An Electron Spin Resonance Investigation of Free Radicals with Oxygen- and Sulphur-containing Substituents

Athelstan L. J. Beckwith * **and Steven Brumby**
Research School of Chemistry, Australian National University, Canberra, Australia, A.C.T. 2601

Electron spin resonance (e.s.r.) spectra have been recorded during the photolysis of di-t-butyl peroxide in the presence of a number of organic substrates with oxygen- and sulphur-containing functional groups. By hydrogen-atom abstraction, many of the substrates yield more than one species of free radical, the relative concentrations of which have been estimated. These relative concentrations are influenced by the electrophilic character of the t-butoxyl radical, and by the stabilities of the radicals generated. Bis(methylthio)methane (**2**) gives rise to tris(methylthio)methyl radicals (**5a**), in addition to the two species expected by direct abstraction. Tris(methylthio)methane (**5**) gives rise to tris(methylthio)methyl radicals (**5a**) only, which, from the measured $\alpha^{13}C$ hyperfine splitting constant, appear to be approximately planar. Several of the substrates used give rise to captodative free radicals. The data indicate that alkylcarbonyl groups are more effective than the methoxycarbonyl group in the capto role. The acyclic captodative radicals all exist in two distinct conformations, the likely geometries of which are discussed. Observations on two cyclic radicals suggest that relatively small deviations from a suitable planar conformation can significantly diminish the importance of the captodative effect.

We are interested in the factors which influence the rates of abstraction of hydrogen atoms from molecules by free radicals such as t-butoxyl. In this connection, we have recorded e.s.r. spectra during the photolysis of solutions of substrates (**1**)—(**14**)

$CH_2(OMe)_2$ (**1**)
$CH_2(SMe)_2$ (**2**)
$MeSCH_2OMe$ (**3**)
$CH(OMe)_3$ (**4**)
$CH(SMe)_3$ (**5**)
$MeOCH_2CH_2OMe$ (**6**)
$MeOCH_2OCOMe$ (**7**)
$MeCO_2Me$ (**8**)
$MeOCH_2CO_2Me$ (**9**)
$MeSCH_2CO_2Me$ (**10**)
$MeOCH_2COMe$ (**11**)
$MeSCH_2COMe$ (**12**)
$C(O)-[CH_2]_3-CH(OMe)$ (**13**)
$C(O)-[CH_2]_3-O-CH_2$ (**14**)

in di-t-butyl peroxide. Under these conditions, many of the substrates gave rise to more than one species of free radical. In most instances it seems likely that the different species undergo radical-radical termination at approximately the same diffusion controlled rate, since even free radicals which are thought to be strongly stabilized by the captodative effect have been found to terminate at close to the diffusion-controlled limit.[1] In this circumstance, and with the additional assumption that the free radicals derived from the substrates are consumed only by radical-radical termination, the relative steady-state concentrations of the different free radicals in solution give a direct indication of the relative rates of hydrogen-atom abstraction from the different positions of a substrate molecule.

Literature e.s.r. parameters are given in Table 1 for radicals (**15**)—(**17**), which are related to those we have investigated. Each of these free radicals has a substituent with a two-fold barrier to rotation about its bond to the trigonal carbon atom, and this gives rise to linewidth alternation in the e.s.r. spectra recorded at low temperatures; the rotational energy barriers shown in Table 1 are based on analyses of these linewidth variations. The same types of restricted internal rotation exist in several of the free radicals we have investigated, with the result that the radicals can exist in distinct rotational conformations.

Experimental

The following substrates were prepared by literature methods: (**3**),[6] (**5**),[7] (**7**),[8] (**9**),[9] (**12**),[10] (**13**),[11] and (**14**).[12] Substrate (**10**) was prepared by the reaction of methyl chloroacetate with sodium methanethiolate in methanol at 0 °C. The other materials were obtained commercially, and in some cases required purification. Usually, an e.s.r. sample consisted only of the substrate and di-t-butyl peroxide, typically in the ratio 1:2 by volume. With substrates (**8**), (**12**), and (**14**), cyclopropane was also included as a solvent.

