Electron Spin Resonance Studies of Radicals derived from Trialkyl Phosphorimidates, $(RO)_3P{=}NR$. Phosphazene Formation by β-Scission of an Aminophosphoranyl Radical

By **Robyn S. Hay, Brian P. Roberts,* Karamjit Singh,** and **Jeremy P. T. Wilkinson**, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

Using e.s.r. spectroscopy it has been shown that the phosphoranyl radical $(EtO)_3\dot{P}N(CH_2Ph)SiMe_3$ undergoes β scission to form a benzyl radical and the phosphorimidate $(EtO)_3P{=}NSiMe_3$ (identified by ^{31}P n.m.r. spectroscopy). Methyl and diethoxyphosphonyl radicals do not add sufficiently rapidly to nitrogen in $(EtO)_3P{=}NMe$ to produce a detectable concentration of phosphoranyl radicals, but the phosphonyl radical adduct has been generated indirectly by addition of ethoxyl radicals to the trivalent phosphorus atom in $(EtO)_2P(O)N(Me)P(OEt)_2$, itself prepared by the reaction of $(EtO)_2PCl$ with $(EtO)_3P{=}NMe$. Hydrogen abstraction from trialkyl phosphorimidates $(RO)_3P{=}NC(H)R_2$ a potential route to iminophosphoranyl radicals $(RO)_3\dot{P}N{=}CR_2$, gives rise to π-radicals $(RO)_3P{=}N\dot{C}R_2$ which may be regarded as imine radical anions carrying a phosphonium substituent on nitrogen. These species do not break down readily to give iminyl radicals and phosphite, and addition of $R_2C{=}N\cdot$ to $(RO)_3P$ is not detectable by e.s.r. spectroscopy.

PHOSPHAZENES of the type $(RO)_3P{=}NR$ (1) are nitrogen analogues of the better known trialkyl phosphates, $(RO)_3P{=}O$.[1] Tetra-alkoxyphosphoranyl radicals (2) readily undergo β-scission to give alkyl radicals and phosphate [equation (1)] [2,3] and it appeared of interest to determine whether phosphazenes could be formed by the analogous fragmentation of aminophosphoranyl radicals of the type (3) [equation (2)].

$$\underset{(2)}{(RO)_4P\cdot} \longrightarrow (RO)_3P{=}O + R\cdot \qquad (1)$$

$$\underset{(3)}{(RO)_3\dot{P}NR_2} \longrightarrow (RO)_3P{=}NR + R\cdot \qquad (2)$$

We also considered that hydrogen abstraction from the *N*-alkyl group of (1) might give rise to radicals of the type (4), and that e.s.r. spectroscopy could provide information regarding the electronic structures of these species. In particular, radical (4) might be better described as an iminophosphoranyl radical, $(RO)_3P{-}N{=}CR_2$. Whatever its electronic structure, this species might be formed from and/or fragment to give trialkyl phosphite and an iminyl radical, $R_2C{=}N\cdot$.

$$Bu^tO\cdot + (RO)_3P{=}N{-}C(H)R_2 \longrightarrow Bu^tOH + \underset{(4)}{(RO)_3P{=}N{-}\dot{C}R_2} \qquad (3)$$

RESULTS

E.s.r. spectra were recorded during continuous u.v. irradiation of samples, usually in cyclopropane as solvent, in the cavity of the spectrometer. The following primary photochemical sources of free radicals were employed: di-t-butyl peroxide ($Bu^tO\cdot$), diethyl peroxide ($EtO\cdot$), dicumyl peroxide ($PhMe_2CO\cdot$), and azomethane ($Me\cdot$).

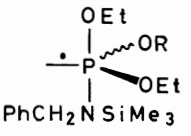
(a) *β-Scission of Aminophosphoranyl Radicals.*—We chose to examine phosphoranyl radicals with the structure (6) since there was some evidence that an *N*-trimethylsilyl substituent would strengthen the P=N bond in a phosphazene of the type $(RO)_3P{=}NSiMe_3$,[4] because the $N{-}CH_2Ph$ bond would be relatively weak, and because cleavage of the P–N bond in (6) should occur less readily than for a dialkylaminophosphoranyl radical of the type $(RO)_3\dot{P}NR_2$.[5,†]

$$RO\cdot + \underset{(5)}{(EtO)_2PN(CH_2Ph)SiMe_3} \longrightarrow \underset{(6)}{RO(EtO)_2\dot{P}N(CH_2Ph)SiMe_3} \qquad (4)$$

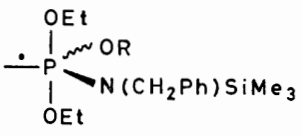
Photolysis of the aminophosphine (5) in cyclopropane gave rise only to a barely detectable spectrum of the benzyl radical. Thus, it appears that the P–N bond in (5) undergoes direct photochemical cleavage, although the rate of radical production must be very small under the conditions employed.

$$(EtO)_2PN(CH_2Ph)SiMe_3 \xrightarrow{h\nu} (EtO)_2\dot{P}{=}NSiMe_3 + PhCH_2\cdot \qquad (5)$$

Photolysis of di-t-butyl peroxide in the presence of (5) at 193 K gave rise to signals which we assign to two isomers, (7a) and (7b), of the phosphoranyl radical (6; R = Bu^t). The radical showing the larger nitrogen splitting is identified [5] as (7a; R = Bu^t) in which the amino-ligand occupies an apical site in the trigonal bipyramid.‡



(7a)



(7b)

The second signal, which showed a larger phosphorus and a smaller nitrogen splitting, is ascribed [5] to (7b; R = Bu^t) in which the amino-ligand is in an equatorial site. At 190 K the concentration ratio [(7a)]/[(7b)] was *ca.* 2, probably close to the value corresponding to equilibrium between the two isomers.[5,7] The e.s.r. parameters for all the phosphoranyl radicals detected in this work are gathered in Table 1.

