# Phenylphosphoranyl Radicals: Are they Tetrahedral or Trigonal Bipyramidal?

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Summary The e.s.r. spectra of phenylphosphoranyl radicals $[Ph_nPX_{3-n}Y]\cdot$ show that, depending on the nature of X and Y, these radicals fall into two types in which the unpaired electron is centred mainly on phosphorus or on the aromatic ring.

THE structure of phenylphosphoranyl radicals, as deduced from their e.s.r. spectra, has been the subject of two recent communications.[1,2] Boeckestein et al.[1] assigned the e.s.r.

(1)

(2)
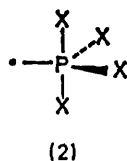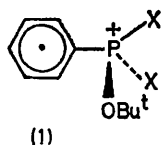
spectrum observed during photolysis of di-t-butyl peroxide in the presence of phenyldimethoxyphosphine to the species

$[PhP(OMe)_2OBu^t]\cdot$. Because the value of the hyperfine coupling to phosphorus was low, and that to the aromatic protons was significant, they proposed that the electron was located on the aromatic ring, and that the radical had an approximately tetrahedral disposition of bonds about phosphorus (1; X = OMe); the assignment however was questionable because it involved the assumption that $a(P) = a(p\text{-H})$.

In contrast, phosphoranyl radicals without aromatic ligands normally exhibit large phosphorus splittings (usually 500—1000 G) indicating that the unpaired electron occupies an orbital which possesses appreciable (15—30%) phosphorus 3s-character, consistent with an approximately trigonal bipyramidal structure (2) with the unpaired electron acting as an equatorial 'phantom' ligand.[3] The apical ligand orbitals also contribute to the molecular orbital containing the unpaired electron.†

Mishra and Symons[2] have suggested that electron capture by phenylphosphorus compounds can occur either at P or at the aromatic ring, and have emphasized the role

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† The isotropic e.s.r. spectra of phosphoranyl radicals containing an apical hydrogen ligand (see Table and refs. 3b, d) exhibit large (120—140 G) proton hyperfine splitting, indicating appreciable spin density in the hydrogen 1s-orbital. Approximate molecular orbital calculations (CNDO/2) on $MeOPH_3$ using the partially optimised geometry derived by Krusic and Meakin (see Figure 2 of ref. 3d) gave orbital spin densities of 0·28 (P, 3s), 0·29 (P, $3p_x$) (the x axis is the bisector of $\angle\ H_{eq}$ P H_{eq}), 0·26 (H_{ap}, 1s). The electronic structure implied by (2) is thus only a convenient approximation.

of constraints imposed by the solid state in determining the site of electron attachment.

Using e.s.r. spectroscopy, we have investigated the structure and reactions of a series of phenylphosphoranyl radicals in fluid solution, where the effect of a rigid matrix is avoided. Photochemically generated t-butoxyl radicals add to phenyldiethoxyphosphine [equation (2), $n = 1$, X = OEt, Y = OBu^t] and an e.s.r. spectrum (see Table) may be detected which can be confidently assigned to the radical (1; X = OEt) because (a) the spectrum derived from $C_6D_5P(OEt)_2$ (see Table) confirms that $a(P)$ indeed is equal to $a(p$-H), and (b) kinetic analysis of the system demon-

produce only a species exhibiting the very large value of $a(P)$ (see Table) expected for the trigonal bipyramidal phosphoranyl radical [type (2)].
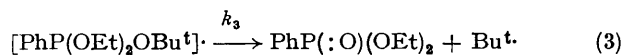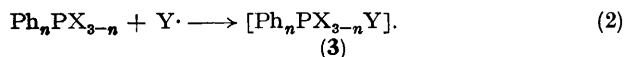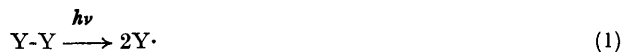
The Table also lists a selection of other mono-, di-, and tri-phenylphosphoranyl radicals which have been detected, together with their hyperfine splitting constants. On the basis of these data we conclude that phenylphosphoranyl radicals fall into two general types with the unpaired electron centred either mainly on phosphorus or on the benzene ring. It appears that ligands (X and Y) in (3) which are capable of inductive or conjugative stabilisation of a positive charge on phosphorus favour benzene radical

