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SPIN ADDUCTS BETWEEN THIOKETONES AND PHOSPHORUS CENTRED RADICALS. PART II.

AN ELECTRON SPIN RESONANCE STUDY OF THE ADDITION OF PHOSPHINYL, PHOSPHONYL AND THIOPHOSPHONYL RADICALS TO DIARYL AND DIALKYL THIOKETONES.

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Abstract. The paramagnetic adducts between a variety of phosphinyl, phosphonyl or thiophosphonyl radicals and thiobenzophenone, 9,H-xanthen-9-thione, 9,H-thiaxanthen-9-thione, 9,H-selenaxanthen-9-thione and di-tert-butyl thioketone have been generated and studied by means of ESR spectroscopy. Attention has been focused on the variations of $a(^{31}P)$ with the nature of the ligands L in the attacking $\cdot PL_n$ radicals and with the nature of the thiocarbonylic substrates.

In all cases the reactions with the precursors of phosphinyl radicals afforded, beside the expected adducts, additional paramagnetic species, identified as the corresponding phosphonyl and thiophosphonyl adducts: while the formation of the former reflects the high sensitivity of tervalent phosphorus compounds to oxidizing agents, the latter adducts are believed to originate from desulfuration of the thioketones by the starting phosphines.

It is well established that thioketones, owing to the presence of the readily assailable C=S double bond, possess a pronounced ability to act as spin traps for a variety of free radicals, and indeed adducts with species centred at elements ranging from Group IV to Group VI and at transition metal atoms have been studied by means of Electron Spin Resonance (ESR) spectroscopy.[1-13] Although several different thiocarbonyls have been used in these studies as substrates for radical addition, a major drawback preventing a general use of this class of compounds as routine spin traps is represented by the relatively low stability of its members, which must, with few exceptions, be handled at low temperatures and in inert atmospheres.

As the result of the several aforementioned ESR investigations, a substantial body of information is now available concerning the structural and electronic properties of the spin adducts between thioketones and carbon,[1-5,7,9] silicon,[2,5-9] germanium,[6-9] tin,[2,5-9] lead,[7] oxygen,[13] or sulphur[13] centred radicals as well as the adducts with metal carbonyls.[11,12] Fewer reports have however dealt with the spin adducts with phosphorus centred radicals, i.e. that of the diethoxyphosphonyl adduct of di-tert-butyl thioketone[2] and of three different tri-thiocarbonates[5] by Ingold and coworkers, and a previous study by some of us concerning the adducts of

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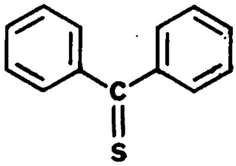
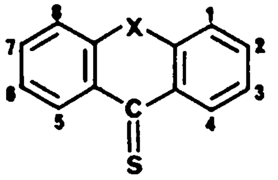
4,4'-dimethoxythiobenzophenone and bis(ethoxythiocarbonyl)sulphide[10] with diphenyl, dimethoxy-, and diethoxy-phosphonyl radicals and with diphenyl and dicyclohexyl phosphinyl radicals, where the choice of the substrates had been based either on the foreseeable persistence of the resulting adducts or on the commercial availability of the thioketones.

Following our previous study and in order to gain a more detailed picture of the adducts between phosphorus radicals and thioketones, we extended our ESR investigation to the reactions of some relatively stable thiocarbonyl compounds, namely thiobenzophenone (TBP), 9,H-xanthen-9-thione (XT), 9,H-thiaxanthen-9-thione (TXT), and 9,H-selenaxanthen-9-thione (SXT) with a larger selection of phosphorus centred radicals:

(TBP)





X = O (XT)
X = S (TXT)
X = Se (SXT)

Some new phosphinyl, phosphonyl and thiophosphonyl radical adducts to di-*tert*-butyl thiokétone have also been studied for comparative purposes.

