# An Electron Spin Resonance Study of Radical Addition to Vinylphosphines

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E.s.r. spectroscopy has been used to show that alkoxyl and methyl radicals add to phosphorus in the vinylic phosphines $R_2C=C(H)PX_2$ (X = MeO, EtO, or Me_2N) to form ' phosphoranyl ' radicals in which the unpaired electron is centred mainly on the remote carbon. These adducts are π-radicals and can be regarded as alkene radical anions which carry a phosphonium substituent, although there is significant spin density on phosphorus. The adducts $R_2\dot{C}-C(H)=P(OR')_2OBu^t$ (R = H or Me) undergo fragmentation to give t-butyl radicals and the phosphonate ester $R_2C=C(H)P(O)(OR')_2$.

t-Butyl radicals add to the unsubstituted carbon of the vinyl group in $H_2C=C(H)PX_2$ (X = RO, Me_2N, or Et) to give α-phosphinoalkyl radicals $Bu^tCH_2\dot{C}(H)PX_2$, the e.s.r. spectra of which exhibit relatively large splitting from ^{31}P. There appears to be appreciable delocalisation of the unpaired electron onto phosphorus, a result which was not anticipated on the basis of previous reports of e.s.r. spectra ascribed to α-phosphinoalkyl radicals.

PHOSPHORANYL radicals (1) are formed readily by radical addition to compounds of trivalent phosphorus [equation (1)].[1,2]

$$X\cdot + PX_3 \longrightarrow X_4P\cdot \qquad (1)$$

(1)
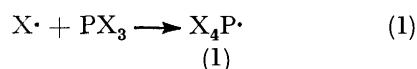
Examples of three types of electronic structure are known for (1). The first, and most common, type of

(2)   (3)
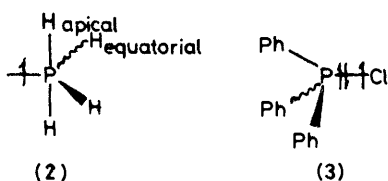
phosphoranyl radical has a quasi trigonal bipyramidal structure [e.g. (2) [3]] in which the unpaired electron is in a molecular orbital comprised mainly of an anti-bonding combination of P-3s, P-3p_σ, and apical ligand orbitals of appropriate symmetry.[4-6] For convenience, the unpaired electron is shown as occupying an equatorially directed orbital.[6,7]

Alternatively, the unpaired electron may be confined to one anti-bonding P-ligand σ^*-orbital with local C_{3v} symmetry at phosphorus,[8,9] and this electronic structure has been proposed for the chlorotriphenylphosphoranyl radical (3).[8] The probability of the existence of structures intermediate between those represented by (2) and (3) must be recognised.

The e.s.r. spectra of phosphoranyl radicals of types (2) and (3) are characterised by large isotropic splittings from ^{31}P (500—1 300 G), but certain phenylphosphoranyl radicals, in which the other ligands are not very electronegative, exhibit much smaller phosphorus splittings and the unpaired electron appears to be centred mainly on the benzene ring.[7,10] For example,[7] the radical (4)
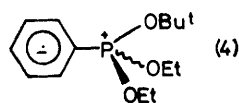
shows $a(P)$ 9.25, $a(1H_p)$ 9.25, $a(2H_o)$ 5.15, and $a(2H_m)$ 1.10 G at 193 K and it is best considered as a phosphonium-substituted benzene radical-anion.

Radical addition to vinylphosphines might take place either at phosphorus or at carbon in the vinyl group, and addition to phosphorus could give rise to a phosphoranyl radical with an electronic structure analogous to those of (2) [or (3)] or (4).

RESULTS

The reactions of alkyl and alkoxyl radicals with the vinylic phosphines (5; X = MeO, EtO, Me_2N, or Et) and (6) were investigated using e.s.r. spectroscopy.

Solutions, generally in cyclopropane, containing the phosphine and the primary photochemical source of radicals (usually an azoalkane or a dialkyl peroxide) were irradiated with u.v. light whilst the sample was in the

FIGURE 1   E.s.r. spectrum of the radical $H_2\dot{C}-CH=P(OMe)_2OBu^t$ obtained by photolysis of di-t-butyl peroxide in the presence of (5; X = MeO) in cyclopropane at 170 K

cavity of the spectrometer. The radical adducts were all transient and their e.s.r. spectra were recorded during continuous photolysis. Irradiation of (5) or (6) alone did not give rise to any e.s.r. spectra.

(a) *Reactions with Alkoxyl Radicals.*—Photolysis of

(5)   (6)

di-t-butyl peroxide in the presence of (5; X = MeO) below 250 K gave rise to the e.s.r. spectrum shown in Figure 1.

