

Unstable Intermediates. Part 173.^{1,†} Triphenyl-phosphonium and -arsonium Cations and Various Phosphoranyl and Arsonanyl Radicals derived from Triphenylphosphine and its Oxide, Sulphide, and Selenide and Triphenylarsine and its Oxide by the Action of Ionizing Radiation

By George W. Eastland and Martyn C. R. Symons,* Department of Chemistry, The University, Leicester LE1 7RH

Exposure of solutions of triphenyl-phosphine and -arsine in sulphuric acid at 77 K to ⁶⁰Co γ -rays gave the corresponding cations, characterised by their e.s.r. spectra. Triphenylphosphine oxide, sulphide, and selenide also gave $\text{Ph}_3\text{P}^{\cdot+}$ radicals together with species thought to be $\text{Ph}_3\text{P}^{\cdot}\text{SH}$ and $\text{Ph}_3\text{P}^{\cdot}\text{SeH}$ from the sulphide and selenide. These species are thought to have a near tetrahedral, σ^* , structure rather than the 'normal' trigonal bipyramidal structure. Diphenylmethyl- and phenyldimethyl-phosphine gave cations with e.s.r. parameters between the extremes for $\text{Ph}_3\text{P}^{\cdot+}$ and $\text{Me}_3\text{P}^{\cdot+}$. Triphenylarsine oxide in sulphuric acid also gave $\text{Ph}_3\text{As}^{\cdot+}$, but in methanol either Ph_3AsO^- or Ph_3AsOR was formed. Tetraphenylarsonium cations in methanolic solution at 77 K gave $\text{Ph}_4\text{As}^{\cdot}$ but no such species was obtained from tetraphenylphosphonium cations. From these results various modes of electron addition to the parent compounds are deduced and discussed.

ELECTRON spin resonance spectra for phosphoryl ($\cdot\text{PL}_3$) radicals,²⁻⁴ phosphoranyl ($\cdot\text{PL}_4$) radicals,⁵⁻⁷ and phosphinyl ($\cdot\text{PL}_2$) radicals⁸⁻¹⁰ are now well established, for radicals in the liquid and solid states. Similar arsenic centred radicals have also been described,¹¹⁻¹³ including $\cdot\text{AsPh}_4$.¹⁴ An interesting dichotomy arises when phosphoranyl radicals having aromatic ligands are potentially formed, since, depending on the nature of the other

ligands, the excess electron may be localised primarily on phosphorus as in normal phosphoranyl radicals, or primarily on the aromatic ring as in aromatic radical anions.¹⁵⁻¹⁹ Yet another method of accommodating an excess electron is in a fairly localised σ orbital, as for radicals of the type $\text{R}_3\text{P}-\text{PR}_3^+$.^{20,21} This method of

[†] The paper by D. Nelson and M. C. R. Symons (*J.C.S. Perkin II*, 1977, 286) designated Part 169 (in error) should be regarded as Part 170.

¹ Part 172, M. C. R. Symons, D. X. West, and J. G. Wilkinson, *Internat. J. Radiation Phys. Chem.*, 1976, **8**, 375.

² A. G. Davies, D. Griller, and B. P. Roberts, *J. Amer. Chem. Soc.*, 1972, **94**, 1782.

³ I. S. Ginns, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2509.

⁴ A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1971, 2290.

⁵ P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

⁶ A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993; 2224.

⁷ A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738.

⁸ B. W. Fullam, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 2145.

⁹ M. C. R. Symons, *Mol. Phys.*, 1972, **24**, 885.

¹⁰ D. Griller, B. P. Roberts, A. G. Davies, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 554.

¹¹ A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1973, **95**, 3483.

¹² E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, 1973, **95**, 6574.

¹³ A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometallic Chem.*, 1972, **38**, C8.

¹⁴ S. A. Fieldhouse, H. C. Starkie, and M. C. R. Symons, *Chem. Phys. Letters*, 1973, **23**, 508.

¹⁵ S. P. Mishra and M. C. R. Symons, *J.C.S. Dalton*, 1973, 1494.

¹⁶ G. Bockstein, E. H. J. Jansen, and H. M. Buck, *J.C.S. Chem. Comm.*, 1974, 118.

¹⁷ A. G. Davies, M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1974, 973.

