An Electron Spin Resonance Study of the Regioselectivity of the Cyclization of Protonated and Unprotonated Pent-4-en-1-oxyl and Pent-4-en-1-peroxyl Radicals

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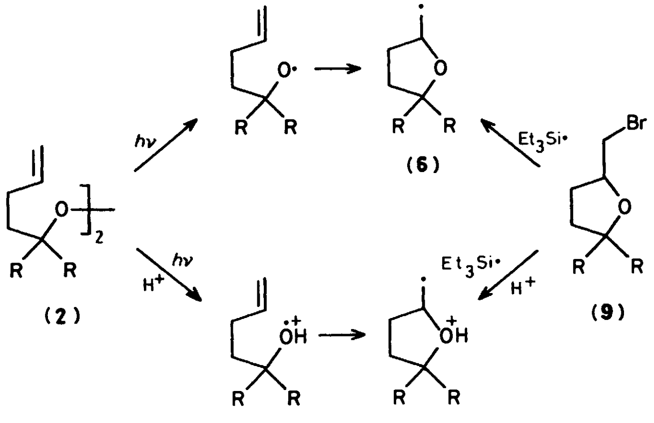
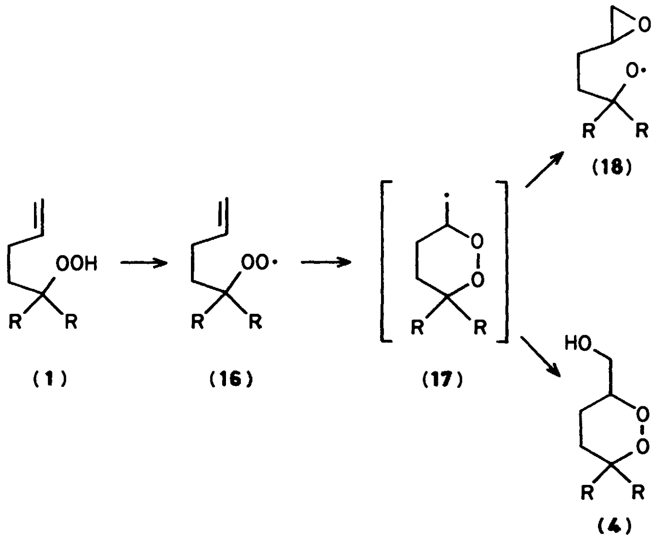
The regioselectivity of the ring closure of protonated and unprotonated pent-4-en-1-oxyl radicals has been determined by monitoring by e.s.r. spectroscopy the radicals which are formed when the corresponding pent-4-enyl peroxides (**2**; R = H or Me) are photolysed in solution.



Under neutral conditions, the spectra of the corresponding tetrahydrofuran-2-ylmethyl radicals (**6**) are observed, confirming the preferential 5-*exo* mode of cyclization. When trifluoroacetic acid is present, the different spectra of the protonated tetrahydrofuran-2-ylmethyl radicals (**8**) are observed, and it is argued that this reflects the similar regioselectivity of the intramolecular addition of the protonated alkoxyl radicals.

The identity of the radicals (**6**) and (**8**) was confirmed by generating them independently by abstracting bromine atoms from the corresponding bromides (**9**).

Similar experiments with the hydroperoxides (**1**) failed to show the spectra of the dioxan-3-ylmethyl radicals (**17**), perhaps because they rapidly undergo γ-scission to the oxygen-centred radicals (**18**). However, (**17**) could be trapped with oxygen to afford, after Ph$_3$P reduction, 1,2-dioxanes (**4**).



(**4**)

No evidence could be found for the protonation of alkylperoxyl radicals by trifluoroacetic acid.

Preliminary e.s.r. evidence has indicated that different radicals are formed when di-t-butyl peroxide is photolysed in the absence or in the presence of trifluoroacetic acid.[1] Thus, under acid conditions, the species obtained added to an alkene and underwent β-scission more readily than does the t-butoxyl radical. It was suggested that the modified chemistry results from the formation of the protonated t-butoxyl radical [equation (1)].[1,2]

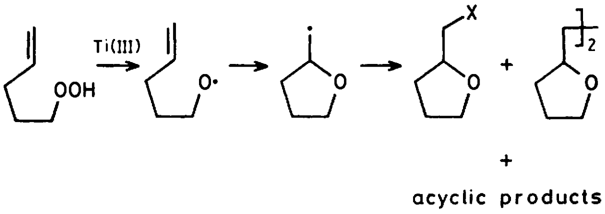
$$\mathrm{Bu^tO{-}OBu^t} \xrightarrow[\mathrm{H^+}]{h\nu} \mathrm{Bu^t\overset{\bullet +}{O}H} \qquad (1)$$