EXPERIMENTAL

The aromatic thioketones were prepared either by reaction of the corresponding ketones with H_2S and HCl in alcoholic solution[14] or with P_2S_5 in xylene,[15] while di-*tert*-butyl thioketone was prepared from the corresponding imine;[16] all phosphorus compounds were commercially available, with the exception of diphenylphosphine sulphide and di(cyclohexyl)phosphine sulphide which were prepared as previously described.[17]

The ESR spectra were recorded on either a Varian E-104 or a Bruker ER-200 D spectrometer equipped with standard devices for field calibration, *g*-factor determination and temperature control. UV irradiation was achieved by focusing on the ESR cavity the light from high pressure 250 W or 1 KW mercury lamps. It should be noted that shorter irradiation times often led to cleaner ESR spectra.

The thioketones were reacted with several different phosphorus centred radicals, *i.e.* diphenylphosphinyl, $\cdot PPh_2$, diphenylphosphonyl, $\cdot P(O)Ph_2$, diphenylthiophosphonyl, $\cdot P(S)Ph_2$, diethoxyphosphinyl, $\cdot P(OEt)_2$, and diethoxyphosphonyl, $\cdot P(O)(OEt)_2$. In the case of TBP and XT we were able to observe the adducts with three additional phosphorus centred species, that is di(cyclohexyl)phosphinyl, $\cdot P(c\text{-}C_6H_{11})_2$, di(cyclohexyl)thiophosphonyl, $\cdot P(S)(c\text{-}C_6H_{11})_2$, and diethtylthiophosphonyl radicals, $\cdot P(S)Et_2$.

The various $\cdot PL_n$ radicals were generated *in situ* by the simple photolytic reactions shown in eq.s 1-9.

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2\ t\text{-BuO}\cdot \qquad (1)$$

$$t\text{-BuO}\cdot + HPL_2 \longrightarrow t\text{-BuOH} + \cdot PL_2\ (L = Ph,\ c\text{-Hex}) \qquad (2)$$

$$t\text{-BuO}\cdot + HP(O)L_2 \longrightarrow t\text{-BuOH} + \cdot P(O)L_2\ (L = Ph,\ OEt) \qquad (3)$$

$$t\text{-BuO}\cdot + HP(S)L_2 \longrightarrow t\text{-BuOH} + \cdot P(S)L_2\ (L = Ph,\ c\text{-Hex}) \qquad (4)$$

$$t\text{-BuO}\cdot + ((EtO)_2P_2)O \longrightarrow t\text{-BuOP(OEt)}_2 + \cdot P(O)(OEt)_2 \qquad (5)$$

$$Ph_2PPPh_2 \xrightarrow{h\nu} 2\ \cdot PPh_2 \qquad (6)$$

$$(CO)_5M\text{-}M(CO)_5 \xrightarrow{h\nu} 2\ \cdot M(CO)_5\ (M = Mn,\ Re) \qquad (7)$$

$$\cdot M(CO)_5 + ClPPh_2 \longrightarrow ClM(CO)_5 + \cdot PPh_2 \qquad (8)$$

$$Et_2P(S)\text{-}P(S)Et_2 \xrightarrow{h\nu} 2\ \cdot P(S)Et_2 \qquad (9)$$

Typical samples consisted of quartz tubes containing degassed benzene, toluene or *t*-butyl benzene solutions of a thioketone (*ca*. 10^{-3} M) and the appropriate precursor(s) of the desired phosphorus radical.

The thioketones were also photoreacted with tetraethylpyrophosphite in the absence of peroxide; under these conditions the diethoxyphosphonyl adduct was observed together with a second radical which, on the basis of its spectral parameters, is believed to be the diethoxyphosphinyl adduct.

$$R_2C{=}S \xrightarrow{h\nu} R_2C{=}S^{*} \tag{10}$$

$$R_2C{=}S^{*} + ((EtO)_2P_2)O \longrightarrow R_2\dot{C}{-}SP(OEt)_2 + \cdot P(O)(OEt)_2 \tag{11}$$

$$R_2C{=}S + \cdot P(O)(OEt)_2 \longrightarrow R_2\dot{C}{-}SP(O)(OEt)_2 \tag{12}$$