¹⁸ S. P. Mishra and M. C. R. Symons, *J.C.S. Perkin II*, 1976, 21.

¹⁹ M. C. R. Symons, *Mol. Phys.*, 1975, **30**, 1921.

²⁰ A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 1589.

²¹ T. A. Claxton, B. W. Fullam, E. Platt, and M. C. R. Symons, *J.C.S. Dalton*, 1975, 1395.

addition has recently been recognised for R_3P-Cl and R_3P-Br molecules, the phosphorus-halogen bond acting as the electron acceptor.^{22,23}

Recently, e.s.r. data have been reported for the triphenylphosphonium cation, Ph_3P^+ .²⁴ The species thus identified were prepared by irradiating Ph_3P-BF_3 and Ph_3P-BCl_3 at room temperature. Our own studies of these materials²⁵ have also revealed the formation of such radicals, but we do not consider the formulation $Ph_3P^{+\cdot}$ to be probable, particularly because the parameters are markedly dependent upon the $B(hal)_3$ group (see Table I). The $Ph_3Ge\cdot$ radical has also been recently

Triphenylphosphine sulphide was prepared by the method of Vanderveer and Jellinek²⁹ and triphenylphosphine selenide was prepared by the method of Nicpon and Meek.³⁰ Dimethylphenyl- and methylidiphenyl-phosphine were kindly provided by Dr. R. Kemmitt. 98% Sulphuric acid was reagent grade.

All solutions in sulphuric acid were prepared by freezing a small amount of the acid and adding the solute to the top of the frozen acid. The acid was warmed until the solute dissolved and beads of the solution were prepared immediately in liquid nitrogen.

Samples were irradiated at 77 K in a Vickrad ⁶⁰Co γ -ray source for up to 4 h at a dose rate of 1.7 Mrad h⁻¹.

TABLE I

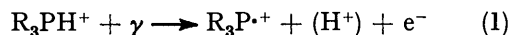
E.s.r. Parameters for various phosphoryl and phosphoranyl radicals and related species

Radical	Substrate-medium	Hyperfine coupling (G) ^{a-c}			g Values ^b
			⊥	iso	
$Ph_3P^{\cdot+}$	$Ph_3P-H_2SO_4$	439	214	289 (³¹ P)	2.003, 2.007
	$Ph_3PO-H_2SO_4$	440	220	293 (³¹ P)	
	$Ph_3PS-H_2SO_4$	457	222	300 (³¹ P)	
	$Ph_3PSe-H_2SO_4$	434	219	291 (³¹ P)	
$Ph_3P^{\cdot}SH$	$Ph_3PS-H_2SO_4$	553	310	391 (³¹ P)	2.000, 2.003
	$Ph_3PSe-H_2SO_4$	568	349	322 (³¹ P)	
$Ph_3P^{\cdot}SeH$	$Ph_3PSe-H_2SO_4$	170	<30	(⁷⁷ Se)	2.005, 2.013
$Ph_2MeP^{\cdot+}$	$Ph_2MeP-H_2SO_4$	504	244	331 (³¹ P)	2.003, 2.008
$PhMe_2P^{\cdot+}$	$PhMe_2P-H_2SO_4$	524	254	344 (³¹ P)	2.003, 2.009
$Me_3P^{\cdot+}$	$Me_3P-H_2SO_4$ ^d	600	290	393 (³¹ P)	1.993, 2.012
$Ph_3P^{\cdot+}$	Ph_3P-BF_3 ^e	499	265	343 (³¹ P)	2.001, 2.005
	Ph_3P-BCl_3	555	316	396 (³¹ P)	2.002, 2.005
$Ph_3As^{\cdot+}$	$Ph_3As-H_2SO_4$	465	231	309	1.995, 2.017
	$Ph_3AsO-H_2SO_4$				
$Et_3As^{\cdot+f}$	$Et_3As-H_2SO_4$	550	280	370	2.00, 2.03
Ph_4As^{\cdot}	$Ph_4As^+Cl^-$	592.6	605	534	1.97, 2.014/2.027
$Me_3PhP^{\cdot}OR$ (B)	$Me_3PhP-CD_3OD$	630	390	470	1.998, 2.012
$Ph_3AsO^{\cdot-}$	$Ph_3AsO-CD_3OD$	751	625	667	1.993, 2.021
Ph_3AsOR^{\cdot}				670	
$Me_3PO^{\cdot-}$	Me_3PO-CD_3OD	738	548	611	1.997, 2.015
$R_3PBr^{\cdot-}$	$(MeO)_2P(S)Br$	780	600	660	

