^{13}C Nuclear Magnetic Resonance of Organophosphorus Compounds: Dihedral Dependence of the $^2J_{PCC}$ Spin Coupling in Four-membered Cyclic Phosphines

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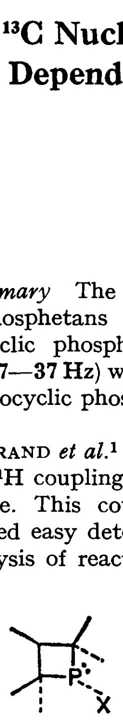
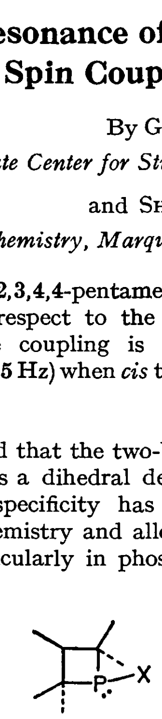
Summary The α-methyl $^2J_{PCC}$ in 2,2,3,4,4-pentamethylphosphetans is stereospecific with respect to the exocyclic phosphorus substituent; the coupling is large (27—37 Hz) when *trans* and small (0—5 Hz) when *cis* to the exocyclic phosphorus substituent.

ALBRAND *et al.*[1] have previously showed that the two-bond ^{31}P–^{1}H coupling in phosphines exhibits a dihedral dependence. This coupling-constant stereospecificity has permitted easy determination of stereochemistry and allowed analysis of reaction mechanisms, particularly in phosphetans. We have noted a similar stereospecificity in the methyl $^2J_{PCC}$ in (Ia—c) and (IIa—c).



(I)

a : X = Ph
b : X = Me
c : X = Cl



(II)

The data are given in the Table and were obtained from high-resolution 25·1 MHz ^{13}C natural abundance spectra using an HA-100 with noise-decoupling and time-averaging. Full details will be provided in a subsequent publication. The α-methyls were assigned on the basis of intensity and upfield shift of axial with respect to equatorial methyls in cyclic systems.[2]

There is a possibility that a sign reversal may occur as a function of the dihedral angle, as shown by Albrand *et al.*[1] However, the couplings are different by an order of magnitude in size so that a knowledge of the coupling sign is not critical for obtaining stereochemical orientation to the exocyclic phosphorus substituent. This can be extended to singly substituted α-carbon atoms. *E.g.*, in 2,2,3,3,-4-pentamethyl-1-phenylphosphetan the 4-methyl has a $^2J_{PCC}$ of 19·4 Hz, suggesting a *trans*-relationship to the phenyl substituent. *X*-Ray studies[3] of its stereochemically related[4] oxide bear out this orientation; ^{1}H n.m.r. studies are also in agreement with this stereo-chemical assignment.[4]

TABLE. $^2J_{PCC}$ *in 2,2,3,4,4-pentamethylphosphetans* ($\pm 0{\cdot}1$ Hz)c

Methyl Orientation	Isomer (I) Axial	Isomer (I) Equatorial	Isomer (II) Axial	Isomer (II) Equatorial
a: X=Ph ..	31·8	2·5	4·9	27·8
b: X=Me ..	30·5	2·1	4·3	26·9
c: X=Cl ..	37·1	0·0	2·5	33·5

Stereospecificities in coupling data such as this, not only have great theoretical value in exploring the nature of bonding, but also in filling the very practical need for reliable techniques in structure assignment. The stereospecificity noted for $^2J_{PCC}$ will prove especially useful in cases where the $^2J_{PCH}$ is difficult to obtain from complicated ^{1}H spectra.

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