An Electron Spin Resonance Study of the Addition of Alkoxyl and Siloxyl Radicals to Pyrrolylphosphines

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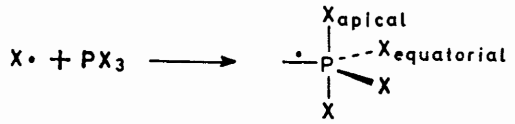
E.s.r. spectra are reported for phosphoranyl radicals generated by addition of Bu^{t}O·, EtO·, or Me$_3$SiO· to the pyrrolylphosphines (EtO)$_2$PNC$_4$H$_4$ and OCH$_2$CH$_2$OPNC$_4$H$_4$ in hydrocarbon solution. The pyrrolylphosphoranyl radicals have trigonal–bipyramidal structures, in which the unpaired electron is centred mainly on phosphorus and the apical ligands, rather than the ligand-π electronic structure adopted by the analogous phenylphosphoranyl radicals. For RO(EtO)$_2\dot{P}$NC$_4$H$_4$ (4; R = Bu^t, Et, or Me$_3$Si) at low temperatures, separate signals were detected from isomeric radicals in which the pyrrolyl group is either apical or equatorial, and at higher temperatures rapid interconversion of these isomers gives rise to lineshape effects in their e.s.r. spectra. Above *ca.* 260 K, the spectra correspond to the concentration-weighted average from the pairs of isomers. Similar effects were observed for the cyclic radicals RO(OCH$_2$CH$_2$O–)$\dot{P}$NC$_4$H$_4$ (6), in which the ring bridges apical and equatorial sites, although these species could not be examined at temperatures sufficiently low to allow detection of separate signals from the two isomers. The apicophilicity of the pyrrolyl group is similar to that of RO, and for (6) the proportion of the isomer in which RO is apical decreases in the order Bu^{t}O > EtO > Me$_3$SiO. Factors which might cause this trend are discussed and the relevance to previous conclusions regarding site-selectivity of β-scission of alkoxyphosphoranyl radicals is pointed out. The radicals (4; R = Bu^t or Et) undergo β-scission to give R· and (EtO)$_2$P(O)NC$_4$H$_4$ at high temperatures.

RADICAL addition to compounds of trivalent phosphorus gives rise to phosphoranyl radicals, the structures of which can often be deduced from their e.s.r. spectra.[1,2] Many phosphoranyl radicals adopt a quasi-trigonal–bipyramidal (TBP) structure in which, for convenience, the unpaired electron is shown as occupying an equatorially directed orbital as in (1).

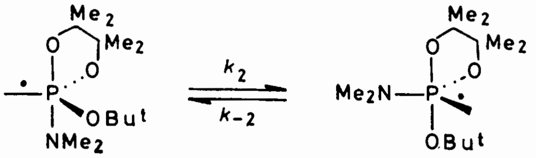


(1)

(1)

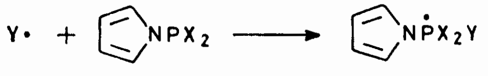
The preference of a particular ligand to occupy an apical rather than an equatorial site in a TBP phosphoranyl radical is referred to as its *apicophilicity* and, in general, this increases with group electronegativity.[1] The apicophilicities of RO and R$_2$N ligands are rather similar. For example,[3,4] addition of t-butoxyl radicals to OCMe$_2$CMe$_2$OPNMe$_2$ gives rise to an equilibrium mixture of two isomers of the phosphoranyl radical (2) [equation (2)]. At 193 K interconversion of (2a and e) is rapid (k_2 3.3 × 10^8 s^{-1}) and K_2 (= k_2/k_{-2}) is 3.3.

In this paper we report an investigation of the structures of phosphoranyl radicals containing the unsaturated pyrrolyl ligand. The apicophilicity of the pyrrolyl group has been determined relative to that of each of the groups Bu^{t}O, EtO, and Me$_3$SiO, and the electronic structures of pyrrolyl- and phenyl-phosphoranyl radicals are compared.



(2a) (2e)

(2)



(3)

RESULTS

E.s.r. spectra were recorded during continuous u.v. photolysis of solutions containing a peroxide ROOR (R = Bu^t, Et, or Me$_3$Si) and one of the phosphines (3) and (5) (C$_4$H$_4$N = pyrrol-1-yl throughout). The solvent was cyclopropane, propane, or ethylene, sometimes with benzene or toluene co-solvent to increase phosphine solubility at low temperatures.

$$\mathrm{ROOR} \xrightarrow{h\nu} 2\mathrm{RO}\cdot \qquad (4)$$

$$\underset{(3)}{\mathrm{RO}\cdot + (\mathrm{EtO})_2\mathrm{PNC_4H_4}} \longrightarrow \underset{(4)}{\mathrm{RO(EtO)_2\dot{P}NC_4H_4}} \qquad (5)$$

