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Nucleophilic fluorination of alkoxysilane with alkali metal hexafluorophosphate [1]—part 1

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Abstract

Alkali metal hexafluorophosphates were used to effect nucleophilic fluorination of a few selected alkoxysilanes both in the presence and absence of polar solvents. Near-quantitative yields of fluorinated silanes were obtained using both alkoxy-equivalent of the complex salt and fluoride equivalents of alkoxysilanes. Some of the intermediate fluorosilanes and fluorophosphorus compounds were identified and the mechanism of fluorination is proposed. © 1997 Elsevier Science S.A.

Keywords: Alkali metal hexafluorophosphates; Fluorination; Alkoxysilanes; Fluorosilanes

1. Introduction

Anhydrous hydrogen fluoride, antimony trifluoride and pentafluoride were used by Frost [1] and others [2,3] for the preparation of aromatic fluorosilanes from appropriate haloprecursors. Fluorinations of alkoxysilanes were investigated in fluorosulfonic acid at low to ambient temperatures in sulfur dioxide medium [4]. Alkoxy- and siloxysilanes, by the reactions with alkyl- and arylfluorophosphoranes give fluorosilanes in high yield [5–9]. Metal fluorides were used [10,11] for the high-yield preparation of fluorosilanes by exchange reactions of alkoxy-, halo-, hydroxy-, amino-, cyano-, thio- or siloxy-organosilanes in the presence of HCl or H_2SO_4.

Carbonyl fluorides were used as fluorinating reagent in organosilicon chemistry. Thus, alkyl- and phenylsilanols and alkylalkoxysilanes were converted to the corresponding fluorosilanes in respectable yields ($>80\%$) [12]. Sulfur tetrafluoride was used to convert siloxyadamantane derivatives to the corresponding fluoroadamantanes in near-quantitative yield [13].

Oligomeric organosiloxanes were converted to organofluorosilanes by the action of boron trifluoride-etherate under heating in respectable yield ($\approx 78\%$) [14]. The latter was also used in the fluorinations of functionalized organosilanes $R_{4-n}SiX_n$ [X = H, OR, Cl, Br] [15,16]. Graphite-intercalated SbF_5 was used to fluorinate organosilicon compounds involving Si–O and Si–Cl bonds in high yields (73–85%) [17]. Under mild conditions, phosphorus pentafluoride was found to fluorinate Si–H bond in $(SiH_3)_2O$ and in $(SiRH_2)_2O$ to obtain fluorosiloxanes [18,19]. Boron trifluoride-etherate has also been used in the fluorination of Si–H bond, e.g., in α-naphthyl ferrocenylfluorosilane (α-NpFcSiHF) [20].

Perfluorinated complex anions, e.g., BF_4^-, PF_6^-, SbF_6^-, and AsF_6^-, have been regarded as non-nucleophilic and inert or 'innocent' anions. Electrochemical experiments [21,22] from several controlled-potential oxidations, have demonstrated that tetrafluoroborate anion is not truly inert and that high yields of fluorinated products result from the participation of this anion in the 'follow up' reactions of electrode intermediates. Some of these anions were used [23,24] as their (expensive) silver salts, for halogen-exchange fluorination of chlorosilicon and chlorogermanium transition-metal complexes. In these reactions, silver-ion assisted rapid elimination of halogen is seemingly obvious in accounting for the reasonable yield of the fluorinated products. Tetrafluoroborate anion as its triphenylmethyl salt, under mild reaction conditions, has been reported [25] to fluorinate Si–H bond(s) of trialkyl- and dialkylsilanes to give high yield (95–100%) of fluorosilanes. The reagent was further used for successful fluorination of $HSiMe_2CH_2Fe(CO)_2Cp$ [Cp = π-cyclopentadienyl] [25]. Potassium tetrafluoroborate, under similar conditions, failed to fluorinate Si–H bond in trialkylsilane [25].

We have recently reported the use of alkali metal salts of perfluorinated complex anions for the conversion of halosi-

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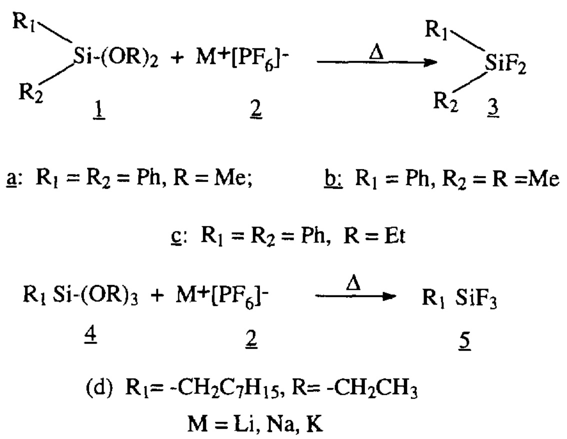

Scheme 1.

lanes [26] and haloboranes [27] to the corresponding fluorosilanes and fluoroboranes in high yield. To our knowledge, salts of perfluorinated complex anion, e.g., PF_6^- have not been used as a source of fluoride ion for nucleophilic fluorination of alkoxysilanes. We now want to report the use of alkali metal hexafluorophosphate as potential source of anhydrous fluoride ions for the effective conversion of alkoxysilanes to the corresponding fluorosilanes.

2. Discussion

When a mixture of diphenyldimethoxysilane, **1a**, (Scheme 1) and sodium hexafluorophosphate in the ratio 1:2 in tetraglyme was heated to about 200°C for 1/4 h, a brownish reaction mixture resulted. This was diluted with methylene chloride and filtered. Removal of solvent gives diphenyldifluorosilane, **3a**, as a single product by ^{29}Si NMR spectra. ^{31}P NMR spectra show two doublets at δ^{31}P -5.58 (d, J_{P-F} 979 Hz) and -6.51 (d, J_{P-F} 976 Hz) in the ratio 76:24. The major signal at δ^{31}P -5.58 is due to dimethylfluorophosphate as was confirmed by using an authentic sample [28].[2] The reaction mixture after work up (see Section 3) and vacuum distillation gave diphenyldifluorosilane in 92% yield (Table 1).