The e.s.r. parameters (see Table 1) are typical of a carbon-centred radical, and we assign the spectrum to the
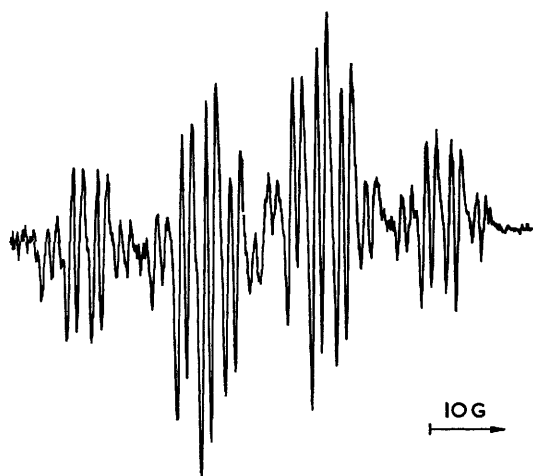
species (7; R = Bu^t) formed by addition of the t-butoxyl radical to phosphorus.

(2)

(7)

The splittings from H$_\beta$ and P$_\beta$ are temperature-dependent; the former decreases and the latter increases as the temperature increases. Non-equivalence of the α-hydrogens could be detected under conditions of high resolution and the average value of $a(H_\alpha)$ was almost independent of temperature. As the temperature was increased from 250 to 290 K, the spectrum of (7; R = Bu^t) became progressively weaker and was replaced by the spectrum assigned to the t-butyl radical adduct of dimethoxyvinylphosphine (see below). We conclude that (7; R = Bu^t), like (4),[7] undergoes fragmentation (β-scission) to form the t-butyl radical, which then adds

(7; R = Bu^t). Above 193 K the spectrum of the t-butyl radical was observed alongside that of (8; R = Bu^t), but no addition of this alkyl radical to (6) was detectable. The radical (8; R = Bu^t) appears to undergo β-scission more rapidly than (7; R = Bu^t), perhaps as a result of the stabilisation of the developing carbon–carbon double bond by the geminal methyl groups in the former radical.

(5)

(6)   (8)

Diethoxyvinylphosphine (5; X = EtO) behaved in a similar way to the methoxy-analogue. Photolysis of di-t-butyl peroxide in the presence of bis(dimethyl-amino)vinylphosphine (5; X = Me$_2$N) gave rise to a spectrum consisting of four broad lines (g 2.0026) and which we assign to the adduct (9).

TABLE 1

E.s.r. parameters for radicals formed by addition of alkoxyl radicals to vinylic phosphines in cyclopropane solvent

Radical	T/K	g-Factor	Hyperfine splittings/G				d$|a(P)|$/dT mGK^{-1}	d$|a(1H_\beta)|$/dT mGK^{-1}
			$a(P)$	$a(2H\alpha)$ [a]	$a(1H_\beta)$	$a(6H_\beta)$ [b]		
H$_2$Ċ–CH=P(OMe)$_2$OBu^t	213	2.0025	13.9	14.9 [c]	1.67		+30	−3.4
H$_2$Ċ–CH=P(OMe)$_2$OBu^s	213	2.0026	13.5	15.0	1.53		+29	−2.9
H$_2$Ċ–CH=P(OMe)$_2$OEt	218	2.0026	13.5	15.0 [d]	1.51		+32	−3.4
H$_2$Ċ–CH=P(OEt)$_2$OBu^t	203	2.0026	13.2	15.0	1.85		+28	−3.1
H$_2$Ċ–CH=P(OEt)$_3$	203	2.0025	12.7	15.0	1.63		+27	−3.3
H$_2$Ċ–CH=P(NMe$_2$)$_2$OBu^t	230	2.0027	14.7 [e]	14.7 [e]	f			
Me$_2$Ċ–CH=P(OMe)$_2$OBu^t	204	2.0027	19.3		f	17.2	+60	
Me$_2$Ċ–CH=P(OMe)$_2$OEt	218	2.0026	19.5		f	17.2	+54	

[a] Mean value for the two non-equivalent protons. [b] The splittings from the two methyl groups were the same within the limits imposed by the line width. [c] At 213 K, $a(1H\alpha)$ 14.8, $a(1H'\alpha)$ 15.0 G. [d] At 218 K, $a(1H_\sigma)$ 14.90, $a(1H'\alpha)$ 15.15 G. [e] Approximate values, line width 2.8 G. [f] Not resolved.

to the vinyl group of the phosphine [equations (3) and (4)].

