

# Fluorination of organochlorophosphorus compounds with alkali metal salts of perfluorinated complex anions. Part 2\*†

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Alkali metal salts of perfluorinated complex anions were used to fluorinate a few selected organochlorophosphorus compounds in the presence and absence of a multifunctional ethereal solvent. Together with oxidative products, low to moderate yields of the desired monofluorinated products were obtained.

Fluorination of various types of organic compounds, including organosilicon and organophosphorus compounds is usually carried out by halogen metathesis with metal fluorides.<sup>1</sup> Chlorine-fluorine exchange on appropriate dichlorophosphines leads to fluorophosphines.<sup>2a</sup> This exchange is commonly carried out with sodium fluoride in aprotic polar solvents of high dielectric constant. Reaction of dichlorophenylphosphine with sodium fluoride in tetramethylenesulfone<sup>2a</sup> leads to the corresponding fluoride in 74% yield. Chlorodiphenylphosphine reacts with sodium fluoride in boiling acetonitrile to give a mixture of products consisting of fluorodiphenylphosphine and other multiple fluorophosphorus compounds.<sup>2b</sup> Diphenylphosphinic fluoride has been conveniently prepared in respectable yield (70%) by dissolving the corresponding chloride in benzene and heating the reaction mixture under reflux with dry ammonium fluoride.<sup>2b</sup> The chlorine-fluorine exchange reaction between bis(diethylamino)chlorophosphine and sodium fluoride in tetramethylenesulfone gives bis(diethylamino)fluorophosphine in poor yield (35%).<sup>2c</sup>

2-Substituted aryldichlorophosphines have been converted into the corresponding difluorophosphines using sodium fluoride in acetonitrile in the presence of a catalytic amount of a crown ether.<sup>3a</sup> Exclusive solvation of the alkali metal cation by the chelating crown ether enhances anion activation. The unsolvated fluoride ion ("naked fluoride") is strongly nucleophilic. The procedure allowed the preparation of 2-methoxyphenyl- and 2-*N,N*-dimethylaminophenyldifluorophosphines in 76% and 82% yield, respectively, from the corresponding dichlorides. Fluorination of 2,5-dimethylphenyldichlorophosphine was also accomplished in high yield (87%) using the sodium fluoride-crown ether procedure under ambient condition.<sup>3b</sup>

Fluorophosphoranes, *via* an oxidation-reduction mechanism, were prepared by the reaction of chlorophosphines with arsenic or antimony trifluoride. Thus, phenyltetrafluoro- and diphenyltrifluorophosphoranes were prepared from phenylchloro- and diphenylchlorophosphines in 94% and 77% yield, respectively.<sup>4a</sup> Both (dimethylamino)- and (diethylamino)chlorofluorophosphines have been prepared in 6% and 3% yield, respectively, from the corresponding dichloride using antimony trifluoride.<sup>4b</sup> The latter has also been used to

prepare difluorophenylphosphine in 14% yield from the corresponding chloro derivative in benzene solution.<sup>4c</sup> Substituted phosphorus fluorides such as (dimethylamino)difluorophosphine, (diethylamino)difluorophosphine and piperidylfluorophosphines were prepared by fluorinating the corresponding chlorides with antimony trifluoride or with sodium fluoride in tetramethylenesulfone in 50–70% yields.<sup>5a</sup> Some aryltetrafluorophosphoranes and difluorides of phenyl-, *p*-tolyl- and *p*-chlorophenylphosphonic acid were prepared in respectable yields by the reaction of the corresponding chlorides with antimony trifluorides.<sup>4a,5b</sup>

The ready availability of halodifluorophosphines allowed the study of fluorination reactions of alkyl/alkenyl compounds in the presence of certain organometallic reagents. The synthesis of alkyl, alkenyl and alkyl difluorophosphines by the reaction of solid organometallic reagents, for example organolithium, -mercury, and -magnesium compounds, with halodifluorophosphine between  $-78^{\circ}\text{C}$  and room temperature is possible.<sup>6</sup> Mercuric fluoride was used to effect fluorination of trialkyl and triarylphosphines. Using this reagent, a facile procedure has been reported for the preparation of difluorotriorgano phosphoranes, such as difluorotrialkyl- and -triarylphosphoranes, in respectable yields (60–70%).<sup>7</sup>