When a mixture of methylphenyldimethoxysilane, **1b**, (Scheme 1) and sodium hexafluorophosphate in the ratio 1:2 was similarly heated in tetraglyme for 3/4 h, methylphenyldifluorosilane, **3b**, was formed as the single product in 98% yield (Table 1) and was obtained by vacuum distillation after usual work up. The two examples show that use of alkoxy equivalent of sodium hexafluorophosphate smoothly converts the alkoxysilanes to the corresponding fluorosilanes in near quantitative yield. Under similar reaction conditions, a mixture of *n*-octyltriethoxysilane, **4d**, (Scheme 1) and sodium hexafluorophosphate in the ratio 1:3 when heated in tetraglyme for 1/2 h, gave a somewhat dark reaction mixture. ^{29}Si NMR spectra of the product mixture shows *n*-octyltrifluorosilane in 96% yield. The trifluorinated silane was obtained by vacuum distillation after usual work up.

At the alkoxy-equivalent ratio of the hexafluorophosphate salt, it is not only the sodium hexafluorophosphate but also the other alkali metal hexafluorophosphate salts can effect fluorinations to the quantitative yield. Thus, using lithium and potassium hexafluorophosphate salts with diphenyldimethoxy- and methylphenyldimethoxysilane, respectively, in tetraglyme, quantitative yield of the corresponding fluorosilanes were obtained (Table 1).

It was of interest to prepare diphenylmethoxyfluorosilane from diphenyldimethoxysilane. When diphenyldimethoxysilane, **1a**, was reacted with sodium hexafluorophosphate in the ratio 1:1 for 2 h in tetraglyme, diphenyldifluorosilane was obtained as the single product in 98% yield (Table 1) on vacuum distillation and as characterized by its ^{29}Si NMR spectra. It shows that more than one fluoride ion from the PF_6^- anion can be utilized for fluorination of the dialkoxysilane. At 1:1 molar ratio, diphenyldimethoxysilane with hexafluorophosphate, in the absence of solvent for 2 h reaction, also gives only diphenyldifluorosilane in 98% yield as obtained by vacuum distillation. ^{31}P NMR spectra of this distillate shows a doublet, a triplet and a singlet at δ^{31}P -5.51 (d, J_{P-F} 979 Hz), -17.62 (t, J_{P-F} 1014 Hz) and 3.62 (s) in the ratio 80:18:2. The ^{3}P NMR signals were assigned to dimethylfluorophosphate, methyldifluorophosphate and trimethylphosphate (Table 2) respectively by using authentic samples [28].

It was of interest to utilize all the available fluoride ions in the complex anion for fluorination and to identify some of the organophosphorus intermediates in the reactions of alkox-

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[2] Methyldifluoro- and dimethylfuorophophates were prepared according to literature procedure. The compounds were also prepared by the action of sodium hexafluorophosphate on the corresponding chlorides and will be reported elsewhere.

Table 1
Fluorination of alkoxysilanes using alkoxy equivalent of hexafluorophosphate salts

Alkoxysilane	MPF_6	Ratio (alkoxysilane:salt)	Reaction time (h)	Fluorosilane	Yield (%)
$Ph_2Si(OMe)_2$	$NaPF_6$	1:2	1/4	Ph_2SiF_2	92
	$NaPF_6$	1:1	2	Ph_2SiF_2	98
	$LiPF_6$	1:2	1/2	Ph_2SiF_2	98
$PhMeSi(OMe)_2$	$NaPF_6$	1:2	3/4	$PhMeSiF_2$	98
	NH_4PF_6	1:2	1/2	$PhMeSiF_2$	97
n-$C_8H_{17}Si(OEt)_3$	$NaPF_6$	1:3	1/2	n-C_8SiF_3	96
	KPF_6	1:3	3/4	n-C_8SiF_3	98

Table 2
NMR spectra of fluorophosphorus compounds

Reaction intermediate	δ^1H, ppm (J_{H-P} Hz)	δ^{31}P, ppm (J_{P-F} Hz)	δ^{19}F, ppm (J_{F-P} Hz)
$(CH_3O)_2FP{=}O$	3.85 (d, 10 Hz)	−5.58 (d, 979 Hz) [a]	−82.30 (d, J_{F-P} 893 Hz)
$(CH_3O)F_2P{=}O$	3.70 (s) [b]	−17.62 (t, J_{P-F} 1014 Hz; J_{P-H} 12 Hz)	−85.86 (d, J_{F-P} 896 Hz) [Ref. [29] −87.5]
$NaPF_6$		−143.19 (hepta, 710 Hz)	−71.32 (d, J_{F-P} 708 Hz) [Ref. [29,30] −71.0]
$(CH_3O)_3P{=}O$	3.62 (d, 11 Hz)	3.83 (sext, 9 Hz)	–
$Na_2[PO_3F]$	–	−2.89 (d, 907 Hz) [Ref. [31] −2.0]	−73.80 (d, J_{F-P} 865 Hz) [Ref. [29,30] −73.0]
$Na[PO_2F_2]$	–	−13.62 (t, J_{P-F} 951 Hz)	−82.60 (d, J_{F-P} 897 Hz) [Ref. [29] −82.0]

[a] Proton.
[b] Phosphorous decoupled.