+ Bu^t• (3)

(4)

The radicals (7; R = Bu^s or Et), formed by addition of s-butoxyl or ethoxyl radicals to dimethoxyvinyl-phosphine, were more stable towards fragmentation and no signals attributable to alkyl radical adducts of the vinylic phosphine could be detected even at 293 K. As expected, the stability of (7) towards β-scission increases with the strength of the R–O bond. The only signal that could be identified during photolysis of dicumyl peroxide in the presence of dimethoxyvinylphosphine, even at 190 K, was that of the cumyl radical and thus [7; R = Ph(Me$_2$)C] is very unstable with respect to cleavage of the weak R–O bond.

Addition of alkoxyl radicals to (6) gave rise to spectra ascribed to (8). For (8; R = Bu^t) at a given temperature, the magnitude of $a(P_\beta)$ was larger than that for

The magnitudes of $a(H_\alpha)$ and $a(P_\beta)$ are expected to be similar and the splittings from the β-proton and the magnetic nuclei in the dimethylamino-groups are unresolved, but presumably contribute to the line width.

(6)

(9)

(b) *Reactions with Alkyl Radicals.*—Photolysis of azo-isobutane in the presence of dimethoxyvinylphosphine (5; X = MeO) afforded the spectrum shown in Figure 2.

At 290 K a residual concentration of the t-butyl radical is present along with a radical which exhibits a large phosphorus splitting (91.4 G) and splittings from one proton (18.8 G) and from two apparently equivalent protons (20.8 G). As the temperature was decreased the phosphorus splitting increased, the unique proton splitting remained unchanged, and the splitting from the pair of protons decreased accompanied by relative broadening of the lines associated with $M_I(2H) = 0$, indicating that the protons are in fact non-equivalent. Three possible structures for this radical merit consideration and these are shown in equations (7)—(9).

$$Bu^{t}\cdot + \underset{(5)}{\overset{H}{\underset{H}{>}}=\overset{H}{\underset{PX_2}{<}}} \longrightarrow \begin{array}{l} Bu^{t}CH_2\dot{C}(H)PX_2 \quad (7) \\ \qquad\qquad (10) \\ \\ H_2\dot{C}C(H)(Bu^{t})PX_2 \quad (8) \\ \qquad\qquad (11) \end{array}$$

$$(11) \xrightarrow{\quad} X_2PCH_2\dot{C}(H)Bu^{t} \qquad (9)$$
$$\qquad\qquad (12)$$

Reaction (7) seems most likely, but the magnitudes of the e.s.r. parameters are not inconsistent with the structures (11) and (12), and all three radicals could

FIGURE 2 E.s.r. spectrum of the radical Bu^{t}CH$_2$ĊHP(OMe)$_2$ obtained by photolysis of azoisobutane in the presence of (5; X = MeO) in cyclopropane at 283 K. The lines marked with asterisks are due to the t-butyl radical

exhibit the line-shape effects described above. However, the splitting from the unique proton does not vary with temperature, whilst that from the pair of apparently

X = MeO) to the α-phosphino-alkyl radical (10; X = MeO).

The radical (10; X = MeO) was also detected during photolysis of di-t-butyl ketone or of a mixture of t-butyl bromide and hexabutylditin in the presence of (5; X = MeO), although the signals were weaker than that obtained using azoisobutane. However, all attempts to generate type (10) adducts of radicals other than t-alkyl failed, because we could not find sufficiently efficient sources of such radicals (isopropyl or ethyl) for use in the presence of (5).

Similar adducts (10) were produced by addition of t-butyl radicals to the vinylic phosphines (5; X = EtO, Me$_2$N, Et). The spectrum of the adduct (10; X = Me$_2$N) showed additional splitting from two apparently equivalent nitrogen nuclei, whilst coupling with four protons of the P-ethyl groups was detected for (10; X = Et). The spectroscopic parameters for the adducts (10) are given in Table 2.

Addition of t-butyl radicals to (6) was not detectable by e.s.r. spectroscopy and only a strong spectrum of this alkyl radical was observed when azoisobutane was photolysed in the presence of the phosphine. The lower rate of addition of t-butyl radicals to the double bond in (6) compared with that in (5) is presumably a steric effect, resulting from the presence of the two methyl groups on carbon in (6).

