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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

#### 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<sub>4</sub>, C<sub>6</sub>F<sub>5</sub>X and hexafluoropropene oxide. These have disadvantages in that isolation of the pure products is difficult [1-3]. Metathesis reactions with bromophosphonium bromides, [R<sub>3</sub>PBr] + Br -, using NaF in boiling CH<sub>3</sub>CN usually take more than 1 d and work only in the case of R=alkyl [4]. Use [(Et<sub>2</sub>N)<sub>3</sub>PBr]+Br<sup>-</sup>, for example, led to the formation of [(Et<sub>2</sub>N)<sub>3</sub>PF]+Br<sup>-</sup>; however, when AgF was used, the difluorophosphorane (Et<sub>2</sub>N)<sub>3</sub>PF<sub>2</sub> was obtained [5]. More recently, it has been shown that anhydrous ZnF<sub>2</sub> in pyridine is a very useful non-oxidizing fluorinating agent [6]. We have investigated the ZnF<sub>2</sub>/pyridine system and the fluorinating potential of anhydrous pure  $Me_{\lambda}N^{+}F^{-}$ .

## 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<sub>4</sub> removed by filtration and the solvent pumped off [8]. Methanol was removed from the remaining  $[Me_4N]^+F^- \cdot nMeOH$  (see Experimental details). Tetramethylammonium fluoride and the bromophosphonium bromides  $[R_3PBr]^+Br^-$  (1a: R=nBu; 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.

$$[R_{3}PBr]^{+}Br^{-} \xrightarrow{A, B} [R_{3}PF]^{+}Br^{-} \xrightarrow{A, B} R_{3}PF_{2}$$

$$(1a-c) \qquad (2a-c) \qquad (3a-c)$$

$$R$$

$$a \qquad \qquad ^{n}Bu$$

$$b \qquad \qquad NMe_{2}$$

$$c \qquad \qquad NEt_{2}$$

Method A: ZnF<sub>2</sub>/py. Method B: Me<sub>4</sub>N<sup>+</sup>F<sup>-</sup>/CH<sub>2</sub>Cl<sub>2</sub>.

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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 (<sup>1</sup>H, internal standard TMS), 75.39 MHz (<sup>19</sup>F, internal standard CCl<sub>3</sub>F) and 32.44 MHz (<sup>31</sup>P, external standard 85% H<sub>3</sub>PO<sub>4</sub>). The compounds [R<sub>3</sub>PBr] + Br - (R = <sup>n</sup>Bu, Me<sub>2</sub>N, Et<sub>2</sub>N) were synthesized using literature procedures [4]. Commercially available ZnF<sub>2</sub> was used after drying [6]. Methanol was distilled firstly from MeONa and then from CaH<sub>2</sub>.

## 3.1. Fluorination procedures

Method A (for experimental details see Table 1)

A mixture of ZnF<sub>2</sub> [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<sub>2</sub>N)<sub>3</sub>PF<sub>2</sub>).

#### 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<sub>4</sub>N<sup>+</sup>-BF<sub>4</sub><sup>-</sup> (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<sub>4</sub> 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<sub>4</sub> ions (19F NMR spectroscopy), more ether (10 ml) should be added, the solution stirred for 0.5 h and checked again for a BF<sub>4</sub> 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<sub>4</sub>N<sup>+</sup>F<sup>-</sup>·nMeOH [7], which was heated slowly to 80-90 °C over 6 h to give Me<sub>4</sub>N<sup>+</sup>F<sup>-</sup>·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)<sup>2</sup> (the methanol content being checked by <sup>1</sup>H NMR spectroscopy). <sup>1</sup>H NMR δ: 3.1 (CD<sub>3</sub>CN) ppm. <sup>19</sup>F NMR  $\delta$ : -73.2 (CH<sub>3</sub>CN); -119 (H<sub>2</sub>O) ppm. The yield of Me<sub>4</sub>N<sup>+</sup>F<sup>-</sup> 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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Table 1
Experimental details regarding the fluorination of 1a-c

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

 $<sup>^{</sup>a~31}P~NMR~\delta:~-14.7~(^{1}J_{PF}{=}581~Hz)~ppm.~^{19}F~NMR~\delta:~-38.6~ppm~[4].$ 

<sup>&</sup>lt;sup>1</sup> Tetrafluoroborates have also been used for phosphazenium fluoride synthesis [8].

 $<sup>^2\,\</sup>mbox{Above 150}$  °C, Me<sub>4</sub>N+F- decomposed slowly to give MeF and Me<sub>3</sub>N.

<sup>&</sup>lt;sup>b</sup> B.p. 75 °C/5 mmHg [4].

<sup>° [(</sup>Me<sub>2</sub>N)<sub>3</sub>PF] +Br - (2b) was found exclusively at 20 °C.

<sup>&</sup>lt;sup>d 31</sup>P NMR  $\delta$ : -65.0 ( ${}^{1}J_{PF}$ =697 Hz) ppm.  ${}^{19}F$  NMR  $\delta$ : -57.0 ppm [5].

<sup>°</sup> B.p. 35 °C/3 mmHg [1].

f After 15 min [(Et<sub>2</sub>N)<sub>3</sub>PF]+Br- (2c) was obtained exclusively.

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

<sup>&</sup>lt;sup>h</sup> B.p. 70 °C/5 mmHg, m.p. 21–22 °C [5].

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#### References

- [1] F. Ramirez, C.P. Smith and S. Meyerson, *Tetrahedron Lett.*, (1966) 3651.
- [2] L.N. Markovskii, G.G. Furin, Yu.G. Shermolovich, O.N. Tychkina and G.G. Yakobson, Zh. Obshch. Khim., 49 (1979) 710.

- [3] L.N. Lermontov, Izv. Akad. Nauk SSSR, Ser. Khim., (1990) 2845.
- [4] R. Bartsch, O. Stelzer and R. Schmutzler, J. Fluorine Chem., 20 (1982) 85.
- [5] R. Bartsch, O. Stelzer and R. Schmutzler, Z. Naturforsch., 36b (1981) 1349.
- [6] A. Sekiya and N. Ishikawa, Bull. Chem. Soc. Jpn., 51 (1978) 1267.
- [7] K. Christe, W. Wilson, R. Wilson, R. Bau and Jin-an Feng, J. Am. Chem. Soc., 112 (1990) 7619.
- [8] B. Schwesinger, R. Zink, G. Thiele, H. Rotter, D. Honert, H. Zimbach and F. Männle, Angew. Chem., 103 (1991) 1376.