^a 1G = 10⁴ T. ^b Estimated using the Breit-Rabi equation. ^c Errors ca. ± 4 G. ^d Ref. 4. ^e Ref. 24. ^f Ref. 11. ^g Ref. 12.

reported,²⁶ and the results compared with those for Ph_3Si .²⁷

One aim of the present study was to prepare $Ph_3P^{\cdot+}$ and $Ph_3As^{\cdot+}$ by the method found to be successful for preparing trialkylphosphonium cations,⁴ namely from the protonated species in sulphuric acid [reaction (1)].



Another aim was to prepare electron adducts from Ph_3PO , Ph_3PS , Ph_3PSe , and Ph_3AsO molecules in the expectation that the three modes of addition mentioned above would be in active competition.

EXPERIMENTAL

Triphenylphosphine, triphenylarsine, and triphenylarsine oxide (Koch-Light) were recrystallized from ethanol and dried *in vacuo*. Triphenylphosphine oxide was prepared by alkaline hydrolysis of an acetone solution of dibromotriphenylphosphorane, and was recrystallized from alcohol.²⁸

* 1G = 10⁴ T.

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.

²⁴ T. Berclaz and M. Geoffroy, *Mol. Phys.*, 1975, **30**, 549.

²⁵ J. Drake and M. C. R. Symons, unpublished results.

E.s.r. spectra were measured with a Varian E3 spectrometer at 77 K. Samples were annealed in the insert Dewar flask with continuous monitoring of the e.s.r. spectrum and cooled to 77 K whenever significant spectral changes were observed.

RESULTS AND DISCUSSION

Typical e.s.r. spectra are shown in the Figures and the derived data are summarised in Table I. In general, $\cdot PL_3$ and $\cdot PL_4$ radicals were not obtained from the pure materials or, if they were, the spectra were poorly defined, and will not be considered herein. Solutions in sulphuric acid (98%) gave intense central lines assignable primarily to H_2SO_4 and $\cdot SO_3^-$ (H_2SO_3) radicals. Wing lines separated by ca. 100 G * and comprising 10 G multiplets were invariably detected which can be safely assigned to substituted cyclohexadienyl radicals, formed either by hydrogen atom addition or by electron addition

²⁶ M. Geoffroy, L. Ginet, and E. A. C. Lucken, *Chem. Phys. Letters*, 1976, **38**, 321.

²⁷ M. Geoffroy and E. A. C. Lucken, *Helv. Chim. Acta*, 1970, **52**, 813.

²⁸ A. Michaelis and L. Gleichmann, *Ber.*, 1882, **15**, 801.

²⁹ W. Vanderveer and F. Jellinek, *Rec. Trav. chim.*, 1966, **85**, 842.

³⁰ P. Nicpon and D. W. Meek, *Inorg. Synth.*, 1967, **10**, 157.

followed by protonation. Outer lines shown in Figures 1—4 are assigned to $\text{Ph}_3\text{P}^{\cdot+}$ or $\text{Ph}_3\text{As}^{\cdot+}$ radicals (^{31}P has

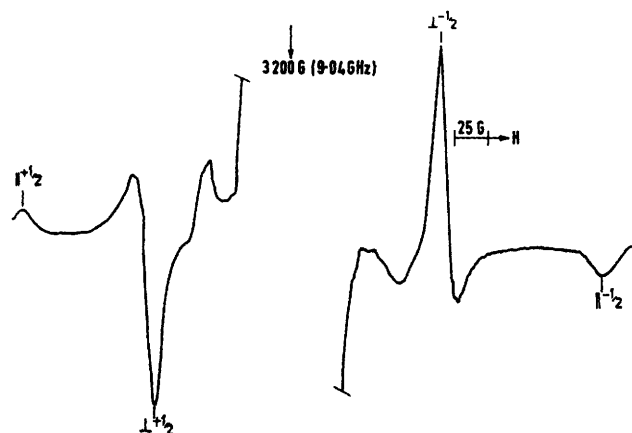


FIGURE 1 First derivative X-band e.s.r. spectrum for Ph_3P in sulphuric acid at 77 K after exposure to ^{60}Co γ -rays, assigned to $\text{Ph}_3\text{P}^{\cdot+}$ radicals. The spectra from Ph_3PO solutions were identical