In contrast with the formation of adducts (10) by addition of t-butyl radicals to carbon, methyl radicals underwent exclusive (as judged by e.s.r. spectroscopy) addition to the phosphorus atom of dialkoxyvinyl-

TABLE 2

E.s.r. parameters for radicals formed by addition of alkyl radicals to vinylic phosphines in cyclopropane solvent

Radical	T/K	g-Factor	$a(P)$	$a(H\alpha)$	$a(H\beta)$	Others	$\frac{d|a(P)|/dT}{mGK^{-1}}$	$\frac{d|a(H\beta)|/dT}{mGK^{-1}}$
				Hyperfine splittings/G ^{a}				
Bu^{t}CH$_2$Ċ(H)P(OMe)$_2$	292	2.0026	91.4	18.8	20.8(2) ^{b}		−51	+11
Bu^{t}CH$_2$Ċ(H)P(OEt)$_2$	285	2.0025	95.8	18.9	20.7(2)		−55	+10
Bu^{t}CH$_2$Ċ(H)P(NMe$_2$)$_2$	338 ^{c}	2.0027	109.8	17.8	19.1(2)	6.0 (2 N)	+7	
Bu^{t}CH$_2$Ċ(H)PEt$_2$	300	2.0024	63.6	18.7	18.7(2)	0.73 (4 H)	−29 ^{d}	
ĊH$_2$–CH=P(OMe)$_2$Me	173	2.0027	17.9	14.8(2) ^{e}	1.30	3.30 (3 H)		
ĊH$_2$–CH=P(OEt)$_2$Me	165	2.0028	18.1	14.9(2)	1.50	3.15 (3 H)		

^{a} Number of nuclei coupling is shown in parentheses where different from one. ^{b} Below 253 K the lines corresponding to $M_{\mathrm{I}}(H\beta)$ = 0 were broadened beyond detectability. ^{c} Cyclopentane solvent. Widths of all lines were approximately equal at this temperature: at lower temperatures there was selective line broadening due to non-equivalence of the β-protons and, probably, of the two nitrogen nuclei. ^{d} Over a range of 28 K. ^{e} Average value; $a(1H\alpha)$ 14.6, $a(1H'\alpha)$ 15.0 G.

equivalent protons is temperature dependent, and these observations indicate strongly against structure (11), in which the unique proton is β and the pair of protons α to the radical centre. The radical (12) is more difficult to eliminate, but when the spectrum was generated by photolysis of perdeuteriodi-t-butyl peroxide in the presence of (5; X = MeO) the line width (0.4 G) was identical with that measured from the spectrum obtained from the protio peroxide. If the structure were (12) we would expect a significant contribution to the line width from coupling to the nine δ-protons of the t-butyl group, whereas the t-butyl proton splitting in (10) is expected to be very small. We, therefore, assign the spectrum resulting from reaction of t-butyl radicals with (5;

phosphines. Thus, photolysis of azomethane in the presence of (5; X = MeO or EtO) afforded spectra which we assign to the adducts (13) [equation (10)].

$$Me\cdot + \underset{H}{\overset{H}{>}}=\underset{P(OR)_2}{\overset{H}{<}} \longrightarrow \underset{H}{\overset{H}{>}}\cdot=\underset{P(OR)_2Me}{\overset{H}{<}} \qquad (10)$$
$$\qquad\qquad\qquad\qquad\qquad (13)$$

Although methyl radicals appeared to add to (5; X = Me$_2$N or Et) and to (6) the resulting spectra were too complex and weak to analyse. The spectrum of (13; R = Me) is shown in Figure 3 and the e.s.r. parameters of the methyl adducts are included in Table 2.

FIGURE 3 E.s.r. spectrum of the radical $H_2\dot{C}-CH=P(OMe)_2Me$ obtained by photolysis of azomethane in the presence of (5; X = MeO) in cyclopropane at 170 K

DISCUSSION

Radical Addition to Phosphorus.—The e.s.r. parameters for the ' phosphoranyl ' radicals * formed by addition of alkoxyl or methyl radicals to the vinylic phosphines are in accord with a planar arrangement of the bonds which formed the parent vinyl group, as shown in (14).
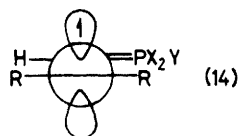
The nature of the P=C bond in (14) is probably similar to that in the diamagnetic alkylidene phosphoranes $R_2C=PX_3$. On the basis of *ab initio* SCF–MO calculations on the model ylid $H_2\bar{C}-\overset{+}{P}H_3$, it has been concluded that a stabilising and bond-shortening interaction exists between the lone pair of electrons on carbon and a $\pi * PH_3$ group orbital.[11] The basis set employed did not include P-3d functions and consequently no conclusions could be drawn regarding the importance of $p_\pi{\rightarrow}d_\pi$ bonding, although structural trends were adequately reproduced without their inclusion.

