An Electron Spin Resonance Study of the Electrochemical Oxidation of Phosphorus(III) Compounds

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Radical cations generated during electrochemical oxidation of a series of trivalent phosphorus compounds, alone or in the presence of 3,3-dimethyl-2-t-butylbut-1-ene, have been studied using e.s.r. spectroscopy. The oxidations were carried out in nitrile or dichloromethane solvents and the cell containing the working electrode was situated in the cavity of the spectrometer. Oxidation of X_3P alone gives rise to the spectrum of the phosphine dimer cation radical, $(X_3PPX_3)^{+\cdot}$, produced by rapid reaction of the initially formed phosphinium radical cation, $X_3P^{+\cdot}$, with a further molecule of phosphine. Trialkyl phosphites did not give detectable concentrations of dimer cation radicals in nitrile solvents, probably because of preferential reaction of $(RO)_3P^{+\cdot}$ with the solvent. In the presence of 3,3-dimethyl-2-t-butylbut-1-ene the spectra of the dimer cation radicals were completely or partially quenched and replaced by those of the adducts $\mathrm{Bu^t{}_2\dot{C}CH_2\overset{+}{P}X_3}$. The phosphorus hyperfine splittings of both $(X_3PPX_3)^{+\cdot}$ and $\mathrm{Bu^t{}_2\dot{C}CH_2\overset{+}{P}X_3}$ increased with the electronegativity of the ligands X, and these trends are interpreted in terms of changes in hybridisation at phosphorus.

THE overall homolytic substitution reaction (i) may be a concerted or a stepwise process in which the species (1) represents a transition state or an intermediate adduct radical, respectively.[1] The degree of charge separation

$$\mathrm{X\cdot + Y{-}Z \longrightarrow \underset{(1)}{[X{-}Y{-}Z]\cdot} \longrightarrow X{-}Y + Z\cdot} \qquad \text{(i)}$$

in (1) may vary considerably, and may be sufficiently large that the interaction of the radical X· with the molecule Y–Z is best considered to be an electron transfer process [*e.g.* reaction (ii), in which X· acts as a one-electron oxidising agent].

$$\mathrm{X\cdot + Y{-}Z \longrightarrow \bar{X}\colon + (Y{-}Z)^{+\cdot}} \qquad \text{(ii)}$$

Phosphoranyl radicals, $X_4P\cdot$, are intermediates in the homolytic substitution reactions of trivalent phosphorus compounds,[1] *e.g.* the radical (2) is involved in the t-butoxydealkylation of trimethylphosphine [equation (iii)].[2,3] The polar canonical form $\mathrm{Me_3P^{+\cdot}\ \colon\!\bar{O}Bu^t}$ probably also makes a substantial contribution to the electronic structure of the intermediate, although there is no evidence for radical cation formation in non-polar solvents. Electrochemical oxidation of phosphorus(III) compounds in solution provides a means of generating phosphinium radical cations ($X_3P^{+\cdot}$) in the absence of nucleophilic counter ions, and in this paper we report results obtained using this technique. A preliminary account of some of this work has already appeared.[4] The electrolyses were carried out with the anode compartment in the cavity of an e.s.r. spectrometer, enabling the spectra of the transient paramagnetic oxidation products to be detected.

$$\mathrm{Bu^tO\cdot + Me_3P \longrightarrow \underset{(2)}{Bu^tO\dot{P}Me_3} \longrightarrow Bu^tOPMe_2 + Me\cdot} \qquad \text{(iii)}$$

RESULTS

Electrochemical oxidation of triethylphosphine at 193 K in a mixture of butyronitrile and propionitrile (70 : 30 v/v), using tetrabutylammonium tetrafluoroborate as carrier electrolyte, gave rise to an e.s.r. spectrum showing coupling to two equivalent phosphorus nuclei [a(2P) 468.8 G, g 2.003 2]. Because of the large magnitude of the phosphorus hyperfine splitting, the $M_I = 0$ transition appeared as a doublet corresponding to $I = 0$ or 1, that is to the singlet

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[1] K. U. Ingold and B. P. Roberts, ' Free Radical Substitution Reactions ', Wiley–Interscience, New York, 1971.