Table 3
NMR spectra of some fluorosilicon intermediates

Reaction intermediate	^{1}H NMR, ppm (J_{H-H}; J_{H-P-F}, Hz)	^{29}Si NMR, ppm (J_{Si-F} Hz)
MePh(OMe)SiF	7.54 (d, 7.5 Hz; dd, 1.5 Hz), 7.34 (t, 8 Hz; tt, 2.0 Hz), 7.30 (t, 7.3 Hz), 3.48 (d, 7.0 Hz), 0.35 (d, 6.0 Hz)	−12.02 (d, J_{Si-F} 287 Hz)
MePh(OH)SiF	1.24 (d, 5.4 Hz), 5.16 (s)	−20.88 (d, J_{Si-F} 280 Hz)
$(MePhFSi)_2O$		−19.66 (d, J_{Si-F} 282 Hz)
$MePhSi(OH)_2$		−22.23 (s)
$MePhSi(OMe)_2$	0.35, 3.55	−13.62 (s)

ysilanes with sodium hexafluorophosphate. Methylphenyldimethoxysilane with sodium hexafluorophosphate in the ratio 3:1 (fluoride equivalent) was heated to about 200°C in tetraglyme for 1 h and the solution part of the product mixture was analyzed by ^{1}H, ^{29}Si, ^{19}F and ^{31}P NMR spectra. ^{1}H and ^{29}Si NMR spectra indicated methylphenyldifluorosilane, methylphenylmethoxyfluorosilane, methylphenylfluorosilanol and the unreacted methylphenyldimethoxysilane (Table 3). The methylphenyldifluorosilane and methylphenylmethoxyfluorosilanes were formed in the ratio 45:5, the remaining being unreacted starting material with methylphenylfluorosilanol in $<1\%$.

The fluorosilicon intermediates were separated in a GC-MS column and their mass spectra are presented in Table 4. In the ^{1}H and ^{31}P NMR spectra also were identified methyldifluorophosphate [28] and soluble part of sodium hexafluorophosphate.[3] The presence of these fluorophosphorus intermediates was further ascertained by their ^{31}P and ^{19}F NMR spectra (Table 2). In the discussed example, after 4 h reaction, ^{29}Si NMR shows about 80% conversion of the starting siloxane to the fluorinated products consisting of methylphenyldifluoro-, methylphenylmethoxyfluoro-, methylphenylfluorosilanol, methylphenylsilanediol and bis(methylphenylfluoro)disiloxane in the ratio 40:20:30:4:5. Mass spectral analysis also shows the presence of $MePhSi[OSiFMePh]_2$ (Table 4) in the product mixture. The ^{31}P NMR signals due to methyldifluorophosphate and sodium hexafluorophosphates were significantly reduced to 1 and 2% as were also found in the ^{19}F NMR spectra. The ^{31}P and ^{19}F

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[3] Sodium hexafluorophosphate is soluble in tetraglyme, with 0.03 g of $NaPF_6$ dissolved in 2.0 g of tetraglyme at room temperature [solubility ≈ 1.5%].

Table 4
Mass spectra of some fluorosilicon intermediates

Organofluorosilanes	Mass spectra (m/e)
MePh(OMe)SiF	170–173(45%), 155–157(100%), 139–141(12%), 125–127(31%), 91–93(23%), 77–79(13%), 63–65(20%), 47–49(42%)
MePh(OH)SiF	156–158(25%), 141–143(100%), 77–79(14%)
$MePhSi(OH)_2$	154(10%), 127–129(100%), 109–111(72%), 79–81(16%), 58–60(100%), 45–47(75%)
$MePhSi(OMe)_2$	182–183(12%), 167–168(100%), 137–139(45%), 121–122(10%), 105–107(20%), 75(16%), 59(25%)
$(MePhFSi)_2O$	294–296(73%), 279–281(82%), 201–203(100%), 187–189(12%), 143–145(15%), 125–127(20%), 91–93(25%)
$MePhSi[OSiFMePh]_2$	430–432(12%), 415–417(90%), 337–339(36%), 276–278(27%), 259–261(45%), 201–203(25%), 197–199(100%), 161(23%), 139–141(12%), 135–137(22%), 91–93(17%), 77–79(12%)

Table 5
NMR spectra of fluorophosphoric acid–tetraglyme complexes

Complexes	δ^{1}H, ppm	δ^{13}C, ppm	δ^{31}P, ppm	δ^{19}F
$(HO)(O)F_2P$:TG[a,b]	13.00 (s)	71.56, 70.18, 69.95, 58.64	-19.59 (t, J_{P-F} 981 Hz)	-75.82 (d, J_{F-P} 914 Hz)
$(HO)_2(O)FP$:TG[a,b]	12.06 (s)	71.58, 70.22, 70.10, 58.63	-7.97 (d, J_{P-F} 954 Hz)	-83.92(d, J_{F-P} 971 Hz)

[a] TG: $CH_3O\text{-}(OCH_2CH_2)_4\text{-}OCH_3$.

[b] Difluorophosphoric acid was mixed with tetraglyme in 1:1 ratio at room temperature. ^{1}H NMR ($CDCl_3$) of the resulting solution shows a relatively broad signal at δ^{1}H 13.04; ^{31}P NMR shows one triplet at δ^{31}P -20.34 (t, J_{P-F} 972 Hz). ^{19}F NMR shows two signals: one at δ^{19}F -76.75 (d, J_{F-P} 926 Hz), the other relatively broad at δ^{19}F -77.07 (d, J_{F-P} 931 Hz). A similar mixture of monofluorophosphoric acid in the ^{1}H NMR ($CDCl_3$) shows two signals: one at δ^{1}H 11.54, the other broad signal at δ^{1}H 11.86. ^{31}P NMR shows two signals: one at δ^{31} -7.02 (d, J_{P-F} 967 Hz), the other relatively broad at δ^{31}P -8.58 (d, J_{P-F} 968 Hz). ^{19}F NMR shows two signals: one at δ^{19}F -84.33 (d, J_{F-P} 983 Hz), the other at δ^{19}F -84.28 (d, J_{F-P} 982 Hz). The NMR data show equilibrium between protonated and unprotonated but complexed forms of fluorophosphoric acids with tetraglyme. Literature values for the aqueous solution of fluorophosphoric acids are as follows:$(HO)(O)PF_2$: δ^{31}P -22.30 [31], δ^{19}F -76.6 [31]; $(HO)_2(O)PF$: δ^{31}P -8.10 [31], δ^{19}F -74.30 [30,31].

