Asymmetry in Alkoxyfluorophosphoranes

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Summary The apical fluorine atoms are shown to be convenient, sensitive n.m.r. probes for investigating the stereochemistry of alkoxyfluorophosphoranes of types (I)—(IV) having 1, 2, or 3 identical or different fast-rotating asymmetric alkyl or alkoxy groups.

LITTLE attention has so far been paid to asymmetric fluorophosphoranes. The apical fluorine atoms are diastereotopic in bipyramidal five-co-ordinate phosphorus derivatives having three different substituents in the equatorial plane if one of them is asymmetric.[1] We report that these apical fluorine atoms are convenient sensitive probes for investigating the stereochemistry and isomerism in such structures by low temperature n.m.r. spectroscopy. Contrary to what is observed in the case of diastereotopic methylene protons, the nonequivalent apical fluorine atoms generally give well resolved first-order spectra (Figure). Taking advantage of this feature, we studied a series of alkoxyfluorophosphoranes containing 1, 2, or 3 identical or different asymmetric groups.

$R^1PF_3OR^2$ (I)

$PhEtPF_2(OCHMeCN)$ (II)

$PhPF_2(OCHMeCN)_2$ (III)

$PhPF(OCHMeCN)_3$ (IV)

Spectrum (a) is a typical low-temperature ^{19}F n.m.r. spectrum (low temperature spectra are necessary to prevent exchange of F_{eq} and F_{ax}) of an alkoxyfluorophosphorane of type $R^1PF_3OR_2$ (I) having no asymmetric substituents. It exhibits a doublet of doublets for the equivalent apical fluorine atoms [$\delta(F_{ax})$ 42·3 p.p.m., $J(PF_{ax})$ 824, $J(F_{ax}F_{eq}$ 64 Hz] and a doublet of triplets for the equatorial fluorine atom [$\delta(F_{eq})$ 65·4 p.p.m., $J(PF_{eq})$ 952 Hz] as expected for structure (I) if the rotation of the alkoxy-group around the P–O bond is rapid.

The introduction of an asymmetric R^2 group makes the apical ^{19}F atoms diastereotopic, *i.e.* they cannot be interchanged by a symmetry operation in any conformation. This results in their being non-equivalent in the n.m.r. spectra, as clearly shown in spectrum (b) [$\delta(F_{ax})$ 42·7, $\delta(F'_{ax})$ 44·8, $\delta(F_{eq})$ 67·6 p.p.m.; $J(PF_{ax})$ 840, $J(PF'_{ax})$ 847, $J(PF_{eq})$ 980, $J(F_{ax}F'_{ax})$ 11, $J(F_{ax}F_{eq}) = J(F'_{ax}F_{eq})$ 63 Hz]. Note that the equatorial fluorine atom signals remain unaffected.

The same type of pattern was observed for (I) with R^1 = Ph; R^2 = CHMeEt, CHMePr, CHMePr^i, $CHMeCH_2Cl$, $CHMeCH_2OMe$, $CHMeCH_2NO_2$, $CHMeCH_2CO_2Et$, CHMeCN, 2-chlorocyclohexyl, bornyl, and menthyl. With R^1 = Me; R^2 = CHMeEt, $CHMeCO_2Et$, an additional splitting [(*H*CP-*F*) *ca.* 9 Hz] is observed. The same non-equivalence of the apical fluorine atoms is observed when the equatorial fluorine is substituted by a group different from R^1, as for example in the compound $PhEtPF_2(OCHMeCN)$ (II) [$\delta(F_{ax})$ 34·4, $\delta(F_{ax})$ 44·6 p.p.m., $J(PF_{ax}) = J(PF'_{ax}) = 742$, $J(F_{ax}H) \simeq J(F_{ax}F'_{ax}) \simeq 10$ Hz].

