Electron Spin Resonance Study of the Fragmentation of Some Cyclic and Acyclic Dialkoxyalkyl Radicals. The Mechanism of 1,2-Rearrangement of β-Acyloxyalkyl Radicals

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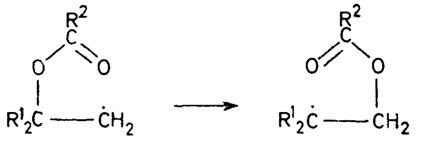
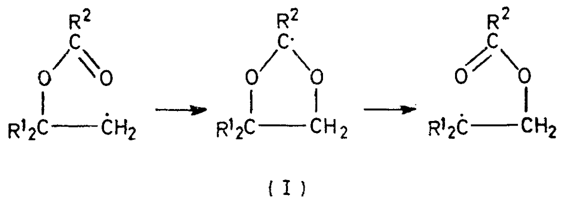
The di-t-butoxymethyl radical and a series of 1,3-dioxolanyl and 1,3-dioxanyl radicals have been generated and studied by e.s.r. spectroscopy in solution. All of these radicals undergo β-scission under appropriate conditions. β-acyloxyalkyl radicals resulting from the 1,3-dioxolanyl radicals. The kinetics of β-scission of these dialkoxyalkyl radicals have been measured, and it is found that the di-t-butoxymethyl radical decomposes much more readily than the analogous cyclic 4,4,5,5-tetramethyldioxolanyl radical undergoes ring opening. The relevance of these results to the mechanism of vicinal rearrangement of β-acyloxyalkyl radicals is discussed. The rate constant for addition of the di-t-butoxymethyl radical to nitrosobutane is found to be about 10^6 l mol^{-1} s^{-1} at 40° in benzene.

UNDER certain conditions β-acyloxyalkyl radicals undergo rearrangement involving a 1,2-shift of the acyloxy-group.[1] This rearrangement is most rapid when the acyloxy-group migrates from a tertiary or benzylic carbon to a primary carbon radical centre.



(1)



(2)

(I)

The most likely mechanism for this rearrangement would appear to be by way of an intermediate dioxolanyl radical (I), which undergoes subsequent β-scission to give the more stable alkyl radical. However, recent work by Beckwith and his co-workers [2,3] has shown that dioxolanyl radicals are probably not intermediates in the vicinal rearrangement of β-acyloxyalkyl radicals. In an e.s.r. study,[2] radical (II) was generated and the spectra of both (II) and the rearranged radical (III) were observed simultaneously at room temperature, although no signal from (I; $R^1 = R^2 = Me$) could be detected. In a separate experiment (I; $R^1 = R^2 = Me$) was generated and no (III) could be detected in the system. Making reasonable assumptions about the

$\cdot CH_2CMe_2OAc$ (II) $AcOCH_2\dot{C}Me_2$ (III)

magnitudes of radical–radical rate constants, it was possible to show that (I; $R^1 = R^2 = Me$) was not on the reaction pathway from (II) to (III). More recently, it has been shown [3] that the vicinal acyloxy-migration takes place with inversion of the labelling pattern if the carbonyl group is labelled with ^{18}O. From kinetic and product studies of the radical chain reduction of a series of 2-bromoalkyl esters with tributyltin hydride, Beckwith and Thomas [3] have adduced further evidence for a one-step rearrangement *via* a five-membered ring transition state (IV) without the intermediacy of a dioxolanyl racial.

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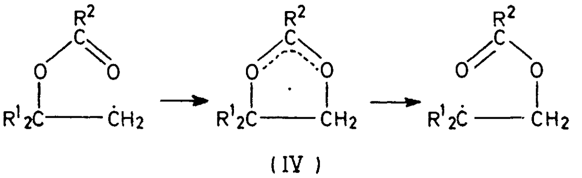
[1] J. W. Wilt in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 1, ch. 8.

[2] A. L. J. Beckwith and P. L. Tindal, *Austral. J. Chem.*, 1971, **24**, 2099.

[3] A. L. J. Beckwith and C. B. Thomas, *J.C.S. Perkin II*, 1973, 861.

However, dioxolanyl radicals do undergo β-scission to give β-acyloxyalkyl radicals under appropriate conditions,[1] and we felt that rearrangement by way of (IV) cannot be much favoured energetically over the route by way of (I) as an intermediate. Against this background we undertook a study of the fragmentation of the di-t-butoxymethyl radical and of a series of cyclic dialkoxyalkyl radicals in which the oxygen atoms form part of a five- or six-membered ring.


(3)

(IV)

In our present work the dialkoxyalkyl radicals were generated by high intensity u.v. irradiation of solutions containing di-t-butyl peroxide and di-t-butoxymethane, or a 1,3-dioxolan, or a 1,3-dioxan, while the sample was in the cavity of the e.s.r. spectrometer.[4]

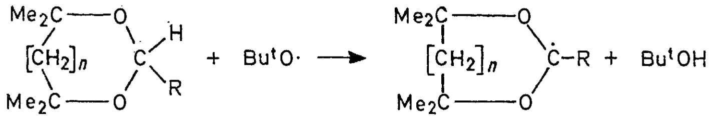
$$\mathrm{Bu^tOOBu^t} \xrightarrow{h\nu} 2\mathrm{Bu^tO\cdot} \qquad (4)$$

$$\mathrm{Bu^tO\cdot} + (\mathrm{R^1O})_2\mathrm{CHR^2} \longrightarrow (\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2} + \mathrm{Bu^tOH} \qquad (5)$$