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

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

[4] W. B. Gara and B. P. Roberts, *J.C.S. Chem. Comm.*, 1975, 949.

or triplet states, respectively, of the two coupled phosphorus nuclei. To second order the separation between the (0,0) transition and the (1,0) transition, which appears at lower magnetic field, is given[5] by $[a(P)]^2/B$, where B is the magnetic flux density. At 203 K further hyperfine splitting was detected [best resolution was obtained for the (0,0) transition] which was interpreted in terms of interaction with twelve equivalent protons [a(12H) 3.6 G, 9 lines observed]. As the temperature was lowered, these lines broadened, and at 148 K a 1 : 2 : 1 triplet splitting was observed [a(2H) 16.8 G]. This e.s.r. spectrum is assigned to the triethylphosphine dimer cation radical (3).

TABLE 1

E.s.r. parameters for the dimer cations $(X_3P{-}PX_3)^{+\cdot}$, obtained by electrochemical oxidation of phosphines using $Bu^n{}_4N^+BF_4{}^-$ carrier electrolyte

Phosphine	Solvent [a]	T/K	g Factor [b]	Hyperfine splitting constants (G) a(2P) [c]	Others
$MeNCH_2CH_2N(Me)PPr^n$	N	213	2.003 0 [d]	340.0 [d]	*ca.* 6 (4N)
$MeNCH_2CH_2N(Me)PPh$	N	203	2.002	344	7.5 (4N)
$MeNCH_2CH_2N(Me)PBu^t$	N	190	2.002	380	*ca.* 6 (4N)
Et_3P	N	193	2.003 2	468.8 [e]	3.6 (12H) [f]
Et_2POEt	N	210	2.002	482	
$OCMe_2CMe_2OPNMe_2$	N	183	2.002	540	
$PhP(OEt)_2$	N	183	2.002	540	
$MeNCH_2CH_2N(Me)POBu^t$	N	173	2.002	544	7.4 (4N)
$MeNCH_2CH_2N(Me)POEt$	N	190	2.002 4 [g]	547.7 [g]	7.5 (4N)
$PhP(OCH_2CF_3)_2$	N	163	2.002	566	
$Me_2NP(OEt)_2$	N	183	2.001 7	600.0	
$(EtO)_3P$	D	224	2.001 7	670.6 [h]	
$(MeO)_3P$	D	179	2.001 5	676.0 [i]	
$(Me_3Si)_2NP(OEt)_2$	D	181	2.001 6	678.5	9.9 (2N)

[a] N = Butyronitrile–propionitrile (70 : 30 v/v); D = dichloromethane. [b] Obtained from the position of the (0,0) transition. Values quoted to four decimal places are accurate to ±0.0001; others are accurate to ±0.0005. [c] Mean of the independent values obtained from the positions of the (1, −1) and 1, +1) transitions, using the g value obtained from the (0,0) transition and the Breit–Rabi equation. Accuracy ±1.0 and ±0.2 G for values quoted to three and four significant figures, respectively. Some values differ from those given in our preliminary communication,[4] since more accurate measurements of magnetic field are now possible (see Experimental section). [d] At 101 K in the solid state, $g_{\parallel}$ 1.996, $g_{\perp}$ 2.005; $A_{\parallel}$ 389, $A_{\perp}$ 294 G. [e] Ref. 13 gives a(P) 460, a(2H) 18 G at 77 K in the solid state. [f] a(2H) 16.8 G at low temperatures, see text. [g] At 144 K in the solid state, $g_{\parallel}$ 1.992, $g_{\perp}$ 2.007; $A_{\parallel}$ 598, $A_{\perp}$ 490 G. [h] a(P) increases with temperature; 673.6 (243 K), 676.1 G (264 K). [i] Ref. 11 gives a(P) 655 G at 77 K in the solid state.

$$Et_3P\colon \xrightarrow{-e} Et_3P^{+\cdot} \qquad \text{(iv)}$$

$$Et_3P^{+\cdot} + Et_3P\colon \longrightarrow \underset{(3)}{(Et_3P{-}PEt_3)^{+\cdot}} \qquad \text{(v)}$$

A series of phosphorus(III) compounds was subjected to anodic oxidation in a similar manner, and the e.s.r. parameters of the phosphine dimer cation radicals which were produced are given in Table 1. Certain compounds, for example trialkyl phosphites, gave no e.s.r. spectra in nitrile solvent, although strong signals were detected in dichloromethane.

