Synthesis of Alkylaminobisdichloro- and Alkylaminobisdifluoro-phosphines

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PRIMARY aliphatic amines can react with phosphorus trichloride to produce phosphorus imide–amide dimers $[P(NR)NHR]_2$, triamides $P(NHR)_3$, phosphoramidous dichlorides $RNHPCl_2$, or cage structures, *e.g.*, $P_4N_6R_6$,[1] but alkylaminobisdichlorophosphines, $RN(PCl_2)_2$, have not so far been isolated. I now report a convenient synthesis of these compounds and their fluoro-analogues.

Prolonged heating of an excess of phosphorus trichloride under reflux with the appropriate amine hydrochloride in 1,1,2,2-tetrachloroethane leads to steady hydrogen chloride evolution and formation of alkylaminobisdichlorophosphines $RN(PCl_2)_2$ (I; R = Me, Et).

$$RNH_3Cl + 2PCl_3 \rightarrow \underset{(I)}{RN(PCl_2)_2} + 3HCl$$

R = Me, b.p. 47°/0·5 mm. (48%) [based on RNH_3Cl].

R = Et, b.p. 62/0·5 mm. (51%).

Confirmation of the formulation comes from elemental analysis and ^1H and ^{31}P n.m.r. spectroscopy. The proton n.m.r. spectrum of (I; R = Me) shows a simple 1–2–1 triplet ($J_{PH} = 3{\cdot}0$ c./sec.) from coupling with two equivalent phosphorus nuclei, while for (I; R = Et) the methylene resonance is the expected 1–2–1 triplet of 1–3–3–1 quartets ($J_{PH} = 5{\cdot}7$, $J_{HH} = 7{\cdot}4$ c./sec.) from coupling with two phosphorus and three hydrogen nuclei. The methyl resonance is a simple triplet ($J_{HH} = 7{\cdot}4$ c./sec.).

Fluorination of (I) with antimony trifluoride leads to the new alkylaminobisdifluorophosphines, $RN(PF_2)_2$ (II), which represent the first examples of this class of compounds, and are closely related to the very recently described F_2POPF_2 and $F_2P{-}PF_2$.[2,3] Their identity was confirmed by vapour-phase molecular-weight measurements. The ^1H n.m.r. spectrum of (II; R = Me) shows a symmetrical nine-line pattern from perfect overlap of three quintuplets which arise from spin-coupling with two phosphorus and four fluorine nuclei ($J_{PH} = 3{\cdot}2$, $J_{FH} = 1{\cdot}6$ c./sec.). Both the ^{19}F and ^{31}P n.m.r. spectra show the complexity expected for an $X_2AA'X_2'$ system.

$$3RN(PCl_2)_2 + 4SbF_3 \rightarrow \underset{(II)}{3RN(PF_2)_2} + 4SbCl_3$$

R = Me, b.p. 42—43° (75%).

R = Et, b.p. 62—63° (71%).]

The identity of (II; R = Et) was further established by its essentially quantitative reaction with hydrogen chloride with cleavage of both phosphorus–nitrogen bonds. Further studies under way indicate that these bifunctional fluorophosphines readily form co-ordination complexes with metal carbonyls.

$$\begin{array}{llll} EtN(PF_2)_2 & + \; 3HCl & \rightarrow & \\ 1{\cdot}239 \text{ mmoles} & 3{\cdot}716 \text{ mmoles} & & \\ & & 2PF_2Cl \; + & EtNH_3Cl \\ & & 2{\cdot}477 \text{ mmoles} & 1{\cdot}239 \text{ mmoles} \end{array}$$

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[1] See, for example, Reviews by G. M. Kosolapoff, "Organophosphorus Compounds", Wiley, New York, 1950; E. Fluck, "Topics in Phosphorus Chemistry" vol. 4, Wiley, New York, 1967, p. 291; M. L. Nielsen, "Developments in Inorganic Nitrogen Chemistry," vol. 1, Elsevier, Amsterdam, 1966, p. 307.

[2] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, 1966, **88**, 3729.

[3] M. Lustig, J. K. Ruff, and C. B. Colburn, *J. Amer. Chem. Soc.*, 1966, **88**, 3875.