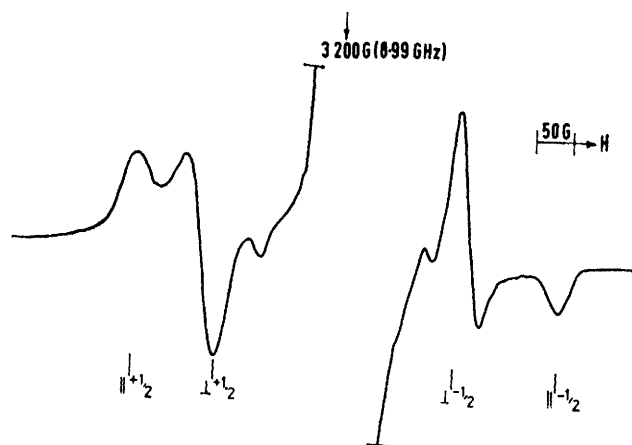


FIGURE 2 First derivative X-band e.s.r. spectrum for Ph_3PS in sulphuric acid at 77 K after exposure to ^{60}Co γ -rays, assigned to Ph_3PSH radicals

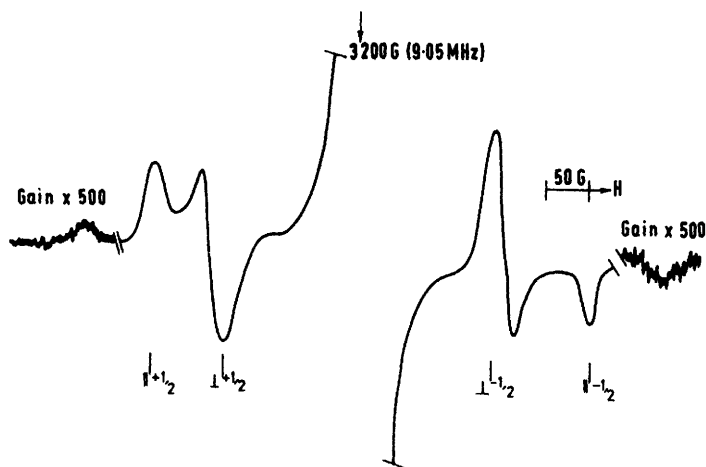


FIGURE 3 First derivative X-band e.s.r. spectrum for Ph_3PSe in sulphuric acid at 77 K after exposure to ^{60}Co γ -rays, assigned to Ph_3PSeH radicals. Parallel features for radicals containing ^{77}Se are indicated on the high and low field sides of the main spectrum

$I \frac{1}{2}$, and ^{75}As has $I \frac{3}{2}$; both are 100% abundant), together, in some cases to other radicals of the phosphoryl or phosphoranyl type (Figures 2 and 3).

$\text{Ph}_3\text{P}^{\cdot+}$ and $\text{Ph}_3\text{As}^{\cdot+}$ Radicals.—The results attributed to these species can be used to obtain approximate orbital populations using calculated hyperfine coupling constants for unit population of the appropriate atomic orbitals. [$A^0(^{31}\text{P})$ 3 650, $2B^0(^{31}\text{P})$ 207, $A^0(^{75}\text{As})$ 3 415, and $2B^0(^{75}\text{As})$ 179 G, estimated from the wavefunctions of Froese.³¹] The results, given in Table 2, are appreciably different from those previously reported,²⁴ and in

