

Stable Monoalkoxyfluorophosphoranes

By DOMINIQUE U. ROBERT, GILLES N. FLATAU, CLAIRE DEMAY, and JEAN G. RIESS*

(Département de Chimie, Institut de Mathématiques et Sciences Physiques, Parc Valrose, 06034 Nice Cedex, France)

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.

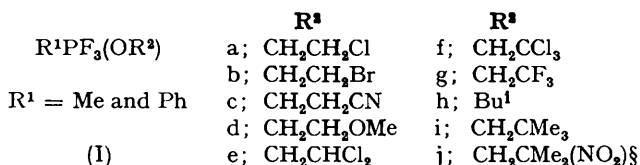
As yet, only a limited number of alkoxyfluorophosphoranes has been reported,¹ mostly as n.m.r.-detected unstable

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

† 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° .



products (>95%) of the cleavage reaction of the trimethylsilyl ether of the alcohols by a stoichiometric amount of both methyl- and phenyl-tetrafluorophosphorane (II), according to equation (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 [ΔG^\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 \pm 1, δF_e 67 \pm 1; for $R^1 = Ph$, δF_a 41 \pm 2, δF_e 66 \pm 1;

§ The corresponding alcohol was kindly supplied by Dr. H. Quast (Würzburg).

¹ (a) S. C. Peake, M. Fild, M. J. C. Hewson, and R. Schmutzler, *Inorg. Chem.*, 1971, **10**, 2723; (b) G. I. Drozd, V. V. Sheluchenko, and S. Z. Ivin, *Uspekhi Khim.*, 1970, **2**, 5; G. I. Drozd, S. Z. Ivin, and M. A. Sokalskii, *Zhur. obshchei. Khim.*, 1969, **39**, 1177; (c) D. H. Brown, K. D. Crosbie, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1969, 872; (d) L. Kolditz, K. Lehmann, W. Wieker, and A. R. Grimmer, *Z. anorg. Chem.*, 1968, **360**, 259.

² H. Koop and R. Schmutzler, *J. Fluorine Chem.*, 1971/72, **1**, 252; D. U. Robert and J. G. Riess, *Tetrahedron Letters*, 1972, 847.

³ D. E. Young and W. B. Fox, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1033.

⁴ I. L. Knunyants, V. V. Tyuleneva, E. Y. Pervova, and R. N. Sterlin, *Izvest. Akad. Nauk S.S.S.R.*, 1964, 1797.

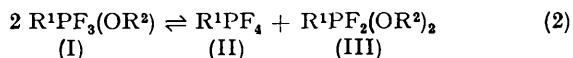
⁵ R. Schmutzler, *J. Chem. Soc.*, 1965, 5630; M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, *Zhur. strukt. Khim.*, 1967, **8**, 1097.

⁶ S. C. Peake and R. Schmutzler, *J. Chem. Soc. (A)*, 1970, 1049.

in both cases $J(P-F_a)$ 830 \pm 15, $J(P-F_e)$ 975 \pm 15, $J(F_a-F_e)$ 64 \pm 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



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

(Received, 24th July 1972; Com. 1271.)