# Fluorophosphoranes: A New Synthesis. Diequatorial Four-membered Ring in a Difluorophosphorane

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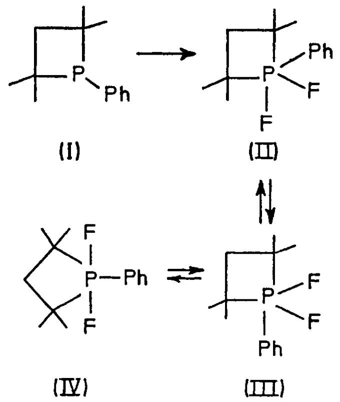
*Summary* Reactions of trisubstituted phosphines with bis(trifluoromethyl) peroxide and bis(trifluoromethyl) disulphide proceed rapidly at −78° to give difluorophosphoranes, one of which (II) exists as a slowly equilibrating mixture at low temperatures.

FLUOROPHOSPHORANES constitute one of the largest classes of pentasubstituted phosphorus compounds, and they have been very useful in studies of the chemistry and permutational isomerizations of pentaco-ordinate phosphorus compounds.[1]

We report that triphenylphosphine, tri-n-butylphosphine, and the phosphetan (I) react at −78° in methylene dichloride with bis(trifluoromethyl) peroxide and bis(trifluoromethyl) disulphide to give the appropriate difluorophosphoranes. The products from triphenyl- and tri-n-butyl-phosphine are known and the materials obtained in this study had the reported physical and spectral properties.[2] Quite pure products were obtained in high yield. In general, bis(trifluoromethyl) peroxide appears to give a somewhat cleaner product.

The product from (I) is assigned the structure of a difluorophosphorane by its method of preparation and its spectral properties. At room temperature the $^{1}$H n.m.r. spectrum (100 MHz) shows resonances at $\delta$ 1·35 (12H, d, $J_{\mathrm{PCCH}}$ 19·5 Hz, 4 equivalent Me), 1·68 (2H, d, $J_{\mathrm{PCCH}}$ 35 Hz, $CH_2$), and



(I) (II)

(IV) (III)

7·3—8·0 (5H, Ar-*H*). The $^{31}P$ n.m.r. spectrum at room temperature shows one broad absorption, 40 p.p.m. wide. The $^{19}F$ n.m.r. spectrum at ambient temperature shows a broad absorption at +50 p.p.m. relative to $CCl_3F$. The $^1H$ n.m.r. spectrum can arise if the phosphorane is undergoing permutational isomerization, *i.e.* pseudorotation. For example conversion of (II) into (III) and/or (IV) allows the hydrogen atoms of the methyl groups to become equivalent, as do the hydrogen atoms of the methylene group.[3] The broadness of the absorptions in the $^{31}P$ and $^{19}F$ n.m.r. spectra is probably due to coupling and coalescence of the absorptions of the permutational isomers.

The low-temperature spectra are particularly interesting. At *ca.* −100° the $^{31}P$ n.m.r. spectrum shows two triplets, one at −3 p.p.m. (relative to 85% $H_3PO_4$) ($J_{PF}$ 932 ± 10 Hz), and one at +30 p.p.m. ($J_{PF}$ 769 ± 10 Hz) in the ratio 2·3:1. The $^{19}F$ n.m.r. spectrum at *ca.* −95° shows two doublets, one at +36·3 p.p.m. ($J_{PF}$ 775 ± 10 Hz), and one at +63·5 p.p.m. ($J_{PF}$ 933 ± 10 Hz) in the ratio 1:2·4. The $^1H$ n.m.r. spectrum at −100° shows six absorptions in the methyl region. These are tentatively assigned as three doublets, $\delta$ 1·56 ($J_{POCH}$ 15·5 Hz), 1·47 ($J_{POCH}$ 25 Hz), and 1·14 p.p.m. ($J_{POCH}$ 22 Hz). The low-temperature n.m.r. spectra are uniquely satisfied if two conformers are present, (II) and (IV), which are interconverting slowly on the n.m.r. time scale; (II) must also be undergoing isomerization between the two equivalent forms in which the phenyl group remains in an equatorial position. These restrictions lead to a doublet for the methyl absorptions of (IV) and two doublets for the methyl absorptions of (II). The $^{19}F$ n.m.r. spectra support this conclusion and suggest that the minor component is (IV) and the major component is (II). In particular, $J_{PF}$ for the minor component is in the range of those reported for axial fluorine atoms and $J_{PF}$ for the major component is intermediate between axial and equatorial P–F coupling constants.[4]

Although the ring of (IV) must be more highly strained than that of (II) apical placing of the fluorine atoms helps to overcome the strain effect.[4,5] Other factors should not be discounted without further study.

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