RESULTS

When a cyclopropane solution of di-t-butoxymethane and di-t-butyl peroxide was irradiated with u.v. light at low temperatures (*ca.* −100°) a two line spectrum assigned to the di-t-butoxymethyl radical was observed [equation (5; $R^1 = Bu^t$, $R^2 = H$)]. As the temperature was increased the spectrum of the t-butyl radical also became apparent, this species being formed by fragmentation of the dialkoxyalkyl radical. Under these conditions, after prolonged reaction the single line spectrum of the t-butoxycarbonyl radical[5] was also evident. This is formed by hydrogen abstraction from the t-butyl formate produced in reaction (6).

$$(\mathrm{Bu^tO})_2\dot{\mathrm{C}}\mathrm{H} \longrightarrow \mathrm{Bu^t\cdot} + \mathrm{Bu^tOCHO} \qquad (6)$$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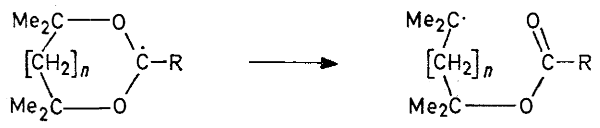

(8)

(V)

The magnitude of the hyperfine splitting from the α-hydrogen in the di-t-butoxymethyl radical showed pronounced temperature dependence, increasing as the temperature decreased.

Qualitatively similar results were obtained when a series of methyl substituted 1,3-dioxolans and 1,3-dioxans were allowed to react with t-butoxyl radicals in the spectrometer cavity [equation (7; R = H or Me, n = 1 or 0)].

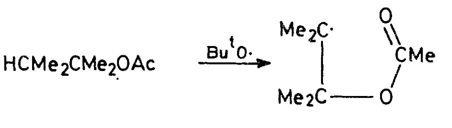
The β-scission of the cyclic radicals (V) was detectable only at much higher temperatures than those required to induce the fragmentation of the di-t-butoxymethyl radical. The spectroscopic parameters of all the dialkoxyalkyl radicals and of the radicals produced by their β-scission are gathered in Table 1.

Abstraction of the tertiary hydrogen atom from 1,1,2-trimethylpropyl acetate by photolytically generated t-butoxyl radicals [equation (9)] gave rise to an e.s.r. spectrum identical to that detected during β-scission of the 2,4,4,5,5-pentamethyldioxolanyl radical (see Table 1). When the β-acetoxyalkyl radical was generated from the acetate at +72°, no signal from the dioxolanyl radical was detectable.

For purposes of comparison, a similar radical [a(β-H) 22·5 G at −80° in cyclopropane] was generated from 2,3-dimethylbutan-2-ol. This radical showed further splittings [a(γ-H) 0·65, a(OH) 0·33 G at +56° in benzene] which were best resolved at high temperatures. The radical $\cdot\mathrm{CMe_2CMe_2OD}$ showed only the splittings from β- and γ-H.

The β-acetoxyethyl radical may be readily generated by photolysis of a mixture containing di-t-butyl peroxide, triethylsilane, and 2-bromoethyl acetate[6] [equation (11)]. Although the strength of the signal from the acetoxyethyl radical declined as the temperature increased, in the range −34 to +46° no signals from the 2-methyldioxolanyl radical were detected, neither were any spectral changes attributable to rapid exchange of the α- and β-methylene hydrogens observed.

Radical (II) [a(α-H) 22·2, a(γ-H) 1·13 G at −30°] was generated in a similar manner from 1-bromomethyl-1-methylethyl acetate. No 1,3-dioxolanyl radical (I; R^1 = R^2 = Me) was detectable up to +36° in this system. The rearranged radical (III) was not detectable up to +40° in benzene solution, whereas Beckwith and Tindal[2] were able to detect (II) and (III) simultaneously at room temperature in aqueous solution when (II) was generated by hydrogen abstraction from t-butyl acetate. However, (III) may have escaped detection in our system because of the relatively low radical concentrations obtainable using the silane–halide method of generation at high temperatures.


(9)

$$\mathrm{Bu^tO\cdot} + \mathrm{HCMe_2CMe_2OH} \longrightarrow \mathrm{Bu^tOH} + \cdot\mathrm{CMe_2CMe_2OH} \qquad (10)$$

$$\mathrm{Et_3Si\cdot} + \mathrm{BrCH_2CH_2OAc} \longrightarrow \mathrm{Et_3SiBr} + \cdot\mathrm{CH_2CH_2OAc} \qquad (11)$$

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[4] See for example, A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224.

[5] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1972, 747.

[6] D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 7695.

It is also possible that a more polar solvent facilitates the rearrangement of (II) to (III).

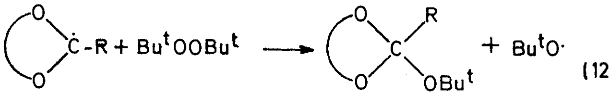
In some spectra obtained from the 1,3-dioxolans and 1,3-dioxans anomalous intensity patterns were observed, the lines to high field of the centre of the spectrum being more intense than those to low field. Such polarisation effects in e.s.r. spectra have been observed many times previously,[7] although a universally accepted theory to account for the phenomenon has not yet appeared. The polarisation was most apparent in the spectrum obtained from paraldehyde (see Table 1) and in all cases the degree of distortion was reduced on decreasing the steady-state radical concentrations by reducing the light intensity incident upon the sample. The degree of polarisation was increased somewhat by the use of neat di-t-butyl peroxide as the solvent, and this may be connected with the observation that at high temperature (*ca.* +80°) the rate of sample depletion was rather high, perhaps indicating the onset of radical induced decomposition of the peroxide giving rise to a chain reaction [reaction (12) may involve initial electron transfer].

