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## The Preparation of Dialkylaminofluorophosphoranes by the Thermal Decomposition of Dialkylamine-Phosphorus Pentafluoride Adducts

By D. H. Brown, G. W. Fraser, and D. W. A. Sharp

Phosphorus pentafluoride forms adducts with secondary amines. When heated, these break down to give dialkylaminotetrafluorophosphoranes. The action of excess of secondary amine on phosphorus pentafluoride or dialkylaminotetrafluorophosphoranes gives bisdialkylaminotrifluorophosphoranes. Physical properties are reported for the dialkylaminofluorophosphoranes, and the bonding is discussed.

PHOSPHORUS PENTAFLUORIDE readily forms adducts with amines and other Lewis bases,<sup>1</sup> but the thermal decompositions of these adducts have been little studied. The chemistry of phosphorus pentafluoride is often similar to that of boron trifluoride, and since, for example, the thermal decomposition of the adducts formed between secondary amines and boron trifluoride gives <sup>2</sup> dialkylaminodifluoroboranes,  $BF_2NR_2$ , the adducts between secondary amines and phosphorus pentafluoride should decompose to give dialkylaminofluorophosphoranes.

<sup>1</sup> R. Schmutzler, Adv. Fluorine Chem., 1965, 5, in the press. <sup>2</sup> J. F. Brown, J. Amer. Chem. Soc., 1952, 74, 1219. Dialkylaminobromophosphoranes have been briefly reported to result from the action of bromine on the appropriate phosphines,<sup>3</sup> and in a preliminary account of the present work<sup>4</sup> it was shown that dialkylaminophosphoranes could be prepared by the series of reactions outlined above. Recently, dialkylaminofluorophosphoranes have also been prepared by the action of dialkylaminotrimethylsilanes <sup>5,6</sup> or trisdialkylaminophosphines 7 on phosphorus pentafluoride. Dialkylaminofluorophosphines result from the action of dialkylamine on phosphorus trifluoride.8

Phosphorus pentafluoride forms a 1:1 adduct with dimethylamine, and adducts having similar spectroscopic properties are formed by diethylamine and di-npropylamine. When heated to 100-120° the adducts melt and eventually resolidify after evolution of gaseous products which have been identified as dialkylaminotetrafluorophosphoranes,  $F_4 PNR_2$  (R = Me, Et, and Pr<sup>n</sup>). The solid material which remains contains hexafluorophosphate ion and seems to result from the action of hydrogen fluoride, which has been abstracted from the adduct, upon a further molecule of adduct. The

$$2\mathsf{PF}_5,\mathsf{NR}_2\mathsf{H} \longrightarrow \mathsf{PF}_4\mathsf{NR}_2 + \mathsf{+}\mathsf{NR}_2\mathsf{H}_2\mathsf{PF}_6$$

dialkylaminotetrafluorophosphoranes form solid adducts with further dialkylamine, but these adducts are unstable at room temperature and disproportionate bisdialkylaminotrifluorophosphoranes,  $F_{2}P(NR_{2})_{2}$ to (R = Me and Et) and the appropriate dialkylamine adduct of phosphorus pentafluoride. If the reaction is

$$2\mathsf{PF}_4\mathsf{NR}_2 \longrightarrow \mathsf{PF}_3(\mathsf{NR}_2)_2 + \mathsf{PF}_5$$

carried out at 100° there is further aminolysis of the phosphorus pentafluoride to give dialkylaminofluorophosphoranes and hexafluorophosphate ion. The bisdialkylaminotrifluorophosphoranes are very inert and do not react further with base; they are apparently not even hydrolysed by atmospheric moisture. It has not yet proved possible to introduce more than two dialkylamino-groups into phosphorus pentafluoride.

It appears well established that most five-co-ordinate phosphorus(v) derivatives have a trigonal-bipyramidal co-ordination about the phosphorus atom, at least in the liquid and gas phases.<sup>9,10</sup> The <sup>19</sup>F n.m.r. spectrum of diethylaminotetrafluorophosphorane has been reported <sup>10</sup> both at room temperature and at  $-85^{\circ}$ , and, although at room temperature all the fluorine atoms appear equivalent, at low temperatures the rate of intramolecular exchange has dropped so that there are two distinguishable fluorine atom environments each of which contains

<sup>6</sup> G. C. Demitras, C. A. Kent, and A. G. MacDiarmid, Chem. and Ind., 1964, 1712.

