An EPR Study of Free Radicals Derived from 1,3-Dioxolan-4-one and Related Compounds

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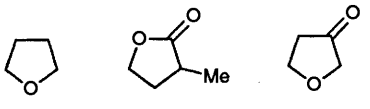
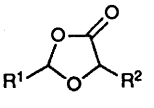
Electron paramagnetic resonance (EPR) spectra have been recorded during UV irradiation of di-*tert*-butyl peroxide in the presence of α-methyl-γ-butyrolactone (**2**), tetrahydrofuran-3-one (**3**), and the substituted 1,3-dioxolan-4-ones **4–10**. *tert*-Butoxyl radicals abstract hydrogen atoms from the α-position of **2**, position 2 of **3**, and positions 2 and 5 of **4–10**. The EPR parameters determined from the spectra include exceptionally large hyperfine splitting constants due to the γ-protons in the radicals derived from **4–10**. The reactivities per equivalent hydrogen atom of tetrahydrofuran (**1**) and the substrates, **2–20**, relative to the reactivity of a methoxy hydrogen atom of *tert*-butyl methyl ether (**11**) have been estimated from digitised EPR spectra, and these reactivities are discussed.

In connection with our work [1] on the application of free-radical methodology to the enantioselective synthesis of α-hydroxy acids we required fundamental information on the behaviour of dioxolanones and related compounds. The principal aim of the present study was to improve our understanding of the factors which influence the rates of hydrogen atom abstraction by *tert*-butoxyl radicals. Previous studies [2,3] have suggested that the captodative effect [4,5] in a free radical is enhanced when its structure is such that the trigonal carbon atom and the capto and dative substituents are coplanar, or nearly so. Such a disposition should be readily attained in radicals derived from 1,3-dioxolan-4-one and related five-membered heterocyclic compounds. With this in mind we have used EPR spectroscopy to investigate the abstraction of hydrogen atoms by *tert*-butoxyl radicals from the substrates **1–10**.



1 **2** **3**



4; R^1 = H, R^2 = H
5; R^1 = H, R^2 = Me
6; R^1 = Me, R^2 = H
7; R^1 = Bu^t, R^2 = H
8; R^1 = Pr^i, R^2 = H
9; R^1 = Me, R^2 = Me
10; R^1 = Bu^t, R^2 = Me

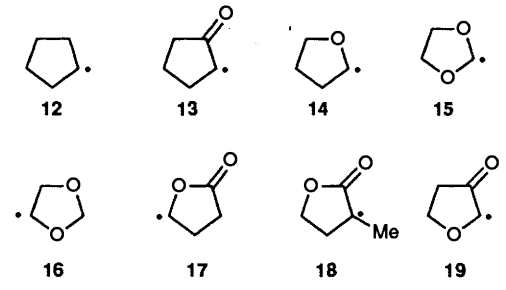
11

First we consider the EPR spectral features of radicals derived from the cyclic compounds **2–10**. Then, we discuss the selectivity of abstraction and compare the reactivities of the hydrogen atoms in the substrates **1–10** with the reactivity of the methoxy hydrogen atoms in *tert*-butyl methyl ether, **11**.

Results and Discussion

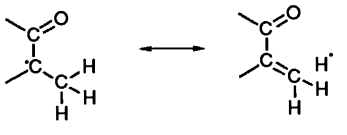
The EPR spectral parameters for the free radicals generated when solutions containing the substrates **2–10** in di-*tert*-butyl peroxide were irradiated with UV light in the cavity of the spectrometer are recorded in Table 1. For comparison, data taken from the literature for the radicals **12–17** are listed in Table 2. Data for the *tert*-butoxymethyl radical derived from **11** are available.[6]

It has been shown previously [7] that the only radical detectable by EPR spectroscopy when solutions of γ-butyrolactone and di-*tert*-butyl peroxide in ethylene oxide are photolysed is **17**, arising by loss of a hydrogen atom from the methylene group adjacent to the ether oxygen. However, under similar conditions in the present experiments, the substituted butyrolactone **2** underwent exclusive attack at the position adjacent to the carbonyl group to give the radical **18**, which was identified unambiguously from its EPR spectrum. Clearly the introduction of the methyl substituent strongly activates the α-proton towards attack by *tert*-butoxyl radicals. Possibly this reflects the favourable contribution of the electron-donating methyl group to dipolar transition structures involving the electrophilic *tert*-butoxyl radical. Also, it is possible that hyperconjugative stabilisation by the methyl group is enhanced by the adjacent carbonyl group in **18**, as indicated in Scheme 1.