The e.s.r. spectrometer and associated equipment has been described elsewhere.[13] The on-line data system was acquired during the course of this work. The relative concentrations shown in parentheses in the Tables were estimated approximately by spectrum simulation, without the benefit of the data system. Other relative concentrations were determined more reliably by a numerical method which has been described.[14]

Results and Discussion

Substrates (**1**)—(**7**).—E.s.r. data for radicals derived from substrates (**1**)—(**7**) are summarized in Table 2. Most of the spectra were consistent with generation of the expected free radicals, but the formation of radical (**5a**) from substrate (**2**) was unexpected. Spectra recorded using substrate (**5**) supported the view that this radical was correctly identified as tris(methylthio)methyl. With substrate (**2**), we found that the relative concentration of (**5a**) increased as the duration of irradiation increased. Furthermore, spectra attributable chiefly to (**5a**) were observed during the photolysis of neat (**2**). The products from the photolysis (at 254 nm) of neat (**2**) were analysed by gas chromatography, using a capillary column coated with OV-101. By comparing the retention times with those of authentic materials, the compounds MeSMe, MeSSMe, and $CH(SMe)_3$ were identified among the products, together with a trace of MeSH. These observations appear to be consistent with equation (1) as the primary photolytic process. Equations (2) and (3) may be important among the subsequent reactions,

$$CH_2(SMe)_2 \longrightarrow {}^{\bullet}SMe + {}^{\bullet}CH_2SMe \qquad (1)$$

$${}^{\bullet}CH_2SMe + CH_2(SMe)_2 \longrightarrow MeSMe + {}^{\bullet}CH(SMe)_2 \qquad (2)$$

Table 1. Literature data for free radicals (**15**)—(**17**)

Radical	T/°C	Hyperfine splitting constants/G		Rotational barrier kJ mol^{-1}	Ref.
		α-H	γ-H		
$^{\bullet}$CH$_2$OMe (**15**)	−80	17.99; 16.61	2.02	24	2
$^{\bullet}$CH$_2$SMe (**16**)	?	17.5; 16.7	3.1	>30	3
$^{\bullet}$CH$_2$COMe (**17**)	−49.5	19.95; 19.48	0.27	39	4, 5

Table 2. Data from e.s.r. spectra recorded with substrates (**1**)—(**7**)

Substrate	T/°C	Radical	Rel. conc.	Hyperfine splitting constants/G			g
				α-H	γ-H	other	
(**1**)[a]	−35	$^{\bullet}$CH(OMe)$_2$ (**1a**)	8.0	11.90	0.795	—	2.003 16
		$^{\bullet}$CH$_2$OCH$_2$OMe (**1b**)	10.0	17.84	0.78	—	2.003 27
(**2**)[b]	−43	$^{\bullet}$CH(SMe)$_2$ (**2a**)	(10)	14.80	1.745	—	2.005 34
		$^{\bullet}$CH$_2$SCH$_2$SMe (**2b**)	(1.5)	16.72	2.00	—	2.005 18
		$^{\bullet}$C(SMe)$_3$ (**5a**)	(3.4)	—	1.18	—	2.005 42
(**3**)	−43	$^{\bullet}$CH(OMe)SMe (**3a**)	10.0	14.44	1.53; 0.47	—	2.003 48
		$^{\bullet}$CH$_2$SCH$_2$OMe (**3b**)	3.9	17.35	1.02	—	2.004 65
		$^{\bullet}$CH$_2$OCH$_2$SMe (**3c**)	1.7	17.54	1.147	—	2.003 62
(**4**)[e]	−26	$^{\bullet}$C(OMe)$_3$ (**4a**)	(10)	—	0.34	154.13;[c] 3.69[d]	2.002 85
		$^{\bullet}$CH$_2$OCH(OMe)$_2$ (**4b**)	(1.9)	18.13	0.96	—	2.003 21
(**5**)	−26	$^{\bullet}$C(SMe)$_3$ (**5a**)	—	—	1.16	39.25;[c] 9.25[d]	2.005 45
(**6**)[g]	−43	$^{\bullet}$CH(OMe)CH$_2$OMe (**6a**)	10.0	17.08	1.95	7.98[f]	2.003 12
		$^{\bullet}$CH$_2$O(CH$_2$)$_2$OMe (**6b**)	11.3	16.92	2.20	0.11[h]	2.003 30
	−111	(**6a**)	10.0	17.50	2.07	6.67; 6.83[f]	—
		(**6b**)	7.6	16.78; 18.14	2.56	0.12[h]	—
(**7**)	−26	$^{\bullet}$CH(OMe)OCOMe (**7a**)	4.5	5.99	1.205	1.056[h]	2.003 07
		$^{\bullet}$CH$_2$OCH$_2$OCOMe (**7b**)	10.0	18.25	0.67	—	2.003 26