At higher temperatures the spectra assigned to (7; R = Bu^t) became weaker and the signal from the t-butyl radical became apparent. At 269 K the spectrum of $Bu^t\cdot$

† The N–X bond in molecules of the types $R(Me_3Si)NX$ and $(Me_3Si)_2NX$ appears to be stronger than that in R_2NX.[6]

‡ The t-butoxy-ligand is shown in an equatorial site for convenience, no evidence exists for such a preference.[7]

TABLE 1

E.s.r. parameters of phosphoranyl radicals in cyclopropane solvent

Radical	Temp. (K)	g-Factor [a]	Hyperfine splittings/G a(P) [a]	a(N)	Others [b]
(7a; R = Bu^t)	190	2.0016	726.5	19.2	
(7b; R = Bu^t)	190	2.0022	857.5	*c*	
(7a; R = Et)	190	2.0014	736.8	19.4	
(7b; R = Et)	190	2.0019	848.9	*c*	
(11)	190	2.0024	950.7	32.5	7.8 (1 P)
(12)	190	2.0027	937.8	33.5	7.9 (1 P); 2.2 (3 H) [d]
(EtO)$_2$Bu^{t}OP$\dot{N}$(Pr^n)-P(O)(OEt)$_2$	228	2.002 [e]	948 [e]	32.5	7.5 (1 P); 4.0 (2 H)
(17a) [f,g]	123	2.003 [e]	697 [e]	12.7	
(17b) [f]	153	2.003 [e]	841 [e]	2.8	

[a] Calculated using the Breit–Rabi equation; *g*-values and phosphorus splittings accurate to ±0.0002 and ±0.5 G, respectively, unless otherwise stated. [b] Number of nuclei coupling shown in parentheses. [c] Very poorly resolved; *a*(N) *ca.* 2—3 G. [d] At 230 K. [e] *g*-Factor ±0.001, *a*(P) ±1—2 G. [f] Data from ref. 5. [g] In propane solvent.

was very intense whilst any signal from the benzyl radical was so weak that it could not be assigned with certainty. The radical (6; R = Bu^t) thus undergoes β-scission with C–O cleavage [equation (6)].

$$Bu^tO(EtO)_2\dot{P}N(CH_2Ph)SiMe_3 \longrightarrow \underset{(8)}{(EtO)_2P(O)N(CH_2Ph)SiMe_3} + Bu^t\cdot \quad (6)$$

In an attempt to decrease the rate of C–O cleavage, and thus possibly to detect C–N cleavage, we generated the phosphoranyl radical (6; R = Et) by photolysis of diethyl peroxide in the presence of (5). Signals ascribed to (7a; R = Et) and (7b; R = Et) were detected and at 191 K the ratio [(7a)]/[(7b)] was *ca.* 6. Similar increases in relative concentration of an isomer with an apical amino-group have been noted previously [5,8] when Bu^{t}O ligands were replaced by EtO groups. As expected (6; R = Et) did not fragment as readily as (6; R = Bu^t), however, at 269 K overlapping spectra from ethyl and benzyl radicals were detected and [Et·]/[PhCH$_2$·] was *ca.* 1.5. The spectrum of the benzyl radical was much more intense than that obtained in the absence of diethyl peroxide or in the presence of di-t-butyl peroxide. We conclude that (6; R = Et) undergoes competing C–O and C–N cleavage to form (8) and the phosphazene (9), respectively.

$$(6;\ R = Et) \longrightarrow \begin{cases} \longrightarrow (8) + Et\cdot & (7) \\ \longrightarrow \underset{(9)}{(EtO)_3P{=}NSiMe_3} + PhCH_2\cdot & (8) \end{cases}$$

Since the rate constants for removal of ethyl and benzyl radicals from the system will be very similar,[9] the rate of cleavage (7) is approximately 1.5 times that of (8) at 269 K.

In order to confirm the occurrence of the novel fragmentation (8) we attempted to detect the cleavage products by ^{31}P n.m.r. spectroscopy. Photolysis of (5) in pentane at 273 K, under similar conditions to those of the e.s.r. experiments, did not yield detectable quantities of (8) or (9) (δ^{31}P −10.4 and +6.6 p.p.m., respectively). Photolysis of a mixture of (5) and diethyl peroxide gave rise to a mixture of (8) and (9) in the molar ratio *ca.* 1.5 : 1 and in good total yield. When a mixture of (5) and di-t-butyl peroxide was photolysed, (8) was the only product identified by ^{31}P n.m.r. spectroscopy and no (EtO)$_2$Bu^{t}OP=NSiMe$_3$ [assumed to have a chemical shift similar to that of (9)] could be detected.

(b) *Radical Addition to Phosphazenes.*—Using e.s.r. spectroscopy we have also attempted to determine whether radical addition to the P=N group of a phosphazene can occur to produce an aminophosphoranyl radical. When azomethane was photolysed in the presence of triethyl *N*-methylphosphorimidate (10) only the spectrum of the methyl radical was observed at low temperatures, and the radical (EtO)$_3\dot{P}$NMe$_2$ [5] [*a*(P) 843, *a*(N) 3.5 G at 153 K] was not detected.

$$Me\cdot + \underset{(10)}{(EtO)_3P{=}NMe} \xrightarrow{k_9} (EtO)_3\dot{P}NMe_2 \quad (9)$$

$$(EtO)_3\dot{P}NMe_2 \longrightarrow (EtO)_3P + Me_2N\cdot \quad (10)$$

At higher temperatures (258 K) a weak signal from the radical (EtO)$_3$P=N$\dot{C}$H$_2$ [presumably formed by hydrogen-abstraction from (10), see below] was observed in addition to that of the methyl radical, but the spectrum of the dimethylaminyl radical, the product of α-scission [5] of (EtO)$_3\dot{P}$NMe$_2$ [equation (10)] was not detected. It thus appears that the methyl radical does not add rapidly to (10), and we estimate that k_9 is less than *ca.* 2×10^2 l mol^{-1} s^{-1} at 258 K.