The oxidative fluorination of phosphines and halo-phosphines<sup>8</sup> has been carried out using the powerful reagent xenon difluoride. Using xenon difluoride, certain fluorinated phosphates (*e.g.*, dialkylfluorophosphates), dialkylfluorophosphazenes and diarylphosphonic fluoride compounds were obtained in moderate yields under mild conditions.<sup>9</sup>

The fluorination of certain phosphites has been effected, using picryl fluoride.<sup>10</sup> Thus, diethyl-3-pyridyl phosphite [ $\text{C}_5\text{H}_4\text{N}-\text{OP}(\text{OEt})_2$ ] reacts with picryl fluoride to give the first diethyl fluorophosphite, which subsequently reacts further with picryl fluoride, thus complicating the process. A preparative procedure for diethyl fluorophosphite has been described by the action of boron trifluoride-etherate on diethyl-3-pyridyl phosphite.<sup>10</sup>

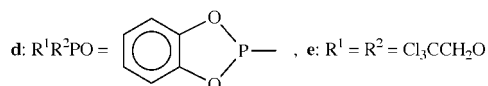
We have previously reported the use of alkali metal salts of perfluorinated complex anions as effective fluorinating agents for nucleophilic fluorination of organosilicon<sup>11–14</sup> and organoboron<sup>15</sup> compounds to obtain the corresponding fluoro compounds in high yields. Recently, we have also reported the use of sodium hexafluoroarsenate and alkali metal salts of perfluorinated complex anions for fluorination of organochlorophosphorus compounds.<sup>16,17</sup> We now wish to report the use of alkali metal salts of perfluorinated complex anions as effective fluorinating agents for the nucleophilic

\* Part of this work was presented in the fluorine Division, ACS National Meeting, New Orleans, 1996. For parts 1 and 3 see references 16 and 17

† Non-SI unit employed: 1 Torr = 133 Pa.



a:  $\text{R}^1 = \text{R}^2 = \text{Me}_2\text{N}$ , b:  $\text{R}^1 = \text{R}^2 = \text{EtO}$ , c:  $\text{R}^1 = \text{R}^2 = \text{PhO}$



M = B, P, Sb;  $n = 3$  (for B), 5 (for P and Sb)

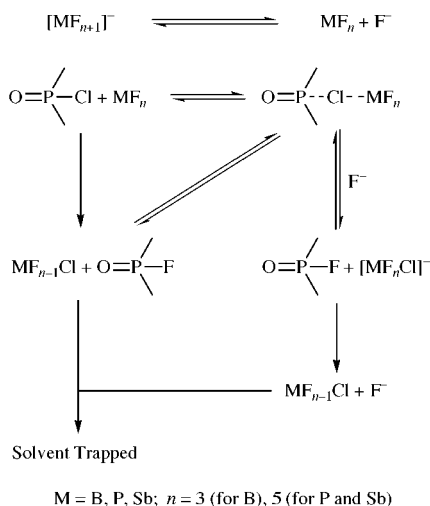
**Scheme 1**

fluorination of some selected organochlorophosphorus compounds.

## Results and discussion

Reactions of alkali metal salts of perfluorinated complex anions with various organochlorophosphorus compounds were carried out in heterogeneous phase in the absence and presence of a high boiling multifunctional ethereal solvent.

When a heterogeneous mixture of bis(dimethylamino)phosphoro chloridate and sodium tetrafluoroborate in a 1 : 1 molar ratio was heated in tetraethyleneglycol dimethyl ether (tetraglyme) to about 200 °C under argon for 15 min, bis(dimethylamino)phosphoro fluoridate **2a** (Scheme 1) was formed and distilled (Table 1). The distillate, within a boiling point range of 45–52 °C at 0.5 Torr, was analyzed by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , and  $^{19}\text{F}$  NMR spectroscopy. The  $^{31}\text{P}$  NMR spectrum shows a doublet (1 : 1) at 15.65 ppm ( $J_{\text{P-F}}$  958 Hz) and the  $^{19}\text{F}$  NMR spectrum displays a doublet at –85.21 ppm ( $J_{\text{F-P}}$  948 Hz). Further, analysis of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and comparison of the NMR chemical shift values with those of an authentic sample substantiate the formation of the said



**Scheme 2**

fluorophosphorus compound. In the reaction with sodium hexafluorophosphate, in addition to the desired product, dimethylamino phosphonic difluoride  $[(\text{Me}_2\text{N})\text{P}(\text{O})\text{F}_2]$  and tris(dimethylamino)phosphate  $[(\text{Me}_2\text{N})_3\text{P}(\text{O})]$  were formed in 15 and 2% yield, respectively. These products are believed to be formed by disproportionation of either the reactant (followed by fluorination), or the product.