12 **13** **14** **15**

16 **17** **18** **19**



Scheme 1

As expected from previous work,[2] the substrate **3** underwent attack by *tert*-butoxyl radicals exclusively at the methylene group flanked by both the carbonyl and ether functions to give the captodative radical **19**. An interesting feature of the spectral data for **19** (Table 1) is that the γ-proton hyperfine splittings are considerably larger than those for the non-captodative radicals **13** and **14**. We see this as a manifestation of the increased delocalisation of the free spin onto oxygen arising from the captodative effect. On this basis the larger of the γ-splittings (5.67 G) is tentatively assigned to the protons adjacent to the ether oxygen.

The usual treatment of each of the substrates **4–10** gave an EPR spectrum comprising overlapping signals for two radicals

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Table 1 Hyperfine splitting constants for radicals in di-*tert*-butyl peroxide/ethylene oxide at −31 °C

Substrate	Radical	a(α-H)/G[a]	a(β-H)/G[a]	a(γ-H)/G[a]	a(δ/ε-H)/G[a]	g
2	**18**		37.00(2); 21.60(3)	0.62(2)	—	2.0032
3	**19**	14.92(1)	—	3.27(2); 5.67(2)	—	2.0052
4	**4A**	17.41(1)	—	9.66(2)	—	2.0043
4	**4B**	16.99(1)	—	7.07(2)	—	2.0032
5	**5A**	—	17.32(3)	8.41(2)	—	2.0042
5	**5B**	16.19(1)	—	7.23(1)	0.11(3)	2.0032
6	**6A**	17.47(1)	—	9.98(1)	0.30(3)	2.0042
6	**6B**	—	14.24(3)	5.94(2)[b]	—	2.0030
7	**7A**	17.49(1)	—	10.31(1)	0.21(3)	2.0046
7	**7B**	—	—	6.71(1); 5.47(1)[b,c]	—	2.0034
8	**8A**	17.45(1)	—	10.08(1)	0.25(1); 0.10(6)	2.0046
8	**8B**	—	13.87(1)	0.25(6); 6.05(2)[b]	—	2.0034
9	**9A**	—	17.30(3)	8.82(1)	0.28(3)	2.0043
9	**9B**	—	14.22(3)	6.12(1)	*c*	2.0031
10	**10A**	—	17.40(3)	9.28(1)	0.20(3)	2.0044
10	**10B**	—	—	6.32(1)	*c*	2.0033

[a] Numbers of equivalent nuclei in parentheses. [b] Lines with $M_\gamma = 0$ selectively broadened. [c] Other splittings not resolved.

Table 2 Literature values of hyperfine splitting constants

Radical	T/°C	a(α-H)/G[a]	a(β-H)/G[a]	a(γ-H)/G[a]	Ref.
12	−40	21.48(1)	35.16(4)	0.53(4)	31
13	19	18.27(1)	36.40(2)	2.76(2); 0.36(2)	7
14	8	12.29(1)	28.57(2)	0.82(2); 1.64(2)	32
15	20	21.5(1)	—	1.4(4)	8
20	20	10.9(1)	27.0(2)	1.6(2)	8
17	−31	15.81(1)	31.47(2)	0.07(2)	7

[a] Numbers of equivalent nuclei in parentheses.