The phosphorus–nitrogen bond in (10) is strongly polar in the sense $\overset{\delta+}{P}{=}\overset{\delta-}{N}$ and we considered that the more electrophilic diethoxyphosphonyl radical might add [equation (11)] more rapidly to the phosphazene than does methyl.

$$(EtO)_2\dot{P}O + (EtO)_3P{=}NMe \longrightarrow \underset{(11)}{(EtO)_3\dot{P}N(Me)P(O)(OEt)_2} \quad (11)$$

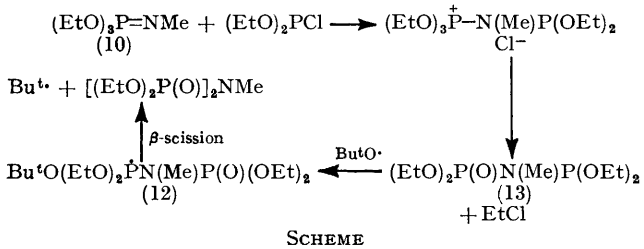
Photolysis of a mixture containing (10), di-t-butyl peroxide, and tetraethyl pyrophosphite (the last two reagents providing the source of phosphonyl radicals [10]) gave only a weak uninterpretable spectrum apart from signals due to the t-butyl radical and the phosphoranyl radical (EtO)$_2\dot{P}$(OBu^t)$_2$ (secondary products of the reaction of Bu^{t}O· with the pyrophosphite [10]).* However, if the pyrophosphite contained some diethyl chlorophosphite † an e.s.r. spectrum ascribed to the phosphoranyl radical (12), which is very similar to (11), was detected. N.m.r. studies (^{1}H and ^{31}P) showed that diethyl chlorophosphite reacted rapidly with (10) to form ethyl chloride and (13), which was isolated from a preparative scale reaction. Addition of t-butoxyl radicals to (13) yielded the phosphoranyl radical (12) (see Scheme). Similar results were obtained with the phosphazene (EtO)$_3$P=NPr^n.

Photolysis of di-t-butyl peroxide in the presence of pure (13) at *ca.* 180 K gave rise only to the spectrum of (12), whereas at higher temperatures the signal from the t-butyl radical became apparent indicating that (12) undergoes β-scission as shown in the Scheme. Repetition of the experiment with diethyl peroxide afforded the spectrum of

* In separate experiments it was shown that the phosphazene (10) did not react with the pyrophosphite in the absence of peroxide and light.

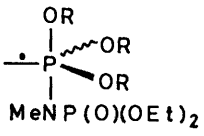
† Tetraethyl pyrophosphite prepared from the chlorophosphite and silver carbonate [11] was so contaminated.

the phosphoranyl radical (11), which underwent β-scission less readily than (12), and the nitrogen splittings for (11) and for related radicals indicate [5,7] that the phosphonyl-amino-ligand occupies an apical site as shown in (14).



SCHEME

Hydrogen Abstraction from N-Alkylphosphazenes.—U.v. irradiation of di-t-butyl peroxide in the presence of phosphazenes of the type $(RO)_3P{=}NC(H)R^1R^2$ gave rise to intense



(14)

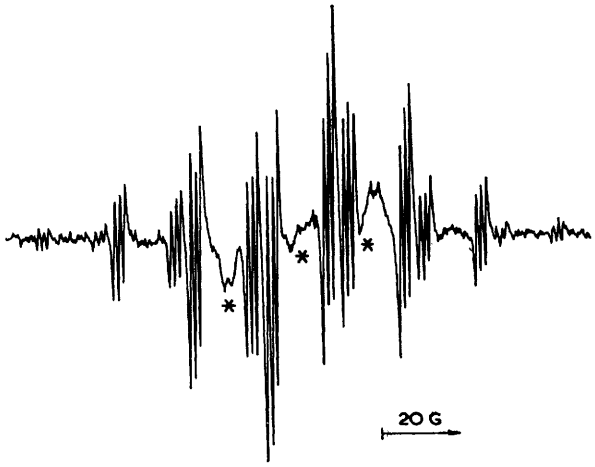
e.s.r. spectra which are assigned to the radicals (15) [equation (12)].

$$Bu^tO\cdot + (RO)_3P{=}NC(H)R^1R^2 \longrightarrow Bu^tOH + (RO)_3P{=}N\dot{C}R^1R^1 \quad (12)$$
(15)

Identical spectra were obtained when dicumyl peroxide, bistrimethylsilyl peroxide, or acetone replaced the di-t-butyl peroxide. With acetone the spectrum of the radical $Me_2\dot{C}OH$ was also detected. With the *N*-methyl- and *N*-n-propyl-phosphazenes, e.s.r. signals from secondary reaction products (*g ca.* 2.002 9) built-up rapidly during photolysis when di-t-butyl peroxide was the source of hydrogen-abstracting radicals, but secondary spectra were unobtrusive with dicumyl peroxide or acetone. The build-up of secondary signals, some of which were detectable for a considerable time after shuttering the light, was rapid for the phosphazene $(MeO)_3P{=}NPr^i$ with both di-t-butyl and dicumyl peroxides. At present no attempt has been made to assign these secondary spectra.