To seek further evidence for the existence and behaviour of alcohol radical cations ($\overset{+\bullet}{\mathrm{ROH}}$) distinct from the corresponding neutral alkoxyl radicals (RO$^\bullet$), we have prepared unsaturated dialkyl peroxides $[\mathrm{CH_2{=}CH(CH_2)_2CR_2O}]_2$ (R = H or Me) and photolysed them in the absence or presence of trifluoroacetic acid, and used e.s.r. spectroscopy to characterize the resultant carbon-centred radicals, which might be expected to be formed by 5-*exo-trig* or 6-*endo-trig* intramolecular addition of the oxygen-centred species to the carbon–carbon double bond.

Using similar techniques with the corresponding unsaturated hydroperoxides $\mathrm{CH_2{=}CH(CH_2)_2CR_2OOH}$ (R = H or Me), we have additionally looked for evidence to differentiate the behaviour of neutral and protonated alkylperoxyl radicals, ROO$^\bullet$ and $\overset{\bullet\,+}{\mathrm{ROOH}}$ respectively.

The most relevant work in the literature is the e.s.r. study by Gilbert and Norman and their co-workers[3] of the reduction of pent-4-enyl hydroperoxide by the titanium(III) ion.

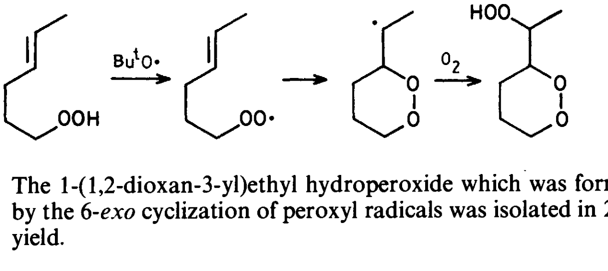
They observed a spectrum with a(2H) 21.9 G and a(1H) 18.5 G, g 2.0025, which was assigned to the tetrahydrofuran-2-ylmethyl radical [equation (2)]. Surzur and his colleagues[4] studied the products which were formed when the hydroperoxide was reduced with $\mathrm{TiCl_3}$, $\mathrm{FeCl_2}$, or $\mathrm{FeI_2}$, or when it was photolysed. Under various conditions, between 11 and 80% of tetrahydrofuran-2-ylmethyl compounds were isolated as shown in equation (2), and these products were thought to be formed through the 5-*exo-trig* cyclization of the pent-4-en-1-oxyl radical.



(2)

The interpretation of these results is complicated somewhat by the fact that the pent-4-en-1-oxyl radicals may be complexed to the titanium or iron ions, and, under Surzur's photolytic conditions, may also abstract hydrogen from the hydroperoxide to give pent-4-en-1-peroxyl radicals, which may themselves cyclize.

Porter and his colleages have studied the products which are formed when hex-4-en-1-yl hydroperoxide is caused to react in the presence of oxygen with t-butoxyl radicals [equation (3)].[5]

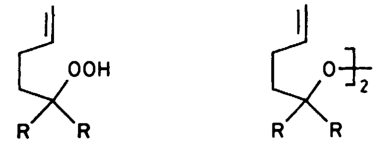


(3)

The 1-(1,2-dioxan-3-yl)ethyl hydroperoxide which was formed by the 6-*exo* cyclization of peroxyl radicals was isolated in 23% yield.

Results and Discussion

Preparation of the Peroxides.—The oxyl and peroxyl radicals described in this paper were generated from one of the four peroxides (**1a**), (**1b**), (**2a**), and (**2b**).

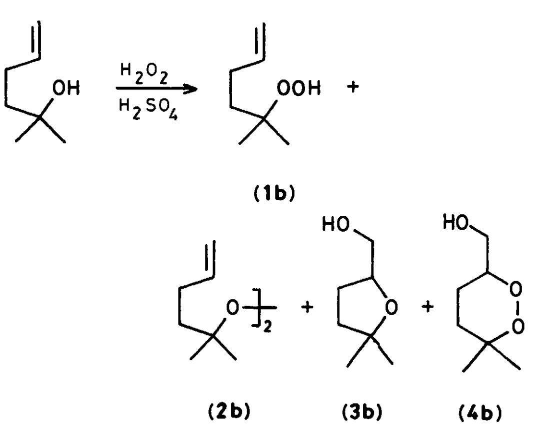


(**1**) (**2**)

a; R = H

b; R = Me

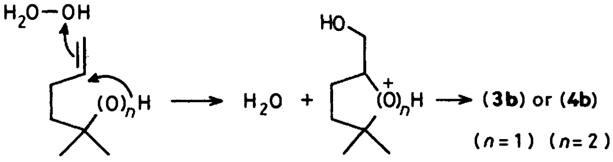
The primary alkyl peroxides (**1a**) and (**2a**) were prepared by alkylating basic hydrogen peroxide with a methanesulphonate,[6] here derived from pent-4-en-1-ol. An attempt to prepare the tertiary alkyl peroxides (**1b**) and (**2b**) using the classical conditions of hydrogen peroxide, alcohol, and acid[7] gave an interesting result [equation (4)].



