Stable Monoalkoxyfluorophosphoranes

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Summary Thermally stable monoalkoxyfluorophosphoranes, $R^1PF_3(OR^2)$, with R^1 = Me and Ph, are obtained when R^2 is either an electron-attractive group or a neopentyl group; the fluorophosphoranes undergo slow redistribution reactions of fluorine *vs.* alkoxy-groups in which the five-co-ordinate state of the phosphorus atom is preserved.

As yet, only a limited number of alkoxyfluorophosphoranes has been reported,[1] mostly as n.m.r.-detected unstable reaction intermediates. The lack of a general route for their preparation has been attributed to the instability[1,2] of these compounds with respect to the formation of the corresponding fluorophosphoryl derivatives, especially in the case of the monoalkoxy-compounds.†

We have found that the stability of the monoalkoxyfluorophosphoranes, $R^1PF_3(OR^2)$ (R^1 = Me or Ph), is considerably improved when R^2 is either an electron-attractive group or an isobutyl‡ or a neopentyl group. Thus, the compounds (Ia—j) were the predominant

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† The perfluoroalkoxy-[3] *or* perfluoroalkyl-[4] fluorophosphoranes, and the aryloxyfluorophosphoranes[1a] appear to be more stable; however, the monoaryloxy-derivatives of formula $RPF_3(OPh)$ were not obtained.

‡ With R^2 = t-butyl rapid decomposition of the phosphorane occurs above −50°.

	R^2	R^2
$R^1PF_3(OR^2)$	a; CH_2CH_2Cl	f; CH_2CCl_3
	b; CH_2CH_2Br	g; CH_2CF_3
R^1 = Me and Ph	c; CH_2CH_2CN	h; Bu^t
	d; CH_2CH_2OMe	i; CH_2CMe_3
(I)	e; CH_2CHCl_2	j; $CH_2CMe_2(NO_2)$§

products (>95%) of the cleavage reaction of the trimethylsilyl ether of the alcohols by a stoicheiometric amount of both methyl- and phenyl-tetrafluorophosphorane (II), according to equation (1).

$$\underset{\text{(II)}}{R^1PF_4} + Me_3SiOR^2 \longrightarrow \underset{\text{(I)}}{R^1PF_3(OR^2)} + Me_3SiF \qquad (1)$$

The structure of these highly air-sensitive derivatives was established by low temperature ^1H and ^{19}F n.m.r. as well as by m.s. analysis. At low temperatures the structure consists of a trigonal bipyramid, with two fluorine atoms in the apical positions, and this undergoes rapid pseudorotation at room temperature [$\Delta G^{\ddagger}$ *ca.* 12·5 kcal mol^{-1} for (If)]. This is in marked contrast to the slowness of the pseudorotation process in the corresponding amino-[5] or alkylthio-[6] derivatives, for which no fluorine exchange is observed at room temperature on the n.m.r. scale. This implies that the more electronegative alkoxy-groups can assume the apical positions more easily. The ^{19}F n.m.r. data from low temperature spectra (δ in p.p.m. from $CFCl_3$, J in Hz) show little dependence on the nature of R^2: for R^1 = Me, δF_a 26 ± 1, δF_e 67 ± 1; for R^1 = Ph, δF_a 41 ± 2, δF_e 66 ± 1; in both cases $J(P\text{–}F_a)$ 830 ± 15, $J(P\text{–}F_e)$ 975 ± 15, $J(F_a\text{–}F_e)$ 64 ± 2. No evidence for ionic isomers was found.

Thermal decomposition, with loss of the pentaco-ordinate state of the phosphorus atom, sets in near 60° for (Ih), 120° for (Ii), in the range of 150—170° for (Ia—e), while heating to *ca.* 200° is necessary to decompose (If), (Ig), and (Ij). The decomposition products depend on R^2: with (Ia), (Ih), and (Ii), $R^1P(O)F_2$ and R^2F are formed almost exclusively; with (Ib) they are accompanied by some dibromoethane; with (Ic) an elimination process yields mainly acrylonitrile; in the other cases, additional compounds, such as the ether R^2OR^2 and the alkoxyfluorophosphonate $R^1P(O)F(OR^2)$, were identified.

At lower temperatures [0° for (Ih), up to 100° for (If) or (Ig)] a slow interconversion among fluorophosphoranes, without loss of the pentaco-ordinate character of the phosphorus atom, is observed. This implies the redistribution of fluorine atoms *vs.* alkoxy-groups, according to equation (2). The equilibrium (2) lies to the right and may

$$2\,\underset{\text{(I)}}{R^1PF_3(OR^2)} \rightleftharpoons \underset{\text{(II)}}{R^1PF_4} + \underset{\text{(III)}}{R^1PF_2(OR^2)_2} \qquad (2)$$

be shifted by continuously pumping off the more volatile tetrafluorophosphorane (II), thus providing an interesting route for the synthesis of the dialkoxyfluorophosphoranes (III).

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