# Homolytic Reactions of Ligated Boranes. Part 4.[1] Electron Spin Resonance Studies of Radicals derived from Secondary Phosphine–Boranes

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Radicals produced by reaction of photochemically or thermally generated t-butoxyl radicals with dimethyl-, diethyl-, and diphenyl-phosphine–boranes have been studied in solution by e.s.r. spectroscopy. Hydrogen abstraction from $R_2PH\rightarrow BH_3$ appears to yield the phosphinyl-borane radical $R_2\dot{P}\rightarrow BH_3$ as the major product, although its e.s.r. spectrum is difficult to detect. Evidence for the competitive formation of an isomeric phosphoranyl radical $[R_2P(BH_2)H]^\bullet$ was found for dimethylphosphine–borane. No phosphine–boryl radical $R_2PH\rightarrow\dot{B}H_2$, analogous to $R_3P\rightarrow\dot{B}H_2$ obtained from the reaction of $Bu^tO^\bullet$ with a trialkylphosphine–borane, was detected. Like the isoelectronic silyl and phosphonyl radicals, $R_2\dot{P}\rightarrow BH_3$ abstracts halogen from alkyl bromides and adds readily to alkenes and isocyanides to give alkyl and imidoyl radical adducts, respectively. Spin-trapping of $R_2\dot{P}\rightarrow BH_3$ with 2-methyl-2-nitrosopropane or phenyl-*N*-t-butylnitrone affords the appropriate nitroxides, whilst with 1-nitroso-2,4,6-tri-t-butylbenzene addition takes place exclusively at oxygen to give an oxyaminyl radical.

In Part 3[1] we reported that t-butoxyl radicals react with secondary amine–boranes $R_2NH\rightarrow BH_3$ to give initially the amine–boryl radical $R_2NH\rightarrow\dot{B}H_2$ as the kinetically controlled product and that this radical rapidly abstracts hydrogen from the parent to yield the more stable isomeric aminyl–borane radical $R_2\dot{N}\rightarrow BH_3$.

The reaction of t-butoxyl radicals with tertiary phosphine–boranes affords the corresponding phosphine–boryl radicals (**1**) by abstraction of hydrogen from boron.[2] The e.s.r. parameters for (**1**) indicate that the radicals are effectively

$$Bu^tO^\bullet + R_3P\rightarrow BH_3 \longrightarrow \underset{(\mathbf{1})}{R_3P\rightarrow\dot{B}H_2} + Bu^tOH \quad (1)$$

planar at the boron centre, in contrast to the amine–boryl radicals $R_3N\rightarrow\dot{B}H_2$ which are pyramidal at boron.[3] Tertiary phosphine–boryl radicals readily abstract halogen atoms from alkyl bromides, but addition to ethylene or to other alkenes was not detected by e.s.r. spectroscopy.[2] However, phosphine–boryls do add readily through boron to *C*-nitroso or nitrone 'spin-traps' and the resulting nitroxides exhibit rich e.s.r. spectra characteristic of the particular addendum.[4]

The P→B moiety is isoelectronic[5] with Si–C; in particular, secondary phosphine–boranes $R_2PH\rightarrow BH_3$ (**2**) are isoelectronic with the diorgano(methyl)silanes $R_2SiHCH_3$ which react with t-butoxyl radicals to yield mainly silyl radicals $R_2\dot{S}iCH_3$.[6] The aims of the present work were to determine the site of hydrogen abstraction from (**2**) and to investigate the structures and chemical reactions of the radicals produced.

## Results and Discussion

E.s.r. spectra were recorded during continuous u.v. irradiation of liquid samples directly in the microwave cavity of the spectrometer.[7] The primary source of radicals was di-t-butyl peroxide (DTBP; *ca.* 15% v/v) [equation (2)], the phosphine–borane concentration was *ca.* 1M, and the solvent was generally cyclopropane–oxirane (1:1 v/v). The secondary phosphine–boranes (**2**; R = Me, Et, or Ph) were examined; u.v. irradiation

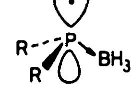
$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^\bullet \quad (2)$$

of the phosphine–boranes in the absence of DTBP afforded no e.s.r. spectra.