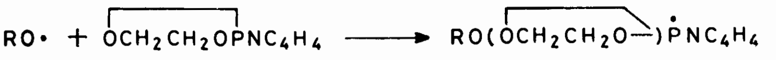

$$\mathrm{RO}\cdot + \underset{(5)}{\mathrm{OCH_2CH_2OPNC_4H_4}} \longrightarrow \underset{(6)}{\mathrm{RO(OCH_2CH_2O\!-\!)\dot{P}NC_4H_4}} \qquad (6)$$

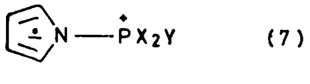
TABLE 1

E.s.r. parameters for (4a and e) in ethylene solvent

R	T/K	(4a)			(4e)			K_7
		g Factor [a]	a(P) [a]/G	a(N)/G	g Factor [a]	a(P) [a]/G	a(N)/G	
Bu^t	130	2.0023	901.4	31.0	2.0022	838.7	3.3	0.25
Et	130	2.0019	901.2	30.0	2.0017	841.4	4.3	0.16
Me$_3$Si [b]	133	2.0022	895.3	29.5	c	c	c	c

[a] Calculated using the Breit–Rabi equation. [b] Cyclopropane–propane (1 : 1 v/v) solvent. [c] (4e; R = Me$_3$Si) was undetectable.

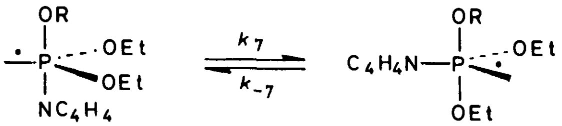
The spectra of the phosphoranyl radicals (4) and (6) exhibited very large splittings from ^{31}P and indicated that the radicals have TBP structures.[1,*] No signals which might be attributed to radicals having a ligand-π electronic structure (7) [compare [5,6] $(RO)_3\overset{+}{P}\overset{\cdot\,-}{Ph}$] were detected.


(7)

The site of the pyrrolyl ligand in the trigonal bipyramid was inferred from the magnitude of the nitrogen hyperfine splitting,[4,7] a value of 25—30 G being typical of an apical sp^2-hybridised nitrogen and 3—6 G indicating equatorial attachment.

(i) *Diethoxy(pyrrolyl)phosphine* (3).—Addition of ethoxyl or t-butoxyl radicals to (3) at low temperatures (*ca.* 160 K) gave rise to overlapping spectra of (4a and e), but for addition of trimethylsiloxyl radicals only (4a) could be detected, although the presence of (4e; R = Me$_3$Si) could be inferred from the linewidth effects apparent at higher temperatures (see below). The spectroscopic parameters for (4) are gathered in Table 1.†

The isomers (4a and e) must be present in their equilibrium concentrations, since their interconversion is much more rapid (see below) than radical decay under these conditions,[7] and between 130 and 260 K the value of K_7 (= k_7/k_{-7}) decreased along the series R = Bu^t > Et > Me$_3$Si (see Tables 1 and 2).


(7)

(4a) (4e)

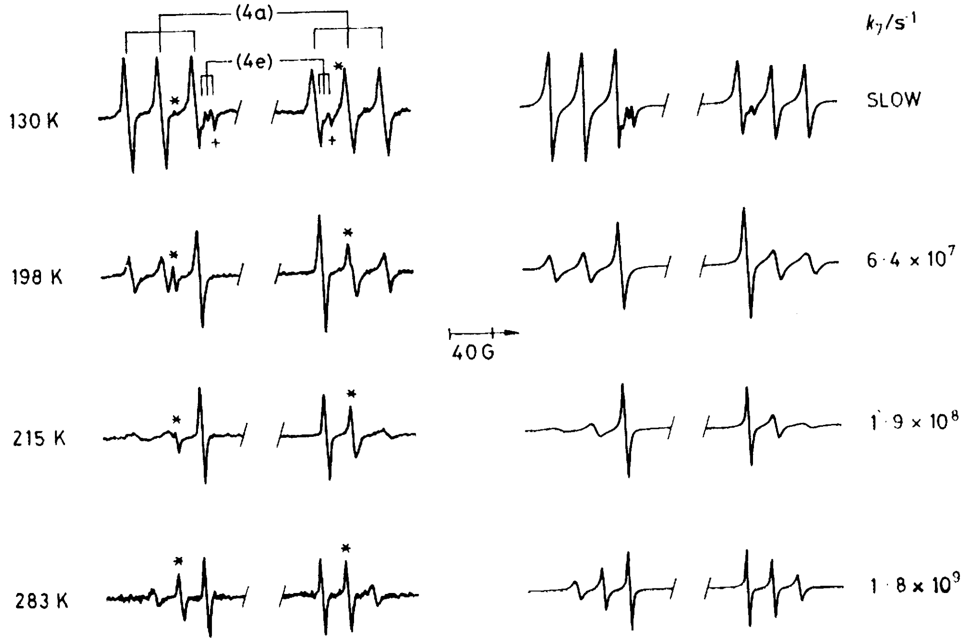


FIGURE 1 E.s.r. spectra of the radical (4; R = Et) in ethylene (at 130 K) or cyclopropane (other temperatures) solvent. Experimental spectra are on the left, computer simulations on the right with corresponding values of k_7/s^{-1} shown alongside. The positions of the lines due to (EtO)$_4$P· are indicated with an asterisk; the lines marked + are corrupted by an unidentified signal

E.s.r. spectra obtained during photolysis of diethyl peroxide in the presence of (3) are shown in Figure 1 and, at 130 K, separate signals from (4a; R = Et) and (4e; R = Et) can be seen. In addition, a weak spectrum due to (EtO)$_4$P·[8] [a(P) 882.8 G, g 2.0019] ‡ and an unidentified signal corresponding to a(P) 842 G, g 2.000 were detected.

