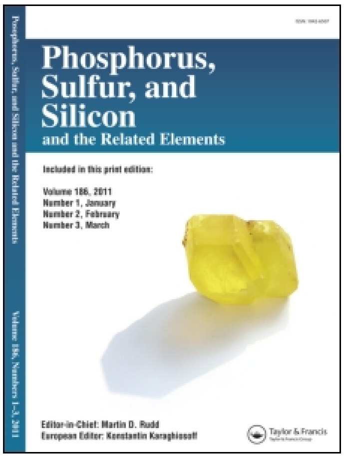

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AN ELECTRON SPIN RESONANCE STUDY OF THE REACTIONS OF PHOSPHORUS CENTERED RADICALS WITH THIOKETONES

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AN ELECTRON SPIN RESONANCE STUDY OF THE REACTIONS OF PHOSPHORUS CENTERED RADICALS WITH THIOKETONES

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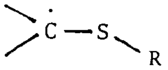
The utility of thioketones as traps for intermediate phosphorus-centered radicals is illustrated by an e.s.r. study of the phosphorus–thioketone radical adducts. The direct evidence of the P—S bond formation in the adduct is clearly supported by the large phosphorus hyperfine splittings which vary with the nature of the organophosphorus moiety. The method also readily detects impurities in the organophosphorus compounds which are susceptible to thermal oxidation. The direct photochemical reactions of thioketones with dialkoxyphosphites are shown to involve free radical mechanisms.

INTRODUCTION

It has been recognized for some time that thioketones are good spin traps for carbon-centered radicals as well as some organometallic radicals.[1–6] Ingold and coworkers, for example, have reported the e.s.r. observations of several carbon and organometallic radical adducts with di-*t*-butylthioketone[2] and trithiocarbonates.[5] Bolton and coworkers,[1] and investigators in this laboratory[6] have observed the e.s.r. spectra of similar radical adducts with 4,4′-dimethoxythiobenzophenone. The e.s.r. parameters were consistent with structure **I**, where R was the parent carbon-centered or organometallic radical.



(I)

Although there have been e.s.r. studies of radical adducts formed by the addition of phosphorus-centered radicals to carbon–carbon and carbon–oxygen double bonds,[7,8] the only e.s.r. observation of phosphorus radical addition to thioketones was that of the $(EtO)_2\dot{P}(O)$ radical[3,5] which demonstrated the direct bonding of the phosphorus to the sulfur showing a large ^{31}P hyperfine coupling constant in the resulting radical adduct. In this report we have carried out a systematic e.s.r. study of the reactions of photochemically generated phosphorus-centered radicals with several thioketones. With some thioketones, especially 4,4′-dimethoxythiobenzophenone, phosphorus radical adduct formation was facile, thus making such systems ideal for e.s.r. study. Furthermore, since organophosphorus compounds are known to participate in many free radical reactions, the efficient trapping of the intermediate phosphorous radicals would be of great utility and interest to mechanistic studies of phosphorus chemistry.