The electronic structure of the radical adducts may be represented as a resonance hybrid of structures (15)—(18).

$$R_2\dot{C}-C(H)=PX_2Y \qquad R_2\dot{C}-\bar{C}(H)-\overset{+}{P}X_2Y$$
$$(15) \qquad\qquad (16)$$
$$R_2\bar{C}-\overset{+}{C}(H)-\dot{P}X_2Y \qquad R_2C=C(H)-\dot{P}X_2Y$$
$$(17) \qquad\qquad (18)$$
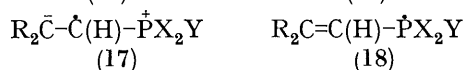
Structure (18) is intended as a convenient representation of the ' phosphoranyl radical ' contribution to the electronic structure. The involvement of phosphorus atomic orbitals in the MO occupied by the unpaired

* It can be argued that these species should not be referred to as phosphoranyl radicals and that this name should be reserved for radicals having the electronic structures typified by (2) and (3).

electron must be effectively or completely [depending on the conformation about the P=C bond in (14)] limited to P-3p_π and P-3d_π. Some involvement of ligand orbitals is also to be expected. A simple picture of the electronic structure is to regard the adduct as an alkene radical-anion with a phosphonium substituent, the presence of which causes localisation of spin density on the remote carbon atom. The radicals formed by addition to phosphorus in vinylic phosphines are thus analogous to (4) and to the radicals (19), produced by abstraction of hydrogen from N-alkylphosphazenes [equation (11)].[12]

$$Bu^tO\cdot + R_2C(H)N=P(OR)_3 \longrightarrow$$
$$R_2\dot{C}-N=P(OR)_3 + Bu^tOH \quad (11)$$
$$(19)$$
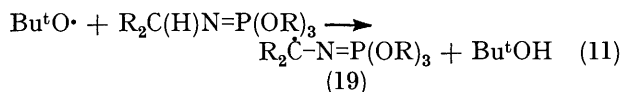
The β-hydrogen and β-phosphorus atoms are situated in the nodal plane of the π-orbital occupied by the unpaired electron in (14), and the stereochemistry about phosphorus is probably close to tetrahedral. For all adduct radicals the magnitude of $a(P)$ increases with temperature, a trend which may be attributed to the increasing amplitude of torsional motion about the C_α–C_β bond, which brings both P_β and H_β out of the nodal plane and gives rise to a positive (hyperconjugative) contribution to the coupling constants of both nuclei. We conclude that the sign of $a(P_\beta)$ is positive for all adducts whilst that of $a(H_\beta)$ is probably negative (spin-polarisation of the C–H σ bond by positive π spin density on C_β predominates) for the adducts of (5). For (14; R = Me) we would expect the amplitude of the torsional motion taking H_β and P_β out of the nodal plane to be greater than for (14; R = H), and thus we may understand the relatively large value of $a(P_\beta)$ in the adducts of dimethoxy-(2-methylpropenyl)phosphine (6).

The value of $a(6H_\beta)$ for (20) can be used to estimate[13] a

$$(20) \qquad\qquad (21)$$
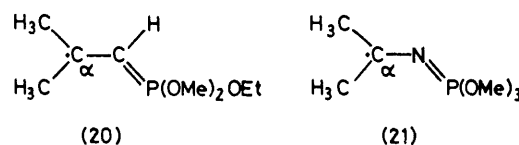
π-spin density on C_α ($\rho_{C\alpha}{}^\pi$) of 0.59, and if we consider (20) as a substituted isopropyl radical the spin-withdrawing power of the $C(H)=P(OR)_3$ substituent, ΔX as defined by equation (12),[13] is equal to 0.30.

$$\rho_{C\alpha}{}^\pi = 0.845 \ (1-\Delta X) \qquad (12)$$

The corresponding value of ΔX for the $N=P(OR)_3$ substituent in (21) is smaller (0.21),[12] and this is in accord with the expected increase in the contributions from canonical structures of the type (15) and (16) when the CH group is replaced by the more electronegative nitrogen atom.

Thus about 70% of the unpaired spin density is on the α-carbon atom in the radical adducts of (5) and (6), with the remaining 30% on the $C(H)=PX_2Y$ group. The relatively large magnitude of the splitting from the P-methyl group in (13) and the line-broadening caused by coupling to nitrogen in (9) both point to the presence

of significant π-spin density on phosphorus in the adducts (14).

The above conclusions are supported by the results of INDO calculations * on the model radical $(HO)_3P=C(H)-\dot{C}H_2$ in the conformation (22).