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[*] A σ* electronic structure, in which the unpaired electron is confined to one phosphorus–ligand σ* orbital, would also exhibit a large ^{31}P splitting, and TBP and σ* structures are often difficult to distinguish on the basis of isotropic e.s.r. data.[1] However, the ring proton splittings detected for (6) strongly indicate a TBP type structure, and the similarity of the spectra from (4) and (6) implies that these species have similar structures.

† The site of attachment of RO is arbitrarily shown as apical.

‡ The (EtO)$_2$PNC$_4$H$_4$, although analytically pure, appeared to contain a trace of triethyl phosphite, since a weak signal assigned to $(EtO)_3\dot{P}OR$ (easily detected because of its relatively sharp lines) was observed immediately upon beginning photolysis.

At higher temperatures the lines due to (4a and e) broaden, those of the latter to the greater extent, and we ascribe this lineshape effect to the decreased lifetimes of the radicals as a result of their interconversion. Differential line-broadening effects and shifts in resonance fields are clearly observable in the spectrum of (4a); the outer lines which shift most upon exchange with (4e) show the greatest increase in width. Above *ca.* 260 K, the lines begin to sharpen at positions corresponding to the concentration-weighted average spectra of (4a and e), and the widths of the six lines continue to decrease towards the natural linewidth up to the highest accessible temperature. The e.s.r. parameters for the averaged spectra of (4a and e) are given in Table 2.

TABLE 2

Averaged e.s.r. parameters for (4a and e) in cyclopropane solvent

R	T/K	g Factor [a]	$\bar{a}$(P) [a]/ G	$\bar{a}$(N)/ G	K_7 [b]
Bu^t	265	2.0022	888.3	22.3	0.45
Et	283	2.0019	884.3	22.9	0.37
Me_3Si	260	2.0020	893.0	26.5	0.12

[a] Calculated using the Breit–Rabi equation. [b] Calculated from the average nitrogen splitting using equation (9).

The spectral changes for (4; R = Et) have been computer-simulated on the basis of the following assumptions. (A) The values * of $a(N_a)$ and $a(N_e)$ have the same sign and are independent of temperature. (B) The difference between the phosphorus splittings of (4a and e) is independent of temperature. (C) The equilibrium constant K_7 varies according to equation (8) between the directly measured value of 0.16 at 130 K and 0.37 at 283 K, the latter value being calculated, using equation (9), from the average nitrogen splitting at this temperature. For (4; R = Et) the values of $\Delta H_7^{\ominus}$ and $\Delta S_7^{\ominus}$ are 1.7 kJ mol^{-1} and -2.5 J mol^{-1} K^{-1}, respectively.

$$\log_{10} K_7 = \Delta S_7^{\ominus}/2.303R - \Delta H_7^{\ominus}/2.303RT \qquad (8)$$

$$K_7 = [a(N_a) - \bar{a}(N)]/[\bar{a}(N) - a(N_e)] \qquad (9)$$

The simulations are shown alongside the experimental spectra in Figure 1 and, between 180 and 290 K, k_7 is given by equation (10), in which $\theta = 2.303RT$ kJ mol.$^{-1}$

$$\log_{10} (k_7/s^{-1}) = 12.7 - 18.5/\theta \qquad (10)$$

The e.s.r. signal of (4; R = Et) could not be detected above 290 K because of rapid β-scission to give ethyl radicals [equation (11; R = Et)] and no spectrum ascribable to the pyrrolyl radical,[9] the product of possible P–N cleavage, could be observed.

$$RO(EtO)_2\dot{P}NC_4H_4 \longrightarrow R\cdot + (EtO)_2P(O)NC_4H_4 \qquad (11)$$

Addition of photochemically generated t-butoxyl radicals to (3) gave similar results, and again a weak unidentified signal corresponding to a(P) *ca.* 845 G was detected in addition to the spectra of (4a and e) (see Figure 2).

The temperature dependence of the spectrum indicated rapid exchange of (4a and e), although signals could not be obtained above *ca.* 270 K because of the onset of rapid β-scission to give t-butyl radicals [equation (11; R = Bu^t)].

Weaker spectra were obtained during photolysis of bis(trimethylsilyl) peroxide in the presence of (3), and the phosphine and peroxide appeared to react directly in the absence of light above *ca.* 265 K. Only (4a) was detectable at low temperatures and the six lines had similar widths at 170 K. However, at higher temperatures linewidth effects indicated exchange with an undetected (4e) isomer having a(P) *ca.* 840 G, and differential broadening was marked at 210 K. Spectra could not be detected above 265 K, at which temperature the lines were more equal in width (especially at high field) and correspond to the weighted average spectrum of (4a and e). Taking $a(N_e)$ as *ca.* 4 G, K_7 (R = Me_3Si) was calculated to be *ca.* 0.12 at 260 K.