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two fluorine atoms. This spectrum has been taken to indicate an equatorially substituted trigonal-bipyramidal model. The room-temperature <sup>19</sup>F n.m.r. spectra of dimethylaminoand di-n-propylamino-tetrafluorophosphorane show only apparently equivalent fluorine atoms but the spectrum of bisdimethylaminotrifluorophosphorane shows that one fluorine atom is in a different environment from the other two. Formally, all these results could arise from substitution into a squarepyramidal configuration, but the chemical shifts and <sup>31</sup>P-<sup>19</sup>F coupling constants follow the patterns set by other RPF<sub>4</sub> and R<sub>2</sub>PF<sub>3</sub> derivatives, and it appears very likely that all the present compounds have trigonalbipyramidal co-ordination about the phosphorus atom and that substitution is into the equatorial plane. The values of the chemical shifts and coupling constants observed in the present work are in Table 1.

The infrared spectra of the compounds prepared in the present work are too complex to allow complete analysis, but identification of many of the vibrational bands may be made by comparison with the spectra of the closely related compounds dimethylaminodifluoroborane,  $\mathrm{BF}_2\mathrm{NMe}_2,^{11}$ dimethylaminodifluorophosphine,  $PF_2NMe_2^{,8}$  chlorotetrafluorophosphorane,  $PF_4Cl_1^{,12}$  and dichlorotrifluorophosphorane, PF3Cl2.13 Table 2 gives the details of the infrared spectra of the dimethylaminofluorophosphoranes prepared; the spectra of the ethyl and n-propyl derivatives are very similar to these, and detailed values are not included. Peaks occurring at frequencies above 1000 cm.<sup>-1</sup> are, apart from possible overtones, associated with the dimethylamino-groups. The peaks at 2860 and 2840 cm.<sup>-1</sup> in the spectra of dimethylaminotetrafluorophosphorane and bisdimethylaminotrifluorophosphorane, respectively, are in the range which is characteristic of the N-CH<sub>3</sub> group.<sup>14</sup> The presence of this band does not preclude interaction between the lone-pair of electrons on the nitrogen and a vacant *d*-orbital on the phosphorus, as the band has been reported for methylanilines and silylamines, in which there will be extensive delocalisation of the lone-pair. A band occurs between 1000 and 1070 cm.<sup>-1</sup> for all the compounds containing a N-C2 group, and, following previous workers,<sup>8</sup> this is assigned to the antisymmetric stretching mode of this group.

The spectra at frequencies below 1000 cm.<sup>-1</sup> consist mainly of broad intense bands which appear to originate from P-F vibrations. The spectrum of thionyl tetrafluoride,  $F_4SO$ , is of a similar shape to that expected for dimethylaminotetrafluorophosphorane, and the infrared spectrum of the former compound 15 shows four (two

<sup>&</sup>lt;sup>8</sup> H. Nöth and H. J. Vetter, *Chem. Ber.*, 1963, **96**, 1109, 1816. <sup>4</sup> D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *Chem.* and Ind., 1964, 367.

<sup>&</sup>lt;sup>5</sup> R. Schmutzler, Angew. Chem., 1964, **76**, 893.

G. W. Fraser, unpublished work.

<sup>&</sup>lt;sup>8</sup> M. A. Fleming, R. J. Wyma, and R. C. Taylor, Spectrochim. Acta, 1965, 21, 1189. 9 E. L. Muetterties, W. Mahler, and R. Schmutzler, Inorg.

Chem., 1963, 2, 613.

<sup>&</sup>lt;sup>10</sup> E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298. <sup>11</sup> A. J. Banister, N. N. Greenwood, B. P. Straughan, and J.

Walker, J. Chem. Soc., 1964, 995. <sup>12</sup> R. P. Carter and R. R. Holmes, Inorg. Chem., 1965, **4**, 738.

<sup>&</sup>lt;sup>13</sup> J. E. Griffiths, R. P. Carter, and R. R. Holmes, J. Chem.

