Stereospecificity of Two-bond Carbon-13 Coupling with Phosphorus-31 in Some Cyclic Phosphines

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Summary The ^{13}C–^{31}P coupling constant is *ca.* 30 Hz for a *trans* 2-Me group in a 1-substituted Δ^3-phospholene and is negligible in the *cis*-isomer; the corresponding isomeric oxides show no appreciable differences in $^2J_{PCC}$.

^{1}H NUCLEAR MAGNETIC RESONANCE spectroscopy has been widely used in stereochemical studies of cyclic phosphines and their oxides, but the value of pulse Fourier transform ^{13}C n.m.r. measurements in such studies remains to be fully appreciated. We present evidence here that clearly shows a dependence of both ^{13}C chemical shifts and ^{13}C–^{31}P coupling constants on structural parameters in phosphines† of the phospholene family, and that points out real utility in this technique for making structural assignments to certain types of *cis,trans*-isomers.

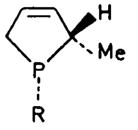
The *cis* (Ia) and *trans* (Ib) isomers of 1,2-dimethyl-Δ^3-phospholene[1] gave distinctly different ^{13}C n.m.r. spectra.‡ Consistent with observations in carbocyclic systems,[2] the more crowded *cis*-isomer possessed signals for *P*-Me (186·5 p.p.m.) and 2-Me (180·1 p.p.m.) upfield relative to the *trans*-isomer (180·1 and 173·1 p.p.m., respectively). More striking, however, was the difference in coupling between phosphorus and carbon of the 2-Me group. The 2-Me signal for the *cis*-isomer was a singlet, while that for the *trans*-isomer was a doublet, J_{PCC} 32 Hz. This coupling constant appears to be the largest yet reported for P–C coupling in any phosphine.

cis-Compound (IIIa)§ also gave a singlet (178·0 p.p.m.) for the methyl carbon atoms while the *trans*-isomer (IIIb) gave a doublet (170·8 p.p.m.; *J* 30 Hz), and that isomer of 2-methyl-1-phenyl-Δ^3-phospholene known[1] to be *cis* (II) gave a singlet for its methyl carbon at 178·0 p.p.m.

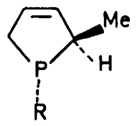
The coupling effect is clearly to be associated with the trivalent state of phosphorus; use of the lone pair in oxide formation results not only in greatly diminished coupling with the 2-methyl carbon, but also in nearly equal values of J_{PCC} in an isomeric pair [*cf.* Me in (IVa) 182·1 p.p.m. *J* 5·0 Hz, with (IVb), 178·8 p.p.m., *J* 4·0 Hz]. One-bond ^{31}P–^{13}C coupling in the phospholene oxides, however, is much greater than that in the corresponding phosphines [Me doublet in (Ia) oxide at 183·6 p.p.m., *J* 63·0 Hz; in (Ib) oxide, 179·4 p.p.m., *J* 61·5 Hz].

Further examination of the P–Me chemical shift values reveals that relief of steric crowding in a phosphine has a more pronounced deshielding effect than does a change in oxidation state of phosphorus [(Ia) *vs.* (Ib), −6·4 p.p.m.; (Ia) *vs.* its oxide, −2·9 p.p.m.; (Ib) *vs.* its oxide, −0·7 p.p.m.].

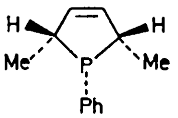
In a study of some four-membered cyclic phosphine oxides, Gray and Cremer[3] pointed out that one-bond ^{13}C–^{31}P coupling constants differed by several Hz for a pair of *cis,trans*-isomers. This unusual effect was not observed in their study or in the present one for the isomeric 1,2,5-trimethyl-Δ^3-phospholene oxides. We have found, however, that differences in $^1J_{PC}$ do prevail among isomeric phosphines in the phospholene series; for P–Me of (Ia), J_{PC} is 21·5 Hz, while in (Ib) J_{PC} is 17·5 Hz.



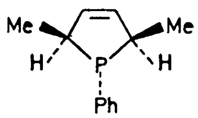
(Ia; R = Me)
(II; R = Ph)



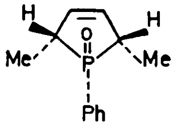
(Ib, R = Me)



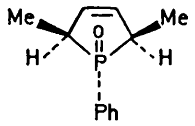
(IIIa)



(IIIb)



(IVa)



(IVb)

While our observation of strong steric control of $^2J_{P-C}$ is unique, stereospecificity in $^2J_{PH}$ for geminal ring protons[4] [as well as for $^3J_{PH}$ in C(2)–methyl protons[3]] has been observed among phospholenes. The orientation of the substituent on phosphorus (and hence of the lone-pair orbital on phosphorus) relative to the substituting atom (H or C) on the adjacent carbon is therefore important in defining the size of the phosphorus coupling; the direction of the effect is the same for both ^{1}H and ^{13}C, and is a useful device for structure assignment.

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† We know of only one other report on the ^{13}C spectrum of a cyclic phosphine (1-phenyl-4,4-dimethoxyphosphorinan; A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, jun., and L. D. Quin, *Chem. Comm.*, 1971, 1020). *Added in proof:* G. A. Grey and S. E. Cremer (*J.C.S. Chem. Comm.*, 1972, 367) have now reported ^{13}C values for some phosphetans, where a steric control of $^2J_{PC}$ is also observed.

‡ Proton noise-decoupled ^{13}C n.m.r. spectra were obtained at 22·62 MHz with a Bruker HFX-10 spectrometer for $CHCl_3$ solutions with C_6F_6 in a 3 mm coaxial capillary as an external heteronuclear lock. The Fourier transform of an ensemble average of several thousand scans (100 μs per point, with 4096 points per scan) was calculated. Chemical shift values are upfield relative to CS_2 [δ (CS_2) = 115·2 + δ ($CHCl_3$)] and are accurate to ±0·1 p.p.m. Coupling constants (±1·2 Hz) with ^{31}P are given in parentheses. Samples of (Ia), (Ib), (II), (IIIb), and (IVb) were of isomeric purity greater than 90%. The samples of (IIIa) and of (IVa) contained 27% of the *trans*-isomer.

§ Preparations and stereochemical assignments were similar to procedures used previously.[1]

[1] L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.*, 1970, **92**, 4303.
[2] A. S. Perlin and H. J. Koch, *Canad. J. Chem.*, 1970, **48**, 2639.
[3] G. A. Gray and S. E. Cremer, *Tetrahedron Letters*, 1971, 3061.
[4] J. P. Albrand, D. Gagnaire, M. Picard, and J. B. Robert, *Tetrahedron Letters*, 1970, 4593.