The formation of these two radicals might be attributed to a homolytic displacement reaction brought about by the photoexcited thiocarbonyl compound, a process akin to the reaction between photoexcited triplet carbonyls and tetraethylpyrophosphite;[18] relaxation taking place too quickly in these systems made it however impossible to detect triplet polarization in previous CIDEP studies of the photoreactions between some thioketones and pyrophosphite.[10]

RESULTS and DISCUSSION

When the thioketones were allowed to react inside the cavity of an ESR spectrometer with the different photolytically generated phosphorus radicals, the corresponding adducts resulting from addition of P-centred radicals to the sulphur atom of the C=S double bond were observed:

$$R_2C{=}S + \cdot PL_n \longrightarrow R_2\dot{C}{-}SPL_n \ (1{-}32) \tag{13}$$

The adducts were in most cases fairly persistent and gave rise to ESR spectra, that could also be detected when the photolysis was interrupted; indeed, prolonging the UV irradiation over longer periods often resulted in the appearence of other radical species arising from degradation and/or further reaction of the initially formed adducts.

Although there are no available values for the rate constants for addition of phosphonyl or phosphinyl radicals to the C=S double bond, this appears to be a fast process even at low temperatures. Actually, in agreement with what observed previously,[10] we found that in no case could the signals from the attacking phosphorus radical and from the related adduct be detected simultaneously, and that the spectrum of the phosphorus centred radical, when observed, was immediately replaced by that of the adduct upon introduction of a small amount of thioketone into the system.

The reaction between the examined thioketones and the precursors of the thiophosphonyl radicals, $\cdot P(S)L_2$, led exclusively to the observation of the expected spin adducts; this was true also for the precursors of the phosphonyl radicals $\cdot P(O)L_2$, although prolonged irradiation resulted in some istances in the appearence of other radicals species characterized by larger phosphorus splittings. With compounds of tervalent phosphorus, such as phosphines or tetraethylpyrophosphite, on the other hand, two, or more often three paramagnetic species were observed shortly after starting the reaction. It was actually found that the expected phosphinyl adducts were in nearly all cases accompanied by the corresponding phosphonyl adducts, in amounts that varied significantly with the way in which each individual sample had been prepared; the formation of these last derivatives is certainly to be attributed to the fact that secondary phosphines[19] and polyphosphines[20] are extremely sensitive to oxidizing agents, and in particular to molecular oxygen. The third radical species formed were identified as the thiophosphonyl adducts corresponding to the starting phosphinyl radicals. The identification of these adventitious species was based on the measured values of their $\underline{a}(^{31}P)$ splitting and was confirmed by generating, where possible, the authentic thiophosphonyl adducts by adding to the thioketones the proper $\cdot P(S)L_2$ radicals. As the precursors of the $\cdot PL_2$ radicals were free from any impurity which might lead to their $\cdot P(S)L_2$ analogs, the formation of the thiophosphonyl adducts detected in the reactions with phosphinyl precursors is somewhat surprising. Although the unexpected adducts might be thought to originate through a process common to all the phosphinyl adducts of the investigated thioketones, it seems more likely that the tervalent phosphorus compounds react with the thioketone during the preparation of the samples to afford the precursors of the thiophosphonyl radicals. A possible mechanism may involve desulfuration of the thioketones by the phosphine to give a carbene and the phosphine sulphide; this desulfuration reaction is analogous to that reported for phosphites.[21]

$$R_2C{=}S \;+\; PL_2H \longrightarrow R_2\bar{C}{-}S{-}\overset{+}{P}L_2H \longrightarrow R_2C: \;+\; P(S)L_2H \qquad (14)$$

Similar processes can be envisaged for tetraphenylbiphosphine and tetraethylpyrophosphite, in order to explain the formation of the corresponding thiophosphonyl adducts.