[a] Earlier studies: references 15—17. [b] References 16 and 18. [c] α^{13}C Splitting. [d] γ^{13}C Splitting. [e] Reference 19. [f] β-H Splittings. [g] References 17 and 20. [h] δ-H Splitting.

$$^{\bullet}CH(SMe)_2 + {}^{\bullet}SMe \longrightarrow CH(SMe)_3 \tag{3}$$

explaining the gradual build-up of (**5**), with a concomitant increase in the concentration of the derived free radical (**5a**). Direct formation of (**5**) by S_H2 attack of (**2a**) on MeSSMe or (**2**) is another possibility. Since the radical (**5a**) was detectable when the concentration of (**5**) was very small, we consider that the rates of biradical termination reactions involving this free radical may be slower than the diffusion-controlled limit.

In the e.s.r. spectrum of radical (**3a**) the larger of the two γ-H splitting constants presumably belongs to the methylthio-substituent. The γ-H splitting constants for this radical are similar in magnitude to those for 2-methyl-1,3-oxathiolan-2-yl,[18] but it is puzzling that for 1,3-oxathiolan-2-yl the two types of γ-proton appear equivalent.[16,18] The assignment of the e.s.r. parameters to the radicals (**3b**) and (**3c**) is not defined by the multiplicities. The tentative assignment we have made is chiefly based on a consideration of the relative concentrations of the two radicals, since we consider that hydrogen abstraction leading to (**3b**) is likely to be faster than abstraction leading to (**3c**).[21] The measured g-factors are consistent with this assignment, because a β-sulphur atom is generally more effective than a β-oxygen atom in augmenting g.[3,16,18]

The kinetics of hydrogen-atom abstraction from ethers, especially cyclic ethers, is a topic which has received attention,[22,23] and the influence on abstraction rates of the dihedral angle θ, between a C–H bond of the substrate ether and the p-type lone pair of an adjacent oxygen atom has been stressed. Substrate (**1**) was included in one of these studies,[22] and the ratio of the reactivity per methylene hydrogen atom to the reactivity per methyl hydrogen atom was 5:1 at −60 °C, which may be compared with a ratio of 2.4:1 based on our observations at −35 °C (Table 2); the difference may be attributed to the lower selectivity of abstraction at the higher temperature. An electron diffraction study[24] of (**1**) suggests that the molecule exists chiefly in a *gauche-gauche* conformation, with the methyl groups on opposite sides of the O–C–O plane. This corresponds to θ = 30° and 90°, for both the methylene hydrogen atoms. Therefore, it is interesting to note in reference 22, that the relative reactivity per equivalent hydrogen atom is similar for the methylene hydrogens of (**1**), and for two types of hydrogen atoms belonging to cyclic ethers, for which θ = 30° and 90°.

In our previous discussion of radical (**1a**),[14] it was argued that, at −35 °C, the preferred conformation was of the *cis-cis* type, but with a significant steady-state concentration of *cis-trans* type. At temperatures lower than *ca.* −100 °C, the spectra showed no trace of the minor conformation. The e.s.r. spectra of the radicals (**2a**) and (**3a**) did not show evidence of similar conformational equilibria under our conditions.