The four lines resulting from coupling to two equivalent phosphorus nuclei were of unequal widths at the temperatures employed. This effect is due to incomplete averaging of the anisotropic phosphorus hyperfine splitting; the wing lines were always the broadest and the (0,0) transition the sharpest. The spectrum of the dimer cation radical obtained by oxidation of $MeNCH_2CH_2N(Me)POBu^t$ is shown in our preliminary communication.[4] The cation radicals were fairly long lived in the absence of oxygen and water, and often gave strong spectra for several minutes at low temperatures after the current had been switched off.

In the presence of 3,3-dimethyl-2-t-butylbut-1-ene (*ca.* 0.1M) the e.s.r. spectra of the phosphine dimer cations were completely or partially quenched and replaced by signals assigned to the alkene adduct (5) of the phosphine monomer cation radical. Similar results were obtained in both nitrile and dichloromethane solvents.

$$\underset{(4)}{X_3P^{+\cdot}} + Bu^t{}_2C{=}CH_2 \longrightarrow \underset{(5)}{Bu^t{}_2C{-}\dot{C}H_2\overset{+}{P}X_3} \qquad \text{(vi)}$$

An alternative mode of adduct formation could involve oxidation of the alkene to the radical cation which then reacts with phosphine to produce (5). This route seems much less likely than trapping of (4) by the alkene, since the phosphines would be expected to undergo oxidation more readily than 3,3-dimethyl-2-t-butylbut-1-ene. Whilst the spectrum of (5) was the major signal detected during oxidation of a mixture of phosphine and 3,3-dimethyl-2-t-butylbut-1-ene, addition of the alkene to the sample cell after generation of $[MeNCH_2CH_2N(Me)PPr^n]_2{}^{\cdot}$ (6), at low temperature did not give rise to the spectrum of the adduct of the monomeric phosphinium cation radical, although the spectrum of (6) was still apparent. When current was passed the signal of the alkene adduct appeared. These results demonstrate that the dimer cation neither adds directly to 3,3-dimethyl-2-t-butylbut-1-ene to produce a detectable adduct, nor dissociates to give (4) which undergoes subsequent addition to the alkene to produce (5).

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[5] R. W. Fessenden, *J. Chem. Phys.*, 1962, **37**, 747.

The radicals (5), which were very persistent,[6,7] gave rise to e.s.r. spectra showing a large phosphorus splitting [a(P) 90—130 G] and splitting from two equivalent β-hydrogens [a(2H) *ca.* 13.5 G]. The phosphorus and proton splittings did not vary significantly with temperature. The results are summarised in Table 2.

TABLE 2

E.s.r. parameters for the 3,3-dimethyl-2-t-butylbut-1-ene adducts $Bu^t{}_2\dot{C}{-}CH_2\overset{+}{P}X_3$ derived from phosphine radical cations

Phosphine	Solvent [a]	T/K	g Factor [b]	Hyperfine splitting constants (G) a(P) [b]	a(2Hβ)
$EtC(CH_2O)_3P$	N	163		131.0	13.4
$(MeO)_3P$	D	183	2.002 5	127.2	13.5
$(EtO)_3P$	D	244		126.2	13.4 [c]
$(EtO)_3P$	N	193	2.002 4	125.8 [d]	13.4
$Me_2NP(OEt)_2$	N	244	2.002 6	121.0	13.6
$(Me_3Si)_2NP(OEt)_2$	D	265	2.002 4	119.3	14.1 [e]
$\overline{OCH_2CH_2O}PNMe_2$	D	228	2.002 4	115.4	13.9
$Me\overline{NCH_2CH_2N(Me)P}Pr^n$	N	213	2.002 4	99.5	14.2
$(Me_2N)_3P$	D	183	2.002 5	93.1	13.6
Et_3P	N	183	2.002 5	89.5	13.3

[a] N = Butyronitrile–propionitrile (70 : 30 v/v); D = dichloromethane. [b] Obtained using the Breit–Rabi equation; ±0.2 G [c] a(18 H_γ) 0.43 G. [d] a(P) 125.5 G at 243 K. [e] a(18 H_γ) 0.38 G.

