The Electron Spin Resonance Spectra and Structure of Chlorophosphoranyl Radicals in Solution

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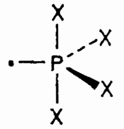
Chlorophosphoranyl radicals of the types $Bu^tO(R)_n\dot{P}Cl_{3-n}$ and $Bu^tO(RO)_n\dot{P}Cl_{3-n}$ have been prepared by addition of photochemically generated t-butoxyl radicals to chlorophosphines in fluid solution. The e.s.r. spectra of these radicals are characterised by very large phosphorus-31 hyperfine splittings (*ca.* 1000 G) and readily resolvable ^{35}Cl and ^{37}Cl splittings (*ca.* 40 G). The chlorine atoms are probably held rigidly (on the e.s.r. time scale) at apical sites in these chlorophosphoranyl radicals, the apicophilicity of chlorine being greater than that of an alkoxy-group. The reactions of chlorophosphoranyl radicals are discussed.

THERE have been several recent e.s.r. studies of the structure and reactivity of phosphoranyl radicals in solution.[1-7] The evidence suggests that phosphoranyl radicals (I) possess distorted trigonal bipyramidal structures in which the unpaired electron is stereochemically active and occupies an equatorial, rather than apical, ligand site.[1-8] The degree of distortion from a regular trigonal bipyramidal structure depends on the nature of the ligands.[2,9]



(I)

Phosphoranes PX_5 also possess a trigonal bipyramidal structure in solution and a large body of data is available concerning their configuration and stereochemical nonrigidity. These data may be summarised in the form of rules governing which is the most stable isomer of a particular phosphorane.[10] When the ligands around phosphorus are of differing electronegativity the most electronegative groups preferentially occupy apical sites. When the phosphorus atom in the phosphorane is incorporated into a four- or five-membered ring, the most favourable placing of the ring is when it spans apical and equatorial positions.

The results obtained so far suggest that the structures of phosphoranyl radicals are governed by the same stereoelectronic preference rules.[1-7] In an acyclic phosphorane in which all five ligands are the same, the angles $X_{ap}\widehat{P}X_{eq}$ and $X_{eq}\widehat{P}X_{eq}$ are 90 and 120° respectively. In cyclic phosphoranes therefore a small (four- or five-membered) ring should bridge apical and equatorial ligand sites preferentially; however, the degree of preference would be expected to depend upon the nature, particularly electronegativity differences, of the groups around phosphorus. In a phosphoranyl radical (I) the angles $X_{ap}\widehat{P}X_{eq}$ and $X_{eq}\widehat{P}X_{eq}$ may be somewhat less than 90 and 120° respectively, the deviation being greater for $X_{eq}\widehat{P}X_{eq}$,[8] but these angles are probably close to their values in the protic parent HPX_4.[4b] The preference of a small ring to bridge apical and equatorial sites might be similar in a phosphoranyl radical and its protic parent.

In general † the isotropic phosphorus-31 hyperfine

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† A recent report [11] claims the detection of $\dot{P}H_4$ trapped in solid krypton at *ca.* 10 K, the value of $a(^{31})P$ being 973·8 ± 2 G. Such a large phosphorus splitting seems very unlikely to us in view of the trends discussed above and the values of $a(^{31}P)$ for related radicals in solution,[7] *e.g.* $Bu^tO\dot{P}H_3$ (626·7 G; −100 °C), $(Bu^tO)_2\dot{P}H_2$ (672·5 G; −100 °C), and $Me(Bu^tO)\dot{P}H_2$ (631·5 G; −85 °C). We feel that further studies of the purported $\dot{P}H_4$ radical are needed in particular to show that the spectrum obtained is not due to an oxygen-containing impurity in the original phosphine.

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

[2] A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738; *J.C.S. Perkin II*, 1972, 993.

[3] A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometallic Chem.*, 1972, **40**, C33.

[4] (*a*) A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224; (*b*) A. G. Davies, R. W. Dennis, D. Griller, K. U. Ingold, and B. P. Roberts, *Mol. Phys.*, in the press.