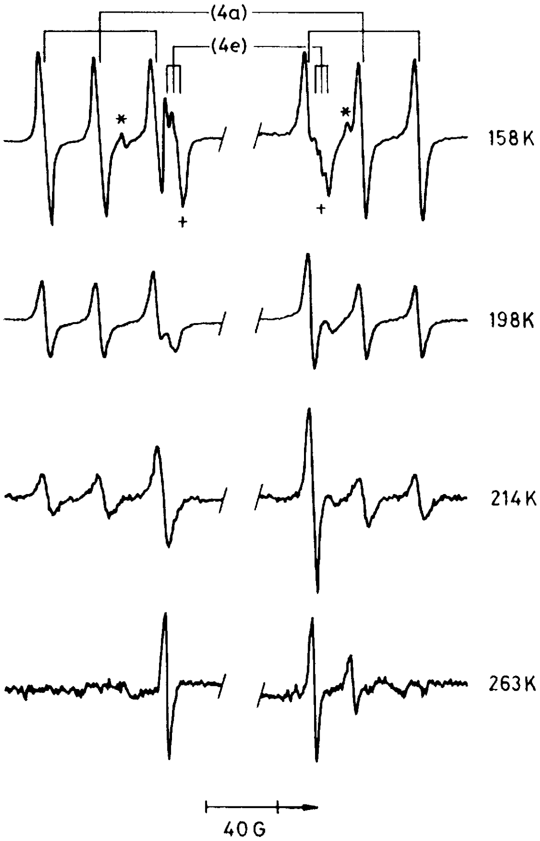
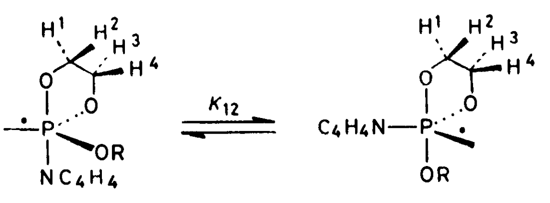


FIGURE 2 E.s.r. spectra of the radical (4; R = Bu^t) in ethylene (at 158 K) or cyclopropane (other temperatures) solvent. The lines marked * are due to $(EtO)_3POBu^t$, those marked + are corrupted by an unidentified signal



(12)

(6a) (6e)

(ii) *2-Pyrrol-1-yl-1,3,2-dioxaphospholan* (5).—The cyclic phosphine (5) was less soluble than (3) in hydrocarbon solvents and spectra could not be obtained at very low temperatures when separate signals from (6a and e) might have been detectable. It also appears that exchange of (6a and e) is somewhat more rapid than exchange of (4a and e).

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* N_a and N_e refer to apical and equatorial nitrogen nuclei, respectively.

At high temperatures (262 K) addition of ethoxyl radicals to (5) afforded the spectrum shown in Figure 3a and corresponding to the weighted average of the signals from (6a; R = Et) and (6e; R = Et) (some differential broadening is still apparent).

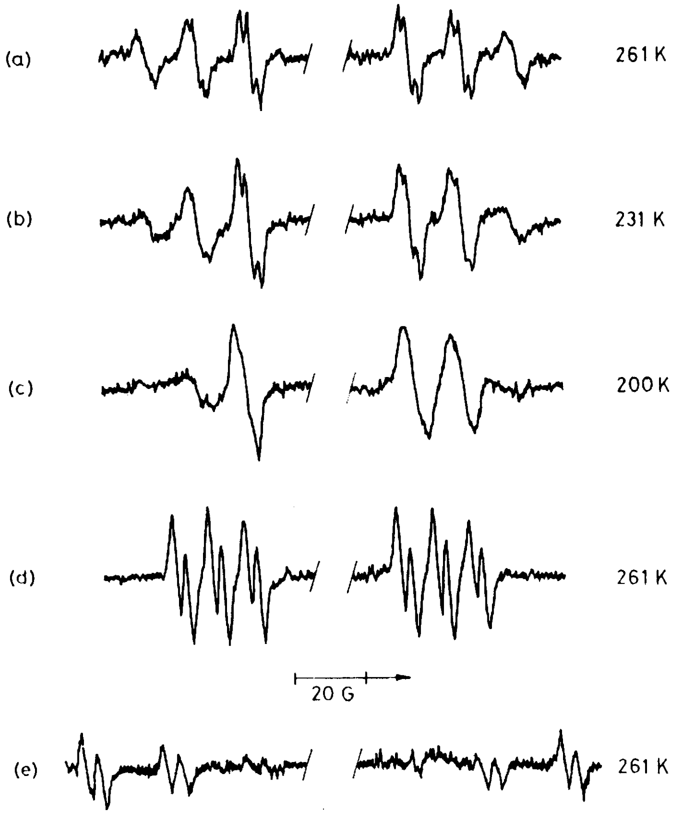


FIGURE 3 E.s.r. spectra of the radicals (6) in toluene–cyclopropane (1 : 1 v/v): (a)—(c), R = Et; (d), R = Bu^t; (e), R = Me_3Si

The average value of a(N) (15.0 G at 262 K) indicates that similar concentrations of (6a and e) are present at equilibrium. As the temperature was decreased differential line-broadening became marked (see Figure 3) and the average nitrogen splitting decreased, indicating that (6e; R = Et) is the more stable isomer if it is assumed that $a(N_a)$ and $a(N_e)$ are independent of temperature.

