Cyclisation of Unsaturated Phosphoranyl Radicals [1]

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The reactions of a series of allylic and homoallylic phosphites and related compounds with t-butoxyl, ethoxyl, and methyl radicals have been studied by e.s.r. spectroscopy. Triallyl phosphite reacts to give detectable phosphoranyl radicals which undergo competitive β-scission (giving allyl radicals) and cyclisation to give oxaphosphetanylmethyl radicals (four-membered ring). Tris-1-methylallyl and tribut-2-enyl phosphites behave similarly, but tris-2-methylallyl phosphite does not give rise to a cyclised species, probably as a result of steric inhibition of the intramolecular addition. The phosphoranyl radical from tribut-3-enyl phosphite cyclises to give an oxaphospholanylmethyl radical (five-membered ring), but not when the addendum radical is the bulky t-butoxyl. The phosphoranyl radical from tripent-4-enyl phosphite does not give rise to detectable cyclised product. Intramolecular competition experiments show that the four-membered ring is formed more readily than the five in the cyclised radicals. Diallylamino(trialkoxy)phosphoranyl radicals also cyclise to give azaphosphetanylmethyl radicals (four-membered ring).

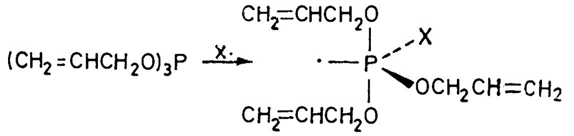
CYCLISATION reactions are rather common in free radical chemistry, and the factors which affect these processes are currently attracting much attention.[2] Most work has been carried out on reactions involving the intramolecular addition of an alkyl radical to an olefinic group, particularly in the hex-5-enyl and related systems, but reactions involving heteroatoms are also known.

Much information is now available on the structures and reactivities of phosphoranyl radicals ($X_4P\cdot$),[3,4] and some intermolecular addition reactions between spirocyclic (but not acyclic) phosphoranyl radicals and terminal alkenes have been reported.[5] As a continuation of our studies on phosphoranyl radicals, we have examined the generation of such species with unsaturated ligands, with the aim of establishing new cyclisation reactions. A number of such systems have been identified, and the factors which govern their behaviour have been investigated.

RESULTS

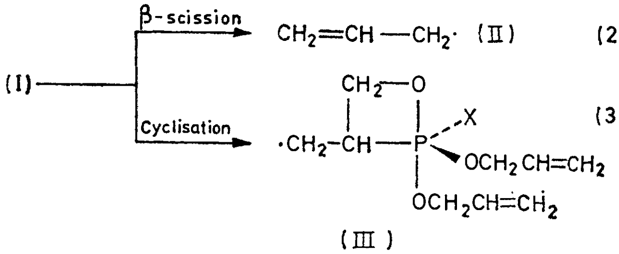
A series of alkenyl phosphites and some related compounds were synthesised, varying the structure of the alkenyl groups in a systematic way. Di-t-butyl peroxide, diethyl peroxide, and azomethane were photolysed in the presence of these phosphites in an e.s.r. cavity, and the spectra of the radicals resulting from the interaction of the compounds with the t-butoxyl, ethoxyl, or methyl radicals were observed. Propane was used as a solvent for the reactions involving the peroxides, and a 70 : 30 propane–toluene mixture for the reactions involving azomethane; most experiments were conducted at −120°. The results are collected in Table 1.

Allylic Phosphites.—The reaction of triallyl phosphite (1) (Table 1) with t-butoxyl radicals in cyclopropane has been studied previously,[6,7] but the spectrum of only the allyl radical (II), resulting from β-scission of the phosphoranyl radical (I) was detected. Using propane as a solvent, we have now detected also the e.s.r. spectra of the phosphoranyl radical itself (I; X = Bu^{t}O) and of a third radical which analyses as a doublet (180 G) of doublets (20 G) of triplets (20 G), and to which we ascribe the oxaphosphetan structure (III; X = Bu^{t}O).† This splitting pattern would not be compatible with cyclisation to give a five-membered (oxaphospholan) ring, and our assignment is supported by the fact that the spectra of all other analogous radicals which we have detected can be interpreted consistently on the same basis (see below).



(1)

(I)



(2)

(3)

(III)

Under similar conditions with ethoxyl radicals the primary phosphoranyl radical (I; X = EtO) could not be detected, but the spectrum of the secondary (cyclised) radical (III; X = EtO) was stronger than with t-butoxyl radicals. Methyl radicals from azomethane similarly produced a relatively strong spectrum of the cyclised radical (III; X = Me) together with that of the allyl radical, but no species (I; X = Me) could be detected.