In the reaction of diethylchlorophosphate, **1b**, with sodium hexafluorophosphate, diethylfluorophosphate  $[(\text{EtO})_2\text{POF}]$ , **2b** and ethyldifluorophosphate  $[(\text{EtO})\text{POF}_2]$  were formed in a 38 : 52 ratio. The yield of the desired fluoro product in this reaction is low and is attributed to the thermally labile nature of ethylchloro- and ethylfluorophosphorus products. Reaction of diphenylchlorophosphate, **1c** with sodium tetrafluoroborate gives almost exclusively the corresponding fluoro product  $[\text{Ph}_2\text{P}(\text{O})\text{F}]$ , **2c** in 25% yield (Table 1), the remainder being unreacted starting material. There is no side product in this reaction. Reaction of diphenylchlorophosphate, **1c**, with sodium hexafluorophosphate in a 3 : 1 molar ratio, in the absence of any solvent, gives the same product in 50% yield (Table 1). Increasing both the ratio of the reagent : reactant to 1 : 2 and the reaction time resulted in an increase in the yield (Table 1).

In the reaction of 1,2-phenylene phosphorochloridite, **1d**, with sodium tetrafluoroborate, the corresponding fluoro product **2d** was obtained in 99% purity, the yield of the oxidation product being about 1%. In the reaction of bis(2,2,2-trichloroethyl)phosphoro chloridate, **1e**, with sodium hexafluorophosphate in a 1 : 1 molar ratio, the corresponding fluoridate **2e** was formed in 30% yield (Table 1) with 2,2,2-trichloroethyldifluorophosphate  $[(\text{Cl}_3\text{CCH}_2\text{O})\text{P}(\text{O})\text{F}_2]$  as a minor product (~4% yield).

In the course of nucleophilic fluorinations of chlorosilanes,<sup>11</sup> alkoxy- and siloxysilanes,<sup>12–14</sup> and haloboranes<sup>15</sup> with alkali metal salts of perfluorinated complex anions, we have previously reported that the Lewis acids and the anhydrous fluoride ions are thermally liberated from the complex anions. The *in situ* generated Lewis acid undergoes complexation with silyl or boron derivatives and polarizes the silicon or the boron center on which the nucleophilic fluorination with the anhydrous fluoride ion readily takes place. In this case too, the thermally liberated fluoride ion undergoes similar ion exchange with chlorophosphorus compounds *via* a polarized phosphorous center, leading to fluorophosphorus compounds (Scheme 2). The halogenated boron and phosphorus Lewis acids remain solvated (solvent trapped).

In conclusion, the well-recognized “inert” and “non-nucleophilic” perfluorinated complex anions are thermally labile and undergo decomposition leading to the Lewis acids and the fluoride ions, which effect nucleophilic fluorination of the chlorophosphorus compounds.

**Table 1** Yield of organofluorophosphorus compounds

X in NaX	Organochloro-phosphorus precursor	Reaction time/min	Organofluoro-phosphorus product	Yield (%)
$\text{BF}_4^-$	$(\text{Me}_2\text{N})_2\text{POCl}$	15	$(\text{Me}_2\text{N})_2\text{POF}$	66
$\text{PF}_6^-$	$(\text{Me}_2\text{N})_2\text{POCl}$	15	$(\text{Me}_2\text{N})_2\text{POF}$	77
$\text{PF}_6^-$	$(\text{EtO})_2\text{POCl}$	10	$(\text{EtO})_2\text{POF}$	12
$\text{BF}_4^-$	$(\text{PhO})_2\text{POCl}$	15	$(\text{PhO})_2\text{POF}$	25
$\text{PF}_6^-$	$(\text{PhO})_2\text{POCl}$	60	$(\text{PhO})_2\text{POF}$	50 <sup>a</sup>
$\text{BF}_4^-$	1,2-Phenylene phosphorochloridite	15	1,2-Phenylene phosphorofluoridite	45
$\text{PF}_6^-$	$(\text{Cl}_3\text{CCH}_2\text{O})_2\text{P}(\text{O})\text{Cl}$	10	$(\text{Cl}_3\text{CCH}_2\text{O})_2\text{P}(\text{O})\text{F}$	30

