The Use of Spin Traps to characterize Sulphur- and Phosphorus-containing Radicals from *OO*-Dialkyl Hydrogen Phosphorodithioates, Zinc Bis-(*OO*-di-isopropyl phosphorodithioate), and Related Compounds

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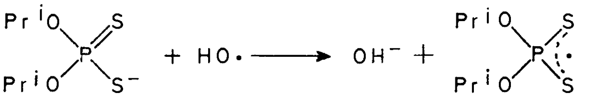
A spin-trapping method, in conjunction with e.s.r. spectroscopy, has been employed to demonstrate that thiyl radicals are formed in the reactions of the hydroxyl radical with a variety of sulphur-containing compounds: radicals trapped with the nitromethane *aci*-anion have been characterised on the basis of the *g* values and β-proton splittings of the resulting adducts. The approach has been extended to the detection of radicals formed in the oxidation of some dialkyl phosphonates and in the photolytic decomposition of sulphur- and phosphorus-containing substrates; the magnitude of $a(^{31}P)$ in the resulting adducts is particularly informative. Complicating features which arise from nucleophilic attack by substrates on the traps have been noted. Finally the spin trapping–e.s.r. technique has been applied to the detection of radicals formed from the antioxidant zinc bis-(*OO*-di-isopropyl phosphorodithioate) by electrochemical oxidation and by reaction with t-butyl hydroperoxide.

ALKANETHIYL radicals (RS•), like alkoxyl radicals,[1] are not directly detectable in solution by e.s.r. spectroscopy, probably on account of the large anisotropy in their *g* values.[2] The technique of spin-trapping (employing the nitromethane *aci*-anion) has however been employed [3] in conjunction with e.s.r. spectroscopy to demonstrate that thiyl radicals are formed as primary intermediates in the oxidation of both thiols and disulphides by the hydroxyl radical and in the reaction between thiols and Ce^{IV}. Sulphur-centred radicals have been proposed as possible intermediates in the decomposition of more complex sulphur-containing species which find widespread use as antioxidants:[4] for example, it has been suggested that the decomposition of zinc bis-(*OO*-dialkyl phosphorodithioate)s, $Zn[(RO)_2P(S)S]_2$, proceeds *via* radicals of the type $(RO)_2P(S)S•$ (see refs. 5 and 6) and that the radical-initiated reaction between zinc diethyldithiocarbamate and tetralin hydroperoxide may involve $Et_2NC(S)S•$ as an intermediate.[7] We now report experiments designed to detect sulphur- (and, where appropriate, phosphorus-) centred radicals if these are formed in the reactions of *OO*-dialkyl hydrogen phosphorodithioates (which are themselves autoxidation inhibitors [5]), their zinc complexes, and some related compounds. In particular, reactions under photolytic conditions and reactions with the hydroxyl radical have been investigated, both in the presence and in the absence of a variety of spin-trapping agents.

RESULTS AND DISCUSSION

Oxidation with the Hydroxyl Radical:—(a) *In the absence of spin traps*. In view of the ease with which the hydroxyl radical [from the titanium (III)-hydrogen peroxide couple] effects one-electron oxidation of a range of sulphur-containing compounds (see, for example, ref. 3) it might be anticipated that species such as the *OO*-di-isopropyl phosphorodithioate anion (1) would undergo a similar oxidation process [reactions (1) and (2)].

$$Ti^{III} + H_2O_2 \longrightarrow Ti^{IV} + HO• + OH^- \qquad (1)$$



(1) (2) (2)

When an aqueous solution of *OO*-di-isopropyl ammonium phosphorodithioate (0.02M) † flowed together with solutions of titanium(III) chloride (0.008M) and hydrogen peroxide (0.03M), with a pH after mixing of *ca.* 9, through the cavity of an e.s.r. spectrometer under normal flow-system conditions (see Experimental section), no e.s.r. spectrum could be detected. Despite this, the absence of the signals [8] expected from the complexed forms of $•O_2H$ (S_1 and S_2) indicates that the substrate nevertheless acts as an effective scavenger for the hydroxyl radicals formed in reaction (1), preventing them from reacting with further hydrogen peroxide. Under similar conditions, no signals could be detected in the corresponding reactions of the diethyldithiocarbamate and ethyl xanthate anions (employed as their sodium and potassium salts, respectively). Nor could signals be detected when the parent acids were used in place of their anions (here the pH of the solutions after mixing was *ca.* 1).

One would expect the scavenging of hydroxyl by these substrates to lead to the formation of organic radicals. Failure to detect such radicals by e.s.r. spectroscopy may be the result of their further rapid reaction (*e.g.* oxidation [9] by H_2O_2 or reduction [10] by Ti^{III}); alternatively, it

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† Concentrations quoted here and elsewhere are those before mixing.

[1] M. C. R. Symons, *J. Amer. Chem. Soc.*, 1969, **91**, 5924.

[2] T. Kawamura, P. J. Krusic, and J. K. Kochi, *Tetrahedron Letters*, 1972, 4075; A. J. Elliot and F. C. Adam, *Canad. J. Chem.*, 1974, **52**, 102.

[3] B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 892.

[4] G. Scott, *Chem. and Ind.*, 1963, 271.

[5] J. A. Howard, Y. Ohkatsu, J. H. B. Chenier, and K. U. Ingold, *Canad. J. Chem.*, 1973, **51**, 1543.

[6] P. I. Sanin, I. F. Blagovidov, A. B. Vipper, A. M. Kuliev, S. E. Krein, K. S. Ramaya, G. I. Shor, V. V. Sher, and Yu. S. Zaslavski, Proceedings of the Eighth World Petroleum Congress, 1971, vol. 5, p. 91.

[7] J. D. Holdsworth, G. Scott, and D. Williams, *J. Chem. Soc.*, 1964, 4692.

[8] R. O. C. Norman and B. C. Gilbert, *Adv. Phys. Org. Chem.*, 1967, **5**, 53.

[9] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1974, 824.

[10] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1973, 2174.