NMR spectra further show dimethylfluorophosphate [28] in 11% of the total two phosphorus products—the other being a singlet due to trimethylphosphate (Table 2).

In presence of such solvent as tetraglyme, the above discussed reaction is slow. Thus, when fluoride equivalent of the alkoxysilane is used, continuation of the reaction for a long time, e.g., 96 h converted all the alkoxysilane to the fluorosilanes consisting of methylphenyldifluorosilane, methylphenylmethoxyfluorosilane and methylphenylhydroxyfluorosilane in the ratio 45:37:18 by ^{29}Si NMR. The expected fluorinated product viz., methylphenyldifluorosilane could not be obtained as a single product. ^{31}P NMR spectra shows trimethylphosphate and does not show any fluorophosphorus component in the organic phase. The solid residue of the above discussed reaction mixture, after 4 h reaction, was filtered off, washed with ether and dried in the air. ^{31}P NMR of the sample in deuterium oxide shows a doublet in 10% of the total phosphorus NMR signals which are all singlets. The doublet ^{31}P NMR signal is due to sodium fluorophosphate (Table 2) as was confirmed by comparing the ^{31}P and ^{19}F NMR signals of an authentic sample. The singlet ^{31}P NMR signals are due to sodium phosphates. The ^{19}F NMR spectra also show NaF at δ^{19}F -122.7 as the major fluorinated product in the residue. The solid residue of the reaction mixture, after 96 h reaction, gave similar results.

Observation and identification of a few fluorophosphorus intermediates in the reactions of sodium hexafluorophosphate with an alkoxysilane suggested an investigation of its reaction with tetraglyme alone under the same reaction condition. The reaction mixture as obtained from the reaction of sodium hexafluorophosphate with tetraglyme for 1.5 h is a black-brown thick liquid solution part of which shows two ^{31}P NMR signals at δ^{31}P -8.67 (d, J_{P-F} 956 Hz) and -19.94 (t, J_{P-F} 980 Hz). The solution part of the reaction mixture obtained in small amount was resolved to four fractions (see Section 3): fraction-II shows acidic proton in the ^{1}H NMR spectra, a triplet and a doublet in the ^{31}P and ^{19}F NMR spectra respectively. ^{13}C NMR spectra of the sample show somewhat de-shielded ^{13}C NMR signals of tetraglyme typical of ether-complexation. The species is assigned to difluorophosphoric acid, $HOPOF_2$ as a tetraglyme complex. Fraction-IV similarly shows an acidic proton and based on its ^{31}P, ^{19}F and ^{13}C NMR spectra, this fraction was assigned to monofluoro-phosphoric acid, $(HO)_2POF$ as a tetraglyme complex. Formation of fluorophosphoric acid–tetraglyme complex was further ascertained by control reactions of the acids with tetraglyme under the same sets of reaction conditions. The NMR spectra of the intermediate tetraglyme complexes as found in the reaction mixture are shown in (Table 5). It is to be mentioned here that the tetraglyme complexes are not formed in presence of alkoxysilane precursor. The solid residue from ether extraction is usually insoluble and was further extracted with acetone. Acetone soluble part (see Section 3) shows trimethylphosphate and the soluble part of sodium phosphates. The remaining white residue, largely insoluble, shows sodium phosphates and fluorophosphate in the ratio 85:15 by ^{31}P NMR. Formation of trimethylphosphate in this reaction suggests decomposition of the tetraglyme.

When the above reaction of sodium hexafluorophosphate with tetraglyme continued for a longer time, e.g., 3–4 h, the difluorophosphoric product was not found in the reaction product. A series of fluorophosphorus compounds were identified in the ^{31}P NMR spectra—all consisting of J_{P-F} doublets. The GC-MASS analysis could not identify any monofluorinated phosphorus compound, apparently suggesting their decomposition in the GC column—only trimethylphosphate was identified.

Moisture sensitivity of the reaction resulting the obvious protonated products is unavoidable. Even when the very dry solvent and the dry salt were used, formation of the similar products remain unchanged under the reaction conditions used.

It was of interest to effect reactions of alkoxysilane with sodium hexafluorophosphate in a low-boiling solvent, e.g., acetonitrile. In an attempt to utilize all the fluoride ions, methylphenyldimethoxysilane was allowed to react with sodium hexafluorophosphate in the ratio 3:1 in acetonitrile for 2 days. The solution part of the reaction mixture when analyzed by ^{29}Si NMR, shows only 17% conversion to methylphenylmethoxyfluorosilane and the ^{31}P NMR spectra shows the

Table 6
NMR spectra of nitrilium fluorophosphates

Nitrilium Salt	δ^1H, ppm	δ^{13}C, ppm	δ^{31}P, ppm	δ^{19}F
$[CH_3\text{-}CNH]^+[PO_2F_2]^-$	13.4, 2.35	179.40, 19.45	-19.71 (t, $J_{P\text{-}F}$ 973 Hz)	-83.20 (d, $J_{F\text{-}P}$ 952 Hz) [Ref. [29] -82.0]
$[CH_3\text{-}CNH]_2^+[PO_3F]^{-2}$			-7.68 (d, $J_{P\text{-}F}$ 934 Hz)	-75.32 (d, $J_{F\text{-}P}$ 920 Hz) [Ref. [29,30] -73.0]

soluble part[4] of sodium hexafluorophosphate and trimethylphosphate. Continuing the reaction for another 5 days shows 94% conversion to the fluorinated silanes consisting of methylphenyldifluoro- and methylphenylfluorosilanol in the ratio 38:56 by ^{29}Si NMR. ^{31}P NMR spectra shows only trimethylphosphate. The reaction mixture was diluted with ether and filtered. The solid residue in deuterium oxide shows sodium fluorophosphate and sodium phosphates in the ratio 8:92. ^{19}F NMR spectra shows a doublet at δ^{19}F -72.20 (d, $J_{P\text{-}F}$ 708) and two singlets at δ^{19}F -122.70(s) and -132.80(s). The first two ^{19}F NMR signals are due to $Na_2[PO_3F]$ and NaF, the later being the major product.