<sup>a</sup> The ratio of the reagent : reactant = 1 : 3

## Experimental

### General

Bis(dimethylamino)phosphoro chloridate, diethyl chlorophosphate, diphenyl chlorophosphate, 1,2-phenylene phosphorochloridite, bis(2,2,2-trichloroethyl)phosphoro chloridate, the sodium salts of the perfluorinated complex anions, tetrabutylammonium fluoride, and tetraglyme were commercially available as reagents from Aldrich. Tetraglyme was dried over sodium according to literature procedure.<sup>18</sup> Boiling and melting points are uncorrected. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>19</sup>F NMR spectra were recorded on a Varian superconducting NMR spectrometer at 400 MHz operating frequency for <sup>1</sup>H, 100.58 MHz for <sup>13</sup>C, 162 MHz for <sup>31</sup>P and 376 MHz for <sup>19</sup>F NMR spectroscopy. In these experiments, TMS (internal) was used for <sup>1</sup>H and <sup>13</sup>C, 85% phosphoric acid (external) for <sup>31</sup>P and CFC1<sub>3</sub> (external) for <sup>19</sup>F NMR spectroscopy as references, respectively.

### Syntheses and reactions

**Preparation of bis(dimethylamino)phosphoro fluoridate.** To a solution of 5.23 g (20 mmol) (20 g of 1 M) tetrabutylammonium fluoride in THF was added 2.90 g (17 mmol) of bis(dimethylamino)phosphoro chloridate under dry argon and the mixture was heated to reflux for 14 h. An aliquot of the reaction mixture showed only a doublet in the <sup>31</sup>P NMR spectrum at 17.1 ppm. From the reaction mixture, THF was removed in vacuum and the remaining was subjected to vacuum distillation. Bis(dimethylamino)phosphoro fluoridate, **2a**, was distilled at 60–65 °C (6 Torr) as a colorless liquid, which was further characterized by its NMR spectra. [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>P(:O)F: <sup>1</sup>H NMR δ 1.95 (d, 10.3 Hz; td, 1.7 Hz); <sup>13</sup>C NMR, δ 34.39; <sup>31</sup>P NMR, δ 16.85 (d, J<sub>P-F</sub> 947 Hz, quint, J<sub>H-P-F</sub> 11 Hz); <sup>19</sup>F NMR, δ –86.65 (d, J<sub>F-P</sub> 946 Hz).

**Fluorination reaction of bis(dimethylamino)phosphoro chloridate.** To a solution of 5 g (29.3 mmol) **1a** in 5 ml tetraglyme was added 3.5 g (32.2 mmol) sodium tetrafluoroborate and the reaction mixture was heated to about 200 °C for 15 min. The reaction mixture, when analyzed by <sup>31</sup>P NMR spectroscopy, was found to consist of different fluorophosphorus components. Bis(dimethylamino)phosphoro fluoridate, **2a**, was distilled at 45–52 °C (0.5 Torr) in 66% yield and characterized by comparing its NMR spectra with those of an authentic sample prepared as described above. The reaction of **1a** with sodium hexafluorophosphate was carried out in a similar fashion and bis(dimethylamino)phosphoro fluoridate was obtained in 77% yield. [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>P(:O)F: <sup>1</sup>H NMR, δ 2.46 (d, 10.5 Hz, td, 1.6 Hz); <sup>13</sup>C NMR, δ 33.70; <sup>31</sup>P NMR, δ 15.65 (d, J<sub>P-F</sub> 958 Hz, quint, J<sub>H-P-F</sub> 10 Hz); <sup>19</sup>F NMR, δ –85.34 (d, J<sub>F-P</sub> 952 Hz). [(CH<sub>3</sub>)<sub>2</sub>N]P(:O)F<sub>2</sub>: <sup>1</sup>H NMR, δ 2.84 (d, 11.0 Hz); <sup>31</sup>P NMR, δ –6.65 (t, J<sub>P-F</sub> 999 Hz).