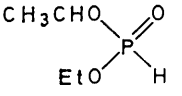
may be due to the operation of relaxation processes which cause large line-widths. Since in radical (2), and in related radicals from the other substrates, the unpaired electron should be localised to a large extent on the sulphur atoms, the latter explanation may well be the correct one. [On the basis of the data for the anisotropic spectra of radicals of type (2), detected[11] during the u.v. irradiation of *OO*-dialkyl hydrogen phosphorodithioates glasses (*e.g.* g 2.0023, 2.015, 2.014; A 2.4, 2.6, 2.6 mT), broad isotropic spectra for these species would be anticipated; we note that a doublet (a 2.5 mT) has been detected[5] during the photolysis of an *OO*-dialkyl hydrogen phosphorodithioate and a zinc bis-(*OO*-dialkyl phosphorodithioate) (though the precise conditions used were not described)].

Excessive line broadening cannot explain the failure to detect carbon-centred radicals from (1) and related compounds: nor would we expect them to be rapidly destroyed by oxidation or reduction processes. We conclude that such radicals are not formed to any significant extent and therefore that oxidation at sulphur [reaction (2)] represents the major reaction pathway.

It has been demonstrated[3] that sulphinyl (RSO•) and sulphonyl (RSO_2•) radicals may be formed by subsequent oxidation of alkanethiyl (RS•) radicals, for example by excess of hydrogen peroxide; however, we could not detect such species in a series of experiments with *OO*-dialkyl phosphorodithioate, diethyldithiocarbamate, and ethyl xanthate anions in which reagent concentrations were varied substantially ([substrate] 0.005—0.1M; [H_2O_2] 0.03—0.06M; [Ti^{III}] constant at 0.008M).

We have also investigated the reaction between the hydroxyl radical and diethyl phosphonate, $(EtO)_2P(O)H$. At pH *ca.* 9, oxidation of this substrate (0.05M) with hydroxyl resulted in the observation of e.s.r. signals from •CHMeOH and $\cdot CH_2CH_2OH$ (in the concentration ratio *ca.* 10 : 1); since the oxidation of ethanol under these conditions yields •CHMeOH and $\cdot CH_2CH_2OH$ in a similar ratio, it seems likely that these species are not direct products of a reaction between •OH and $(EtO)_2P(O)H$ but result from subsequent reaction of ethanol formed by base-catalysed hydrolysis of the phosphonate ester. We have also detected the formation of phenoxyl radicals[12] in the oxidation of diphenyl phosphonate under similar conditions.

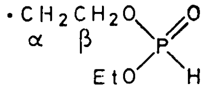
Under acid conditions (pH 1.5) no radicals could be detected by e.s.r. spectroscopy in the oxidation of diethyl phosphonate (0.05M) but when the concentration of substrate was increased to 0.3M signals attributable to the radicals (3) and (4) were detected [splittings ±0.01 mT, $g \pm 0.000\,1$]. These are the radicals characterised previously in this system by Metcalfe and Waters.[13] A feature of note is that the concentration of substrate needed for their detection is much greater (by a factor of *ca.* 10) than the concentrations typically employed for the detection of carbon-centred radicals from related substrates (*e.g.* ethanol); this suggests that the radicals detected are not formed in the main oxidation sequence. No radicals were detected in the oxidation of diphenyl phosphonate under similar conditions.



(3)

a(3H)	2·46 mT
a(1H)	1·77 mT
a(P)	1·77 mT

g 2·0029



(4)

a(2H)	2·44 mT (β)
a(2H)	2·24 mT (α)

g 2·0026

Dialkoxyphosphoryl radicals, $(RO)_2\dot{P}{=}O$, which would be formed by abstraction of the phosphorus-bonded hydrogen atom, have been detected in low-temperature photolytic studies[14] and can be recognised by their g values (2.004—2.005) and large ^{31}P splittings (*ca.* 70.0 mT). It is possible that these radicals are formed in our system but that their spectra are undetectable either because of the operation of a line-broadening process or because of further rapid reaction (*e.g.* fragmentation, or reaction with Ti^{III} or H_2O_2). Attempts to confirm the mediation of phosphorus-centred radicals are described in the next section.

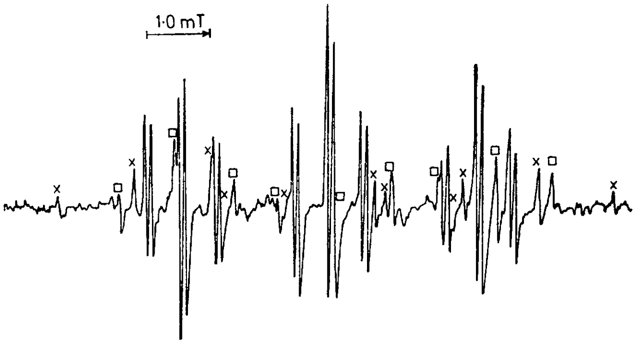


FIGURE 1 E.s.r. spectrum of the spin adduct (5) formed from the oxidation of *OO*-di-isopropyl ammonium phosphorodithioate with •OH in the presence of the *aci*-anion of nitromethane. Signals from $CH_3NO_2^{\cdot-}$ (×) and $HOCH_2NO_2^{\cdot-}$ (□) are indicated

(b) *Reactions in the presence of nitroalkane* aci-*anions.* The anion $^-CH_2NO_2$ is a convenient spin-trap for a wide range of radicals (R•) generated in aqueous flow systems at pH *ca.* 9: the first formed radicals can be characterised on the basis of the values of a(β-H), long-range splittings (where appropriate) and, in some cases, g values, of the resulting adducts $RCH_2NO_2^{\cdot-}$.[15,16]

Oxidation of *OO*-di-isopropyl ammonium phosphorodithioate by the hydroxyl radical in the presence of nitromethane at pH *ca.* 9 results in the detection of an e.s.r. spectrum (Figure 1) which we believe to be that of

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[11] M. Sato, M. Yanagita, Y. Fujita, and T. Kwan, *Bull. Chem. Soc. Japan*, 1971, **44**, 1423.

[12] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

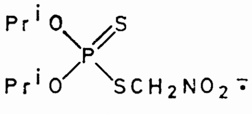
[13] A. R. Metcalfe and W. A. Waters, *J. Chem. Soc.* (*B*), 1967, 340.

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

[15] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

[16] B. C. Gilbert, J. P. Larkin, R. O. C. Norman, and P. M. Storey, *J.C.S. Perkin II*, 1972, 1508.