TABLE 1

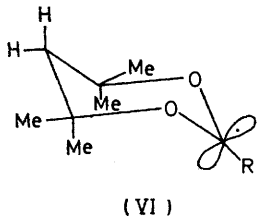
Spectroscopic parameters of cyclic and acyclic dialkoxyalkyl radicals and of the radicals formed by their β-scission

Dialkoxyalkyl radical [a]	Temp. (°C)	Hyperfine splittings (G)	Radical formed by β-scission [b]	Temp. (°C)	Hyperfine splittings (G)
$(Bu^tO)_2\dot{C}H$	−110	a(α-H) 11·1 [c]	$Bu^t\cdot$ [d]	−42	a(β-H) 23·1
$\dot{C}H$ $O{-}[CMe_2]_2{-}O$	−124	a(α-H) 21·7 [e]	$O{=}CH{\cdot}O{-}CMe_2{-}\dot{C}Me_2$	+80	a(β-H) 21·8 a(γ-H) 0·7 a(C*H*O) 2·2
$\dot{C}Me$ $O{-}[CMe_2]_2{-}O$	−60	a(β-H) 13·5 [f]	$O{=}CMe{-}O{-}CMe_2{-}\dot{C}Me_2$	+80	a(β-H) 22·3 a(γ-H) 0·7
$\dot{C}H$ $O{-}CMe_2{-}CH_2{-}CMe_2{-}O$	−136	a(α-H) 1·2 [g]	$O{=}CH{-}O{-}CMe_2{-}CH_2'{-}\dot{C}Me_2$	+56	a(β-H) 23·1 a(β-H′) 13·4
$\dot{C}Me$ $O{-}CMe_2{-}CH_2{-}CMe_2{-}O$	−64	a(β-H) 14·1 [h]	$O{=}CMe{-}O{-}CMe_2{-}CH_2'{-}\dot{C}Me_2$	+56	a(β-H) 23·1 a(β-H′) 13·4
$\dot{C}Me$ $O{-}CH_2{-}CMe_2{-}O$	−80 [i]	a(β-H) 13·1, a(γ-H) 1·3	$O{=}CMe{-}O{-}CH_2'{-}\dot{C}Me_2$	+70	a(β-H) 23·1 a(β-H′) 15·0
$\dot{C}Me$ $O{-}CHMe{-}O{-}CHMe{-}O$	−30	a(β-H) 14·3	*j*		

[a] Solvent cyclopropane unless otherwise stated. [b] Solvent benzene unless otherwise stated. [c] a(β-H) 9·1 G at −60°. [d] Cyclopropane solvent. [e] a(β-H) 21·3 at −40 in cyclopropane and 21·1 G at +60° in benzene. No further fine structure but a line-width of 0·37 G at −104°. [f] a(β-H) 13·5 G at +40° in di-t-butyl peroxide. [g] As the temperature was increased a(α-H) decreased as did the line-width, and further splittings became apparent (see text). [h] a(β-H) 14·1 at −124 and 14·0 G at −4°. Further fine structure was also detectable and resolution was optimised at *ca.* −100° when the splitting gave rise to an odd number of lines (5, 7, or 9) spaced by *ca.* 0·35 G. [i] n-Hexane solvent; no abstraction of hydrogen from the solvent was detected with a dioxolan concentration of *ca.* 1M. [j] No β-scission was detectable even at +90° in di-t-butyl peroxide solvent.



(12)



(VI)

The smallest splittings (see Table 1) in the spectra of the dialkoxyalkyl radicals derived from the 1,3-dioxans are rather difficult to assign. These radicals will probably exist in chair conformations (VI) in which the groups in axial and equatorial positions on C-4, -5, and -6 are instantaneously non-equivalent, although chair–chair interconversion may be important on the e.s.r. time scale.

The value of a(α-H) in (VI; R = H) is close to zero[8] and similar in magnitude to the long-range splittings, except at very low temperatures when the smallest splittings are no longer resolved. The smallest splittings (*ca.* 0·2 G) in (VI; R = H) in the temperature range −10 to −120°, and those (*ca.* 0·35 G) in (VI; R = Me) at −86 to −106° must be due to long range coupling with δ-H, but for our present purposes definite assignment was not necessary.

Kinetics of β-*Scission of Dialkoxyalkyl Radicals*.—With the photolytic methods of radical generation employed in this work, it is possible to determine the kinetic order of the reaction responsible for removing a radical from the system by measurement of the dependence of radical concentration upon incident light intensity. For example, the concentration of the radical (VI; R = H) was proportional to the square-root of the light intensity at −64°, whilst at +6° it was proportional to the first power. At the lower temperature the radical is removed by a second-order process, presumably self-reaction, whilst at +6° decay is a first-order process, namely β-scission. Similar dependences of radical concentration upon light intensity at different temperatures were obtained for the other dialkoxyalkyl radicals studied.

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[7] For references see H. Fischer in ref. 1, vol. 2, ch. 19; J. K. S. Wan, S.-K. Wong, and D. A. Hutchinson, *Accounts Chem. Res.*, 1974, **7**, 58.

[8] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124.

