Generation and E.S.R. Spectra of Some New Phosphorus-centred Radicals $\dot{\mathrm{P}}_2\mathrm{Ar}_2\mathrm{X}$, $\dot{\mathrm{P}}(\mathrm{Ar})\mathrm{X}$, $\dot{\mathrm{P}}(\mathrm{OAr})_2$, $\dot{\mathrm{P}}\mathrm{Ar}_2(:\mathrm{O})$, $\dot{\mathrm{P}}\mathrm{Ar}[\mathrm{N}(\mathrm{SiMe}_3)_2](:\mathrm{NSiMe}_3)$, and $[\mathrm{P}_2\mathrm{Ar}_2]^{\cdot-}$ derived from the Bulky Group $\mathrm{C_6H_2Bu^t{}_3}$-2,4,6 (= Ar)†

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The photochemical reaction of X_2 and the diphosphene *trans*-ArP=PAr (Ar = $\mathrm{C_6H_2Bu^t{}_3}$), (**1**), leads successively to $\dot{\mathrm{P}}_2\mathrm{Ar}_2\mathrm{X}$, (**2**), $\dot{\mathrm{P}}(\mathrm{Ar})\mathrm{X}$, (**3**), and upon cooling $[\mathrm{P(Ar)X}]_2$ [for X = OBu^t, $\Delta H_{\mathrm{diss}} = 107 \pm 7$ kJ mol^{-1}] for X = OBu^t or SPr^n, whereas for X = SBu^t only (**3**) was detected; the radicals $\dot{\mathrm{P}}(\mathrm{Ar})\mathrm{X}$, $\dot{\mathrm{P}}(\mathrm{OAr})_2$, and $\dot{\mathrm{P}}\mathrm{Ar}_2(:\mathrm{O})$ were formed by reduction of the appropriate diamagnetic P$^{\mathrm{III}}$ or P$^{\mathrm{V}}$ chloride, while $[\mathrm{P_2Ar_2}]^{\cdot-}$ was obtained from (**1**) and $\mathrm{Na[C_{10}H_8]}$.

We describe the preparation and characterisation by e.s.r. spectroscopy of persistent radical intermediates formed by addition to the P=P double bond of the novel[1] ArP=PAr, (**1**), (Ar = 2,4,6-tri-t-butylphenyl). A number of phosphorus-centred radicals stabilised by the bulky Ar ligand are also reported: $\dot{\mathrm{P}}_2\mathrm{Ar}_2\mathrm{X}$ (**2**), $\dot{\mathrm{P}}(\mathrm{Ar})\mathrm{X}$ (**3**), $\dot{\mathrm{P}}(\mathrm{OAr})_2$, $\dot{\mathrm{P}}\mathrm{Ar}_2(:\mathrm{O})$, $\dot{\mathrm{P}}\mathrm{Ar}[\mathrm{N}(\mathrm{SiMe}_3)_2](:\mathrm{NSiMe}_3)$, and $[\mathrm{P_2Ar_2}]^{\cdot-}$. E.s.r. data on these radicals are in Table 1. The preparation of the diamagnetic precursors will be described in a forthcoming communication[2] or in ref. 3 for $\mathrm{PAr_2(Cl)(:O)}$.

Photolysis of di-t-butyl peroxide in a toluene solution of (**1**) at ambient temperature gave an e.s.r. spectrum consisting of a doublet of doublets [see (A) in Figure 1, and Table 1], and a less intense doublet [(B) in Figure 1]. The larger splitting in (A) is characteristic of phosphinyl radicals[4] and the spectrum is assigned to the adduct (**2**; X = OBu^t), equation (1). [Photolysis of (**1**) under identical conditions (1 kW Hanovia Hg–Xe lamp) but without $\mathrm{Bu^t{}_2O_2}$ did not afford a paramagnetic species.] The concentration of the doublet (B), assigned to the species (**3**), increased as that of (**2**) diminished. The intensity of this e.s.r. signal (B) was also found to depend reversibly on temperature; it was barely detectable at 0 °C but was strong at 50 °C. We attribute this to the phosphinyl radical (**3**; X = OBu^t) being in equilibrium with its dimer, equation (2). From the temperature dependence of the e.s.r. signal intensity we estimate $\Delta H_{\mathrm{diss}} = 107 \pm 10$ kJ mol^{-1} for the equilibrium (2).