Reaction in acetonitrile is very slow and neither monofluoro- nor difluorinated silane could be obtained in high to near-quantitative yield. It is to be mentioned here that reactions with even 1:1 ratio is also slow. Thus, at 1:1 ratio of sodium hexafluorophosphate:methylphenyldimethoxysilane, only 16% conversion to monofluorinated compound was obtained after 20 h reaction.

To identify some of the fluorophosphorus intermediates in the reaction of methylphenyldimethoxysilane with sodium hexafluorophosphate in acetonitrile, the reaction was monitored for 3 days by intermittently analyzing the reaction mixture by ^{31}P NMR spectra. Throughout this period of reaction, ^{31}P NMR signal at ^{31}P -143.4 due to the soluble part of sodium hexafluorophosphate was observed as the major signal together with a minor singlet at ^{31}P 3.61 due to trimethylphosphate except for the reaction for 3 h period. For this later period of reaction, a triplet in the ^{31}P NMR spectra was observed at δ^{31}P -13.62 (t, $J_{P\text{-}F}$ 951 Hz) due to soluble part of sodium difluorophosphate (Table 2) as was confirmed by matching with an authentic sample.

To trap any intermediate fluorophosphorus component in the reaction of sodium hexafluorophosphate with acetonitrile, the reaction was carried out in the absence of silicon precursor. Sodium hexafluorophosphate was heated in acetonitrile for 48 h and the solution part of the product mixture obtained in small amount was analyzed by NMR. ^{1}H NMR spectra shows acidic proton at δ^1H 13.4 and ^{13}C NMR shows deshielded signal at δ^{13}C 179.40 (s). ^{31}P NMR spectra shows a doublet at δ^{31}P -7.68 (d, $J_{P\text{-}F}$ 934 Hz), a triplet at δ^{31}P -19.71 (t, $J_{P\text{-}F}$ 973 Hz) and a septuplet at δ^{31}P -143.0 (sept. $J_{P\text{-}F}$ 710 Hz) in the ratio 48:20:32. ^{19}F NMR spectra shows three doublets at δ^{19}F -83.20 (d, $J_{P\text{-}F}$ 952 Hz), -75.32(d, $J_{P\text{-}F}$ 920 Hz) and -71.32 (d, $J_{P\text{-}F}$ 708 Hz) in the ratio 11:11:70. The ^{31}P and ^{19}F NMR signals were assigned to PO_3F^-, $PO_2F_2^-$ and PF_6^- anions [29,30], respectively. The acetonitrile is thus protonated and forms intermediate nitrilium salts of fluorophosphate anions. Moisture contamination is the proton source for the intermediate fluorophosphoric acids. Detail NMR spectra of the nitrilium salts are shown in Table 6.

Formation of nitrilium monofluorophosphate was further ascertained by preparing the authentic sample from the corresponding acid and acetonitrile under reaction conditions (see Section 3). Although ^{31}P NMR shows difluoro- and monofluorophosphate anion in the main reaction mixture in the ratio 95:5, yet existence of the nitrilium monofluorophosphate is inferred due to the fact that the authentic sample could be prepared and its ^{13}C NMR is identical to that with the difluorophosphate salt. The solid residue of the discussed reaction, analyzed by ^{31}P NMR, was found to consist of sodium monofluorophosphate and sodium difluorophosphate together with unreacted sodium hexafluorophosphate. The mono- and difluorinated salts were found in the ratio 1:11, with the remainder being unreacted starting material.

As reaction in the absence of solvent is faster, it was of further interest to utilize all the fluoride ion from PF_6 complex anion for enhanced fluorination under such condition. Accordingly, diphenyldimethoxysilane was allowed to react with sodium hexafluorophosphate in the molar ratio 3:1 (fluoride equivalent) for 6 h in the absence of solvent when a clear solution was obtained. ^{29}Si NMR spectra of this reaction mixture shows diphenyldifluorosilane as the only fluorosilicon product and ^{31}P NMR shows trimethylphosphate as the only organophosphorus compound. Usual aqueous work up and removal of solvent gave diphenyldifluorosilane in 95% yield (Table 7) containing no phosphorus component. In the reaction of diphenyldiethoxysilane with sodium hexafluorophosphate, 96% yield of the corresponding difluorosilane was obtained for a 6 h reaction in the absence of any solvent.

That all the available fluoride ion in PF_6 can be utilized has further been examined in a few other organoalkoxysilanes. When methylphenyldimethoxysilane was heated with sodium hexafluorophosphate in the molar ratio of 3:1 for 3/4 h in the absence of any solvent, only 30% conversion to fluorosilanes was observed by ^{29}Si NMR. The relative percentages of the methylphenyldifluoro-, methylphenylmetho-

