Tetrahedron Letters No. 48, pp 4845 - 4848.
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0040-4039/78/1122-4845$02.00/0

EQUILIBRIUM BETWEEN THE COVALENT AND IONIC FORMS OF ALKOXYFLUOROPHOSPHORANES

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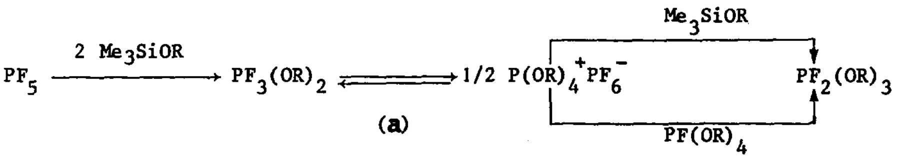
The alkoxyfluorophosphoranes, in contrast to some of their amino[1] and aryloxy[2] analogues, show little tendency to give ionic species[3]. In two cases, however, the ionic compounds $P(OR)_4^+PF_6^-$ where R = CH_3 or C_2H_5, were the only species observed both in the solid and in solution[4], and no evidence has so far been found to support the existence of an equilibrium between the covalent and ionic forms[2,4].

We now wish to report : 1) that the neutral covalent compounds $PF_3(OR)_2$ can be obtained and isolated at low temperatures in the cases of R = CH_2CCl_3 and CH_2CF_3; 2) the existence of an equilibrium between these and their ionic forms in CD_2Cl_2 solutions, and 3) some reactions in which the ionic compounds are reconverted into other covalent pentaco-ordinated phosphorus compounds of the $PF_{5-n}(OR)_n$ series in smooth conditions.

When PF_5 was allowed to react with two equivalents of Me_3SiOR (R = CH_2CCl_3 or CH_2CF_3) at temperatures below 0°, the neutral dialkoxytrifluorophosphoranes 1 were formed and, in the case of CH_2CF_3, isolated by distillation.



$$PF_5 \xrightarrow{2\,Me_3SiOR} PF_3(OR)_2 \underset{(a)}{\rightleftarrows} 1/2\ P(OR)_4^+PF_6^- \xrightarrow[PF(OR)_4]{Me_3SiOR} PF_2(OR)_3$$

1 2 3

(a : R = CH_2CCl_3 ; b : R = CH_2CF_3)

Their structures were established by low temperature ^1H, ^{19}F and ^{31}P NMR. The ^{31}P NMR spectra for example (fig. 1A) show at -70° the characteristic doublet of triplets due to the coupling of the phosphorus with the two apical and one equatorial fluorine atoms, as expected for a trigonal bipyramidal structure under slow exchange conditions. But at room temperature, after *ca* two hours these products converted quantitatively into crystalline compounds, which analysed