TABLE 3

Averaged e.s.r. parameters for (6a and e) in toluene–cyclopropane (1 : 1) solvent

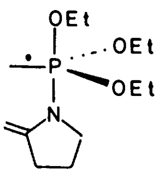
R	T/K	g Factor [a]	Hyperfine splittings/G				K_{12} [b]
			$\bar{a}$(P) [a]	$\bar{a}$(N)	$\bar{a}(H^2)$	$\bar{a}(H^1)$	
Bu^t	232	2.0022	875.7	8.9	3.5	c	6.1
	261	2.0021	878.2	9.8	3.4	c	4.4
Et	231	2.0018	888.8	14.4	*ca.* 2.2	*ca.* 2.2	1.5
	262	2.0019	890.8	15.0	*ca.* 2.2	*ca.* 2.2	1.3
Me_3Si	232	2.0022	906.4	22.8	c	4.4	0.23
	263	2.0021	910.5	22.5	c	4.3	0.25

[a] Calculated using the Breit–Rabi equation. [b] Calculated from the average nitrogen splitting. [c] Not resolved.

Similarly, only the averaged spectra of (6a and e) were obtained for (6; R = Bu^t), but the smaller nitrogen splitting (9.8 G at 262 K) implies a much smaller proportion of (6a; R = Bu^t) at equilibrium. Similar temperature-dependent linewidth effects were apparent in the spectra of (6; R = Et) and (6; R = Bu^t), and the form of the differential broadening indicates that a(P) for (6a) is *greater than* a(P) for (6e), the same order as found for the acyclic radicals (4a and e) when R = Bu^t, Et, or Me_3Si.

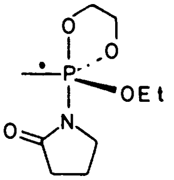
It was difficult to obtain spectra of (6; R = Me_3Si) on account of a thermal reaction between (5) and $Me_3SiOOSiMe_3$. The spectra between 230 and 262 K (see Figure 3) indicated that the averaged signals from (6a and e) were again being detected, and the high value of a(N) (22.5 G at 262 K) implies that K_{12} is smaller for (6; R = Me_3Si) than for (6; R = Et or Bu^t). The differential broadening observed in the spectrum of (6; R = Me_3Si) indicates that a(P) for (6a) is *less than* that for (6e). The e.s.r. parameters for (6) are collected in Table 3.

Since separate signals for (6a and e) could not be obtained at low temperatures, it was necessary to assume nitrogen splittings for each isomer in order to estimate K_{12} from $\bar{a}$(N). We chose the individual splittings by comparison with those [7] for the phosphoranyl radicals (7)—(9), which contain a 2-oxopyrrolidin-1-yl ligand.



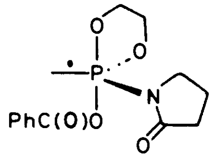
(7)

a(N)/G 25·8



(8)

22·8



(9)

ca. 6

An estimate (26.6 G) of $a(N_a)$ for (6a) was obtained by multiplying the value for (4a; R = Et) by 22.8/25.8, and $a(N_e)$ for (6e) was taken as 6 G. The values of K_{12} were then calculated from $\bar{a}$(N) using a relationship analogous to equation (9)

The proton splittings observed for (6) are in accord with apical–equatorial attachment of the ring [7] and, qualitatively, with the values of K_{12} calculated from $\bar{a}$(N). On average, splitting from H^1 and H^2 [see equation (12)] would be expected and the magnitudes would be given by equations (13) and (14), assuming that only the apical methyleneoxy proton *cis* to the unpaired electron gives rise to non-zero splitting [of 4.5 G, as in (8)].[7]

Thus, the average spectra, from (6a and e), show a doublet from H^2 (R = Bu^t), a doublet from H^1 (R = Me_3Si), and an

$$\bar{a}(H^1) = 4.5/(K_{12} + 1) \qquad (13)$$

$$\bar{a}(H^2) = 4.5K_{12}/(K_{12} + 1) \qquad (14)$$

apparent triplet as a result of approximately equal splittings from H^1 and H^2 (R = Et).

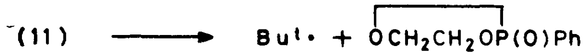
(iii) 2-*Phenyl*-1,3,2-*dioxaphospholan* (10).—These experiments were carried out to permit a comparison to be made with the results from the pyrrolylphosphines.