[5] D. Griller and B. P. Roberts, *J. Organometallic Chem.*, 1972, **42**, C47.

[6] R. W. Dennis and B. P. Roberts, *J. Organometallic Chem.*, 1972, **43**, C2.

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

[8] J. Higuchi, *J. Chem. Phys.*, 1969, **50**, 1001.

[9] G. F. Kokoszka and F. Brinckman, *J. Amer. Chem. Soc.*, 1970, **92**, 1199.

[10] E. L. Muetterties, *Accounts Chem. Res.*, 1970, **3**, 266 and references cited therein.

[11] C. A. McDowell, K. A. R. Mitchell, and P. Raghunathan, *J. Chem. Phys.*, 1972, **57**, 1699.

splitting in a phosphoranyl radical increases as the electronegativity of the substituents increase.[1-7,9]

RESULTS AND DISCUSSION

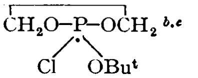
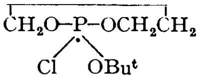
We report here an e.s.r. study of a series of chlorophosphoranyl radicals generated by the addition of t-butoxyl radicals to chlorophosphites or chlorophosphines [equation (1; X = alkyl or alkoxy)]. Although some phos-

$$\mathrm{Bu^tO\cdot + X_{\mathit{n}}PCl_{3-\mathit{n}} \longrightarrow Bu^tO(X_{\mathit{n}})\dot{P}Cl_{3-\mathit{n}}} \qquad (1)$$

phoranyl radicals containing P–Cl bonds have been detected by e.s.r. in the solid state,[9,12] no comparable solution study exists. The experimental method has been described in detail elsewhere and involves irradiation of a mixture of di-t-butyl peroxide and the chlorophosphine in a solvent (usually cyclopropane or propane) with high intensity u.v. light whilst the sample is in the cavity of the spectrometer.[2] The Figure shows the e.s.r. spectrum obtained from the reaction of t-butoxyl radicals with diethyl chlorophosphite and the results are presented in the Table

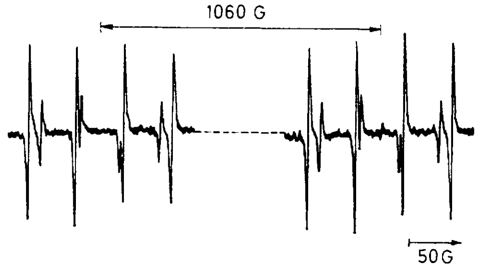
As chlorine atoms are successively substituted for the alkoxy-groups in a tetra-alkoxyphosphoranyl radical the isotropic phosphorus hyperfine splitting increases from 890 [in $\mathrm{Bu^tO\dot{P}(OEt)_3}$][2] to 1217 G (in $\mathrm{\dot{P}Cl_4}$).[12a] This trend is in accord with the relative electronegativities of the chlorine and alkoxy-substituents [3·16 and 2·53 (for EtO) respectively[13]]. The ligand sites in a phosphoranyl radical are non-equivalent and the question arises as to whether the preference of chlorine for an apical site (its apicophilicity[14]) is greater or less than that of an alkoxy-group. Apicophilicity generally parallels electronegativity and thus we might expect the preference of chlorine substituent for apical placement to be greater than that of an alkoxy-group.

