Stereochemical Non-rigidity of Phosphoranyl Radicals: Relative Ligand Apicophilicities

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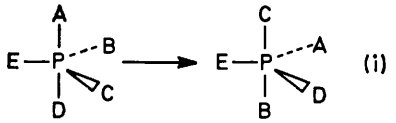
A series of phosphoranyl radicals, produced by addition of photochemically generated alkoxyl or benzoyloxyl radicals to substituted 1,3,2-dioxaphospholans, have been studied by e.s.r. spectroscopy. The spectra of certain of these radicals exhibit line-shape effects which are interpreted in terms of intramolecular ligand exchange at phosphorus. On the basis of deuterium labelling studies, two types of apical–equatorial ligand exchange have been identified, involving interchange of exocyclic or of endocyclic substituents, respectively. The spectra derived from 4,4-dimethyl-1,3,2-dioxaphospholans show the presence of an approximately equimolar mixture of two isomeric phosphoranyl radicals, in which the endocyclic CH_2O group is sited either apically or equatorially. The e.s.r. spectra of some cyclic and acyclic phosphoranyl radicals show that, in general, ligand apicophilicity decreases in the order F–, Cl–, RC(O)O–> $\overset{|}{C}H_2CH_2CH_2C(O)\overset{|}{N}$–, OCN–> RO–, R_2N>H–>H_3C–, closely paralleling group electronegativity. Rate constants for exchange of apical with equatorial H and Me_2N ligands, repectively, in the acyclic radicals $H_2(Me)$-$POBu^t$ and $(Me_2N)_2ClPOBu^t$ have been estimated.

THE structures and stereochemical non-rigidity of penta-co-ordinated phosphoranes (PX_5) have been studied extensively, from both experimental and theoretical standpoints.[1] Phosphoranes may be isolable (*e.g.* PF_5) or may occur as transient intermediates (*e.g.* in phosphate ester hydrolysis), where they play a key role in determining the products, stereochemistry, and rate of the overall reaction. The related phosphoranyl radicals ($\cdot PX_4$), which are intermediates in the homolytic reactions of trivalent phosphorus compounds, have so far received less attention.[2]

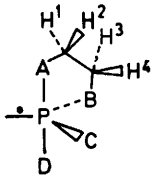
Although the mechanistic details of ligand exchange in phosphoranes are still somewhat controversial,[1,3] it appears in general that the permutational mode [4,5] (M1 mode †) is that exemplified in equation (i) for the chiral



(i)

phosphorane P(ABCDE).[1,6] To account for this mode of ligand exchange two general mechanisms are commonly discussed, Berry pseudo-rotation [7] and turnstile rotation.[3]

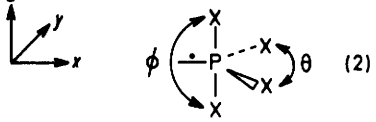
A knowledge of the rate, mode, and mechanism of ligand exchange in phosphoranyl radicals is clearly important for our understanding of the homolytic chemistry of phosphorus, and there are an increasing number of instances where ligand exchange occurs at a rate such that its effects are apparent in the e.s.r. spectra of these radicals.[8–12] The e.s.r. spectra of phosphoranyl radicals of the type (1) [10] exhibit hyperfine splitting from a quasi-apical ring proton H^1 or H^2, which provides a means for probing the stereochemical non-rigidity of these radicals.



(1) A, B = O or NMe

RESULTS AND DISCUSSION

(a) *Structure of Phosphoranyl Radicals.*—Phosphoranyl radicals possess quasi-trigonal bipyramidal geometry in which, for convenience, we represent the unpaired



(2)

electron as occupying an equatorially directed orbital as shown in the valence bond canonical structure (2).[10]

More realistically, the unpaired electron may be envisaged as occupying a molecular orbital which is symmetrical with respect to reflection in the equatorial (*xy*) plane, and which is made up predominantly of contributions from P(3*s*), P(3p_x), P(3p_y), and apical ligand orbitals of appropriate symmetry.[13,14] Gillbro

† There are five distinguishable modes of rearrangement for a trigonal bipyramidal phosphorane P(ABCDE), designated by Musher [4] as M1—M5.

[1] (*a*) R. Luckenbach, ' Dynamic Stereochemistry of Pentaco-ordinated Phosphorus and Related Elements,' Thieme, Stuttgart, 1973; (*b*) S. Trippett, *Pure Appl. Chem.*, 1974, **40**, 595.

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

[3] P. Gillespie, P. Hoffman, H. Klusackek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687; F. Ramirez and I. Ugi, *Bull. Soc. chim. France*, 1974, 453.

[4] J. I. Musher, *J. Chem. Educ.*, 1974, **51**, 94.

[5] D. Britton and J. D. Dunitz, *J. Amer. Chem. Soc.*, 1975, **97**, 3836.

[6] M. Eisenhut, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutch, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 5385; G. M. Whitesides, M. Eisenhut, and W. M. Bunting, *ibid.*, p. 5398.

[7] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

[8] P. J. Krusic and P. Meakin, *Chem. Phys. Letters*, 1973, **18**, 347.

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

[10] R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140.

[11] I. H. Elson. M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1975, 586.

[12] J. W. Cooper and B. P. Roberts, *J.C.S. Perkin II*, 1976, 808.

[13] T. Gillbro and F. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 5032.

[14] A. G. Davies, M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1974, 973.

and Williams [13] have examined the single-crystal e.s.r. spectrum of $[OPCl_3]^{-\cdot}$ and concluded that, to a good degree of approximation, the unpaired electron residues in a molecular orbital which is essentially non-bonding and made up of P(3*s*) and apical Cl(3p_z) atomic orbitals. Clearly (2) is a poor description of this radical, but it seems likely that the contribution from P(3p_σ) orbitals will increase when the ligands are less electronegative.[15] There seems to be no good reason to discard (2) as a convenient representation for chemical studies, provided that we realise its obvious limitations.

The degree of distortion of phosphoranyl radicals from regular trigonal bipyramidal geometry is difficult to determine from isotropic e.s.r. spectra. Nelson and Symons [16] have shown that the apical chlorine ligands and the phosphorus in $[ROP(O)Cl_2]^{-\cdot}$ must be approximately collinear, and a study [17] of $\cdot PF_4$ in a single crystal of PF_3 indicates that the angle ϕ in (2; X = F) is close to 180°. Whilst INDO molecular orbital calculations predict [18,19] ϕ *ca.* 156° for $\cdot PF_4$, more recent *ab initio* calculations [20] give ϕ 166 for $\cdot PF_4$ and 173° for $\cdot PH_4$. Calculations also suggest that the angle θ is appreciably <120°, a value of *ca.* 100° being obtained by several groups of workers for ligands of differing electronegativity.[18-21] Recently, Berclaz *et al.*[22] have obtained the e.s.r. spectrum of $Ph_3\dot{P}Cl$ by *X*-irradiation of a single crystal of Ph_3P,BCl_3, and have concluded that this radical has close to local C_{3v} symmetry at phosphorus with the unpaired electron located in a P–Cl σ^* orbital. Symons [23] has confirmed this result, and further, shown that other monohalogenophosphoranyl radicals are perhaps better described as having distorted tetrahedral rather than trigonal bipyramidal structures. The degree of distortion from regular trigonal bipyramidal geometry may thus be quite marked for some phosphoranyl radicals, and will probably depend upon the nature of the ligands.

(b) *Generation of Phosphoranyl Radicals.*—The phosphoranyl radicals described in this paper were produced *in situ* by addition of photochemically generated ethoxyl (from EtOOEt), t-butoxyl (from Bu^tOOBu^t), or benzoyloxyl [from PhC(O)OOC(O)Ph] radicals to the appropriate trivalent phosphorus compound, whilst the sample was in the cavity of an e.s.r. spectrometer.[10]

$$ROOR \xrightarrow{h\nu} 2RO\cdot \qquad \text{(ii)}$$

$$RO\cdot + PX_3 \longrightarrow RO\dot{P}X_3 \qquad \text{(iii)}$$

The e.s.r. spectra were normally obtained in cyclopropane solution during continuous u.v. irradiation of the sample. At the maximum rate of generation a phosphoranyl radical must have a lifetime >*ca.* 10^{-4} s for its concentration to reach a detectable level (*ca.* 10^{-7}M). Thermoneutral or exothermic exchanges of apical and equatorial ligands appear to be rapid processes [8-12] ($k_{exch.} > 10^5$ s^{-1} at 173 K), and hence if the spectrum of only one isomer of a phosphoranyl radical is detected this may be assumed to be the most stable thermodynamically. In addition, if two or more isomers are detected then these may be assumed to be present in close to their equilibrium concentrations.