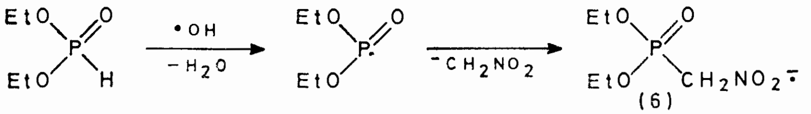
the adduct (5), formed by addition of the radical (2) to the trap. The assignment of this structure is made on the basis of the g value, which is typical of nitro radical-anions with a sulphur substituent in the β-position, and the unusually low β-proton splitting [3,15,17] [a(H) for $CH_3NO_2^{\cdot-}$ is 1.20 mT]. The spectrum also shows a very small doublet splitting consistent with the presence of a γ-phosphorus atom [contrast the much larger splittings from ^{31}P when it is in the β-position with respect to the radical centre, *e.g.* in (3), for which hyperconjugative interaction [16] plays an important role in spin transmission].



(5)

a(N) 2·325 mT
a(2H) 0·538 mT
a(P) 0·100 mT
g 2·0055

The results of oxidation studies on other sulphur-containing substrates in the presence of nitroalkane *aci*-anions are summarised in Table 1: assignments are based on the considerations outlined above. [The observed signals are accompanied by weak signals from the radical-anion of the parent nitroalkane and, in the reactions in the presence of $^{-}CH_2NO_2$, by signals from the hydroxyl spin-adduct ($HOCH_2NO_2^{\cdot-}$)[18]]



(3)

(6)

a(N) 2·470 mT
a(2H) 0·980 mT
a(P) 3·773 mT
g 2·0050

These findings suggest that electron transfer from the sulphur-containing anions to the hydroxyl radical [see equation (2)] is rapid and that these anions compete effectively with $^{-}CH_2NO_2$ as scavengers for ·OH. We conclude that the thiyl radicals, though not directly detected, are nevertheless important intermediates in the oxidation of *OO*-dialkyl phosphorodithioates and related substrates.

TABLE 1

E.s.r. parameters of spin-adducts of nitroalkane *aci*-anions [a]

Substrate	Trap	Spin-adduct	Hyperfine splittings (mT) [b] a(N)	a(H)	a(P)	g [c]
$(Pr^iO)_2P(S)S^-$	$^{-}CH_2NO_2$	$(Pr^iO)_2P(S)SCH_2NO_2^{\cdot-}$	2.325	0.538(2)	0.100	2.005 5
$(Pr^iO)_2P(S)S^-$	$^{-}CHMeNO_2$	$(Pr^iO)_2P(S)SCHMeNO_2^{\cdot-}$	2.562	0.425(1)	0.075	2.005 1
$Et_2NC(S)S^-$	$^{-}CH_2NO_2$	$Et_2NC(S)SCH_2NO_2^{\cdot-}$	2.403	0.600(2)		2.005 5
$EtOC(S)S^-$	$^{-}CH_2NO_2$	$EtOC(S)SCH_2NO_2^{\cdot-}$	2.400	0.587(2)		2.005 5
$(EtO)_2P(O)H$	$^{-}CH_2NO_2$	$(EtO)_2P(O)CH_2NO_2^{\cdot-}$	2.470	0.980(2)	3.773	2.005 0
$(EtO)_2P(O)H$	$^{-}CHMeNO_2$	$(EtO)_2P(O)CHMeNO_2^{\cdot-}$	2.500	0.367(1) 0.032(3)	3.387	2.005 0
$(PhO)_2P(O)H$	$^{-}CH_2NO_2$	$(PhO)_2P(O)CH_2NO_2^{\cdot-}$	2.470	0.980(2)	3.773	2.005 0
$(PhO)_2P(O)H$	$^{-}CHMeNO_2$	$(PhO)_2P(O)CHMeNO_2^{\cdot-}$	2.500	0.367(1)	3.387	2.005 0

[a] From reaction with ·OH at pH 9. [b] ±0.005 mT. [c] ±0.0001.

The reactions between dialkyl phosphonates and hydroxyl were similarly investigated. In the case of diethyl phosphonate the spin adduct obtained using $^{-}CH_2NO_2$ has a large doublet splitting (a 3.773 mT), evidently from ^{31}P. We believe that this adduct has the structure (6), the phosphorus splitting being in the range expected [16] for a substituent placed β to the radical centre: the magnitudes of nitrogen and proton splittings are also as expected.[16] We envisage that radical (6) is formed by way of the sequence shown in reaction (3) [*cf.* the ready addition of $(RO)_2P(O)\cdot$ to alkenes [14]]: a relatively intense spectrum from (6) was detected at much lower concentrations (<0.1M) of diethyl phosphonate than was needed to detect the (different) radicals formed in the absence of trap [*i.e.* (3) and (4)], which suggests that the major radical involved in the oxidation is indeed the phosphorus-centred species (*cf.* also ref. 14). The conclusion of Metcalfe and Waters [13] that the C–H bond is more readily oxidised than the P–H bond is not apparently substantiated by the spin-trapping results.

Splittings for the sulphur- and phosphorus-containing spin adducts of nitro-*aci*-anions are collected in Table 1. Comparison of the sizes of the methylene-proton splittings for adducts of $^{-}CH_2NO_2$ with sulphur- and phosphorus-centred radicals indicates that the former (which have considerably smaller splittings) show a greater tendency to adopt a conformation (7) with the heteroatom eclipsing the orbital of the unpaired electron on nitrogen [a(β-H) depends on $\langle\cos^2\theta\rangle$ where θ is the dihedral angle between the unpaired electron's orbital and the C–H bond]. This conclusion is also reinforced by the enhanced g value and the lower nitrogen splittings for the β-sulphur substituted anions; these features may result

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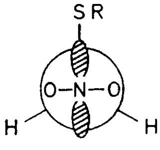
[17] R. O. C. Norman and P. M. Storey, *J. Chem. Soc.* (*B*), 1971, 1009.