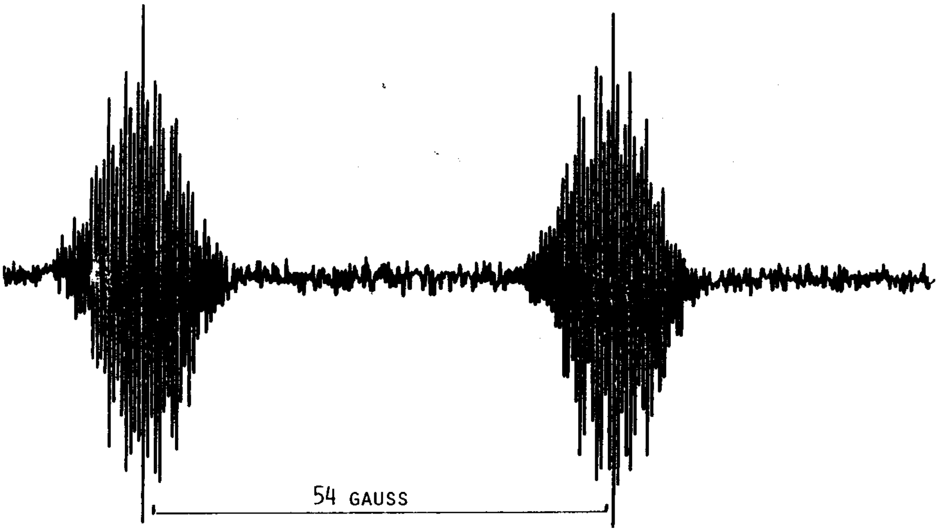


FIGURE 1 A typical e.s.r. spectrum of the dialkoxyphosphonyl-- DMBS radical adduct in toluene at 25°C.

RESULTS AND DISCUSSION

1. The Reactions of Phosphorus-Centered Radicals with 4,4′-Dimethoxythiobenzophenone

Photolysis of a toluene solution containing dimethyl and diethyl phosphite and di-*t*-butylperoxide at −60°C gave an e.s.r. spectrum of a doublet which has been previously assigned to the dialkoxyphosphonyl radical,[10] $(RO)_2\dot{P}(O)$. When 4,4′-dimethoxythiobenzophenone, DMBS, was added to the solution and irradiated at 23°C, the large doublet spectrum of the dialkoxyphosphonyl radical was replaced by a new e.s.r. spectrum consisting of a smaller doublet of complex multiplets. A typical e.s.r. spectrum is shown in Figure 1 and the e.s.r. parameters of the parent phosphonyl radical and the phosphorus–sulfur radical adducts are given in Table I. The e.s.r. observations are consistent with the following reactions:

$$\mathrm{Me_3COOCMe_3} \xrightarrow{h\nu} 2\ \mathrm{Me_3C\dot{O}} \qquad (1)$$

$$\mathrm{Me_3C\dot{O}} + \mathrm{(RO)_2P(O)H} \longrightarrow \mathrm{Me_3COH} + \mathrm{(RO)_2\dot{P}(O)} \qquad (2)$$

$$\mathrm{(RO)_2\dot{P}(O)} + \mathrm{DMBS} \longrightarrow \mathrm{(MeO\text{-}C_6H_4)_2\dot{C}\text{-}S\text{-}P(O)(RO)_2} \qquad (3)$$

(II)

TABLE I

Hyperfine coupling constants for phosphorus$\dot{-}$ DMBS radical adducts in toluene

Organophosphorus substrate	Radical(s) observed	a_P(gauss)	a^o_H	a^m_H	a^p_H (gauss)
$(MeO)_2P(O)H$	$(MeO)_2(O)\dot{P}$	700 ± 0.03			
	$(MeO)_2(O)P\dot{-}$ DMBS	56.2	2.92	1.08	0.37
$(EtO)_2P(O)H$	$(EtO)_2(O)\dot{P}$	690			
	$(EtO)_2(O)P\dot{-}$ DMBS	54.1	2.91	1.08	0.37
$(EtO)_2POP(EtO)_2$	$(EtO)_2(O)P\dot{-}$ DMBS	54.1	2.91	1.08	0.37
	$(EtO)_2P\dot{-}$ DMBS	30.0	2.86	1.06	0.36
	Unassigned	12.0	2.88	1.07	0.36
$Ph_2P(O)H$	$Ph_2(O)\dot{P}$	355			
	$Ph_2(O)P\dot{-}$ DMBS	39.5	2.94	1.09	0.35
Ph_2PH	$Ph_2P\dot{-}$ DMBS	19.9	2.84	1.05	0.35
	$Ph_2(O)P\dot{-}$ DMBS	39.5	2.87	1.08	0.36
Ph_2PPPh_2	$Ph_2P\dot{-}$ DMBS	19.8	2.85	1.05	0.35
	$Ph_2(O)P\dot{-}$ DMBS	39.7	2.88	1.06	0.35
Ph_2PCl (with $Re_2(CO)_{10}$)	$Ph_2P\dot{-}$ DMBS	19.9	2.86	1.06	0.37
(Cyclo-$C_6H_{11})_2PH$	$(C_6H_{11})_2P\dot{-}$ DMBS	15.6	not resolved		
	$(C_6H_{11})_2(O)P\dot{-}$ DMBS	46.0	not resolved		
Tertiary Phosphines	$Ph_2P\dot{-}$ DMBS	19.8	2.85	1.06	0.35
	$(PhO)_2(O)P\dot{-}$ DMBS	52.4	2.85	1.03	0.36
	$R\dot{-}$ DMBS	—	2.89	1.08	0.37