When a mixture of triethylphosphine and di-t-butyl peroxide in butyronitrile solution was photolysed with high intensity u.v. light, whilst the sample was in the spectrometer cavity, the only spectra observed were those of the ethyl radical and the phosphoranyl radical $Et_2\dot{P}(OBu^t)_2$.[2,3] No further signals, in particular no spectrum of (5; X = Et), were obtained when 3,3-dimethyl-2-t-butylbut-1-ene was also present. It thus appears that reactions of the types (vii) and (viii) take place very slowly, even in the relatively polar nitrile solvent.

$$X_3P\colon + X_3\dot{P}{-}OBu^t \longrightarrow (X_3P{-}PX_3)^{\dot{+}} + Bu^tO^- \quad \text{(vii)}$$

$$Bu^t{}_2C{=}CH_2 + X_3\dot{P}{-}OBu^t \longrightarrow Bu^t{}_2\dot{C}{-}CH_2\overset{+}{P}X_3 + Bu^tO^- \quad \text{(viii)}$$

DISCUSSION

Several reports of e.s.r. spectra assigned to phosphine dimer radical cations have appeared previously.[8-13] However, all the species detected so far have been generated in the solid state by γ-irradiation of the parent phosphine. Anisotropic spectra were obtained and other radicals, the spectra of which often obscured part of the region of interest, were generated simultaneously. A phosphinium radical cation (4) is presumably the initial product of electron loss for both electrolytic and γ-radiolytic methods of generation, but this reacts rapidly with a second molecule of phosphine to produce the dimer cation radical (7).

$$X_3P\colon \xrightarrow{-e} X_3P^{\dot{+}}\ (4) \quad \text{(ix)}$$

$$X_3P^{\dot{+}} + {:}PX_3 \longrightarrow \underset{(7)}{(X_3P{-}PX_3)^{\dot{+}}} \quad \text{(x)}$$

E.s.r. spectra assigned to the phosphinium cation monomers (4) have been detected after γ-radiolysis of phosphine and of trialkylphosphines in concentrated sulphuric acid.[14] Dimeric cation radicals of the type $(X_nMMX_n)^{\dot{+}}$ have also been detected by e.s.r. spectroscopy during chemical [15,16] and electrochemical [16] oxidation of dialkyl sulphides ($X_nM = R_2S$), and γ-radiolysis of dimethyl selenide [17] ($X_nM = Me_2Se$) or of triethylarsine ($X_nM = Et_3As$).[9]

Electrochemical oxidation of phosphorus(III) compounds provides a convenient general route to the phosphine dimer cation radicals (7), free from unwanted paramagnetic side-products. These cation radicals may be studied in fluid solution or glassy matrix (by freezing the solution after generation) and their chemical reactions may be examined in solution. No system could be found in which the spectrum of the monomer cation (4) was detectable. The relatively narrow lines which were characteristic of the solution spectra enabled ligand hyperfine splitting to be detected in many cases (see Table 1). In particular, the spectrum of the dimer cation (3) from triethylphosphine exhibited coupling to all 12 methylene protons at high temperatures, although these are clearly non-equivalent in the most stable conformation, as shown by the low temperature spectrum of this species generated electrochemically or, previously,[13] by γ-radiolysis.

It has been shown [8-13] that the unpaired electron in the dimer cations (7) resides in a symmetrical anti-bonding σ*-molecular orbital composed predominantly of phosphorus 3s and 3p atomic orbitals. The phosphorus atoms are equivalent with the deviation from planarity of the X_3P fragment intermediate between that found for $X_3P\colon$ and $X_3P^{\dot{+}}$.[9,11] Analysis of the anisotropic spectra of the trialkylphosphine dimer cations (7; X = Me, Et, Bu^n) reveals that the unpaired electron is essentially entirely confined to the two phosphorus atoms in an orbital for which the hybridisation ratio (c_{3p}/c_{3s}) is *ca.* 3.4.[9,13] An elegant study of the dimer cation (7; X = MeO) derived from trimethyl phosphite in both glassy matrix and as a single crystal, has shown that the unpaired electron again appears to be confined to phos-

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[6] G. D. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 2441.

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

[8] M. C. R. Symons, *Mol. Phys.*, 1972, **24**, 885.

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

[10] B. W. Fullam and M. C. R. Symons, *J.C.S. Dalton*, 1975, 861.