(22)
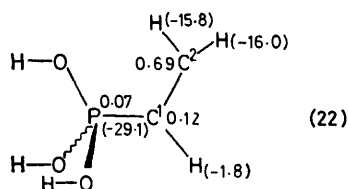
The distances P–C^1 and C^1–C^2 were varied, whilst other bond lengths were fixed standard values; the angles HOP and OPC^1 were taken as 109.5° and other bond angles as 120°. The basis set did not include P-3d orbitals. The best agreement with the proton splittings observed for $H_2\dot{C}C(H)=P(OR)_3$ was obtained with P–C^1 1.70 and C^1–C^2 1.45 Å. The calculated SOMO is a π-orbital, antibonding between C^1 and C^2 but bonding between C^1 and P. The π-spin densities on P, C^1, and C^2 are indicated on (22); there is also some spin density on the oxygen atoms. The calculated splitting constants are shown in parentheses on (22) and the charges on P, C^1, and C^2 are +1.29, −0.34, and −0.12, respectively.

The calculated value of $a(P)$ for (22) is in poor agreement with the positive splitting observed for $H_2\dot{C}C(H)=P(OR)_3$, but this is not surprising in view of the approximations involved and the neglect of torsional motion about the C–C bond.

The t-butoxyl radical adducts of (5; X = RO) and (6) undergo fragmentation to form t-butyl radicals and the corresponding phosphonates [equation (13)].

$$R^1_2\dot{C}-C(H)=P(OR^2)_2OBu^t \xrightarrow{\beta\text{-scission}}$$

(23)

$$R_2^1C=C(H)-P(O)(OR^2)_3 + Bu^{t\cdot} \quad (13)$$
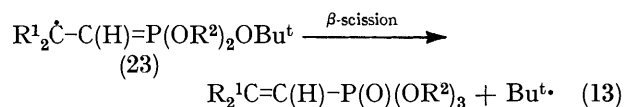
The trigonal bipyramidal phosphoranyl radical (24) and the phenyl substituted ' phosphoranyl ' radical (4) undergo β-scission at similar rates.†

$$(EtO)_3\dot{P}OBu^t \longrightarrow (EtO)_3P=O + Bu^{t\cdot} \quad (14)$$

(24)

$$C_6\bar{H}_5-\overset{+}{\dot{P}}(OEt)_2OBu^t \longrightarrow C_6H_5P(O)(OEt)_2 + Bu^{t\cdot} \quad (15)$$

(4)
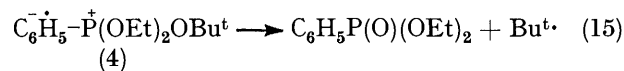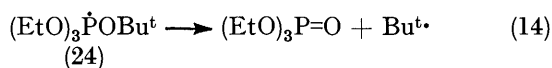
The vinylic ' phosphoranyl ' radicals (23; R^1 = H or Me, R^2 = MeO) undergo fragmentation less readily than does (24), as judged qualitatively from the temperature dependence of radical concentrations. The t-butyl radicals thus formed add to the vinyl group in the parent phosphine (5; X = RO), but not at a detectable rate to

dimethoxy-(2-methylpropenyl)phosphine (6) presumably for steric reasons. t-Butyl radicals also add readily to diethyl vinylphosphonate [equation (16)] but the e.s.r. spectra are readily distinguishable from those of the vinylphosphine adducts.[14]

(16)

Radical Addition to the Vinyl Group.—Addition of t-butyl radicals to (5) gives rise to the carbon-centred radicals $Bu^tCH_2\dot{C}(H)PX_2$ (10), in which a phosphino-substituent is attached to the radical centre. The most stable conformation about the C–P bond is probably that shown in (25).

(25a)   (25b)
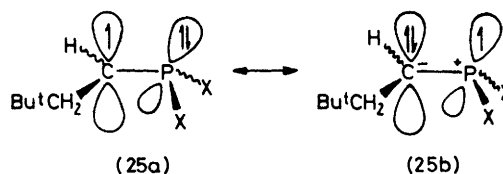
The unpaired electron is in an antibonding π*-orbital formed by overlap of the C-2p_π orbital with the sp-hybrid orbital on phosphorus. There will be two major contributions to $a(P)$, a negative one resulting from spin-polarisation of the C–P σ-bonding electrons by the spin on C$_\alpha$ and a positive one from spin density in the sp-hybrid orbital on phosphorus, and the latter contribution must outweigh the former. Evidence for spin delocalisation onto phosphorus is provided by the observation of a relatively large coupling to two nitrogen nuclei in (10; X = Me$_2$N) and to four protons in (10; X = Et).