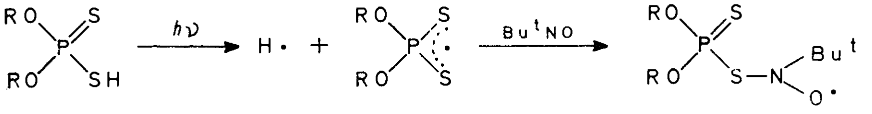
[18] D. J. Edge and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 182.

from 1,3-interaction between the radical centre and the heteroatom.[15,17]



(7)

Photolytic Studies.—When solutions of *OO*-dialkyl hydrogen phosphorodithioates [$(RO)_2P(S)SH$; R = Et or Pr^i] in benzene were photolysed at room temperature in cavity of an e.s.r. spectrometer, no radicals could be detected. The photolyses were repeated in the presence of various spin traps [2-methyl-2-nitrosopropane, Bu^{t}NO,[19] and the nitrones *N*-methylene-[20] and *N*-benzylidene-t-butylamine *N*-oxide,[21] RCH=N(Bu^t)O, where R = H and Ph, respectively]; although Bu^{t}NO suffers from the disadvantage [19] that di-t-butyl nitroxide is produced during its photolysis, it has the advantage that the radical centre of any species trapped is directly attached to nitrogen in the resulting nitroxide adduct, so that characterisation of sulphur- and phosphorus-centred radicals should be facilitated.



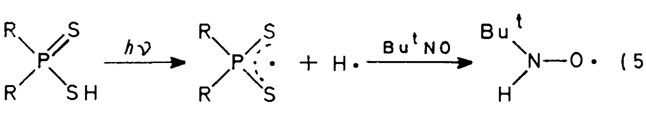
(8)

(4)

(a) *Use of 2-methyl-2-nitrosopropane. In situ* photolysis at room temperature of a benzene solution of either *OO*-diethyl or *OO*-di-isopropyl hydrogen phosphorodithioate (*ca.* 0.1M) containing 2-methyl-2-nitrosopropane (0.01M) resulted in the detection of e.s.r. signals from two species. One signal, common to both systems, is attributed to di-t-butyl nitroxide [22] [*a*(N) 1.550 mT, *g* 2.006 0], formed by photolysis of the trap: the other radical detected has, in each case, a six-line spectrum (*d* 2.006 3) with a large doublet splitting (3.662 mT), evidently from ^{31}P, and a nitroxide-like nitrogen splitting of 1.537 mT. The magnitude of *a*(P) strongly supports the assignment of these signals to species (8; R = Et or Pr^i), which have a phosphorus substituent in the β-position [*cf.* (6)]. These species are presumably formed as shown in reaction (4). Radicals (8) have much smaller nitrogen splittings than those (*ca.* 2.8 mT) for analogous alkoxynitroxide radicals $R^1N(OR^2)O\cdot$: the smaller values probably reflect increased delocalisation onto the heteroatom (which would also account for the higher *g* value) together with some flattening of the geometry around nitrogen.[23] The radical Bu^{t}N(SBu^n)O•, formed in the photolysis of mixtures of the same trap and either butanethiol or dibutyl disulphide, has [24] *a*(N) 1.85 mT, *g* 2.007 1.

The e.s.r. spectrum detected during the photolysis of either diethyl- or diphenyl-phosphinodithioic acid in the presence of Bu^{t}NO was identified as that of Bu^{t}NHO• [*a*(N), *a*(H) 1.11 mT, *g* 2.006 3; *cf.* ref. 25], formed apparently *via* hydrogen-transfer to the trap [reaction (5; R = Et or Ph)]. It is not clear why the thiyl radicals are not trapped in concentrations sufficient for detection but we note that in the photolysis of thiophenol under similar conditions only H•, and not PhS•, is trapped.[25]

(b) *Spin trapping with nitrones. In situ* photolysis of benzene solutions containing *OO*-diethyl hydrogen phosphorodithioate (*ca.* 0.1M) and *N*-methylene-t-butylamine *N*-oxide (*ca.* 0.01M) resulted in the detection of the e.s.r. signals of two radicals (see Figure 2). The radical present in higher concentration is assigned structure (9), with a sulphur substituent in the β-position (and a preferred conformation with the β-C–S bond eclipsing the orbital of the unpaired electron) on the basis of the *g* value (higher than that for a simple dialkyl nitroxide, *g ca.* 2.006 0) and the low values of *a*(N) and *a*(β-H) [for $CH_3N(Bu^t)O\cdot$, for example, the methyl group proton splitting is 1.13 mT [26]]. The other radical is assigned



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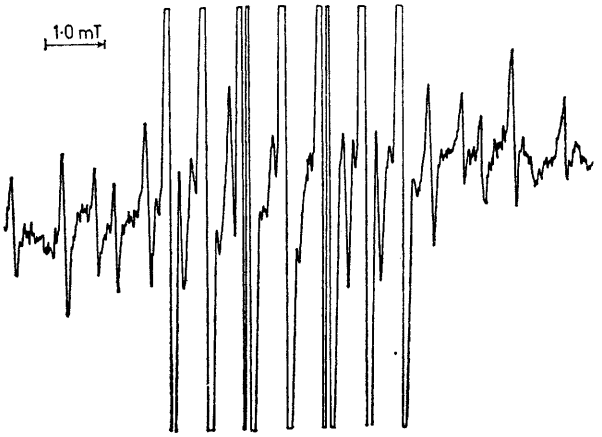

FIGURE 2 E.s.r. spectra from the mixture of radicals formed when a solution of *OO*-diethyl hydrogen phosphorodithioate and *N*-methylene-t-butylamine *N*-oxide in benzene is photolysed *in situ*: the spectrum is recorded at high gain to reveal the relatively weak signal from (10) in addition to that from (9)

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[19] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31.

[20] G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 401.

[21] E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 1968, **90**, 5909; 1969, **91**, 4481.

[22] H. Lemaire, A. Rassat, P. Servoz-Gavin, and G. Berthier, *J. Chim. phys.*, 1962, **59**, 1247.

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[24] I. H. Leaver, G. C. Ramsay, and E. Suzuki, *Austral. J. Chem.*, 1969, **22**, 1891.

[25] Th. A. J. W. Wajer, A. Mackor, and Th. J. de Boer, *Tetrahedron*, 1969, **25**, 175.

[26] M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 395.

structure (10) on the basis of the *g* value [somewhat lower than that for (9)] and the large (β) phosphorus splitting [*cf.* data for substituted nitro-radical-anions in Table 1]: the preference for an eclipsed conformation of the bond between the β-carbon atom and the heteroatom is clearly less in (10) than it is in the case of radical (9).