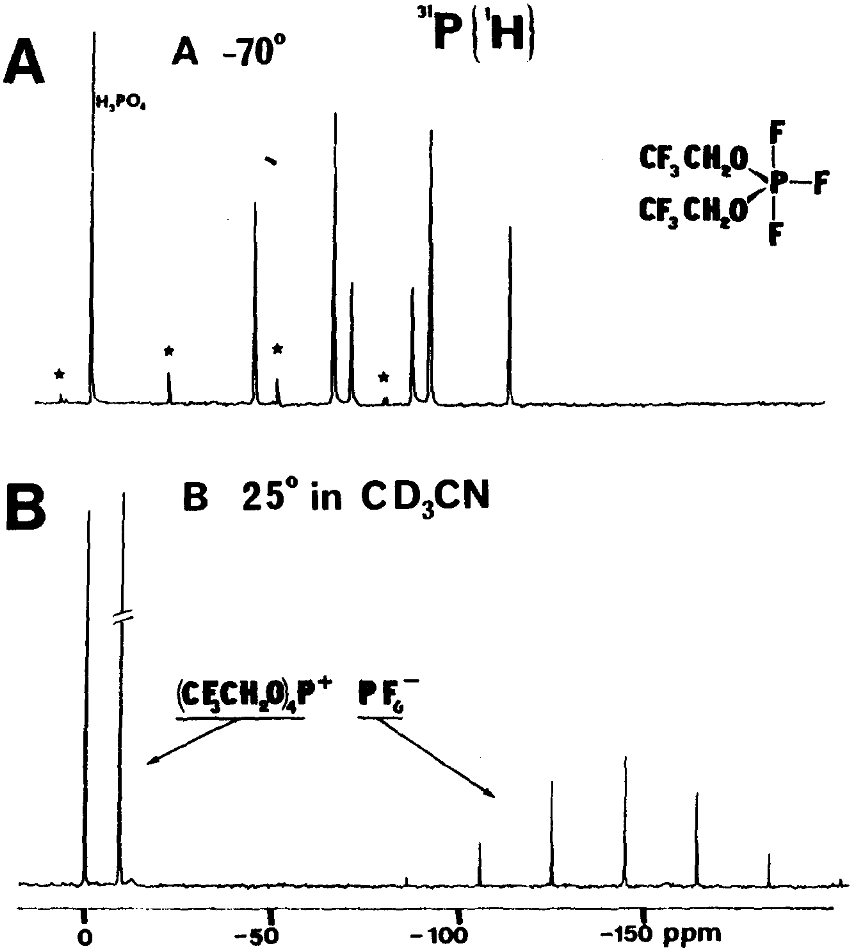


Fig. 1 : ^{1}H decoupled ^{31}P NMR spectra A) of neat $PF_3(OCH_2CCl_3)_2$ at -70°C; B) of the same sample after conversion to the ionic form and dissolution in CD_3CN (0.5 M) at 25°C.

as "$PF_2(OR)_3$" but differed from the initial products by their involatility and by the fact that they dissolved best in polar solvents such as acetonitrile. The PF_6^- anion was identified in their 0.5 M solutions in CD_3CN by its very characteristic septuplet (δ = -145 ppm, J = 715 Hz)^2; in the ^{31}P NMR spectra (fig. 1B); this is confirmed by the ^{19}F NMR data (δ = 72 ppm, J = 712 Hz). The cations exhibit a single phosphorus signal, sharp when decoupled from ^{1}H (at -9.8 ppm for R = CH_2CF_3, and -12.6 for R = CH_2CCl_3) (δ from H_3PO_4, CCl_3F and TMS).

While no other signals were detected (less than 2% of total peak intensity) in the CD_3CN solutions, the signals assigned to the covalent species $PF_3(OR)_2$ (40 mol%), $PF_4(OR)$ (16%) and $PF_2(OR)_3$ (18%) appeared and slowly developed in the ^{19}F NMR spectra next to those of the ionic species (27%), when the crystalline material 2a was dissolved in CD_2Cl_2 (0.13 mol) (fig. 2).

