PERKIN 1 COMMUNICATION

Fluorination of organodichlorophosphorus compounds with sodium hexafluorosilicate, Part 1[1a]

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Sodium hexafluorosilicate was used as a source of fluoride ion for nucleophilic fluorination of some selected organodichlorophosphorus compounds in the presence and absence of a multifunctional ethereal solvent, giving fluoro derivatives in low to moderate yields.

Halogen-exchange fluorination with metal fluorides is widely used for fluorination of various types of organic compounds including organosilicon and organophosphorus compounds.[1b] The exchange is commonly carried out using sodium fluoride in an aprotic polar solvent.[2a] Chlorine–fluorine exchange on such chlorophosphines as phenyldichlorophosphine and bis[diethylamino]chlorophosphines with sodium fluoride in tetramethylene sulfone (tetrahydrothiophene 1,1-dioxide) led to the corresponding fluorides in 74% and 35% respectively.[2a,b]

In the fluorination with sodium fluoride, crown-ether solvation affords advantages. Exclusive solvation of sodium ion by the chelating crown ether enhances anion activation. The unsolvated fluoride ion (‘naked fluoride’) is strongly nucleophilic. The procedure allowed the preparation of 2,5-dimethylphenyldifluorophosphine in 87% and 2-methoxyphenyl- and 2-(*N*,*N*-dimethylamino)phenyl-difluorophosphines in 76% and 82% yield respectively.[3a,b]

Reaction of chlorophosphines with arsenic or antimony trifluoride provides a simple route to fluorophosphoranes *via* an oxidation–reduction mechanism. Thus, phenyltetrafluoro- and diphenyltrifluoro-phosphoranes were prepared from phenylchloro- and diphenylchloro-phosphines in 94% and 77% yield respectively.[4a] Both (dimethylamino)- and (diethylamino)-chlorofluorophosphines have been prepared in 6% and 3% yield respectively from the corresponding dichloride using antimony trifluoride.[4b] The procedure has been extended to prepare other substituted difluoro- and monofluoro-phosphines in poor to moderate yields.[4c,d]

Hexafluorosilicate anion as its sodium or ammonium salt has been used to effect nucleophilic fluorination of organosilicon compounds.[5] We have previously reported the use of alkali metal salts of perfluorinated complex anions as effective fluorinating agents for nucleophilic fluorination of organosilicon compounds[6–8] and organoboron compounds[9] to obtain the corresponding fluoro compounds in high yields. We now report the use of sodium hexafluorosilicate as an effective fluorinating agent for nucleophilic fluorination of some organodichlorophosphorus compounds.

Reactions of various organochlorophosphorus compounds with sodium hexafluorosilicate were carried out as a heterogenous mixture in the absence and presence of a high boiling multifunctional ethereal solvent. A mixture of phenylphosphonic dichloride and sodium hexafluorosilicate (Scheme 1) in a molar ratio 1 : 1 was heated to about 200 °C for 1.5 h in the absence of solvent and then was subjected to distillation. The distillate, collected within boiling point range 55–65 °C/0.5 Torr, was analyzed by ^{1}H, ^{31}P and ^{19}F NMR spectroscopy. The ^{31}P NMR spectrum gave a triplet (1 : 2 : 1) at δ_P 10.64 (t, $J_{P\text{–}F}$ 1103 Hz). By comparison of this and the ^{19}F NMR spectrum at δ_F −65.41 (d, $J_{F\text{–}P}$ 1104 Hz) with those of an authentic sample,[10a] the compound was assigned as phenylphosphonic difluoride. Phenylphosphonic chloride fluoride [δ_P 29.13 (J_{PF} 1137 Hz)] was formed in trace amounts (<1%). Redistillation gave phenylphosphonic difluoride in 99% purity. When the same reaction was repeated using 2 equiv. of sodium hexafluorosilicate in presence of a multifunctional ether [tetraethylene glycol dimethyl ether (tetraglyme)] for 15 min, only phenylphosphonic difluoride was formed as a single product in 61% yield. No monofluorinated product could be identified.

$$\text{R–POCl}_2 + \text{Na}_2\text{SiF}_6 \longrightarrow \text{R–POF}_2 + \text{R–POClF}$$

$$\text{R} = \text{Ph, PhO, EtO, C}_3\text{H}_7, p\text{-NO}_2\text{PhO, CBr}_3\text{CH}_2\text{O}$$

Scheme 1

In the reaction of phenyl dichlorophosphate with sodium hexafluorosilicate in 1 : 1 molar ratio for 15 min, analysis of the distillate within a boiling point range of 80–95 °C/0.5 Torr shows two products: phenyl difluorophosphate and phenyl chlorofluorophosphate in the ratio 88 : 12. Redistillation of the distillate gave phenyl difluorophosphate in 45% yield. The NMR parameters of the product is shown in the Experimental section.

