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Simple preparation of difluorophosphoranes using anhydrous zinc and tetramethylammonium fluorides

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Abstract

Bromophosphonium bromides, $R_3PBr^+Br^-$ ($R={}^nBu$, NMe_2, NEt_2) are easily fluorinated using zinc difluoride in pyridine or tetramethylammonium fluoride in methylene chloride to give the corresponding difluorophosphoranes R_3PF_2 in high yield. A simple procedure for preparing pure tetramethylammonium fluoride is described.

Keywords: Preparation; Difluorophosphoranes; Anhydrous zinc; Tetramethylammonium fluorides; NMR spectroscopy

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1. Introduction

To the best of our knowledge, convenient methods for the preparation of tris(dialkylamino)difluorophosphoranes have not been developed. Literature procedures are based on the oxidation of phosphorus(III) amides using SF_4, C_6F_5X and hexafluoropropene oxide. These have disadvantages in that isolation of the pure products is difficult [1–3]. Metathesis reactions with bromophosphonium bromides, $[R_3PBr]^+Br^-$, using NaF in boiling CH_3CN usually take more than 1 d and work only in the case of R = alkyl [4]. Use of $[(Et_2N)_3PBr]^+Br^-$, for example, led to the formation of $[(Et_2N)_3PF]^+Br^-$; however, when AgF was used, the difluorophosphorane $(Et_2N)_3PF_2$ was obtained [5]. More recently, it has been shown that anhydrous ZnF_2 in pyridine is a very useful non-oxidizing fluorinating agent [6]. We have investigated the ZnF_2/pyridine system and the fluorinating potential of anhydrous pure $Me_4N^+F^-$.

2. Results

Fluorination of tri-n-butylbromophosphonium bromide, $[{}^nBu_3PBr^+]Br^-$ (**1a**), using ZnF_2 in pyridine was complete within 2 h at 20 °C. In contrast, tris(diethylamido)bromophosphonium bromide (**1c**) could be fluorinated in a stepwise manner. Thus, after 15 min $[(Et_2N)_3PF]^+Br^-$ (**2c**) [5] was formed exclusively, whilst after 2 d pure $(Et_2N)_3PF_2$ (**3c**) was obtained. In the case of $[(Me_2N)_3PBr]^+Br^-$ (**1b**), only $[(Me_2N)_3PF]^+Br^-$ (**2b**) was found at 20 °C (**2b**), while at 60–80 °C $(Me_2N)_3PF_2$ (**3b**) could be isolated in 37% yield.

Anhydrous $[Me_4N]^+F^-$ has only been prepared recently [7]. In order to exclude HF_2^- and halide impurities, $[Me_4N]^+BF_4^-$ has been treated with KF in methanol, the precipitated KBF_4 removed by filtration and the solvent pumped off [8]. Methanol was removed from the remaining $[Me_4N]^+F^-\cdot n$MeOH (see Experimental details). Tetramethylammonium fluoride and the bromophosphonium bromides $[R_3PBr]^+Br^-$ (**1a**: $R=n$Bu; **1b**: $R=Me_2N$; **1c**: $R=Et_2N$) reacted exothermally in a 1:1 ratio to give $[R_3PF]^+Br^-$ (**2a**: $R={}^nBu$; **2b**: $R=Me_2N$; **2c**: $R=Et_2N$) [5]. When a 2:1 ratio was employed, R_3PF_2 (**3a**: $R={}^nBu$; **3b**: $R=Me_2N$; **3c**: $R=Et_2N$) was found within 15 min at 5 °C. Silver(I) fluoride showed a similar reactivity, but disadvantages were observed in separating the products.

$$\begin{array}{ccccc} & \text{Methods} & & \text{Methods} & \\ [R_3PBr]^+Br^- & \xrightarrow{\text{A, B}} & [R_3PF]^+Br^- & \xrightarrow{\text{A, B}} & R_3PF_2 \\ \textbf{(1a–c)} & & \textbf{(2a–c)} & & \textbf{(3a–c)} \end{array}$$

	R
a	^nBu
b	NMe_2
c	NEt_2

Method A: ZnF_2/py. Method B: $Me_4N^+F^-/CH_2Cl_2$.

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3. Experimental details

The appropriate precautions in handling moisture-sensitive compounds were observed throughout this work. NMR spectra were obtained on a Bruker AC-80 instrument operating at 80.13 MHz (^1H, internal standard TMS), 75.39 MHz (^{19}F, internal standard CCl_3F) and 32.44 MHz (^{31}P, external standard 85% H_3PO_4). The compounds $[R_3PBr]^+Br^-$ ($R = {}^nBu$, Me_2N, Et_2N) were synthesized using literature procedures [4]. Commercially available ZnF_2 was used after drying [6]. Methanol was distilled firstly from MeONa and then from CaH_2.