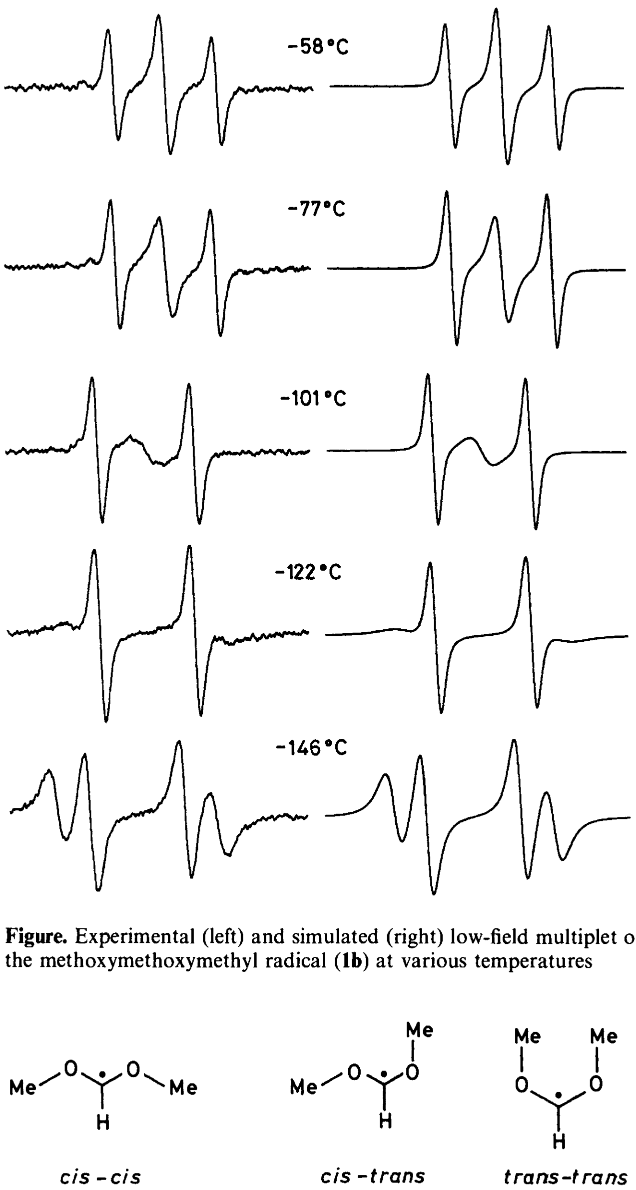
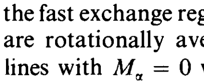
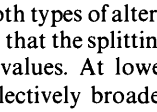


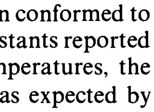
Figure. Experimental (left) and simulated (right) low-field multiplet of the methoxymethoxymethyl radical (**1b**) at various temperatures



cis-cis

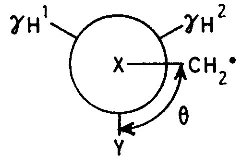


cis-trans

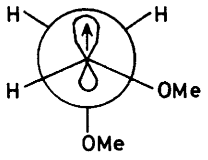


trans-trans

The e.s.r. spectra of the radicals (**1b**), (**2b**), (**3b**), and (**3c**) displayed two types of linewidth alternation, as discussed for (**1b**) by Gaze and Gilbert.[17] The data reported in Table 2 apply to temperatures at which both types of alternation conformed to the fast exchange regime, so that the splitting constants reported are rotationally averaged values. At lower temperatures, the lines with $M_\alpha = 0$ were selectively broadened, as expected by analogy with radicals (**15**) and (**16**), and the lines with $M_\gamma = 0$ were also selectively broadened; this is illustrated for (**1b**) in the Figure. The radicals appear to prefer conformations of the type (**18**) (X = S or O, Y = SMe or OMe), and show linewidth alternation due to restricted rotation about the O_β–C_γ bond. We have carried out MNDO calculations[25] for (**1b**) which indicate that the preferred dihedral angle θ is 82°; this compares with θ = 60° found using INDO calculations.[17] Our calculations suggest that $a_\gamma(1)$ is negative and $a_\gamma(2)$ is positive, in agreement with the INDO calculations. The simulated multiplets, shown in the Figure, were calculated by the fast Fourier transform method,[2] using the Simplex algorithm[13] to optimize the parameters. At temperatures higher than −146 °C, we found it necessary to assume that $|a_\gamma(1) - a_\gamma(2)|$ did not deviate from its value at −146 °C (2.27 G). Although this assumption is unlikely to be strictly correct, in view of the fact that $|a_\gamma(1) + a_\gamma(2)|$ increased from 1.34 G at −146 °C to 1.46 G at −58 °C, we estimate that the exchange rates, determined by the simulation method, are not likely to be seriously in error. A least-squares fit of these exchange rates to the Arrhenius equation yielded, for rotation about $O_\beta - C_\gamma$, an activation energy of (16.1 ± 0.2) kJ mol^{-1} (*cf.* 19 ± 2 kJ mol^{-1} found by Gaze and Gilbert[17]) and a pre-exponential factor of $(3.2 \pm 0.4) \times 10^{12}$ s^{-1}. [The errors quoted do not take account of possible variations in $|a_\gamma(1) - a_\gamma(2)|$.]