The behaviour of most of the other unsaturated phosphites which are listed in Table 1 can be understood on a similar basis, generalised in the Scheme.

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† When X is an alkoxy-group this ligand may occupy an apical site instead of the allyloxy-group, or ligand exchange may be rapid on the e.s.r. time scale.

[1] Preliminary report, A. G. Davies, M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1974, 27.

[2] J. W. Wilt, 'Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, vol. I, ch. 8.

[3] A. G. Davies, R. W. Dennis, and B. P. Roberts, *J.C.S. Perkin II*, 1974, 1101; R. W. Dennis and B. P. Roberts, *ibid.*, 1975, 140.

[4] W. G. Bentrude, 'Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, vol. II, ch. 22.

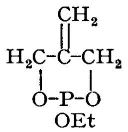
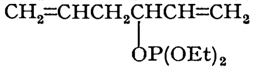
[5] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1416.

[6] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969, **91**, 3944.

[7] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993.

TABLE 1

E.s.r. spectra obtained from the reactions of radicals (X•) with unsaturated phosphites and related compounds[a]

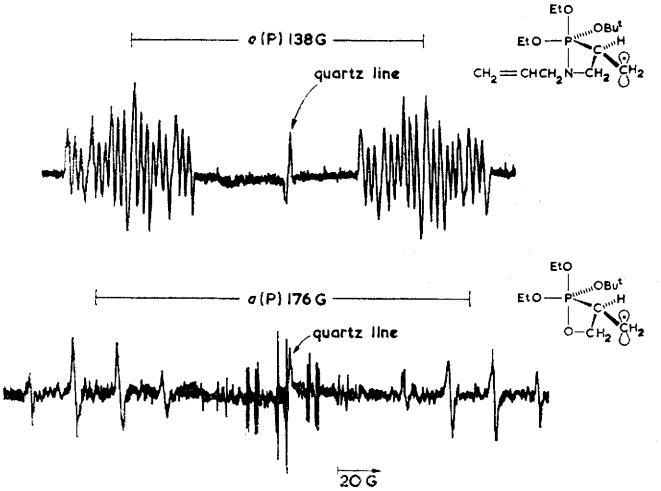
		Radical				
		(IV)	(VI)			
Compound	X•	a(P)[b]	a(H$_\alpha$)[b]	a(H$_\beta$)[b]	a(P)[b]	(V) *etc.*
(1) $(CH_2{=}CHCH_2O)_3P$	Bu^{t}O•	897	20.5	20.5	179.0	$CH_2{=}CH{-}\dot{C}H_2$
	EtO•		20.0	20.0	182	$CH_2{=}CH{-}\dot{C}H_2$
	Me•		20.0	20.0	180	$CH_2{=}CH{-}\dot{C}H_2$
(2) $CH_2{=}CHCH_2OP(OEt)_2$	Bu^{t}O•	884	20.0	20.0	176	$CH_2{=}CH{-}\dot{C}H_2$
	EtO•	865	20.0	20.0	181	$CH_2{=}CH{-}\dot{C}H_2$
	Me•		20.0	20.0	180	$CH_2{=}CH{-}\dot{C}H_2$,Me•
(3) $(MeCH{=}CHCH_2O)_3P$	Bu^{t}O•		19.9	14.3[c]	190	$MeCH{=}CH\dot{C}H_2$
	EtO•		19.9	14.3[c]	199	$MeCH{=}CH\dot{C}H_2$
	Me•		20.0	14.3[c]	195	$MeCH{=}CH\dot{C}H_2$
(4) $(CH_2{=}CMeCH_2O)_3P$	Bu^{t}O•	898				$CH_2{=}CMe\dot{C}H_2$
	EtO•	899				$CH_2{=}CMe\dot{C}H_2$
	Me•	804				$CH_2{=}CMe\dot{C}H_2$
(5) $CH_2{=}CHCHMeOP(OEt)_2$	Bu^{t}O•	882	20.7	20.7	174[d]	$MeCH{=}CH\dot{C}H_2$
			20.5	20.5	176.5[d]	
	EtO•	881	20.4	20.4	178.5	$MeCH{=}CH\dot{C}H_2$
	Me•		20.8	20.8	117	$MeCH{=}CH\dot{C}H_2$,Me•
(6) $CH_2{=}CHCH_2OPEt_2$	Bu^{t}O•	710[e]				$CH_2{=}CH{-}\dot{C}H_2$,Et•
	EtO•	701[f]				$CH_2{=}CH{-}\dot{C}H_2$,Et•
	Me•	585[g]				$CH_2{=}CH{-}\dot{C}H_2$,Me•,Et•
(7) 	Bu^{t}O•	886				 $EtO(X)P(O)OCH_2\overset{\overset{CH_2}{\Vert}}{C}{-}\dot{C}H_2$[h]
	EtO•	885	18.0		221	 $EtO(X)P(O)OCH_2\overset{\overset{CH_2}{\Vert}}{C}{-}\dot{C}H_2$[h]
	Me•					 $EtO(X)P(O)OCH_2\overset{\overset{CH_2}{\Vert}}{C}{-}\dot{C}H_2$[h]
(8) $(CH_2{=}CHCH_2)_2NP(OEt)_2$	Bu^{t}O•	857	19.5	10.7	138[i]	$(CH_2{=}CHCH_2)_2N$•[j]
	EtO•		19.5	11.3	139[i]	$(CH_2{=}CHCH_2)_2N$•
	Me•					Me•
(9) $[CH_2{=}CH(CH_2)_2O]_3P$	Bu^{t}O•	884				Bu^t•[k]
	EtO•	883	21.0	25.0	127	Et•[k]
	Me•		21.0	25.0	136	Me•
(10) $[CH_2{=}CH(CH_2)_3O]P$	Bu^{t}O•	893				Bu^t•[k]
	EtO•	890				$CH_2{=}CH(CH_2)_2\dot{C}H_2$,Et•[k]
	Me•	794				Me•
(11) $CH_2{=}CH(CH_2)_4OP(OEt)_2$	Bu^{t}O•	887				Bu^t•[k]
(12)  $CH_2{=}CHCH_2\underset{\underset{OP(OEt)_2}{\vert}}{C}HCH{=}CH_2$	Bu^{t}O•	887[l]	20.5	20.5	174[l]	$CH_2{=}CHCH_2\dot{C}HCH{=}CH_2$[m]
		891[l]	20.0	20.0	177[l]	$CH_2{=}CHCH_2\dot{C}HCH{=}CH_2$[m]
	EtO•	881	20.7	20.7	178.3	$CH_2{=}CHCH_2\dot{C}HCH/{=}CH_2$[m]
	Me•		20.8	20.8	175.5	$CH_2{=}CHCH_2\dot{C}HCH/{=}CH_2$,Me•[m]
(13) $(PhO)_3P$	Bu^{t}O•	962[n]				PhO•
	EtO•	969				PhO•
	Me•					[o]
(14) $PhCH_2OP(OEt)_2$	Bu^{t}O•	887				$PhCH_2$•