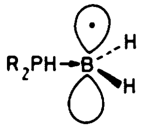
Abstraction of hydrogen from phosphorus in (**2**) would give the phosphinyl–borane radical (**3**), isoelectronic with both $R_2\dot{S}iCH_3$ and $R_2\dot{P}\rightarrow O$, whilst abstraction from boron might give a phosphine–boryl radical (**4**), analogous to (**1**). However, as we have pointed out previously,[2] alternative electronic configurations involving hypervalent phosphorus must be considered for species of the type $[X_3PBH_2]^\bullet$. Thus, it appears likely that the σ* phosphoranyl radicals[8,9] (**5**) and (**6**) or the

$R_2PH\rightarrow BH_3$

(**2**)

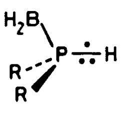


(**3**)

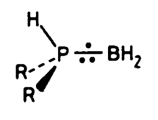


(**4**)

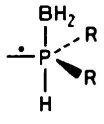
'trigonal bipyramidal' species (**7**) will be fairly close in energy to (**4**). In fact, the relatively low *g* factors (*ca.* 2.0020, less than free-spin) obtained for $R_3P\rightarrow\dot{B}H_2$ and $(RO)_3P\rightarrow\dot{B}H_2$ were taken as evidence for the existence of energetically proximate excited states of the type (**6**) for the tertiary phosphine- and trialkyl phosphite–boryl radicals.[2]



(**5**)



(**6**)



(**7**)

No e.s.r. spectra attributable to boron-centred radicals of the type (**4**) were observed during photolysis of DTBP in the presence of any of the three secondary phosphine–boranes, nor were any lines detectable within 50 G on either side of *g* = 2, even at very high gain. With diethylphosphine–borane at 183—208 K, spectra of two phosphorus-centred radicals were observed. One of these radicals [*a*(P) 708.9, *a*(4H) 2.2 G, *g* 2.0036 at 206 K] was very long-lived and persisted after u.v. irradiation ceased; it is identified as the phosphoranyl radical $Et_2\dot{P}(OBu^t)_2$,[10] presumably formed as a minor product of secondary reactions.[2] The other spectrum appeared as two groups of weak, broad lines ($\Delta B_{p-p}$ *ca.* 5 G) to low and high field of *g* = 2 and corresponded to *a*(P) 208 G; the two groups of lines were superimposable within the limits dictated by the

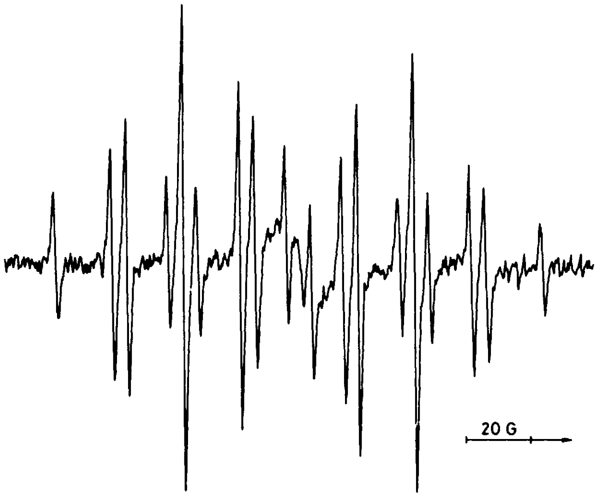


**Figure 1.** E.s.r. spectrum of the adduct radical obtained during u.v. irradiation of DTBP and dimethylphosphine–borane in ethylene–oxirane (1:1 v/v) at 183 K

noise level. Line spacings of *ca.* 12 and 18 G could be identified within each group, but a complete analysis was not possible. We tentatively assign this spectrum to the pyramidal diethylphosphinyl–borane (**3**; R = Et), since the phosphorus splitting falls within the range expected on the basis of the linear correlation [equation (3)] previously established between $a$(P) (in G) for $L_nP^{\bullet}$ and $^1J_{P-H}$ (in Hz) for its protic parent $L_nPH$.[11,12] Thus, a phosphorus splitting of 187 G would be predicted for (**3**; R = Et) since $^1J_{P-H}$ for $Et_2PH \rightarrow BH_3$ is 353 Hz.