It is possible to obtain the rate constant for a unimolecular fragmentation or rearrangement process relative to the rate constant for self-reaction of the product radical by measurement of steady-state radical concentrations.*[,5] For the pertinent reactions shown in equations (13)—(17)

$$(\mathrm{R^1O})_2\mathrm{CHR^2} + \mathrm{Bu^tO\cdot} \longrightarrow \mathrm{Bu^tOH} + (\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2} \tag{13}$$

$$(\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2} \longrightarrow \mathrm{R^1\cdot} + \mathrm{R^1OCR^2O} \tag{14}$$

$$\left.\begin{array}{r} \mathrm{R^1\cdot} + \mathrm{R^1\cdot} \longrightarrow \\ \mathrm{R^1\cdot} + (\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2} \longrightarrow \\ \mathrm{R^1\cdot} + \mathrm{Bu^tO\cdot} \longrightarrow \end{array}\right\}\text{non-radical products} \qquad \begin{array}{r}(15)\\(16)\\(17)\end{array}$$

it may readily be demonstrated that equation (18) holds.[5]

$$\frac{1}{[\mathrm{R^1\cdot}]} = \frac{2k_{15}}{k_{14}}\,\frac{[\mathrm{R^1\cdot}]}{[(\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2}]} + \frac{k_{16}}{k_{14}} + \frac{k_{17}}{k_{14}}\,\frac{[\mathrm{Bu^tO\cdot}]}{[(\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2}]} \tag{18}$$

Reaction (17), and hence the last term in equation (18), is included because the C–H bond adjacent to two oxygen atoms in the acyclic dialkoxyalkanes does not appear to be as reactive towards t-butoxyl radicals as might be expected on the basis of polar effects,[10] and thus the steady-state concentration of t-butoxyl radicals may not be negligible. Under conditions where the major reaction removing the radical $(\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2}$ is β-scission [equation (14)], we may write equation (19). Combining equations (18) and (19)

$$\frac{[\mathrm{Bu^tO\cdot}]}{[(\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2}]} \simeq \frac{k_{14}}{k_{13}[(\mathrm{R^1O})_2\mathrm{CHR^2}]} \tag{19}$$

we obtain equation (20), and a plot of $1/[\mathrm{R^1\cdot}]$ against

$$\frac{1}{[\mathrm{R^1\cdot}]} = \frac{2k_{15}}{k_{14}}\,\frac{[\mathrm{R^1\cdot}]}{[(\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2}]} + \frac{k_{16}}{k_{14}} + \frac{k_{17}}{k_{13}[(\mathrm{R^1O})_2\mathrm{CHR^2}]} \tag{20}$$

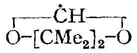
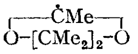
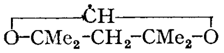
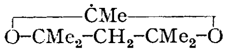
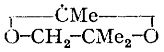
$[\mathrm{R^1\cdot}]/[(\mathrm{R^1O})_2\dot{\mathrm{C}}\mathrm{R^2}]$ for varying light intensities at a constant temperature yields a straight line of slope $(2k_{15}/k_{14})$.

Di-t-butoxymethane appeared to be the least reactive compound towards t-butoxyl radicals, and by competition against cyclopentane [11] it was shown to be about half as reactive as the hydrocarbon at −64°. The rate constant for hydrogen abstraction from cyclopentane at −64° may be derived from data in the literature,[12,13] and we obtain a value for k_{13} at −64° of *ca.* 2×10^3 l mol^{-1} s^{-1}. The steady-state concentration of t-butoxyl radicals will be lower in the reactions involving the cyclic dialkoxyalkyl radicals at higher temperatures.

The relative rate constants obtained using equation (20) are given in Table 2. The accuracy of these values is not thought to be high because of the assumptions involved in deriving equation (20), and problems of low signal strength at low light intensities and high temperatures. The possible occurrence to a small extent of a chain reaction involving induced decomposition of the peroxide [equation (12)] should not affect the results. In cases where signal strengths were affected by polarisation effects (see above)

TABLE 2

Kinetics of β-scission of cyclic and acyclic dialkoxyalkyl radicals

Dialkoxyalkyl radical [a]	Temp. (°C)	$2k_{15}(k_{14})^{-1}$/ l mol^{-1}	k_{14}/s^{-1}	$\log_{10}[2A_{15}(A_{14})^{-1}$/ l mol^{-1}]	$(E_{14} - E_{15})$/ kcal mol^{-1}
$(\mathrm{Bu^tO})_2\dot{\mathrm{C}}\mathrm{H}$ [b]	−24	$6{\cdot}5 \times 10^5$		−1·0	+7·7
	−44	$1{\cdot}9 \times 10^6$			
	−54	$4{\cdot}9 \times 10^6$			
	−64	$9{\cdot}8 \times 10^6$			
	+72 [d]		$5{\cdot}0 \times 10^5$ [e]		
 $\overset{\dot{\mathrm{C}}\mathrm{H}}{\mathrm{O{-}[CMe_2]_2{-}O}}$	+72	$3{\cdot}4 \times 10^5$	$5{\cdot}8 \times 10^3$ [e,f,g]		
 $\overset{\dot{\mathrm{C}}\mathrm{Me}}{\mathrm{O{-}[CMe_2]_2{-}O}}$	+72	$9{\cdot}7 \times 10^5$	$2{\cdot}1 \times 10^3$ [e]		
 $\overset{\dot{\mathrm{C}}\mathrm{H}}{\mathrm{O{-}CMe_2{-}CH_2{-}CMe_2{-}O}}$	+31	$1{\cdot}0 \times 10^5$		+0·5	+6·5
	+41	$9{\cdot}3 \times 10^4$			
	+58	$5{\cdot}1 \times 10^4$			
	+75	$3{\cdot}3 \times 10^4$			
	+72 [h]	$3{\cdot}5 \times 10^4$	$5{\cdot}7 \times 10^4$ [e]		
	+40	$1{\cdot}3 \times 10^6$		+1·2	+7·0
 $\overset{\dot{\mathrm{C}}\mathrm{Me}}{\mathrm{O{-}CMe_2{-}CH_2{-}CMe_2{-}O}}$	+58	$5{\cdot}1 \times 10^5$			
	+76	$3{\cdot}4 \times 10^5$			
	+72 [h]	$3{\cdot}8 \times 10^5$	$5{\cdot}3 \times 10^3$ [e]		
 $\overset{\dot{\mathrm{C}}\mathrm{Me}}{\mathrm{O{-}CH_2{-}CMe_2{-}O}}$	+72	*ca.* 3×10^6	*ca.* 7×10^2 [e]		