[a] Reactions involving Bu^{t}O• and EtO• were carried out in propane and those involving Me• in propane–toluene, at −100 to −120° unless otherwise stated. [b] Hyperfine splittings are quoted in G; the Breit–Rabi equation has been used where appropriate. All phosphoranyl radicals had g factors of 2.003 ± 0.001. [c] $a(CH_3)$ 23.0 G (3 H). [d] Two isomers, intensity ratio 3 : 2. [e] $a(CH_2)$ 2.3 G (4 H). [f] $a(CH_2)$ 2.4 G (4 H). [g] Line width *ca.* 40 G at −133°; no resolvable fine structure. [h] Coupling constants for X = Bu^{t}O, EtO, or Me; 13.6 (2 H), 14.4 (2 H), 2.7 G (2 H). [i] a(N) 3 G. [j] Coupling constants at −50°; a(N) 14.0, a(H$_\beta$) 34.5 (4 H), a(H) 2.8 G (3 H). [k] At *ca.* −20°. [l] Two isomers detected, intensity ratio 3 : 1. [m] Approximate coupling constants for a mixture of two isomers; 15.8 (3 H), 14.6 (1 H), 13.2 (2 H), 3.5 G (1 H). [n] A spectrum assigned to $(PhO)_2\dot{P}(OBu^t)_2$, a(P) 930 G, developed with time. [o] Weak, poorly resolved, unidentified multi-line spectrum, g *ca.* 2.00, width *ca.* 80 G.

Spectra of the cyclised species (VI; $n = 1$) were usually stronger when X = EtO or Me than when X = Bu^{t}O, and, when X = Bu^{t}O, allyl diethyl phosphite (2) gave a stronger spectrum (see Figure) than did triallyl phosphite (1). Whereas tris-3-methylallyl phosphite (3) gave a cyclised radical with all three reagents, tris-2-methylallyl phosphite (4) gave only the primary phosphoranyl radical (IV), and none of the cyclised radical (VI).

