



### 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 ( $^1\text{H}$ , internal standard TMS), 75.39 MHz ( $^{19}\text{F}$ , internal standard  $\text{CCl}_3\text{F}$ ) and 32.44 MHz ( $^{31}\text{P}$ , external standard 85%  $\text{H}_3\text{PO}_4$ ). The compounds  $[\text{R}_3\text{PBr}]^+\text{Br}^-$  ( $\text{R} = ^n\text{Bu}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) were synthesized using literature procedures [4]. Commercially available  $\text{ZnF}_2$  was used after drying [6]. Methanol was distilled firstly from  $\text{MeONa}$  and then from  $\text{CaH}_2$ .

#### 3.1. Fluorination procedures

##### Method A (for experimental details see Table 1)

A mixture of  $\text{ZnF}_2$  [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  $(\text{Me}_2\text{N})_3\text{PF}_2$ ).

##### Method B

To an ice-cooled solution of compounds **1a–c** (10 mmol) in  $\text{CH}_2\text{Cl}_2$  (12 ml),  $\text{Me}_4\text{N}^+\text{F}^-$  (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  $[\text{Me}_4\text{N}]^+\text{F}^-$  (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<sup>1</sup>,  $\text{Me}_4\text{N}^+\text{BF}_4^-$  (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  $\text{KBF}_4$  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  $\text{BF}_4^-$  ions ( $^{19}\text{F}$  NMR spectroscopy), more ether (10 ml) should be added, the solution stirred for 0.5 h and checked again for a  $\text{BF}_4^-$  impurity). The precipitate was filtered off, the solvent removed in vacuo (0.01 mmHg) at 20 °C to yield a white low-melting solid,  $\text{Me}_4\text{N}^+\text{F}^- \cdot n\text{MeOH}$  [7], which was heated slowly to 80–90 °C over 6 h to give  $\text{Me}_4\text{N}^+\text{F}^- \cdot \text{MeOH}$  [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  $^1\text{H}$  NMR spectroscopy).  $^1\text{H}$  NMR  $\delta$ : 3.1 ( $\text{CD}_3\text{CN}$ ) ppm.  $^{19}\text{F}$  NMR  $\delta$ : –73.2 ( $\text{CH}_3\text{CN}$ ); –119 ( $\text{H}_2\text{O}$ ) ppm. The yield of  $\text{Me}_4\text{N}^+\text{F}^-$  free from  $\text{MeOH}$ ,  $\text{HF}_2^-$ ,  $\text{BF}_4^-$  or  $\text{SiF}_6^{2-}$  as impurities was 8.8 g (95%) ( $\text{H}_2\text{O}$  impurity 0.058–0.060 wt.%).

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<sup>1</sup> Tetrafluoroborates have also been used for phosphazanium fluoride synthesis [8].

<sup>2</sup> Above 150 °C,  $\text{Me}_4\text{N}^+\text{F}^-$  decomposed slowly to give  $\text{MeF}$  and  $\text{Me}_3\text{N}$ .

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

| Compound<br>$\text{R}_3\text{PF}_2$          | Method: reactant<br>g (mmol) | Reaction<br>conditions   | Yield<br>[g (%)]       | Boiling point<br>(°C/mmHg) |
|--|------------------------------|--------------------------|------------------------|----------------------------|
| <b>3a</b> : $\text{R} = ^n\text{Bu}$         | A: <b>1a</b> 1.19 (3.3)      | 2h/20 °C                 | 0.58 (74) <sup>a</sup> | 73–75/0.02 <sup>b</sup>    |
|  | B: <b>1a</b> 3.62 (10)       | 15 min/5 °C              | 0.59 (75) <sup>a</sup> |                            |
| <b>3b</b> : $\text{R} = \text{Me}_2\text{N}$ | A: <b>1b</b> 1.07 (3.3)      | 10 h/60 °C <sup>c</sup>  | 0.25 (37) <sup>d</sup> | 34–35/2 <sup>c</sup>       |
|  | B: <b>1b</b> 3.23 (10)       | 15 min/5 °C <sup>c</sup> | 0.54 (81) <sup>d</sup> |                            |
| <b>3c</b> : $\text{R} = \text{Et}_2\text{N}$ | A: <b>1c</b> 1.34 (3.3)      | 48 h/20 °C <sup>f</sup>  | 0.50 (53) <sup>g</sup> | 74–75/0.02 <sup>h</sup>    |
|  | B: <b>1c</b> 4.07 (10)       | 15 min/5 °C              | 0.68 (72) <sup>g</sup> |                            |

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

<sup>b</sup> B.p. 75 °C/5 mmHg [4].

<sup>c</sup>  $[(\text{Me}_2\text{N})_3\text{PF}]^+\text{Br}^-$  (**2b**) was found exclusively at 20 °C.

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

<sup>e</sup> B.p. 35 °C/3 mmHg [1].

<sup>f</sup> After 15 min  $[(\text{Et}_2\text{N})_3\text{PF}]^+\text{Br}^-$  (**2c**) was obtained exclusively.

<sup>g</sup>  $^{31}\text{P}$  NMR  $\delta$ : –60.0 ( $J_{\text{PF}} = 700$  Hz) ppm.  $^{19}\text{F}$  NMR  $\delta$ : –65.0 ppm [5].

<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. Ty-chkina 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.