In the e.s.r. spectrum of radical adduct **II**, the complex multiplets arise from the methoxy protons and the ring protons hyperfine interactions while the larger doublet splitting is due to the phosphorus ^{31}P. The proton splittings of the DMBS moiety appear to be quite insensitive to the substituents on the P atom. Such an insensitivity has also been observed for carbon-centered radical adducts with DMBS.[6,11] Figure 2 shows a typical e.s.r. spectrum of a carbon-centered radical-DMBS adduct. The

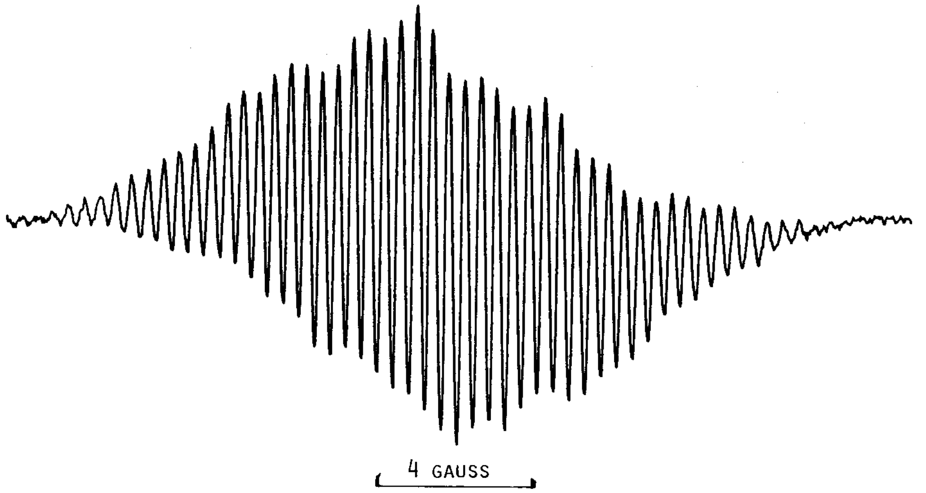


FIGURE 2 A typical e.s.r. spectrum of a radical adduct formed by the addition of a carbon-centered radical to DMBS in toluene.

proton coupling constants of the carbon radical adducts (Table I) are practically identical to those for radical adduct **II**. This fact indicates that there is considerable spin delocalization among the DMBS moiety. In comparison, Scaiano and Ingold[2] have characterized the dialkoxyphosphonyl radicals added to di-*t*-butylthioketone in which the radical adducts showed a large ^{31}P splitting of 101 gauss. In the latter case, spin densities on the thioketone moiety were much less and thus a much larger spin density on the P nucleus was expected.

The reactions of tetraethylpyrophosphite with DMBS in the presence of di-*t*-butylperoxide led to the observation of the same radical adduct **II**. As expected, the diethoxyphosphonyl radical was generated by the Davies, Griller and Roberts mechanism:[10]

$$\mathrm{Me_3C\dot{O}} + \mathrm{(EtO)_2POP(EtO)_2} \longrightarrow \mathrm{(EtO)_2(Me_3CO)\dot{P}OP(EtO)_2} \qquad (4)$$

$$\mathrm{(EtO)_2(Me_3CO)\dot{P}OP(EtO)_2} \xrightarrow{\alpha\ \mathrm{scission}} \mathrm{(EtO)_2(Me_3CO)P} + \dot{\mathbf{(II)}} \qquad (5)$$