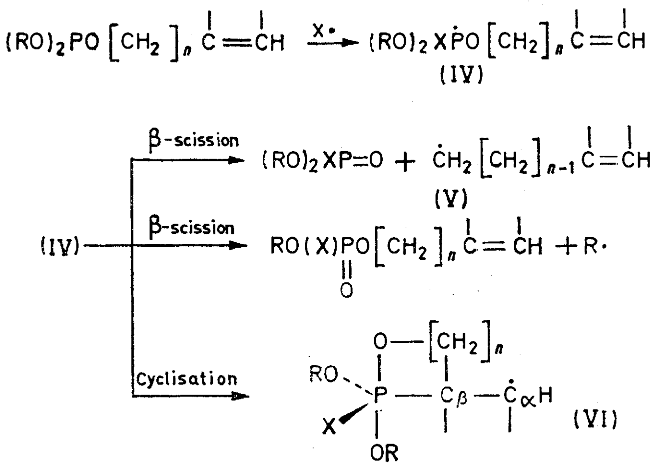
Diethyl 1-methylallyl phosphite (5) reacted with methyl radicals to give the cyclised radical (VI; X = Me, R = Et), but no spectra of the primary phosphoranyl radical or the 1-methylallyl radical were detected. With ethoxyl radicals, a primary phosphoranyl radical, a cyclised species, and the 1-methylallyl radical were all present. t-Butoxyl radicals gave rise to similar spectra, but there were two forms of the cyclised radical with slightly different splitting constants. These are discussed below.

In the reactions involving photolysis of azomethane, triallyl (1), tris-2-methylallyl (4), and tribut-2-enyl phosphite (3) showed no spectrum of the methyl radical alongside that of the appropriate allyl radical, but allyl diethyl phosphite (2) showed the presence of both allyl and methyl radicals. With methyl, ethoxyl, or t-butoxyl radicals, allyloxydiethylphosphine (6) showed the presence of the primary phosphoranyl radical, $Et_2X\dot{P}OCH_2CH{=}CH_2$, methyl (X = Me), ethyl, and allyl radicals (X = EtO, Bu^{t}O, Me), but no spectrum of the cyclised radical was apparent with any of the reagents.



E.s.r. spectra obtained by the photolysis of di-t-butyl peroxide in propane at −120° in the presence of the following phosphorus compounds. Upper spectrum: diethoxydiallylaminophosphine (8) showing the presence of the cyclised radical (XI). Lower spectrum: allyl diethyl phosphite (2), showing the presence of the cyclised radical, and, in the centre, the allyl radical

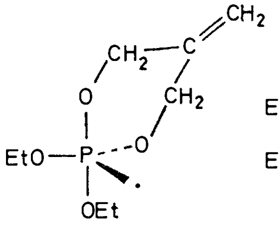
The phosphoranyl radicals resulting from the interaction of ethoxyl or t-butoxyl radicals with allyloxydiethylphosphine exhibited fine structure due to coupling with the four methylene protons of the two equatorial ethyl groups,[3] and, in common with the detected isomers of other dialkoxydialkylphosphoranyl radicals [3] were relatively long lived: the radical $(CH_2{=}CH{-}CH_2O)\dot{P}Et_2OBu^t$ decayed at −120° with a first-order rate constant of $8.6 \times 10^{-2}\ s^{-1}$.



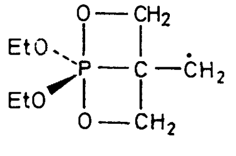
SCHEME

2-Ethoxy-5-methylene-1,3,2-dioxaphosphorinan (7) reacted with ethoxyl radicals to give rise to the spectra of the phosphoranyl radical (VII), of the bicyclic product of ring closure (VIII) (which showed an unusually large β-phosphorus splitting of 221 G), and of an allylic radical (IX) arising from the β-scission of (VII). A similar allylic radical was detected in the reactions of the phosphorinan with t-butoxyl and methyl radicals.

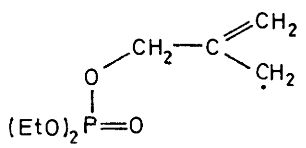
To determine whether the cyclisation could produce a heterocyclic radical involving nitrogen rather than oxygen, the reaction of diethoxy(diallylamino)phosphine (8) was investigated. t-Butoxyl radicals reacted to give the phosphoranyl radical (X) and its product of cyclisation (XI) (see Figure) and, above −100°, the diallylaminyl radical resulting [3,8] from the α-scission of (X). The other product of α-scission is diethyl t-butyl phosphite, and after prolonged photolysis, this gives rise to the spectrum of the phosphoranyl radical [8] $(EtO)_2\dot{P}(OBu^t)_2$.