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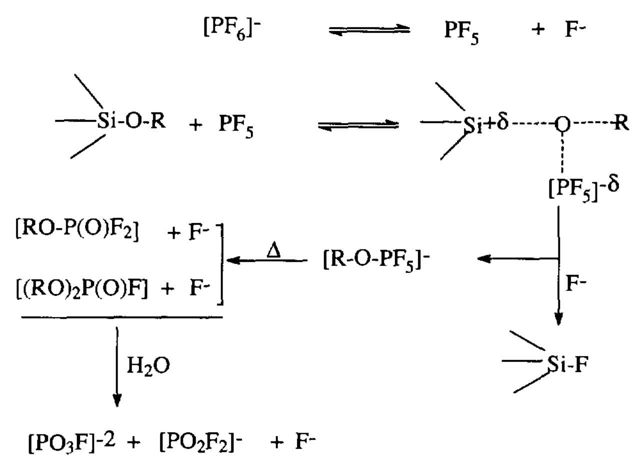
[4] Sodium hexafluorophosphate is also soluble in acetonitrile, with 0.01 g of sodium hexafluorophosphate dissolved in 0.5 g acetonitrile-d_3 on brief heating [solubility ≈ 2.0%] in an NMR tube to give ^{31}P NMR signal at δ^{31}P -143.02 (hepta, $J_{P\text{-}F}$ 710 Hz).

xyfluoro-, and methylphenylfluorosilanol are in the ratio 3:24:2. When the same reaction was repeated for 9 h, methyphenyldifluorosilane was obtained as the only product. ^{31}P NMR spectra show a singlet due to trimethylphosphate. Usual aqueous work up of this reaction mixture gave methylphenyldifluorosilane as the only product in 93% yield (Table 7). *n*-Octadecyldimethylethoxysilane was heated for 6 h, in the absence of solvent, with sodium hexafluorophosphate in the molar ratio 6:1. In the product mixture was obtained *n*-octadecyldimethylfluorosilane as the only product as evidenced by its ^{29}Si NMR spectra at $\delta^{29}Si$ 33.77 (d, J_{Si-F} 279 Hz). Usual aqueous work up and subsequent vacuum distillation gave *n*-octadecyldimethylfluorosilane in 92% yield as the only product (Table 7). This shows that using one equivalent of the complex salt of PF_6^- anion, six equivalent of ethoxysilane can completely be converted to the corresponding fluorosilane. The discussed examples show that all the available fluoride ions in the PF_6^- complex anion can be utilized in the fluorination process.

When *n*-octyltriethoxysilane was reacted with sodium hexafluorophosphate under the reaction conditions previously described in the molar ratio 4:1 for 16 h, a mixture of fluorinated silicon products were obtained as identified by their ^{29}Si NMR spectra. These components were identified as unreacted *n*-octyltriethoxysilane, *n*-octyldiethoxyfluorosilane, *n*-octylethoxydifluorosilane and *n*-octyltrifluorosilane in the ratio 20:50:26:4. From the ^{29}Si NMR spectra, the silicon chemical shifts at $\delta^{29}Si$ −43.85 (s), −47.28 (d, J_{Si-F} 277 Hz), −52.03 (t, J_{Si-F} 282 Hz) and −58.40 (q, J_{Si-F} 275 Hz) were assigned to the fluorosilanes respectively. The reaction was repeated using the alkoxysilane and hexafluorophosphate in the molar ratio 2:1 for 12 h. Usual aqueous work up and subsequent vacuum distillation gave *n*-octyltrifluorosilane in 94% yield (Table 7).

Partial fluorination in alkoxysilane has also been carried out. When methylphenyldimethoxysilane was heated with sodium hexafluorophosphate in the molar ratio 6:1 for 4 h, in the absence of any solvent, high conversion to fluorosilanes was obtained. ^{29}Si NMR shows difluoro- and monofluorinated products in relative percentages of 5 and 78% respectively. ^{31}P NMR shows trimethylphosphate as the only organophosphorus compound. Continuing the reaction for 20 h did not significantly improve the conversion—only 85% conversion to the fluorinated compounds were obtained. The residue after distillation was diluted with ether, filtered and the solid was dried in air. ^{31}P and ^{19}F NMR spectra in deuterium oxide show sodium fluorophosphate and sodium hexafluorophosphate in the ratio 5:6. ^{19}F NMR spectra show two singlets at $\delta^{19}F$ − 122.7 and − 133.4. The former was identified for NaF as the major product.



Scheme 2.

We previously reported [26] that when alkyl- or arylchlorosilane was heated with alkali metal salts of perfluorinated complex anion, e.g., $[BF_4]^-$ in the presence or absence of any multifunctional etheral solvent (e.g., tetraglyme), corresponding fluorosilane was formed in near quantitative yield. The reactions in the absence of solvent have shown evolution of boron trifluoride gas and the release of fluoride ion from the thermal decomposition of the complex $[BF_4]^-$ anion. The fluoride ion causes nucleophilic halogen-exchange fluorination in the halosilanes. In the present reactions, under similar conditions, thermally liberated Lewis acid, PF_5 undergoes complexation with alkoxysilane wherein the silicon center becomes more polarized for nucleophilic attack by the liberated fluoride ion (Scheme 2). The fluorinated ate-anion undergoes further thermal decomposition liberating alkylfluorophosphates and more fluoride ions for further fluorination.

The well-recognized perfluorinated 'non-nucleophilic' complex anion $[PF_6]^-$ is thermally labile and decomposes to give fluoride ions as has been illustrated in this paper. The

Table 7
Fluorination of alkoxysilanes using fluoride equivalent of alkoxysilanes

Alkoxysilane	Complex salt	Ratio (alkoxysilane:salt)	Reaction time (h)	Fluorosilane	% Yield
$Ph_2Si(OMe)_2$	$NaPF_6$	1:1	2	Ph_2SiF_2	92
		3:1	6	Ph_2SiF_2	95
$Ph_2Si(OEt)_2$	$NaPF_6$	3:1	3	Ph_2SiF_2	85
		3:1	6		96
$MePhSi(OMe)_2$	$NaPF_6$	3:1	5	$MePhSiF_2$	72
		3:1	9	$MePhSiF_2$	93
n-$C_{18}H_{37}Si(Me)_2Oet$	$NaPF_6$	6:1	6	n-$C_{18}H_{37}(Me)_2SiF$	92
n-$C_8H_{17}Si(OEt)_3$	$NaPF_6$	2:1	5	n-$C_8H_{37}Si(OEt)F_2$	80
		2:1	12	n-$C_8H_{17}SiF_3$	94

complex $[PF_6]^-$ anion is a potential source of anhydrous fluoride ions and all the fluoride ions in the anion can be utilized for effective fluorination of alkoxysilanes leading to high yield preparation of organofluorosilanes.