(c) *Phosphoranyl Radicals derived from* 1,3,2-*Dioxaphospholans.*—The e.s.r. spectrum of the cyclic phosphoranyl radical (3; $R^1 = R^2$ = Et or Bu^t) exhibits a temperature dependence which may be interpreted in terms of the ligand exchange mode shown in equation (iv).[10] This mode will be referred to as the M4(exocyclic) mode [4] of ligand exchange, indicating that the apical and equatorial exocyclic ligands exchange sites. The analogous exchange of endocyclic ligands [equation (v)], which was not detected for (3), will be referred to as the M4(ring) mode.

In order to gain further insight into the nature of ligand exchange in phosphoranyl radicals, we have examined the e.s.r. spectra of a series of radicals derived from 1,3,2-dioxaphospholans (4).

The structure, (5a or b), adopted by the phosphoranyl radicals depends upon the relative apicophilicities [1b,10] of the substituents RO and X. The structure can usually be inferred [10] from the magnitudes of the hyperfine splittings from phosphorus and from the ligand X (providing this contains magnetic nuclei which give resolvable splittings).

Hyperfine splitting of *ca.* 4 G from one ring proton [either H^1 of H^2, see section (e)] was apparent in the low temperature spectra of (5), when X and RO were of different apicophilicity. When X and RO were the same, splitting from two apparently equivalent protons (*ca.* 2 G) was detected, which is consistent [10] with rapid exchange of H^1 and H^2 as shown in equation (vii).

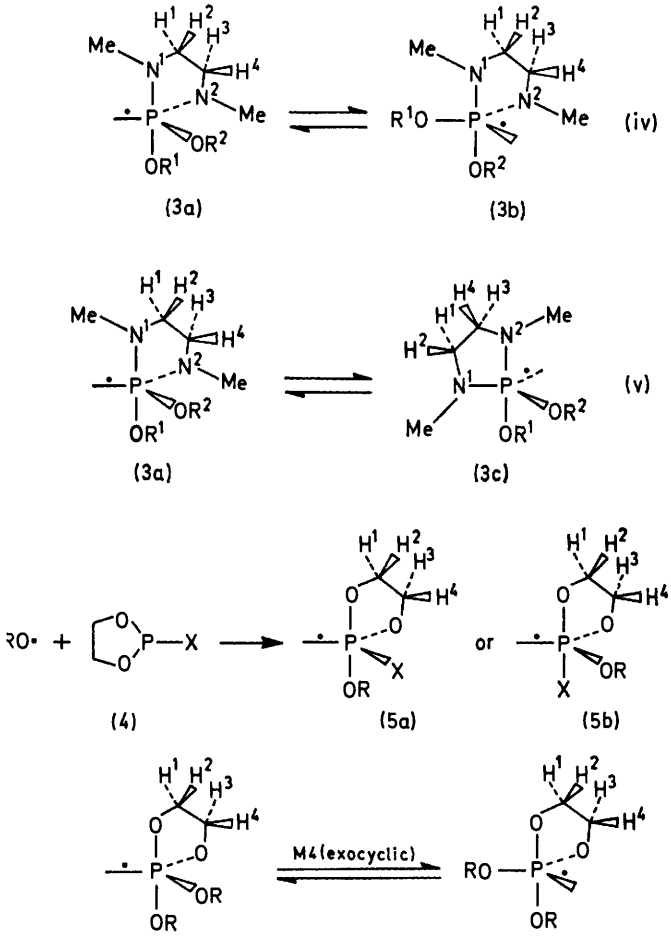
The e.s.r. parameters for the series of phosphoranyl radicals (5) are given in Table 1. The assignments of structure given in Table 1 were made on the basis of the following observations and assumptions.[10] (I) The five-membered ring bridges apical and equatorial sites. (II) The magnitude of a(P) increases with increasing ligand electronegativity, provided that the ligands of highest electronegativity occupy apical sites. (III) When X contains a magnetic nucleus directly bound to phosphorus, the isotropic hyperfine splitting from this nucleus is larger when the ligand is apical than when it is equatorial. (IV) When ligand hyperfine splitting is not detectable it may sometimes be necessary to *assume* a structure based upon the empirical rule that ligand apicophilicity parallels ligand electronegativity. Such

[15] K. Nishikida and F. Williams, *J. Amer. Chem. Soc.*, 1975, **97**, 5462.
[16] D. J. Nelson and M. C. R. Symons, *J.C.S. Dalton*, 1975, 1164.
[17] A. Hasegawa, K. Ohnishi, K. Sogabe, and M. Miura, *Molecular Phys.*, 1975, **30**, 1367.
[18] A. Hudson and J. T. Wiffen, *Chem. Phys. Letters*, 1974, **29**, 113.
[19] A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1975, **62**, 2004.
[20] A. Hudson and R. F. Treweek, *Chem. Phys. Letters*, 1976, **39**, 248.
[21] Y. I. Gorlov and V. V. Penkovsky, *Chem. Phys. Letters*, 1975, **35**, 25.
[22] T. Berclaz, M. Geoffroy, and E. A. C. Lucken, *Chem. Phys. Letters*, 1975, **36**, 677.
[23] M. C. R. Symons, *Chem. Phys. Letters*, 1976, **40**, 226.

assignments are supported by internal consistency [see section (g)] and arguments based on (II) above.

The spectra of radicals (6) and (7) (see Figure 1) exhibit splitting from two ring protons and do not show line-shape changes attributable to the slowing of exchange, at low temperatures, before the onset of viscosity broadening. This result is expected if the radicals are undergoing rapid M4(exocyclic) exchange of identical alkoxy-groups. Because of the much higher electronegativity of F compared with RO, the radicals (10) even at low temperatures (200 K), although the spectrum of (8) shows a doublet splitting (3.6 G) from one ring proton at 143 K in ethylene solvent. Since the chlorine splittings are essentially independent of temperature, and the phosphorus splittings vary only slightly with temperature,[24] the rapid exchange of two ring protons, which occurs even at low temperatures, cannot be the result of an M4(exocyclic) process.

Below *ca.* 253 K the spectra of the radicals (16)—(19) are temperature independent [*cf.* radicals (10) and



and (11) would be expected to adopt structures in which the fluorine substituents are apical, and not to undergo the endothermic M4(exocyclic) mode of ligand exchange at a significant rate. The spectra of (10) and (11) (see Figure 1) are consistent with these proposals.

The radicals (12)—(15) give e.s.r. spectra which are basically similar to those of the fluorophosphoranyls (10) and (11). The phosphorus and nitrogen splittings are consistent with these radicals containing an apical nitrogen ligand, in which the nitrogen is essentially sp^2-hybridised and is more electronegative and apicophilic than that in a dialkylamino-substituent.[10]

The results for the radicals (8) and (9) were somewhat unexpected. The spectra of both radicals exhibit splittings from two apparently equivalent ring protons, (11)], but at higher temperatures they exhibit line-shape changes expected for the exchange of the ring proton giving rise to the resolvable (*ca.* 4 G) splitting with another ring proton with a negligible splitting constant, and above *ca.* 280—300 K the fast exchange limit is approached (see Figure 2).

Both acetate and trifluoroacetate ligands probably have significantly higher apicophilicities than alkoxy-groups, and thus the ring proton exchange detected for (16)—(19) cannot be brought about by an M4(exocyclic) process. We suggest that an M4(ring) exchange occurs in these radicals and that this process is also responsible for the proton exchange detected for the chlorophosphoranyl radicals (8) and (9) at much lower tem-

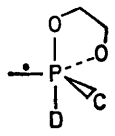
[24] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1339.

peratures. An alternative explanation, inversion of configuration at phosphorus, is eliminated by the deuterium labelling experiments described below.