However, in the absence of di-*t*-butylperoxide, the photochemical reactions of tetraethylpyrophosphite with DMBS gave a typical e.s.r. spectrum (Figure 3) which consisted of three phosphorus radical adducts. The major and the most intense e.s.r. signal (a_P = 54 gauss) is clearly associated with radical adduct **II**, while the identities

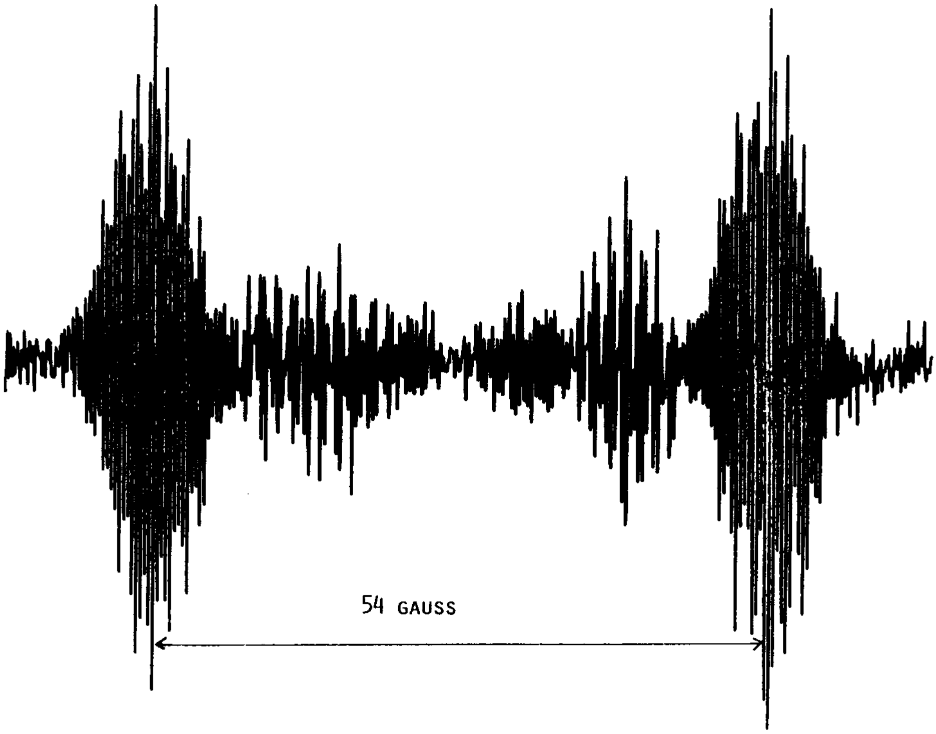


FIGURE 3 The e.s.r. spectrum of the phosphorus–DMBS radical adducts generated by the photochemical reaction of DMBS and tetraethylpyrophosphite in the absence of di-*t*-butylperoxide in toluene at 25°C.

of the other two radical adducts remain uncertain at the present time. Since photolysis of tetraethylpyrophosphite alone did not yield any observable phosphonyl radicals, the free radical reactions must be sensitized by DMBS, probably in its excited singlet state:

$$\mathrm{DMBS} + h\nu \longrightarrow {}^{1}\mathrm{DMBS}^{*} \tag{6}$$

$${}^{1}\mathrm{DMBS}^{*} + \mathrm{(EtO)_2POP(EtO)_2} \longrightarrow \dot{(\mathbf{II})} + \mathrm{(EtO)_2\dot{P}} \tag{7}$$

$$\mathrm{(EtO)_2\dot{P}} + \mathrm{DMBS} \longrightarrow \underset{(\mathbf{IIa})}{\mathrm{(MeO\text{-}C_6H_4)_2\dot{C}\text{-}S\text{-}P(EtO)_2}} \tag{8}$$

$${}^{1}\mathrm{DMBS}^{*} + \mathrm{(EtO)_2POP(EtO)_2} \qquad (\mathbf{IIa}) + \mathrm{(EtO)_2\dot{P}(O)} \tag{8a}$$

The involvement of an excited singlet DMBS in reaction (7) accounts for the lack of triplet polarization mechanism in the time-resolved e.s.r. observation of radical adduct **II**. The possible formation of the radical **IIa** and the subsequent trapping by DMBS could account for the additional radical species (Figure 3). Alternatively, radical **IIa** may also be formed directly by reaction (8a).