$$a(^{31}P) = 1.52\,{}^1J_{P-H} - 350 \qquad (3)$$

With dimethylphosphine–borane no spectrum corresponding to $a$(P) *ca.* 200 G was observable, although (**3**; R = Me) will also prove very difficult to detect on account of its complex spectrum [the isoelectronic $Me_2\dot{P} \rightarrow O$ shows[13] $a$(P) 373 G and $a$(6H) 5.6 G]. However, apart from that of the extremely persistent phosphoranyl[10] $Me_2\dot{P}(OBu^t)_2$ [$a$(P) 708.5, $a$(6H) 2.6 G, $g$ 2.0036 at 202 K], the spectrum of a second phosphorus-centred radical was apparent for which no analogue from $Et_2PH \rightarrow BH_3$ was detected. This second radical gave rise to a doublet of doublets, presumably because of coupling to one $^{31}P$ nucleus and one proton [$a$(P) 576.1, $a$(H) 211.1 G, $g$ 2.0038 at 177 K]; no further fine structure was resolvable, although the lines were very broad ($\Delta B_{p-p}$ 16—18 G), and the radical was short-lived, decaying within the fall-time of the spectrometer (1 s) at 177 K when u.v. irradiation ceased. We suggest that this radical is the σ* phosphoranyl (**5**; R = Me), probably solvent-stabilised by co-ordination of oxirane to the boron, produced by hydrogen atom abstraction from the $BH_3$ group of $Me_2PH \rightarrow BH_3$. However, at this time we cannot exclude the alternative assignment to the radical anion of the phosphine–borane $[Me_2PH \rightarrow BH_3]^{-\bullet}$. Nishikida and Williams[14] have reported generally similar e.s.r. parameters for the trimethylphosphoranyl radical $[Me_3PH]^{\bullet}$ [$a$(P) 484, $a$(H) 182 G, $g$ 2.0035 at 77 K]. It is noteworthy that whilst $[PhP(OEt)_2OBu^t]^{\bullet}$ has a 'ligand π' SOMO, analogous to that of the tertiary phosphine–boryl (**1**), in which the unpaired electron is centred on the benzene ring, the presence of a hydrogen ligand as in $[PhPH_2OBu^t]^{\bullet}$ induces a switch to a hypervalent phosphoranyl ground state analogous to (**5**).[15]

With diphenylphosphine–borane no e.s.r. signals were detected under high gain within ±500 G of $g$ = 2 between 173 and 253 K. However, the solution became pale yellow during u.v. irradiation and thus the DTBP may have been 'screened' to some extent.

**Table 1.** E.s.r. parameters for $L_nPCH_2\dot{C}R_2$ formed by addition of phosphinyl–borane radicals to ethylene or 1,1-di-t-butylethylene

| | | | | Hyperfine splittings (G) | | |
|---|---|---|---|---|---|---|
| $L_nP$ | R[a] | $T$/K | $g$ Factor[b] | $a(^{31}P)$[b] | $a(2H_{\alpha})$ | $a(2H_{\beta})$ |
| $Me_2P(\rightarrow BH_3)$ | H | 165 | 2.0027 | 71.3 | 22.0 | 17.3 |
| | H | 185 | 2.0027 | 70.8 | 22.0 | 17.5 |
| | Bu$^t$[c] | 171 | 2.0024 | 85.9 | | 13.4 |
| | Bu$^t$[c] | 205 | 2.0024 | 84.2 | | 13.4 |
| | Bu$^t$[c] | 260 | 2.0024 | 81.9 | | 13.5 |
| $Et_2P(\rightarrow BH_3)$ | H | 185 | 2.0027 | 64.3 | 22.0 | 17.8 |
| | Bu$^t$ | 207 | 2.0024 | 79.5 | | 13.4 |
| | Bu$^t$ | 263 | 2.0024 | 77.4 | | 13.4 |
| $Ph_2P(\rightarrow BH_3)$ | Bu$^t$[d] | 171 | 2.0025 | 93.6 | | 13.1 |
| | Bu$^t$[d] | 205 | 2.0025 | 91.8 | | 13.1 |
| | Bu$^t$[d] | 260 | 2.0025 | 89.5 | | 13.2 |

[a] For R = H the solvent was ethylene–oxirane (1:1 v/v); for R = Bu$^t$ it was cyclopropane–oxirane (1:1 v/v). [b] Corrected using the Breit-Rabi equation. [c] First half-life for decay at 234 K was *ca.* 114 s. [d] Approximate first half-lives for decay at 182, 214, and 234 K were 120, 4, and 1 s, respectively.