The results for the photolysis of other substrates with this trap are included in Table 2: in particular we note that radicals with (β) phosphorus splittings of *ca.* 4.0 mT, derived formally by addition of phosphorus-centred radicals to the trap, were obtained from $(RO)_2P(O)H$ (R = Et or Ph), $Ph_2P(S)H$, and $[Et_2P(S)]_2$.

TABLE 2

E.s.r. parameters of sulphur- and phosphorus-containing adducts of *N*-methylene-t-butylamine *N*-oxide [a]

Substrate	Radical	Hyperfine splittings (mT) [b] a(N)	a(H)	a(P)	g [c]
$(EtO)_2P(S)SH$	$(EtO)_2P(S)SCH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.350	0.613(2)		2.006 5
	$(EtO)_2P(S)CH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.443	0.875(2)	4.770	2.006 1
$(PhO)_2P(S)SH$	$(PhO)_2P(S)SCH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.337	0.612(2		2.006 4
	$(PhO)_2P(S)CH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.425	0.875(2)	5.200	2.006 0
$Et_2P(S)SH$	$Et_2P(S)SCH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.370	0.637(2)	0.062	2.006 4
$Ph_2P(S)SH$	$Ph_2P(S)SCH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.362	0.675(2)	0.062	2.006 5
	$Ph_2P(S)CH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.425	0.912(2)	3.892	2.006 1
$[Et_2P(S)]_2$	$Et_2P(S)CH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.475	1.087(2)	2.550	2.006 1
$(EtO)_2P(O)H$	$(EtO)_2P(O)CH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.450	0.900(2)	4.412	2.006 0
$(PhO)_2P(O)H$	$(PhO)_2P(O)CH_2{-}N{<}^{Bu^t}_{O\cdot}$	1.442	0.912(2)	4.625	2.006 0

[a] Generated by photolysis of solutions in benzene; see text. [b] ±0.005 mT. [c] ±0.0001.

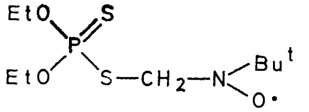
TABLE 3

E.s.r. parameters of sulphur- and phosphorus-containing adducts of *N*-benzylidene-t-butylamine *N*-oxide [a]

Substrate	Radical	Hyperfine splitting (mT) [b] a(N)	a(H)	a(P)	g [c]
$(EtO)_2P(S)SH$	$(EtO)_2P(S)SCHPhN{<}^{Bu^t}_{O\cdot}$	1.400	0.138(1)	0.175	2.006 4
	$(EtO)_2P(S)CHPhN{<}^{Bu^t}_{O\cdot}$	1.450	0.275(1)	2.588	2.006 0
$(PhO)_2P(S)SH$	$(PhO)_2P(S)CHPhN{<}^{Bu^t}_{O\cdot}$	1.418	0.262(1)	2.812	2.005 9
$Et_2P(S)SH$ $[Et_2P(S)]_2$	$Et_2P(S)CHPhN{<}^{Bu^t}_{O\cdot}$	1.410	0.338(1)	1.430	2.005 8
$(EtO)_2P(O)H$	$(EtO)_2P(O)CHPhN{<}^{Bu^t}_{O\cdot}$	1.475	0.318(1)	2.475	2.005 9
$(PhO)_2P(O)H$	$(PhO)_2P(O)CHPhN{<}^{Bu^t}_{O\cdot}$	1.430	0.325(1)	2.525	2.005 9

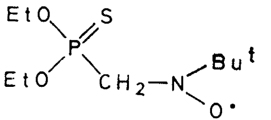
[a] Generated by photolysis of solutions in benzene. [b] ±0.005 mT. [c] ±0.0001.

Photolysis of *OO*-diethyl hydrogen phosphorodithioate in the presence of the nitrone $\mathrm{PhCH{=}N(Bu^t)O}$ resulted, at low trap concentrations (0.01—0.05M), in the detection



(9)

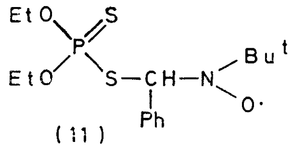
a(N) 1·350 mT
a(2H) 0·613 mT
g 2·0065



(10)

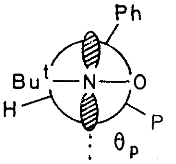
a(N) 1·443 mT
a(P) 4·770 mT
a(2H) 0·875 mT
g 2·0061

of a signal attributed to (11). At higher concentrations of trap, photolysis led to the appearance of a different signal, characterised by a larger phosphorus splitting (see Table 3) and attributed to the adduct $\mathrm{(EtO)_2P(S)}$-$\mathrm{CHPhN(Bu^t)O\cdot}$. Other radicals with β-phosphorus substituents were obtained from similar experiments



(11)

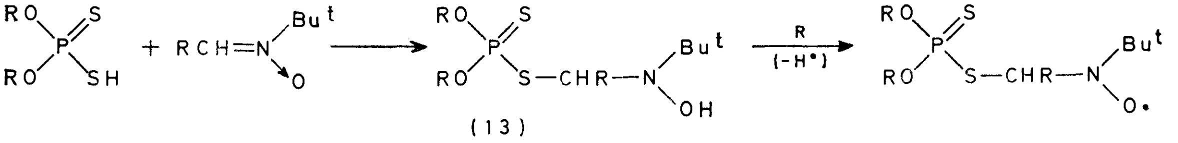
a(N) 1·400 mT
a(P) 0·175 mT
a(H) 0·138 mT
g 2·0064



(12)

employing diethyl phosphonate, diphenyl phosphonate, and tetraethyldiphosphinyl disulphide as substrates. These radicals have somewhat lower values for a(β-P) than the corresponding methylene nitrone adducts (Table 2) and the g values are also lower. This is understandable in terms of increased steric compression in the adducts of the phenyl-substituted nitrone so that conformations of the type (12), in which θ_P is large (and $\cos^2\theta_P$ small), are favoured.

$$\mathrm{AcO^- + PhCH{=}N(Bu^t)O \longrightarrow AcOCHPh{-}N(Bu^t)O^- \xrightarrow{O_2} AcOCHPh{-}N(Bu^t)O\cdot} \qquad (6)$$



(13)

(7)

