)	—	—	—	183
$C_{21}H_{12}SiClF_9$	$(m\text{-}CF_3C_6H_4)_3SiCl$	174.2(0,7)	—	—	1.5018[25]	166,167
$C_{21}H_{12}SiF_{10}$	$(m\text{-}CF_3C_6H_4)_3SiF$	168—174(1—2)	—	1.4008[25]	1.4858[25]	161
$C_{21}H_{13}SiF_9$	$(m\text{-}CF_3C_6H_4)_3SiH$	322—325	—	1.3500	1.4948	178
$C_{21}H_{13}SiF_9$	$(p\text{-}CF_3C_6H_4)_3SiH$	—	82—83	—	—	162
$C_{21}H_{21}SiF$	$(o\text{-}CH_3C_6H_4)_3SiF$	—	86,5	—	—	100
$C_{21}H_{21}SiF$	$(p\text{-}CH_3C_6H_4)_3SiF$	324—327	108—109	—	—	132,146
$C_{21}H_{21}SiF$	$(C_6H_5CH_2)_3SiF$	235.5(7.5)	79	—	—	121,136
$C_{22}H_{15}SiF_9$	$CH_3(p\text{-}CF_3C_6H_4)_3Si$	—	106—107,5	—	—	162
$C_{24}H_9SiClF_{18}$	$[2,5\text{-}(CF_3)_2C_6H_3]_3SiCl$	155—160(3)	—	—	1.4549[30]	166,167
$C_{24}H_9SiClF_{18}$	$[3,5\text{-}(CF_3)_2C_6H_3]_3SiCl$	186—188(20)	—	1.5523[30]	1.4445[30]	165,166,167
$C_{24}H_{51}SiF$	$(n\text{-}C_8H_{17})_3SiF$	177—180(0.5—1)	—	—	1.4455[25]	133
$C_{25}H_{19}SiF_3$	$(C_6H_5)_3(m\text{-}CF_3C_6H_4)Si$	—	101	—	—	173
$C_{26}H_{18}SiF_6$	$(C_6H_5)_2(m\text{-}CF_3C_6H_4)Si$	375—378	97—98	—	—	178
$C_{27}H_{17}SiF_9$	$C_6H_5(m\text{-}CF_3C_6H_4)_2Si$	370—374	81	—	—	178
$C_{28}H_{14}SiF_{12}$	$(m\text{-}CF_3C_6H_4)_4Si$	362	102—103	—	—	161,178
$C_{30}H_{21}SiF$	$(\alpha\text{-}C_{10}H_7)_3SiF$	290—292(3)	224	—	—	127,128
$C_{36}H_{75}SiF$	$(n\text{-}C_{12}H_{25})_3SiF$	275—295(2)	18,6	—	1.4530[25]	133
$C_{42}H_{87}SiF$	$(n\text{-}C_{14}H_{29})SiF$	310—330(3)	61—62	0.834	—	133
$C_{54}H_{111}SiF$	$(n\text{-}C_{18}H_{37})_3SiF$		64—66	—	—	133

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ADVANCES IN THE SYNTHESIS OF ALKYLPYRIDINES

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I. INTRODUCTION

By virtue of their valuable properties the pyridine bases are acquiring an increasing importance in chemical industry. Pyridine and its homologues are widely used as solvents, and in the synthesis of rubber, plastics, and drugs. Interest in the synthesis of pyridine bases has been stimulated by the discovery that α-vinylpyridine, 2-methyl-5-vinylpyridine, and other vinylpyridines may act as valuable copolymers in the manufacture of synthetic rubber and plastics[1-11]. For instance, copolymers of butadiene and 2-methyl-5-vinylpyridine, and tripolymers of butadiene, styrene, and 2-methyl-5-vinylpyridine are used as latex for the impregnation of tyre cord because they increase the strength of the resin bond with the cord by 80–100%. Nicotinic and isonicotinic acids are of special significance. The former is a constituent of vitamin PP, which prevents and cures pellagra, and fortifies the nervous system. The latter is the main starting material in the synthesis of a series of antitubercular preparations of the isoniazid type[12].

Wider application of pyridine bases in organic synthesis is limited by the fact that the starting alkylpyridines are difficult to obtain.

The preparation of alkylpyridines has not been discussed in sufficient detail, although there are several reviews on the chemistry of pyridine derivatives[13-19]. We have therefore undertaken to describe systematically all the most important methods for the synthesis of alkyl- and aryl--pyridines which had appeared up to 1959. We divided these methods into two groups: (1) synthesis of pyridine bases from compounds not containing a pyridine ring; (2) synthesis from compounds containing a pyridine ring.

Compounds of the pyridine series can also be obtained by pyrolysis. Pyrolysis of coals and shales yields tar containing small quantities of a complex mixture of alkylpyridines which are difficult to separate. Although methods for the separation of individual compounds from the mixture of bases have been studied for many years[20], the problem is still not completely solved, and the practical use of mixtures of pyrogenic pyridines is still out of the question.

II. SYNTHESIS OF PYRIDINE BASES FROM COMPOUNDS NOT CONTAINING A PYRIDINE RING

1. Synthesis Based on the Chichibabin Reaction

In 1869 Baeyer[21,22] carried out one of the first syntheses of pyridine, by passing acrolein through an aqueous solution of ammonia. He identified β-picoline in the reaction products by means of chloroplatinate. Dürkopf[23-25] carried out an analogous reaction, at almost the same time, by heating a mixture of aliphatic aldehydes and ammonium acetate in sealed tubes to 200°, and obtained a mixture of pyridine bases. He obtained the best results using paraldehyde, when he isolated 2-methyl-5-ethylpyridine from the mixture of reaction products.

Chichibabin and his collaborators carried out a good deal of work in this field. They synthesised pyridine by two methods: (1) heating aldehydes with aqueous ammonia in sealed tubes; (2) passing a mixture of aldehyde vapours and ammonia over a dehydration catalyst. Using the first method[27-30] they obtained α- and γ-methylpyridines and