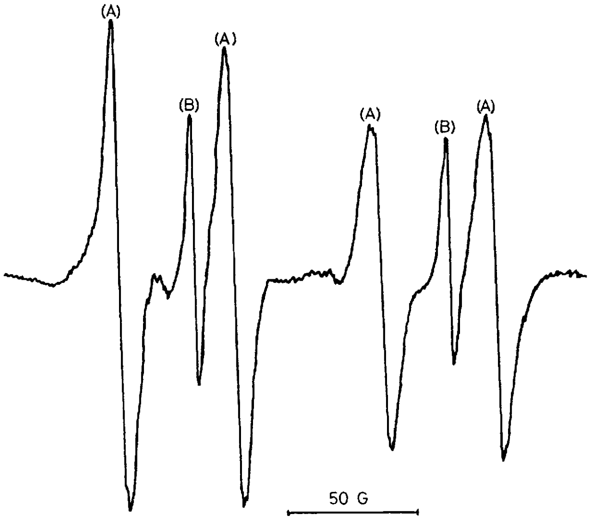
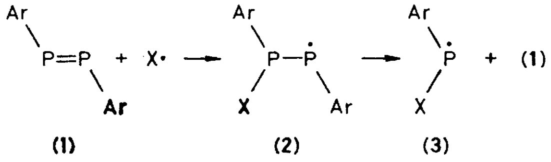


Figure 1. The e.s.r. spectrum of radicals produced by photolysis of ArP=PAr + Bu^{t}OOBu^t in toluene at 30 °C; the signals marked (A) are attributed to $\mathrm{Ar(Bu^tO)P\dot{P}Ar}$ (**2**; X = OBu^t), and (B) to $\dot{\mathrm{P}}(\mathrm{Ar})\mathrm{OBu^t}$ (**3**; X = OBu^t).

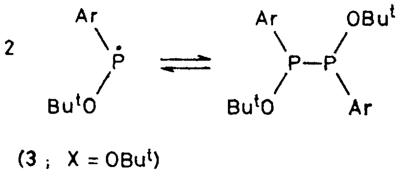
Analogous radicals were detected when di-t-butyl peroxide was replaced by di-n-propyl disulphide but no marked temperature dependence was found for the concentration of (**3**; X = SPr). When di-t-butyl disulphide was employed as a radical source the spectrum of the adduct (**2**; X = SBu^t) was very weak and only (**3**; X = SBu^t) was readily detectable. These observations are consistent with increased steric requirements for SBu^t compared with OBu^t, leading to an enhanced formation of (**3**) from (**2**); the decreased tendency for (**3**) to dimerise may in part be due to stabilisation by the neighbouring sulphur.

A series of persistent phosphinyl radicals (**3**) was formed when a solution of PAr(Cl)X [X = Cl, Ph, $\mathrm{C_6H_2Me_3}$-2,4,6, $\mathrm{OC_6H_2Bu^t{}_3}$-2,4,6, or $\mathrm{CH(SiMe_3)_2}$] was photolysed in toluene in the presence of the electron-rich olefin (**4**) at *ca.* 25 °C, equation (3). {We had previously used this procedure for the synthesis of the persistent radicals $\dot{\mathrm{M}}\mathrm{R}_2$ [M = P or As, R = $\mathrm{CH(SiMe_3)_2}$ or $\mathrm{N(SiMe_3)_2}$].[4]} Similarly, the radical $\dot{\mathrm{P}}(\mathrm{OAr})_2$ was obtained at *ca.* 28 °C from $\mathrm{PCl(OAr)_2}$ + (**4**) in toluene by photolysis.

