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Preliminary Note

Preparation of C–F compounds by the reaction of silyl ethers or tetra-alkoxysilanes with fluorophosphoranes

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A new preparation of C–F compounds which involves the reaction of silyl ethers or silicic acid esters with fluorophosphoranes is described.

During a study of the reactions of phosphorus pentafluoride and its derivatives, R_nPF_{5-n} ($n = 0, 1, 2, 3$; R = hydrocarbon group), with trimethylsilyl ethers it has been observed that, instead of the alkoxy-substituted fluorophosphoranes, $R_nPF_{4-n}OR'$, their decomposition products, $R_nP(:O)F_{3-n}$ and R'F, are formed[1,2],

$$R_nPF_{5-n} + R'OSiMe_3 \begin{array}{ll} \nrightarrow R_nPF_{4-n}OR' + Me_3SiF & \text{(1a)} \\ \longrightarrow R_nP(:O)F_{3-n} + R'F + Me_3SiF & \text{(1b)} \end{array}$$

We have now undertaken a closer study of this reaction which, in many instances, occurs at or below room temperature, and find that it provides a facile synthesis of C–F compounds, by the conversion of a hydroxy compound to the corresponding fluoro derivative, *viz.*

$$\equiv C{-}OH \xrightarrow{\text{silylation}} \equiv C{-}O{-}SiMe_3 \xrightarrow{R_n\,PF_{5-n}} \equiv C{-}F \qquad (2)$$

Trimethylsilyl ethers of primary (RCH_2OH; R = H, Me, 5-norbornenyl-2), secondary (R^1R^2CHOH; $R^1 = R^2$ = Me, Pr^i; R^1 = Me, $R^2 = Pr^n$; R^1R^2 = cyclohexyl), and tertiary (Bu^tOH) alcohols were allowed to react with phenyl- and ethyl-tetrafluorophosphorane in a 1:1 molar ratio, without the use of a solvent and normally at room temperature. The reactions were found to proceed quantitatively with regard to formation of the C–F compound in almost every instance (eqn. 1(b)). ^1H, ^{19}F, and ^{31}P NMR spectroscopy were employed to identify the products.

A side reaction which caused a decrease in the yield of C–F species[3],

$$RP(:O)F_2 + R'OSiMe_3 \rightarrow RP(:O)(F)(OR') + Me_3SiF \qquad (3)$$

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could be virtually eliminated when excess tetrafluorophosphorane was employed.

Trifluorophosphoranes were found to react with alkyltrimethylsilyl ethers in an analogous manner, but more vigorous reaction conditions were required, presumably as a consequence of the lower acceptor strength of R_2PF_3[2],

$$R_2PF_3 + R'OSiMe_3 \xrightarrow{\text{ca. } 100^\circ} R_2P(:O)F + R'F + Me_3SiF \tag{4}$$

In most cases, diphenyltrifluorophosphorane (R = Ph) was employed. The intermediate diphenylalkoxyfluorophosphoranes, Ph_2PF_2OR', were of such stability in a number of cases that their formation and subsequent decomposition (in the 60–100°C temperature range) could clearly be demonstrated by NMR spectroscopy[2,4–6],

$$R_2PF_3 + R'OSiMe_3 \xrightarrow{-Me_3SiF} R_2PF_2OR' \xrightarrow{60\text{–}100^\circ} R_2P(:O)F + R'F \tag{5}$$

When R′ originated from a secondary alcohol, formation of olefins was invariably observed to some extent. The expected C–F compounds were always formed when silyl ethers derived from unsaturated alcohols were allowed to react with tetra- or tri-fluorophosphoranes, but simultaneous polymerization of the olefinic compounds was found to occur.

It may be noted that in the reaction of alkyl esters of silicic acid, $Si(OR')_4$, with tetra- and tri-fluorophosphoranes, formation of C–F compounds also took place[3],

$$R_nPF_{5-n} + (R'O)_3SiOR' \rightarrow R_nP(:O)F_{3-n} + R'F + (R'O)_3SiF \tag{6}$$

Even under vigorous conditions, the reaction did not normally involve all four R′O groups of the silicate ester, and formation of SiF_4 occurred to a small extent only. Also, the side reaction,

$$RP(:O)F_2 + (R'O)_3SiOR' \rightarrow RP(:O)(F)(OR') + (R'O)_3SiF \tag{7}$$

was rather marked[3].

Consideration was given, finally, to the possibility of synthesising aromatic C–F compounds by the pyrolysis of a stable aryloxyfluorophosphorane[7] (eqn. 8 (a)),

$$PhPF_2(OPh)_2 \begin{array}{ll} \xrightarrow{?} PhF + PhP(:O)(F)(OPh) & \text{(8a)} \\ \xrightarrow{350^\circ} PhP(:O)F_2 + PhOPh & \text{(8b)} \end{array}$$

The reaction, however, was found to proceed in accord with eqn. 8(b), to the exclusion of reaction 8(a).

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