[a] Solvent benzene except where otherwise stated. [b] Cyclopropane solvent. Qualitatively similar rates in neat di-t-butyl peroxide solvent. [c] Taking $2k_{15}$ (Bu$^t\cdot$) as $1{\cdot}6 \times 10^9$ l mol^{-1} s^{-1} at −60° and E_{15} as 1 ± 1 kcal mol^{-1}. [d] Extrapolated value. [e] Taking $2k_{15}$ as 2×10^9 l mol^{-1} s^{-1} at +72°. [f] The rate of β-scission was similar in t-butyl alcohol solvent. [g] $E_{14} - E_{15}$ was *ca.* 7—8 kcal mol^{-1}. [h] Interpolated value.

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* The direct decay of a transient radical intermediate may also be monitored by e.s.r. spectroscopy using computer averaging techniques to improve the signal to noise ratio.[9] This technique is often somewhat superior to the steady-state method described here.

[9] K. U. Ingold in ref. 1, vol. 1, ch. 2.

[10] A. Hudson and K. D. J. Root, *Tetrahedron*, 1969, **25**, 5311.

[11] A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1823.

[12] J. A. Howard, *Adv. Free Radical Chem.*, 1972, **4**, 49.

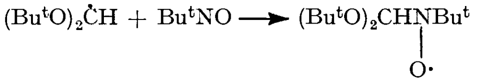
[13] A. A. Zavitsas and J. D. Blank, *J. Amer. Chem. Soc.*, 1972, **94**, 4603; A. A. Zavitsas and J. A. Pinto, *ibid.*, p. 7390.

the mean strength of the corresponding high and low field lines was taken to represent the true radical concentration.[14]

The absolute value of $2k_{15}$ has been measured in the case of the t-butyl radical.[15] The result obtained was $2k_{15}(Bu^t\cdot) = 1{\cdot}6 \times 10^9$ l mol^{-1} s^{-1} at $-60°$ with an activation energy of 1 ± 1 kcal mol^{-1}, in a solvent mixture which must have a similar viscosity to that employed in our work.* Combination of this result with the temperature dependence of $(2k_{15}/k_{14})$ for $(Bu^tO)_2\dot{C}H$ given in Table 2, gives $\log_{10}(k_{14}/s^{-1}) = 11{\cdot}2 - 7{\cdot}7/\theta$, where $\theta = 2{\cdot}303RT$/kcal mol^{-1}. For the radicals produced by β-scission of the cyclic dialkoxyalkyl radicals, $2k_{15}$ has not been measured, but it must be close to 2×10^9 l mol^{-1} s^{-1} at $+72°$ with an activation energy of *ca.* 2 ± 1 kcal mol^{-1} in benzene.[9] The lower rates of β-scission of the cyclic radicals compared with $(Bu^tO)_2\dot{C}H$ appear to derive mainly from a relatively low *A* factor, although the accuracy of the activation parameters hardly justifies further consideration at this point.

The intercept from plots made according to equation (20) can provide an estimate of $(2k_{15}/k_{16})$. For the di-t-butoxymethyl radical at $-64°$, the intercept was *ca.* 7×10^6 l mol^{-1}. The rate constant k_{17} must be similar to k_{16},[9] and for a 1M-solution of di-t-butoxymethane the last term in equation (20) will be small compared to (k_{16}/k_{14}), and the latter will correspond to the intercept. Hence at $-64°$, $(2k_{15}/k_{16})$ is close to unity for reactions of the t-butyl and di-t-butoxymethyl radicals.

Rate of Addition of the Di-t-butoxymethyl Radical to 2-Methyl-2-nitrosopropane (' Nitrosobutane ').—Having determined the rate constant for the fragmentation of the di-t-butoxymethyl radical, it was possible to estimate the rate of spin-trapping[17] of this radical by nitrosobutane.



$$(Bu^tO)_2\dot{C}H + Bu^tNO \longrightarrow (Bu^tO)_2CH\underset{\underset{\textstyle O\cdot}{|}}{N}Bu^t \qquad (21)$$

(VII)

We have recently measured the rate constant for spin-trapping of the t-butoxycarbonyl radical by competitive scavenging and decarboxylation of this species.[16] The e.s.r. spectrum of the nitroxide (VII) showed $a(N) = 14{\cdot}4$ G in benzene at $+40°$ with no resolvable splitting from the hydrogen β to nitrogen, even when [$^2H_9$]nitrosobutane was used. Fragmentation of the di-t-butoxymethyl radical gives t-butyl radicals which are scavenged to give di-t-butyl nitroxide. Benzene solutions containing nitrosobutane, di-t-butoxymethane, and di-t-butyl hyponitrite (as a thermal source of t-butoxyl radicals) were warmed to $+40°$ in the cavity of the e.s.r. spectrometer, and the increasing concentrations of (VII) and (VIII) were monitored. After correcting for any (VIII) formed from t-butyl radicals resulting from the decomposition of t-butoxy t-butyl nitroxide also present in the system,[16] (k_{21}/k_{14}) was

$$Bu^t\cdot + Bu^tNO \longrightarrow \underset{(VIII)}{Bu^t{}_2NO\cdot} \qquad (22)$$

found to be 6 l mol^{-1} at $+40°$. Taking the value of k_{14} extrapolated to $+40°$ as $1{\cdot}5 \times 10^6$ s^{-1} we obtain $k_{21} = 9 \times 10^5$ l mol^{-1} s^{-1} at 40°.