The radical $\dot{\mathrm{P}}\mathrm{Ar}_2$ was most readily prepared by treating $\mathrm{PArCl_2}$ with an excess of LiAr. It was also slowly formed when



(1)



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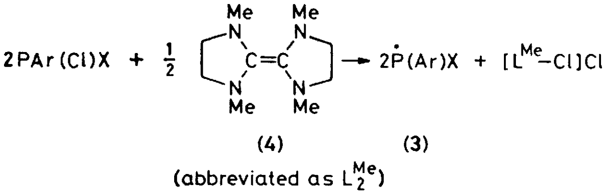

(3)

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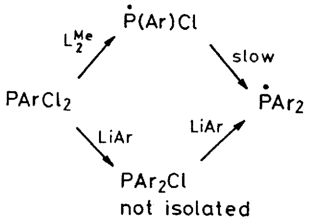
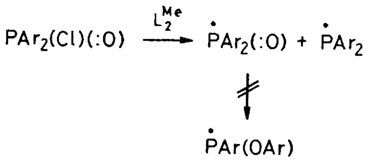
† No reprints available.



(4)



(5)

a solution of $\dot{P}(Ar)Cl$ was kept for 1 week at room temperature, presumably by disproportionation. These findings are interpreted in terms of equations (4).

When $PAr_2(Cl)(:O)$ was reduced with the electron-rich olefin L_2^{Me} a 365 G doublet ($g_{av.} = 2.005$) was observed, which we assign to $\dot{P}Ar_2(:O)$ [*cf.*, $\dot{P}Me_2(:O)$ which has[5] $a(^{31}P) = 375$ G, $g_{av.} =$ *ca.* 2.005]. A second smaller doublet found in this system proved to be due to $\dot{P}Ar_2$. An alternative possibility, that instead of deoxygenative reduction a molecular rearrangement takes place to afford $\dot{P}(Ar)OAr$, is discounted, since (**3**; X = OAr) has significantly smaller $a(^{31}P)$ (see Table 1). Hence the reduction is interpreted in terms of equations (5).

When $PArCl_2$ was treated with $LiN(SiMe_3)_2$ a large doublet (336 G) signal with superimposed hyperfine structure was observed. This is assigned to a phosphorimidoyl radical, probably $\dot{P}Ar[N(SiMe_3)_2](:NSiMe_3)$ {*cf.*,[6] $\dot{P}Bu^t[N(SiMe_3)_2](:NSiMe_3)$ which has $a(^{31}P) = 336.5$, $a(^{14}N) = 5.2$, $a(^{14}N') = 4.0$ G, $g_{av.} = 2.0032$}. A smaller doublet detected in this reaction is attributed to the phosphinyl [**3**; X = $N(SiMe_3)_2$].

Addition of sodium naphthalide in THF to ArP=PAr gave a signal which we assign to the radical anion $[ArP{=}PAr]^{\bullet-}$.

The stabilisation of metal-centred radicals by Ar is not limited to phosphorus. A 50 G quartet was obtained when $AsCl_3$ was treated with LiAr and is provisionally assigned to $\dot{A}sAr_2$. However, photolysis of $AsCl(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_2$ with the electron-rich olefin (**4**) in PhMe at *ca.* 20 °C afforded the persistent aryloxy-radical[7] [a quartet of triplets: *a*(quartet), 10.83 G; *a*(triplet), 1.71 G; $g_{av.}$, 2.0039].

Table 1. Hyperfine splittings (G) and $g_{av.}$-factors for some phosphorus-centred radicals in PhMe (or in one case THF) at *ca.* 25 °C (Ar = $C_6H_2Bu^t_3$-2,4,6).

Radical	X	$a(^{31}P)$	*a*(other)	$g_{av.}$
(**2**)	OBu^t	102	44	2.008
(**2**)	SPr	100	44	2.009
(**3**)	OBu^t	100	—	2.005
(**3**)	SPr	98	—	2.011
(**3**)	SBu^t	99	—	2.012
(**3**)	Cl	92	—	2.005
(**3**)	$N(SiMe_3)_2$	108	—	2.006
(**3**)	$CH(SiMe_3)_2$	104	13.5	2.008
(**3**)	Ph	105	—	2.007
(**3**)	$C_6H_2Me_3$-2,4,6	103	—	2.007
(**3**)	Ar	103	—	2.007
(**3**)	OAr	94	—	2.006
$\dot{P}(OAr)_2$		82	—	1.999
$\dot{P}Ar_2(:O)$		365	—	2.005
$\dot{P}Ar[N(SiMe_3)_2](:NSiMe_3)$		336	—	2.004
$[ArP{=}PAr]^{\bullet-\,a}$		55	—	2.010

[a] In tetrahydrofuran (THF).

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