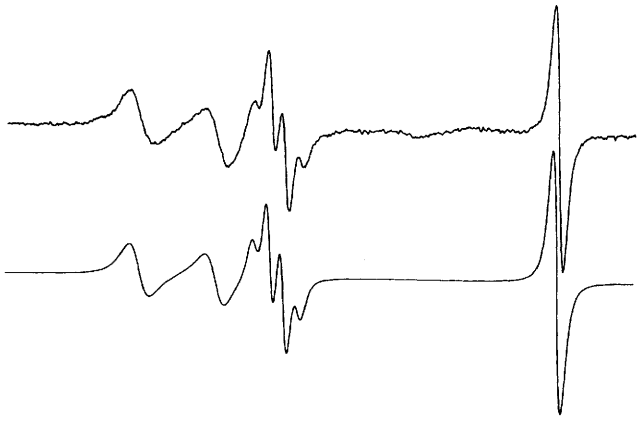
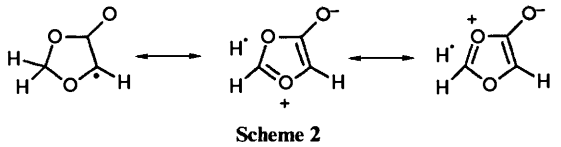


Fig. 1 A portion of the spectrum (width: 10 G) recorded at 242 K using substrate **7**, comprising one of the four quartets due to **7A** and three of the four lines of the slow regime spectrum of **7B**. Experimental spectrum above, calculated spectrum below.

of type **A** and type **B**. For most of the radicals, the assignments were clear from the multiplicities alone. However, for those generated from **4** and **9** the g factors and the magnitudes of the splittings were helpful in allowing unambiguous assignments to be made.



Scheme 2

For the free radicals derived from the substrates **4**–**10**, the splittings due to the α- and β-protons are unreliable indicators of α-carbon atom spin densities because of the sensitivity of the splittings to small deviations from planarity at the radical

A **B**

4; R^1 = H, R^2 = H
5; R^1 = H, R^2 = Me
6; R^1 = Me, R^2 = H
7; R^1 = Bu^t, R^2 = H
8; R^1 = Pr^i, R^2 = H
9; R^1 = Me, R^2 = Me
10; R^1 = Bu^t, R^2 = Me

centre.[8] On the basis of earlier work with dioxolanyl radicals and related species,[8–10] it seems likely that type **B** radicals are more planar than **15**, and that type **A** radicals are somewhat more planar than **14**. Of considerable interest are the γ-proton splittings in both **A** and **B** type radicals, which are about four to six times larger than analogous splittings in **15** and **16**. The abnormally large values of a(γ-H) in **19** and some related radicals have previously been rationalised in terms of the captodative effect.[2] However, for the radicals **4A**–**10A** the values are too large for such an explanation to be plausible; furthermore, the radicals **4B**–**10B** show similarly large splittings even though they are not captodative species. Variations in geometry have an important influence on the magnitude of γ-proton splitting,[11] but it does not seem likely that the geometry of the five-membered ring systems under consideration would vary significantly. The saturated γ-carbons are the only atoms in the ring systems of the radicals **4A**–**10A** and **4B**–**10B** which do not formally possess orbitals of π-symmetry. In view of this, we speculate that hyperconjugation involving groups, including hydrogen, attached to the γ-carbon atom may be unusually favourable because of the contribution of conjugated structures, as illustrated for radical **4A** in Scheme 2. In these terms the radicals **4A**–**10A** and **4B**–**10B** can be regarded as possessing an element of aromatic character with six π electrons partially delocalised over a five-membered cyclic structure. This would lead to enhanced γ-proton hyperfine splitting and cause significant stabilisation of the radicals. The same argument could alternatively be presented in molecular orbital terms, and would be similar to the explanation provided by Whiffen[12] for the unexpectedly large hyperfine splitting constant due to the methylene protons of cyclohexadienyl. However, when we carried out semi-empirical molecular orbital calculations of the AM1-UHF[13] and INDO[14] types for the radicals **4A** and **4B**