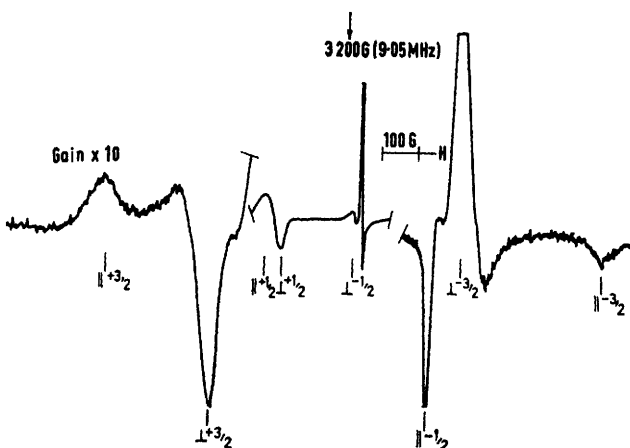


FIGURE 4 First derivative X-band e.s.r. spectrum for Ph_3As in sulphuric acid at 77 K after exposure to ^{60}Co γ -rays, assigned to $\text{Ph}_3\text{As}^{\cdot+}$ radicals

particular, the calculated $3s$ character is smaller for $\text{Ph}_3\text{P}^{\cdot+}$. The estimation of s -character is more reliable than that of p -character, so we draw attention to the

TABLE 2

Approximate orbital parameters for the unpaired electron in some of the radicals listed in Table 1

Radical	a_s^2 (%)	a_p^2 (%)	$\lambda^{2a,b}$
$\text{Ph}_3\text{P}^{\cdot+}$	8.1	72.5	9.0
Ph_3PSH	10.7	78.3	7.3
Ph_3PSeH	11.6	70.5	6.1
$\text{Ph}_2\text{MeP}^{\cdot+}$	9.1	83.6	9.2
$\text{PhMe}_2\text{P}^{\cdot+}$	9.5	87.0	9.2
$\text{Me}_2\text{P}^{\cdot+}$	10.8	100	9.3
$\text{Ph}_3\text{P}^{\cdot+ c}$ (BF_3)	9	75	8.3
(BCl_3)	10	77	7.7
$\text{Ph}_3\text{As}^{\cdot+}$	11	97	8.8
$\text{Et}_3\text{As}^{\cdot+}$	10	91	9.1
$\text{Ph}_4\text{As}^{\cdot}$	16	33	2.0
Ph_2AsO^-	19.5	46	2.4
$\text{Me}_2\text{PhP}^{\cdot\text{OR}}(\text{B})$	12.9	77.3	6.0
Me_3PO^-	19.0	54.0	2.85
$\text{R}_3\text{PBR}^-(\sigma^*)$	18.0	59.0	3.28
$\text{Ph}_3\text{Si}^{\cdot d}$	6	65	11
$\text{Ph}_3\text{Ge}^{\cdot e}$	15	96	6.4

^a $\lambda^2 = a_p^2/a_s^2$. ^b Using $A^0(^{31}\text{P})$ 3 650, $2B^0(^{31}\text{P})$ 207; $A^0(^{75}\text{As})$ 3 415, $2B^0(^{75}\text{As})$ 179 G. ^c Ref. 24. ^d Ref. 27. ^e Ref. 26.

variation in s -character estimated for the isostructural species $\text{Ph}_3\text{Si}^{\cdot}$, $\text{Ph}_3\text{Ge}^{\cdot}$, $\text{Ph}_3\text{P}^{\cdot+}$, and $\text{Ph}_3\text{As}^{\cdot+}$. We have previously shown⁴ that for the series $\text{Me}_3\text{Al}^{\cdot-}$, $\text{Me}_3\text{Si}^{\cdot}$,

³¹ Calculated from the data of C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

and Me_3P^+ there is a steady fall in s -character for the unpaired electron (32, 15, and 10% respectively). The results for the germanium and arsenic derivatives fit in well with this trend, but clearly the results reported for $\text{Ph}_3\text{Si}^{\cdot}$ are quite out of line. Since there were severe difficulties in the extraction of ^{29}Si data for this radical, which was trapped in pairs in crystals of Ph_3SiH , irradiated at room temperature,²⁷ we suggest that the value of *ca.* 6% $3s$ -character is in error. Preliminary results for Ph_3SiH irradiated at 77 K confirm this, the estimated $3s$ -character being *ca.* 12%.