DISCUSSION

Several authors have found evidence for the non-planarity of the bonds about the radical centre from studies of the e.s.r. spectra of dialkoxyalkyl radicals.[2,8,10] This non-planarity affects the magnitude of the α-hydrogen hyperfine splitting, a direct (positive) contribution becoming larger as the deviation from planarity increases. The α-hydrogen splitting in the di-t-butoxymethyl radical has a significant direct contribution, although the predominant coupling mechanism is still spin-polarisation giving rise to a net negative coupling constant. The quantity $|a(\alpha\text{-H})|$ for the di-t-butoxymethyl radical increases as the temperature is reduced. This may be associated with a $C\text{-}H_\alpha$ bending vibration which gives rise to larger time average deviations from planarity at higher temperatures.

In the radical (VI; R = H), obtained by abstraction of hydrogen from 4,4,6,6-tetramethyl-1,3-dioxan, $a(\alpha\text{-H})$ is close to zero except at very low temperatures. This probably results from the near equality of the positive and negative contributions to the splitting constant, indicating a greater degree of non-planarity at the radical centre than in the acyclic dialkoxyalkyl radicals.[8] The analogous dioxolanyl radicals exhibit an even greater degree of non-planarity,[8] and this has been associated with the favourable disposition of the (essentially) $2p_\pi$ orbital of the unpaired electron and the filled $2p_\pi$ orbitals on the adjacent oxygens, allowing maximal interaction leading to non-planarity in the five-membered ring system.[8] The sign of $a(\alpha\text{-H})$ in the 1,3-dioxolanyl radicals is thought to be positive, the contribution from the spin-polarisation mechanism now being smaller than that from the direct interaction. These conclusions are also supported by the magnitudes of $a(\alpha\text{-}^{13}C)$ in such radicals.[2,8]

Huyser and his co-workers[18] have studied the competition between the two possible modes of β-scission of the radicals $(R^1O)(R^2O)\dot{C}Me$. They found that the ease of C–O fission increased along the series $R^p < R^s < R^t$. The rate of fragmentation of the di-t-butoxymethyl

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* Recent measurements of $2k_{15}(Bu^t\cdot)$ (J. E. Bennett, J. A. Eyre, C. P. Rimmer, and R. Summers, *Chem. Phys. Letters*, 1974, **26**, 69 and references cited therein) indicate that a value of *ca.* 10^{10} l mol^{-1} s^{-1} at 25°, with an activation energy close to that for diffusion in the medium, may be more reasonable. If this higher value is accepted, rate constants derived relative to $2k_{15}(Bu^t\cdot)$ taken as *ca.* 2×10^9 l mol^{-1} s^{-1} at 25° would have to be increased by a factor of *ca.* 5 (fairly independent of temperature). Such rate constants include those for reactions (i)—(iii).

$$Bu^tO\dot{C}O \longrightarrow Bu^t\cdot + CO_2 \text{ (ref. 5)} \qquad \text{(i)}$$

$$Bu^tO\dot{C}O + Bu^tNO \longrightarrow Bu^tO{\cdot}CO{\cdot}N\dot{O}{\cdot}Bu^t \text{ (ref. 16)} \qquad \text{(ii)}$$

$$(Bu^tO)_2\dot{C}H + Bu^tNO \longrightarrow (Bu^tO)_2CH{\cdot}N\dot{O}{\cdot}Bu^t \text{ (this work)} \qquad \text{(iii)}$$

[14] F. J. Adrian, *J. Chem. Phys.*, 1971, **54**, 3918.

[15] G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 8784.

[16] M. J. Perkins and B. P. Roberts, *J.C.S. Chem. Comm.*, 1973, 173; *J.C.S. Perkin II*, 1974, 297.

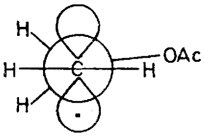
[17] M. J. Perkins, ' Essays in Free Radical Chemistry,' Chem. Soc. Special Publication No, 24, The Chemical Society, London, 1970, ch. 5.

[18] E. S. Huyser and D. T. Wang, *J. Org. Chem.*, 1964, **29**, 2720.

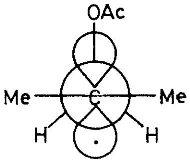
radical is expected to be relatively high because of the formation of the stable t-butyl radical.

The 1,3-dioxolanyl and 1,3-dioxanyl radicals give β- and γ-acyloxyalkyl radicals upon ring opening, but their rates of β-scission are much lower than that of the *di-t*-butoxymethyl radical, even though tertiary carbon radicals are formed in all cases.

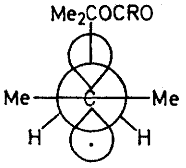
The e.s.r. spectra of the acyloxyalkyl radicals give some information on the most stable conformations of these species. Edge and Kochi[6] have shown that the β-acetoxyethyl radical [a(β-H) 28·44 G at −108°] has a preferred conformation (IX); the carbonyl group lies close to the plane of the radical centre and changes position so as to cause in-phase modulation of the hyperfine splittings from the pair of β-hydrogens. However, the β-hydrogen splitting in the 1,1-dimethyl-2-acetoxyethyl radical (Table 1 and ref. 2) indicates that the preferred conformation is (X).[19] The steric effect of the methyl groups in (X) is presumably the major factor responsible for the change in conformation. A similar change of preferred conformation is encountered on going from $HOCH_2CH_2\cdot$[19] to $HOCH_2\dot{C}Me_2$,[2] and from $MeCH_2CH_2\cdot$ to $MeCH_2\dot{C}Me_2$.[19] Any interaction between the ester carbonyl group in (IX) and the radical centre to maintain this conformation must be quite small. From the magnitudes of the β-methylene hyperfine splittings the two γ-acyloxyalkyl radicals derived from the 1,3-dioxanyl radicals (Table 1) have preferred conformations as shown in (XI; R = H or Me).