Addition of photochemically-generated t-butoxyl radicals to (10) in cyclopropane–toluene solvent (3 : 1 v/v) at low temperatures gave rise to the spectrum of the ligand-π phosphoranyl radical (11) [$a(\mathrm{P}) \simeq a(1\mathrm{H}_p)$ 14.6, $a(2\mathrm{H}_o)$ 5.5, $a(2\mathrm{H}_m)$ *ca.* 0.9 G, *g* 2.0026 at 165 K]. No isomeric radical exhibiting large ^{31}P splitting was detectable.

At 165 K a weak signal from the t-butyl radical was also apparent [equation (16)] and [$\mathrm{Bu^t\cdot}$]/[(11)] increased with temperature until above *ca.* 200 K only the β-scission product was detectable.

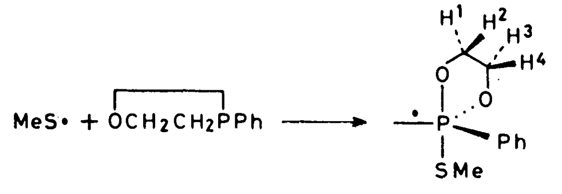
$$\mathrm{Bu^tO\cdot + \overline{OCH_2CH_2OP}Ph \longrightarrow Bu^tO(\overline{OCH_2CH_2O-})\overset{+}{P}-\overset{\bullet\,-}{Ph}} \quad (15)$$

(10) (11)



$$\mathrm{(11) \longrightarrow Bu^t\cdot + \overline{OCH_2CH_2OP}(O)Ph} \quad (16)$$

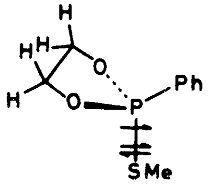
Repetition of the above experiment with dimethyl disulphide (as a source of MeS·) instead of $\mathrm{Bu^tOOBu^t}$, afforded the spectrum of the TBP phosphoranyl radical (12) [a(P) 623.7, a(1H) 3.8 G, *g* 2.0047 at 207 K] and no ligand-π species were detectable.



(17)

(12)

The splitting from one ring proton (probably H^1), still apparent at 260 K, indicates a TBP radical rather than a σ* structure (13), which would probably not exhibit splitting from a ***unique*** ring proton at high temperatures.



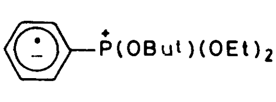
(13)

DISCUSSION

The pyrrolylphosphoranyl radicals all appear to adopt TBP structures and exhibit large phosphorus hyperfine splittings: no species having a ligand-π electronic structure could be detected by e.s.r. spectroscopy. In contrast, phenylphosphoranyl radicals of the type $[\mathrm{PhP(OR)_3}]^\bullet$ are most stable as ligand-π structures, which are best regarded as benzene radical anions carrying a $\overset{+}{\mathrm{P}}\mathrm{(OR)_3}$ substituent. The phosphorus atom lies in the nodal plane of the unpaired electron orbital and *a*(P) is small (*ca.* 10 G), although there must be appreciable delocalisation of the unpaired electron into vacant π-orbitals of the $\overset{+}{\mathrm{P}}\mathrm{(OR)_3}$ group.† However, the energetic difference between ligand-π and TBP structures must be quite small, since when H, Cl, or RS ligands are attached to phosphorus the latter structure (or the related σ* structure) becomes preferred.[1,5] For example, the only structures detected by e.s.r. spectroscopy for $[\mathrm{PhP(OBu^t)(OEt)_2}]^\bullet$ and $[\mathrm{PhP(OBu^t)Cl_2}]^\bullet$ are (14) and (15), respectively.[5]

There is evidence [10] that less strain is present in a five-membered ring when it bridges apical and equatorial sites in a TBP phosphorane than when the endocyclic phosphorus atom is tetrahedral. Hence, we considered it possible that $[\mathrm{PhP(\overline{-OCH_2CH_2O})OBu^t}]^\bullet$ might adopt the TBP structure (16) rather than the ligand-π structure (11) analogous to (14). However, the e.s.r. spectrum shows conclusively that the ligand-π structure is still preferred, although recent work [13] has shown that the constraints imposed by the cage in (17) result in the adoption of a TBP structure, in contrast to the ligand-π structure (18) preferred by the acyclic analogue.

The radical $[\mathrm{PhP(\overline{-OCH_2CH_2O})SMe}]^\bullet$ has an alkylthiyl ligand and adopts the TBP structure (12), as expected on the basis of earlier results.[5]



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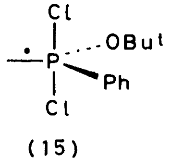

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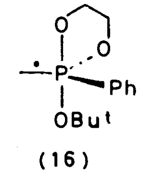

(16)

The calculated electron affinity of pyrrole (−2.39 eV) is much smaller than that of benzene (−1.14 eV),[14] and