The extra species detected upon prolnged photoreaction of thioketones with diphenylphosphine oxide and *t*-BuOO-*t*-Bu could again be positively identified as the corresponding diphenylthiophosphonyl adducts. Because we were lacking a suitable precursor, we could not generate *in situ* the diethoxythiophosphonyl radicals, $\cdot P(S)(OEt)_2$; nevertheless, on the basis of the measured $\underline{a}(^{31}P)$ splittings and by analogy with what found with $\cdot P(O)Ph_2$ radicals, it seems conceivable to us that the species observed along with the diethoxyphosphonyl adducts be identified as their thiophosphonyl analogs. The formation of the $\cdot P(S)L_2$ adducts in the reactions of $\cdot P(O)L_2$ radicals, or their precursors, with thioketones is a puzzling finding, and at the present time we prefer not to speculate on this matter.

General Remarks on the ESR Spectra.

The ESR spectral parameters (hyperfine splitting constants and *g*-factors) of all the observed species are collected in Table 1. In nearly all cases the spectra were intense and well resolved; within each group of aromatic substrates the spectra were very similar and showed, besides the coupling with a ^{31}P nucleus which varied with the nature of the attacking phosphorus centred radical, couplings with the expected number of protons. Assignment to the different positions in the adducts from XT, TXT, and SXT was made by analogy with that of the related Group IVB adducts, which followed from McLachlan spin density calculations.[9]

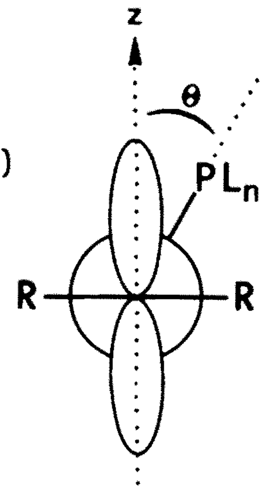
The increase of the *g*-factors observed in adducts 1-26 when changing from TBP to XT, TXT and SXT is consistent with the presence of the heteroatom in the molecular framework of the last three thioketones and with the fact that oxygen, sulphur and selenium are characterized by increasing spin-orbit coupling.

The data collected in Table 1 are also indicative of a somewhat higher spin density on the rings of the cyclic adducts than on those of TBP. This is due to the fact that in the latter derivatives the aromatic rings are partially twisted out of the molecular plane to relieve steric hindrance, thus making conjugation less efficient than in the more planar cyclic adducts.

Preferred Conformation of the Adducts.

An examination of Table 1 shows that the phosphorus splittings vary according to two distinct trends. In particular, for each attacking radical, the larger values of $\underline{a}(^{31}P)$ are found in the adduct of *t*-$Bu_2C{=}S$, while in the series of the aromatic thioketones the phosphorus coupling increases slightly when changing the substrate from TBP to XT, and decreases noticeably when passing to TXT and to SXT. On the other hand, $\underline{a}(^{31}P)$ increases markedly when going from a phosphinyl adduct of an individual thioketone to the corresponding phosphonyl and thiophosphonyl adducts.

(A)



The phosphorus atom in adducts 1-32 is β to the radical centre, and therefore its hyperfine splitting will be dependent on both the spin density on the α carbon and the degree of overlap between the SOMO and the phosphorus orbitals, that is on the dihedral angle θ between the S-P bond and the simmetry axys of the $2p_z$ on C_α as shown in structure (A).

The preferred geometry of the S-P bond in the different adducts can be estimated from the measured values of a(^{31}P), assuming for the β phosphorus hyperfine splitting constant a dependence on θ similar to that of β protons,[22] i.e.

$$a(^{31}P) = \varrho_C B \langle \cos^2 \theta \rangle \qquad (15)$$

with ϱ_C being the spin density on the α-carbon, B a constant, and $\langle \cos^2\theta \rangle$ the ensemble average over the thermally populated torsional leveles.