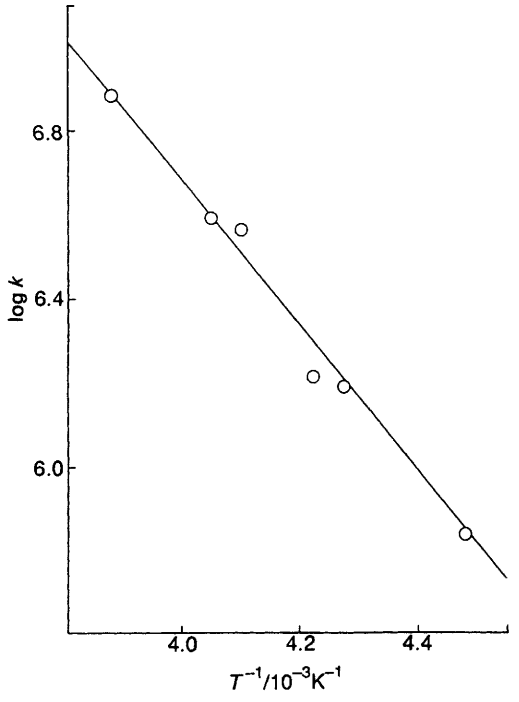


Fig. 2 Arrhenius plot of the logarithm of the rate of exchange of the γ protons in **7B** against the reciprocal of the absolute temperature

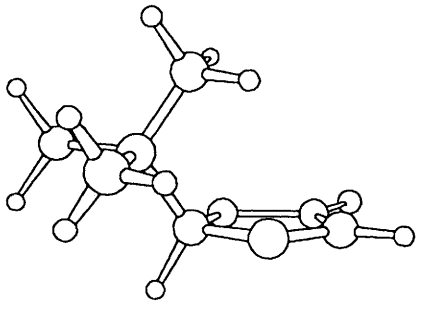
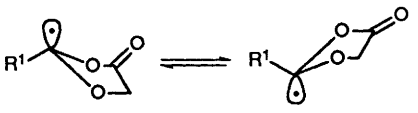


Fig. 3 The structure of radical **7A** as optimized by the AM1–UHF method

the calculated γ-proton coupling constants were considerably smaller than those observed and were in the range usually regarded as normal.

It has been reported[15] that radicals in which the sequence –C(O)–ĊH–O– is incorporated into six-membered rings show splittings of *ca.* 5 G, attributable to the axial γ protons. These splittings were seen as a result of favourable steric and electronic factors. However, the γ splittings for **4A**–**10A** are approximately twice as large, possibly supporting the extended delocalization proposal (Scheme 2).

The EPR spectra of the radicals **6B**, **7B** and **8B** showed selective broadening of the line with M_γ = O. Part of the spectrum of **7B** is shown in Fig. 1. It seems likely that the γ-protons are exchanged by conformational equilibria involving simultaneous ring inversion and inversion at the radical centre (Scheme 3), as has been proposed to explain the exchange of β and γ protons in analogous five-membered cyclic radicals.[16–18] Evidently the rate of inversion depends strongly on the nature of R^1: when R^1 was hydrogen (radical **4B**) no evidence for inequivalent γ-protons could be found at the lowest temperatures attainable, but when R^1 was methyl (**6B**) or *tert*-butyl (**7B**) fast and slow regime spectra respectively were observed at −31 °C (Table 1). We examined the temperature dependence of the spectra of **7B** in greatest detail. In this type of work, it is often assumed that the difference between the



Scheme 3

exchanging hyperfine splitting constants is temperature invariant. In this case however such an assumption was not justified.* Below the coalescence temperature, there was no real problem, because our iterative method of analysing the spectra[19] optimized the difference in splitting constants along with the other spectral parameters. We estimated differences above the coalescence temperature by extrapolation of the data acquired below the coalescence temperature; however the extrapolation was considered too hazardous for temperatures above −15.6 °C. The exchange rates obtained in this way (*e.g.* 3.67×10^6 s^{-1} at −29.3 °C) were fitted to the Arrhenius equation as shown in Fig. 2, and a pre-exponential factor of $(3.9 \pm 3.8) \times 10^{13}$ s^{-1} and an activation energy of (33.1 ± 2.0) kJ mol^{-1} were calculated. This activation energy is larger than the activation energies for inversion of 2-methyl-1,3-dioxolan-2-yl radical (23.4 kJ mol^{-1}),[16] and is also larger than the activation energies for exchange of β protons in substituted cyclopentyl radicals.[18] However, for the cyclopentyl radicals, the activation energy was found to increase with the size of the substituent (with one exception), and since no substituent as large as Bu^t was investigated the two sets of results do not necessarily disagree.