The radicals (15) were characterised by *g*-factors of *ca.* 2.002 9, by small nitrogen splittings, and by highly temperature-dependent phosphorus splittings. The spectrum of the radical $(MeO)_3P{=}N\dot{C}Me_2$ is shown in the Figure and the spectroscopic parameters for radicals of type (15) are given in Table 2.

For none of the radicals (15) were we able to resolve different splittings from the groups R^1 and R^2 when these were chemically identical, however, the lines corresponding to $M_I(H\alpha)=0$ in the spectrum of $(EtO)_3P{=}N\dot{C}H_2$ broadened relative to the other lines at very low temperatures (148 to 128 K in liquid ethylene). This line-shape effect may result either from a decrease in the rate of exchange of the α-hydrogens by rotation about the N–C bond, or from a small increase (as the temperature decreases) in the difference between the splittings from these two protons in a radical which is undergoing rotation about the N–C bond slowly on the e.s.r. time scale. At least, we may conclude that the α-hydrogens are probably magnetically non-equivalent.



E.s.r. spectrum of the radical $(MeO)_3P{=}N{-}\dot{C}Me_2$ in cyclopropane at 180 K. The lines marked with an asterisk are from relatively long-lived secondary radicals

Fragmentation of radicals of the type (15) to give iminyl radicals [equation (13)] was undetected even at high temperatures. Thus, the signals from $(EtO)_3P{=}N\dot{C}H_2$ and $(MeO)_3P{=}N\dot{C}Me_2$ were still strong at 300 K and the spectra of $H_2C{=}N\cdot$ and $Me_2C{=}N\cdot$, respectively, were not detected.

$$(RO)_3P{=}N\dot{C}R^1R^2 \longrightarrow (RO)_3P + R^1R^2C{=}N\cdot \quad (13)$$

TABLE 2

E.s.r. parameters for radicals of the type $(RO)_3P{=}N\dot{C}R_2$ in cyclopropane

Radical	Temp. (K)	*g*-Factor	Hyperfine splittings [a]/G *a*(Hα)	*a*(Hβ)	*a*(N)	*a*(P)	d|*a*(P)|/dT (mGK^{-1})	d|*a*(N)|/dT (mGK^{-1})
$(MeO)_3P{=}N\dot{C}H_2$	197	2.0028	18.2(2)		[b]	12.8	+38	
$(EtO)_3P{=}N\dot{C}H_2$	223	2.0029	18.1(2)		0.14	13.9	+40	+3.0
$(MeO)_3P{=}N\dot{C}(H)CH_2CH_3$	197		17.6	22.3(2)	[c]	13.5		
$(EtO)_3P{=}N\dot{C}(H)CH_2CH_3$	213	2.0029	17.5	21.5(2)	[c]	15.5	+50	
$(MeO)_3P{=}N\dot{C}Me_2$	188	2.0028		19.4(6)	1.30	16.2	+90	−3.5
$(MeO)_3P{=}N\dot{C}(H)Me$	190	2.0030	18.6	21.7(3)	0.85	14.4	+58	−3.7

[a] Numbers of nuclei given in parentheses if different from unity. [b] Not resolved. [c] Not resolved; *a*(3Hγ) 0.5 G.

Neither does the reverse of the cleavage (13) occur readily, since photolysis of acetone or formaldehyde azines * (16; R = Me or H) in the presence of trimethyl or triethyl phosphite over a range of temperatures gave rise only to the spectra of the iminyl radicals $R_2C{=}N\cdot$.

$$R_2C{=}N{-}N{=}CR_2 \xrightarrow{h\nu} 2R_2C{=}N\cdot \quad (14)$$
(16)

* Azines provide reasonably good photochemical sources of certain iminyl radicals for e.s.r. studies in solution [12] (compare ref. 13).

DISCUSSION

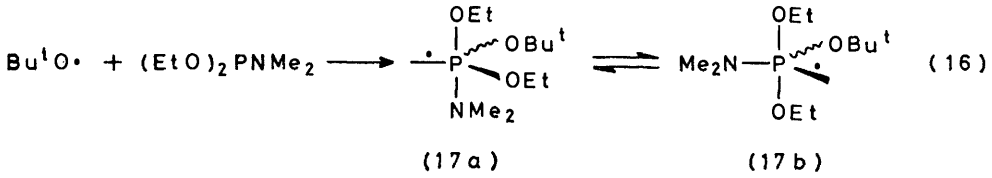
Fragmentation of the radical (6; R = Et) to give benzyl radicals and (9) represents the first reported β-scission of a phosphoranyl radical to form a phosphazene. Benzyloxyphosphoranyl radicals undergo β-scission extremely readily [14] [*e.g.* equation (15)], and the

$$PhCH_2O\dot{P}(OEt)_3 \longrightarrow Ph\dot{C}H_2 + O{=}P(OEt)_3 \quad (15)$$

lower rate of N–C cleavage for (6; R = Et) is presumably mainly a result of the larger difference in bond strengths * [D(P=X) − D(P–X)] for X = O than for X = N.[2,15]