The radicals (21)—(23), generated by addition of benzoyloxyl radicals to the appropriate dioxaphospholan, place at *lower* temperatures when the phosphoranyl radicals contained tertiary alkoxy-ligands [radicals (9), (17), (19), and (23)] than for the analogous radicals bearing primary alkoxy-substituents [radicals (8), (16), (18), (21), and (22)]. Some approximate rate constants

TABLE 1

E.s.r. parameters for phosphoranyl radicals derived from 1,3,2-dioxaphospholans



Radical[a]	C	D	Addendum radical	Line-shape changes detected	T/K	Hyperfine splitting (G) a(P)[b]	a(H)	Other
(6)	EtO	EtO	EtO·	No	193	904	2.0 (2 H)	
(7)[c]	Bu^{t}O	Bu^{t}O	Bu^{t}O·	No	203	903	1.7 (2 H)	
(8)[d]	EtO	Cl	EtO·	Yes	203	1 050	1.5 (2 H)[e]	43.1 (^{35}Cl)[f]
(9)[g]	Bu^{t}O	Cl	Bu^{t}O·	No	223	1 032	1.5 (2 H)	42.8 (^{35}Cl)[h]
(10)	EtO	F	EtO·	No	187	1 062	4.2 (1 H)	280 (1 F)
(11)	Bu^{t}O	F	Bu^{t}O·	No	173	1 050	4.0 (1 H)	282 (1 F)
(12)	EtO	OCN	EtO·	No	210	997	4.2 (1 H)	23.8 (1 N)
(13)	Bu^{t}O	OCN	Bu^{t}O·	No	204	971	4.0 (1 H)	24.4 (1 N)
(14)	EtO	$CH_2(CH_2)_2C(O)N$	EtO·	No	222	926	4.5 (1 H)	22.8 (1 N)
(15)	Bu^{t}O	$CH_2(CH_2)_2C(O)N$	Bu^{t}O·	No	203	908	5.2 (1 H)	23.6 (1 N)
(16)	EtO	$MeCO_2$	EtO·	Yes	212	1 032	4.0 (1 H)	
(17)	Bu^{t}O	$MeCO_2$	Bu^{t}O·	Yes	193	1 009	4.0 (1 H)	
(18)	EtO	CF_3CO_2	EtO·	Yes	183	1 060	4.4 (1 H)	
(19)	Bu^{t}O	CF_3CO_2	Bu^{t}O·	Yes	188	1 031	4.4 (1 H)	
(20)[i]	Bu^{t}O	$(EtO)_2P(O)O$	Bu^{t}O·	Yes	173	1 028	4.2 (1 H)	
(21)[j]	EtO	BzO	BzO·	Yes	228	1 039	4.2 (1 H)	
(22)[j]	Bu^{t}CH$_2$O	BzO	BzO·	Yes	234	1 042	4.0 (1 H)	
(23)[j]	Bu^{t}O	BzO	BzO·	Yes	223	1 013	3.9 (1 H)	
(24)[j]	$CH_2(CH_2)_2C(O)N$	BzO	BzO·	No	253	982	*ca.* 4 (1 H)[k]	*ca.* 6[k] (1 N)

[a] Cyclopropane solvent unless otherwise stated. [b] Obtained using the Breit–Rabi equation: $g = 2.003 \pm 0.001$ unless otherwise stated. [c] Propane solvent. [d] $g = 2.009$. [e] At 143 K in ethylene solvent a(H) = 3.6 G (1 H). [f] $a(^{37}Cl) = 36.0$ G. [g] $g = 2.010$. [h] $a(^{37}Cl) = 35.9$ G. [i] A. G. Davies, M. J. Parrott, B. P. Roberts, and A. Skowronska, *J.C.S. Perkin II*, 1976, 1154. [j] Toluene solvent. [k] Approximate values, line-width *ca.* 2 G.

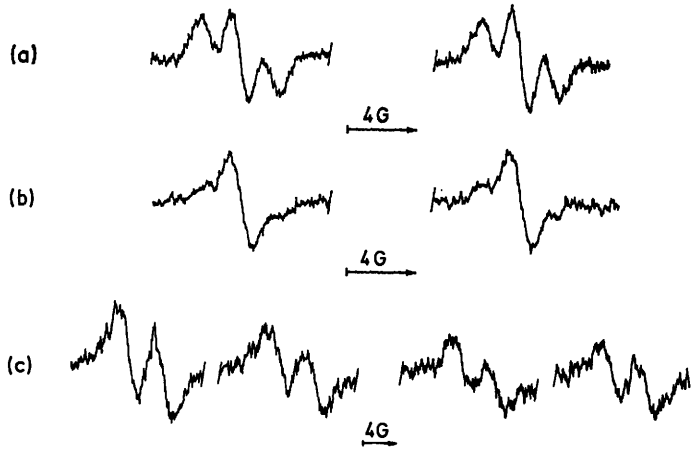


FIGURE 1 E.s.r. spectra of phosphoranyl radicals derived from 1,3,2- and 4,4-dideuterio-1,3,2-dioxaphospholans in cyclopropane solution: (a) radical (6) at 263 K; (b) radical (27) at 263 K; (c) radical (10) at 216 K

exhibited spectra which were very similar to those of the acetoxy- and trifluoroacetoxy-phosphoranyl radicals (16)—(19). Above *ca.* 253 K ligand exchange caused two ring protons to become equivalent on the e.s.r. time scale. It is noteworthy that the line-shape changes attributed to the M4(ring) ligand exchange took for ring proton exchange, obtained by computer simulation based on the low temperature coupling constants given in Table 1 and assuming exchange with a proton which itself gives rise to an unresolved splitting of 0.1 G, are given in Table 2.

The e.s.r. spectrum of the phosphoranyl radical (24)

was consistent with a rigid structure in which the benzoyloxy-group was apical [see also section (g)].

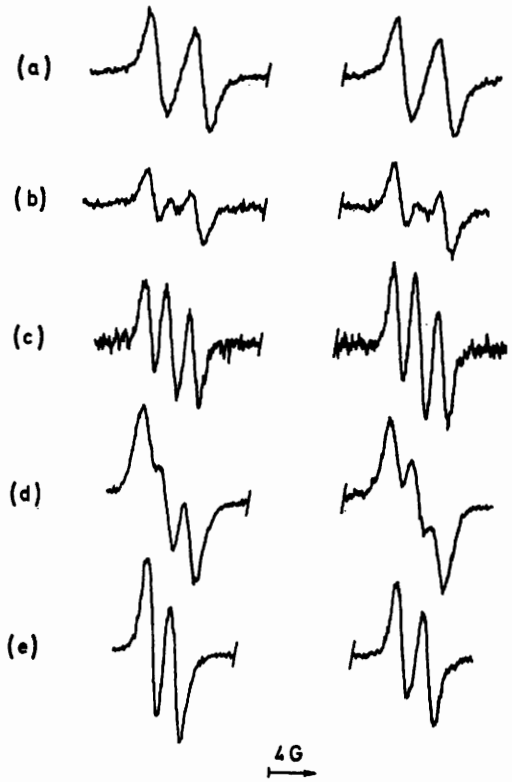
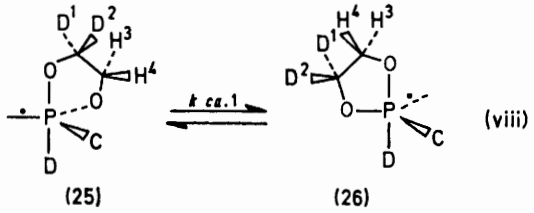
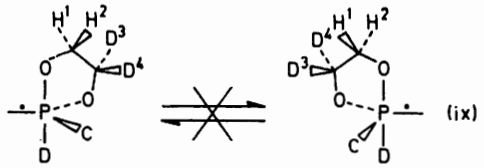


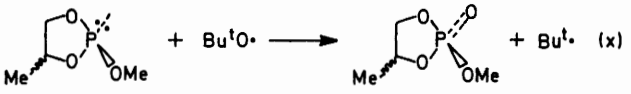
FIGURE 2 E.s.r. spectra in cyclopropane solution of: (a) radical (17) at 225 K; (b) radical (17) at 265 K; (c) radical (17) at 285 K; (d) radical (33) at 225 K; (e) radical (33) at 285 K

In order to examine the possibility that inversion of configuration at phosphorus might be responsible for ring-proton exchange in (5), we generated deuterium labelled phosphoranyl radicals from a series of 4,4-dideuterio-1,3,2-dioxaphospholans. The e.s.r. spectra were consistent with the expected equimolar mixture of (25) and (26) [equation (viii) also assumes an M4(ring) exchange]. The results are summarised in Table 3 and typical spectra are shown in Figures 1 and 2.



The spectra of the fluorophosphoranyl radicals (30) and (31) show that these species do not undergo ring–proton exchange on the e.s.r. time scale, and the spectra of isomers of the types (25) and (26) were seen superimposed. The radicals (32)—(35) exhibit similar spectra to those of the fluorophosphoranyl radicals below 253 K, but at temperatures where the unlabelled analogues of (32)—(35) underwent ring proton exchange such that the 1 : 1 (*ca.* 4 G) splitting became a 1 : 2 : 1 (*ca.* 2 G) splitting, the spectra of the two isomers of the labelled radicals became indistinguishable, and at high temperatures a 1 : 1 (*ca.* 2 G) doublet was observed. The form of the high temperature spectra of (32)—(35) requires that H–D rather than H–H exchange is occurring rapidly on the e.s.r. time scale, and hence the exchange process is not simple inversion of configuration at phosphorus [equation (ix)], however this result is consistent with a rapid M4(ring) exchange [equation (viii)].