An interesting feature of the spectra of the radicals **7A** and **10A** is that in each case splitting by only three of the *tert*-butyl protons was detected. One of the quartets of **7A** may be seen in Fig. 1. The structure of one of the enantiomeric forms of **7A** optimised by the AM1–UHF method[13] is shown in Fig. 3. A reasonable interpretation of the observations is that rotation of the *tert*-butyl group is restricted, and that only the protons of the methyl group above the ring give resolvable splittings. In accord with this view, spin densities calculated by the AM1–UHF[13] and INDO[14] methods corresponded to unresolvably small splittings for the protons of the two methyl groups directed away from the ring. The average calculated splitting for the protons of the interacting methyl group was about half as large as that observed experimentally; possibly, the difference arises from through-space interactions.

Spectra of radical **7A** were examined over a range of temperatures. Above −31 °C, the lines of the quartets broadened and the multiplet appeared to collapse to a single line. On closer examination, barely resolved hyperfine structure could be discerned. A multiplet recorded at 10 °C is shown in Fig. 4 (top). Immediately below is a resolution-enhanced version of the experimental spectrum, calculated by the method of Roth and Kirste,[20] and at the bottom of the diagram is a calculated sub-spectrum corresponding to nine equivalent hydrogen atoms each with a splitting constant of 0.087 G. The observations are indicative of slow rotation of the *tert*-butyl group below −31 °C, and relatively fast rotation, on the EPR time scale, above 10 °C.

The unexpected spectral data for the *tert*-butyl groups in the radicals **7A** and **10A** prompted us to examine carefully the features of the EPR spectrum of the isopropyl-substituted radical **8A**. At −31 °C the spectrum of **8A** could be accurately simulated on the basis of equivalent methyl groups. At lower temperatures the observed linewidth increased, and at the lowest temperatures attainable no splitting attributable to the isopropyl protons could be resolved. It is not clear whether this was due to restricted rotation of the isopropyl substituent, or to other factors.

* We are indebted to a referee for pointing this out.

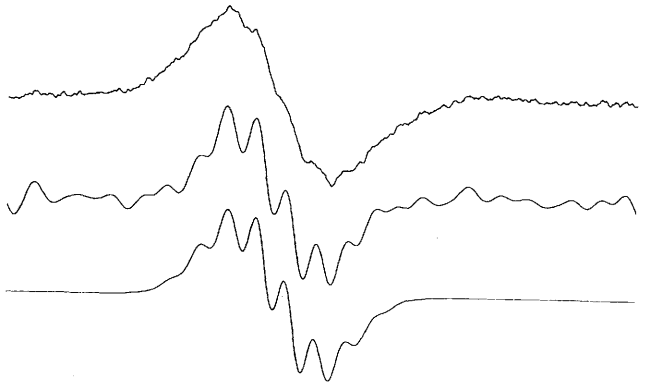


Fig. 4 Above, the high field multiplet of radical **7A** recorded at 283 K (width: 2 G). Below this, a resolution enhanced version of the spectrum is shown. At the bottom, a spectrum calculated on the basis of nine equivalent spin-1/2 nuclei, each with a hyperfine splitting constant of 0.087 G, is plotted.

Table 3 Ratio of concentrations of type **A** (captodative) to type **B** radicals from reactions with *tert*-butoxyl radicals at −31 °C

Substrate	[A]:[B]
4	1.42
5	6.94
6	1.74
7	2.19
8	1.30
9	6.57
10	11.25

Table 4 Relative reactivities per hydrogen atom (ρ) for the reaction RH + Bu^{t}O$^\bullet$ ⟶ R$^\bullet$ + Bu^{t}OH at −31 °C

R$^\bullet$	ρ
14	15.67
19	8.62
18	5.37
5A (Type A, R^2 = Me)	4.04
Bu^{t}OCH$_2^\bullet$	1.00
8B (Type B, R^1 = Pr^i)	0.54
6B (Type B, R^1 = Me)	0.41
4A (Type A, R^2 = H)	0.35
7B (Type B, R^1 = Bu^t)	0.32
4B (Type B, R^1 = H)	0.29