Reaction of ethyl dichlorophosphate with sodium hexafluorosilicate was carried out in 1 : 2 molar ratio for a few minutes (0.1 h). The distillate within a boiling point range 85–95 °C/760 Torr gave several products as identified in the ^{31}P NMR spectra. Ethyl difluorophosphate, difluorophosphoric and monofluorophosphoric acids were formed in the ratio 90 : 7 : 3 to give a total conversion of 33% to the fluorinated products. The reaction products are very sensitive to moisture. Careful redistillation gave ethyl difluorophosphate in 18% yield. Propylphosphonic dichloride was allowed to react, under the similar conditions, with sodium hexafluorosilicate in 1 : 2 molar ratio for 1 h to give the corresponding difluoride in 71% yield and 98% purity.

In the reaction of *p*-nitrophenyl dichlorophosphate with sodium hexafluorosilicate in 1 : 1 molar ratio for 0.5 h, the corresponding difluoride, together with monofluoride, was formed in 35% yield. Redistillation gave *p*-nitrophenyl difluoride in 22% yield. In the reaction of 2,2,2-tribromoethyl dichlorophosphate in 1 : 1 molar ratio for 0.5 h, the desired difluorinated product is formed in relatively higher yield (75%). The only by-product as identified in the ^{31}P NMR spectra is the monofluorophosphoric acid formed in a trace amount.

Experimental

Phenylphosphonic dichloride, phenyl dichlorophosphate, ethyl dichlorophosphate, propylphosphonic dichloride, *p*-nitrophenyl dichlorophosphate, 2,2,2-tribromoethyl dichlorophosphate, sodium hexafluorosilicate were made available from Aldrich as reagent grade chemicals. Tetraglyme, prior to use, was dried over sodium. ^{1}H, ^{31}P and ^{19}F NMR spectra were recorded on a Varian 400 MHz superconducting NMR spectrometer. TMS (internal) for ^1H, 85% phosphoric acid (external) for ^{31}P and $CFCl_3$ (external) for ^{19}F NMR spectra were used as references.

General procedure of fluorination of organodichlorophosphorus compounds

To 2 g (10.3 mmol) phenylphosphonic dichloride was added 2.1 g (11.2 mmol) sodium hexafluorosilicate and the mixture was heated to about 200 °C for 1.5 h. The distillate collected within bp 55–65 °C/0.5 Torr consisted of phenylphosphonic difluoride in 98% purity. Redistillation gave the product in 44% yield [bp 55–60 °C/0.5 Torr (lit.,[10a,b] 78 °C/15 mmHg, 69 °C/10 mmHg)]. Reaction in the presence of tetraglyme was similarly carried out for 15 min to obtain the product in 61% yield. The product was identified by comparison of its NMR spectra with those of an authentic sample.[10a] Reactions of other organodichlorophosphorus compounds were similarly carried out and analyzed. The NMR spectra of various organofluorophosphorus compounds are as follows.†

$PhPOF_2$: δ_H(400 MHz, $CDCl_3$) 7.76 (2H, ddd, J 15, 7.0, 1.4), 7.63 (1H, dt, J 8.0, 1.2), 7.47 (2H, dq, J 6.5, 1.2); δ_P(400 MHz, $CDCl_3$) 10.64 (t, $J_{P–F}$ 1103) [lit.,[11] 10.82 ($J_{P–F}$ 1103)]; δ_F(400 MHz, $CDCl_3$) −65.41 (d, $J_{P–F}$ 1104) [lit.,[2a] −65.40 ($J_{P–F}$ 1107)].

$PhOPOF_2$: δ_H(400 MHz, $CDCl_3$) 7.34 (t, J 8), 7.22 (t, J 6.2), 7.16 (d, J 7.8); δ_P(400 MHz, $CDCl_3$) −28.3 (t, $J_{P–F}$ 1032) [lit.,[12] −27.1 ($J_{P–F}$ 1030)]; δ_F(400 MHz, $CDCl_3$) −83.70 (d, $J_{F–P}$ 1032) [lit.,[10a] −84.1 ($J_{F–P}$ 102)].

$EtOPOF_2$: δ_H(400 MHz, $CDCl_3$) 1.11 (t, J 5.3), 4.38 (q, J 7.2); δ_P(400 MHz, $CDCl_3$) −21.35 (t, $J_{P–F}$ 1014) [lit.,[10a] −20.2 ($J_{P–F}$ 1014)]; δ_F(400 MHz, $CDCl_3$) −84.6 ($J_{F–P}$ 1034) [lit.,[10a] −85.0 ($J_{F–P}$ 1008)].

n-$C_3H_7POF_2$: δ_H(400 MHz, $CDCl_3$) 2.13 (m, J 7.3), 1.77 (m, J 6.3), 1.09 (t, J 5.3); δ_P(400 MHz, $CDCl_3$) 23.68 (tm, including J 1135, 18.4); δ_F(400 MHz, $CDCl_3$) −65.15 (d, $J_{F–P}$ 1134).

p-$NO_2PhOPOF_2$: δ_H(400 MHz, $CDCl_3$) 8.12 (d, J 9.03), 6.94 (d, J 9.03); δ_P(400 MHz, $CDCl_3$) −20.04 (t, $J_{P–F}$ 1012).

$CBr_3CH_2OPOF_2$: δ_P(400 MHz, $CDCl_3$) −19.63 (t, $J_{P–F}$ 978).

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Paper 8/00243F
Received 8*th January* 1998
Accepted 8*th January* 1998

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† J Values are given in Hz.