Bentrude and his co-workers [25,26] have concluded, from product studies of the oxidation of certain cyclic phosphites by t-butoxyl radicals, that inversion of an intermediate tetra-alkoxyphosphoranyl radical does not compete with its fragmentation to yield phosphate. In particular, oxidation of *cis*- or *trans*-2-methoxy-4-methyl-1,3,2-dioxaphospholan by t-butoxyl radicals is almost stereospecific with retention of configuration about phosphorus [26] [equation (x)]. It should also be

TABLE 2

Rate constants for ring proton exchange in some phosphoranyl radicals derived from 1,3,2-dioxaphospholans

Radical [a]	k_{exch}/s^{-1} [b]	T/K	k_{exch}/s^{-1} at 273 K [c]	Process responsible for exchange
(6)	$>2 \times 10^8$	188	$>6 \times 10^9$	M4(exocyclic)
(8) [d]	*ca.* 2×10^7 [e]	153	*ca.* 6×10^9	M4(ring)
(10) [f]	$<1 \times 10^7$	328	$<6 \times 10^5$	
(12)	$<1 \times 10^7$	220	$<1 \times 10^8$	
(14) [g]	$<1 \times 10^7$	253	$<3 \times 10^7$	
(16)	5.5×10^7 [h]	313	9.3×10^8	M4(ring)
(17)	1.5×10^8 [i]	313	2.9×10^7	M4(ring)
(18)	3.0×10^7	306	6.4×10^6	M4(ring)
(19)	2.0×10^8 [j]	308	5.0×10^7	M4(ring)
(21) [k]	6.0×10^7	322	6.9×10^6	M4(ring)
(22) [k]	2.5×10^7 [l]	305	5.5×10^6	M4(ring)
(23) [k]	6.0×10^7 [m]	300	1.8×10^7	M4(ring)

[a] Cyclopropane solvent unless otherwise stated. [b] Obtained by computer simulation of spectra. [c] Obtained by extrapolation or interpolation taking $\log_{10}(A_{exch}/s^{-1}) = 13.0$. [d] Ethylene solvent. [e] $k_{exch.}$ *ca.* 8×10^7 s^{-1} at 203 K. [f] Iso-octane solvent. [g] Toluene–cyclopropane solvent. [h] Measurements in the range 273—329 K give $\log_{10}(k_{exch}/s^{-1}) = 12.9—29.8/\theta$, where $\theta = 2.303RT$ kJ mol^{-1}. [i] Measurements in the range 263—313 K give $\log_{10}(k_{exch.}/s^{-1}) = 12.9—26.9/\theta$. [j] $k_{exch.}$ *ca.* 4×10^7 s^{-1} at 280 K. [k] Toluene solvent. [l] $k_{exch.}$ *ca.* 1×10^7 s^{-1} at 290 K. [m] Measurements in the range 265—308 K give $\log_{10}(k_{exch.}/s^{-1}) = 13.7—32.7/\theta$.

[25] W. G. Bentrude, J. H. Hargis, and P. E. Rusek, jun., *Chem. Comm.*, 1969, 296.

[26] H.-W. Tan and W. G. Bentrude, *J. Amer. Chem. Soc.*, 1974, **96**, 5950.

noted that whilst this result appears to exclude the possibility of rapid rearrangement of the intermediate phosphoranyl radical in an M1 mode[4] [as would be combination of M4(ring) and M4(exocyclic) exchanges should average the couplings from all four ring protons lead to a 1 : 4 : 6 : 4 : 1 (*ca.* 1 G) quintet splitting.

TABLE 3

E.s.r. parameters for phosphoranyl radicals based on isomers (25) and (26) derived from 4,4-dideuterio-1,3,2-dioxaphospholans

Radical[a]	C	D	Addendum radical	Line-shape changes detected[b]	T/K	Hyperfine splitting (G) a(P)[c]	a(H)	Other
(27)	EtO	EtO	EtO·	No	193	904[d]	*ca.* 2 (2 H)[d]	
(28)	EtO	Cl	EtO·	Yes[e]	178	1 084[f]	1.8 (1 H)[f]	42.5 (^{35}Cl)[g]
(29)	Bu^{t}O	Cl	Bu^{t}O·	No	223	1 032[f]	1.6 (1 H)[f]	43.0 (^{35}Cl)[h]
(30)	EtO	F	EtO·	No	243	1 064[i]	3.9 (1 H)[j]	280 (1 F)
(31)	Bu^{t}O	F	Bu^{t}O·	No	203	1 054[i]	3.9 (1 H)[j]	280 (1 F)
(32)	EtO	$MeCO_2$	EtO·	Yes	303	1 037[f,k]	2.3 (1 H)[f]	
(33)	Bu^{t}O	$MeCO_2$	Bu^{t}O·	Yes	263	1 010[f,k]	2.1 (1 H)[f]	
(34)[l]	EtO	BzO	BzO·	Yes	263	1 040[f,k]	2.3 (1 H)[f]	
(35)[l]	Bu^{t}O	BzO	BzO·	Yes	273	1 016[f,k]	2.3 (1 H)[f]	

[a] Cyclopropane solvent unless otherwise stated. [b] Effects due to exchange of ring hydrogen and/or deuterium atoms. [c] Obtained using the Breit–Rabi equation: *g* factors were similar to those of the undeuteriated analogues. [d] a(P) was similar for isomers (25) and (26), a(H) refers to isomer (26). [e] Evidence for line-shape changes at low temperatures was inconclusive. [f] a(P) and a(H) are average values for isomers (25) and (26) which exchange rapidly at the temperatures quoted. [g] a(^{37}Cl) 35.2 G. [h] a(^{37}Cl) 35.8 G. [i] Values quoted refer to isomer (25); for isomer (26) a(P) was *ca.* 1 G smaller. [j] Values quoted refer to isomer (26) [k] At lower temperatures, when separate spectra could be detected for isomers (25) and (26) a small isotope effect on a(P) was apparent, such that the phosphorus splitting for (25) was *ca.* 1 G larger than that for (26). [l] Toluene solvent.

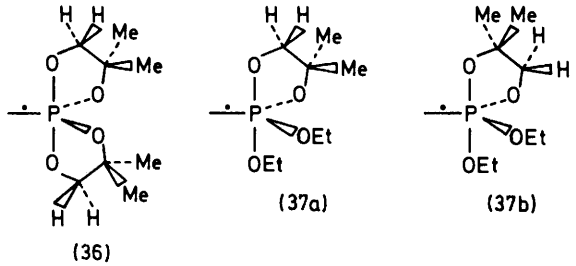
brought about by Berry pseudo-rotation with the 'unpaired electron orbital' as pivot, see equation (i)],[26] it does *not* preclude an M4 rearrangement being rapid compared with β-scission of the intermediate.

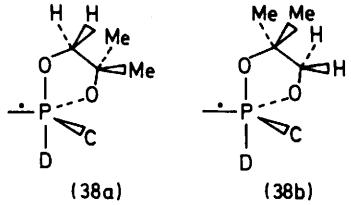
The chlorophosphoranyl radicals (28) and (29) appeared to behave in a similar manner to (32)—(35). At temperatures where the spectra of the unlabelled species showed 1 : 2 : 1 proton splittings (*ca.* 1.5 G), those of the labelled phosphoranyl radicals exhibited 1 : 1 splittings (*ca.* 1.7 G). This result is consistent with the M4(ring) exchange being rapid for the chlorophosphoranyl radicals at much lower temperatures than for (32)—(35). It is possible that the presence of a chlorine ligand brings about marked changes in electron distribution and in the degree of distortion from trigonal bipyramidal geometry.[22,23]

For radical (6), the unlabelled analogue of (27), we suggested[10] that rapid M4(exocyclic) exchange averages the splittings from the quasi-apical ring protons, such that a 1 : 2 : 1 pattern is observed even at low temperatures (down to 163 K below which viscosity broadening precludes detection of proton splittings). In accord with this proposal, at temperatures where the unlabelled radical exhibited this 1 : 2 : 1 (2 G) pattern, the deuteriated radical (27) gave rise to a spectrum which could be interpreted as a superposition of the spectra of (25) and (26) (C = D = EtO). A singlet [from isomer (25)] and a 1 : 2 : 1 (2 G) triplet [from isomer (26) undergoing rapid M4(exocyclic) exchange of ethoxy-groups] of equal integrated intensities combine to give the appearance of a 1 : 6 : 1 triplet (see Figure 1).