In order to ascertain whether captodative radicals are generated more rapidly than other types of radicals, carefully selected portions of the EPR spectra obtained from substrates **4**–**10** were recorded digitally and a simulation method[21] was used to determine the relative concentrations of type **A** and **B** free radicals. The results are shown in Table 3. In some cases the concentration ratios were also estimated by double integration; the results of the two methods were found to be in reasonable agreement. It may be shown[2,22] that such concentration ratios provide accurate indices of the relative rate constants for the formation of the radicals involved provided that there is no interconversion between them and that they have identical radical–radical termination constants. To confirm that these prerequisites were met we determined the concentration ratio [**4A**]:[**4B**] with varying intensity of UV irradiation. As required for the method to be valid, the observed ratio varied by less than the experimental uncertainties. It appears reasonable, therefore, to conclude that the concentration ratios presented in Table 3 are a direct indication of the relative rates of hydrogen atom abstraction from positions 2 and 5 of the substrates.

To compare the reactivities of abstractable hydrogen atoms in different substrates, *tert*-butyl methyl ether **11** was used as a suitable reference compound. EPR spectra were recorded while solutions of the substrate, the reference compound **11**, and di-*tert*-butyl peroxide in ethylene oxide were subjected to UV irradiation. In preliminary experiments with tetrahydrofuran **1**, a portion of the spectrum suitable for estimating the relative concentrations of the two radicals was selected, and the approximate relative amounts of **1** and **11** required to give lines of similar intensity were determined. Finally, a sample containing accurately weighed quantities of **1** and **11** was irradiated, and the selected portions of the spectrum were used to calculate the relative concentrations of radicals by the simulation method. This procedure was then applied to the substrates **2**, **3** and **4** with **11** as reference compound in each case.

From these experiments it was possible to calculate the relative reactivities per hydrogen atom in the various substrates, a concept used previously by Malatesta and Ingold.[22] Six of the entries in Table 4 (R$^\bullet$ = **14**, **18**, **19**, **4A**, **4B** and Bu^{t}OCH$_2^\bullet$) were obtained in this way. For the substrates **4**–**10** we considered that the hydrogen atom reactivities were unlikely to be significantly influenced by the nature of the substituent, R^1 or R^2, furthest away from the hydrogen atom under consideration. On this assumption it was possible to use data presented in Table 3 to calculate the remaining four entries in Table 4. There are some minor inconsistencies between some of the data in Tables 3 and 4. For example, the ratio [**4A**]:[**4B**] predicted on the basis of data in Table 4 is 1:1.21 whereas the value in Table 3 is 1:1.42. While the discrepancies may be partly due to experimental error, it is possible that the selectivity of hydrogen atom abstraction may be influenced by the physical characteristics of the reaction medium, such as the relative permittivity. In our experiments, no attempt was made to standardise the relative permittivity of the reaction media.

Several interesting points arise from the data presented in Table 4. The generally higher reactivity of protons in five-membered rings compared with six-membered rings has been explained on the basis that radical formation in the former relieves ring strain whereas in the latter it does not.[23] However, except for tetrahydrofuran **1**, all the substrates with five-membered rings considered here have a carbonyl group in the ring, which may be expected to relieve ring strain in a similar manner to a free radical carbon. The absence of significant strain in 1,3-dioxolan-4-one rings may help explain their facile formation during the cationic ring-opening polymerization of 6,8-dioxabicyclo[3.2.1]octan-7-one.[24] Molecular mechanics calculations confirm that a carbonyl group in a five-membered ring significantly lowers the strain energy whereas the introduction of a second sp^2 carbon in the form of a radical centre has a relatively small effect. This provides a plausible explanation for the relatively high reactivity of tetrahydrofuran towards hydrogen-atom abstraction by *tert*-butoxyl radicals.