The adducts between phosphorus centred radicals and di-tert-butyl thioketone can be used to derive the proper values of B since, due to the large bulk of the tert-butyl group, they are compelled to adopt the orthogonal conformation (θ = 0 deg.) where the S-P bond is eclipsed with the $2p_z$ orbital on the α-carbon. The spin densities ϱ_C in the thioketone adducts may be assumed to vary in a way similar to the β-hydrogen splitting in the corresponding hydrocarbon radicals, i.e. t-$Bu_2\dot{C}$-H (21.89 Gauss),[16] diphenylmethyl (14.7),[17] xanthyl (12.7),[18] and thioxanthyl (11.82).[19] For selenaxanthyl no values are available. The $\varrho_C B$ values in the adducts of TBP, XT, and SXT with the various $\cdot PL_n$ radicals may therefore be obtained simply by multiplying the phosphorus hfs constant measured in the t-$Bu_2\dot{C}$-SPL_n adducts by 0.67, 0.58 and 0.54 respectively.

As t-$Bu_2\dot{C}$-SP(O)(OEt)$_2$ was the only adduct between phosphorus centred radicals and di-tert-butyl thioketone for which the ESR spectral parameters were available,[2] we have generated radicals 27-32 in order to get the necessary a(^{31}P) coupling constants. The last column in Table 1 collects the θ angle calculated by using the above procedure. Not surprisingly, the larger deviations from the eclipsed conformation are found for the three diphenylphosphinyl adducts, that is for the species characterized by the lower steric hindrance, and for the adducts to thiobenzophenone where the phosphorus substituent is less rigidly held in the orthogonal conformation, owing to the mobility of the aromatic rings. The small values of the θ angle found in the cyclic derivatives have to be considered more as an indication of the extent of torsional oscillation around the equilibrium position rather than as a measure of the actual deviations from the orthogonal conformation.

The g-factors of the adducts 1-26 also suggest that these radicals adopt a conformation very close to the orthogonal one, since their values are only slightly larger than 2.0025, which is typical of hydrocarbon radicals. Actually, much larger g-factors would be expected for the geometry with the S-P bond lying in the plane of the sp^2 hybrid on C_α, owing to easy delocalization of the unpaired electron on the sulphur atom.[27,28]

Rationalizing the variation of a(^{31}P) with the groups bonded to the phosphorus atom in a series of adducts with the same substrate is a somewhat more intriguing task. It is known that increasing the electronegativity of the L substituents in

TABLE 1. ESR spectral parameters[a,b] for radical adducts from TBP (1-6), XT (7-15), TXT (16-20), SXT (21-26), and di-*tert*-butyl thioketone (27-32) and calculated deviation angles, θ.

Rad.	PR_n	a_o	a_m	a_p	$a(^{31}P)$	g	θ[c]
1	PPh_2	2.91	1.24	3.27	16.59	2.0033	51
2	$P(O)Ph_2$	3.00	1.25	3.32	35.69	2.0029	34
3	$P(S)Ph_2$	2.91	1.22	3.30	49.23	2.0032	31
4	$P(O)(OEt)_2$	2.98	1.23	3.29	51.17	2.0028	29
5	[d]$P(S)(OEt)_2$	3.02	1.24	3.34	56.88	2.0029	31
6	$P(S)Et_2$	2.95	1.27	3.28	41.88	2.0032	33