2. *The Diphenyl Phosphonyl-DMBS Radical Adduct*

Photolysis of a toluene solution of diphenylphosphine oxide in the presence of di-*t*-butyl peroxide at 23°C gave an e.s.r. doublet spectrum which has been assigned to the diphenylphosphonyl radical.[12] When DMBS was added to the solution before photolysis, the diphenylphosphonyl radical spectrum was replaced by a new e.s.r. spectrum similar to that shown in Figure 1. The e.s.r. parameters of the parent phosphonyl radical and its radical adduct to DMBS are given in Table I. The ^{31}P hyperfine splittings in both the radical and the radical adduct are significantly smaller than the corresponding dialkoxy analogs. Similar observations have also been obtained in the additions of phosphonyl radicals to carbon–carbon double bonds of *p*-benzoquinone[8] and ascorbic acid.[13] The results indicate that the diphenyl substitution in the organophosphorus moiety facilitates the spin delocalization from the P atom.

3. *The Diphenylphosphinyl-DMBS Radical Adduct*

(i) Reactions with Diphenylphosphine—The photolysis of a toluene solution containing diphenylphosphine, di-*t*-butylperoxide and DMBS gave an e.s.r. spectrum of a large doublet of multiplets, consistent with the following reactions:

$$\mathrm{Me_3C\dot{O}} + \mathrm{Ph_2PH} \longrightarrow \mathrm{Me_3COH} + \mathrm{Ph_2\dot{P}} \tag{9}$$

$$\mathrm{Ph_2\dot{P}} + \mathrm{DMBS} \longrightarrow \mathrm{(MeO\text{-}C_6H_4)_2\dot{C}\text{-}S\text{\textbackslash}PPh_2} \tag{10}$$

(**III**)

The e.s.r. parameters of radical adduct **III** are given in Table I. In the absence of DMBS, direct e.s.r. observation of the $Ph_2\dot{P}$ has been reported in a low temperature solid matrix.[14]

When the same solution was bubbled with oxygen before photolysis, the photochemical reactions led to an e.s.r. spectrum shown in Figure 4, which consisted of two phosphorus radical adducts. Their e.s.r. parameters are given in Table I. One of the two phosphorus radical adducts can be identified by its ^{31}P splitting as the diphenylphosphinyl–DMBS radical **III**, while the other has a ^{31}P splitting identical to that of the diphenylphosphonyl–DMBS radical adduct. The intensity ratio of the phosphonyl–DMBS radical adduct and that of the phosphinyl–DMBS radical increased with the length of time for which oxygen was bubbled through the sample solution. The results demonstrate the ease of thermal oxidation of diphenyl phosphine to diphenylphosphine oxide[15] in the presence of oxygen. The e.s.r. technique offers a good means of monitoring such an oxidation. Also, the same observation of the two diphenylphosphinyl and diphenylphosphonyl–DMBS radical adducts was obtained when a toluene solution of tetraphenylbiphosphine and DMBS was photolysed in the presence of oxygen. In fact, an old stock of biphosphine led to the formation of both radical adducts even without the passing of oxygen through the solution. Since biphosphines are known to undergo thermal oxidation to the corre-

