^{18}O Isotopic Shifts in the ^{31}P N.M.R. Spectra of Five-co-ordinate Oxyphosphoranes

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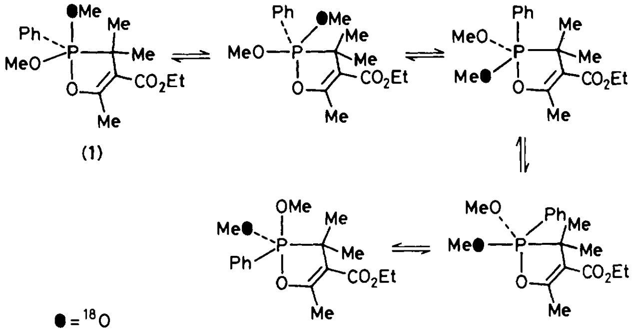
Apical and equatorial ^{18}O produce different isotopic shifts in the ^{31}P n.m.r. spectra of oxyphosphoranes; this difference can be used to follow permutational isomerisation by means of variable temperature ^{31}P n.m.r. spectroscopy.

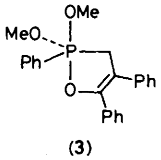
Replacement of the ^{16}O of a PO bond by ^{18}O produces an upfield isotopic shift in the ^{31}P n.m.r. spectrum which, in a given phosphoryl compound, is greater for a $P^{18}O$ double bond than for a $P^{18}O$ single bond.[1] This distinction has served as the basis of a number of stereochemical investigations of substitutions at phosphoryl centres.[2] We now show that, in five co-ordinate trigonal-bipyramidal phosphoranes, different isotopic shifts are produced by apical and equatorial $P^{18}O$ single bonds and that this difference can be used to follow permutational isomerisation in these compounds by means of variable temperature ^{31}P n.m.r. spectroscopy.

Dimethyl phenylphosphonite, $PhP(OMe)_2$, was prepared using methanol containing 50% of ^{18}O.[3] Its ^{31}P n.m.r. spectrum† shows three peaks in the ratio 1:2:1 with an isotopic shift due to a single $P^{18}O$ bond of 11.2 Hz. The adduct[4] with ethyl isopropylideneacetoacetate shows in its ^{31}P n.m.r. spectrum at 0 °C four peaks of equal intensity with shifts, relative to the lowest field, of 4.3, 6.5, and 10.8 Hz. The lowest and highest field peaks are due to unlabelled and doubly labelled adduct respectively; the central peaks are due to adduct having a single ^{18}O either apical (**1**) or equatorial (**2**). These central peaks coalesce at 19 °C leading to ΔG^* for the pseudorotation process (**1**) $\rightleftharpoons$ (**2**) of 16.1 kcal mol^{-1} (1 cal = 4.184 J) in agreement with that deduced from variable temperature ^{1}H n.m.r. spectroscopy.[4] Similarly the adduct (**3**) of the above labelled phenylphosphonite with methylenedeoxybenzoin shows, in its ^{31}P n.m.r. spectrum at room temperature, three peaks in the ratio of 1:2:1. Pseudorota-



(1)

(2)



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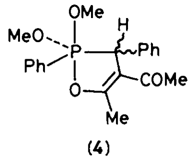

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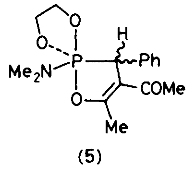

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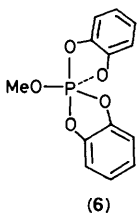

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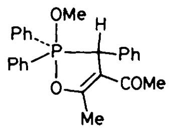

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† All ^{31}P n.m.r. spectra were determined at 162 MHz (^{1}H decoupled).

tion to equilibrate apically and equatorially labelled phosphoranes is rapid on the n.m.r. time scale under these conditions. However, at −90 °C, when this pseudorotation is slow, the central peak is split into two with $\Delta\delta$ 1.7 Hz; the isotopic shifts of equatorial and apical ^{18}O in this phosphorane are 5.3 and 7.0 Hz, although not necessarily in that order. The corresponding isotopic shifts in the two geometrical isomers of the phosphorane (**4**)[5] are 3.7 and 6.8 Hz (low-field isomer) and 4.5 and 6.4 Hz (high-field isomer).

The size of isotopic shifts produced on ^{13}C nuclei decreases with an increase in the s character of the ^{13}C orbital bonding to the isotope.[6] If this is so with ^{31}P nuclei, and the large shift observed in $PhP(OMe)_2$ supports this, then the larger isotopic shifts in the above phosphoranes are due to apical ^{18}O. Most trigonal-bipyramidal phosphoranes are distorted along the Berry pseudorotation pathway towards square-pyramidal geometry[7] and this would be expected to affect isotopic shifts. The shifts in the two isomers of the phosphorane (**5**), prepared from ethylene glycol labelled in one position with 50% ^{18}O,‡ of 3.6 and 4.2 Hz (low-field isomer) and 3.5 and 4.9 Hz (high-field isomer) would then be consistent with distortion towards the square pyramids with axial dimethylamino groups, this distortion decreasing the difference between apical and equatorial positions. It may ultimately be possible to correlate isotopic shifts with geometry within a given type of phosphorane. The isotopic shifts of 4.2 Hz in (**6**), which has an equatorial methoxy, and of 3.6 Hz in (**7**), which has an apical methoxy group, show that, if in a given phosphorane apical ^{18}O produces the greater isotopic shift, then in different phosphoranes the ranges of apical and equatorial shifts overlap.

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References

1 G. Lowe, B. V. L. Potter, B. S. Sproat, and W. B. Hull, *J. Chem. Soc., Chem. Commun.*, 1979, 733.
2 G. Lowe, *Acc. Chem. Res.*, 1983, **16**, 244; S. Trippett and C. L. White, *J. Chem. Soc., Chem. Commun.*, 1984, 251.
3 C. B. Sawyer, *J. Org. Chem.*, 1972, **37**, 4225.
4 D. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, 1970, **92**, 634.
5 F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *J. Am. Chem. Soc.*, 1968, **90**, 1275.
6 H. Batiz-Hernandez and R. A. Bernheim, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1967, **3**, 63; J. M. Risley and R. L. Van Etten, *J. Am. Chem. Soc.*, 1980, **102**, 4609.
7 R. R. Holmes, *Acc. Chem. Res.*, 1979, **12**, 257.

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‡ Prepared from ethylene glycol and $H_2{}^{18}O$ in the presence of CF_3SO_3H at 0 °C and purified by preparative g.l.c. (Peg 4, 180 °C).