Phenylphosphoranyl radicals $Ph_n\dot{P}X_{3-n}Y$

Ph_nPX_{3-n}					Y·	$a(P)$	Hyperfine coupling constants/G[a]		
						Type (1)		Others	
PhP(OMe)$_2$	..	..	..	..	Bu^{t}O·	9·7[b]	9·7 (p-H)[b]	5·5(o-H)[b]	0·9(m-H)[b]
PhP(OEt)$_2$	..	..	..	..	Bu^{t}O·	9·25	9·25(p-H)	5·15(o-H)	1·10(m-H)
C$_6$D$_5$P(OEt)$_2$	..	..	..	..	Bu^{t}O·	10·10	1·50(p-D)	0·90(o-D)	<0·3(m-D)
Ph$_2$POEt	..	..	..	..	Bu^{t}O·	23·0		c	
Ph$_3$P	..	..	..	..	Bu^{t}O·	45·0	3·1(p-H)[d]	1·7(o-H)[d]	<0·5(m-H)[d]
						Type (2)			
PhPCl$_2$	..	..	..	..	Bu^{t}O·	1009·0	31·5(^{35}Cl)[e]	26·2(^{37}Cl)[e]	
PhP(OCH$_2$CF$_3$)$_2$	..	..	..	..	Bu^{t}O·	703·0			
PhPH$_2$	..	..	..	..	Bu^{t}O·	557·0	126·5(H$_{ap}$)	10·2(H$_{eq}$)	
PhP(SMe)$_2$	..	..	..	..	Bu^{t}O·	687·0			
Ph$_2$POEt	..	..	..	..	MeS·	643·0			
Ph$_2$PCl	..	..	..	..	Bu^{t}O·	808·3	41·0(^{35}Cl)	34·0(^{37}Cl)	
Ph$_3$P	..	..	..	..	MeS·	622·7			

[a] In propane solvent at -80 °C. Coupling constants depended on solvent and temperature. [b] Coupling constants from ref. 1. [c] Ring proton splittings poorly resolved. [d] The rings appear to be equivalent. The coupling constants were determined by computer simulation, and deuterium labelling studies are in progress to confirm them. [e] Two equivalent apical chlorine atoms.

strates that the species which gives rise to the spectrum is the source of the t-butyl radicals which are also detected,‡

$$Y-Y \xrightarrow{h\nu} 2Y· \quad (1)$$

$$Ph_nPX_{3-n} + Y· \longrightarrow [Ph_nPX_{3-n}Y]· \quad (2)$$
$$(3)$$

$$[PhP(OEt)_2OBu^t]· \xrightarrow{k_3} PhP(:O)(OEt)_2 + Bu^t· \quad (3)$$

However, phenyldichlorophosphine reacted with t-butoxyl radicals [equation (2), $n = 1$, X = Cl, Y = OBu^t] to

anions carrying tetrahedral phosphonium substituents (1), whilst electron withdrawing ligands favour trigonal bipyramidal radicals of the type (2), in which the valence shell of phosphorus contains nine electrons.

It should be noted that the essential difference between species of types (1) and (2) is one of unpaired electron distribution. The isotropic e.s.r. spectra do not give precise information regarding bond angles, and when differentiating[1] into 'tetrahedral' and 'trigonal bipyramidal' types the probability of distortion of both species from regular geometry must be borne in mind.

‡ The phenyl group markedly accelerates β-scission; $\log_{10}(k_3/s^{-1}) = 10·6 - 3·9/\theta$ where $\theta = 2·303RT$ kcal mol^{-1} [compare the rate[3c] of β-scission of $(EtO)_3\dot{P}OBu^t$].

[1] G. Boeckestein, E. H. J. M. Jansen, and H. M. Buck, J.C.S. Chem. Comm., 1974, 118.
[2] S. P. Mishra and M. C. R. Symons, J.C.S. Chem. Comm., 1974, 606.
[3] (a) A. G. Davies, D. Griller, and B. P. Roberts, J.C.S. Perkin II, 1972, 993, 2225, (b) P. J. Krusic, W. Mahler, and J. K. Kochi, J. Amer. Chem. Soc., 1972, 94, 6033, (c) G. B. Watts, D. Griller, and K. U. Ingold, ibid., p. 8784, (d) P. J. Krusic and P. Meakin, Chem. Phys. Letters, 1973, 18, 347.