The M4(ring) mode of exchange appears to be slower for (6) and (27) than for (16) and (32). Even at the highest accessible temperature (338 K in hexane) the radical (6) showed a 1 : 2 : 1 (2 G) triplet, whilst a

(d) *Phosphoranyl Radicals derived from 4,4-Dimethyl-1,3,2-dioxaphospholans.*—The e.s.r. spectra of the radicals $(\overline{OCMe_2CH_2O}-)_2P\cdot$ and $\overline{OCMe_2CH_2O}\dot{P}(OEt)_2$ have previously been interpreted in terms of the structures (36) and (37a), implying that the CH_2O group is more apicophilic than the CMe_2O group.[10,27]





Whilst this conclusion appears to remain essentially correct for the spirocyclic radical, closer examination of the spectrum obtained from $\overline{OCMe_2CH_2O}\dot{P}(OEt)_2$ reveals some asymmetry such that (37b) may also be present. The spectrum of (37a) would appear (apart from phosphorus splitting) as a 1 : 2 : 1 triplet [a(H) *ca.* 2 G] arising from coupling to two quasi-apical ring protons [this would imply fast M4(exocyclic) exchange], and (37b) would give rise to a singlet. If the phosphorus splitting for (37b) were *ca.* 4 G larger than that for (37a), their superimposed spectra would appear as a

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

distorted triplet with line spacings of *ca.* 2 G, as observed. In order to probe this question further, we examined the e.s.r. spectra of a series of phosphoranyl radicals (38), generated by radical additions to 4,4-dimethyl-1,3,2-dioxaphospholans.

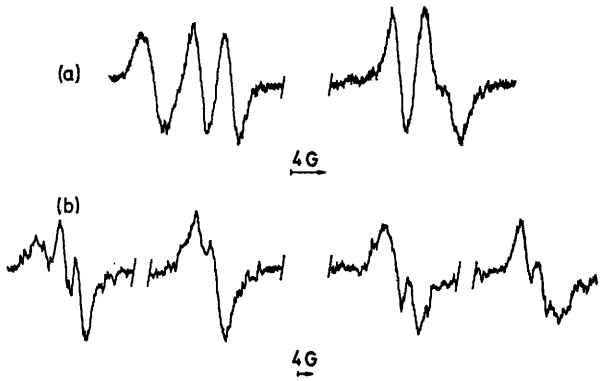


FIGURE 3 E.s.r. spectra in cyclopropane solution of: (a) radical (39) at 240 K; (b) radical (45) at 178 K

The spectroscopic parameters are given in Table 4 and some typical spectra are shown in Figure 3. The spectra of the radicals (39)—(43) clearly show in each case the presence of two isomers (see Figure 3), and the concentration ratio [(38a)]/[(38b)] is close to unity for each phosphoranyl radical. By analogy with the unsubstituted phosphoranyl radicals, the species showing the 1 : 1 doublet splitting of *ca.* 4 G is assigned as the isomer (38a), and that giving rise to a singlet as (38b); the phosphorus splitting for (38b) is always somewhat larger than that for (38a). Hence it appears that in (39)—(43) the apicophilicities of the CH_2O and CMe_2O groups are almost identical. The spectra of (39)—(43) showed no clearly defined line-shape changes even up to 300 K.

The fluorophosphoranyl radicals (44) and (45) similarly each exist in the two isomeric forms (38a) and (38b), although the similarities in phosphorus splittings for the two isomers lead to overlap of their e.s.r. spectra (see Figure 3). Again, the apicophilicities of the CH_2O and CMe_2O groups are very similar. The chlorophosphoranyl radicals (46) and (47) each showed only one set of e.s.r. signals (peak–peak line-width *ca.* 3 G) without resolvable proton splittings, and hence it was not possible to obtain further structural information.

Returning to the problem of the radical $\overline{OCMe_2CH_2O}\dot{P}(OEt)_2$, it now appears most likely that the spectrum detected is indeed a superposition of signals from (37a and b), where radical (37a) is undergoing rapid M4(exocyclic) exchange, in a similar way to the unsubstituted analogue (6). Under conditions of maximum resolution (dilute solutions, low power and modulation amplitude) it is possible to detect separate signals from (37a and b) (see Table 4).

The spirocyclic radical $(\overline{OCMe_2CH_2O}^-)_2P^\bullet$ appears to exist predominantly as structure (36); however re-examination of the spectra [27] reveals weak signals from species with a larger ^{31}P hyperfine splitting (just visible in the Figure in ref. 37) which may be assigned to one or both of the other possible isomers of (36). The appearance of these weaker signals was unaffected by repeated distillation of or the origin * of the spirophosphorane precursor.[27]

TABLE 4

E.s.r. parameters for phosphoranyl radicals based on (38) derived from 4,4-dimethyl-1,3,2-dioxaphospholans

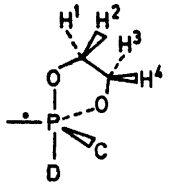
Radical [a]	C	D	T/K	Hyperfine splitting [b] (G) a(P)	a(H)	Other	Ratio [c] [(38a) : (38b)]
(37a)	EtO	EtO	223	902	1.9 (2 H)		*ca.* 1
(37b)			223	907			
(39a)	EtO	$MeCO_2$	198	1 026	3.7 (1 H)		1.1
(39b)			198	1 030			
(40a)	Bu^{t}O	$MeCO_2$	181	997	3.4 (1 H)		0.9
(40b)			181	1 000			
(41a) [d]	EtO	BzO	248	1 032	3.7 (1 H)		1.3
(41b)			248	1 040			
(42a)	EtO	CF_3CO_2	183	1 052	4.3 (1 H)		1.0
(42b)			183	1 057			
(43a)	Bu^{t}O	CF_3CO_2	193	1 017	4.3 (1 H)		0.9
(43b)			193	1 027			
(44a)	EtO	F	203	1 050	4.4 (1 H)	276 (1 F)	0.8
(44b)			203	1 062		284 (1 F)	
(45a)	Bu^{t}O	F	173	1 043	4.6 (1 H)	275 (1 F)	*ca.* 0.8
(45b)			173	1 047		283 (1 F)	
(46a, b)	EtO	Cl	238	1 044	*e*	42.8 [f] (^{35}Cl)	*e*
(47a, b) [g]	Bu^{t}O	Cl	283	1 036	*e*	42.7 [g] (^{35}Cl)	*e*

[a] Cyclopropane solvent unless otherwise stated. [b] Calculated using the Breit–Rabi equation: g 2.003 ± 0.001 unless otherwise stated. [c] Measured by electronic integration of the derivative spectra, and cutting out and weighing the resulting absorption peaks. [d] In toluene solution: obtained by addition of photochemically generated benzoyloxyl radicals to 2-ethoxy-4,4-dimethyl-1,3,2-dioxaphospholan. [e] Only one set of signals could be detected, with no resolution of proton hyperfine splitting. [f] $a(^{37}Cl)$ 35.6 G; g 2.008. [g] $a(^{37}Cl)$ 35.6 G; g 2.008.

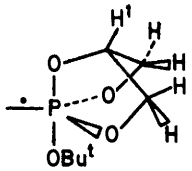
* 2,2,7,7-Tetramethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]-nonane $[(\overline{OCMe_2CH_2O}^-)_2PH]$ was prepared either from $P(NMe_2)_3$ and 2-methylpropane-1,2-diol [27] or from PCl_3 and the diol in the presence of triethylamine. Some of the ^1H n.m.r. parameters for this spirophosphorane were incorrectly reported in ref. 27. The correct data are τ (C_6H_6; 35 °C) 2.6 (d, $^1J_{HP}$ 818 Hz, PH), 8.87 (s, CH_3^A) and 8.91 (s, CH_3^B); the methylene ring protons appeared as the AB part of an ABX pattern (X ≡ ^{31}P), τ_A 6.61, τ_B 6.47 (J_{AB} 8.7, J_{AX} 16.8, J_{BX} 11.2 Hz).

We conclude that the apicophilicities of primary and tertiary alkoxy-ligands are more similar than previously supposed,[27] but that their relative apicophilicity depends upon the nature of the particular phosphoranyl radical concerned. Trippett [1b] has come to similar conclusions regarding the relative apicophilicities of primary and tertiary alkoxy-substituents in pentaco-ordinated phosphoranes.

(e) *Assignment of Proton Hyperfine Splittings in Cyclic Phosphoranyl Radicals.*—There is good evidence [10,27] that the hyperfine splitting (*ca.* 4 G) from a single proton, detected in the e.s.r. spectra of phosphoranyl radicals of the type (48) when ring proton exchange is slow, is due to H^1 or H^2, that is to one of the quasi-apical ring protons.

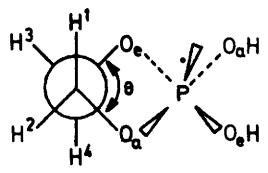


(48)

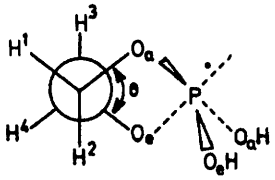


(49)

This assignment is further supported by the observation [28] of a doublet splitting from the unique proton in (49), and an INDO calculation for the hydroxy-analogue of (49) gave $a(H^1)$ +8.5 G, and predicted that the pairs of *exo-* (+0.2 G) and *endo-* (+0.3 G) quasi-equatorial protons would give rise to negligible splittings.