(IX)



(X)

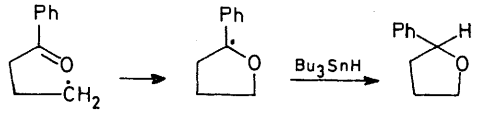


(XI)

In (XI) the bulky group in the γ-position probably plays a part in establishing the most stable conformation. The conformations of the radicals $\cdot CMe_2CMe_2OCRO$ are more difficult to establish, but they are probably similar to (IX) for steric reasons. The relatively large splitting from the formyloxy-hydrogen in $\cdot CMe_2CMe_2OCHO$ and from the hydroxy-hydrogen in $\cdot CMe_2CMe_2OH$ are noteworthy.

Kinetics of β-Scission of Dialkoxyalkyl Radicals.—The activation parameters given in Table 2 are probably not very accurate, although they are useful for estimating rate constants at temperatures fairly close to the experimental range. There seems little reason to expect that A_{14} will be much smaller than 10^{12}—10^{13} s^{-1} and thus $(2A_{15}/A_{14})$ would be expected to be *ca.* 10^{-2}—10^{-3} l mol^{-1} in all cases.

The major result evident from Table 2 is the large difference in rate of β-scission between the cyclic radicals and the di-t-butoxymethyl radical. The radical $\cdot CMe_2CMe_2OAc$, showed no tendency to cyclise under the conditions of the e.s.r. experiments. No evidence was found for cyclisation of the radicals $\cdot CH_2CH_2OAc$ or $\cdot CH_2CMe_2OAc$. The apparent low rate of β-scission of the 1,3-dioxolanyl radicals is not then due to reversibility of the reaction under our conditions. Ring closure of a δ-carbonylalkyl radical is found in the tin hydride reduction of 3-chloropropyl phenyl ketone,[20] but here benzylic stabilisation of the cyclised radical is undoubtedly important, as is the higher reactivity of ketone compared with ester carbonyl groups toward radical addition.[21]



(23)

Several possible reasons may be cited for the relatively low rate of β-scission of the cyclic radicals, although the accuracy of the Arrhenius parameters obtained in this work does not permit us to determine whether this difference results predominantly from changes in the entropy or enthalpy of activation. A relatively ' loose ' transition state might be expected to lead to a higher A factor for β-scission of the acyclic dialkoxyalkyl radicals.

As pointed out above, the radical centres in the cyclic radicals are significantly less planar than that in the di-t-butoxymethyl radical. Formation of the transition state for β-scission should involve movement towards coplanarity of the bonds about the potential ester carbonyl carbon atom, and some of the reticence of the cyclic radicals to undergo β-scission may be attributed to non-planarity of the radical centre. However, the radical centres in the 1,3-dioxanyl radicals are more nearly planar than those in the 1,3-dioxolanyl radicals (see above) and we might have expected a larger difference between the rates of β-scission of the five- and six-membered ring species.

We suggest that an important factor controlling the rates of scission of the cyclic radicals is the relatively small degree of overlap between the (approximately) $2p_\pi$ orbital of the unpaired electron and the antibonding σ orbital of the β-O–C bond. Similar stereoelectronic requirements for ring opening in carbocyclic systems have been discussed.[22] The transition state for β-scission will be formed by overlap of the $2p_\pi$ orbital of the unpaired electron with the σ* orbital on the adjacent oxygen, and this will be maximised in a conformation such as (XII) in which the axis of the $2p_\pi$

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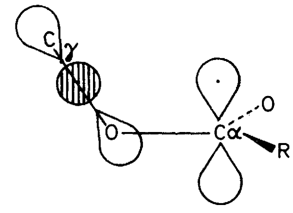
[19] J. K. Kochi and P. J. Krusic, ref. 17, ch. 7; P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

[20] L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, 1964, **86**, 3047.

[21] J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1933.

[22] A. L. J. Beckwith, ref. 17, ch. 9; D. L. Strubble, A. L. J Beckwith, and G. E. Gream, *Tetrahedron Letters*, 1968, 3701; 1970, 4795.

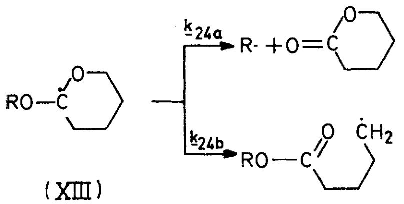
orbital and the C_α–O and O–C_γ bonds are coplanar. Such a conformation can be achieved in an acyclic



(XII)

dialkoxyalkyl radical, but in a 1,3-dioxolanyl radical the σ^* and $2p_\pi$ orbitals are close to orthogonal, with the 1,3-dioxanyl radicals representing an intermediate situation.

The relative rates of exo- and endo-cyclic cleavage of the radicals (XIII) at room temperature in benzene have been measured by product analysis.[23] For R = Bu^n



(XIII)

(24)

the ratio (k_{24a}/k_{24b}) is 17 showing that exocyclic cleavage of (XIII) is favoured when the radicals produced have similar stability.