**Fluorination reaction of diethylchlorophosphate.** To a solution of 2 g (11.6 mmol) **1b** in 1 ml of tetraglyme was added 2.1 g (12.7 mmol) sodium hexafluorophosphate and the reaction mixture was heated as described above for 10 min. Distillation *in vacuo* gave a mixture of products within the range 70–80 °C (0.5 Torr). Diethylfluorophosphate, **2b**, was obtained in about 12% yield. The products were identified by their NMR spectra. (EtO)<sub>2</sub>P(:O)F: <sup>1</sup>H NMR, δ 1.41 (t, 7 Hz), 4.3 (q, 8 Hz); <sup>31</sup>P NMR, δ –13.17 (d, J<sub>P-F</sub> 977 Hz, td, J<sub>H-P-F</sub> 10 Hz); <sup>19</sup>F NMR, δ –78.60 (d, J<sub>F-P</sub> 995 Hz) [Lit.<sup>19</sup> –77.5]. EtOP(:O)F<sub>2</sub>: <sup>1</sup>H NMR, δ 1.21 (t, 7 Hz), 4.34 (q, 8 Hz) [Lit.<sup>16</sup> 1.11 (t, 5.3 Hz), 4.38 (q, 7.2 Hz)]; <sup>31</sup>P NMR, δ –22.92 (t, J<sub>P-F</sub> 993 Hz, tt, J<sub>H-P-F</sub> 10 Hz) [Lit.<sup>16</sup> –21.35 (t, J<sub>P-F</sub> 1014 Hz), Lit.<sup>19</sup> –20.20 (J<sub>P-F</sub> 1014 Hz)]; <sup>19</sup>F NMR, δ –85.31 (d, J<sub>F-P</sub> 1017 Hz) [Lit.<sup>16</sup> –84.60 (d, J<sub>F-P</sub> 1034 Hz), Lit.<sup>19</sup> –85.0 (d, J<sub>F-P</sub> 1008 Hz)].

**Fluorination reaction of diphenylchlorophosphate.** To a solution of 5 g (18.6 mmol) **1c** in 5 ml tetraglyme was added 2.25 g (20.5 mmol) of sodium tetrafluoroborate and the mixture was heated, under nitrogen, as described above for 15 min. The distillate (b.p. 125–130 °C at 0.5 Torr) consisted of diphenylfluorophosphate (25% yield). [(C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>]P(:O)F: <sup>1</sup>H NMR, δ 7.17 (d, 8 Hz), 7.05 (q, 7 Hz), 6.97 (t, 8 Hz); <sup>31</sup>P NMR, δ –24.52 (d, J<sub>P-F</sub> 1001 Hz); <sup>19</sup>F NMR, δ –77.20 (d, J<sub>F-P</sub> 1012 Hz) [Lit.<sup>20</sup> –78.40].

**Fluorination reaction of 1,2-phenylene phosphorochloridite.** To a solution of 4 g (22.9 mmol) **1d** in 4 ml tetraglyme was added 2.77 g (25.5 mmol) of sodium tetrafluoroborate and the mixture was heated for 15 min as described above. The reaction mixture was analyzed for both 1,2-phenylene phosphorofluoridite and -fluoridate. Vacuum distillation gave 1,2-phenylene phosphorofluoridite in 35% yield (b.p. 30 °C at 1 Torr) [Lit.<sup>21</sup> b.p. 38 °C at Torr]. 1,2-C<sub>6</sub>H<sub>4</sub>(O)<sub>2</sub>PF: <sup>1</sup>H NMR, δ 7.13 (t, 10 Hz), 7.02 (t, 10 Hz) [Lit.<sup>22</sup> 7.0 and 6.8]; <sup>31</sup>P NMR, δ 120.72 (d, J<sub>P-F</sub> 1306 Hz) [Lit.<sup>22</sup> 123.1 (d, J<sub>P-F</sub> 1306 Hz)]; <sup>19</sup>F NMR, δ –37.72 (d, J<sub>F-P</sub> 1306 Hz) [Lit.<sup>22</sup> –37.0 (d, J<sub>F-P</sub> 1207 Hz)]. 1,2-C<sub>6</sub>H<sub>4</sub>(O)<sub>2</sub>P(:O)F: <sup>31</sup>P NMR, δ –24.37 (d, J<sub>P-F</sub> 901 Hz).