We conclude that t-butoxyl radicals abstract hydrogen from the PH group of $R_2PH \rightarrow BH_3$ and that abstraction from the $BH_3$ group may take place competitively, at least with $Me_2PH \rightarrow BH_3$, although the results are not entirely conclusive on the latter point. Certainly, hydrogen abstraction from boron does not afford a phosphine–boryl radical, as it does with a tertiary phosphine–borane.[2]

t-Butoxyl radicals are known to abstract hydrogen rapidly from phosphorus in a dialkylphosphine oxide and in a variety of other disubstituted phosphine oxides to yield phosphonyl radicals of the type $X_2\dot{P} \rightarrow O$.[11,12,16,17]

A number of experiments in which a third reactant was present along with the phosphine–borane and DTBP were carried out in the hope of further characterising the radicals formed from $R_2PH \rightarrow BH_3$; the results are described in the following sections.

*Reactions with Alkenes.*—Phosphine–boryl radicals (**1**) do not add to ethylene[2] whereas silyl and phosphonyl radicals add readily.[6,12] U.v. irradiation of an ethylene–oxirane (1:1 v/v) solution containing dimethylphosphine–borane and DTBP gave rise to the spectrum shown in Figure 1 and assigned to the β-phosphorus-substituted ethyl radical $Me_2P(\rightarrow BH_3)CH_2\dot{C}H_2$. The alternative assignment to $Me_2P(BH_2)(H)CH_2\dot{C}H_2$ is considered less probable and it seems likely that rearrangement of the $R_2P(BH_2)H$ moiety to an $R_2P(\rightarrow BH_3)$ group would accompany or rapidly follow addition of (**5**) to an alkene or to the other unsaturated molecules discussed later, since there is no evidence that $R_3P(BH_2)H$ is present alongside $R_3P \rightarrow BH_3$ even in donor solvents. A similar transient adduct was obtained from $Et_2PH \rightarrow BH_3$, and persistent[18] radicals of the type $R_2P(\rightarrow BH_3)CH_2\dot{C}Bu^t_2$ were derived by analogous addition to $Bu^t_2C{=}CH_2$. E.s.r. parameters for the adducts are collected in Table 1 and the spectrum of the radical derived from $Me_2PH \rightarrow BH_3$ and $Bu^t_2C{=}CH_2$ is shown in Figure 2. Only *one* adduct spectrum was obtained from each phosphine–borane.

The eclipsed conformation (**8**), in which hyperconjugative interaction between the unpaired electron on $C_{\alpha}$ and the β-C–P σ orbital is maximised, is favoured for the adducts to both

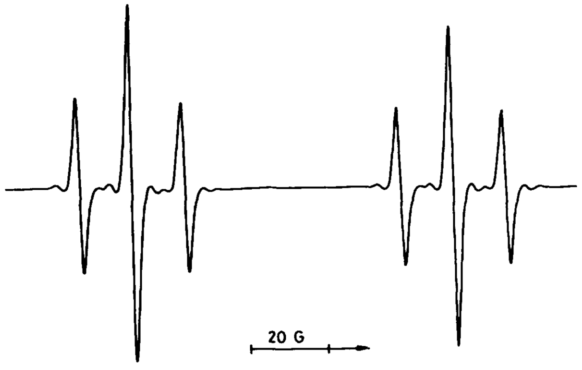
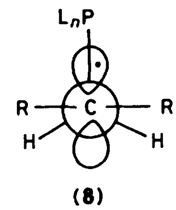


Figure 2. E.s.r. spectrum of the adduct radical obtained during u.v. irradiation of DTBP, dimethylphosphine–borane, and 1,1-di-t-butylethylene in cyclopropane–oxirane (1:1 v/v) at 260 K