The diastereotopy of the apical fluorine atoms may also be provoked by an asymmetric R^1 group, as for example in $Bu^sPF_3(OR^2)$ with $R^2 = CHMe_2$ [$\delta(F_{ax})$ 44·1, $\delta(F'_{ax})$ 45·3, $\delta(F_{eq})$ 69·2 p.p.m.; $J(PF_{ax})$ 875, $J(PF'_{ax})$ 882, $J(PF_{eq})$ 945, $J(F_{ax}F_{eq}) = J(F'_{ax}F_{eq}) = 70$, $J(F_{ax}F_{ax})$ 14 Hz] or $R^2 = CHCCl_3$ [$\delta(F_{ax})$ 42·2, $\delta(F'_{ax})$ 43·4, $\delta(F_{eq})$ 71·5 p.p.m.; $J(PF_{ax} = J(PF'_{ax}) = 1176$, $J(F'_{ax}F_{eq}) = J(F'_{ax}F_{eq}) = 70$, $J(F_{ax}F'_{ax})$ 14 Hz]. The coupling due to the tertiary Bu^s proton is also detected [$J(F_{ax}H)$ *ca.* 14 Hz].

When two different asymmetric centres are present in (I), two pairs of diastereoisomers can form (1)[1] and (2), both of which have diastereotopic apical fluorine atoms. This expectation was borne out, as shown in Figure (c), by the presence of two sets of signals, of equal area, in the apical fluorine atom region [R^1 = Bu^s, R^2 = $CHMeCO_2Et$; superscripts 1 and 2 refer to the diastereoisomers (1) and (2): $\delta(F_{ax}^1)$ 38·8, $\delta(F'^1_{ax})$ 41·65, $\delta(F_{ax}^2)$ 48·65, $\delta(F'^2_{ax})$ 49·8, $\delta(F_{eq})$ 71·5 p.p.m.; $J(PF_{ax}^1)$ 886, $J(PF'^1_{ax})$ 875, $J(PF_{ax}^2) = J(PF'^2_{ax}) = 889$, $J(PF_{eq}) = 1036$, $J(F_{ax}F_{eq})$ 70, $J(F_{ax}F'_{ax})$ 14 Hz]. The difference in chemical shifts for the two diastereoisomers is notable and further depends on the nature of R^2 [CHMeCN: ($\delta F_{ax}^1 - \delta(F_{ax}^2)$ = 1·4, CHMeEt 2·5, $CHMeCH_2Cl$ 3·3, $CHMeCO_2Et$ 9·5 p.p.m.] This again illustrates the sensitivity of the apical fluorine atoms as stereochemical probes, while, on the contrary, the equatorial fluorine signal was neither resolved nor significantly shifted in these experiments. Likewise the low-temperature ^{31}P n.m.r. spectrum appeared to be of little use for this purpose.

When two identical asymmetric R^2 groups are present as in compound $PhPF_2(OCHMeCN)_2$ (III), two sets of signals of equal overall area are again observed for the fluorines. One of them, which consists of two doublets [$\delta(F_{ax})$ = 38·9, $\delta(F'_{ax})$ = 39·5 p.p.m., $J(PF_{ax}) = J(PF'_{ax}) = 803$ Hz] of doublets [$J(F_{ax}F'_{ax})$ 11 Hz], is assigned to the *RS meso* isomer in which the fluorine atoms are nevertheless inequivalent. The other, which reduces to simply one doublet [$\delta(F_{ax})$ 39·4 p.p.m., $J(PF_{ax})$ 803 Hz], is consistent with the existence of the pair of enantiomers (*RR* and *SS*) in each of which the two F atoms experience identical environments. Note that the presence of a unique signal for (III) (*RR* + *SS*) further implies that the rotation of the alkoxy-groups is rapid. In the absence of asymmetric groups (R^1 = Ph; R^2 = Et, CH_2CCl_3, $CH_2CMe_2NO_2$) a single doublet is observed even with the most bulky substituents.