E.s.r. spectroscopic parameters of chlorophosphoranyl radicals in solution

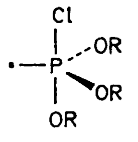
Phosphoranyl radical	Solvent	Temp. (°C)	$a(^{31}P)/G$ [a]	$a(^{35}Cl)/G$	$a(^{37}Cl)/G$	g [a]
$\mathrm{Bu^tO(EtO)_2\dot{P}Cl}$ [b]	Cyclopentane	−50	1037	47·2	39·3	2·009
	Cyclopropane	−60	1034	47·2	39·2	2·010
 [b,c]	Cyclopropane	−30	1033	42·8	35·9	2·010
	Cyclopropane	−40	1070	44·8	37·1	2·007
$\mathrm{Bu^tO(EtO)\dot{P}Cl_2}$ [d]	Propane	−70	1145	34·1	28·1	2·011
$\mathrm{Bu^tO(Me)\dot{P}Cl_2}$ [d]	Propane	−70	1023	30·9	25·8	2·010
$\mathrm{Bu^tO(Et)\dot{P}Cl_2}$ [d]	Propane	−70	1003	31·3	26·0	2·010
$\mathrm{Bu^tO(Et_2)\dot{P}Cl}$ [e]	Cyclopropane	−40	794	38·9	32·2	2·008
$\mathrm{Bu^tO\dot{P}(OEt)_3}$	Cyclopentane	−70	890			2·003
$\mathrm{\dot{P}Cl_4}$ [f]	Solid state	−196	1217	[g]		2·013
$\mathrm{[O\dot{P}Cl_3]^{\overline{\cdot}}}$ [f]	Solid state	−196	1367	[h]		2·014

[a] Calculated using the Breit–Rabi formula. [b] a(Cl) Did not not vary significantly (> ±0·5 G) in the temperature range −120 to +40°. [c] Each line was further split into a 1 : 2 : 1 triplet, a(H) = 1·3 G. See text. [d] Two equivalent chlorine atoms. [e] When irradiation was carried out at higher temperatures (*ca.* −10°) a second chlorophosphoranyl radical [$a(^{31}P)$ 943 G; $a(^{35}Cl)$ 30 G; $a(^{37}Cl)$ 25 G] was also present. This was assigned the structure $\mathrm{(Bu^tO)_2Et\dot{P}Cl}$ derived by addition of t-butoxyl radicals to $\mathrm{Bu^tO(Et)PCl}$, the product of α-scission of the primary radical. [f] Ref. 12*a*. [g] $a(^{35}Cl)_{ap}$ 60 G; $a(^{35}Cl)_{eq}$ not resolved. [h] $a(^{35}Cl)_{ap}$ 67 G; $a(^{35}Cl)_{eq}$ 14 G.

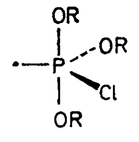
The structure of $\mathrm{Bu^tO(EtO)_2\dot{P}Cl}$ could be represented by (II) or (III) (neglecting any difference in apicophilicity of Bu^tO and EtO) or exchange between these two isomers could be rapid on the e.s.r. time scale giving rise to averaged spectroscopic parameters. The chlorine splitting in (II) and (III) would be expected to be very different[8,9,12] (see Table) and the essential independence of the observed value of a(Cl) with changing temperature militates against a rapid exchange between (II) and (III).



E.s.r. spectrum at 9·130 GHz produced by photolysis of di-t-butyl peroxide in the presence of diethyl chlorophosphite in cyclopropane at −60°



(II)



(III)

Only if the rate of exchange were extremely rapid and the

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[12] C. M. L. Kerr and F. Williams, *J. Phys. Chem.*, 1971, **75**, 3023; (*b*) A. Begum and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2065.

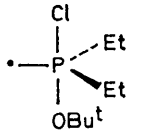
[13] J. E. Huheey, *J. Phys. Chem.*, 1965, **69**, 3284; 1966, **70**, 2086.

[14] P. Gillespie, P. Hoffman, H. Klysacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687.

equilibrium constant close to unity at all accessible temperatures (*i.e.* ΔH° *ca.* 0) would a(Cl) be likely to be independent of temperature. However, the chlorine splittings obtained in our work are close to the mean of the values for apical and equatorial chlorines in $\dot{\mathrm{P}}\mathrm{Cl}_4$ and $(\mathrm{POCl}_3)^-$, lending some support to the possibility that in the radicals we have detected the chlorine atoms are rapidly switching between apical and equatorial sites, spending equal times in each position.