[11] T. Gillbro, C. M. L. Kerr, and F. Williams, *Mol. Phys.*, 1974, **28**, 1225.

[12] C. M. L. Kerr, K. Webster, and F. Williams, *J. Phys. Chem.*, 1975, **79**, 2650.

[13] M. Iwaizumi, T. Kishi, F. Watari, and T. Isobe, *Bull. Chem. Soc. Japan*, 1975, **48**, 3483.

[14] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2290; M. Iwaizumi, T. Kishi, and T. Isobe, *J.C.S. Faraday II*, 1976, 113.

[15] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.

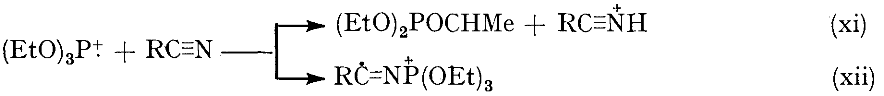
[16] W. B. Gara and B. P. Roberts, unpublished work.

[17] K. Nishikida and F. Williams, *Chem. Phys. Letters*, 1975, **34**, 302.

phorus, and (c_{3p}/c_{3s}) is 2.0.[11] This increase in 3*s*-character is expected on account of the higher electronegativity of the alkoxy-group compared with that of the alkyl group. Inspection of the isotropic phosphorus coupling constants listed in Table 1 indicates that the variations are mainly to be ascribed to changes in the hybridisation ratio for the orbital of the unpaired electron, brought about by changes in ligand electronegativity. Thus, the value of a(P) for $[(EtO)_2XP]_2^{+\cdot}$ increases along the series * X = Ph < Me$_2$N < EtO < (Me$_3$Si)$_2$N, and the phosphorus splitting for $[(EtO)_2PhP]_2^{+\cdot}$ is 26 G less than that for $[(CF_3CH_2O)_2PhP]_2^{+\cdot}$. The dimer cation containing a dioxaphospholan ring, $(\overline{OCMe_2CMe_2OP}NMe_2)_2^{+\cdot}$, had an isotropic phosphorus splitting *ca.* 60 G less than that for the acyclic analogue $[(EtO)_2Me_2NP]_2^{+\cdot}$.

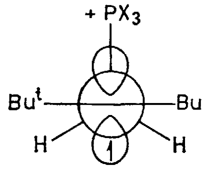
On the basis of isotropic e.s.r. data alone it is difficult to rationalise the low phosphorus splittings (340—380 G) obtained for the radicals $[Me\overline{NCH_2CH_2N(Me)P}R]_2^{+\cdot}$ (8; R = Pr^n, Bu^t, Ph), since the values for (8; R = EtO, Bu^{t}O) agree well with those expected from consideration of ligand electronegativity, and the nitrogen splittings are essentially independent of the nature of R. At low temperatures in frozen nitrile solvents anisotropic spectra typical of radicals with axially symmetric *g* and phosphorus hyperfine splitting tensors were obtained for the radical cations (8; R = Pr^n, EtO). The e.s.r. parameters, determined at temperatures below which the spectra underwent no further shifts in line positions, are given as footnotes to Table 1. The orbital populations and hybridisation ratios derived † from these measurements are c_{3s} 9.0, c_{3p} 30.7%, (c_{3p}/c_{3s}) 3.4 for (8; R = Pr^n), and c_{3s} 14.5, c_{3p} 35.0%, (c_{3p}/c_{3s}) 2.4 for (8; R = EtO). It thus appears that substitution of an n-propyl group for the ethoxy-group brings about a relatively large change in the hybridisation ratio [(c_{3p}/c_{3s}) 3.4 for $(Et_3PPEt_3)^{+\cdot}$ [13]] and an increase in the degree of delocalisation onto the nitrogen atoms. The similar magnitudes of a(N) for (8; R = Pr^n, EtO) appear to be fortuitous and probably result from compensating changes in spin-density on and hybridisation of the nitrogen atoms.

Whereas the e.s.r. spectra of a number of phosphine dimer cations could be readily detected in nitrile solvent, no signal was observed during anodic oxidation of triethyl phosphite. However, in dichloromethane solvent strong spectra of trialkyl phosphite dimer cations were observed. We suggest that our inability to detect these species in nitrile solvent is due to the preferential reaction of the monomer cation with the solvent rather than with the phosphite. This reaction with the solvent could be deprotonation [equation (xi)] or addition [equation (xii)], followed by rapid removal of the radical products.