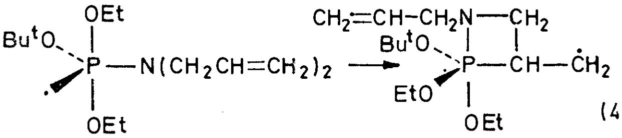
(VII)



(VIII)



(IX)



(X) (XI) (4)

Homoallylic Phosphites and Related Compounds.—To examine the effect of size on the ease of ring closure, some homoallylic phosphites were investigated. Tribut-3-enyl phosphite (9) reacted with ethoxyl and methyl radicals to give the phosphoranyl radicals (XII; X = EtO or Me), which cyclised to give the heterocycloalkylmethyl radicals (XIII) rather than the alternative heterocycloalkyl radicals (XIV).

Tripent-4-enyl phosphite (10) and diethyl hex-5-enyl phosphite (11) both yielded phosphoranyl radicals, but neither gave any indication of cyclisation.

To investigate the relative ease of cyclisation to give a four- or a five-membered ring, diethyl 1-vinylbut-3-enyl phosphite (12) was investigated. With methyl radicals, no phosphoranyl radical was detected, but spectra of a cyclised species and of the methyl radical were observed. With ethoxyl radicals, a phosphoranyl radical spectrum was observed together with spectra of a cyclised radical and of an allylic radical. t-Butoxyl radicals gave rise to *two* phosphoranyl radicals with similar phosphorus hyperfine split-

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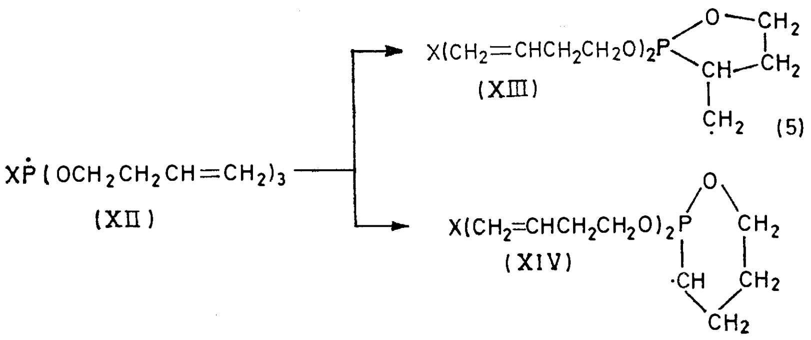
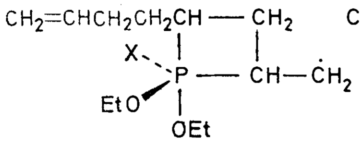
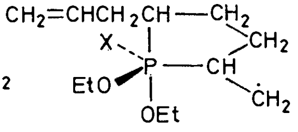
[8] R. W. Dennis and B. P. Roberts, *J. Organometallic Chem.*, 1973, **47**, C8.

tings and to *two* similar cyclised radical spectra [*cf.* the reaction of (5) with t-butoxyl radicals]. All the cyclised radicals from (12) had a(P) in the range 175—185 G, a value which appears to be characteristic of the four-membered ring system [*e.g.* 175—188 G from compounds (1)—(3) and (5)] rather than the five-membered ring [*e.g.* 127—136 G from compound (9)]. Although this evidence is not entirely conclusive, it appears very likely that cyclisation gives (XV) rather than (XVI) (X = Me, EtO, Bu^{t}O).





(XV)



(XVI)

The possibility that intramolecular attack could occur at a benzene ring was also briefly explored. Alkoxyl radicals reacted with triphenyl phosphite (13) and with benzyl diethyl phosphite (14) to give primary phosphoranyl radicals whose e.s.r. spectra could be detected in propane solvent at low temperatures, but no cyclised species were apparent. It is noteworthy that neither of these phosphoranyl radicals have been detected previously by e.s.r. spectroscopy, and this detection rules out the possibility of concerted processes in the overall displacement of phenoxyl radicals from triphenyl phosphite or the overall oxidation of benzyl diethyl phosphite to t-butyl diethyl phosphate.

DISCUSSION

Whereas only spirocyclic phosphoranyl radicals normally add readily to olefins,[5] intramolecular addition can occur with the acyclic species. Cyclisation of the radicals $X_3\dot{P}O[CH_2]_nC{=}C$, always to give the exocyclic radicals $X_3\overline{\dot{P}O[CH_2]_nC}{-}C\cdot$, took place when $n = 1$ or 2, but not when $n = 3$ or 4, and the phosphorane containing the four-membered ring ($n = 1$) appears to be formed more readily than that containing the five-membered ring ($n = 2$). Phosphoranes in which the phosphorus is part of a four- or five-membered ring bridging between apical and equatorial positions are well known[9] and often possess higher stability than their acyclic analogues.