**Fluorination reaction of bis(2,2,2-trichloroethyl)phosphoro chloridate.** To a solution of 2 g (5.27 mmol) **1e** in 2 ml tetraglyme was added 0.89 g (5.30 mmol) of sodium hexafluorophosphate and the mixture was heated as described above for 10 min. The reaction mixture was analyzed for both bis(2,2,2-trichloroethyl)fluorophosphate and 2,2,2-trichloroethylidifluorophosphate. Distillation *in vacuo* gave bis(2,2,2-trichloroethyl)fluorophosphate in 30% yield (b.p. 98–104 °C at 0.5 Torr). (Cl<sub>3</sub>CCH<sub>2</sub>O)<sub>2</sub>P(:O)F: <sup>1</sup>H NMR, δ 4.78 (d, 8.3 Hz); <sup>31</sup>P NMR, δ –12.15 (d, J<sub>P-F</sub> 997 Hz). Cl<sub>3</sub>CCH<sub>2</sub>OP(:O)F<sub>2</sub>: <sup>31</sup>P NMR, δ –21.22 (t, J<sub>P-F</sub> 1025 Hz).

### References

- 1 M. R. C. Gerstenberger and A. Haas, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 647.
- 2 (a) R. Schmutzler, *Chem. Ber.*, 1965, **98**, 552; (b) C. Brown, M. Murray and R. Schmutzler, *J. Chem. Soc. (C)*, 1970, 878; (c) H. W. Roesky, *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 891.
- 3 (a) L. Heuer, M. Sell, R. Schmutzler and D. Schomburg, *Polyhedron*, 1987, **6**, 1295; (b) L. Heuer, P. G. Jones and R. Schmutzler, *New J. Chem.*, 1990, **14**, 891.
- 4 (a) R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 410; (b) W. Albers, W. Kruger, W. Storzer and R. Schmutzler, *Synth. React. Inorg. Met.-Org. Chem.*, 1985, **15**, 187; (c) K. Sasse, *Organische Phosphorverbindungen, Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1963, vol. XII, pt 1.
- 5 (a) R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 415; (b) L. M. Yagupol'skii and Z. M. Ivanova, *Zh. Obshch. Khim.*, 1959, **29**, 3766 (*Gen. Chem. USSR*, 1959, **29**, 3726).
- 6 (a) E. L. Lines and L. F. Centofanti, *Inorg. Chem.*, 1973, **12**, 598; (b) E. L. Lines and L. F. Centofanti, *ibid.*, 1974, **13**, 1517; (c) E. L. Lines and L. F. Centofanti, *ibid.*, 1974, **13**, 2796.
- 7 K. M. Doxsee, E. M. Hanawalt and T. J. R. Weakley, *Inorg. Chem.*, 1992, **31**, 4420.
- 8 J. A. Gibson, R. K. Marat and A. F. Janzen, *Can. J. Chem.*, 1975, **53**, 3044.
- 9 S. A. Lermontov, A. V. Popov, S. I. Zavorin, I. I. Sukhojenko, N. V. Kuryleva, I. V. Martynov, N. S. Zefirov and P. Stang, *J. Fluorine Chem.*, 1994, **66**, 233.
- 10 P. P. Onys'ko, E. A. Suvalova, T. I. Chudakova and A. D. Sinitsa, *Zh. Obshch. Khim.*, 1992, **62**, 577 (*J. Gen. Chem.*, 1992, **62**, 473).
- 11 O. Farooq and G. V. D. Tiers, *J. Org. Chem.*, 1994, **59**, 2122.
- 12 O. Farooq, *J. Fluorine Chem.*, 1997, **86**, 189.
- 13 O. Farooq, *J. Chem. Soc., Perkin Trans. 1*, 1998, 661.
- 14 O. Farooq, *J. Fluorine Chem.*, submitted.
- 15 O. Farooq, *J. Fluorine Chem.*, 1995, **70**, 225.
- 16 O. Farooq, *J. Chem. Soc., Perkin Trans. 1*, 1998, 839.

- 17 O. Farooq, *Inorg. Chim. Acta*, in press.  
18 D. D. Perrin and W. L. F. Armarego, *Purification of Solvents*, Pergamon, New York, 3rd edn., 1988.  
19 R. Schmutzler, *J. Chem. Soc.*, 1964, 4551.  
20 C. H. Dungan and J. R. Van Wazer, *Compilation of Reported  $^{19}\text{F}$  NMR Chemical Shifts*, Wiley Interscience, New York, 1970.  
21 R. Schmutzler, *Chem. Ber.*, 1963, **96**, 2435.  
22 G. S. Reddy and R. Schmutzler, *Z. Naturforsch. B*, 1965, **20**, 104; b.p. 50–51°C at 50 Torr.

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