Hydrogen Abstraction from N-*Alkylphosphazenes*.—The e.s.r. parameters indicate that the species $(RO)_3P{=}N{-}\dot{C}R_2$ (4) are π-radicals in which the unpaired electron is centred mainly on carbon; the g-factors are similar to those of α-aminoalkyl radicals [19] [$Me_2N\dot{C}H_2$; a(2Hα) 13.4, a(N) 7.0, a(6Hγ) 3.7 G, g 2.002 8: $H_2N\dot{C}Me_2$; a(6Hβ) 18.3, a(2Hβ) 4.9, a(N) 2.9 G, g 2.002 9]. For radicals of the type $CH_3\dot{C}(X^1)(X^2)$, which have a planar arrangement of bonds to C-α, the magnitude of a(Hβ) is given approximately by equations (17) and (18).[20]

The parameter ΔX measures the spin-withdrawing



The radicals (6) do not undergo α-scission to give detectable concentrations of alkyl(silyl)aminyl radicals, in sharp contrast to the ready fragmentation [5] of radicals of the type $(RO)_3\dot{P}NR_2$ to give $R_2N^{\cdot}$. The *N*-silyl group appears to strengthen the P–N bond in (6) relative to that in the dialkylamino-analogue.[6] The alkyl(silyl)-amino-ligand is somewhat more apicophilic than the dimethylamino-group.[5] Addition of t-butoxyl radicals to $(EtO)_2PNMe_2$ gives spectra which are assigned to the isomers (17a) and (17b), and at 123 K the concentration ratio [(17a)]/[(17b)] is *ca.* 0.1.[5,†]

Ligand apicophilicity in phosphoranyl radicals generally increases with group electronegativity, and the greater apicophilicity of the $PhCH_2(Me_3Si)N$ group may be explained in terms of $p_\pi \rightarrow d_\pi$ bonding between nitrogen and silicon, which removes electron density from the nitrogen and increases its effective electronegativity.[16] The magnitude of a(N) observed for the isomer (7a) is as expected for a trigonal planar nitrogen in the silylamino-ligand.[7] The values of a(P) for (7a) and (7b) are larger than those for (17a) and (17b), respectively, as expected [7] if the electronegativities of the substituents are in the order R_2N < $R(Me_3Si)N$ < RO. The electronegativities of $R(Me_3Si)N$ and RO groups are probably quite similar [a(P) for $(MeO)_3\dot{P}OBu^t$ is 887 G at 187 K [17]], and the differences in the apicophilicities of these ligands, like those of different alkoxy-groups, appear to result from a subtle interplay of relatively small electronic and steric effects.

The phosphonylamino-substituent is, like amido-[7] and isocyanato-ligands,[7] more apicophilic than either R_2N or RO groups. The splitting from the phosphonyl-phosphorus in (14) is similar to that detected for radicals of the type $(RO)_3\dot{P}OP(O)(OR)_2$, for which we have argued that the phosphonyloxy ligand also occupies an apical site.[18]

* For $Me_3P{=}NEt$ and $Ph_3P{=}NEt$, D(P=N) has been estimated to be 405 and 525 kJ mol^{-1}, respectively.[15] The value [2] of D(P–N) in $(Me_2N)_3P$ is *ca.* 289 kJ mol^{-1}. For comparison, D(P–O) 351 kJ mol^{-1} [in $(EtO)_3P$] and D(P=O) 619 kJ mol^{-1} [in $EtO)_3P{=}O$].[2]

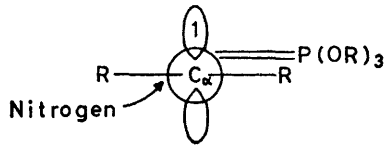
effect of the substituent X, and ΔX is 0.081 for a methyl group and zero for hydrogen. Hence, the β-hydrogen splitting constants for $(MeO)_3P{=}N{-}\dot{C}(H)CH_3$ and

$$a(H\beta) = 29.3\ \rho_{C\alpha}{}^{\pi} \quad (17)$$

$$\rho_{C\alpha}{}^{\pi} = 0.919(1 - \Delta X^1)(1 - \Delta X^2) \quad (18)$$

$(MeO)_3P{=}N{-}\dot{C}(CH_3)_2$ indicate that the π-spin densities on the α-carbons are 0.74 and 0.66, respectively. The value of ΔX for the $(MeO)_3P{=}N{-}$ substituent is *ca.* 0.21, compared with 0.26 and 0.20 for $H_2N{-}$ [19] and $O{=}C{=}N{-}$ [21] groups, respectively. It is difficult to estimate the spin density on phosphorus on the basis of the present evidence, but by analogy with the related radicals $X_3P{=}C(H){-}\dot{C}R_2$ [22] it is probably significant.

The most stable conformation of the radicals (4) appears to be (18), in which the phosphorus atom and the atoms directly bonded to C-α are coplanar, and the P=N–C-α system is bent as it is the parent phosphazenes.[23]

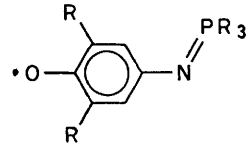


(18)

For the conformation (18) there would be two major contributions of opposite sign to a(P). Spin polarisation of the N–P σ-bond by positive π-spin density on N will induce negative spin density in the P-3s orbital. Positive spin density in the P-3p_π and P-3d_π orbitals, produced by delocalisation of the unpaired electron onto phorphorus, will induce positive spin density in the P-3s orbital. Thermally-induced torsional motion about the C(α)–N bond will bring the phosphorus atom out of the plane and allow hyper-conjugative interaction between the π-orbital of the unpaired electron and the P–N σ-bond, which will give rise to a positive contribution to a(P) that increases with temperature.

