

Preliminary communication

HYPERCONJUGATION AND HOMOCONJUGATION IN ALKYL RADICALS BEARING β -PHOSPHORUS SUBSTITUENTS

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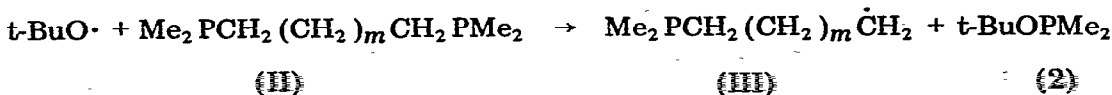
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Summary

The isotropic ^{31}P hyperfine splitting constants derived from the ESR spectra of a series of β -phosphorus-substituted alkyl radicals are in the order expected for hyperconjugative spin transmission.

There has been much discussion [1] concerning the mechanism of interaction between a β -substituent, MX_n , and the unpaired electron in alkyl radicals of the type $\text{X}_n\text{MCH}_2\dot{\text{C}}\text{R}_2$. Whilst it appears likely that the hyperfine splitting (hfs) from phosphorus(V), detected in the ESR spectra of radicals of the type $\equiv\text{PV}-\text{CH}_2\dot{\text{C}}\text{R}_2$, is predominantly hyperconjugative in origin [2], it has been suggested that $p_\pi-p_\pi$ homoconjugation, involving the lone-pair on phosphorus and the 2 p -electron on carbon, is responsible for the large ^{31}P -hfs (251 G) reported [2,3] for the radical $\text{Et}_2\text{PCH}_2\dot{\text{C}}\text{H}_2$.

We report here a preliminary study of a series of β -phosphorus-substituted alkyl radicals and related species in solution, which supports the view that hyperconjugation is mainly responsible for the detected ^{31}P -hfs, regardless of whether the oxidation state of the phosphorus atom is three or five. The radicals were generated photochemically in the cavity of an ESR spectrometer, either by addition of the appropriate phosphorus-centred radical to an alkene [4] (eq. 1) or by displacement [5a] from phosphorus(III) in a diphosphine of the type (II; $m = 0-2$) (eq. 2). The spectroscopic parameters are listed in Table 1.



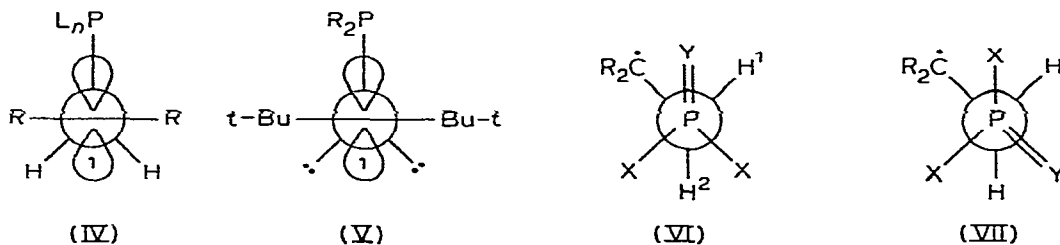
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TABLE 1
ESR PARAMETERS FOR β -PHOSPHORUS ALKYL RADICALS IN CYCLOPROPANE

Radical	Source ^a	T(°C)	Hyperfine splittings (G)			
			$a(P)$	$a(H_\alpha)$	$a(H_\beta)$	Others
$Me_2PCH_2\dot{C}H_2$ ^b	A, B	-5	45.5	20.5	17.5	
	A, B	-66	46.9	20.5	16.1	
$Me_2PCH_2\dot{C}Me_2$	B	-51	54.5		13.0	22.0(6H)
$Me_2PO\dot{C}-t-Bu_2$	C	-115	45.9			0.3(18H)
$Et_2PO\dot{C}-t-Bu_2$	C	-125	41.5			0.3(18H)
$(OCH_2CMe_2O)_2PCH_2\dot{C}-t-Bu_2$	B	-25	127.3		13.3	0.6(18H)
	B	-75	127.5		13.2	0.6(18H)
$(EtO)_2P(O)CH_2\dot{C}H_2$	B	-46	84.3	21.3	18.8	
	B	-112	89.5	21.2	17.0	
$(EtO)_2P(O)CH_2\dot{C}Me_2$	B	-21	104.6		13.9	22.6(6H)
	B	-60	105.8		13.8	22.4(6H)
$(EtO)_2P(O)CH_2\dot{C}-t-Bu_2$	B	+20	106.5		13.7	0.4(18H)
	B	-116	109.5		13.7	0.4(18H)
$(Me_2N)_2P(O)CH_2\dot{C}H_2$	B	-75	79.0	21.2	18.5	
$(Me_2N)_2P(O)CH_2\dot{C}-t-Bu_2$	B	-75	94.0		14.0	0.5(18H)
$Et_2P(O)CH_2\dot{C}H_2$	B	-90	77.0	21.4	17.0	
$Et_2P(O)CH_2\dot{C}-t-Bu_2$	B	-95	77.5		14.4	0.5(18H)
$Me_2PCH_2CH_2\dot{C}H_2$	A	-60	1.6	22.0	28.0	0.75(2H)
$Me_2PCH_2CH_2CH_2\dot{C}H_2$	A	-70	1.5	22.0	28.5	0.7(2H)