3. Experimental

3.1. General aspects

Diphenyldiethoxy-, diphenyldimethoxy-, methylphenyldimethoxy-, *n*-octyltriethoxy-, *n*-dodecyldimethylethoxysilane were available from Petrarch Chemicals as reagent grades and were used as such. Dimethylchlorophosphate (Toronto Research Chemicals, Ontario, Canada), methyldichlorophosphate (Aldrich), difluoro- and monofluorophosphoric acids (Pfaltz and Bauer) were of analytical grades and were used as received. Sodium hexafluorophosphate, tetraglyme, acetonitrile were made available from Aldrich. Tetraglyme and acetonitrile were dried over calcium hydride/sodium according to the literature procedure [32]. Sodium hexafluorophosphate was dried in a vacuum line under heating. Boiling and melting points are uncorrected. NMR spectra were recorded on a 400 and 500 MHz Varian superconducting NMR spectrometer using TMS (internal) for ^1H, ^{13}C and ^{29}Si, 85% phosphoric acid (external) for ^{31}P and $CFCl_3$ (internal) for ^{19}F NMR spectra.

GC-MS spectra was analyzed on a HP-5972 instrument. The sample was injected in a split mode onto the analytical column, 30 meter DB-5MS (0.2 mm i.d., 1.0 μm film) heated from 50° to 310°C (5 min hold) at 10°C/min. The separated components were subjected to electron bombardment at 70 eV. Full scan unit resolution mass spectra from 29 to 600 m/e were recorded.

Various reactions and general procedure for the preparation of organofluorosilanes from the corresponding alkoxysilanes and sodium hexafluorophosphate are as follows.

3.1.1. Diphenyldifluorosilane

To a solution of 2 g (8.2 mmole) diphenyldimethoxysilane in 2 g tetraglyme was added 2.9 g (17.2 mmole) sodium hexafluorophosphate and the heterogenous mixture, under argon, was heated to about 200°C for 1/4 h. The brownish reaction mixture was cooled to room temperature, diluted with methylene chloride, quenched in water, organic layer was separated and dried over anhydrous magnesium sulfate. Organic layer was concentrated in a rotavapor and the product was distilled under reduced pressure (b.p. 60–68°C/0.4 Torr) to obtain diphenyldifluorosilane, 1.6 g (92%) (Table 1). The reaction was repeated in the absence of tetraglyme using 6 g (24.5 mmole) diphenyldimethoxysilane and 1.37 g (8.27 mmole) sodium hexafluorophosphate for 6 h and worked up as described in Section 3.1. Distillation under reduced pressure gave diphenyldifluorosilane, 5.1 g (95%) (Table 7).

Ph_2SiF_2: ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (m), 7.32 (t), 7.16 (t); ^{29}Si NMR (400 MHz, $CDCl_3$) δ −28.65 (t, J_{Si-F} 292 Hz), [Ref. [26] δ −28.50 (t, J_{Si-F} 290 Hz)].

3.1.2. Methylphenyldifluorosilane

To a solution of 2 g (10.9 mmole) methylphenyldimethoxysilane in 2 g tetraglyme was added 3.8 g (22.9 mmole) sodium hexafluorophosphate and the heterogenous mixture was heated, under argon, to about 200°C for 3/4 h. The reaction mixture, on cooling down to room temperature, was worked up as described in Section 3.1. Product was distilled in vacuo (b.p. 112–118/760 Torr) to obtain 1.7 g (98%) (Table 1) methylphenyldifluorosilane. The reaction was repeated using 6 g (65.4 mmole) methylphenyldimethoxysilane and 3.8 g (22.9 mmole) sodium hexafluorophosphate in the absence of tetraglyme and worked up as usual. Methylphenyldifluorosilane was obtained in 72% and 93% yield for 5 h and 9 h reactions, respectively (Table 7). $MePhSiF_2$: ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, 8.1; dd, 1.5 Hz), 7.42 (t, 7.5; tt, 2.2 Hz), 7.32 (t, 7.5 Hz), 0.49 (t, 7.5 Hz); ^{29}Si NMR (400 MHz, $CDCl_3$) δ −10.95 (t, J_{Si-F} 291 Hz) [Ref. [26] δ −10.94 (t, J_{Si-F} 289 Hz)].

3.1.3. n-Octadecyldimethylfluorosilane

To 5 g (14.0 mmole) *n*-octadecyldimethylmethoxysilane was added 0.43 g (2.5 mmole) sodium hexafluorophosphate and the heterogenous mixture, under argon, was heated to about 200°C for 6 h. On cooling down to room temperature the reaction mixture was worked up as described in Section 3.1. Organic solvent was removed and product was distilled in in vacuo to obtain 4.2 g, (92%) (Table 7) of *n*-octadecyldimethyl-fluorosilane.

n-$C_{18}H_{37}(Me)_2SiF$: ^{29}Si NMR (400 MHz, $CDCl_3$) δ 33.77 (d, J_{Si-F} 279 Hz).

3.1.4. n-Octyltrifluorosilane

A heterogenous mixture of 3.0 g (10.8 mmole) *n*-Octyltriethoxysilane and 0.9 g (5.4 mmole) sodium hexafluorophosphate was heated to about 200°C as described in Section 3.1 for 5 h. Usual work up and subsequent vacuum distillation gave *n*-octyltrifluorosilane 1.72 g (80%) (Table 7). The reaction was repeated for 12 h to obtain *n*-octyltrifluorosilane in 94% yield (Table 7). ^{29}Si NMR (400 MHz, $CDCl_3$) −57.42 (q, J_{Si-F} 285 Hz).