When cyclisation did occur, the intensity of the spectra of the phosphoranyl radicals was thereby reduced, and the superimposed spectra of the acyclic parent and the cyclic product radicals could usually be observed only below —100°. Above this temperature, only fragments arising from the α- or β-scission of the phosphoranyl radical could generally be detected. As an exception to this, however, the spectrum of the cyclic radical when $n = 2$ [derived from compound (9)] could be observed up to —70°.

For comparison, alkenyl radicals $\dot{C}H_2CH_2[CH_2]_nC{=}C$ also cyclise to give exocyclic radicals $\overline{CH_2CH_2[CH_2]_nC}{-}C\cdot$, and the reaction occurs most readily when $n = 2$. This propensity for forming the less thermodynamically stable of the two possible alkyl radicals is usually ascribed[10] to the requirement that, in the transition state, the p-orbital containing the unpaired electron must overlap with the π^*-orbital of the double bond, and that this interaction is more effective in the configuration which leads to the exocyclic radical. No data are available on the relative thermodynamic stabilities of the various possible products of phosphoranyl radical cyclisation, and it is not clear whether they are formed under conditions of kinetic or thermodynamic control. However, stereoelectronic factors may well be involved to some extent in determining the products of cyclisation of unsaturated phosphoranyl radicals.

The spectra of the cyclised radicals were stronger when the attacking radical was ethoxyl rather than t-butoxyl, probably as a result of steric inhibition of the intramolecular addition reaction. Similarly, our failure to detect the cyclised radicals from tris-2-methylallyl phosphite (X· = EtO·, Bu^{t}O·, or Me·) and from tribut-3-enyl phosphite (X· = Bu^{t}O·) may be reasonably attributed to steric effects. Electronic effects are probably important in some systems, for example the failure of $(Et)_2X\dot{P}OCH_2CH{=}CH_2$ to cyclise is presumably in part a reflection of the lower stability of alkylphosphoranes compared with alkoxyphosphoranes.[11]

The e.s.r. parameters of the unsaturated phosphoranyl radicals are in line with those previously reported for the saturated analogues,[3] and are consistent with a trigonal

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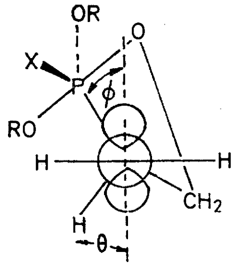
[9] B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelmann, R. L. Powell, and D. W. White, *J. Amer. Chem. Soc.*, 1971, **93**, 4004.

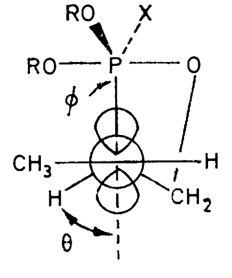
[10] A. L. J. Beckwith, G. E. Gream, and D. S. Struble, *Austral. J. Chem.*, 1972, **25**, 1081.

[11] B. J. Walker, 'Organophosphorus Chemistry,' Penguin, Harmondsworth, 1972.

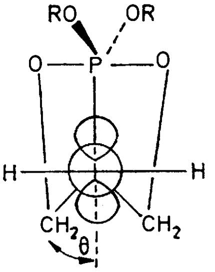
bipyramidal structure. It should be noted that an unsaturated oxygen or nitrogen ligand must presumably be located apically for cyclisation to occur.



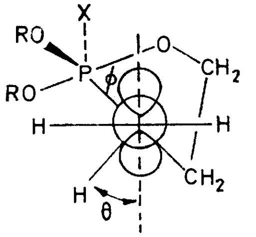
(XVII) a(P) $\sim$ 180 G
$a(H_\alpha) \sim$ 20 G
$a(H_\beta) \sim$ 20 G
$\theta \sim 50°$, $\phi \sim 10°$



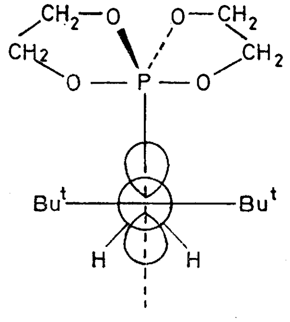
a(P) $\sim$ 195 G (XVIII)
$a(H_\alpha) \sim$ 20 G
$a(H_\beta) \sim$ 14 G
$a(H_\beta) \sim$ 23 G
$\theta \sim 55$-$60°$, $\phi \sim 0$ - $5°$