MePh_2P^+ and Me_2PhP^+ Radicals.—Results for these radicals trapped in sulphuric acid are compared with those for Me_3P^+ and Ph_3P^+ in Figure 5. There is a

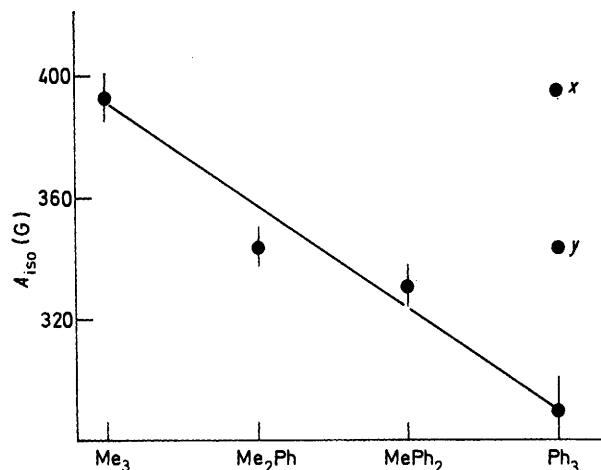


FIGURE 5 Display of the isotropic ^{31}P hyperfine coupling constants for R_3P^+ radicals. x and y are taken from ref. 24

steady decrease with increasing number of phenyl groups, possibly reflecting a small π -delocalisation onto the aromatic rings. The previous results assigned to Ph_3P^+ , also included, are seen to be less satisfactory.

The fall on replacing alkyl by phenyl is opposite to that previously noted for oxy-radicals of this type.³ These radicals are more pyramidal and delocalisation into the π -system of the aromatic rings is less likely. However, such delocalisation was thought to be small even for phosphinyl radicals, when the unpaired electron on phosphorus is in a pure $3p(\pi)$ orbital ideally suited for π -overlap.⁸ The reason for these contrary trends remains obscure.

Phosphoranyl and Related Radicals.—Although Ph_3P , Ph_3As , Ph_3PO , and Ph_3AsO gave only the triphenyl cations in sulphuric acid, Ph_3PS and Ph_3PSe gave another species (A) with a greater hyperfine coupling (Figure 2). This increased coupling suggests the presence of a phosphoranyl radical, and Ph_3PSH and Ph_3PSeH are most probable. However, species (A) do not have the magnetic properties that we would expect for normal phosphoranyl radicals. Thus, A_{iso} for R_3POR radicals is always in the 620 G region.³ Replacing OR by SR causes A_{iso} to fall by *ca.* 20 G,⁸ so we predict an isotropic coupling of *ca.* 600 G for Ph_3PSH radicals, and a value of

391 G is clearly too small. Again, most phosphoranyl radicals have $3p : 3s$ ratios (λ^2) in the range 2–3, whilst for species (A) $\lambda^2 = 6$ –7. These results are, in fact, strikingly close to those for the σ^* phosphoranyl radicals recently described²³ (see Table 1), and hence we tentatively postulate structures in which the excess electron is largely in the P-S or P-Se σ^* orbital.

In an attempt to shed more light on this suggestion we have examined the spectra assigned to Ph_3PSeH for satellite lines from radicals containing ^{77}Se (Figure 3). (^{77}Se has $I = \frac{1}{2}$ and is 7.6% abundant.) Clear parallel type features are apparent on the high and low field sides of the main $\pm \frac{1}{2}$ transitions which give $A_{\parallel}(^{77}\text{Se}) = 170$ G. However, we were unable to detect any satellites to the main perpendicular features, which means that $A_{\perp}(^{77}\text{Se})$ for this direction is ≤ 30 G.

These values, although too imprecise to warrant derivation of orbital populations are nevertheless quite reasonable for the σ^* structure. They establish that the parallel ^{77}Se coupling has a similar direction to that for ^{31}P . This would be impossible for the normal phosphoranyl structure,³² but is required for the σ^* structure,^{22,23} which therefore receives strong support.

When these solutions were annealed, the Ph_3P^+ radicals were lost prior to the σ^* phosphoranyl radicals. There was no sign of conversion of these to Ph_3P^+ or to normal phosphoranyl radicals prior to complete loss.

Solutions in Methanol.—In many cases the solubility was too low and the resulting e.s.r. spectra were untrustworthy (there is a danger with sparingly soluble substrates that more soluble impurities are preferentially extracted.) However, good, reproducible results were obtained from Me_2PhP and Ph_3AsO solutions and we consider that these are worthy of discussion.