(18)

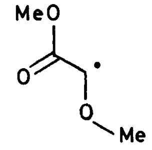
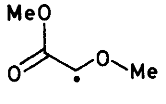
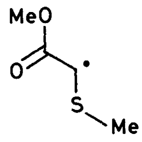
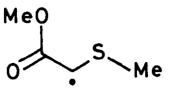


(19)

In a previous investigation of radical (**4a**),[19] no value for $a(\gamma^{13}C)$ was reported, and this omission is rectified in Table 2. Our value for $a(\alpha^{13}C)$, at a considerably higher temperature than the previous measurement,[19] demonstrates that $\partial|a(\alpha^{13}C)|/\partial T$ has a small positive value. Substrate (**5**) gave an intense spectrum of radical (**5a**), from which it was possible to determine the splittings due to α and $\gamma^{13}C$ atoms in natural abundance (Table 2). The ^{33}S satellites could not be located, however. The magnitude of $a(\alpha^{13}C)$ is indicative of an approximately planar geometry at the trigonal carbon atom, in contrast to the pyramidal (**4a**).[19] This may signify a smaller antagonistic effect[26] between alkylthio substituents than between alkoxy substituents, and steric factors may also be involved. Both $a(\alpha\text{-H})$ and $a(\gamma^{13}C)$ are larger for (**5a**) than for (**4a**). These observations all point to a greater delocalization of the unpaired electron in (**5a**) than in (**4a**). This presumably explains why no trace of the sulphur analogue of (**4b**) could be found in the experiments with substrate (**5**). Other evidence supports the view that alkylthio substituents are more effective spin delocalizers than alkoxy substituents.[3,27]

Substrate (**6**) is of special interest because of reports[28,29] that an oxygen substituent at the β-position exercises a stabilizing effect on carbon radicals. This might be expected to favour the formation of radical (**6a**) over (**6b**) beyond the preference usually observed for formation of secondary radicals over primary. From Table 2, it may be seen that, at −43 °C, the ratio [(**6a**)]:[(**6b**)] does not differ greatly from the ratio of 2:3 which would be expected if the two types of hydrogen atom were equally reactive in transfer. At −111 °C the t-butoxyl radicals are more selective, and the ratio has shifted in favour of radical (**6a**), but the effect is not dramatic. The smallness of the value of $a(\beta\text{-H})$ for radical (**6a**) indicates that the radical has a preference for conformation (**19**), analogous to the preferred conformations of $^{\bullet}CH(SBu^t)CH_2OMe$,[27] β-fluoro-t-butyl,[30] and 1,2-dihydroxyethyl[31] radicals. A preference for conformation (**19**) is also consistent with the fact that selective broadening of the lines with $M_\beta = 0$ was observed in the spectrum recorded at −111 °C. We conclude that the presence of the β-oxygen

Table 3. Data from e.s.r. spectra recorded with substrates (**8**)—(**10**)

				Hyperfine splitting constants/G			
Substrate	T/°C	Radical	Rel. conc.	α-H	γ-H	δ-H	g
(**8**)	−60	$^{\bullet}CH_2CO_2Me$ (**8a**)	(1.0)	21.28	—	1.36	2.003 54
		$^{\bullet}CH_2OCOMe$ (**8b**)	(1.0)	20.80	—	1.32	2.003 31
		$^{\bullet}\overline{CH\text{-}CH_2CH}_2$ [a]	(1.0)				
(**9**) [b]	−43	 **(9a)**	10.0	17.54	2.83	1.60	2.004 06
		 **(9b)**	2.8	17.30	2.80	1.10	2.004 12
		$^{\bullet}CH_2OCH_2CO_2Me$ **(9c)**	2.3	17.30	1.79	—	2.003 27
(**10**) [c]	−26	 **(10a)**	(10)	14.67	4.07	1.29	2.006 09
		 **(10b)**	(8.0)	14.51	4.08	0.83	2.006 18
		$^{\bullet}CH_2SCH_2CO_2Me$ **(10c)**	(6.5)	16.18	2.21	—	2.004 62

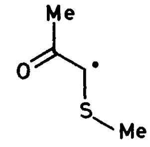
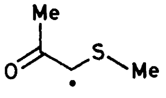
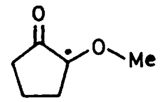
[a] a(α-H) = 6.16; a(β-H) = 22.88. [b] Reference 1. [c] Reference 27.

substituent has only a small influence on the rate of formation of (**6a**), but does affect its conformation.