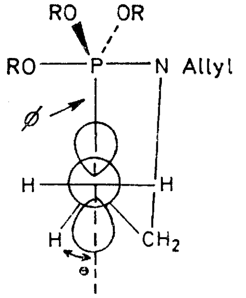
(XIX) a(P) = 221 G
$a(H_\alpha)$ = 18 G
$\theta \sim 60°$, $\phi \sim 0°$



a(P) $\sim$ 127 G (XX)
$a(H_\beta) \sim$ 25 G
$a(H_\alpha) \sim$ 21 G
$\theta \sim 45°$, $\phi \sim 15°$



(XXI) a(P) = 128·9 G
$a(H_\beta)$ = 13·13 G



(XXII) a(P) = 138 G
$a(H_\alpha)$ = 19·5 G
$a(H_\beta)$ = 10·7 G
a(N) = 3 G

The splitting constants for the cyclised radicals provide some evidence concerning their conformations with respect to the C_α–C_β bond. Using the relati [12] $a(H_\beta) = A + B \cos^2\theta$, where A *ca.* 0 G and B *ca.* 54 G, the β-hydrogen splitting constant may be related to the dihedral angle, θ, between the *p*-orbital of the unpaired electron and the C_β–H bond. A similar form of relationship appears to exist for β-phosphorus substituents [13,14] as a result of the predominantly hyperconjugative mechanism of spin transmission. Although it is dangerous to attempt to derive precise values of θ in this way, the following general conclusions appear to be justified.

Both $a(H_\beta)$ and a(P) did not vary substantially with temperature, and the magnitude of $a(H_\beta)$ for the cyclic radicals (XVII) derived from the allyl phosphites implies that their conformations are fairly rigidly held with θ *ca.* 50°, and hence ϕ *ca.* 10°. In the radical (XVIII) derived from tribut-2-enyl phosphite, repulsion occurs between the methyl and PX_4 groups: the value of $a(H_\beta)$ implies that θ has opened up to 55—60° and hence the phosphorus atom is near to eclipsing the half-occupied 2*p*-orbital, with a(P) close to its maximum value for a radical of this type.

In the symmetric bicyclic radical (XIX), the C_β–P bond probably eclipses the orbital of the unpaired electron, but the value of a(P) is increased above that for the radical (XVIII) by ring strain effects (see below).

In the radical (XX) containing a five-membered ring, the value of $a(H_\beta)$ implies that θ *ca.* 45°, and hence ϕ *ca.* 15°. The value of a(P) however is approximately equal to that in the radical [15] (XXI), where because of the bulk of the α-substituents, ϕ must be zero.

It seems likely that, because of angle strain in (XX), the C_β–P bond may have a higher contribution from carbon 2*p* atomic orbitals; hyperconjugative overlap of the 2*p* orbital of the unpaired electron would hence be increased, and a(P) will increase. It should be noted that such an effect will deflect the C_β–H bonds into the nodal plane and hence lower $a(H)_\beta$ for a given value of θ; the value of θ = 45° derived for (XX) would then represent a maximum value. It is partly for this reason that the calculated values of θ for other radicals in this paper, and elsewhere, should be treated with some reserve.

In the cyclic radical (XXII) derived from the allylaminophosphine, the values of $a(H_\beta)$ and of a(P), are incompatibly low for an undistorted radical. It seems likely that θ is close to 60°, and ϕ is close to zero, but $a(H_\beta)$ is reduced by distortion at C_β as described above, and a(P) is reduced as a result of the decreased proportion of the P (3*s*) atomic orbital in the C_β–P bond because of the reduced electronegativity of the nitrogen ligand.

Finally, we consider the structures of the phosphoranyl radicals and cyclised radicals derived from compounds (5) and (12). These have the general structures (XXIII) and (XXIV), and contain chiral carbon centres as indicated.

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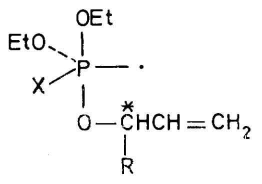
[12] R. W. Fessenden, *J. Chim. phys.*, 1964, **61**, 1570.

[13] W. Demerau and G. Lassmann, *J. Magnetic Resonance*, 1971, **5**, 408.

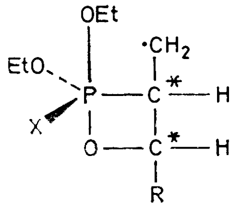
[14] I. G. Neil and B. P. Roberts, *J. Organometallic Chem.*, 1975, **102**, C17.

[15] D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 6715.