Phys., 1964, 41, 863.
<sup>14</sup> J. T. Braunholz, E. Ebsworth, F. Mann, and N. Sheppard, J. Chem. Soc., 1958, 2780.
<sup>15</sup> P. L. Goggin, H. L. Roberts, and L. A. Woodward, Trans. Faraday Soc., 1961, 57, 1877.

of which overlap) bands in this region which are derived from S-F modes. By analogy, the corresponding four strongest bands at 950, 882 (doublet), and 701 cm.<sup>-1</sup> for dimethylaminotetrafluorophosphorane are identified as originating from P-F modes. This leaves a moderately weak band at 806 cm.<sup>-1</sup> unassigned (chlorotetrafluorophosphorane does have a weak band at 817 cm.<sup>-1</sup>, which could mean that both of these bands are also the P-N stretching frequency on going from dimethylaminotetrafluorophosphorane to bisdimethylaminotrifluorophosphorane would be in agreement with a smaller amount of  $p \longrightarrow d$  overlap in each N-P bond in the latter compound. Since, however, there are two N-P bonds, the total electron density at the phosphorus atom could still be sufficiently great for it to be no longer electrondeficient, and combination with bases would be further

		TABLE 1				
	Nuclear mag	gnetic resona	nce spectra			
	$J(^{31}P-^{19}F)$	$J(^{31}P_{-1}H)$	$\int (^{19}\mathrm{F}-^{1}\mathrm{H})$	$J(\mathbf{F}_{\mathbf{A}} - \mathbf{F}_{\mathbf{E}})$	δ <sub>н</sub> *	$\delta_{\mathbf{F}}^{\dagger}$
PF <sub>5</sub> ,NMe <sub>2</sub> H	752(A)			50		+16.7
	808(E)					+7.3
PF <sub>4</sub> NMe <sub>2</sub>	836	11	2		-2.57	+5.3
$PF_3(NMe_2)_2$	752(A)	11	$2 \cdot 8(A)$	42	-2.65	-8.5(A)
	871(E)		1.5(E)			+10.2(E)
PF <sub>5</sub> ,NEt <sub>2</sub> H	756(A)		· · /	50		+16.7
	813(A)					$+4\cdot 2$
PF <sub>4</sub> NEt <sub>2</sub>	868`´					$+4\cdot 2$
$PF_3(NEt_2)_2$	753(A)					-3.0(A)
	876(E)			44		+5.2(E)
PF <sub>4</sub> NPr <sub>2</sub>	856					+3.7

With respect to tetramethylsilane. † With respect to trifluoromethylbenzene. (A) apical fluorines; (E) equatorial fluorines.

			Infrared sp	ectra		
$\mathrm{PF}_{4}\mathrm{NMe}_{2}$	BF2NMe2	$\mathrm{PF_2NMe_2}$	$PF_4Cl$	$\mathrm{PF}_{3}(\mathrm{NMe}_{2})_{2}$	$PF_{3}Cl_{2}$	
2960 2900 2860 1464	$3000 \\ 2947 \\ 2911 \\ 2827 \\ 1473 \\ 1433$	$2925 \\ 2865 \\ 2820 \\ 1507 \\ 1432$		2970 2900 2840 1466		CH stretch CH <sub>3</sub> antisym. deform. CH <sub>3</sub> sym. deform.
1368 1300 1211 1042	$\begin{array}{c} 1209 \\ 1078 \end{array}$	1307 1195 1073		1368 1295 1224 1070 1020		$CH_3$ deform. $CH_3$ rock $CH_2$ antisym. stretch
950		989 814 770	$945 \\ 927 \\ 921$	870 830	925 902	Ĵ
882 (doublet)			903 895 817w	775		P-F modes

TABLE 2

associated with P–F vibrations), and it is preferred to identify this band (and those at 799 and 790 cm.<sup>-1</sup> for the diethylamino- and di-n-propyl-amino-derivatives) with the P–N stretch. Bisdimethylaminotrifluorophosphorane has a much more complicated spectrum than dimethylaminotetrafluorophosphorane but it has a moderately intense band at 722 cm.<sup>-1</sup> which may be identified as the P–N stretch. P–N stretching modes are not well characterised but the P–N stretch in dimethylaminodifluorophosphine is assigned at 705 cm.<sup>-1</sup>.<sup>8</sup>

Dimethylaminodifluoroborane is a solid and is dimeric in the solid state<sup>11</sup> but, as has been pointed out,<sup>10</sup> nearly all the physical properties of the dialkylaminotetrafluorophosphoranes suggest that they are essentially monomeric. Possible dimerisation would be hindered by steric effects which would be greater than in the boranes. A monomeric molecule could also be stabilised by  $p \rightarrow d$  overlap in the N-P bond, and the lowering of hindered by the presence of two bulky dimethylaminogroups (cf. the gross reduction in acceptor strength with increase in the number of alkyl groups in the alkylfluorophosphoranes <sup>16</sup>).

Attempts were made to use dimethylaminotetrafluorophosphorane as a base by way of the lone-pair of electrons on the nitrogen atom, but there is no reaction with methyl iodide, in agreement with participation of the lone-pair in  $p \longrightarrow d$  overlap in the N-P bond with consequent non-availability of electrons for simple electron-pair donation.

