Fluorophosphoranes containing Phosphorus–Sulphur and Phosphorus–Oxygen Bonds

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PREVIOUS evidence has shown that fluorophosphoranes containing alkoxy-groups are not thermally stable, and readily lose alkyl fluoride with formation of the corresponding phosphoryl compound,[1–4] *i.e.*

$$R^1_nPF_{4-n}OR^2 \rightarrow R^1_nP(:O)F_{3-n} + R^2F$$

It seems reasonable to assume that the reaction occurs because of the formation of the polar phosphoryl bond, and that the tendency for the above decomposition would be less pronounced in the case of mercapto-compounds, the thiophosphoryl bond being less polar than the $P=O$ bond.

It has now been found that this assumption is valid and, using the cleavage reaction of trimethyl thioethers[5] with fluorophosphoranes, a series of stable, often distillable pentaco-ordinate fluorides of composition $R^1_nPF_{4-n}SR^2$ ($n = 1,2$; $R^1 = Ph$; $R^2 =$ alkyl, aryl) could be obtained in accordance with the equation

$$R^1_nPF_{5-n} + R^2\text{-S-SiMe}_3 \rightarrow R^1_nPF_{4-n}SR^2 + Me_3SiF$$

Stable fluorophosphoranes, containing an aryloxy-group, were also obtained by a similar synthetic route, using phenyltrimethylsilyl ether. With tetrafluorophosphoranes, the disubstituted derivatives, $RPF_2(OPh)_2$, rather than $RPF_3(OPh)$ were obtained, irrespective of the order of combination of the reactants or of their molar ratio, *viz.*

$$RPF_4 + 2PhOSiMe_3 \rightarrow RPF_2(OPh)_2 + 2Me_3SiF \quad (R = Me, Ph)$$

Diphenyltrifluorophosphorane was found to react in the same way

$$Ph_2PF_3 + PhOSiMe_3 \rightarrow Ph_2PF_2(OPh) + Me_3SiF$$

The novel fluorophosphoranes are obtained in the form of well-shaped crystals which are stable at room temperature and may be recrystallized without change.

The fluorophosphoranes $(MeO)_3PF_2$ and $(PhO)_3PF_2$ have been reported as by-products in the reaction of the respective phosphite $(RO)_3P$ ($R = Me, Ph$), and difluorodiazirine.[3] These compounds were characterized by ^{19}F n.m.r. only. Unstable alkyl compounds, $R_fP(OR)_3F$[3] ($R_f =$ perfluoroalkyl), and $MeOPF_4$[4] have also been described. There is also n.m.r. evidence for a thermally unstable compound, $MeSPF_4$, prepared by the reaction of Me-S-SiMe$_3$ with PF_5.[6]

All new compounds gave satisfactory elemental analyses. ^{19}F n.m.r. spectra were recorded (Table) and, from the observed parameters, we suggest that the compounds are trigonal bipyramids, with two fluorine atoms in axial positions, and the hydrocarbon, mercapto-, or phenoxy-groups in equatorial positions.[7,8] The observed magnitude of the P–F coupling constants and the δ_F values are consistent with this formulation.

Consistent ^{31}P and ^1H n.m.r. data have also been obtained for the new compounds. The δ_P values are strongly positive, as is typical of fluorides of pentaco-ordinate phosphorus.[9] The spectral data

TABLE

^{19}F *N.m.r. data for* $R^1_nPF_{4-n}(SR^2)$ *and* $R^1_nPF_2(OPh)_{3-n}$

Compound	J_{P-F} (c./sec.)	J_{F-F} (c./sec.)	δ_F (p.p.m.)*
$PhPF_3SMe$	942 (axial)	60·5	+15·0 (axial)
	1042 (equat.)		+71·9 (equat.)
$PhPF_3SEt$	938 (axial)	59·3	+15·7 (axial)
	1049 (equat.)		+71·3 (equat.)
$PhPF_3SPh$	970 (axial)	60·0	+13·6 (axial)
	1060 (equat.)		+71·3 (equat.)
Ph_2PF_2SMe	760		+25·0
Ph_2PF_2SEt	752		+25·2
Ph_2PF_2SPh	796		+23·5
$MePF_2(OPh)_2$	825		+18·1
$PhPF_2(OPh)_2$	829		+35·0
$Ph_2PF_2(OPh)$	797		+33·3

* CCl_3F used as internal reference.

also show clearly that the compounds exist in the covalent, pentaco-ordinate form and there is no evidence for the existence of ionic isomers.

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