The phosphorus centre in (XXIII) and (XXIV) is also chiral if the ligand X is not EtO. It appears likely that the two spectra of similar cyclised radicals detected when each of compounds (5) and (12) react with t-butoxyl radicals are due to the existence of these centres of chirality. The simplification of the spectra when X = Me or EtO must be due to accidental equivalence or, less likely, to stereospecific cyclisation, for, although when X = EtO the phosphorus atom is no longer a chiral centre, two chiral carbon centres still remain. Similarly, the two forms of the phosphoranyl radical (XXIII; X = Bu^{t}O, R = allyl) may be accounted for.



(XXIII)



(XXIV)

Table 2

B.p.s and elemental analyses of allylic phosphorus compounds

Compound	B.p./°C (mmHg)	Empirical formula	Found (%) C Required (%) C	H H	P P
(2)	58—59 (10)		lit.,[17] b.p. 60—61° at 2 mmHg		
(3)	88—89 (0.3)		lit.,[18] b.p. 98—99° at 1 mmHg		
(4)	93—94 (0.3)		lit.,[19] b.p. 124° at 4 mmHg		
(5)	42—43 (1.0)		lit.,[20] b.p. 44—46° at 0.5—1 mmHg		
(6)	41—42 (10)		lit.,[21] b.p. 46—47° at 17 mmHg		
(7)	31—33 (0.4)	$C_6H_{11}O_3P$	44.2	7.1	19.6
			44.4	6.8	19.1
(8)	52 (0.4)	$C_{10}H_{20}NO_2P$	55.0	9.4	14.5 [a]
			55.3	9.3	14.3 [a]
(9)	91—92 (0.3)	$C_{12}H_{21}O_3P$	58.8	8.9	13.0
			59.0	8.7	12.7
(10)	95—96 (0.02)		lit.,[22] b.p. 150—152° at 14 mmHg		
(11)	69—70 (0.1)	$C_{10}H_{21}O_3P$	54.5	9.6	14.4
			54.5	9.6	14.1
(12)	49—50 (0.1)	$C_{10}H_{19}O_3P$	55.4	8.4	13.8
			55.0	8.8	14.2

[a] Found: N, 6.5. Required: N, 6.5%.

EXPERIMENTAL

The apparatus and sample handling technique for the photolytic generation of free radicals for e.s.r. study have been previously described.[3,5,7] The determination of the rate constant for first-order decay of a phosphoranyl radical has also been described.[3] Phosphorus hyperfine coupling constants have been obtained using the Breit–Rabi equation.[3]

Diethyl peroxide [9] and azomethane [16] were prepared by standard methods. The azomethane was stored at low temperature as a 30% solution in toluene.

Triallyl phosphite was obtained commercially and purified by distillation. Other phosphorus compounds were prepared from the appropriate alcohol (or diallylamine), and the appropriate chlorophosphine, using triethylamine as hydrogen chloride scavenger, in diethyl ether solvent. A typical preparation is described below. The b.p.s and elemental analyses of new compounds are gathered in Table 2.

Preparation of Diethyl Hex-5-enyl Phosphite.—A solution of diethyl chlorophosphite (7.8 g, 0.05 mol) in dry ether (20 ml) was slowly added, under nitrogen, to a stirred, ice-cold solution of hex-5-enol (5.0 g, 0.05 mol) in ether (25 ml) containing triethylamine (5.1 g, 0.05 mol). After the addition (30 min), stirring was continued for 30 min at room temperature and the mixture was filtered under nitrogen. The solvent was removed from the filtrate by evaporation and the residue was distilled to give diethyl hex-5-enyl phosphite (95%), b.p. 69—70° at 0.1 mmHg.

The e.s.r. spectra of the allyl,[23] 1-methylallyl,[24] and 2-methylallyl [18] radicals have been described previously. The coupling constants for new radicals are given in footnotes to Table 1.

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[16] R. Penaud and L. C. Leitch, *Canad. J. Chem.*, 1954, **32**, 545.

[17] A. N. Pudovik and I. M. Aladzheva, *Zhur. obshchei Khim.*, 1963, **33**, 3096.

[18] A. N. Pudovik, *Zhur. obshchei Khim.*, 1957, **27**, 2755.

[19] U.S.P. 3,184,496 (*Chem. Abs.*, 1965, **63**, 8200a).

[20] E. S. Huyser and J. A. Dieter, *J. Org. Chem.*, 1968, **33**, 4205.

[21] A. N. Pudovik, I. M. Aladzheva, and L. V. Spirina, *Zhur. obshchei Khim.*, 1967, **37**, 700.

[22] R. Burgada, *Ann. Chim.*, 1963, **8**, 347.

[23] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

[24] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1968, **90**, 7157.