Fluoro-1,3,2,4-diazadiphosphetidines

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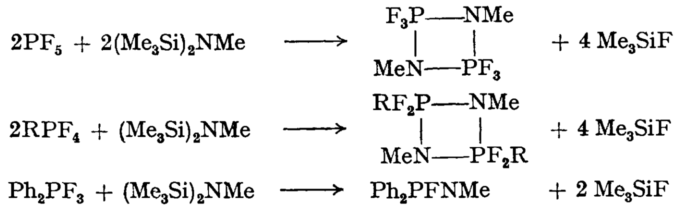
LEWIS ACID phosphorus fluorides, such as PF_5, RPF_4, or Ph_2PF_3, react with hexamethyldisiloxane with cleavage of the Si–O bond, the products being Me_3SiF and POF_3, $RPOF_2$, or Ph_2POF, respectively.[1] The interaction of the same types of phosphorus fluoride with heptamethyldisilazane, where the oxygen of the disiloxane is replaced by the NMe group, has been found to be a very general route into phosphorus–nitrogen chemistry. The following scheme summarizes the types of reactions encountered, the ease of reaction decreasing in the order given:



In a typical preparation, phenyltetrafluorophosphorane reacts with heptamethyldisilazane to give Me_3SiF (95%) and $(PhPF_2NMe)_2$, m.p. 162° [Found: *M* (isopiestic in acetonitrile), 344, 350. Calc.: 350], in 99% yield. Characterization of derivatives of the fluorodiazadiphosphetidine system was by elemental analysis, and infrared and, especially, ^1H, ^{19}F, and ^{31}P n.m.r. spectroscopy.

Especially revealing as to the presence of the *NN'*-dimethyl-1,3,2,4-diazadiphosphetidine ring system is the ^1H n.m.r. spectrum of a saturated solution of $(PhPF_2NMe)_2$ in deuterochloroform: a sharp 1–2–1 triplet is observed at $-2{\cdot}46$ p.p.m., while an aromatic multiplet is centred at *ca.* $-7{\cdot}7$ p.p.m. (external tetramethylsilane standard). Integration gives $H_{\text{aliph.}} : H_{\text{aromat.}} = 3:5$, in confirmation of the composition. The P-H coupling constant is 12·5 c./sec., and there is no indication of spin-spin-splitting between fluorine and the protons of the N-Me group. The same pattern for the ^1H n.m.r. spectrum, due to the N-Me protons, is observed for a variety of other derivatives of *NN'*-dimethyl-1,3,2,4-diazadiphosphetidine. Significant proof for the suggested structure is thus provided, ruling out, for instance, an open chain (N–P–N–P) or an N–N–P–P chain or ring structure.

The ^{19}F n.m.r. spectra of the fluoro-*NN'*-dimethyl-1,3,2,4-diazadiphosphetidines consist of a basic doublet, $J_{P-F} = 880$—900 c./sec., while a 1–2–1 triplet, indicative of a PF_2 group, is observed in the ^{31}P n.m.r. spectrum. The high positive values of the ^{31}P chemical shift (relative to an external phosphoric acid reference) of some typical compounds strongly suggest phosphorus being present in co-ordination number five, *e.g.*,

$(EtPF_2NMe)_2$ (neat), $\delta_P = +45{\cdot}6$ p.p.m.

$(ClCH_2{\cdot}PF_2NMe)_2$ (in benzene), $\delta_P = +56{\cdot}3$ p.p.m.

$(F_3PNMe)_2$ (neat), $\delta_P = +71{\cdot}5$ p.p.m.

The last value may be compared to $\delta_P = +78{\cdot}2$ p.p.m. for the related $(Cl_3PNMe)_2$.[2]

A valuable indication of the presence of an NMe group is provided by a characteristic i.r. stretching frequency in the 2760—2820 cm.$^{-1}$ region, if the nitrogen atom retains its lone-pair of

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[1] R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 410; R. Schmutzler, *J.*, in the press.

[2] E. Fluck, *Z. anorg. Chem.*, 1963, **320**, 64.

electrons.[3] The observation that in a series of our novel fluoro-*NN'*-1,3,2,4-diazadiphosphetidines a distinct i.r. absorption is invariably observed in the 2800—2840 cm.$^{-1}$ region suggests that delocalization of the lone-pair of electrons on the nitrogen into the four-membered ring does not occur to a significant extent.

The stability of the fluorodiazadiphosphetidine ring system, both thermally and toward hydrolysis, is noteworthy. All the compounds are sufficiently stable to be distilled or sublimed with ease.

Further structural information on the diazadiphosphetidine ring system is provided by the investigation of $(F_3PNMe)_2$, b.p. 91·6°/757 mm., m.p. $-8{\cdot}3°$; n_D^{25} 1·3323; d_4^{25} 1·532 (Found: *M* (mass spectr.), 234. Calc.: 234). A 0·0314M-solution of $(F_3PNMe)_2$ in benzene had zero dipole moment. $(F_3PNMe)_2$[4] and the related $(F_3PNPh)_2$[5] have also been obtained independently by other workers.

It is suggested that the ease of reaction between heptamethyldisilazane and phosphorus fluorides is a function of the Lewis acidity of the latter. This is in accord with the observed low reactivity of Ph_2PF_3, and the complete lack of interaction with Me_2PF_3. It may also be noted that PF_3 did not react at all with heptamethyldisilazane, although PCl_3 reacted with the related *N*-ethylhexamethyldisilazane.[6]

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[3] J. T. Braunholtz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppard, *J.*, 1958, 2780.

[4] J. Goubeau and P. Haasemann and G. C. Demitras and A. G. MacDiarmid, personal communications; cf. also G. C. Demitras, R. A. Kent, and A. G. MacDiarmid, *Chem. and Ind.*, 1964, 1712.

[5] J. J. Harris and B. Rudner, Paper presented at the Meeting of the American Chemical Society, Philadelphia, April, 1964 (J. J. Harris, personal communication).

[6] E. W. Abel and G. Willey, *Proc. Chem. Soc.*, 1962, 308.