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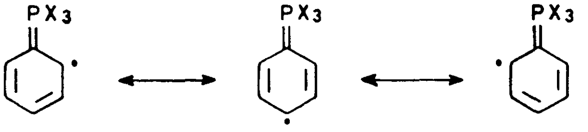
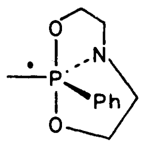
† Both inductive and π-conjugative electron withdrawal by the $\overset{+}{\mathrm{P}}\mathrm{X_3}$ substituent should result in stabilisation of ψ_S relative to ψ_A (the benzene ring π* orbitals which are symmetric and antisymmetric, respectively, to reflection in the plane through C-1 and C-4 and perpendicular to the ring) and consequently result in a build-up of spin density at ring positions 1 and 4 and a reduction at positions 2, 3, 5, and 6.[11] Superimposed on this effect, π-electron transfer to the substituent will result in selective reduction in spin density at positions 3 and 5, as indicated by the inclusion of canonical structures (A)—(C). A similar distribution of spin density is found in the radical anions of $\mathrm{PhSiMe_3}$[12a] and PhCN.[12b]



(A) (B) (C)

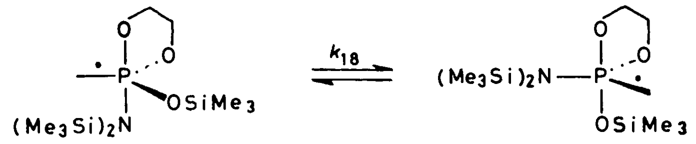
thus it is not surprising that the TBP structure is preferred for the pyrrolylphosphoranyl radicals (4) and (6).


(17)


$(\mathrm{EtO})_2\mathrm{Et_2N\dot{P}{-}\dot{P}h}$

(18)

Permutational Isomerisation and Ligand Apicophilicity.—The high rates of exchange between a and e isomers of (4) and (6) are similar to that for exchange of apical and equatorial Me_2N and Bu^tO groups in (2) (see Introduction). A recent e.s.r. study of (19) has shown that a and e isomers also undergo rapid exchange.[15] At 215 K, k_{18} is 1.9 × 10^8 s^{-1} and its temperature dependence is given by equation (19).

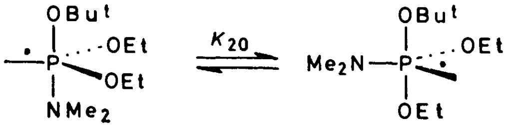

(18)

(19a) (19e)

The apicophilicities of pyrrolyl and alkoxyl ligands are similar and clearly subtle factors will be involved in determining the relative stabilities of a and e isomers of (4) and (6).

$$\log_{10}(k_{18}/\mathrm{s}^{-1}) = 12.7 - 18.2/\theta \qquad (19)$$

The equilibrium constant K_7 ($R = Bu^t$) is much smaller than K_{20} (*ca.* 10 at 123 K)[4] [equation (20)].


(20)

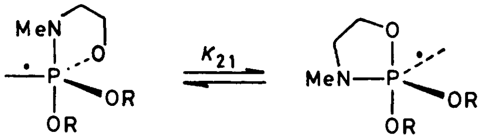
(20a) (20e)

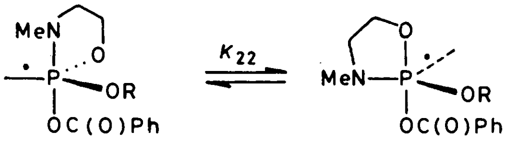
The electronegativity and apicophilicity of a pyramidal Me_2N group would be expected to be less than that of a pyrrolyl ligand, and the lower value (12.8 G) of $a(N_a)$ for (20a) compared with that for (4a) may be indicative of the different states of hybridisation of nitrogen in the two radicals. For the cyclic radical (2a), $a(N_a)$ is 24 G, similar to the estimated value of $a(N_a)$ for (6a), and K_2 is also similar to K_{12} ($R = Bu^t$). The apicophilicities of Me_2N and pyrrolyl ligands and the values of $a(N)$ are thus similar for the cyclic species and this may indicate planarity of the Me_2N group in (2).

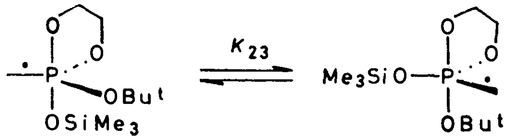
The equilibrium constant K_{12} increases along the series $R = Me_3Si < Et < Bu^t$, and the simplest interpretation of this trend would be to attribute it to an increase in the apicophilicities of the RO ligands in the order $Me_3SiO < EtO < Bu^tO$.* However, this is probably not the only factor involved since the apicophilicity of amino ligands appears to be significantly dependent on the nature of the other ligands present in a phosphoranyl radical. For example, at 178 K the equilibrium constant K_{21} is 3 when $R = Et$, but 38 when $R = Bu^t$.[4] Similarly, K_{22} is 1.5 when $R = Et$, but 3.3 when $R = Bu^t$ at 218 K.[7]

It thus appears that, as expected, apicophilicity is not a ligand property entirely independent of the nature of the other substituents at phosphorus. It is still not possible to disentangle the various steric and electronic effects involved and to predict with certainty the site preferences of RO groups in all phosphoranyl radicals. Changing the nature of R in (6) may alter not only the apicophilicity of RO, but will also have a secondary effect on the apicophilicity of the pyrrolyl group.