3.1. Fluorination procedures

Method A (for experimental details see Table 1)

A mixture of ZnF_2 [6] (1.0 g, 10 mmol) and the corresponding phosphonium bromides **1a–c** (3.3 mmol) in pyridine was stirred, the mixture filtered, the resulting precipitate washed with ether or petroleum ether (5 ml), and the solvents distilled off at 20 °C/10 mmHg (at 30 mmHg in the case of $(Me_2N)_3PF_2$).

Method B

To an ice-cooled solution of compounds **1a–c** (10 mmol) in CH_2Cl_2 (12 ml), $Me_4N^+F^-$ (2.32 g, 25 mmol) was added in portions over 5 min. After stirring for 15 min, the reaction mixture was diluted with diethyl ether or petroleum ether (10 ml). After filtration, the precipitate was washed with ether (5 ml). The solvents were distilled off in vacuo (15 mmHg). Under the same conditions, if $[Me_4N]^+F^-$ (0.93 g, 10 mmol) was added in a 1:1 ratio, the fluorophosphonium bromides **2a–c** [5] were formed in 100% yield.

3.2. *Anhydrous tetramethylammonium fluoride*

Tetramethylammonium tetrafluoroborate [1], $Me_4N^+BF_4^-$ (16.1 g, 0.1 mmol), which had been dried in vacuo at 90–100 °C, was added to a stirred solution consisting of 7.0 g (0.12 mmol) of potassium fluoride, which had been dried in vacuo at 230–250 °C, in 70 ml of methanol. After 1 h the precipitate of KBF_4 formed was filtered off and washed with 15 ml of methanol. The combined solutions were distilled in vacuo (0.01 mmHg) until one-third of the original volume remained. Diethyl ether (30 ml) was added and the mixture again stirred for 0.5 h (if the lower layer still contains BF_4^- ions (^{19}F NMR spectroscopy), more ether (10 ml) should be added, the solution stirred for 0.5 h and checked again for a BF_4^- impurity). The precipitate was filtered off, the solvent removed in vacuo (0.01 mmHg) at 20 °C to yield a white low-melting solid, $Me_4N^+F^- \cdot nMeOH$ [7], which was heated slowly to 80–90 °C over 6 h to give $Me_4N^+F^- \cdot MeOH$ [7]. After pulverizing the solid, the temperature was raised to 100 °C for 1 h and to 130–140 °C for 5 h with pumping in vacuo (0.01 mmHg) [2] (the methanol content being checked by ^1H NMR spectroscopy). ^1H NMR δ: 3.1 (CD_3CN) ppm. ^{19}F NMR δ: -73.2 (CH_3CN); -119 (H_2O) ppm. The yield of $Me_4N^+F^-$ free from MeOH, HF_2^-, BF_4^- or SiF_6^{2-} as impurities was 8.8 g (95%) (H_2O impurity 0.058–0.060 wt.%).

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[1] Tetrafluoroborates have also been used for phosphazenium fluoride synthesis [8].

[2] Above 150 °C, $Me_4N^+F^-$ decomposed slowly to give MeF and Me_3N.

Table 1
Experimental details regarding the fluorination of **1a–c**

Compound R_3PF_2	Method: reactant g (mmol)	Reaction conditions	Yield [g (%)]	Boiling point (°C/mmHg)
3a: $R = {}^nBu$	A: **1a** 1.19 (3.3)	2h/20 °C	0.58 (74) [a]	73–75/0.02 [b]
	B: **1a** 3.62 (10)	15 min/ 5 °C	0.59 (75) [a]	
3b: $R = Me_2N$	A: **1b** 1.07 (3.3)	10 h/60 °C [c]	0.25 (37) [d]	34–35/2 [e]
	B: **1b** 3.23 (10)	15 min/5 °C [c]	0.54 (81) [d]	
3c: $R = Et_2N$	A: **1c** 1.34 (3.3)	48 h/20 °C [f]	0.50 (53) [g]	74–75/0.02 [h]
	B: **1c** 4.07 (10)	15 min/5 °C	0.68 (72) [g]	

[a] ^{31}P NMR δ: -14.7 ($^1J_{PF} = 581$ Hz) ppm. ^{19}F NMR δ: -38.6 ppm [4].

[b] B.p. 75 °C/5 mmHg [4].

[c] $[(Me_2N)_3PF]^+Br^-$ (**2b**) was found exclusively at 20 °C.

[d] ^{31}P NMR δ: -65.0 ($^1J_{PF} = 697$ Hz) ppm. ^{19}F NMR δ: -57.0 ppm [5].

[e] B.p. 35 °C/3 mmHg [1].

[f] After 15 min $[(Et_2N)_3PF]^+Br^-$ (**2c**) was obtained exclusively.

[g] ^{31}P NMR δ: -60.0 ($^1J_{PF} = 700$ Hz) ppm. ^{19}F NMR δ: -65.0 ppm [5].

[h] B.p. 70 °C/5 mmHg, m.p. 21–22 °C [5].

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