The negative values ‡ of $d|a(P)|/dT$ for (10) may be attributed to the effects of torsional motion about the C–P bond. As the temperature increases the average dihedral angle between the axes of the orbitals on C and P will increase and overlap, and hence the positive contribution to $a(P)$, will decrease. The value of $a(P)$ in (10) varies with the nature of X and is expected to depend primarily upon the contribution from (25b) and the hybridisation at phosphorus. Thus, $a(P)$ should increase with a decrease in the ionisation potential corresponding to removal of a lone-pair electron from phosphorus, and with an increase in the P-3s character of the lone-pair orbital.
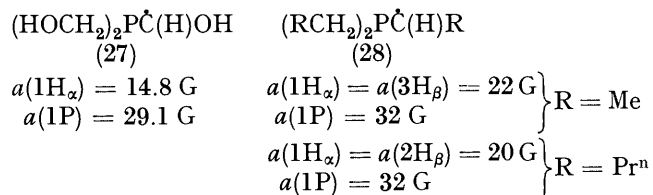

(26)
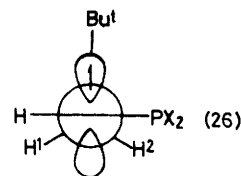
For steric reasons the preferred conformation about the C$_\alpha$–C$_\beta$ bond is probably that shown in (26), for which H^1

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† In reference 7 it is erroneously stated that the radical (4) undergoes β-scission much more rapidly than (24). The correct rate constant for β-scission of (4) [equation (15)] is given by $\log(k_{15}/s^{-1}) - 12.0$—$36.7/\theta$, where $\theta - 2.303RT$ kJ mol^{-1}.

‡ For (10; X = Me$_2$N) $d|a(P)|/dT$ is relatively small and positive. A relatively high barrier to rotation about the P–C bond and the effects of rotation about the P–N bonds are likely to be responsible for this anomalous temperature dependence.

and H^2 are non-equivalent and for which $a(H_\beta)$ will be at a minimum. Exchange of H^1 with H^2 can take place by rotation about C_α–C_β, giving rise to the observed line-shape effects, and exchange with less stable conformations, for which $a(H_\beta)$ is larger, will lead to the observed increase with temperature of the mean β-proton coupling constant.

The large values of $a(P)$ observed for (10) would not have been unexpected had there not been two previous reports of e.s.r. spectra ascribed to α-phosphinoalkyl radicals. Lucken[15] has reported a spectrum which he assigned to the radical (27), formed by reaction of hydroxyl radicals with tris(hydroxymethyl)phosphine in aqueous solution at room temperature.

$(HOCH_2)_2P\dot{C}(H)OH$ $(RCH_2)_2P\dot{C}(H)R$
(27) (28)

$a(1H_\alpha) = 14.8$ G $a(1H_\alpha) = a(3H_\beta) = 22$ G $\left.\right\}$ R = Me
$a(1P) = 29.1$ G $a(1P) = 32$ G

$a(1H_\alpha) = a(2H_\beta) = 20$ G $\left.\right\}$ R = Pr^n
$a(1P) = 32$ G

Symons and his co-workers[16] have reported e.s.r. spectra ascribed to the α-dialkylphosphinoalkyl radicals (28; R = Me or Pr^n), formed by γ-irradiation of trialkylphosphines at 77 K. Both groups of workers found a splitting of about 30 G from the α-phosphorus nucleus, and this must be compared with the value of ca. 64 G found by us for (10; X = Et). The radical (27) is perhaps not directly comparable because of the presence of an α-hydroxy-group, but the low values of $a(P)$ for (28) are more difficult to understand. Possibly the conformation adopted by (28) in the solid state at low temperature is such that the orbitals occupied by the lone pair of electrons on phosphorus and by the unpaired electron on carbon do not overlap effectively.[16]

Addition to Phosphorus versus *Addition to Carbon.*—Both alkyl and alkoxyl radicals add fairly rapidly to (5), whereas the spectra of the adduct radicals may be detected in the presence of (5) with no sign of addition to the latter. Fortunately, it appears that polar and thermodynamic factors result in relatively slow addition of the adduct radicals to the parent phosphine. In fact the addition of t-butyl radicals to (5) is not very rapid, since the spectrum of the addendum may still be detected, and the more stabilised cumyl radical fails to add to (5; X = MeO) under our conditions.

Addition of alkoxyl radicals to trialkyl phosphites is very rapid[17] and essentially irreversible[18] [equation (17); Y = RO].

$$Y\cdot + (RO)_3P \rightleftharpoons (RO)_3\dot{P}Y \qquad (17)$$
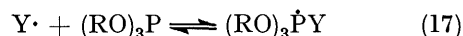
Methyl radicals add reversibly to phosphites [equation (17); Y = CH_3] under e.s.r. conditions,[19] but no phosphoranyl radical can be detected with ethyl (or more highly branched alkyl) radicals. It is, therefore, reasonable that alkoxyl and methyl radicals should add to phosphorus in (5) whilst t-butyl radicals add to carbon. t-Butyl radicals add more rapidly to (5) than to ethylene[14] and this could be due to the stabilisation of (10)

relative to $Bu^t CH_2CH_2\cdot$ as a result of the interaction represented by (25a) $\rightleftharpoons$ (25b) and/or a polar effect which acts to reduce the barrier for addition to (5). Such a polar effect might arise because of contributions to the transition state from structures of type (29), since it is known that a phosphino-substituent stabilises a negative charge on an adjacent carbon atom.