Rad.	PR_n	X[e]	$a_{1,8}$	$a_{2,7}$	$a_{3,6}$	$a_{4,5}$	$a(^{31}P)$	g	θ[c]
7	PPh_2	O	0.72	3.46	0.72	2.92	27.92	----	28
8	$P(O)Ph_2$	O	0.74	3.53	0.74	2.95	38.50	2.0030	22
9	$P(S)Ph_2$	O	0.69	3.49	0.69	2.75	52.15	2.0033	19
10	$P(OEt)_2$	O	0.72	3.43	0.72	2.71	22.19	2.0030	--
11	$P(O)(OEt)_2$	O	0.76	3.57	0.76	2.95	54.86	2.0031	14
12	[d]$P(S)(OEt)_2$	O	0.71	3.69	0.71	2.90	61.38	2.0033	17
13	[f]$P(c\text{-}Hex)_2$	O	0.67	3.57	0.67	2.96	20.72	----	--
14	$P(S)(c\text{-}Hex)_2$	O	0.59[h]	3.42	0.64[h]	2.52	41.13	----	--
15	$P(S)Et_2$	O	0.66	3.55	0.66	2.89	45.61	2.0031	20
16	PPh_2	S	0.86	3.27	0.86	2.83	24.13	2.0038	32
17	$P(O)Ph_2$	S	0.89	3.34	0.89	2.87	34.68	2.0038	24
18	$P(S)Ph_2$	S	0.87	3.29	0.87	2.72	44.40	2.0040	25
19	$P(OEt)_2$	S	0.86	3.26	0.86	2.65	23.58	2.0039	--
20	$P(O)(OEt)_2$	S	0.88	3.40	0.88	2.85	48.83	2.0040	19
21	PPh_2	Se	0.95	3.34	0.95	2.85	24.82	2.0070	--
22	$P(O)Ph_2$	Se	0.89	3.35	0.89	2.79	33.22	2.0074	--
23	$P(S)Ph_2$	Se	0.92	3.22	0.92	2.80	42.43	2.0073	--
24	$P(OEt)_2$	Se	0.93	3.11	0.93	2.65	24.82	2.0068	--
25	$P(O)(OEt)_2$	Se	0.94	3.42	0.94	2.90	46.89	2.0073	--
26	$P(S)(c\text{-}Hex)_2$	Se	0.86	3.32	0.86	2.82	34.81	----	--

Rad.	PR_n	a(18H)	$a(^{31}P)$	g
27	PPh_2	0.47	61.81	2.0024
28	$P(O)Ph_2$	0.47	76.99	2.0027
29	$P(S)Ph_2$	0.47	100.57	2.0028
30	$P(O)(OEt)_2$	0.45	100.84	2.0025
31	$P(S)(OEt)_2$	0.45	115.32	2.0028
32	$P(S)Et_2$	n.r	89.15	2.0030

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a) Couplings in Gauss = 10^{-4} T; b) at room temperature; c) degrees; d) identity assumed; e) heteroatom; f) additional 1:2:1 triplet of 0.33 G; h) may be exchanged.

radicals $\cdot P(X)L_2$ leads to a more pyramidal structure and hence to a higher phosphorus splitting.[29] In radicals containing a β-phosphorus substituent the transmission of spin density from the α-carbon to the P-atom may occur via both spin polarization through the σ skeleton and direct delocalization. If only the former mechanism was operative, a linearrelation between the $a(^{31}P)$ splitting measured in the attacking radicals and in the resulting adducts should be expected, provided that the geometry at phosphorus is retained in the adducts. This is actually what we have found in a recent investigation on iminoxyls containing phosphorus substituents at the methine carbon.[30] Iminoxyls are known to be σ radicals and thus the spin density is transmitted from the radical centre to the phosphorus atom essentially through the σ framework.

Direct spin transfer, on the other hand, will strongly depend only on the radical conformation, i.e. on the overlap between the SOMO and the σ and σ^* orbitals of the S-P bond, but also on the energy difference between these orbitals. Since the latter will change by changing the nature of the phosphorus ligands, the magnitude of the phosphorus splitting cannot be easily predicted even if the radical adducts adopt the same conformation. We may only notice that within each series of adducts to the same substrate, the phosphorus coupling increases in the order $PL_2 < P(O)L_2 < P(S)L_2$ despite the fact that thiophosphonyl radicals $\cdot P(S)L_2$ exhibit[30-32] smaller phosphorus splittings than the related phosphonyl radicals, $\cdot P(O)L_2$.