We believe that caution should be exercised before it is concluded that the adducts obtained using nitrones as spin traps are formed simply by addition of radicals, generated photolytically, to the traps. Thus it has been pointed out [27] that nitroxides can be formed from a nitrone *via* addition of *nucleophiles* to the trap followed by oxidation (for example, by adventitious oxygen) of the resulting anion [see reaction (6)]. The ability of *OO*-dialkyl hydrogen phosphorodithioates to act as nucleophiles towards a range of unsaturated compounds (including, for example, benzaldehyde) has previously been reported.[28] We found that solutions prepared by addition of either of the nitrones to solutions of phosphorodithioic and phosphinodithioic acids become coloured, and spectroscopic observations (n.m.r., i.r.) suggest that a rapid initial reaction takes place. Thus the compounds photolysed are the products of this initial reaction, rather than the parent substrates. We suggest that the radicals detected are formed by the oxidation of an (unisolable) intermediate hydroxylamine [*e.g.* (13)] by radicals produced in the photolytic decomposition either of the hydroxylamine itself or of excess of the parent compound [reaction (7)]. Phosphorus–sulphur bond cleavage by photolysis of the hydroxylamine or the resultant nitroxide also seems possible: this would account for the production of $\mathrm{(EtO)_2P(S)\cdot}$ and its subsequent trapping.

Thus although the data obtained here allow the e.s.r. spectra of sulphur- and phosphorus-containing nitroxides to be characterised, we must reiterate the caveat [27] concerning limitations placed on mechanistic deductions based on results obtained with the trapping method.

Radical Reactions of Zinc Bis-(OO*-dialkyl Phosphorodithioate*)*s*.—We have carried out a preliminary investigation of the application of e.s.r. spectroscopy to the study of reaction of zinc bis-(*OO*-di-isopropyl phosphorodithioate), $\mathrm{Zn[(Pr^iO)_2P(S)S]_2}$: this complex, which is undissociated in non-polar solvents, is a typical member of a class of compound employed for the inhibition of autoxidation in, for example, lubricating oils.[29] Although the mode of action of this type of additive appears to be complicated [4-7,30,31] (the additive appears to be capable both of chain inhibition and of peroxide decomposition) evidence for the involvement of radical reactions, at least in the presence of peroxides, has been presented.[6,30,31] Radical intermediates which may be involved include the radical cation of the zinc complex,[5,30] peroxyl [5,30] or alkoxyl [31] radicals from the peroxide, and $\mathrm{(RO)_2P(S)S\cdot}$ [5,6,31] and $\mathrm{\cdot ZnSP(S)(OR)_2}$.[6]

The possibility [31] that reaction between zinc bis-(*OO*-dialkyl phosphorodithioates) and hydroperoxides might

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[27] A. R. Forrester and S. P. Hepburn, *J. Chem. Soc.* (*C*), 1971, 701.

[28] S. Oae, A. Nakanishi, and N. Tsujimoto, *Chem. and Ind.*, 1972, 575; *Tetrahedron*, 1972, **28**, 2981; A. Nakanishi and S. Oae, *Chem. and Ind.*, 1973, 274.

[29] J. F. Ford, *J. Inst. Petroleum*, 1968, **54**, 198.

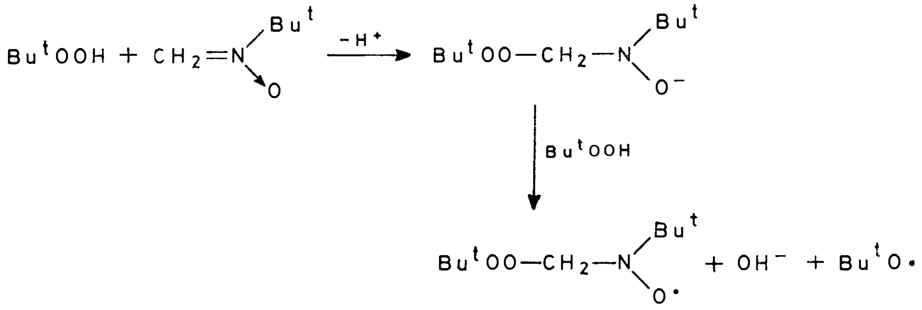
[30] T. Colclough and J. I. Cunneen, *J. Chem. Soc.*, 1964, 4790.

[31] A. J. Burn, R. Cecil, and V. O. Young, *J. Inst. Petroleum*, 1971, **57**, 319.

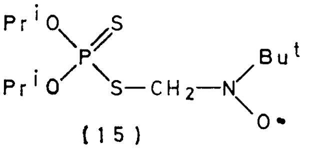
involve initial one-electron transfer [*e.g.* reaction (8)] was investigated. Attempts were made to detect the radical-cation (14) (or radicals derived from it) and also $\cdot\mathrm{CH_3}$ (from $\mathrm{Bu^tO\cdot}$) or $\mathrm{Bu^tO_2\cdot}$ by mixing benzene solutions of both reactants (at a variety of concentrations) in static and flow systems. No radicals could be detected. We found (see also ref. 32) that the products of the reaction are the so-called basic zinc complex, $\mathrm{Zn_4O[S_2P(OPr^i)_2]_6}$ [compounds of this type are formed as by-products of the preparation of zinc bis-(*OO*-dialkyl phosphorodithioate)s from the parent acids [33]] and the disulphide $\mathrm{[(Pr^iO)_2P(S)S]_2}$: the formation of the latter, at least, might be taken as evidence for the involvement of thiyl radicals in the reaction.

$$\mathrm{Zn[(Pr^iO)_2P(S)S]_2} + \mathrm{Bu^tOOH} \longrightarrow \underset{(14)}{\mathrm{Zn[(Pr^iO)_2P(S)S]_2^{+\cdot}}} + \mathrm{Bu^tO^{\cdot}} + \mathrm{OH^-} \quad (8)$$