(4)

The dimethyltetrahydrofuran-3-ylmethanol (**3b**) and the dimethyldioxan-3-ylmethanol (**4b**) were obtained in addition to the expected peroxides (**1b**) and (**2b**). Compounds (**3b**) and (**4b**) most likely arise by electrophilic oxygenation of the double bond coupled with intramolecular nucleophilic capture, the parent alcohol giving rise to compound (**3b**) and the derived hydroperoxide (**1b**) giving rise to the compound (**4b**).

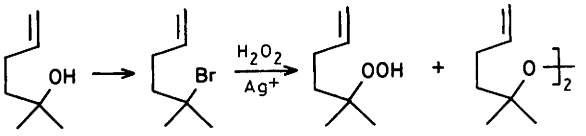
Presumably the reaction mixture contains a low concentration of $\mathrm{H_3O_2^+}$ and although the conditions are not normally conducive to alkene epoxidation, electrophilic attack is promoted by concurrent intramolecular capture [equation (5)].



(5)

Consistent with this picture was the observation that parallel treatment of pent-4-en-1-ol, where conversion into the primary alkyl hydroperoxide (**1a**) is not expected to occur readily, afforded tetrahydrofuran-2-ylmethanol but no 1,2-dioxan-3-ylmethanol. Furthermore, analogous acid-induced transformations of 4,5-epoxy-alcohols and -hydroperoxides into tetrahydrofuran-2-yl- and 1,2-dioxan-3-yl-methanols respectively are well established.[5]

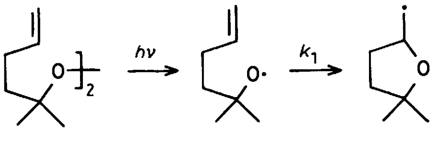
The tertiary alkyl peroxides (**1b**) and (**2b**) were prepared more satisfactorily by converting 2-methylhex-5-en-2-ol into the corresponding alkyl bromide then treating it with hydrogen peroxide and silver tetrafluoroborate [equation (6)].



(6)

(1b) **(2b)**

Radicals derived from Unsaturated Dialkyl Peroxides (**2a**) *and* (**2b**).—Because of its obvious relationship to the di-t-butyl peroxide–alkene system, peroxide (**2b**) was examined first. When a 1:4 mixture of peroxide (**2b**) and cyclopropane was photolysed in the cavity of an e.s.r. spectrometer between 175—213 K, a strong spectrum was observed which consisted of a triplet of doublets with some further small coupling (see Figure 1 and Table), and is assigned to the tetrahydrofuran-2-ylmethyl radical (**6b**), formed by cyclization of the initial alkoxyl radical (**5b**) [equation (7)].



(7)

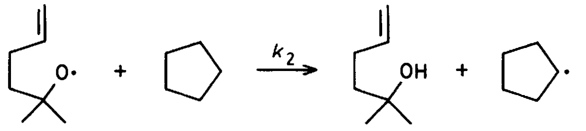
(2b) **(5b)** **(6b)**

If the alternative mode of 6-*exo* cyclization occurred to give a tetrahydropyran-3-yl radical, the e.s.r. spectrum would be predictably substantially different.

This confirms that, in a system which is free from the possible incursion of metal-complexed alkoxyl radicals or of alkylperoxyl radicals, the pent-4-en-1-oxyl radical (**5b**) does undergo a 5-*exo* ring closure.[3,4]

When the peroxide (**2b**) was photolysed at 183 K in cyclopentane (relative concentrations 1:3 by volume), the same spectrum of (**6b**) could be observed, and none of the cyclopentyl radical which might be formed by reaction (8) could be detected.

If it is assumed that the rate constants for the removal of the radical (**6b**) and of the cyclopentyl radical are equal at the diffusion-controlled limit, the competition between the unimolecular ring closure of equation (7), and the bimolecular

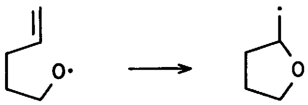


(8)

(5b)

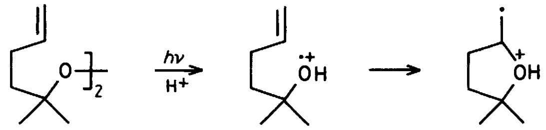
hydrogen abstraction of equation (8), enables the rate constants k_1 and k_2 to be compared.

