Fluorine-19 Nuclear Magnetic Resonance Study of 2-Fluoro-2,2'-spiro-1,3,2-dioxaphosphole; a Trigonal-bipyramidal Molecule with a Single Equatorial Fluorine Atom

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Summary ^{19}F N.m.r. evidence is presented for the compound 2-fluoro-2,2'-spiro-1,3,2-dioxaphosphole having unusual stereochemistry, with the fluorine atom in an equatorial position.

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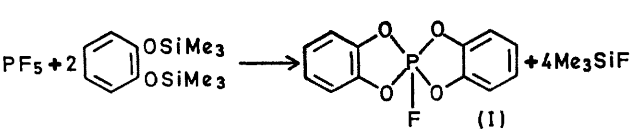
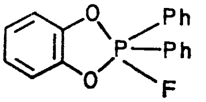
o-PHENYLENEDIOXYBIS(TRIMETHYLSILANE) has been found to react with fluorophosphoranes with the formation of trimethylfluorosilane and 1,3,2-dioxaphospholes. The fluorophosphoranes used in this study include phosphorus pentafluoride; alkyl- and aryl-tetrafluorophosphoranes; dialkyl-, diaryl-, and alkylaryl-trifluorophosphoranes; and trialkyl- and triaryl-difluorophosphoranes. The compound obtained from phosphorus pentafluoride was characterized by elemental analysis and n.m.r. spectroscopy as 2-fluoro-2,2'-spiro-1,3,2-benzodioxaphosphole (I). This same compound has been reported earlier by Evtikhov, Razumova, and Petrov, but the method of synthesis was not given nor are any n.m.r. results listed.[1] This compound is unique in that the ^{19}F n.m.r. values were consistent with the single fluorine atom being in the equatorial position of a trigonal bipyramid, thus, $J_{F-P} = 1018$ Hz; δ_F 70·4 p.p.m. from CCl_3F. These values are considerably higher than the coupling constants and chemical shift values of other monofluoro-derivatives of 1,3,2-dioxaphospholes obtained from dialkyl-, diaryl-,

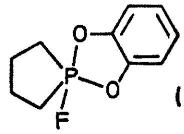


(I)

or alkylaryl-trifluorophosphoranes. For example, 2-fluoro-2,2′-diphenyl-1,3,2-dioxaphosphole (II) has J_{F-P} 797 Hz and δ_F 31 p.p.m. from CCl_3F. Such values are consistent with the fluorine being in an axial position. In the compound 5-fluorospiro(4,5-benzodioxaphole-5,5′-phospholane) (III), the n.m.r. data ($J_{F-P} = 829{\cdot}2$ Hz; $\delta_F = 21{\cdot}65$ p.p.m. from CCl_3F) indicate that the fluorine atom again occupies the axial position, which suggests that the phospholane ring is attached through two equatorial positions. There is ^{19}F n.m.r. evidence that the phospholane ring occupies two equatorial positions in 1,1,1-trifluoro-1,1-dihydrophospholane below −70°.[2]



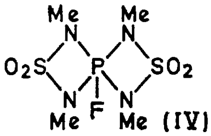
(II)



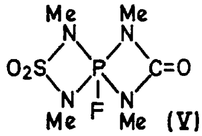
(III)

In compound (I) the steric requirements in each 1,3,2-dioxaphosphole ring are apparently such that one oxygen atom must occupy an axial and one an equatorial position, thus forcing the single fluorine atom into an equatorial position. This seems to be the first example of the most electronegative atom in a trigonal-bipyramidal molecule occupying an equatorial position, as predicted by Muetterties, Mahler, and Schmutzler,[2] who suggested that there may be cases of five-co-ordinate, trigonal bipyramidal systems in which the influence of the electronegativity of substituents such as fluorine may be outweighed by steric factors.

While our work was in progress Becke-Goehring and Weber[3] have reported synthesis and ^{19}F n.m.r. data for the compounds (IV) and (V).



(IV)



(V)

The magnitude of both ^{19}F chemical shifts and P–F coupling constants [δ_F $+88{\cdot}5$ p.p.m., J_{PF} 1035 Hz for (IV); δ_F $+102{\cdot}8$ p.p.m., J_{PF} 1038 Hz for (V)] suggest that in these cases a trigonal-bipyramidal structure with fluorine in an equatorial position may prevail in solution.

Further confirmation of the structures of our compounds (I) and (III) is being sought by an *X*-ray crystal structure determination.

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[1] Zh. L. Evtikhov, N. A. Razumova, and A. A. Petrov, *Doklady Akad. Nauk S.S.S.R.*, 1968, **181**, 1385.

[2] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

[3] M. Becke-Goehring and H. Weber, *Z. anorg. Chem.*, 1969, **365**, 185.