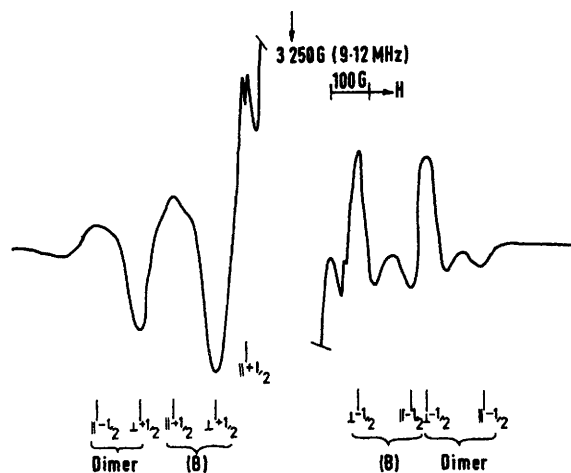


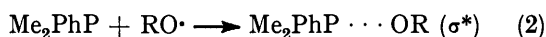
FIGURE 6 First derivative X-band e.s.r. spectrum for Me_2PhP in CD_3OD at 77 K, after exposure to ^{60}Co γ -rays, showing features tentatively assigned to Me_2PhPOR σ^* radicals (B)

Irradiation of methanolic solutions of Me_2PhP gave some dimer cation, $\text{Me}_2\text{PhP-PMe}_2\text{Ph}^+$, which was formed in high yield in the pure material, together with a

³² D. J. Nelson and M. C. R. Symons, *J.C.S. Dalton*, 1975, 1164.

species (B) having A_{\parallel} 630, A_{\perp} 390 G and g values *ca.* 2.00. Some $\text{MePh}\dot{\text{P}}$ radicals were also detected (Figure 6). Although direct electron addition to the benzene rings is expected, nevertheless the anion Me_2PhP^- with the electron on phosphorus is a possible candidate for centre (B). Unfortunately $\cdot\text{PL}_3^-$ centres are not well established, and so we are unable to argue by analogy. However, we confidently expect that A_{iso} (^{31}P) should be appreciably less for $\cdot\text{PR}_3^-$ than for $\cdot\text{PR}_4$ radicals, A_{iso} for $\cdot\text{PH}_4$ is 519.3 G,³³ and replacing H by alkyl is expected to reduce this value.³ Thus an isotropic coupling of 470 G is reasonable for Me_2PhP^- anions. Nevertheless, we consider this to be unlikely since even if electron addition to phosphorus were to compete with ring addition, we would expect ready protonation to give $\text{Me}_2\text{Ph}\dot{\text{P}}\text{H}$ or $\text{Me}_2\text{Ph}\dot{\text{P}}\text{D}$, just as occurs to the ring to give cyclohexadienyl radicals. Since methanolic solutions gave no ^1H hyperfine coupling this seems unlikely.

Another possibility, which we favour, is the σ^* phosphoranyl structure assigned to $\text{Ph}_3\dot{\text{P}}\text{SH}$ and $\text{Ph}_3\dot{\text{P}}\text{SeH}$. The e.s.r. data are quite comparable (Table 1), but we stress that $\text{Ph}_3\dot{\text{P}}\text{OH}^+$ in sulphuric acid failed to give such a species. Possibly reaction (2) is the first step in this



addition process. There was no sign of any change to the 'normal' phosphoranyl radical structure on annealing, although radical (B) was rapidly lost at temperatures close to 77 K. We conclude, if reaction (2) is correct, that electron migration onto the ring to give the thermodynamically favoured aromatic anion occurs rapidly. In the liquid phase the first detectable product between PhPL_2 molecules and alkoxy radicals is the aromatic anion.^{16,17} However, in the particular case of $\text{PhP}(\text{OMe})_2$, one of us¹⁹ has presented evidence that at 77 K $\text{RO}\cdot$ addition proceeds *via* the phosphoranyl radical $\text{Ph}\dot{\text{P}}(\text{OMe})_2(\text{OR})$, which probably has the 'normal' structure. We conclude that the energetic balance between the formation of $\text{PhL}_2\dot{\text{P}}\text{OR}$ σ^* radicals, normal $\text{PhL}_2\dot{\text{P}}\text{OR}$ phosphoranyl radicals, and $\text{PhL}_2\dot{\text{P}}\text{OR}^-$ anions is subtle and that the mechanistic route to the most stable form can vary with substrate and temperature.