Similar conclusions apply to the phosphoranyl radical from 2-chloro-1,3,2-dioxaphospholan except that the ring probably spans apical and equatorial positions in the most stable isomer. The small (1·3 g) triplet splitting in this case probably arises from coupling with a pair of *cis*- or *trans*-hydrogen atoms in the ring which have coupling constants which are equal within the line width.* Whether the six-membered ring in the phosphoranyl radical from 2-chloro-1,3,2-dioxaphosphorinan prefers to span apical and equatorial positions or be diequatorial is uncertain at present.

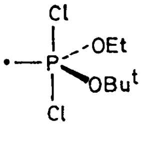
The e.s.r. spectrum of the radical $\mathrm{Bu^tO(Et)_2\dot{P}Cl}$ provides some evidence for the relative apicophilicities of Cl and RO in phosphoranyl radicals. Because of the relatively low electronegativity[13] of the ethyl groups (2·28) the barrier to ligand interchange in this radical is expected to be relatively large[6,7] and the rigid structure (IV) may be assigned to it. An apical chlorine-35 atom

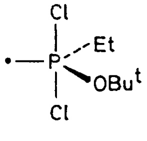

(IV)

in (IV) thus gives rise to a coupling constant of 38·9 G. The values of $a(^{35}\mathrm{Cl})$ in all the other chlorophosphoranyl radicals we have examined fall into the range 31—47 G and it thus seems probable that in these radicals the chlorine atoms are apical. Isomeric radicals with equatorial chlorine atoms would be less stable (they have not been detected) and apical–equatorial chlorine exchange is slow on the e.s.r. time scale.

The electronegativities of chlorine and alkoxy-groups may not be the only factor determining the relative apicophilicities of these ligands in phosphoranyl radicals. The ability of a donor ligand to enter into p_π–d_π bonding with the central phosphorus atom in a phosphorane is greatest when the ligand is in the equatorial plane.[14–16] The oxygen atom of an alkoxy-group may π-bond more effectively than chlorine with the phosphorus atom in a phosphoranyl radical, and this will bring about a further decrease in the apicophilicity of an alkoxy-group relative to chlorine. It is not clear why the phosphorus splitting in the radical ion $[\mathrm{OPCl_3}]^{\cdot}$ should be greater than that in $\dot{\mathrm{P}}\mathrm{Cl}_4$ (see Table).

The dichlorophosphoranyl radicals which we have detected probably have the structures (V)—(VII).


(V)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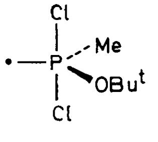
(VII)

To summarise, whilst the results are not entirely unambiguous, the apicophilicity of chlorine is probably greater than that of an alkoxy-group in a phosphoranyl radical as a result of electronegativity differences and the greater degree of π-bonding between oxygen and phosphorus.

Reactions of Chlorophosphoranyl Radicals.—In addition to self-reaction, phosphoranyl radicals readily undergo unimolecular scission reactions in solution.[17]

$$\mathrm{Bu^tO\dot{P}X_3} \left\{ \begin{array}{l} \xrightarrow{\alpha\text{-scission}} \mathrm{Bu^tOPX_2} + \mathrm{X}\cdot \\ \xrightarrow[\beta\text{-scission}]{} \mathrm{Bu^t}\cdot + \mathrm{OPX_3} \end{array} \right. \qquad (2)$$

At temperatures below about −40° and with radical concentrations at full light intensity of *ca.* 10^{-6}M, all the chlorophosphoranyl radicals listed in the Table decayed by second-order processes. This was shown by the radical concentration being proportional to the square root of the light intensity incident on the sample. Under these conditions P–P coupling to form an unstable biphosphoranyl may be the major process responsible for radical removal.[4a,5,18]