(50a)



(50b)

Although only a small number of ring conformations were investigated, it is clear that either H^1 or H^2 could give rise to the resolvable splitting of *ca.* 4 G detected for (48) in the slow exchange limit. However, the similarity of the proton splittings [*ca.* 4 (1 H) or *ca.* 2 G (2 H)] for (48), determined in this work and previously,[10,27] regardless of the nature of C and D or of the substituents on the ring, indicates that the ring conformation is probably similar for all these radicals. In (50b; θ 60°) H^1 is in a position approaching that which it would occupy in (49), and an INDO calculation for the hydroxy-analogue of (49) gave $a(H^1)$ +8.5 G, and predicted that the pairs

TABLE 5

Proton hyperfine coupling constants determined by INDO molecular orbital calculations for (50a and b)

		Hyperfine splitting [b] (G)			
Radical [a]	θ (°)	$a(H^1)$	$a(H^2)$	$a(H^3)$	$a(H^4)$
(50a, b)	0	−0.3 (0.0)	+9.4 (+8.4)	−0.6 (−0.4)	−0.9 (−0.7)
(50a)	30	+1.7 (−1.2)	+7.1 (+6.2)	+0.1 (+0.2)	+0.1 (+0.1)
(50b)	30	+3.5 (+3.1)	+1.6 (+1.5)	−0.1 (−0.1)	−0.2 (−0.1)
(50a)	60	−2.4 (−1.6)	+10.1 (+8.7)	−0.7 (−0.3)	+0.7 (+0.6)
(50b)	60	+9.1 (+7.8)	−0.3 (−0.1)	−0.1 (0.0)	−0.7 (−0.3)

[a] Nuclear co-ordinates were measured from a molecular model constructed to the following dimensions: bond lengths; C–H, 1.09; C–O, 1.43; C–C, 1.54; P–O, 1.65; O–H, 0.96 Å; bond angles; $O_a\widehat{P}O_a$, 180; $O_a\widehat{P}O_e$, 100°; $O_e\widehat{P}O_e$, 90°; all other bond angles were 109.5° before closing the five-membered ring. [b] Values before spin-annihilation; those obtained after spin-annihilation are given in parentheses. Spin densities were converted to splitting constants by multiplication by 555.7 G (pre-annihilation) or 584.7 G (post-annihilation).

the spectrum of (49) [a(P) 895, a(H) = 5.5 G at 218 K in cyclopropane]. In the spectra of (48), when splitting (*ca.* 2 G) is observed from two apparently equivalent protons, this probably results from rapid M4(exocyclic) exchange of H^1 with H^2 or M4(ring) exchange which interchanges H^1 with H^3 and H^2 with H^4. However, it is difficult to decide which of the two quasi-apical ring protons gives rise to the only resolvable splitting when exchange is slow. On the basis that, for most reasonable ring conformations, H^1 forms a better 'W plan arrangement' with the orbital of the unpaired electron in the canonical structure (48), we tentatively suggested [10,27] that this proton gives rise to the splitting of *ca.* 4 G. In view of the fact [13] that such canonical structures can be very poor approximations to the actual unpaired electron distribution [see section (a)], molecular orbital calculations using the INDO approximation * have been carried out in an attempt to assign this splitting more reliably. These calculations were performed for the conformations (50a and b), which are interconverted by ring inversion, of the dihydroxyphosphoranyl radical (50), and the results are given in Table 5.

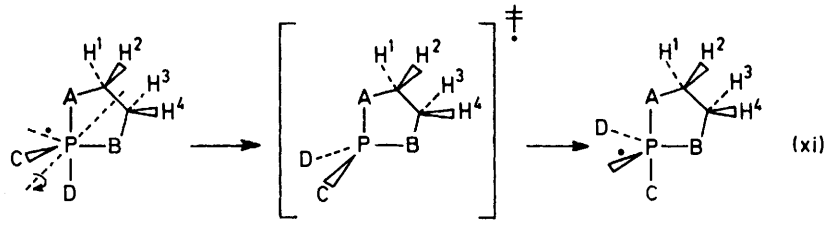
The possibility that changes in ring conformation alone are responsible for the line-shape effects attributed to M4(exocyclic) ligand exchange at phosphorus must be considered. We reject this explanation for the following reasons. Ring conformational changes *alone* do not bring about degenerate exchange of the quasi-apical ring protons. In addition, INDO results indicate that exchange between non-planar conformations similar to (50a and b) is unlikely to account for the line-shape changes obtained experimentally. The phosphorus substituent effects observed in this work and previously [10,27] are those expected if the line-shape changes result from ligand exchange at phosphorus.

* These calculations were performed using the computer program developed by Dr. A. Hudson of the University of Sussex.[18] We are indebted to Dr. Hudson for carrying out these calculations.

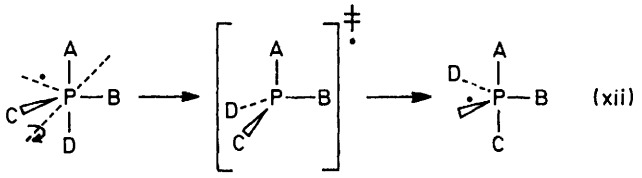
[28] I. G. Neil and B. P. Roberts, unpublished results.

If the ring is appreciably non-planar, then M4 processes alone do not bring about exchange between degenerate conformers. The ring must thus be essentially planar, or be non-planar but inverting rapidly on the e.s.r. time scale, or be non-planar with its inversion coupled to the M4 ligand exchange at phosphorus. At the present time we favour a non-planar ring conformation similar to (50b; θ 60°) for which ring inversion and ligand exchange at phosphorus are coupled processes.

(f) *Mechanisms for Ligand Exchange.*—A mechanism for the M4(exocyclic) mode of ligand exchange in the cyclic phosphoranyl radicals (1), which is consistent with the experimental results so far, is illustrated in equation (xi). Changes in ring conformation may also accompany ligand exchange [see section (e)].



(1) (xi)



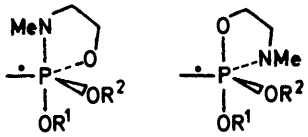
(xii)

This mechanism, which we have previously termed [10] the ' P4 mechanism,' requires that (*a*) ligand A is apical and ligand B is equatorial before and after exchange, (*b*) ligands C and D interchange sites, and (*c*) the ring protons H^1 and H^2 exchange sites. M4(exocyclic) exchange which is fast on the e.s.r. time scale will only be detectable if C and D are identical or have fairly similar apicophilicities.[9,10] The mechanism for the M4(ring) mode could be analogous, and although in principle C and D could be exchanging rapidly at the same temperature as that required for the endocyclic ligands to switch rapidly between apical and equatorial sites, the combination of these two exchange processes has not been detected by experiment [see section (c)]. When apicophilicity constraints are absent, the M4(ring) exchange is slower than the M4(exocyclic) process, and this difference may result from increased ring strain associated with changes in the angle $\widehat{APB}$ on proceeding to the transition state for M4(ring) exchange.

A basically similar mechanism [equation (xii)] will account for the fluxional behaviour of the acyclic phosphoranyl radicals $Bu^tO\dot{P}H_3$,[8] $RO\dot{P}F_3$,[11] $(EtO)_2\dot{P}(NMe_2)_2$,[10] and $RO\dot{P}(CH_3)_3$.[12]

The detailed mechanisms will undoubtedly be different for different radicals; for example when the ligands B, C, and D are identical these may become equivalent in the transition state (C_{3v} symmetry). Recent findings regarding the structures of certain monohalogenophosphoranyl radicals may have important bearing on such mechanistic details.[22,23] A similar mechanism of ligand exchange to that shown in equation (xii) has been proposed for $HO\dot{P}H_3$, on the basis of CNDO molecular orbital calculations.[21] Analysis of the line-shape changes which will accompany ligand exchange in the radicals $\dot{P}H_4$ and $\dot{P}F_4$ may prove important in this regard.

(g) *Ligand Apicophilicity in Phosphoranyl Radicals.*—In general the apicophilicity of a ligand in either a penta-co-ordinated phosphorane (PX_5) [1b] or a phosphoranyl radical [8-12,24,29] parallels its group electronegativity, although ring-strain effects may determine the most stable structure in a cyclic species. However, one notable difference between PX_5 and $\cdot PX_4$ is that for the former a dialkylamino-ligand appears to be much less apicophilic than an alkoxy-ligand, despite the similarities in the group electronegativities.[30] In a phosphoranyl radical these ligands have more similar preferences for apical placement,[10] and which group is the more apicophilic depends upon subtle constitutive effects for the particular radical concerned. For example,[10] we have previously shown for (51; $R^1 = R^2$) that the isomer value [(51a)/(51b)] depends markedly on the nature of R [0.33 for $R^1 = R^2 =$ Et, and 0.026 for $R^1 = R^2 =$ Bu^t at 177 K].