One of the aims of this work was to probe the hypothesis that captodative radicals are synergistically stabilised, and that this stabilisation may have kinetic consequences. The EPR spectral characteristics of type **A** radicals described above, and of other captodative species discussed elsewhere,[5,25] indicate that spin is more extensively delocalised in captodative radicals than in otherwise similar non-captodative radicals. Whether such extended delocalisation is reflected either in the stabilities of captodative radicals or in their ease of formation remains a moot point.[5] The data recorded in Table 4 afford no clear-cut conclusions. Captodative stabilisation of **19** may account for the high rate of its formation and for the very high regioselectivity of attack of *tert*-butoxyl radicals on the substrate **3**. However, when the carbonyl group of **3** is replaced by the alkoxycarbonyl function in **4** there is a dramatic decrease in the observed reactivity at the captodative position. Perhaps this is

an indication that the alkoxycarbonyl function is relatively ineffective in the capto role. In this situation the results reflect an interplay between the influence of the electrophilic character of the *tert*-butoxyl radical and the influence of the stability of the product radical.

The effects of alkyl substitution on reactivity are more easily rationalised. The fact that the methyl group at position 4 in **5**, **9** and **10** appears to accelerate strongly the formation of **A** type radicals is consistent with the extended hyperconjugation of Scheme 1. The methyl group at position 2 in **6** and **9** has a much weaker activating effect. Possibly, in radicals **6B** and **9B** the methyl group may not be able to exert its full potential for stabilisation because of the antagonistic effect.[26] As expected, both the isopropyl and *tert*-butyl groups in **7** and **10** are activating, the latter less so because of steric hindrance. Finally, it is noteworthy that attack on the *tert*-butyl substituted substrate, **10**, is highly regioselective, an observation of possible synthetic significance.

Conclusion

A comparison of the EPR spectral characteristics of cyclic captodative radicals with similar non-captodative species suggests that free-spin delocalisation is more pronounced in the former than the latter. Competition experiments designed to reveal whether such delocalisation in the product radical is reflected in enhanced reactivity of the precursor have been inconclusive. However, the results do confirm the activating nature of alkyl substituents, particularly at the captodative positions, and show that the attack of *tert*-butoxyl radicals on appropriately substituted dioxolanones can occur with high regioselectivity.

Experimental

IR spectra were recorded on a Perkin-Elmer 683 spectrometer. ^{1}H NMR spectra were recorded in deuteriochloroform with tetramethylsilane as internal reference at 200 MHz on a JEOL PNM FX-200 instrument. All *J* values are given in Hz. ^{13}C NMR spectra were recorded in deuteriochloroform with tetramethylsilane as internal reference at 50 MHz on a JEOL PNM FX-200 instrument. Elemental analyses were carried out by the Australian National University Microanalytical Service.

The EPR spectrometer and associated equipment and the methods used have been described elsewhere.[2,19,21] Samples for EPR spectroscopy contained the substrate(s) and di-*tert*-butylperoxide; with substrates **2**–**8**, ethylene oxide was used as a solvent. Substrates were purified by Kugelrohr distillation. The substrates **3**,[27] **4**,[28] **5**,[28,29] **9**,[28,29] and **10**[30] were prepared by literature methods; **9** and **10** were used as mixtures of the *cis* and *trans* isomers. The following compounds were prepared from glycollic acid and the appropriate aldehyde by the general method previously described.[30]

2-*Methyl*-1,3-*dioxolan*-4-*one* **6**. This was obtained as a colourless oil (60%), b.p. 60 °C/200 mmHg (Found: C, 50.0; H, 5.85. $C_4H_6O_3$ requires C, 47.1; H, 5.9%); ν_{max}(neat)/cm^{-1} 1800, 1410, 1225, 1200, 1115, 1080, 920, 820; δ_H 1.57 (3 H, d, *J* 5), 4.22 (1 H, d, *J* 15), 4.36 (1 H, d, *J* 15), 5.73 (1 H, q, *J* 5); δ_C 20.29, 69.14, 104.08, 171.47.