## EXPERIMENTAL

Phosphorus pentafluoride was prepared by heating Phosfluorogen A (Ozark Mahoning Company) or was obtained from a cylinder (Matheson Corporation); it was <sup>16</sup> E. L. Muetterties and W. Mahler, *Inorg. Chem.*, 1965, **4**, 119. purified by low-temperature distillation. All other materials were purified by distillation and were stored over the appropriate drying agent.

The Adducts between Phosphorus Pentafluoride and Secondary Amines.—These were prepared by condensing phosphorus pentafluoride on to a solution of dimethylamine in toluene held at  $-78^{\circ}$ . The adduct was deposited from solution, and when no further absorption occurred the volatile products were removed by pumping at room temperature for several hours, and the adduct was finally sublimed at  $60^{\circ}$  in vacuo. Dimethylamine—phosphorus pentafluoride (Found: C, 14·1; H, 4·3; F, 55·5; N, 8·2; P, 18·1. C<sub>2</sub>H<sub>7</sub>F<sub>5</sub>NP requires C, 14·3; H, 4·1; F, 55·6; N, 8·1; P, 18·1%). The adducts formed between diethylamine and di-n-propylamine and phosphorus pentafluoride were prepared in a similar manner but were not isolated.

Dialkylaminotetrafluorophosphoranes.-These were prepared by heating the dialkylamine-phosphorus pentafluoride adducts to 150° in a closed system under a few mm. pressure. Volatile products were collected in a  $-196^{\circ}$ trap. The solid residue contained hexafluorophosphate ion (identified by n.m.r. spectroscopy). The derivatives were also prepared by forming the adduct in tetramethylene sulphone. Dimethylaminotetrafluorophosphorane (Found: C, 15.7; H, 4.1; N, 9.5; P, 20.9%; M, 157. Calc. for  $C_2H_6F_4NP$ : C, 15.9; H, 3.9; N, 9.3; P, 20.5%; M, 151), m. p.  $<-78^{\circ}$ , b. p. 60° (extrapolated); vapour pressure equation  $\log_{10} p(\text{mm.}) = 8.69 - 1936/T$ . Diethylaminotetrafluorophosphorane (Found: C, 27.0; H, 5.7; F, 42.5; N, 7.9; P, 17.2. C<sub>4</sub>H<sub>10</sub>F<sub>4</sub>NP requires C, 26.8; H, 5.6; F, 42.2; N, 7.8; P, 17.3%), m. p. -73°; vapour pressure 25 mm. at 19°. Di-n-propylaminotetrafluorophosphorane was prepared similarly. Spectroscopic properties were very

similar to those of the diethylamino-derivative and the product was not characterised further; vapour pressure  $4 \text{ mm. at } 19^{\circ}$ .

Bisdialkylaminotrifluorophosphoranes .--- These were prepared by reaction of phosphorus pentafluoride and excess of dialkylamine either alone or using tetramethylene sulphone as solvent. The compounds were also prepared from the interaction of excess of dialkylamine and dialkylaminotetrafluorophosphoranes. This reaction was carried out on a small scale in a nuclear magnetic resonance tube. Bisdimethylaminotrifluorophosphorane (Found: C, 27.1; H, 6.6; F, 33.0; N, 16.0; P, 17.5. Calc. for C<sub>4</sub>H<sub>12</sub>F<sub>3</sub>N<sub>2</sub>P: C, 27·3; H, 6·8; F, 32·4; N, 15·9; P, 17·6%), m. p. -22°; vapour pressure 4 mm. at 20°. Bisdiethylaminotrifluorophosphorane (Found: C, 41.4; H, 8.7; F, 24.4; N, 12.2; P, 13.5.  $C_8H_{20}F_3N_2P$  requires C, 41.4; H, 8.6; F, 24.6; N, 12.1; P, 13.4%), m. p. 5°. There was no reaction between bisdimethylaminotrifluorophosphorane (0.5 g.) and dimethylamine (0.1 g.) when heated in a sealed tube for 12 hr. at 120°.

Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer spectrometer working at 33.5°. Proton spectra were recorded at 40 Mc./sec and <sup>19</sup>F spectra at 37.65 Mc./sec. Samples were sealed into tubes for examination directly from a vacuum line. Infrared spectra were recorded on a Grubb-Parsons model DB2 spectrophotometer.

We thank the U.S. Department of Navy and Messrs. Albright and Wilson for financial support.

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