Substrate (**7**) is unique among the substrates investigated in this work in that abstraction of a methylene hydrogen atom is less favourable than abstraction of a methoxy hydrogen atom. More precisely, a methylene hydrogen atom of (**7**) is about 0.7 times as readily abstracted as a methoxy hydrogen at −26 °C. Again, we consider that the rates of hydrogen transfer may be strongly influenced by factors other than the stability of the product radicals; in this case, the OAc substituent may render the methylene hydrogen atoms less nucleophilic, and therefore less subject to attack by t-butoxyl radicals. A comparison of $|a(\alpha\text{-H})|$ for radical (**7a**) (5.99 G) and radical (**1a**) (11.9 G) is interesting. Radical (**7a**) would be expected to be more nearly planar than radical (**1a**). This implies that a(α-H) for (**1a**) must be positive. In previous work, some authors have considered this coupling to be negative,[15,32,33] whereas others have argued in favour of a positive value.[19,31] The sign of a(α-H) for (**7a**) is not certain.

Substrates (**8**)—(**10**).—Bascetta *et al.*[34] have used a number of carboxylic esters as substrates for hydrogen-atom abstraction by t-butoxyl radicals. The relative concentrations of the free radicals detected by e.s.r. spectroscopy seem to indicate that acyloxy and alkoxycarbonyl substituents have rather similar effects on the rates of abstraction from an adjacent position in a substrate molecule, CO_2R being slightly more activating and OCOR slightly less activating than R. Under our conditions, the two kinds of substituents were similarly activating, since radicals (**8a**) and (**8b**), derived from substrate (**8**), had approximately the same steady-state concentration (Table 3). Cyclopropyl radicals, identified from literature data,[35] were also found; this may be due to the low reactivity of the substrate, resulting in relatively high steady-state concentrations of t-butoxyl radicals. In this connection, we note that there is evidence for abnormally high methoxy C–H bond strengths in methyl esters;[36] however, our observations do not necessarily give a direct indication of bond strengths. Interestingly, when substrate (**8**) was used under different experimental conditions,

Table 4. Data from e.s.r. spectra recorded with substrates (**11**)—(**14**)

Substrate	T/°C	Radical	Rel. conc.	Hyperfine splitting constants/G				g
				α-H	H, XR	H, COR	other	
(**11**)	−43	(**11a**)	(2.0)	15.10	2.83	1.10	—	2.004 83
		(**11b**)	(1.0)	15.39	2.74	2.96	—	2.004 56
	+34	(**11a**)	(2.0)	15.47	2.72	0.85	—	—
		(**11b**)	(1.0)	15.84	2.71	2.71		—
(**12**)	−88	 (**12a**)	(1.2)	13.65	4.03	2.08	—	2.006 25
		 (**12b**)	(1.0)	12.64	5.28	1.87	—	2.006 32
	−52	(**12a**)	(3.0)	13.48	3.95	2.02	—	2.006 23
		(**12b**)	(1.0)	12.47	5.15	1.84	—	2.006 35
(**13**)	−35	 (**13a**)	—	—	2.80	7.00	24.00;[a] 0.40[b]	2.004 75
(**14**)	−60	C(O)–ĊH–O–[CH$_2$]$_2$–CH$_2$ (**14a**)	—	14.09	3.77; 5.08	0.18; 0.47	—	2.004 86

[a] a(β-H). [b] Splitting constant for the γ-protons furthest from the carbonyl group.

and with OH$^{\cdot}$ as the abstracting species, the concentration of (**8b**) was about 10 times larger than that of (**8a**).[37] Further details of the e.s.r. spectra of (**8a**) and (**8b**) will be reported elsewhere.