alkenes, as evidenced by the magnitudes and temperature dependencies of $a(2\mathrm{H}_\beta)$ and $a$(P).[19] This electronic conformational preference is reinforced by steric effects for the di-t-butylethylene adducts and (**8**) is strongly favoured in our temperature range when R = $\mathrm{Bu}^t$. For adducts of the type (**8**; R = $\mathrm{Bu}^t$) we have shown[20] that an approximately linear relationship exists between the P-3*s* character of the β-C–P bond (as measured by $^1J_{\mathrm{P-H}}$ for $\mathrm{L}_n\mathrm{PH}$) and $a$(P), implying that the extent of hyperconjugative unpaired electron delocalisation into this bond is virtually independent of the nature of $\mathrm{L}_n\mathrm{P}$. On this basis we would expect values of $a$(P) for [**8**; $\mathrm{L}_n\mathrm{P} = \mathrm{R}_2\mathrm{P}(\rightarrow\mathrm{BH}_3)$] in the region of 65—70 G, rather smaller than those obtained (Table 1). However, the differences in $a$(P) for the three adducts do parallel the increase in $^1J_{\mathrm{P-H}}$ along the series $\mathrm{Et_2PH{\rightarrow}BH_3 < Me_2PH{\rightarrow}BH_3 < Ph_2PH{\rightarrow}BH_3}$.



(**8**)

It is more difficult to estimate the P-3*s* contribution to the β-C–P σ orbital, and thus to predict $a$(P), if $\mathrm{L}_n\mathrm{P} = \mathrm{R_2P(BH_2)(H)}$, when the geometry at the five-co-ordinate phosphorus will presumably be intermediate between trigonal bipyramidal (TBP) and square pyramidal.[21] The P-3*s* character of an apical P–X bond is much less than that of an equatorial P–X bond in a TBP phosphorane $\mathrm{PX}_5$ and this is reflected by $^1J_{\mathrm{P-H}}$ for apical and equatorial P–H bonds.[22] Although the values of $a$(P) for (**8**) are consistent with a quasi-equatorial P–$\mathrm{C}_\beta$ bond in the adducts to alkenes, further speculation is not warranted at this time.

*Reactions with Alkyl Isocyanides.*—The phosphorus-centred radicals derived from dimethyl- or diethyl-phosphine–borane added to t-butyl or methyl isocyanide to form imidoyl radicals[23] (**9**; R = Me or $\mathrm{Bu}^t$); the e.s.r. parameters are given in

$$\mathrm{RN{=}\dot{C}PL}_n \quad (\mathbf{9})$$

Table 2. Again, it is not certain whether $\mathrm{L}_n\mathrm{P}$ is $\mathrm{R_2P(\rightarrow BH_3)}$ or $\mathrm{R_2P(BH_2)(H)}$, although we favour the former.

**Table 2.** E.s.r. parameters for $\mathrm{L}_n\mathrm{P\dot{C}{=}NR}$ formed by addition of phosphinyl-borane radicals to alkyl isocyanides in cyclopropane–oxirane (1:1 v/v)

| | | | | Hyperfine splittings (G) | |
|---|---|---|---|---|---|
| $\mathrm{L}_n\mathrm{P}$ | R | *T*/K | *g* Factor[a] | $a(^{31}\mathrm{P})$[a] | $a$(N) |
| $\mathrm{Me_2P(\rightarrow BH_3)}$ | Me | 202 | 2.0015 | 87.7[b] | 6.1[b] |
| | $\mathrm{Bu}^t$ | 194 | 2.0016 | 89.7 | 6.3 |
| | $\mathrm{Bu}^t$ | 239 | 2.0016 | 89.7 | 6.3 |
| | $\mathrm{Bu}^t$ | 293[c] | 2.0016 | 89.7 | 6.3 |
| $\mathrm{Et_2P(\rightarrow BH_3)}$ | Me | 210 | 2.0015 | 75.7 | 6.3 |
| | $\mathrm{Bu}^t$ | 194 | 2.0017 | 76.8 | 6.7 |
| | $\mathrm{Bu}^t$ | 249 | | 76.7 | 6.8 |

[a] Corrected using the Breit–Rabi equation. [b] A further splitting (*ca.* 1.2 G) from three equivalent protons was poorly resolved at 206 K. [c] The spectrum of $\mathrm{Bu}^{t\bullet}$ was not detected at this temperature.