† The Bu^{t}O ligand is shown in an equatorial site for convenience; it is probably rapidly exchanging sites with the apical ethoxy-group.[3,7]

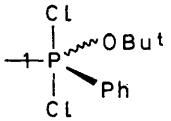
The observed magnitude of a(P) increases rapidly with temperature, and hence a(P) is probably positive. The phosphorus splitting for $(MeO)_3P{=}N\dot{C}Me_2$ is particularly temperature dependent, and this may be associated with the presence of relatively bulky methyl groups on C-α, which serve to reduce the barrier to out-of-plane motion of the phosphorus atom. Scheffler *et al.*[24] have reported e.s.r. studies of phenoxyl radicals of the type (19) and have suggested similar reasons for the temperature dependence of the phosphorus hyperfine splitting in these species.



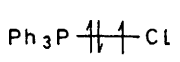
(19)

The electronic nature of the P=X bond (X = O, NR, or CR_2) in phosphorus ylids has long been a subject of controversy, and is still being investigated theoretically.[25] It has been concluded [25b] from recent *ab initio* SCF–MO calculations (4—31G) that a P–C bond-shortening and stabilising interaction exists between the H_3P group and the lone pair of electrons on carbon in the ylid $H_3\overset{+}{P}{-}\bar{C}H_2$. The basis set employed did not contain P-3*d* functions and the acceptor orbital was identified as a π^* H_3P group orbital. Since these calculations adequately account for the structures of phosphorus ylids, it is not clear to what extent, if any, P-3*d* orbitals are involved in P–N π-bonding in phosphazenes or in radicals of type (4).

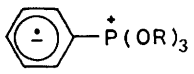
E.s.r. studies of phenylphosphoranyl radicals have identified three different types of electronic structures,[26-31] exemplified by (20)—(22).



(20)



(21)



(22)

The radical (20) appears to possess an approximately trigonal bipyramidal skeleton and the unpaired electron is centred mainly on phosphorus and the two apical ligands,[27] whilst for (21) there is local C_{3v} symmetry at phosphorus with the unpaired electron in an antibonding σ^* P–Cl orbital.[29] However, in phenyltrialkoxyphosphoranyl radical the unpaired electron is mainly on the aromatic ring, and this species is best described as a benzene radical anion with a phosphonium substituent as shown in (22).[27] Similarly, the species (4) may be better described as a phosphonium-substituted imine radical anion, and can be represented as a hybrid of (23a) and (23b) with the former making the major contribution.

$$\underset{\text{(23a)}}{(RO)_3\overset{+}{P}{-}\bar{N}{-}\dot{C}R_2} \longleftrightarrow \underset{\text{(23b)}}{(RO)_3\overset{+}{P}{-}\dot{N}{-}\bar{C}R_2}$$

There would also be considerable charge neutralisation by electron donation into vacant P-3d_π orbitals (and/or into a $\pi^*P(OR)_3$ group orbital [25]). Several contributions, not all of the same sign, to a(N) can be envisaged and it seems likely that the signs of the small nitrogen splittings are opposite for $(EtO)_3P{=}N\dot{C}H_2$ and $(MeO)_3P{=}N\dot{C}(R)Me$ (R = H or Me).

It is of interest that neither the addition of iminyl radicals to phosphites nor the fragmentation of (4) to give iminyl radicals occurs sufficiently rapidly to be detected by e.s.r. spectroscopy in solution. In general, either formation of $(RO)_3\dot{P}X$ from $(RO)_3P$ and X· or the reverse process, phosphoranyl radical fragmentation to give $(RO)_3P$ and X·, is rapid enough to be detected by e.s.r. For example, $(RO)_3\dot{P}NR_2$ undergoes rapid α-scission to give $(RO)_3P$ and $R_2N\cdot$,[5] whilst $(Me_3Si)_2N\cdot$ adds rapidly to $(RO)_3P$ to form $(RO)_3\dot{P}N(SiMe_3)_2$.[6] The different behaviour of the iminyl radical-phosphite system is presumably related to the fact that the adduct (4) has a different structure from phosphoranyl radicals of the type $(RO)_3\dot{P}X$.

EXPERIMENTAL

E.s.r. Spectroscopy.—Samples were sealed *in vacuo* in 4 mm o.d. Suprasil tubes and irradiated, whilst in the cavity of a Varian E-4 spectrometer, with light from a Philips SP500 mercury discharge lamp using fused silica optics. Spectra were recorded during continuous photolysis and relative radical concentrations were measured by electronic integration of suitable derivative signals, followed by manual integration of the absorption peaks so obtained. g-Factors were determined by measurement of the microwave frequency and the magnetic field, and were calculated using the Breit–Rabi equation when large hyperfine splittings from ^{31}P were present.

Samples, usually in cyclopropane solvent, were generally 0.5—1M in phosphorus compound and in the primary photochemical source of radicals.

Materials.—Di-t-butyl peroxide (purified before use), dicumyl peroxide, and acetone were commercially available. Diethyl peroxide [32] bis(trimethylsilyl) peroxide,[33] and azomethane [34] were prepared by standard methods. Acetone azine and formaldehyde azine polymer were prepared from hydrazine hydrate and the appropriate carbonyl compound.[35] Monomeric formaldehyde azine was generated by heating the polymer *in vacuo* and condensing the azine directly into the e.s.r. tube; benzene co-solvent was employed with cyclopropane in these experiments.

Proton-decoupled phosphorus n.m.r. spectra were obtained with a Varian CFT-20 spectrometer equipped with a ^{31}P probe, using a mixture of equal volumes of C_6H_6 and C_6D_6 as solvent. Chemical shifts are quoted relative to 85% H_3PO_4 as external standard, although neat triphenyl phosphite ($\delta^{31}P$ −127 p.p.m.) was sometimes employed as a standard to avoid overlap of signals.