$$\overset{+}{Bu}{}^t \ \dot{C}H_2\text{-}\overset{-}{C}(H)PX_2 \qquad (29)$$
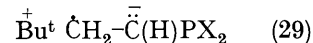
Rephrasing this using the terminology of frontier orbital theory, the predominant interaction for addition of t-butyl radicals to the double bond in (5) or ethylene would be between the SOMO of the radical and the LUMO (π^*-orbital) of the alkene, and the electron-withdrawing substituent would decrease the energy of the LUMO and hence make the interaction more favourable.

EXPERIMENTAL

E.s.r. Spectroscopy.—Samples were sealed *in vacuo* in 4 mm o.d. Suprasil tubes and irradiated, whilst in the cavity of a Varian E-4 spectrometer, with light from a Philips SP 500 mercury discharge lamp using fused silica optics. g-Factors (± 0.0001) were determined by measurement of the microwave frequency and the magnetic field, and were calculated using the Breit–Rabi equation when large hyperfine splittings from ^{31}P were present. Where values of $d|a(X)|/dT$ are given in Tables 1 and 2 these correspond to the slope of the best straight line through points on a plot of $a(X)$ against T (normally over 60—100 K). For no radical was there any marked deviation from linearity. Solutions were 0.5—1M in vinylic phosphine and in the primary photochemical source of radicals.

INDO calculations were carried out using a version of the program (No. 141) available from Quantum Chemistry Program Exchange, modified by Dr. A. R. Gregory to allow calculations for species containing second-row elements. Standard bond lengths employed were: H–O, 0.96; P–O, 1.65; C–H, 1.08 Å. Calculations were carried out for the bond length P–C^1 = 1.45, 1.55, 1.65, 1.70, 1.75, 1.85 Å and C^1–C^2 = 1.25, 1.35, 1.45, 1.55 Å, and all combinations were investigated.

Materials.—Di-t-butyl peroxide and dicumyl peroxide were commercial samples which were purified before use. Perdeuteriodi-t-butyl peroxide,[20] di-s-butyl peroxide,[21] diethyl peroxide,[22] azomethane,[23] and azoisobutane[24] were prepared according to published procedures.

Bis(dimethylamino)vinylphosphine was prepared by the method of King and Masler[25] and was converted to dimethoxy(vinyl)phosphine by treatment with methanol.[25]

Diethoxy(vinyl)phosphine, b.p. 41 °C at 12 Torr, was prepared in the same way as dimethoxy(vinyl)phosphine[25] using ethanol; ^1H n.m.r. (CDCl$_3$) δ 1.25 (t, J 7 Hz), 3.87 (doublet of quartets, J_{H-H} 7, J_{H-P} ca. 7 Hz), 5.4—5.6 (m).

Diethyl(vinyl)phosphine, b.p. 118—120 °C at 760 Torr (lit.,[26] 125 °C at 744 Torr), was prepared by the reaction of ethylmagnesium bromide with dimethoxy(vinyl)phosphine in ether.

Bis(dimethylamino)-2-methylpropenylphosphine, b.p. 77—79.5 °C at 10 Torr, was prepared by treatment of bis-(dimethylamino)chlorophosphine with 1-lithio-2-methylpropene in ether at −70 °C (Found: C, 55.5; H, 10.9; N,

16.3; P, 17.3. $C_8H_{19}N_2P$ requires C, 55.2; H, 11.0; N, 16.1; P, 17.8%); ^1H n.m.r. $(CDCl_3)$ δ 1.70—1.87 (m), 2.62 (d, J_{P-H} 10 Hz), 5.63 (m). Proton decoupled ^{31}P n.m.r. $(C_6H_6 + C_6D_6)$ −87.7 p.p.m. downfield from 85% H_3PO_4. The aminophosphine was converted into *dimethoxy-2-methylpropenylphosphine*, b.p. 83—84 °C at 60 Torr, by treatment with methanol; ^1H n.m.r. $(CDCl_3)$ δ 1.90 (m), 2.00 (broad s), 3.58 (d, J_{P-H} 10 Hz), and 5.73 (m); ^{31}P n.m.r. $(C_6H_6 + C_6D_6)$ −161.9 p.p.m.

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