The radical $\mathrm{Bu^tO\dot{P}(OEt)_3}$ undergoes rapid β-scission at low temperatures.[2] In contrast the chlorophosphoranyl radical $\mathrm{Bu^tO(EtO)_2\dot{P}Cl}$ only gives rise to a detectable concentration of t-butyl radicals at +25° and above. It is possible that a proportion of these t-butyl radicals may have arisen from a secondary source [reactions (3) and (4)]. At these temperatures the phosphoranyl

$$\mathrm{Bu^tO(EtO)_2\dot{P}Cl} \longrightarrow \mathrm{Bu^tOP(OEt)_2} + \mathrm{Cl}\cdot \qquad (3)$$

$$\mathrm{Bu^tOP(OEt)_2} + \mathrm{Bu^tO}\cdot \longrightarrow \mathrm{(Bu^tO)_2\dot{P}(OEt)_2} \longrightarrow$$
$$\mathrm{Bu^t}\cdot + \mathrm{Bu^tO(OEtO)_2P{=}O} \qquad (4)$$

radicals decayed by mixed first- and second-order processes. The decreased rate of β-scission upon replacement of EtO by Cl is probably mainly the result of a polar effect, a reduction in electron density at phosphorus bringing about both ground state stabilisation and transition state destabilisation relative to $\mathrm{Bu^tO\dot{P}(OEt)_3}$.

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* A possible alternative is that apical and equatorial ring methyleneoxy-groups are interchanging position rapidly on the e.s.r. time scale giving rise to an average value of the *cis*-(or *trans*-)hydrogen splitting.

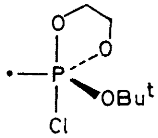
[15] R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047 and references cited therein.

[16] E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1972, **94**, 5674.

[17] K. U. Ingold and B. P. Roberts, ' Free Radical Substitution Reactions,' Wiley-Interscience, New York, 1971, ch. 6.

[18] G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 8784.

There is also evidence from other sources[17] that chlorophosphoranyl radicals may undergo α-scission with loss of a chlorine atom, particularly at higher temperatures. The radical (VIII) did not give a detectable concentration of t-butyl (or other alkyl) radicals at +30° and this is



(VIII)

probably due to the stabilising effect that the five-membered ring system appears to exert on phosphoranyl radicals.[4a,5]

At low temperatures (<−40°) the radical $Bu^tO(Et)_2\dot{P}Cl$ decayed by a second-order process whereas at higher temperatures (−10°) a first-order component was detected. A high temperatures a second chlorophosphoranyl radical was detected in lower concentration and this is assigned the structure $(Bu^tO)_2Et\dot{P}Cl$ on the basis of its ^{31}P hyperfine splitting (943 G). The probable mode of formation of this secondary phosphoranyl radical is set out in equations (5) and (6). The relatively ready loss of Et• from (IV) rather than Cl• is in accord with bond strength data[19] [D(P–C) in $Et_3P = 65$ kcal mol^{-1}; D(P–Cl) in $Cl_3P = 76$ kcal mol^{-1}].

$$\underset{(IV)}{Bu^tO(Et)_2\dot{P}Cl} \begin{cases} \xrightarrow{\text{low temperature}} \text{self reaction} \\ \xrightarrow[\text{high temperature}]{} Bu^tO(Et)PCl + Et\cdot \end{cases} \qquad (5)$$

$$Bu^tO(Et)PCl + Bu^tO\cdot \longrightarrow (Bu^tO)_2Et\dot{P}Cl \qquad (6)$$

In the above discussion we have made no mention of the importance of configurational effects[4a,6] in determining the type and rate of the reactions of phosphoranyl radicals. Although these effects are probably quite significant, our experimental data do not yet justify discussion in these terms. Full kinetic, structural, and product studies are clearly required for these systems.

EXPERIMENTAL

The apparatus used for u.v. irradiation of samples *in situ* in the e.s.r. spectrometer cavity has been described previously.[2] Solutions of reactants in propane and cyclopropane were prepared using a conventional vacuum line.[7] The chlorophosphines used in this work were either commercial products or were prepared by standard procedures.

We are grateful to the Ethyl Corporation for generous gifts of methyl- and ethyl-dichlorophosphines. One of us (D. G.) acknowledges the award of a Salters' Fellowship.

[3/036 *Received, 8th January,* 1973]

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[19] S. B. Hartley, W. S. Holmes, J. K. Jaques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev.*, 1963, **17**, 204.