N-*Benzyl*-N-*trimethylsilylamino*(*diethoxy*)*phosphine* (5). n-Butyl-lithium (58 ml; 2.4M solution in hexane) was added during 0.5 h to a stirred and ice-cooled solution of *N*-trimethylsilylbenzylamine [36] (25 g) in ether (100 ml). The mixture was refluxed for 2 h and then cooled in an ice-bath during addition (over 0.5 h with constant stirring) of a solution of diethyl chlorophosphite (22 g) in ether (100 ml). The mixture was stirred for 1 h at room temperature, the precipitated lithium chloride was filtered off, and the solvents removed from the filtrate under reduced

pressure. Distillation of the residue yielded the phosphine, b.p. 80—82 °C at 0.05 Torr (Found: C, 55.9; H, 8.6; N, 4.8; P, 10.5. $C_{14}H_{26}NO_2PSi$ requires C, 56.2; H, 8.8; N, 4.7; P, 10.3%); $\delta^{31}P$ −143.2 p.p.m.

Diethyl N-benzyl-N-trimethylsilylphosphoramidate (8). This compound was prepared in a similar way to (5) except that diethyl chlorophosphite was replaced by diethyl chlorophosphate which was added at room temperature to the solution of $PhCH_2(Me_3Si)NLi$. The mixture was refluxed for 12 h and worked up as for (5) to yield (8), b.p. 126 °C at 0.2 Torr (Found: C, 53.2; H, 8.3; N, 4.3; P, 9.7. $C_{14}H_{26}NO_3PSi$ requires C, 53.3; H, 8.3; N, 4.4; P, 9.9%); $\delta^{31}P$ −10.4 p.p.m.

Triethyl *N*-trimethylsilylphosphorimidate (9) could not be obtained pure from the reaction of triethyl phosphite with bis(trimethylsilyl)chloramine using the method reported in the literature.[4] This phosphazene was prepared by the method which has proved successful for $(MeO)_3P{=}NSiMe_3$.[37] Trimethylsilyl azide (20 g) was added dropwise with stirring to triethyl phosphite (29 g) at 80—100 °C during 1.5 h. The mixture was stirred for a further 8 h at 100—120 °C, after which no more nitrogen was evolved, and then distilled to yield (9) (20.8 g, 47%), b.p. 54—55 °C at 2.5 Torr (Found: C, 43.0; H, 9.6; N, 5.4; P, 12.5. $C_9H_{24}NO_3PSi$ requires C, 42.7; H, 9.5; N, 5.5; P, 12.3%); $\delta^{31}P$ +6.6 p.p.m.

Trialkyl *N*-alkylphosphorimidates of the type $(R^1O)_3P{=}NR^2$ were prepared by the reaction of the alkyl azide R^2N_3 with the phosphite $(R^1O)_3P$ in ether solvent, as described by Goldwhite *et al.*[1] Those compounds which have not been previously characterised are listed in Table 3.

Tetraethyl pyrophosphite was prepared in a pure state by the method of Anderson *et al.*[38] and, contaminated with diethyl chlorophosphite, by the method of Samuel and Silver.[11]

Reaction between Triethyl N-Methylphosphorimidate and Diethyl Chlorophosphite.—Diethyl chlorophosphite (4.70 g, 0.03 mol) in benzene (20 ml) was added dropwise to a stirred solution of $(EtO)_3P{=}NMe$ (5.86 g, 0.03 mol) in benzene (20 ml) at room temperature under nitrogen. After the addition the solution was heated gradually (oil-bath) to reflux and the ethyl chloride (identified by ^1H n.m.r. spectroscopy) evolved was collected in a trap cooled to −80 °C. After refluxing for 0.5 h, the mixture was allowed to cool and the benzene was removed under reduced pressure. Distillation of the residue yielded *diethyl N-diethoxyphosphonyl-N-methylphosphoramidate* (4.5 g), b.p. 82 °C at 0.01 Torr (Found: C, 37.2; H, 8.3; N, 4.9, P, 21.2. $C_9H_{23}NO_5P_2$ requires C, 37.6; H, 8.1; N, 4.9; P, 21.6%); $\delta^{31}P$ −140.3 (d) and −6.8 (d) p.p.m., $^2J_{P-P}$ 56 Hz; ^1H n.m.r. (in C_6H_6) showed δ 1.12 (t, $^3J_{H-H}$ 7.2 Hz, 12 H), 2.80 (doublet of doublets, $^3J_{H-P}$ 10.8, $^3J_{H-P(O)}$ 2.5 Hz, 3 H), and 3.85 (m, 8 H).

Reaction between Alkoxyl Radicals and N-Benzyl-N-trimethylsilylamino(diethoxy)phosphine.—A pentane solution (0.7 ml) containing (5) (1.7M) and the dialkyl peroxide (*ca.* 2.5M) was sealed under nitrogen in a quartz tube and irradiated with light from a Thorn 250 W ME/D high pressure mercury discharge lamp for 1—2 h. During photolysis the sample was immersed in water at 0 °C contained in a beaker with quartz window. The pentane was removed under reduced pressure and the residue dissolved in C_6H_6–C_6D_6 and examined using ^{31}P n.m.r. spectroscopy. Control experiments with samples that had been stored in the dark at 0 °C for the duration of the photolysis showed no detectable products.