(51a) (51b)

The radicals (51; R^1 = Bz, R^2 = Et or Bu^t) were generated by photolysis of benzoyl peroxide in the presence of the appropriate azaoxaphospholan (see Table 6). Again there was an appreciable difference in the value [(51a)]/[(51b)] (at 218 K) depending on whether R^2 = Et (0.65) or Bu^t (0.30), even though the electro-

[29] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

[30] R. K. Oram and S. Trippett, *J.C.S. Chem. Comm.*, 1972, 554; *J.C.S. Perkin I*, 1973, 1300.

negative benzoyloxy-group is presumably sited apically in both isomers. Changes in the nature of the equatorial, as well as the apical,[12] substituents therefore affect the relative apicophilicities of oxygen and nitrogen ligands.

spectra yields $k_{exch.}$ *ca.* 2×10^7 s^{-1} at 206 K, somewhat slower than exchange of the Me_2N groups in the unsymmetrical isomer of $(EtO)_2\dot{P}(NMe_2)_2$.[10]

The magnitudes of the ^{31}P, ^{14}N, and ^1H splittings

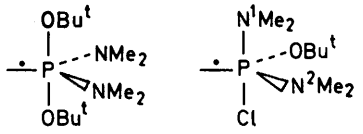
TABLE 6

E.s.r. data for the phosphoranyl radicals discussed in section (g)

Radical [a]	Addendum radical	T/K	Hyperfine splitting (G) a(P) [b]	Other
(51a; R^1 = Bz, R^2 = Et) [c]	BzO·	223	842	a(N) 13.0 (1 N), a(H) 9.0 (1 H)
(51b; R^1 = Bz, R^2 = Et) [c]	BzO·	223	1 025	a(N) *ca.* 4.2 (1 N), a(H) *ca.* 4.2 (1 H)
(51a; R^1 = Bz, R^2 = Bu^t) [c]	BzO·	223	831	a(N) 9.3 (1 N), a(H) 8.0 (1 H)
(51b; R^2 = Bz, R^2 = Bu^t) [c]	BzO·	223	1 014	*d*
(52)	Bu^tO·	163	770	*e*
(53)	Bu^tO·	203	884	$a(N^1)$ 9.5 (1 N), $a(N^2)$ 1.0 (1 N) $a(^{35}Cl)$ 44.0 (1 Cl) [f]
(54) [c]	BzO·	243	1 026	a(N) 20.0 (1 N)
(55) [g]	EtO·	243	932	a(N) 25.8 (1 N)
$Bu^tO\dot{P}(NCO)_3$ (56)	Bu^tO·	169	1 049	a(N) 22.5 (2 N) [h]
(58) [i]	Bu^tO·	183	627	a(H) +139 (1 H), a(H) −9.6 (1 H) a(H) 3.9 (3 H)
(59) [i]	Bu^tO·	193	629	a(H) +139 (1 H), a(H) −11 (2 H)

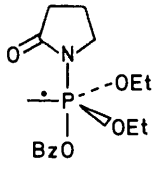
[a] Cyclopropane solvent unless otherwise stated. [b] Calculated using the Breit–Rabi equation; *g* 2.003 ± 0.001 unless otherwise stated. [c] Toluene solvent. [d] Nitrogen and proton splittings not sufficiently resolved to allow analysis; line-width 7 G. [e] From ref. 10; nitrogen splitting not resolved, line-width 5 G. [f] Nitrogen splittings obtained from the low temperature (9.5 G triplet) and high temperature (5.3 G quintet) line spacings: $a(^{37}Cl)$ 36.5 G; *g* 2.010. [g] Cyclopentane solvent. [h] Equatorial nitrogen splitting poorly resolved: a(N) *ca.* 2 G (1 N). [i] See ref. 29 for the original reports of these radicals.

The only detectable isomer of $(Bu^tO)_2\dot{P}(NMe_2)_2$ is (52),[10] whilst $Bu^tO(Cl)\dot{P}(NMe_2)_2$ appears [28] to exist as



(52)

(53)



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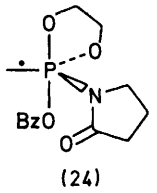
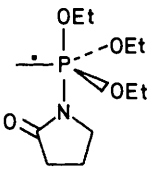
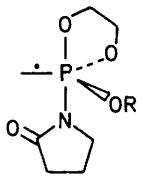


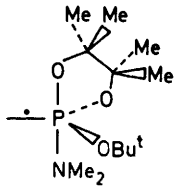
(24)



(55)



(14) R = Et
(15) R = Bu^t



(57)

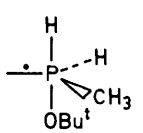
structure (53), because the nitrogen atoms give rise to different splittings at 173 K.*

Line-shape changes attributable to exchange of the dimethylamino-ligands in (53) are evident at higher temperatures, such that the nitrogens are apparently equivalent at 223 K. Computer simulation of the

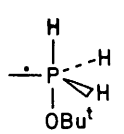
* The structure of (53) may deviate considerably from regular trigonal bipyramidal geometry (see refs. 22 and 23), and clearly anisotropic e.s.r. data for orientated radicals are required.

detected for (54) and (24) indicate that these radicals have the structures shown (see Figure 4). The five-membered ring preferentially bridges apical and equatorial sites, and the apicophilicity of the benzoyloxy-group is shown to be greater than that of the amido-substituent, as expected on the basis of the group electronegativities. The hyperfine splittings for (55), (14), and (15) suggest that all three possess an apical amido-group. The apicophilicity of the amido-group is thus greater than that of the alkoxy group, in accord with the larger ^{31}P splittings detected for (55), (14), and (15) compared with those for analogous tetra-alkoxyphosphoranyl radicals.[31] Similarly, the spectra of $Bu^tO\dot{P}(NCO)_3$ [radical (56), Table 6], (12), and (13) indicate that the isocyanato-group is more apicophilic than an alkoxy-group. For acyclic phosphoranyl radicals, the larger values of a(N) for apical isocyanato- and amido-groups, compared with apical dimethylamino-groups [10] (*ca.* 12 G) are consistent with an increased proportion of N(2*s*) character in the P–N bonds to the former ligands. The nitrogen splittings for the cyclic radicals (15) and (57) [10] are comparable (both *ca.* 24 G), perhaps indicating that the nitrogen atom in both is approximately sp^2 hybridised.

Hydrogen is intermediate in apicophilicity between methyl and alkoxy-ligands, as illustrated by the low-temperature e.s.r. spectra of (58) [29] and (59).[8,29]



(58)



(59)

[31] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224.

We have now shown that, at higher temperatures (>233 K), the spectrum of (58) exhibits the line-shape changes expected to accompany exchange of apical and equatorial hydrogen ligands (see Figure 4), and computer simulation shows that $k_{exch.}$ is *ca.* 1×10^7 s^{-1} at 246 K.

In summary, the apicophilicity of a substituent in a phosphoranyl radical closely parallels its group electronegativity, and in general ligand apicophilicity decreases

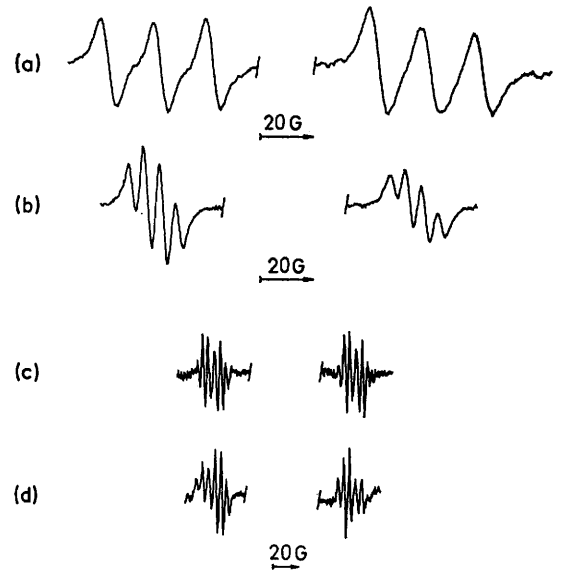


FIGURE 4 E.s.r. spectra of: (a) radical (54) at 228 K in toluene solution; (b) radical (24) at 238 K in toluene solution; (c) radical (58) in cyclopropane at 188 K [Only the low field lines corresponding to $M_I(^{31}P) = +\frac{1}{2}$ are shown]; (d) radical (58) at 246 K

in the order F, Cl, $RCO_2 > RC(O)NR$, $OCN > RO$, $R_2N > H > R$. Identical or closely similar apical and equatorial ligands in a phosphoranyl radical undergo very rapid exchange at temperatures usually employed for chemical studies (>150 K).