2-(1,1-*Dimethylethyl*)-1,3-*dioxolan*-4-*one* **7**. This was obtained as a colourless oil (85%), b.p. 60 °C/200 mmHg (Found: C, 58.25; H, 8.3. $C_7H_{12}O_3$ requires C, 58.3; H, 8.4%); ν_{max}(neat)/cm^{-1} 2980, 1810, 1488, 1409, 1215, 1100, 960; δ_H 0.96 (9 H, s), 4.24 (1 H, d, *J* 15), 4.34 (1 H, d, *J* 15), 5.26 (1 H, s); δ_C 23.26, 35.01, 64.44, 111.82, 171.62.

2-(1-*Methylethyl*)-1,3-*dioxolan*-4-*one* **8**. This was distilled at 100 °C/100 mmHg (Found: C, 55.7; H, 8.0; $C_6H_{10}O_3$ requires C, 55.37; H, 7.74%); ν_{max}(neat)/cm^{-1} 2970, 1810, 1220, 1090, 950; δ_H 0.95 (6 H, d, *J* 15), 1.95 (1 H, m), 4.15 (1 H, d, *J* 16), 4.30 (1 H, d, *J* 16), 5.32 (1 H, d, *J* 16); δ_C 15.54, 32.21, 64.04, 109.89, 171.46.

References

1 A. L. J. Beckwith and C. L. L. Chai, *J. Chem. Soc., Chem. Commun.*, 1990, 1087.
2 A. L. J. Beckwith and S. Brumby, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1801.
3 C. Nootens, R. Merényi, Z. Janousek and H. G. Viehe, *Bull. Soc. Chem. Belg.*, 1988, **97**, 1045.
4 H. G. Viehe, Z. Janousek, R. Merényi and L. Stella, *Acc. Chem. Res.*, 1985, **18**, 148.
5 R. Sustmann and H.-G. Korth, *Adv. Phys. Org. Chem.*, 1990, **26**, 131.
6 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 6161.
7 S. Brumby, in preparation.
8 A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. A*, 1971, 124.
9 A. L. J. Beckwith and P. K. Tindal, *Aust. J. Chem.*, 1971, **24**, 2099.
10 G. Brunton, K. U. Ingold, B. P. Roberts, A. L. J. Beckwith and P. J. Krusic, *J. Am. Chem. Soc.*, 1977, **99**, 3177.
11 F. W. King, *Chem. Rev.*, 1976, **76**, 157.
12 D. H. Whiffen, *Mol. Phys.*, 1963, **6**, 223.
13 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
14 J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
15 B. C. Gilbert, D. M. King and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1186.
16 S. O. Kobayashi and O. Simamura, *Chem. Lett.*, 1973, 699.
17 C. Gaze and B. C. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1161.
18 R. V. Lloyd and D. E. Wood, *J. Am. Chem. Soc.*, 1977, **99**, 8269.
19 A. L. J. Beckwith and S. Brumby, *J. Magn. Reson.*, 1987, **73**, 252.
20 A. L. J. Roth and S. Kirste, *J. Magn. Reson.*, 1985, **63**, 360.
21 A. L. J. Beckwith and S. Brumby, *J. Magn. Reson.*, 1987, **73**, 260.
22 V. Malatesta and K. U. Ingold, *J. Am. Chem. Soc.*, 1981, **103**, 609.
23 V. Malatesta and J. C. Scaiano, *J. Org. Chem.*, 1982, **47**, 1455.
24 A. Okada, H. Sumitomo and M. Atsumi, *Macromolecules*, 1984, **17**, 1840.
25 For example, P. Lommes, R. Sustmann, L. Sylvander and L. Stella, *Nouv. J. Chem.*, 1987, **11**, 365.
26 R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, 1973, **95**, 7182.
27 G. J. Baxter and R. F. C. Brown, *Aust. J. Chem.*, 1978, **31**, 327.
28 M. Farines and J. Soulier, *Bull. Soc. Chim. Fr.*, 1970, 332.
29 T. Połoński, *Tetrahedron*, 1983, **39**, 3131.
30 D. Seebach, R. Naef and G. Calderari, *Tetrahedron*, 1984, **40**, 1313.
31 R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.
32 B. C. Gilbert and M. Trenwith, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1083.

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