Our analysis of the spectrum recorded using substrate (**9**) is closely similar to that of Korth *et al.*[1] The spectrum shows that methoxy(methoxycarbonyl)methyl free radicals exist in two distinct conformations. There is evidence for restricted rotation about both $^{\cdot}$C–OMe[2] and $^{\cdot}$C–CO$_2$Me[38] bonds, and when both kinds of bonds are present it seems possible that the rotations may be more strongly restricted, as a consequence of the captodative effect.[39] Therefore four possible rotamers may be envisaged for this free radical. The rotamers which we have drawn in Table 3 are speculative.

Similar arguments apply to the spectrum recorded with substrate (**10**). This substrate has been used in another investigation,[27] but a complete analysis of the e.s.r. spectrum was not given.

Radicals of the type $^{\cdot}$CR(OH)CO$_2$R′ also exist in two isomeric forms, which have been attributed to restricted rotation of the CO$_2$R′ group about its bond to the trigonal carbon atom.[40]

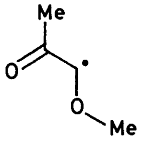
Substrates (**11**)—(**14**).—Whereas substrates (**9**)—(**10**) gave rise to both captodative and non-captodative free radicals, substrates (**11**)—(**14**) (Table 4) did not give rise to any non-captodative free radicals in sufficiently large concentrations for their detection by e.s.r. spectroscopy. It seems possible that this difference between the two classes of substrate may be related to the more weakly capto character of the methoxycarbonyl substituent, as compared with the methylcarbonyl substituent.

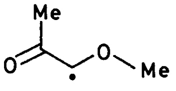
One way of assessing the importance of the captodative effect is by comparing the hyperfine splitting constants associated with substituents in captodative and non-captodative free radicals. Suitable non-captodative free radicals for comparison are (**15**)—(**17**) and (**8a**). The observations with substrates (**9**)—(**12**) suggest that the captodative effect causes enhancement of the splittings associated with the substituents OMe, SMe, and COMe. The effect is most pronounced for the COMe substituent. Judged by this criterion, the captodative effect shows interesting dependencies on conformation (Tables 3 and 4): for the CO$_2$Me substituent, a small enhancement in splitting constant is found in conformation (**9a**), but a decrease is found in (**9b**).

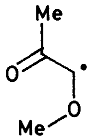
Table 5. Relative energies of conformations of the 1-methoxyacetonyl radical by MO calculations

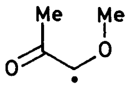
Conformation	Relative energy (kJ mol^{-1})	
	MNDO	INDO
(**11a**)	0	6.1
(**11b**)	0.6	0
(**11c**)	7.8	5.6
(**11d**)	18.9	92.1

The e.s.r. spectra recorded with substrate (**11**) indicated that the methoxy(methylcarbonyl)methyl radical exists in two distinct conformations. In view of the studies which have been made of the radicals (**15**) and (**17**) (Table 1) it seems likely that rotation about both the $^{\cdot}$C–O and $^{\cdot}$C–CO bond is restricted, so that the four conformations (**11a**)—(**11d**) may be envisaged. We have used semi-empirical molecular orbital calculations at the MNDO[25] and INDO[41] levels of approximation to estimate the relative energies of these conformations. The most stable conformation was found to be (**11a**) when the MNDO method was used and (**11b**) when the INDO method was used, as shown in Table 5. We believe the MNDO energies are more reliable; conformations (**11c**) and (**11d**) appear to be destabilized by steric repulsions involving the methyl group bonded to oxygen, and for conformation (**11d**) the MNDO calculations indicate that the repulsion is sufficiently large that the radical backbone is twisted somewhat out of a planar arrangement.


(**11a**)


(**11b**)


(**11c**)


(**11d**)

Based on these considerations, it seems possible that the two conformations which contribute to the e.s.r. spectra are (**11a**) and (**11b**). We consider that the species with the greater steady-state concentration is likely to be (**11a**) (Table 4). For these conformations, the assignments of the splitting constants to the methyl groups is ambiguous. For (**11a**), our assignments are based on the view that the splitting constant for the methoxy protons is likely to be larger than for the non-captodative radical (**15**). For (**11b**) at the lower temperature the difference in magnitude between the splittings is small, and the assignment we have made in Table 4 is arbitrary; at the higher temperature there is no measurable difference in magnitude between the splittings.