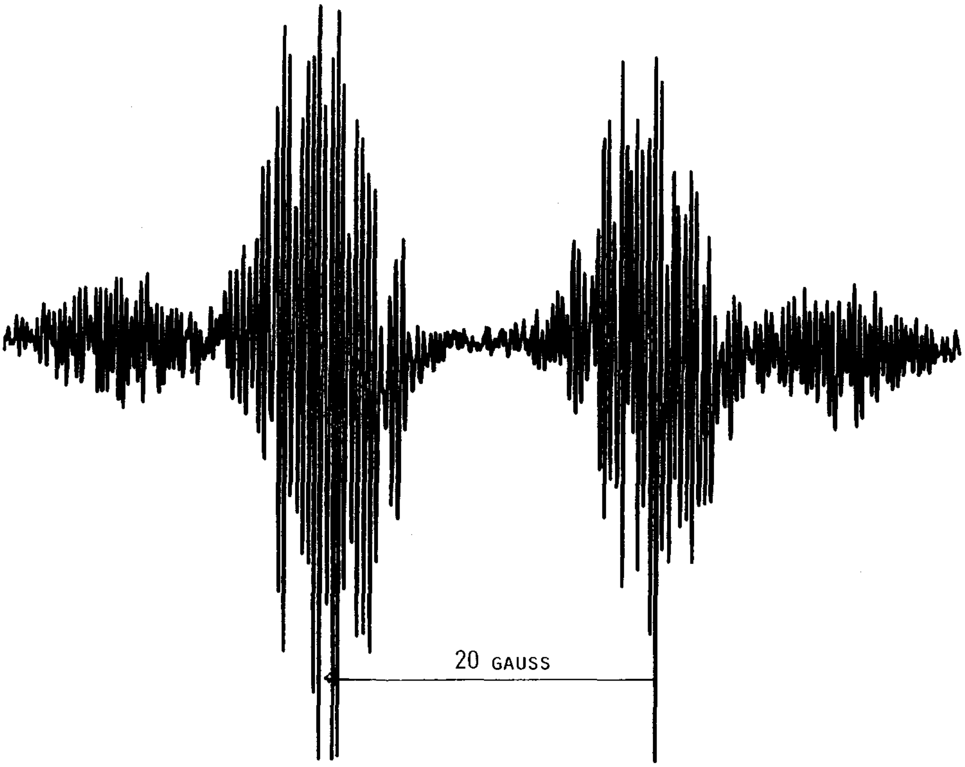


FIGURE 4 The e.s.r. spectrum of the phosphorus–DMBS radical adducts generated by photolysis of an oxygen saturated toluene solution of diphenylphosphine at 25°C.

sponding phosphine oxides,[16] photochemical reactions inducing the breaking of the P—P bond in both the biphosphine and the biphosphine oxide yield the corresponding phosphinyl and phosphonyl radicals. Because of the high sensitivity of the e.s.r. technique, this DMBS trapping method offers a simple way to detect the impurity and the extent of the thermal oxidation of old stocks of phosphines and biphosphines. Similar results are obtained with dialkylphosphines and the e.s.r. parameters of the dicyclohexylphosphinyl and dicyclohexylphosphonyl–DMBS radical adducts are reported in Table I.

(ii) Chlorodiphenylphosphine—Rhenium pentacarbonyl radicals, $\dot{R}e(CO)_5$, are highly reactive towards halogen containing compounds[17] and they can be produced by the photolysis of the stable dimer $Re_2(CO)_{10}$. This fact has been successfully applied to generate organic radicals by the $R\dot{e}(CO)_5$ radicals specifically abstracting a halogen from a variety of alkyl and aryl halides.[11,17] When DMBS was used as a spin trap for the carbon-centered radicals generated by the reaction with $R\dot{e}(CO)_5$ radicals, both the $\dot{R}e(CO)_5$ and the carbon-centered radicals added to DMBS and two radical adducts were observed (Figure 5). The $Re(CO)_5\dot{-}$ DMBS radical adduct exhibited the six broad lines due to the Re nucleus (a_{Re} = 53 gauss). When the $R\dot{e}(CO)_5$ radicals were used to abstract the Cl from a diphenyl phosphine in the presence of DMBS, only the diphenylphosphinyl–DMBS radical adduct was observed. This fact suggests that the reactivity of $R\dot{e}(CO)_5$ radicals towards the Cl—P bond is relatively higher than towards the corresponding Cl—C bond.