**Table 3.** E.s.r. parameters for spin adducts (**10**)—(**12**) in benzene

| | | | | Hyperfine splittings (G) | |
|---|---|---|---|---|---|
| Spin adduct | $\mathrm{L}_n\mathrm{P}$ | *T*/K | *g* Factor | $a$(N) | Others |
| (**10**) | $\mathrm{Me_2P(\rightarrow BH_3)}$ | 298 | 2.0066 | 11.3 | 7.4 (1P) |
| | $\mathrm{Me_2P(\rightarrow BH_3)}$[a] | 313 | 2.0067 | 11.3 | 7.4 (1P) |
| | $\mathrm{Et_2P(\rightarrow BH_3)}$ | 308 | 2.0067 | 10.7 | 9.1 (1P) |
| (**11**) | $\mathrm{Me_2P(\rightarrow BH_3)}$ | 312 | 2.0036 | 9.6 | 2.1 (2H) |
| | $\mathrm{Et_2P(\rightarrow BH_3)}$ | 304 | 2.0036 | 9.5 | 2.0 (2H) |
| (**12**) | $\mathrm{Me_2P(\rightarrow BH_3)}$ | 301 | 2.0059 | 14.4 | 9.7 (1P), 3.5 (1H) |
| | $\mathrm{Et_2P(\rightarrow BH_3)}$ | 304 | 2.0060 | 14.4 | 9.7 (1P), 3.3 (1H) |
| | $\mathrm{(EtO)_2P(\rightarrow O)}$[b] | *ca.* 300 | 2.0059 | 14.75 | 24.75 (1P), 3.18 (1H) |
| | $\mathrm{Et_2P(\rightarrow S)}$[b] | *ca.* 300 | 2.0058 | 14.10 | 14.30 (1P), 3.38 (1H) |

[a] Derived from $[^2\mathrm{H}_9]\mathrm{Bu}^t\mathrm{NO}$; no further splittings were resolved, although the lines were slightly narrower than those obtained from the non-undeuteriated MNP. [b] Data from ref. 30.

A number of other types of phosphorus-centred radicals and trialkylsilyl radicals are known to add in a similar fashion to alkyl isocyanides to give imidoyl radicals.[23] The silicon, but not the phosphorus, adducts with t-butyl isocyanide undergo ready β-scission [equation (4)]. In the present experiments the

$$\mathrm{Bu^tN{=}\dot{C}SiR_3} \longrightarrow \mathrm{Bu^{t\bullet}} + \mathrm{N{\equiv}CSiR_3} \qquad (4)$$

spectrum of the adduct derived from $\mathrm{Bu^tNC}$ and $\mathrm{Me_2PH{\rightarrow}BH_3}$ was still observable at 293 K and $\mathrm{Bu}^{t\bullet}$ was not detectable.

*Reactions with Alkyl Bromides.*—Between 177 and 220 K, u.v. irradiation of cyclopropane–oxirane solutions containing diethylphosphine–borane, DTBP, and an alkyl bromide ($\mathrm{Pr^nBr}$, $\mathrm{Pr^iBr}$, or $\mathrm{Bu^tBr}$, each *ca.* 1.5M) gave rise to the e.s.r. spectrum of the corresponding alkyl radical, probably formed by halogen abstraction by $\mathrm{Et_2\dot{P}{\rightarrow}BH_3}$. Both $\mathrm{(EtO)_2\dot{P}{\rightarrow}O}$[16,17b] and $\mathrm{R_3Si^\bullet}$[24] react similarly with alkyl bromides; the spectra obtained in the present experiments were similar in strength to those derived from the phosphonyl radical, but less intense than those obtained from reactions of the silyl radical.

*Reactions with* C-*Nitroso Compounds and Phenyl*-N-*t-butylnitrone* (N-*t-Butylbenzylideneamine* N-*Oxide*) (PBN).—A number of spin-trapping[25] experiments were carried out by generating $\mathrm{Bu^tO^\bullet}$ thermally from di-t-butyl hyponitrite[26] (TBHN) in the presence of $\mathrm{Me_2PH{\rightarrow}BH_3}$ or $\mathrm{Et_2PH{\rightarrow}BH_3}$ (*ca.* 1.5M) and the spin-trap (*ca.* 0.01M) in benzene solvent. Apart from PBN, 2-methyl-2-nitrosopropane (MNP) and 1-nitroso-2,4,6-tri-t-butylbenzene (TBN) were investigated; the results are summarised in Table 3 and e.s.r. spectra of the spin-adducts