We have recently reported a study of the β-scission of a series of cyclic and acyclic t-butoxyphosphoranyl radicals, from which it was concluded that fragmentation was site-selective in the sense that the C–O bond in a Bu^tO ligand undergoes cleavage more readily when this substituent is apical than when it is equatorial.[16] The radical (21) exhibits an e.s.r. spectrum which indicates that K_{23} is not close to unity, and we assumed K_{23} <1 on the basis of the expected higher group electronegativity of Me_3SiO compared with that of Bu^tO.[16]


(21)


(22)


(23)

(21a) (21b)

However, in view of the present results obtained for (6) it appears much more likely that K_{23} is >1. The

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* The e.s.r. spectra of $\mathrm{Me\overline{NCH_2CH_2XP}(OEt)OBu^t}$ (X = MeN or O) indicate that the apicophilicities of Bu^tO and EtO groups are significantly different for these radicals.[4] However, the apicophilicities of endocyclic Me_2CO and H_2CO groups in radicals of the type $\mathrm{\overline{OCMe_2CH_2OP}(A)B}$ are similar.[7] This may indicate that differences in apicophilicity of primary and tertiary alkoxy-groups is steric, rather than electronic, in origin.

previous experimental evidence [16] would then have to be reinterpreted in terms of *equatorial* site-selectivity in β-scission.

A relatively low apicophilicity for the Me_3SiO group would be understandable if the σ inductive effect [17] of a substituent is more important than its total (resonance + inductive + field effects) electronegativity in governing the preference of a ligand for apical placement.

The reversal in the order of a(P) for (6a and e) when $R = Me_3Si$, compared with the order $[a(P_{6a}) > a(P_{6e})]$ when R = Bu^t or Et, deserves some comment. For TBP phosphoranyl radicals with identical ligands, we have suggested [4] that the permutational isomer with the most electronegative ligands in apical sites will exhibit the largest value of a(P). This would imply that electronegativity increases in the order Bu^{t}O, EtO < C_4H_4N < Me_3SiO.

EXPERIMENTAL

The techniques employed for detection of e.s.r. spectra during continuous u.v. irradiation of samples in the cavity of the Varian E-4 spectrometer have been described previously.[4,18] Photolysis was conducted with light from a Philips CS 500 W/2 mercury lamp, focused using silica lenses and filtered through 8 cm of 0.04M-$NiSO_4$ in distilled water. Samples consisted of phosphine, peroxide (or MeSSMe), and solvent in the volume ratio *ca.* 1 : 1 : 6, and photolysis of solutions containing the phosphines alone afforded no e.s.r. signals.

Spectroscopic parameters, which did not vary significantly with the nature of the hydrocarbon solvent, were measured using a proton magnetometer and a microwave frequency counter. The difference in magnetic fields at the magnetometer probe and at the sample was determined using the pyrene radical anion (Na^+ counter ion) in tetrahydrofuran (g 2.002710) as standard.[19] Relative radical concentrations were determined by electronic integration of the first-derivative spectra followed by manual integration of the derived absorption spectra. Computer simulations were accomplished using the program ESREXN available from QCPE (program no. 209).

Materials.—Di-t-butyl peroxide and dimethyl disulphide were commercial products which were purified before use. Diethyl [20] and bis(trimethylsilyl) [21] peroxides, and 2-pyrrol-1-yl-1,3,2-dioxaphospholan (5) [22] were prepared by methods in the literature. 2-Phenyl-1,3,2-dioxaphospholan, b.p. 93—94 °C at 3.5 Torr, was prepared from ethylene glycol, dichlorophenylphosphine, and triethylamine in ether solvent as described by Dutasta *et al.*[23]

Diethoxy(pyrrolyl)phosphine (3), b.p. 62—63 °C at 2.3 Torr, was prepared in a similar way to (5) [22] from diethyl chlorophosphite, pyrrole, and triethylamine in benzene (Found: C, 51.0; H, 7.5; N, 7.5; P, 16.6. $C_8H_{14}NO_2P$ requires C, 51.3; H, 7.5; N, 7.5; P, 16.6%).

The proton-decoupled ^{13}C n.m.r. spectra of (3) and (5) in perdeuteriocyclohexane with tetramethylsilane internal standard confirmed that both phosphines were N–P bonded (compare ref. 24). Compound (3) showed δ_C −16.7 (J_{C-P} 5.1 Hz, 2CH_3), −60.1 (J_{C-P} 10.1 Hz, 2CH_2), −111.1 (J_{C-P} 3.1 Hz, C-3 and -4), and −120.5 (J_{C-P} 13.3 Hz, C-2 and -5); compound (5) showed δ_C −64.8 (J_{C-P} 9.0 Hz, 2CH_2), −112.0 (J_{C-P} 2.2 Hz, C-3 and -4), and −120.6 (J_{C-P} 12.8 Hz, C-2 and -5).

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