The e.s.r. spectra did not show evidence for interconversion between (**11a**) and (**11b**), even at +34 °C. In contrast, the spectra of (**17**), and other alkanoyl methyl radicals which do not have dative substituents,[42] conform to the fast exchange limit at this temperature, although there is evidence that rotation may be more strongly hindered in aqueous media.[43] The observations seem to be consistent with the view that the captodative effect increases the barriers to internal rotation.

We have remarked on the intriguing conformation dependencies of the splitting constants associated with substituents, especially capto substituents, in the captodative free radicals we have studied. The effect is greatest for the acetyl substituent of (**11a**) and (**11b**). Spin densities calculated for these two conformations by the MNDO and INDO methods did not differ by nearly as much as the measured e.s.r. parameters imply. The large enhancement of a(H, COMe) in both (**11a**) and (**11b**), compared, for example, with (**17**), may be attributed to the captodative effect, which depends for its effectiveness on the atoms of the radical backbone being coplanar: any deviation from this planar arrangement would be expected to result in a smaller enhancement of the splitting constant. Such deviations are inevitable as a consequence of thermal motion, but would not necessarily be similar for different conformations. We speculate that the difference in a(H, COMe) between (**11a**) and (**11b**) may be largely due to the different time-averaged deviations from planarity. These idea will be discussed further in relation to radicals (**13a**) and (**14a**).

The spectra recorded with substrate (**12**) were interpreted in a similar way to the spectra recorded with substrate (**11**) (Table 4). On steric grounds, one would expect the energy difference between (**12a**) and (**12b**) to be greater than between (**11a**) and (**11b**), and the spectra showed intriguing differences regarding the relative concentrations of the rotamers. For the radicals derived from substrate (**11**), the concentration ratio did not vary, within experimental error, over the temperature range −43—+34 °C. In contrast, for the radicals derived from substrate (**12**) the ratio of the concentration of the less abundant rotamer to that of the more abundant rotamer decreased from 0.81 at −88 °C to 0.61 at −77 °C, to 0.33 at −52 °C, and at −26 °C the less abundant rotamer did not make any detectable contribution to the e.s.r. spectrum. It is difficult to comment on these observations without more information than we have on the mobilities of the equilibria between the rotamers. The concentration ratio between two rotamers is expected to depend on two factors: (a) the ratio in which the two rotamers are initially generated, and (b) the equilibrium concentration ratio. The relative importance of these two factors will depend on the mobility of the equilibrium.* A possible interpretation of the observations with substrate (**12**) is that factor (a) is of greater importance at low temperatures, and that factor (b) becomes relatively important at higher temperatures as the equilibrium becomes more mobile. With regard to the observations with substrate (**11**), we speculate that the equilibrium may be less mobile, so that factor (a) is of greater importance throughout the temperature range investigated.

The e.s.r. spectrum recorded using substrate (**13**) shows evidence of only one type of free radical, which we have assumed to be the rotamer (**13a**) (Table 4), expected to be preferred sterically. The assignments of the splittings to the inequivalent pairs of γ-protons is ambiguous, and the assignment in Table 4 is based partly on a consideration of literature data for the hydroxycyclopentyl radical,[44] for which $a(\gamma\text{-H}) = 0.35$ G. Also, the splitting constant due to the γ-protons adjacent to the carbonyl group seems likely to be the larger of the two. At 7.00 G, this splitting constant is considerably greater than the analogous parameter for the species (**11a**) and (**11b**). This is partly, but not entirely, explained by the fact that the γ-protons adjacent to the carbonyl group are constrained by the ring to adopt orientations favourable for a hyperconjugative interaction. Another consideration is that, for the most effective enhancement of a(H, COMe) by the captodative effect, it is necessary for the atoms involved in the π-system to adopt a planar arrangement: in (**13a**), thermal motions which might disturb this planarity are severely restricted by the ring.

Radical (**14a**) also has two pairs of γ-protons, which again leads to ambiguity about the assignments. The assignments we have made in Table 4 are reasonable by comparison with radicals (**15**) and (**17**) (Table 1) if radical (**14a**) is considered to be unable to achieve its captodative potential because of non-planarity in the ring. The fact that both pairs of γ-protons appear inequivalent in the e.s.r. spectrum supports the idea that the radical is non-planar.

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* Also on the average time interval between abstraction and termination, but in e.s.r. work there is limited scope for varying this parameter.

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