Long-range Phosphorus–Hydrogen Spin–Spin Coupling in the N.m.r. Spectra of Some Conjugated Triphenylphosphonium Halides. Some Further Evidence for Hyperconjugation

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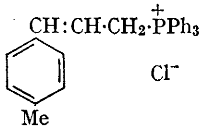
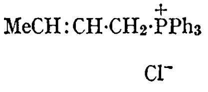
WE have recently reported[1] the n.m.r. spectra of *p*-, *o*-, and *m*-methylbenzyltriphenylphosphonium bromides and the observed order of the variation of the long-range coupling constants, $|J_{\text{P-}p\text{-CH}_3}| > |J_{\text{P-}o\text{-CH}_3}| > |J_{\text{P-}m\text{-CH}_3}|$ has been rationalised in terms of the magnitude of the induced positive charge at the three aromatic positions to which the methyl groups are attached. In this Communication we report some details concerning the n.m.r. spectra of *p*-methylcinnamyltriphenylphosphonium chloride (I) and γ-methylallyltriphenylphosphonium chloride (II) which appear to establish our previous interpretation of these effects with greater certainty. The compounds (I) and (II) were prepared by treating the appropriate chloride with an equivalent amount of triphenylphosphine either in acetone or in ethanol-free chloroform. These phosphonium salts were analysed for C, H, and ionic Cl and the analyses are in good agreement with the formulae.



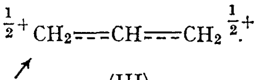
(I)



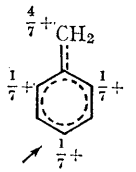
$\text{MeCH:CH·CH}_2\cdot\overset{+}{\text{P}}\text{Ph}_3\ \text{Cl}^-$

(II)

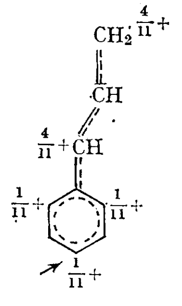
The approximate charge distributions calculated from the HMO theory for the allyl, benzyl, and cinnamyl carbonium ions are shown below (III, IV and V):—



(III)



(IV)



(V)

and hence the relative amounts of positive charge induced by the positive phosphorus atom at the positions to which the methyl group is attached (denoted by an arrow) will be in the ratio, allyl: benzyl: cinnamyl:: 5·50:1·57:1. The observed ^{31}P–^{1}H coupling constants are in the ratio, allyl:

benzyl: cinnamyl::15 : 6·5 : 1, *i.e.*, in the same order. The absolute values of the observed coupling constants are: $|J_{P-CH_3}|$ (I) = 0·40 ± 0·1 c./sec. in $CDCl_3$ ($\tau = 7{\cdot}73$ p.p.m.) and $|J_{P-CH_3}|$ (II) = 6·0 ± 0·2 c./sec. ($\tau = 8{\cdot}38$ p.p.m.) in the same solvent. The data for the *p*-methylbenzyl compound are given in ref. 1.

The observation that $|J_{P-o-CH_3}| < |J_{P-p-CH_3}|$ in the benzyl compounds[1] suggests that the distance between the methyl group and the phosphorus atom is a second-order effect, and that the change in bond order (sp^3–$sp^2 \rightarrow sp^2$–sp^2) of the bond between the methyl group (sp^3) and the ring or unsaturated carbon atom (sp^2) is the dominating factor which influences the magnitude of the coupling constant. This means that the interaction of the methyl group hydrogen spins with the phosphorus spin takes place *via* a π-electron cloud which extends from the methyl group to the phosphorus atom. Such a description of the interaction [over nine bonds in the case of (I)] essentially involves hyperconjugation between the methyl group and the rest of the molecule.

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[1] K. Khaleeluddin and J. M. W. Scott, *Chem. and Ind.*, 1966, 1034.