(iii) Tertiary Phosphines—The tertiary phosphines studied include Ph_3P, $Ph_2P(CH_2)_nPPh_2$ (n = 1–4), benzyldiphenyl phosphine, and 1,1,1-tris-(diphenylphosphino)-methane. In general, the photolysis of a tertiary phosphine with DMBS in the absence of di-*t*-butylperoxide yielded an e.s.r. spectrum consisting of three

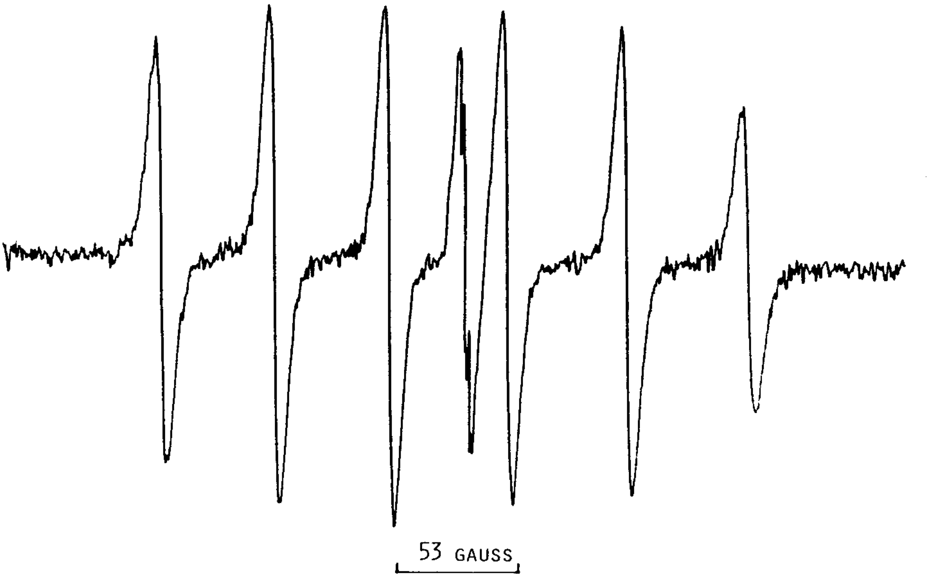


FIGURE 5 A typical e.s.r. spectrum of the $Re(CO)_5$—DMBS radical adduct and a carbon-centered radical–DMBS adduct in toluene at 25°C.

distinct DMBS radical signals. Two of these are due to phosphorus-centered radical adducts and the third is due to a carbon-centered radical adduct. The most intense e.s.r. signal was attributed to the diphenylphosphinyl–DMBS radical adduct; its formation and that of the carbon-centered radical adduct can be accounted for by the following reactions:

$$^{1}\mathrm{DMBS}^{*} + \mathrm{Ph_2PR} \longrightarrow (\mathrm{MeO{-}C_6H_4})_2\dot{\mathrm{C}}{-}\mathrm{S}{\searrow}\mathrm{PPh_2} + \dot{\mathrm{R}} \qquad (11)$$

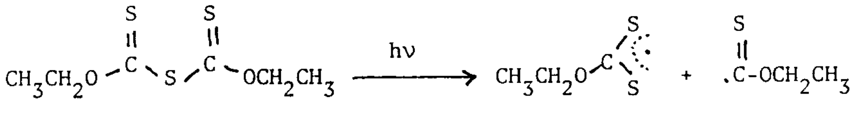
$$\dot{\mathrm{R}} + \mathrm{DMBS} \longrightarrow (\mathrm{Me}){-}\mathrm{C_6H_4})_2\dot{\mathrm{C}}{-}\mathrm{S}{\searrow}\mathrm{R} \qquad (12)$$

where $\dot{R} = \dot{P}h, \dot{C}H_2(CH_2)_{n-1}PPh_2$, etc. The identity of the second phosphorus-centered DMBS radical adduct ($a_P = 52$ gauss) is not known at this time. However, the magnitude of the phosphorus splitting is very similar to that of the dialkoxyphosphonyl-DMBS adduct. It is conceivable that the tert-phosphine used contained some impurity from thermal oxidation which in turn produced the diphenoxyphosphonyl–DMBS radical adduct. Buckler[18] has reported the autoxidation of tertiary phosphines with a variety of products, including the phosphine oxides and phosphites.