TABLE 3

Physical constants of trialkyl *N*-alkylphosphorimidates $(R^1O)_3P{=}NR^2$

				Elemental analysis							
				Found (%)				Required (%)			
R^1	R^2	B.p. (°C/Torr)	^{31}P n.m.r. δ p.p.m.[a]	C	H	N	P	C	H	N	P
Me	Pr^n	34—36/2	+1.9	39.5	8.8	7.6	17.1	39.8	8.9	7.7	17.1
Et	Pr^n	54—56/0.8	+3.9	48.1	9.9	6.2	14.2	48.1	9.9	6.2	13.9
Me	Pr^i	38/1.5	+5.6	39.5	8.9	7.9	16.8	39.8	8.9	7.7	17.1
Et	Me	56—57/1	−0.3	43.4	9.2	7.2		43.1	9.3	7.2	15.9

[a] Relative to 85% aqueous H_3PO_4; C_6H_6 + C_6D_6 solvent.

[8/1207 *Received*, 30*th June*, 1978]

REFERENCES

[1] H. Goldwhite, P. Gysegem, S. Schow, and C. Swyke, *J.C.S. Dalton*, 1975, 12.
[2] For a review see W. G. Bentrude in 'Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, Vol. 2, ch. 22.
[3] R. S. Hay and B. P. Roberts, *J.C.S. Perkin II*, 1978, 770.
[4] A. M. Pinchuk, M. G. Suleimanova, and L. P. Filonenko, *J. Gen. Chem. U.S.S.R.*, 1972, **42**, 2111.
[5] R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140.
[6] B. P. Roberts and J. N. Winter, *J.C.S. Chem. Comm.*, 1978, 545 and unpublished results.
[7] J. W. Cooper, M. J. Parrott, and B. P. Roberts, *J.C.S. Perkin II*, 1977, 730.
[8] J. W. Cooper and B. P. Roberts, *J.C.S. Perkin II*, 1976, 808.
[9] D. Griller and K. U. Ingold, *Internat. J. Chemical Kinetics*. 1974, **6**, 453.
[10] A. G. Davies, D. Griller, and B. P. Roberts, *J. Amer. Chem. Soc.*, 1972, **94**, 1782.
[11] D. Samuel and B. L. Silver, *J. Org. Chem.*, 1963, **28**, 1155.
[12] B. P. Roberts and J. N. Winter, unpublished work.
[13] M. Kamachi, K. Kuwata, and S. Murahashi, *J. Phys. Chem.*, 1971, **75**, 164.
[14] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224.
[15] A. P. Claydon, P. A. Fowell, and C. T. Mortimer, *J. Chem. Soc.*, 1960, 3284.
[16] H. Kwart and K. G. King, 'd-Orbitals in the Chemistry of Silicon, Phosphorus, and Sulfur,' Springer-Verlag, Berlin, 1977; see however K. J. Shea, R. Gobeille, J. Bramblett, and E. Thompson, *J. Amer. Chem. Soc.*, 1978, **100**, 1611 and references cited therein.
[17] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993; B. P. Roberts and K. Singh, *J. Organometallic Chem.*, 1978, **159**, 31.
[18] A. G. Davies, M. J. Parrott, B. P. Roberts, and A. Skowronska, *J.C.S. Perkin II*, 1976, 1154.
[19] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 1970, **53**, 3932.
[20] H. Fischer, *Z. Naturforsch.*, 1965, **20a**, 428.
[21] D. E. Wood, R. V. Lloyd, and W. T. Lathan, *J. Amer. Chem. Soc.*, 1971, **93**, 4145.
[22] J. A. Baban, C. J. Cooksey, and B. P. Roberts, unpublished results.
[23] J. Bragin, S. Chan, E. Mazzola, and H. Goldwhite, *J. Phys. Chem.*, 1973, **77**, 1506.
[24] K. Scheffler, S. Hieke, R. Haller, and H. B. Stegman, *Z. Naturforsch.*, 1975, **30a**, 1175.

[25] (*a*) M.-H. Whangbo, S. Wolfe, and F. Bernardi, *Canad. J. Chem.*, 1975, **53**, 3040; (*b*) F. Bernardi, H. B. Schlegel, M.-H. Whangbo, and S. Wolfe, *J. Amer. Chem. Soc.*, 1977, **99**, 5633.
[26] G. Boekestein, E. H. J. M. Jansen, and H. M. Buck, *J.C.S. Chem. Comm.*, 1974, 118.
[27] A. G. Davies, M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1974, 973.
[28] M. C. R. Symons, *Mol. Phys.*, 1975, **30**, 1921.
[29] T. Berclaz, M. Geoffroy, and E. A. C. Lucken, *Chem. Phys. Letters*, 1975, **36**, 677.
[30] M. C. R. Symons, *Chem. Phys. Letters*, 1976, **40**, 226.
[31] G. W. Eastland and M. C. R. Symons, *J.C.S. Perkin II*, 1977, 833.
[32] B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *J. Amer. Chem. Soc.*, 1971, **93**, 4004.
[33] P. G. Cookson, A. G. Davies, and N. A. Fazal, *J. Organometallic Chem.*, 1975, **99**, C31.
[34] R. Renaud and L. C. Leitch, *Canad. J. Chem.*, 1954, **32**, 545.
[35] Th. Curtius and K. Thun, *J. prakt. Chem.*, 1891, **44**, 161; N. P. Neureiter, *J. Amer. Chem. Soc.*, 1959, **81**, 2910.
[36] P. L. De Benneville and M. Hurwitz, U.S.P. 2,876,209/1959 (*Chem. Abs.*, 1959, **53**, P12321 e).
[37] O. Schlak, W. Stadelmann, O. Stelzer, and R. Schmutzler, *Z. anorg. Chem.*, 1976, **419**, 275.
[38] G. W. Anderson, J. Blodinger, and A. D. Welcher, *J. Amer. Chem. Soc.*, 1952, **74**, 5309.