**Figure 3.** E.s.r. spectrum of the oxyaminyl radical [**11**; $L_nP$ = $Me_2P(\rightarrow BH_3)$] in benzene at 312 K

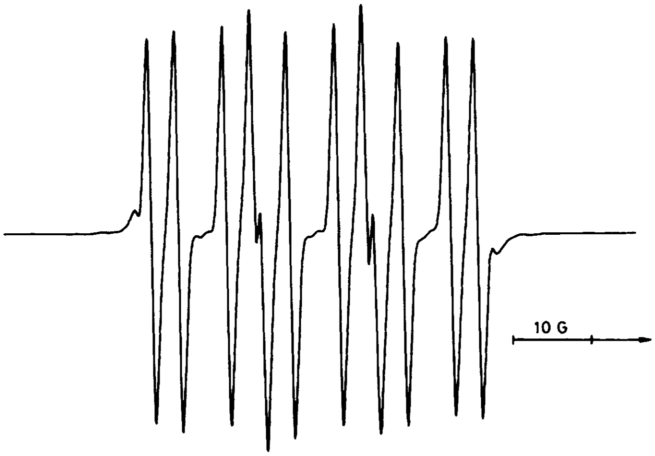
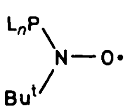


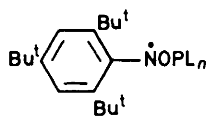
**Figure 4.** E.s.r. spectrum of the nitroxide [**12**; $L_nP$ = $Me_2P(\rightarrow BH_3)$] in benzene at 301 K

formed with TBN and PBN are shown in Figures 3 and 4, respectively. Only one adduct spectrum was observed from each phosphine–borane and no adducts arising from addition through boron[4] were detected with any of the spin-traps. In all the adducts we believe $L_nP = R_2P(\rightarrow BH_3)$, although we cannot completely exclude the presence of the isomeric $R_2P(BH_2)(H)$ moiety on the basis of the spectroscopic data.

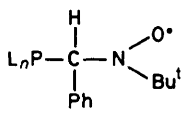
Nitroxides of the type (**10**) are obtained from MNP and the e.s.r. parameters are similar to those[27] of [**10**; $L_nP$ = $(EtO)_2P(\rightarrow O)$] [$a$(N) 9.9, $a$(P) 13.1 G]. With the ambident



**(10)**



**(11)**



**(12)**

spin-trap TBN,[28] oxyaminyl adducts of the type (**11**), rather than nitroxides, were produced. Similar exclusive addition to *oxygen* has been reported[29] for $Et_2\dot{P}\rightarrow O$, whilst the more electrophilic $(EtO)_2\dot{P}\rightarrow O$ adds exclusively to *nitrogen*; $R_2\dot{P}\rightarrow BH_3$ would be expected to behave like $R_2\dot{P}\rightarrow O$. The phosphorus atom in (**11**) appears to be confined to the nodal plane of the SOMO, accounting for the unresolvably small value of $a$(P).

Nitroxides of the type (**12**) are produced by addition of $R_2\dot{P}\rightarrow BH_3$ to PBN; the e.s.r. parameters of the known[30] adducts [**12**; $L_nP$ = $(EtO)_2P(\rightarrow O)$ or $Et_2P(\rightarrow S)$] are included in Table 3. As judged from the magnitude of $a(H_\beta)$,[30–32] the conformations about the N–C$_\beta$ bond are similar for all the PBN adducts listed in Table 3 and thus $a$(P) should reflect the P-3$s$ character of the $L_nP$–C$_\beta$ bond.[20,33] Therefore, a phosphorus splitting of 9.7 G is not unreasonable for [**12**; $L_nP$ = $R_2P(\rightarrow BH_3)$] in comparison with the values of $a$(P) for [**12**; $L_nP$ = $(EtO)_2P(\rightarrow O)$ or $Et_2P(\rightarrow S)$].

## Experimental

E.s.r. spectra were recorded with a Varian E-109 or E-4 instrument operating at *ca.* 9.2 GHz. The techniques used for sample preparation and for the detection of transient photochemically generated free radicals have been described previously.[2,7] Samples were sealed in evacuated Suprasil quartz tubes (4 mm o.d. × 3 mm i.d. or 3 mm o.d. × 2 mm i.d., depending on the dielectric constant of the contents). The light source was an Osram HBO-500 W/2 mercury discharge lamp; after focussing with two 10 cm focal length quartz lenses and passage through an aqueous $NiSO_4$–$CoSO_4$ filter solution, the light incident on the sample was mainly in the wavelength region 240—340 nm.