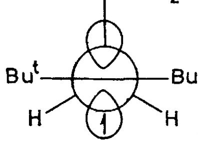
$$(EtO)_3P^{+\cdot} + RC{\equiv}N \longrightarrow (EtO)_2PO\dot{C}HMe + RC{\equiv}\overset{+}{N}H \qquad \text{(xi)}$$
$$(EtO)_3P^{+\cdot} + RC{\equiv}N \longrightarrow R\dot{C}{=}N\overset{+}{P}(OEt)_3 \qquad \text{(xii)}$$

Adducts to 3,3-*Dimethyl*-2-*t*-*butylbut*-1-*ene*.—In the presence of 3,3-dimethyl-2-t-butylbut-1-ene, in either nitrile or dichloromethane solvent, the phosphinium radical cation (4) is trapped to give a long-lived α,α-di-t-butylalkyl radical with a β-phosphonium substituent [equation (vi)]. For steric and electronic reasons [7] these adducts exist in the eclipsed conformation (9), as shown by the magnitudes of $a(H_\beta)$ and $a(P_\beta)$. The β-proton and phosphorus splittings were essentially independent of temperature [$a(P_\beta)$ decreased slightly with increasing temperature], showing that conformations other than (9) are negligibly populated at the temperatures employed.



(9)

Even when the steric constraint is absent, related radicals [*e.g.* $Et_3\overset{+}{P}CH_2CH_2\cdot$ and $Ph_3\overset{+}{P}CH(Me)CH_2\cdot$ [18]] appear to exist predominantly in similar eclipsed conformations for which overlap of the unpaired electron orbital with the β-P–C bond is at a maximum. It appears that the isotropic splitting observed for α,α-di-t-butylalkyl radicals carrying a β-phosphorus substituent arises predominantly by a hyperconjugative mechanism.[19] The P 3*s* character of the β-C–P bond and thus the magnitude of $a(P_\beta)$ increase with the electronegativity of the substituents on phosphorus in a given valency state. For the radical (10), in which the β-phosphorus atom is tetraco-ordinate as it is in the adducts (9), we have found a(P) 109.5, $a(2H_\beta)$ 13.7 G at 157 K.[7, 19]



(10)

In general terms, the phosphorus splittings given in Table 2 show that similar conclusions may be drawn for a

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* The electronegativity of the (Me$_3$Si)$_2$N group is expected to be comparable to that of the EtO group because of p_π–d_π bonding between nitrogen and silicon.

† Calculated taking A_0 = 3 640 G and $2B_0$ = 206 G (P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals', Elsevier, Amsterdam, 1967).

[18] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 622.

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

β-phosphonium substituent; *a*(P) decreases from *ca.* 130 for (9; X = RO) to *ca.* 90 G for (9; X = Et). However, the detailed analysis is probably quite complex and the presence of lone pairs of electrons on the phosphorus ligands may play an important role in determining the P 3*s* character of the β-C–P bond.

EXPERIMENTAL

E.s.r. spectra were recorded during continuous constant current electrolysis of samples in the cavity of a Varian E-4 spectrometer, using the standard variable temperature insert. The electrolysis cell was made from parallel Suprasil quartz flats with a 1 mm gap. The working electrode was a platinum flag (4 × 4 mm), with the top edge positioned in the centre of the microwave cavity, electrically connected by a thin platinum wire insulated from the electrolyte solution by tightly fitting Teflon sleeving. The counter electrode was a larger platinum flag in a compartment, just outside the Dewar insert, separated from the working electrolyte by a fine porosity glass frit.

The potentiostat was constructed from a field effect transistor (f.e.t.) input high-voltage operational amplifier (Teledyne-Philbrick 1022) with an added current-booster output stage, giving an output swing of ±120 V at ±100 mA with a slewing rate of 30 V μs^{-1}, in the follower-with-gain configuration. The working electrode was either connected to earth or to the ' virtual-earth ' of a current follower built from an f.e.t. input operational amplifier (Radiospares Components Ltd.) with an added current-booster output stage.

