A Convenient Route to Monosubstituted and Non-geminal Derivatives of Phosphonitrilic Fluorides

By T. CHIVERS and N. L. PADDOCK*

(*Department of Chemistry, University of British Columbia, Vancouver* 8, *B.C., Canada*)

IN connection with studies of ring-size effects on the properties of phosphonitrilic compounds,[1] we have investigated the reaction between (dimethylamino)trimethylsilane and the phosphonitrilic series $(NPF_2)_n$ (n = 3—6). The reaction leads to hitherto unknown dimethylamino-derivatives of phosphonitrilic fluorides, which provide a convenient route to monofunctional and non-geminally substituted derivatives of phosphonitrilic fluorides, for example by reaction with anhydrous HCl or HBr.

The products obtained from the reaction between equimolar amounts of (dimethylamino)trimethylsilane and the appropriate phosphonitrilic fluoride at 100° in a sealed tube are shown in Table 1. They were separated by vacuum distillation and identified by analysis and by their i.r. and n.m.r. spectra. For n = 3—5, monosubstituted products are obtained in high yield. For n = 6, a pronounced increase in di- and tri-substituted products is observed. With equimolar (dimethylamino)trimethylstannane in diethyl ether at −78°, $N_4P_4F_8$ gives mainly the disubstituted product $N_4P_4F_6(NMe)_2$ (95%) and only a trace of monosubstituted product.

TABLE 1

Percentage composition of the products of the reaction between phosphonitrilic fluorides, and (dimethylamino)trimethylsilane[a]

$(NPF_2)_n$	$N_nP_n(NMe_2)F_{2n-1}$	$N_nP_n(NMe_2)F_{2n-2}$	$N_nP_n(NMe_2)_3F_{2n-3}$
$(NPF_2)_3$	100 (80)	— (20)	—
$(NPF_2)_4$	80 (55)	20 (45)	—
$(NPF_2)_5$	70 (55)	30 (45)	—
$(NPF_2)_6$	20 (45)	45 (45)	35 (10)

[a] Figures in parentheses indicate composition of products from $(NPF_2)_n$ + $2Me_2NH$ in diethyl ether at 0°.

TABLE 2

B.p's of the monohalogeno-fluorophosphonitriles, and the ^{19}F *n.m.r. parameters of the* ≡PFX *group*

	X = Cl			X = Br		
	δ_F[a]	J'_{PF}[b]	B.p.	δ_F[a]	J'_{PF}[b]	B.p.
$N_3P_3F_5X$	32·9	970	82°	19·6	1056	86°
$N_4P_4F_7X$	38·9	925	117	30·6	974	120
$N_5P_5F_9X$	33·9	952	144—145	25·0	1016	107—109/146 mm.
$N_6P_6F_{11}X$	38·2	944	78/25 mm.	23·4	1032	84—86/25 mm.

[a] Relative to CCl_3F.
[b] Apparent coupling constants in Hz.

For comparison, yields of dimethylamino-fluorophosphonitriles obtained from the reaction of the phosphonitrilic fluoride with 2 equivalents of anhydrous dimethylamine in diethyl ether at 0° are also shown in Table 1. Except for $N_6P_6F_{12}$, the yields of monosubstituted derivatives are lower than in the reaction with Me_3SiNMe_2.

The ^1H and ^{19}F n.m.r. spectra of the disubstituted and more highly substituted derivatives prove that successive substitution of dimethylamino-groups takes place non-geminally, in agreement with a simple electrostatic picture of the reaction. In all cases, the ^1H n.m.r. spectra consist of a sharp doublet of doublets at τ 7·2—7·3, (J'_{PH} 12·0—12·7 Hz., J'_{HF} 1·7—2·2 Hz), the central area being occupied by a broad peak.[2] The ^{19}F n.m.r. spectra show a down-field doublet at 57·3—59·5 p.p.m. [$\equiv PF(NMe_2)$] in addition to the $\equiv PF_2$ absorption. For example, $N_6P_6F_{10}(NMe_2)_2$ shows a doublet at 59·0 p.p.m. (J'_{PF} 923 Hz.), which is one-quarter the area of the $\equiv PF_2$ absorption, and the corresponding doublet in $N_6P_6F_9(NMe_2)_3$ has half the area of the $\equiv PF_2$ absorption. In the case of $N_3P_3F_4(NMe_2)_2$, 12% of the geminal derivative (τ 7·41; J'_{PH} 11·9 Hz.; *cf.* ref. 3) was obtained in addition to the *cis*- and *trans*-isomers of the non-geminal derivative.

The dimethylamino-fluorophosphonitriles react with liquid HCl or HBr at 25° to give the corresponding chlorides and bromides in almost quantitative yields. For $N_3P_3F_5$-NMe_2, heating to 100° is necessary. In this way all the compounds $N_nP_nF_{2n-1}X$ (X = Cl, Br; n = 3—6) have been obtained. The monochlorides have hitherto been prepared only in small yields by the partial fluorination of phosphonitrilic chlorides,[4] and there is no report of the monobromides, except[5] $N_3P_3F_5Br$. The ^{19}F n.m.r. spectra of the $N_nP_nF_{2n-1}X$ compounds show a downfield doublet (≡PFX) in addition to the $\equiv PF_2$ doublet. The n.m.r. parameters and b.p.s of the monohalogeno-fluorophosphonitriles are given in Table 2. These compounds readily undergo nucleophilic displacement reactions to give, *e.g.*, the series of monoisothiocyanato-derivatives[6] $N_nP_nF_{2n-1}$(NCS).

(*Received, February* 10*th*, 1969; *Com.* 187.)

---

[1] T. Chivers and N. L. Paddock, *Chem. Comm.*, 1968, 704.
[2] R. K. Harris, *Inorg. Chem.*, 1966, **5**, 701.
[3] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 177.
[4] A. C. Chapman, D. H. Paine, H. T. Searle, D. R. Smith, and R. F. M. White, *J. Chem. Soc.*, 1961, 1768; J. Emsley and N. L. Paddock, *J. Chem. Soc.* (*A*), 1968, 2590.
[5] E. Steger and D. Klemm, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1812.
[6] T. Chivers, R. T. Oakley, N. L. Paddock, and J. Serreqi, unpublished work.