Unfortunately, the results obtained in the present study shed little light on the mechanism of vicinal rearrangement of β-acyloxyalkyl radicals.[2,3] They neither exclude nor require a mechanism in which the cyclic dioxolanyl radicals mediate. The mechanistic pathway may even change from one to the other depending upon the substituents and reaction conditions.

Spin-trapping of the Di-t-butoxymethyl Radical.—Our inability to resolve a splitting from the hydrogen β to nitrogen in the nitroxide (VII) is presumably a result of the presence of the bulky t-butoxy-groups. The corresponding nitroxide adduct of the dimethoxymethyl radical shows a hydrogen splitting of 1·9 G; [24] however, in the spin-adduct of the 4,4,5,5-tetramethyldioxolanyl radical this is reduced to 0·94 G.[24] In (VII) the C–H bond must occupy a position close to the nodal plane of the nitroxide π-system.

The rate constant for addition of the di-t-butoxymethyl radical to nitrosobutane is close to that for spin-trapping of the t-butoxycarbonyl radical [16] (both *ca.* 10^6 l mol^{-1} s^{-1} at 40°). It appears that most small carbon-centred radicals may add to nitrosobutane at similarly high rates.

De Boer and his co-workers [24] attempted to detect the β-acyloxyalkyl radicals formed by β-scission of a series of 1,3-dioxolanyl radicals by spin-trapping with nitrosobutane at 20°. Only the spin-adducts of the dioxolanyl radicals were detected by e.s.r. spectroscopy. This result is not surprising since a rate constant of *ca.* 10^3—10^4 s^{-1} at 20° would have been required to give a detectable signal from the β-acyloxyalkyl radical spin-adduct, even with a nitrosobutane concentration of *ca.* 0·01M. Although the rate constant for β-scission of the dioxolanyl radicals at 20° was not measured quantitatively, it must be significantly lower than this.

EXPERIMENTAL

The techniques used for the photolytic generation of transient radicals for study by e.s.r. spectroscopy in solution have been described elsewhere.[4,5] The source of u.v. irradiation was a Mazda 1 kW ME/D high pressure mercury lamp operated from an a.c. supply, in conjunction with two Spectrosil B silica lenses. The light intensity incident upon the sample could be varied by placing neutral density filters made of metal gauze in the light beam.[5]

Radical concentrations were measured by comparison with standard solutions of *NN*-diphenyl-*N'*-picrylhydrazyl in carbon tetrachloride, using a synthetic ruby fixed to the cavity wall as an internal standard.[4,5] Corrections were made for the difference between sample temperature and that of the *NN*-diphenyl-*N'*-picrylhydrazyl solution by assuming that the e.s.r. signal intensities were proportional to T^{-1}.

The spin-trapping experiments were carried out as described previously,[16] using di-t-butoxymethane instead of t-butyl formate.

Di-t-butoxymethane was prepared from t-butyl alcohol and paraformaldehyde using toluene-*p*-sulphonic acid catalyst.[25] 4,4,5,5-Tetramethyl- and 2,4,4,5,5-pentamethyl-1,3-dioxolan were prepared from pinacol and paraformaldehyde or paraldehyde respectively, using syrupy phosphoric acid as catalyst.[26] 2,4,4-Trimethyl-1,3-dioxolan was prepared by azeotropic distillation of an equimolar solution of 2-methylpropane-1,3-diol [27] and paraldehyde in hexane with toluene-*p*-sulphonic acid catalyst.[28] 4,4,6,6-Tetramethyl- and 2,4,4,6,6-pentamethyl-1,3-dioxan were prepared in a similar way from 2,4-dimethylpentane-2,4-diol [29] using benzene as the azeotropic solvent.[30] 1-Bromomethyl-1-methylethyl acetate was synthesised by the method described by Beckwith and Thomas,[3] and 1,1,2-trimethylpropyl acetate was prepared by esterification of the alcohol (Aldrich) with acetic anhydride.[31]

Di-t-butyl peroxide was the commercial product (Koch-Light) which was washed with acidic potassium iodide, dried ($MgSO_4$), distilled, and finally passed down a column

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[23] T. Yamagishi, T. Yoshimoto, and K. Minami, *Tetrahedron Letters*, 1971, 2795.

[24] J. W. Hartgerink, L. C. J. van der Laan, J. B. F. N. Engberts, and Th. J. de Boer, *Tetrahedron*, 1971, **27**, 4323.

[25] I. Jansson, *Suomen Kem.*, 1964, **37B**, 19.

[26] R. L. Leutner, *Monatsh.*, 1935, **66**, 222.

[27] W. B. Smith, T. J. Kimet, and P. S. Rao, *J. Amer. Chem. Soc.*, 1961, **83**, 2190.

[28] C. S. Rondestvedt, *J. Org. Chem.*, 1961, **26**, 2247.

[29] K. D. Zwahlen, W. J. Horton, and G. I. Fujimoto, *J. Amer. Chem. Soc.*, 1957, **79**, 3131.

[30] K. Pihlaja, *Ann. Univ. Turkuensis Ser. A*, 1967, No. 114.

[31] A. Chablay, *Compt. rend.*, 1964, **258**, 5237.

of alumina (Woelm basic activity 1). Samples for photolysis were made up as described previously[4,5] and were *ca.* 1M in dialkoxyalkane. The solvent was usually 5 : 1 v/v cyclopropane–di-t-butyl peroxide or 3 : 1 v/v benzene–di-t-butyl peroxide.

We are grateful to Mr. R. Tye for preparing 1-bromomethyl-1-methylethyl acetate. We thank the S.R.C. for grants in support of this work.

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