EXPERIMENTAL

The e.s.r. spectra were obtained using a Varian E-4 spectrometer equipped for irradiation of the sample *in situ* with high-intensity u.v. light from either a Thorn 1 kW D.C. (type ME/D) or a Philips 500 W A.C. (type SP 500) mercury discharge lamp. The general technique of sample preparation has been described previously.[10,31]

Spectrum simulation, including the effects of ligand exchange, was accomplished using the computer program ESREXN, written by Dr. J. Heinzer and obtained from QCPE (program no. 209) at Indiana University.

The 4,4-dideuterio-1,3,2-dioxaphospholans were prepared using 1,1-dideuterioethane-1,2-diol which was obtained by reduction of ethyl glycolate with $LiAlD_4$ in ether. A solution of freshly distilled ethyl glycolate (22.5 g) in ether (100 ml) was added during 1 h to a stirred mixture of lithium aluminium deuteride (8.3 g; 99 atom % D) in ether (200 ml) whilst maintaining gentle reflux. After the addition, the mixture was stirred under reflux for 4 h, cooled, and water (10 ml) was added cautiously with stirring and cooling in an ice-bath, followed by 16% aqueous sodium hydroxide (10 ml), and finally water (20 ml). Anhydrous magnesium sulphate (40 g) was added and the mixture stirred for 1 h, filtered, and the solid material on the filter washed thoroughly with acetone (6 × 80 ml). Acetone and ether were removed from the filtrate under reduced pressure and the residual oil distilled to yield 1,1-dideuterioethane-1,2-diol, b.p. 62 °C at 1.5 Torr (5.6 g, 41% based on ethyl glycolate), τ (D_2O; $Me_3Si[CH_2]_2CH_2SO_3Na$ standard; +35 °C), τ 5.29 (s, OH) and 6.35 (s, CH_2); the latter peak resolved into a 1 : 2 : 3 : 2 : 1 quintet at +62 °C ($^3J_{HD}$ *ca.* 1.5 Hz).

The syntheses of new 1,3,2-dioxaphospholans are described below. ^{31}P N.m.r. spectra were determined in C_6D_6 solvent and chemical shifts are quoted relative to 85% H_3PO_4.

2-(2-*Oxopyrrolidin*-1-*yl*)-1,3,2-*dioxaphospholan* was prepared by dropwise addition of 2-chloro-1,3,2-dioxaphospholan (23.4 g) in ether (50 ml) to a well stirred solution of pyrrolidin-2-one (15.7 g) and triethylamine (18.8 g) in ether (100 ml), keeping the temperature at *ca.* 10 °C. After addition, the mixture was stirred for 1 h at 20 °C and then filtered to remove the precipitated triethylamine hydrochloride. The ether was removed under reduced pressure and the residual oil was distilled to yield the product, b.p. 115 °C at 0.1 Torr, as a supercooled liquid, which crystallised on standing to a white solid, m.p. 53 °C (Found: C, 40.9; H, 5.9; N, 8.0; P, 17.8. $C_6H_{10}NO_3P$ requires C, 41.2; H, 5.8; N, 8.0; P, 17.7%). Proton decoupled ^{31}P n.m.r. showed a broad singlet at δ −125 p.p.m.

2-*Neopentoxy*-1,3,2-*dioxaphospholan* was prepared from 2-chloro-1,3,2-dioxaphospholan, neopentyl alcohol, and triethylamine in ether, b.p. 59—60 °C at 5 Torr (Found: C, 47.3; H, 8.5; P, 17.2. $C_7H_{15}O_3P$ requires C, 47.2; H, 8.5; P, 17.4%).

2-*Trifluoroacetoxy*-1,3,2-*dioxaphospholan* was prepared by slow addition of 2-chloro-1,3,2-dioxaphospholan (8.2 g) to a stirred suspension of anhydrous sodium trifluoroacetate (9.0 g) in ether (50 ml) maintained at 0 °C. The mixture was allowed to warm to 20 °C and stirred for 1 h, filtered, and the ether removed from the filtrate under reduced pressure. The residue was distilled to yield the product, b.p. 63—64 °C at 17 Torr (Found: C, 23.5; H, 2.0; P, 14.9. $C_4H_4F_3O_4P$ requires C, 23.5; H, 2.0; P, 15.2%).

2-*Chloro*-4,4-*dideuterio*-1,3,2-*dioxaphospholan* was prepared by slow addition of 1,1-dideuterioethane-1,2-diol (7.0 g) to a stirred, gently refluxing solution of phosphorus trichloride (15.7 g) in dry methylene chloride (40 ml). Removal of the solvent under reduced pressure followed by distillation of the residue yielded the product (8.0 g), b.p. 51—53 °C at 20 Torr. The proton-decoupled ^{31}P n.m.r. spectrum showed a singlet at δ −167.5 p.p.m.

2-*Fluoro*-4,4-*dideuterio*-1,3,2-*dioxaphospholan* was prepared by slow addition of the 2-chloro-compound (2.0 g) to antimony trifluoride (2.0 g). Distillation of the mixture yielded the product, b.p. 25 °C at 15 Torr. The ^{31}P n.m.r. showed δ −124 p.p.m. [$^1J_{PF}$ 1 226 (1 F), $^3J_{PH}$ 8.8 (1 H), $^3J_{PH}$ 1.5 (1 H), $^3J_{PD}$ 1.5 Hz (1 D)].

2-*Ethoxy*-4,4-*dideuterio*-1,3,2-*dioxaphospholan* was prepared from the 2-chloro-compound, ethanol, and triethylamine in ether, b.p. 50 °C at 15 Torr.

2-*Acetoxy*-4,4-*dideuterio*-1,3,2-*dioxaphospholan*, was prepared by the reaction of the 2-chloro-compound with anhydrous sodium acetate in ether at 0 °C. After filtration and removal of the solvent, the residue was distilled to yield the product, b.p. 44 °C at 0.4 Torr. Proton decoupled ^{31}P n.m.r. showed a singlet at δ −127 p.p.m. The

^{1}H n.m.r. spectrum showed a complex multiplet centred at τ 6.40 (2 H) and a doublet ($^4J_{PH}$ 1.1 Hz) at 8.35 (3 H).

2-*Chloro*-4,4-*dimethyl*-1,3,2-*dioxaphospholan* was prepared by dropwise addition during 2 h of phosphorus trichloride (17.4 g) in benzene (150 ml) to a stirred solution of 2-methylpropane-1,2-diol (11.4 g) and triethylamine (25.6 g) in benzene (60 ml) at 0 °C. After addition, the mixture was allowed to warm to room temperature, stirred for a further 1 h, and filtered. The solvent was removed from the filtrate under reduced pressure and the residue distilled to yield the product (12 g), b.p. 57 °C at 19 Torr (Found: C, 31.5; H, 5.4; P, 20.1. $C_4H_8ClO_2P$ requires C, 31.1; H, 5.2; P, 20.2%).

2-*Fluoro*-4,4-*dimethyl*-1,3,2-*dioxaphospholan* was prepared from the 2-chloro-compound and antimony trifluoride, and was purified by trap-to-trap distillation at 20 °C (Found: C, 34.7; H, 5.7. $C_4H_8FO_2P$ requires C, 34.8; H, 5.8%). Analysis of the ^{31}P n.m.r. spectrum gave δ −131 p.p.m. [$^1J_{PF}$ 1 226 (1 F), $^3J_{PH}$ 12.2 Hz (1 H)].

2-Chloro-4,4-dimethyl-1,3,2-dioxaphospholan was converted to (a) 2-*ethoxy*-4,4-*dimethyl*-1,3,2-*dioxaphospholan*, b.p. 44 °C at 6 Torr, by the reaction with ethanol and triethylamine in ether (Found: C, 44.2; H, 8.0; P, 19.3. $C_6H_{13}O_3P$ requires C, 43.9; H, 8.0; P, 18.9%), δ(^{31}P) −141.5 p.p.m.; (b) 2-*trifluoroacetoxy*-4,4-*dimethyl*-1,3,2-*dioxaphospholan*, b.p. 42 °C at 2.8 Torr, by the reaction with anhydrous sodium trifluoroacetate in ether at 0 °C (Found: C, 31.2; H, 3.5. $C_6H_8F_3O_4P$ requires C, 31.3; H, 3.5%), δ(^{31}P) −137 p.p.m.; (c) 2-*acetoxy*-4,4-*dimethyl*-1,3,2-*dioxaphospholan*, b.p. 56 °C at 0.3 Torr, by the reaction with anhydrous sodium acetate in ether at 0 °C (Found: C, 40.0; H, 6.4; P, 17.1. $C_6H_{11}O_4P$ requires C, 40.5; H, 6.2; P, 17.4%).

The awards of a research assistantship (to M. J. P.) and of a research studentship (to J. W. C.) are acknowledged. We are grateful to Dr. A. Hudson, University of Sussex, for carrying out the INDO calculations, and to Professor A. G. Davies and Dr. M. G. Hutchings for helpful discussions.

[6/993 *Received*, 24*th May*, 1976]