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REFERENCES and NOTES

1) N. Kito and A. Ohno, *Bull. Chem. Soc. Jpn.*, 46, 2487 (1973).
2) J.C. Scaiano and K.U. Ingold, *J. Am. Chem. Soc.*, 98, 4727 (1976).
3) J.C. Scaiano, J.P.A. Tremblay, and K.U. Ingold, *Can. J. Chem.*, 54, 3407 (1976).
4) D. Forrest, K.U. Ingold, and D.H.R. Barton, *J. Phys. Chem.*, 81, 915 (1977).
5) D. Forrest and K.U. Ingold, *J. Am. Chem. Soc.*, 100, 3868 (1978).
6) A. Alberti, F.P. Colonna, and G.F. Pedulli, *Tetrahedron*, 36, 3043 (1980).
7) B.B. Adeleke, K.S. Chen, and J.K.S. Wan, *J. Organomet. Chem.*, 208, 317 (1981).
8) A. Alberti, M. Guerra, and G.F. Pedulli, *J. Am. Chem. Soc.*, 103, 6604 (1981).
9) A. Alberti, F.P. Colonna, M. Guerra, B.F. Bonini, G. Mazzanti, Z. Dinya, and G.F. Pedulli, *J. Organomet. Chem.*, 221, 47 (1981).
10) W.G. McGimpsey, M.C. Depew, and J.K.S. Wan, *Phosphorus and Sulphur*, 21, 135 (1984).
11) W.G. McGimpsey, M.C. Depew, and J.K.S. Wan, *Organometallics*, 3, 1684 (1984).
12) A. Alberti, M.C. Depew, A. Hudson, W.G. McGimpsey, and J.K.S. Wan, *J. Organomet. Chem.*, 280, C21, 1985.
13) A. Alberti, B.F. Bonini, and G.F. Pedulli, *Tetrahedron Letters*, 3737 (1987).
14) B.I. Gofton and E.A. Braude, *Org. Synth.*, 35, 97 (1980).
15) N. Lozac'h and G. Guillozo, *Bull. Chim. Soc. France*, 1221 (1957).
16) D.H.R. Barton, F.S. Guziec, Jr., and I. Shahak, *J. Chem. Soc.,Perkin Trans. I*, 1794 (1974).
17) G. Peters, *J. Am. Chem. Soc.*, 82, 4751 (1960).
18) A. Alberti, A. Hudson, G.F. Pedulli, W.G. McGimpsey, and J.K.S. Wan, *Can.J. Chem.*, 63, 917 (1985).
19) M.M. Rauhut and H.A. Currier, *J. Org. Chem.*, 26, 4626 (1961).
20) D.J.H. Smith, in "Comprehensive Organic Chemistry", D.H.R. Barton, W.D. Ollis, and I.O. Sutherland, Ed.s, vol. 2, p. 1159, Pergamon Press, New York, 1979.
21) W.J. Middleton and W.H. Sharkey, *J. Org. Chem.*, 30, 1384 (1955).
22) P.B. Ayscough, in "Electron Spin Resonance in Chemistry", Methuen, London, 1967.
23) D. Griller and K.U. Ingold, *J. Am. Chem. Soc.*, 95, 6459 (1973).
24) A.R. Bassindale, A.J. Bowles, A. Hudson, R.A. Jackson, K.Schreiner, and A. Berndt, *Tetrahedron Letters*, 3185 (1973).
25) H. Masuhara, M. Okuda, M. Koizumi, *Bull. Chem. Soc. Jpn.*, 41, 2319 (1968).
26) P. Devolder, *Can J. Chem.*, 54, 1744 (1976).
27) B.C. Gilbert, J.P. Larkin, and R.O.C. Norman, *J. Chem. Soc., Perkin Trans. II*, 272 (1973).
28) The diethoxyphosphonyl adduct of di-*tert*-butyl thioketone, that for steric reasons adopt an orthogonal conformation, is characterized by $g = 2.0026$.[2]
29) B.P. Roberts and K. Singh, *J. Organomet. Chem.*, 159, 31 (1978).
30) A. Alberti and G.F. Pedulli, *Gazzetta Chim. It.*, 118, 131 (1988).
31) A.G. Davies, R.W. Dennis, D. Griller, K.U. Ingold, and B.P. Roberts, *Mol. Phys.*, 25, 989 (1973).
32) The spectral parameters of the diphenylthiophosphonyl radical have been determined in the course of this work as $a(^{31}P) = 286.94$ G, $g = 2.0114$ at 280 K; the values have been corrected using the full Breit-Rabin equation).