^a A = Photolysis of *t*-Bu OOBu-*t* in the presence of $Me_2PCH_2(CH_2)_mCH_2PMe_2$; B = Photolysis of *t*-Bu OOBu-*t* in the presence of L_nPH or $(EtO)_2POP(OEt)_2$ and $H_2C=CR_2$; C = Photolysis of *t*-Bu₂C=O in the presence of R_2PPR_2 . ^b $g = 2.0026$.

The magnitude and temperature dependence of $a(H_\beta)$ for the β -substituted radicals indicates [1] that the most stable conformation is that shown in IV.



The magnitude of $a(P_\beta)$ increases and that of $a(H_\beta)$ decreases with the bulk of R and with decreasing temperature. For (I; R = Me) and, particularly, (I; R = *t*-Bu) the coupling constants are almost independent of temperature, and the only conformation which is significantly populated appears to be IV. For similar steric reasons, the "eclipsed" conformation V would be adopted by the dialkylphosphinyl radical adducts of di-*t*-butyl ketone (see Table 1). The most stable conformation about the $\beta C-P$ bond is more difficult to ascertain, but the small temperature dependence of $a(P_\beta)$ for (I; R = *t*-Bu) indicates that, for these radicals, different rotamers exhibit similar phosphorus splittings, and/or the relative rotamer populations are not influenced by temperature changes within the range studied. The most stable conformation is probably

VI or VII, where $Y = O$ or a lone-pair. Many of the ESR spectra exhibited selective broadening of the central component of the β -hydrogen triplet at low temperatures, which may be attributable to exchange of H^1 and H^2 in VI.

The variation of $a(P_\beta)$ with the nature of the β -substituent is consistent with a hyperconjugative mechanism of spin-transmission, in which the degree of delocalisation into the $\beta C-P$ bond remains roughly constant, for given α -substituents. Changes in $a(P_\beta)$ reflect changes in the P-3s character of the $\beta C-P$ bond. Thus, there is a decrease in $a(P_\beta)$ for (IV; $R = t\text{-Bu}$ or Me) on going along the series $L_n P = (\overline{OCH_2 CMe_2 O})_2 P > (\text{EtO})_2 P(O) > (\text{Me}_2 N)_2 P(O) > \text{Et}_2 P(O) > \text{Me}_2 P$, in line with the decrease in $^1J(\text{PH})$ for the compounds $L_n P-H$, and in $a(P)$ for the radicals $L_n P\cdot$ [6]. For the phosphorus(V) substituted radicals (I; $R = t\text{-Bu}$), a plot of $a(P_\beta)$ against $^1J(\text{PH})$ gives a good straight line.

The low value of $a(P_\beta)$ which we find for $R_2 PCH_2 \dot{C}H_2$ in solution makes it unnecessary to propose any large homoconjugative contribution to the coupling. The reason for the very large phosphorus splitting obtained for $\text{Et}_2 PCH_2 \dot{C}H_2$ in the solid state is not clear, although it may be the result of the trapping of an unstable conformation [2,3], for which homoconjugation might be important, in the solid matrix at low temperatures.

No evidence was found for the cyclisation of the radicals (III; $m = 0-2$) to give tetraalkylphosphoranyl radicals, and there were no line-shape effects ascribable to α, ω -transfer of the $\text{Me}_2 P$ group at higher temperatures (up to $+40^\circ\text{C}$). The latter result is not surprising, since the α - and ω - CH_2 groups would probably remain non-equivalent in a cyclic phosphoranyl radical intermediate [5b].

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