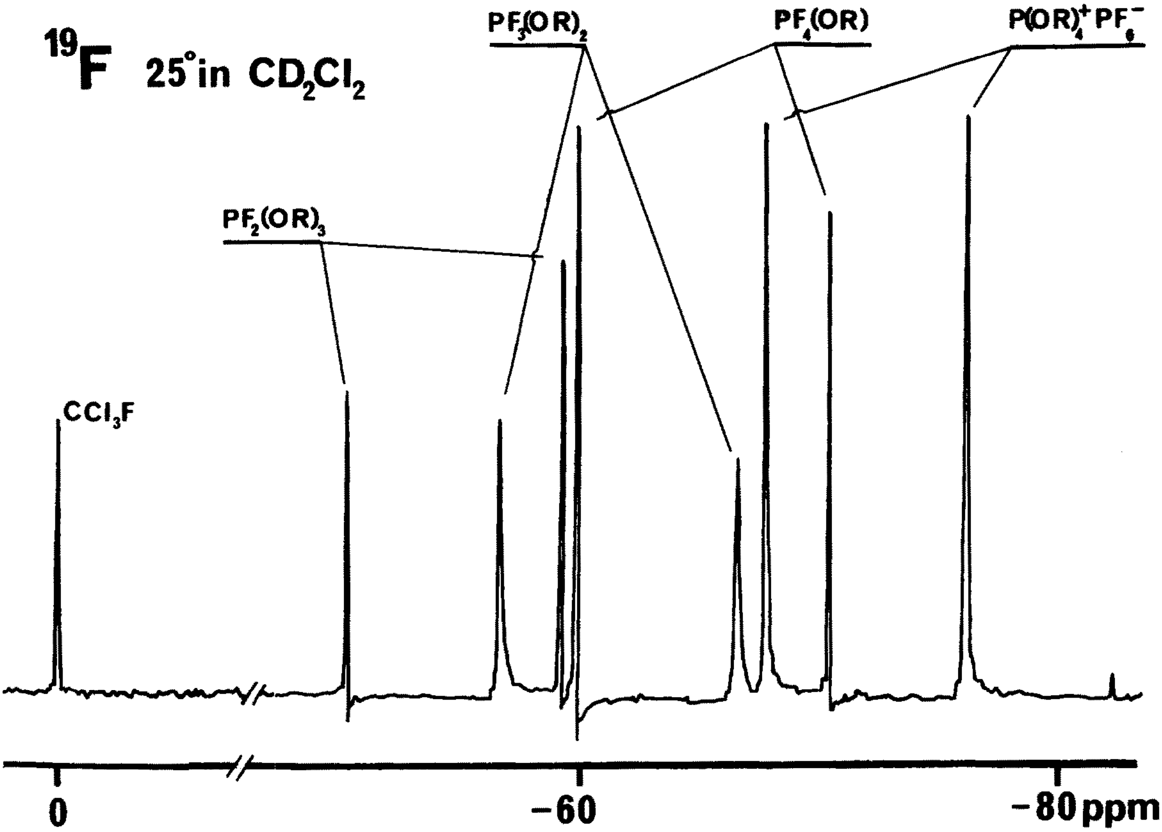


Fig. 2 : ^{19}F NMR spectra measured on a 0.13 mol solution of $P(OCH_2CCl_3)_4^+PF_6^-$ in CD_2Cl_2 at equilibrium at 25°C.

The equilibrium situation was reached after *ca* 15 hours at room temperature, and was characterized by the following constants (where the concentrations are expressed in $mol.l^{-1}$) :

$$K_a = [PF_3(OR)_2]^2/[P(OR)_4^+PF_6^-] = 12 \pm 1.3\ mol.l^{-1} \qquad \text{(derived from (a))}$$

$$K_b = [PF_4(OR)][PF_2(OR)_3]/[PF_3(OR)_2]^2 = 0.9 \pm 0.04$$

$$\text{(derived from } 2PF_3(OR)_2 \rightleftharpoons PF_2(OR)_3 + PF_4(OR) \qquad \text{(b))}$$

A comparable situation was observed with R = CH_2CF_3, but the lower solubility of 2b made the evaluation of meaningful equilibrium constants difficult.

The formation of ionic isomers was not detected for the other members of the $PF_{5-n}(OR)_n$ series. Thus, only the term which can give totally symmetrically substituted phosphorus anion and cation appears to display this behavior.

While the PF_6^- anion is generally reactivity-wise a dead-end, it was expected that, due to the existence of equilibrium (**a**), the ionic compounds $\underline{\underline{2}}$ could react and be reconverted into covalent pentaco-ordinated phosphorus compounds. Thus for example, when a new amount of Me_3SiOR was added to a solution of $\underline{\underline{2a}}$ in CD_2Cl_2, it could be converted into the covalent trialkoxydifluorophosphorane $\underline{\underline{3a}}$. When $\underline{\underline{2a}}$ was mixed in 2:1 ratio with $PF(OCH_2CCl_3)_4$[5] in CD_2Cl_2, the mixture was also quantitatively converted into the covalent $PF_2(OCH_2CCl_3)_3$ (as the only species detected after 24 hours at room temperature), which is the product normally expected from a redistribution of substituents between $PF_3(OR)_2$ and $PF(OR)_4$.

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(Received in UK 18 September 1978)