Controlled-potential electrolysis was not the method of choice for generating radical cation dimers because of a large background e.s.r. signal derived from the silver wire reference electrode that was employed. It was found that constant-current electrogeneration of these radical cations was more satisfactory. The current required for a sufficiently strong e.s.r. signal varied with temperature and the life-times of the radical-ions. In general, the current used was in the region 1—400 μA, equivalent to a current density of 6.3×10^{-6}—2.5×10^{-3} A cm^{-2}, and was optimised to give an e.s.r. signal of satisfactory strength. When necessary fresh electrolyte solution was introduced into the region of the cell near the working electrode. *g* Factors were obtained by measurement of the microwave frequency (using a calibrated wavemeter) and the magnetic field at the centre of resonance, using a specially constructed proton magnetometer containing glycerol, the probe being placed alongside the cavity. The difference in magnetic field experienced by the probe and by the sample was small and was accounted for by determining the *g* factor of the pyrene radical anion (Na^+ counter ion) in tetrahydrofuran (*g* 2.002710).[20]

Electrolyte solutions, *ca.* 0.1M in tetra-n-butylammonium tetrafluoroborate, *ca.* 0.3M in phosphine and *ca.* 0.1M in 3,3-dimethyl-2-t-butylbut-1-ene (if present), were degassed five times using a vacuum line and subsequently handled under an atmosphere of high purity nitrogen.

Butyronitrile and propionitrile (Aldrich) were purified in the manner described by Walter and Rameley (method B).[21] Dichloromethane (B.D.H.) was purified by passage over activated basic alumina. Tetra-n-butylammonium tetrafluoroborate was prepared by neutralising a 40% aqueous solution of tetra-n-butylammonium hydroxide (B.D.H.) with a 40% aqueous fluoroboric acid (Fisons) and recrystallised four times from methanol–water mixture (2 : 1) using activated charcoal to remove the colour. The crystalline product was dried *in vacuo* at 80 °C over phosphoric oxide for two days and stored over phosphoric oxide.

2-Phenyl-*NN*-dimethyl-1,3-diazaphospholidine was prepared from dichloro(phenyl)phosphine and *NN*-dimethylethylenediamine in ether solvent with triethylamine as the tertiary base.[22] *2-t-Butyl-*NN*-dimethyl-*1,3-*diazaphospholidine*, b.p. 72 °C at 10 mmHg, was prepared in a similar manner from dichloro-(t-butyl)phosphine (Found: C, 55.3; H, 11.2; N, 16.4; P, 17.5. $C_8H_{19}N_2P$ requires C, 55.1; H, 11.0; N, 16.1; P, 17.8%). The *2-n-propyl analogue*, b.p. 88 °C at 25 mmHg, was prepared from dichloro-(n-propyl)phosphine (Found: C, 52.8; H, 10.8; N, 17.7; P, 18.9. $C_7H_{17}N_2P$ requires C, 52.5; H, 10.7; N, 17.5; P, 19.3%).

Phenylbis-(2,2,2-*trifluoroethoxy*)*phosphine*, b.p. 60—62 °C at 0.15 mmHg, was prepared from dichloro(phenyl)phosphine and 2,2,2-trifluoroethanol in the presence of triethylamine in ether (Found: C, 39.5; H, 3.1; P, 10.0. $C_{10}H_9F_6O_2P$ requires C, 39.2; H, 3.0; P, 10.1%).

Diethoxy[*bis*(*trimethylsilyl*)*amino*]*phosphine*.—A solution of n-butyl-lithium in hexane (74 ml, 2.1M) was added dropwise with stirring to an ice-cooled solution of hexamethyldisilazane (25 g) in ether (100 ml). After the addition the mixture was refluxed for 1 h and then cooled in an ice-bath during addition, with stirring, of a solution of diethyl phosphorochloridite (24.3 g) in ether (100 ml). After the addition the mixture was stirred for a further 0.5 h at room temperature, filtered, and the solvent removed at reduced pressure. Distillation of the residue gave the product, b.p. 79—80 °C at 4 mmHg (Found: C, 43.0; H, 10.3; N, 4.9; P, 11.1. $C_{10}H_{28}NO_2PSi_2$ requires C, 42.7; H, 10.0; N, 5.0; P, 11.0%).

3,3-Dimethyl-2-t-butylbut-1-ene was prepared by the method of Newman *et al.*[23]

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