Methanolic solutions of Ph_3AsO gave spectra that can be interpreted with greater certainty (Figure 7). The resulting data are close to expectation for Ph_3AsO^- or Ph_3AsOR with the normal phosphoranyl configuration. A_{iso} is close to that for $\text{Ph}_3\text{AsOCMe}_3$ studied by Furimsky *et al.* in the liquid phase,¹² and $\lambda^2 = 2.4$, which is in the region expected for such radicals. We suggest that electron addition occurs on arsenic in preference to the benzene rings, as is the case for Ph_4As^+ . These results point to a considerably greater electron affinity for arsenic than for phosphorus in these compounds, together possibly with a smaller resistance to the bending distortion required to form the stable configuration of these anions. If this is correct, electron addition is

³³ A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1975, **62**, 2004.

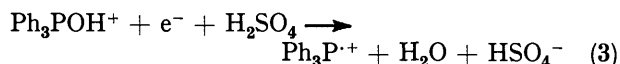
probably followed by protonation. Replacing CD_3OD by CH_3OH resulted in a marked increase in line-width, but no extra hyperfine splitting. This result is similar to that recently noted for AsF_6^- and PF_6^- ions.³⁴ Both react with electrons to give AsF_5^- and PF_5^- respectively, but when the former is present as a dilute impurity in KPF_6 , AsF_5^- ions are formed in preference to PF_5^- , showing the greater effective electron affinity for arsenic.³⁴

Aspects of Mechanism.—The triphenyl radical cations are formed by electron loss followed by proton loss for



FIGURE 7 First derivative X-band e.s.r. spectrum for Ph_3AsO in CD_3OD , at 77 K, after exposure to ^{60}Co γ -rays, showing features assigned to Ph_3AsO^- or Ph_3AsOD radicals

Ph_3PH^+ and Ph_3AsH^+ , but presumably by electron gain for Ph_3POH^+ and Ph_3AsOH^+ [reaction (3)]. Probably



electron addition to the phenyl groups also occurs since cyclohexadienyl radicals are formed, but there is no trace of the parent phosphoranyl radicals. Since these are formed in their σ^* form from the sulphide and selenide derivatives, we suggest that bond stretching is favoured over bond bending due to the presence of a low-lying σ^* orbital in all these cases. Perhaps the σ^* $\text{Ph}_3\dot{\text{P}}\text{-OH}$ radical is an intermediate in process (3), and subsequent protonation gives $\text{Ph}_3\text{P}^{\cdot+} + \text{H}_2\text{O}$. The low basicity of sulphur and selenium would then explain why H_2S and H_2Se are less readily lost from the sulphur and selenium derivatives. The fact that $\text{Ph}_3\text{P}^{\cdot+}$ is not formed from Ph_3PO in methanol, electron capture being entirely on

³⁴ M. C. R. Symons, *Internat. J. Radiation Phys. Chem.*, 1976, **8**, 643.

the aromatic rings, shows how subtle these effects must be. Thus Ph_3PO adds to the ring only, but Ph_3AsO adds to arsenic to give a normal phosphoranyl radical. Ph_3POH^+ adds in part to phosphorus, but sulphuric acid causes dissociative electron capture. Ph_3PSH^+ and Ph_3PSeH^+ again add to phosphorus, but now the σ^* structure is the most stable.

Other Radicals.— Me_2PhP and MePh_2P gave good e.s.r. signals for the dimer cations²⁰ on irradiation at 77 K (*cf.* Figure 6). The data were similar to those previously reported for $\text{R}_3\text{P-PR}_3^+$ species ($\text{R} = \text{alkyl}$) but, as with

the monomer cations themselves, replacing alkyl by phenyl caused a slight fall in A_{iso} (^{31}P).

In several cases evidence for phosphinyl and arsinyl radicals was obtained.^{8,11} These are characterised by well defined parallel features separated by 250—300 G, but generally their perpendicular features were hidden by more intense central lines from other radicals.

G. W. E. thanks the Saginaw Valley State College for leave of absence, and the S.R.C. for a grant.

[6/1233 Received, 25th June, 1976]