We have also investigated the reaction by employing the spin trap *N*-methylene-t-butylamine *N*-oxide, but any mechanistic conclusions are complicated by the observation that, although the zinc complex is inert towards the trap, e.s.r. signals can be detected shortly after mixing benzene solutions of the nitrone and $\mathrm{Bu^tOOH}$; these are attributed to $\mathrm{Bu^tOCH_2{-}N(Bu^t)O\cdot}$ [*a*(N) 1.293, *a*(2H) 0.463 mT, *g* 2.005 9] (to confirm the assignment, the signal was also generated by photolysis of di-t-butyl peroxide in the presence of the trap). This observation suggests that t-butoxyl radicals are formed by reaction of the hydroperoxide with the trap: it seems likely that the reaction involves an initial nucleophilic attack by hydroperoxide, and that the t-butoxyl radicals are generated either by induced decomposition of the hydroperoxide by the intermediate anion or by decomposition of the nitroxide derived from the anion (Scheme). Benzene solutions containing $\mathrm{Zn[(Pr^iO)_2P(S)S]_2}$ (0.01—0.05M), $\mathrm{Bu^tOOH}$ (0.05—0.2M), and the trap (0.01—0.1M) rapidly developed e.s.r. signals attributable to $\mathrm{Bu^tOCH_2{-}N(Bu^t)O\cdot}$ and to (15): the arguments on which the assignment of structure (15) is based are parallel to those for radical (9). Although the origin of $\mathrm{Bu^tO\cdot}$ is not clear (it could derive by reaction of $\mathrm{Bu^tOOH}$ either with the trap or with the zinc complex) the detection of (15) suggests that $\mathrm{(Pr^iO)_2P(S)S\cdot}$ is formed by reaction of $\mathrm{Bu^tO\cdot}$ with the zinc complex (either by S_H2 reaction or *via* an intermediate radical-cation). Mechanistic deductions from reactions employing the nitrone $\mathrm{PhCH{=}N(O)Bu^t}$ are similarly limited by the observation that, in the presence of $\mathrm{Bu^tOOH}$ alone, signals from $\mathrm{Bu^tOCHPh{-}N(Bu^t)O\cdot}$ [*a*(N) 1.425, *a*(H) 0.199 mT, g 2.005 8] were detected.



SCHEME



(15)

a(N) 1·350 mT
a(2H) 0·613 mT
g 2·0065

Although no clear evidence for radical reactions could be obtained from the experiments with the spin traps described here, evidence from *spin scavenging* experiments is more conclusive. Thus we found that, although there was no reaction under our experimental conditions between either zinc bis-(*OO*-di-isopropyl phosphorodithioate) or t-butyl hydroperoxide and the stable free radical 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) (its *e.s.r.* signal was not quenched by either of them), when both the zinc complex and the hydroperoxide were added to a solution of the radical, its signal decayed rapidly (see also ref. 34). This indicates that zinc complex and hydroperoxide *together* produce free radicals which combine with the nitroxide: the radicals concerned are probably $\mathrm{Bu^tO\cdot}$ [produced in the initial step, *e.g.* reaction (8)] and possibly also $\mathrm{(Pr^iO)_2P(S)S\cdot}$ formed either by S_H2 reaction of t-butoxyl with the zinc complex or by decomposition of an intermediate cation-radical (14).

We have investigated the possibility of generating the radical-cation (14) by one-electron transfer reactions. However, no e.s.r. signals could be detected when solutions of zinc bis-(*OO*-dialkyl phosphorodithioate)s were treated with various one-electron oxidants including *p*-benzoquinone and 1,2-dinitrobenzene (both employed as solutions in benzene). With the powerful one-electron

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[32] E. Rossi and L. Imparato, *Chimica e Industria*, 1971, **53**, 838.

[33] (*a*) V. P. Wystrach, E. O. Hook, and G. L. M. Christopher, *J. Org. Chem.*, 1956, **21**, 705; (*b*) A. J. Burn and G. W. Smith, *Chem. Comm.*, 1965, 394.

[34] S. K. Ivanov and I. Kateva, *Doklady Bolg. Akad. Nauk*, 1972, **25**, 645.

oxidant [35] nitrosyl hexafluorophosphate (in acetonitrile) the evolution of NO_2 (from atmospheric oxidation of NO produced in the reaction) and a change in colour of the solution indicated that reaction had taken place, but no e.s.r. signal could be detected and attempts to isolate the product were unsuccessful.

In situ electrochemical oxidation of solutions of zinc bis-(*OO*-di-isopropoxy phosphorodithioate) (0.001—0.01M) in acetonitrile, with tetra-n-butylammonium perchlorate as supporting electrolyte, was also employed, but no radicals were detected. However when a current (*ca.* 10 mA) was passed through a solution of the zinc complex and supporting electrolyte to which *N*-methylene-t-butylamine *N*-oxide (*ca.* 0.01M) had been added, an e.s.r. signal developed within a few minutes. The spectrum [a(N) 1.375, a(2H) 0.650 mT] is attributed to the radical $(Pr^iO)_2P(S)SCH_2N(Bu^t)O\cdot$, probably formed as in reaction (9).

$$\mathrm{Zn[(Pr^iO)_2P(S)S]_2} \longrightarrow \mathrm{Zn[(Pr^iO)_2P(S)S]_2^{+\cdot}} \longrightarrow \mathrm{(Pr^iO)_2P(S)S\cdot} + \mathrm{{}^+Zn[S_2P(OPr^i)_2]} \quad (9)$$

These preliminary investigations suggest that reactive radicals [$Bu^tO\cdot$, $(Pr^iO)_2P(S)S\cdot$] are formed during oxidation reactions of zinc bis-(*OO*-di-isopropyl phosphorodithioate) and also that the radical-cation of the zinc complex may decompose to give the thiyl radical $(Pr^iO)_2P(S)S\cdot$. However, it seems unlikely that the initial stage of the reaction involves simple one-electron transfer from the zinc complex to the hydroperoxide [for example, the E_{p} value for the complex, measured by cyclic voltammetry,[36] is fairly high (1.75 V), *cf.* ref. 37], and no direct evidence for the radical-cation has been obtained. More extensive kinetic studies employing the spin scavenging method are in progress.

EXPERIMENTAL

Solvents used were of AnalaR grade; benzene was dried over sodium wire, distilled, and stored over 4A molecular sieve, and acetonitrile was dried over calcium hydride, distilled, and stored similarly. *OO*-Dialkyl hydrogen phosphorodithioates,[38] *OO*-diphenyl hydrogen phosphorodithioate,[39] diethylphosphinodithioic acid,[40] and diphenylphosphinodithioic acid [41] were prepared by procedures described in the literature. Ammonium salts of these compounds were prepared by dissolving the acids in benzene and passing ammonia through the solutions for *ca.* 0.2 h. The resulting precipitates were removed by filtration, washed with benzene, and dried *in vacuo*. Ethyl potassium xanthate was prepared by adding carbon disulphide, with vigorous stirring, to a solution of potassium hydroxide in absolute ethanol at 0 °C;[42] the precipitate was collected, washed with absolute ethanol, and dried *in vacuo*. Sodium diethyldithiocarbamate (Hopkin and Williams Ltd.) was used without further purification.