For the spin-trapping experiments, a benzene solution containing the trap and the phosphine–borane was deaerated in the sample tube by purging with a fine stream of argon or nitrogen bubbles. After closure of the tube with a self-sealing rubber cap and checking for the absence of e.s.r. signals, a deaerated solution of TBHN in benzene was introduced by syringe, and the sample was rapidly shaken and returned to the spectrometer cavity. The usual precautions to exclude light were taken when working with MNP.

*Materials.*—N.m.r. spectra were obtained with a Varian XL-200 instrument. The solvent was $C_6D_6$ or $C_6D_6$–$C_6H_6$, with tetramethylsilane internal standard ($^1$H) or $BF_3 \cdot Et_2O$ ($^{11}$B) external standard. All preparations and handling of dialkylphosphine–boranes were conducted under dry argon or nitrogen.

The spin-traps MNP, TBN, and PBN were obtained commercially (Aldrich). 1,1-Di-t-butylethylene (b.p. 44—46 °C at 17 Torr) was prepared by dehydration of 2,2,3,4,4-pentamethylpentan-3-ol, as described by Newmann *et al.*;[34] material further purified by preparative g.l.c. gave indistinguishable results. Di-t-butyl hyponitrite[26] and methyl isocyanide[35] were prepared according to published methods; other reagents, apart from the phosphine–boranes, and solvents were commercial products.

*Dimethylphosphine–borane.* This was prepared by reduction of (chloro)dimethylphosphine (Strem) with lithium borohydride by a route similar to that used by Nöth and Vetter[36] to prepare $(Me_2N)_2PH\rightarrow BH_3$. (Chloro)dimethylphosphine (5.0 g, 51.8 mmol) in dry diethyl ether (30 cm$^3$) was added dropwise to a stirred solution of lithium borohydride (1.2 g, 55.1 mmol) in ether (30 cm$^3$) at −40 °C. After the addition, the mixture was allowed to warm to room temperature and stirred for a further 1 h before precipitated lithium chloride was removed by filtration. Removal of ether from the filtrate under reduced pressure and distillation of the residue gave the phosphine–borane [b.p. 45—46 °C at 5 Torr (lit.,[37] vapour pressure 5.6 Torr at 45 °C); yield 26%]; $^{11}$B n.m.r. δ −37.8 (d of q, $^1J_{B-H}$ 97.6, $^1J_{B-P}$ 50.4 Hz); $^1$H n.m.r. essentially as reported previously,[38] in particular δ(P$H$) 4.13 (d of decets, $^1J_{P-H}$ 361 Hz).

*Diethylphosphine–borane.* Diethylphosphine (strem: 2.0 g, 22.2 mmol) in dry ether (10 $cm^3$) was added dropwise with stirring at room temperature to dimethyl sulphide–borane (2.3 $cm^3$ of a 10M solution in $Me_2S$; Aldrich) in ether (10 $cm^3$). The mixture was stirred for 1 h after the addition, ether and dimethyl sulphide were removed under reduced pressure at 25 °C, and the residue was distilled to yield the phosphine–borane (b.p. 45—46 °C at 2 Torr); $^1H$ n.m.r. essentially as described previously[38] [$\delta(PH)$ 3.98 (d of octets, $^1J_{P-H}$ 353 Hz]; $\delta(^{11}B)$ $-41.1$ (d of q, $^1J_{B-H}$ 96.8, $^1J_{B-P}$ 49.6 Hz).

*Diphenylphosphine–borane.* This was prepared from $Me_2S\cdot BH_3$ and diphenylphosphine as described for the diethylphosphine complex. It was isolated as a crystalline solid which was further purified by high performance liquid chromatography on Partisil 5 silica gel with light petroleum (b.p. 40—60 °C)–ethyl acetate (55:45 v/v) as eluant; m.p. 44—45 °C (lit.,[39] 43—44 °C): $\delta(^{11}B)$ $-$ 38.1 (d of q, $^1J_{B-H}$ 94.8, $^1J_{B-P}$ 46.8 Hz); $\delta(PH)$ 5.83 (d of q, $^1J_{P-H}$ 378, $^3J_{P-H}$ 7.3 Hz).

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