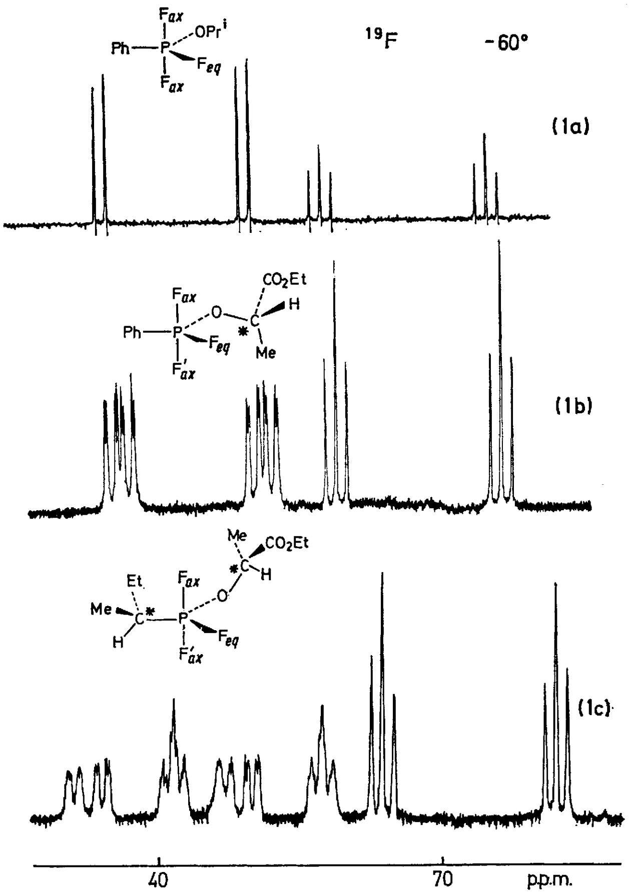

FIGURE. Comparative low-temperature ^{19}F n.m.r. spectra of alkoxyfluorophosphoranes having 0, 1, and 2 asymmetric groups (*ca.* 0·5M in CH_2Cl_2, ref. CCl_3F).

If Ph is replaced by Bu^s in (III) the former *meso* isomer now becomes a pair of enantiomers whose spectra consequently consist of the same pattern as above [$\delta(F_{ax})$ 37·25, $\delta(F'_{ax})$ 37·75 p.p.m., $J(PF_{ax}) = J(PF'_{ax}) = 858$, $J(F_{ax}F_{ax})$ 15 Hz], while the former pair of enantiomers gives place to two pairs of diastereoisomers, each of which gives a single doublet for its apical fluorine atoms [$\delta(F_{ax}^1)$ 37·15, $\delta(F_{ax}^2)$ 37·40 p.p.m., $J(PF_{ax}^1) = J(PF_{ax}^2) = 858$ Hz].

In $PhPF(OCHMeCN)_3$ (IV) one of the asymmetric alkoxy-groups occupies an apical site. The ^{19}F spectra exhibits two doublets [$\delta(F^1)$ 34·25, $\delta(F^2)$ 34·35 p.p.m., $J(PF)$ 800 Hz]. The difference in chemical shifts is comparable to that found for the two diastereoisomers of compound (III), which could mean that the fluorine atom is insensitive to the configuration of the apical alkoxy-group and does not distinguish the diastereoisomers which result from the presence of this group.

Finally, all the observed splitting patterns could be interpreted as originating in asymmetry, while no evidence was ever found for hindered rotation about the P–C or P–O bonds[1,2] in the temperature domain accessible to measurements (−100 to −30°). Bu^sPF_4 [b.p. 76° at 760 mmHg; $\delta(P)$ 31·0 p.p.m.; $\delta(F)$ 55·12 p.p.m.; $J(PF)$ 994 Hz] and $PhEtPF_3$ [b.p. 70° at 9 mmHg; $\delta(P)$ 15·3 p.p.m.; $\delta(F_{ax})$ 31·7; $\delta(F_{eq})$ 85·2 p.p.m.; $J(PF_{ax})$ 818, $J(PF_{eq})$ 958, $J(F_{ax}F_{eq})$ 34, $J(F_{ax}H) = 11$ Hz] were prepared by fluorination of the chlorophosphines with SbF_3. The alkoxyfluorophosphoranes (I)—(IV) were obtained by reaction of the desired fluorophosphoranes with the alkoxytrimethyl silanes.[3–5]

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