4. *Other Thioketones*

(i) Thiobenzophenone (BS)—The purpose of using BS instead of DMBS as spin trap was to simplify the radical adduct spectrum by eliminating the 6 methoxy protons hyperfine splittings. However, the thermal stability of BS was much less than that of DMBS. As well, the BS-radical adducts were found to be much less stable than the corresponding DMBS-radical adducts. The best e.s.r. spectrum obtained using BS is that of the $(EtO)_2P(O)\dot{-}$ Bs radical adduct with $a_P = 51.3$ gauss. Because of the poor intensity, only the ortho-protons in the BS moiety were resolved ($a^{o}_{H} = 2.9$ gauss).

(ii) Bis(ethoxythiocarbonyl)sulfide (BETS)—Photolysis of a toluene solution containing dialkoxyphosphite or tetraethylpyrophosphite, di-*t*-butylperoxide, and BETS at $-60°C$ gave an e.s.r. spectrum exhibiting two radicals. The more intense signal which consisted of a triplet, has been previously assigned[19] to structure **IV** formed by the photochemical cleavage of a C—S bond:

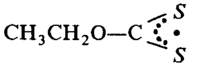


(13)

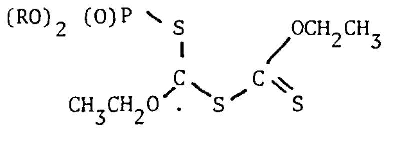
(BETS) **(IV)**

TABLE II

Hyperfine coupling constants for the phosphonyl$\dot{-}$ BETS radical adducts in toluene at −60°C

Radical adducts	a_P (gauss)	$a_H^{CH_2}$ (gauss)
$(MeO)_2(O)P\dot{-}$ BETS	72.3	3.2
$(EtO)_2(O)P\dot{-}$ BETS	70.9	3.2
$(Ph)_2(O)P\dot{-}$ BETS	62.7	3.3
 $CH_3CH_2O{-}C\overset{S}{\underset{S}{\cdot}}$		3.0

The other radical consisted of a doublet of triplets with the doublet splittings similar to that of the phosphorus–DMBS radical adducts. This radical is assigned to the $(RO)_2P(O)\dot{-}$ BETS adduct with the following structure:



(V)

The large doublet is assigned to the phosphorus splitting and the small triplet is due to the methylene protons in the BETS moiety. The e.s.r. parameters of a number of phosphorus$\dot{-}$ BETS radical adducts are given in Table II.

The phosphorus$\dot{-}$ BETS radical adducts are only observable at −60°C or lower. This is in contrast to the metal carbonyl$\dot{-}$ BETS radical adducts which were found to be very stable at room temperature.[19] However, for these stable complexes, the transition metal is coordinated to both the sulfur atoms of the thiocarbonyl groups showing four equivalent methylene protons. With the present phosphorus radical adducts, only two methylene protons are observed, consistent with the structure V.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E104 X-band spectrometer with 100 kHz field modulation. g-Factors were measured using a Hewlett Packard electronic frequency counter and a standard DPPH sample for field calibration.

In a typical experiment a sample containing a few milligrams each of the organophosphorus compound, thioketone, and either di-*t*-butylperoxide or $Re_2(CO)_{10}$, in 1 ml of toluene was degassed with nitrogen and sealed off in a pyrex tube. The sample was continuously irradiated in situ within a temperature probe in the microwave cavity by a 200 watt super pressure mercury arc. The e.s.r. signal was simultaneously digitized by a Nicolet 4094 computer oscilloscope and directly plotted out on a Hewlett Packard 7475A graphic plotter.

Commercially available thioketones were purchased from Aldrich, Pfaltz and Bauer, and Alfa Chemicals. Thiobenzophenone was prepared from benzophenone and Lawesson's reagent by the method of

Pedersen and coworkers.[9] Dimethyl and diethyl phosphites were vacuum distilled before use. Toluene was refluxed over sodium and distilled.

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