3.1.5. Methylphenylmethoxyfluorosilane

To 5 g (27.3 mmol) methylphenyldimethoxysilane was added 0.76 g (4.2 mmole) sodium hexafluorophosphate and the mixture, under argon, was heated to about 200°C for 4 h. The reaction mixture was diluted with dry ether, filtered and concentrated in vacuo. Fractional distillation in vacuo gave methylphenylmethoxyfluorosilane as the first fraction (b.p. 150–155°C/760 Torr) in 60% yield. In the second fraction were co-distilled trimethylphosphate and methylphenyldimethoxysilane.

$CH_3Ph(OCH_3)SiF$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 7.5 Hz; dd, 1.5 Hz), 7.34 (t, 8 Hz; tt, 2.0 Hz), 7.30 (t, 7.0 Hz), 3.48 (d, 7.0 Hz), 0.35 (d, 6.0 Hz); ^{29}Si NMR (400 MHz, $CDCl_3$) δ −12.02 (d, J_{Si-F} 287 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ 133.35, 130.59, 127.99, 50.43, −5.23.

3.1.6. Sodium fluorophosphates

To a solution of 0.5 g difluorophosphoric acid in 2 g deionized water was added equimolar amount (0.2 g) of NaOH [as 30% aqueous solution] with occasional vortex mixing to obtain the neutral point of pH. ^{31}P NMR analysis shows a triplet at δ^{31}P −13.34 (t, J_{P-F} 1008 Hz) for sodium difluorophosphate. To 0.5 g monofluorophosphoric acid (70%) was added 2.0 g deionized water and mixed. To this solution was dropwise added two equivalents (0.28 g) of NaOH [as 30% aqueous solution; 0.95 g] with occasional vortex mixing to obtain the neutral point of pH. ^{31}P NMR shows a doublet at δ^{31}P −2.25 (d, J_{P-F} 911 Hz) for disodium fluorophosphate. Similarly, 0.5 g monofluorophosphoric acid (70%) was added to 2.0 g deionized water and mixed. To this solution was dropwise added one equivalent (0.14 g) of NaOH [as 30% aqueous solution; 0.48 g] with occasional vortex mixing to obtain an acidic solution. ^{31}P NMR shows a doublet at δ^{31}P 1.84 (d, J_{P-F} 871 Hz) for monosodium fluorophosphate. In all cases sodium phosphates were obtained as by-product.

3.1.7. Reaction of sodium hexafluorophosphate with tetraglyme

A heterogenous mixture of 4.0 g sodium hexafluorophosphate with 10 ml dry tetraglyme, under argon, was heated to about 200°C for 1.5 h. The black-brown reaction mixture was cooled and diluted with ether, filtered. Removal of solvent gave a black-brown liquid which was fractionated to four components. Fraction-I and -III were discarded. Fraction-II has b.p. 77–85°C/0.3 Torr and fraction-IV has b.p. 102–108°C/0.3 Torr. The fractions were analyzed by NMR. The combined fractions gave 1.24 g which is equivalent to about 10% yield based on sodium hexafluorophosphate used. The brown-black solid residue ($\approx$ 1.6 g) was washed with ether, further extracted with acetone and filtered. Removal of acetone in vacuo gave a brown-black semisolid (0.32 g) from which acetone-soluble part was analyzed by ^{1}H and ^{31}P NMR spectra. From the remaining white solid (0.80 g), the water-soluble part has been similarly analyzed.

3.1.8. Fluorophosphoric acid–tetraglyme complex

A mixture of 5 g dry tetraglyme and 2 g monofluorophosphoric acid was heated to about 200°C for 1/4 h to obtain a brown-black solution. The solution was cooled, diluted with ether and filtered off the sludge. The filtrate was condensed in a rotavapor and distilled in vacuo to obtain 0.1 g of the complex. $(HO)_2(O)PF$:TG: ^{31}P NMR [400 MHz, $(CDCl_3)$] δ −7.94 (d, J_{P-F} 956 Hz); ^{19}F NMR [400 MHz, $(CDCl_3)$] δ −83.12 (d, J_{F-P} 966 Hz).

3.1.9. Reaction of sodium hexafluorophosphate with acetonitrile

A mixture of 2 g sodium hexafluorophosphate with 5 ml dry acetonitrile, under argon, was heated to vigorous reflux for 48 h. The reaction mixture was cooled to room temperature, diluted with ether, filtered. Removal of solvent gave a semisolid (0.20 g) which is equivalent to about 12% yield based on sodium hexafluorophosphate used. The product was characterized by NMR as the nitrilium fluorophosphates. The white solid residue was dissolved in deuterium oxide, filtered and when characterized by ^{31}P NMR was found to consist of sodium fluorophosphates and unreacted sodium hexafluorophosphate.

3.1.10. Nitrilium fluorophosphates

A mixture of 2 g monofluorophosphoric acid in 5 g dry acetonitrile was heated to vigorous reflux for 24 h. The reaction mixture was cooled to room temperature, dry ether was added, filtered and solvent was removed in a rotavapor. Further removal of solvent in a vacuum line gave off-white semisolid which was characterized as the bis(nitrilium) fluorophosphate; 0.4 g, $\approx$25% yield.

$[CH_3\text{-}CNH]_2^+[PO_3F]^{-2}$: ^{1}H NMR [400 MHz, $(CD_3)_2CO$] δ 11.10, 2.38; ^{13}C NMR [400 MHz, $(CD_3)_2CO$] δ 179.42, 19.29; ^{31}P NMR [400 MHz, $(CD_3)_2$] δ −7.84 (d, J_{P-F} 920 Hz); ^{19}F NMR [400 MHz, $(CD_3)_2CO$] δ −74.21 (d, J_{F-P} 928 Hz).

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