Zinc bis-*OO*-dialkyl phosphorodithioate)s were prepared by a modification of the reported method: [38] aqueous solutions of the ammonium *OO*-dialkyl phosphorodithioate and of zinc sulphate were mixed, with stirring, at room temperature. In each case, the solution was stirred for 1 h and the zinc complex was extracted into ether; the ethereal layer was separated from the aqueous layer, dried ($MgSO_4$), and the ether removed under reduced pressure. The complexes were recrystallised from ethanol.

When t-butyl hydroperoxide (0.09 g) was added to a solution of zinc bis-(*OO*-di-isopropyl phosphorodithioate) (1.97 g) in light petroleum (20 ml) a white precipitate formed. The mixture was stirred for 1 h and the precipitate was removed by filtration, washed with light petroleum, and dried *in vacuo* (yield 1.05 g). The product was shown to be identical with a pure sample of $Zn_4O[S(S)P(OPr^i)_2]_6$ prepared according to reference 33*a*. Removal of the solvent from the filtrate resulted in the isolation of a small quantity (0.1 g) of yellow crystals of the disulphide [31] $[(Pr^iO)_2P(S)S]_2$.

2-Methyl-2-nitrosopropane was prepared by the method of Stowell [43] and *N*-methylene-t-butylamine *N*-oxide was prepared from 2-methyl-2-nitrosopropane and diazomethane [44] by the method of Baldwin *et al.*[45] 2,2,6,6-Tetramethylpiperidin-1-oxyl was prepared by the method of Brière *et al*;[46] the spin trap *N*-benzylidene-t-butylamine *N*-oxide was a gift from Dr. D. K. C. Hodgeman. Tetra-n-butylammonium perchlorate [47] and Fremy's salt [48] were prepared using standard procedures. t-Butyl hydroperoxide (Koch–Light) was dried over molecular sieve; it was de-oxygenated prior to use by purging with nitrogen. Di-t-butyl peroxide (Koch–Light) was passed through a column of activated alumina to remove traces of hydroperoxide impurity.

Satisfactory elemental analyses were obtained for all the compounds mentioned above: these were performed by Mr. R. B. Girling of this Department using a Perkin-Elmer 240 Elemental Analyser (for C, H, and N) and by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany (for Zn, P, and S).

The cyclic voltammetric result was obtained with a TYR-40-3A potentiostat (Chemical Electronics Company) fitted with a linear sweep generator and a Bryans 21005 XY recorder: acetonitrile was employed as solvent, sodium perchlorate (Fisons; AnalaR) was used as supporting electrolyte, the working electrode and stationary cathode

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[42] N. Rabjohn, ' Organic Syntheses,' Wiley, New York, 1963, Coll. Vol. IV, p. 569.

[43] J. C. Stowell, *J. Org. Chem.*, 1971, **36**, 3055.

[44] Th. J. de Boer and H. J. Backer, *Rec. Trav. chim.*, 1954, **73**, 229.

[45] J. E. Baldwin, A. K. Qureshi, and B. Sklarz, *J. Chem. Soc.* (*C*), 1969, 1073.

[46] R. Brière, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1965, 3273.

[47] D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.

[48] H. Zimmer, D. C. Lankin, and S. W. Horgan, *Chem. Rev.*, 1971, **71**, 229.

were made from platinum wire (22 S.W.G., 5.0 mm length, bound into glass tubes containing mercury), and the reference electrode was a standard calomel electrode (separated from the solution under investigation by an agar salt-bridge).

E.s.r. spectra were all recorded on a Varian E-3 spectrometer with 100 kHz modulation and an X-band klystron. Hyperfine splittings (± 0.005 mT unless stated otherwise) and g values ($\pm 0.000\,1$) were obtained by comparison with those of an aqueous solution of Fremy's salt [a(N) 1.309 mT,[49] g 2.005 50 [50]].

The mixing chamber used for the flow studies enabled three streams to be mixed simultaneously *ca.* 0.05 s before passage of the combined solution through the cavity of the spectrometer: the flow rate for each solution was *ca.* 2.5 ml s^{-1} and the initial volume of each solution was typically 3 dm^3. All solutions were de-oxygenated by purging with nitrogen before commencement of the flow. The first solution contained, typically, titanium(III) chloride (0.008M) and, for runs at pH *ca.* 1, concentrated sulphuric acid (*ca.* 25 ml); the second solution contained hydrogen peroxide solution (0.03M), and the third stream contained the substrate (typically *ca.* 0.1M). For experiments at higher pH, the sulphuric acid in the first stream was replaced by the disodium salt of ethylenediaminetetra-acetic acid (15 g), and concentrated ammonia solution was added to adjust the pH to the required value.

For spin-trapping flow-system studies, the nitroalkane (*ca.* 3 ml) was added to the third solution, together with ammonia (*d* 0.880; *ca.* 10 ml) except in the experiments involving diethyl and diphenyl phosphonate. The first stream contained ammonia and disodium ethylenediaminetetra-acetate as above.

For the photolytic studies the source of radiation employed was an Hanovia 400 W medium pressure mercury arc lamp. The chosen spin trap (*ca.* 10^{-5} mol) was dissolved in benzene (1—2 ml) and the solution was purged with nitrogen: the substrate (*ca.* 10^{-4} mol) was then injected into the solution which was transferred to the e.s.r. cell under nitrogen.

The cell system used for the electrochemical e.s.r. investigations was a modification of the standard Varian aqueous sample cell: a piece of platinum wire, bound into the bottom of the cell, acted as a cathode, and the anode was a piece of platinum gauze (surface area *ca.* 75 mm^2) placed in the flat portion of the cell so that radicals formed by anodic oxidation could be immediately detected. The radicals were generated by passing a current between the electrodes: the current was adjusted to obtain the best possible spectra (optimum values 5—10 mA).

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[5/1509 *Received*, 30*th July*, 1975]

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