We estimate that the cyclopentyl radical [a(1H) 21.5 G, a(4H) 35.1 G, a(4H) 0.53 G] would have been detected above the noise level if its concentration were 1/7 of that of radical (**6b**). If the rate constant k_2 at 183 K is taken to be 2.1×10^4 l mol^{-1} s^{-1} (per molecule),[8] a lower limit for k_1 can be estimated to be 1×10^6 s^{-1}. This is to be compared with Gilbert and Norman's estimate[3] of a value of $> 10^8$ s^{-1} for the rate constant for the 5-*exo* cyclization of the pent-4-en-1-oxyl radical in water solvent [reaction (9)].



(9)

A different spectrum from that of (**6b**) was observed when a 1:1:2 mixture of peroxide (**2b**), trifluoroacetic acid, and cyclopropane was similarly photolysed between 216—185 K (see Figure 2 and Table). We ascribe this spectrum to the distonic radical cation (**8b**), formed by the cyclization of the protonated alkoxyl radical (**7b**) [equation (10)].



(10)

(2b) **(7b)** **(8b)**

The same spectrum was obtained when the reaction was carried out with deuteriotrifluoroacetic acid, showing that hyperfine coupling to the OH proton is not observed.

The identities of the radicals (**6b**) and (**8b**) were confirmed by generating then independently from (5,5-dimethyltetrahydrofuran-2-yl)methyl bromide (**9b**). Thus, photolysis of a 1:20:2 mixture of bromide (**9b**), triethylsilane, and di-t-butyl peroxide at 200 K, which should afford radical (**6b**) [equations (11)—(13)], gave a spectrum superimposable upon that from the photolysis of peroxide (**2b**) in cyclopropane [equation (7)].

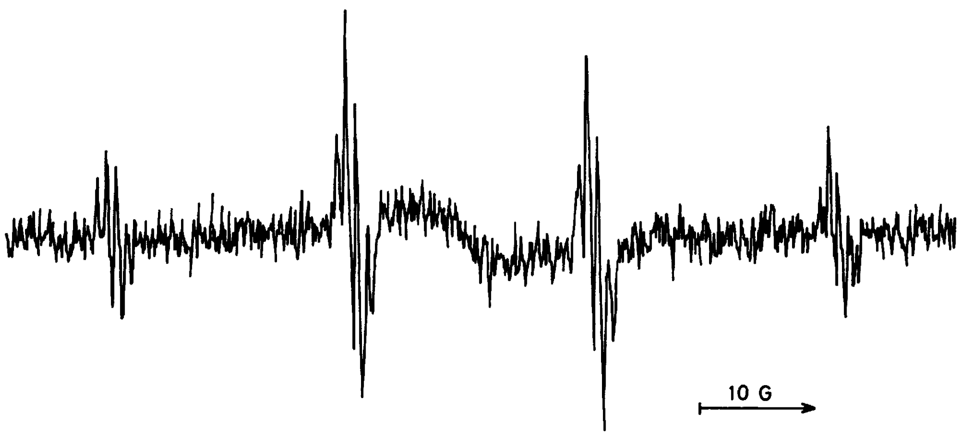


Figure 1. E.s.r. spectrum of the (5,5-dimethyltetrahydrofuran-2-yl)methyl radical (**6b**) in cyclopropane at 175 K

Table. E.s.r. spectra of protonated and unprotonated 2-alkoxyalkyl radicals

	T/K	Solvent	Hyperfine coupling constants/G $a(\mathrm{H}_\alpha)$	$a(\mathrm{H}_\beta)$	a(others)	g-Factor
$\mathrm{Bu^tOCH_2CH_2^{\bullet}}$ [1]	198	C_2H_4	22.0 (2H)	33.2 (2H)		
$\mathrm{Bu^t\underset{H}{\overset{+}{O}}CH_2CH_2^{\bullet}}$ [1]	183	C_2H_4	22.0 (2H)	28.8 (2H)		
(6b)	213—175	c-C_3H_6 or Et_3SiH	21.94 (2H)	21.94 (1H)	0.82 (2H)	2.0025
(8b)	216—165	c-C_3H_6 or Et_3SiH	22.20 (2H)	16.10 (1H)	0.68 (2H)	2.0025
(6a)	181	c-C_5H_{10} or Et_3SiH	22.51 (2H)	22.51 (1H)		2.0025
(8a)	184	c-C_5H_{10}	22.46 (2H)	17.34 (1H)		2.0025

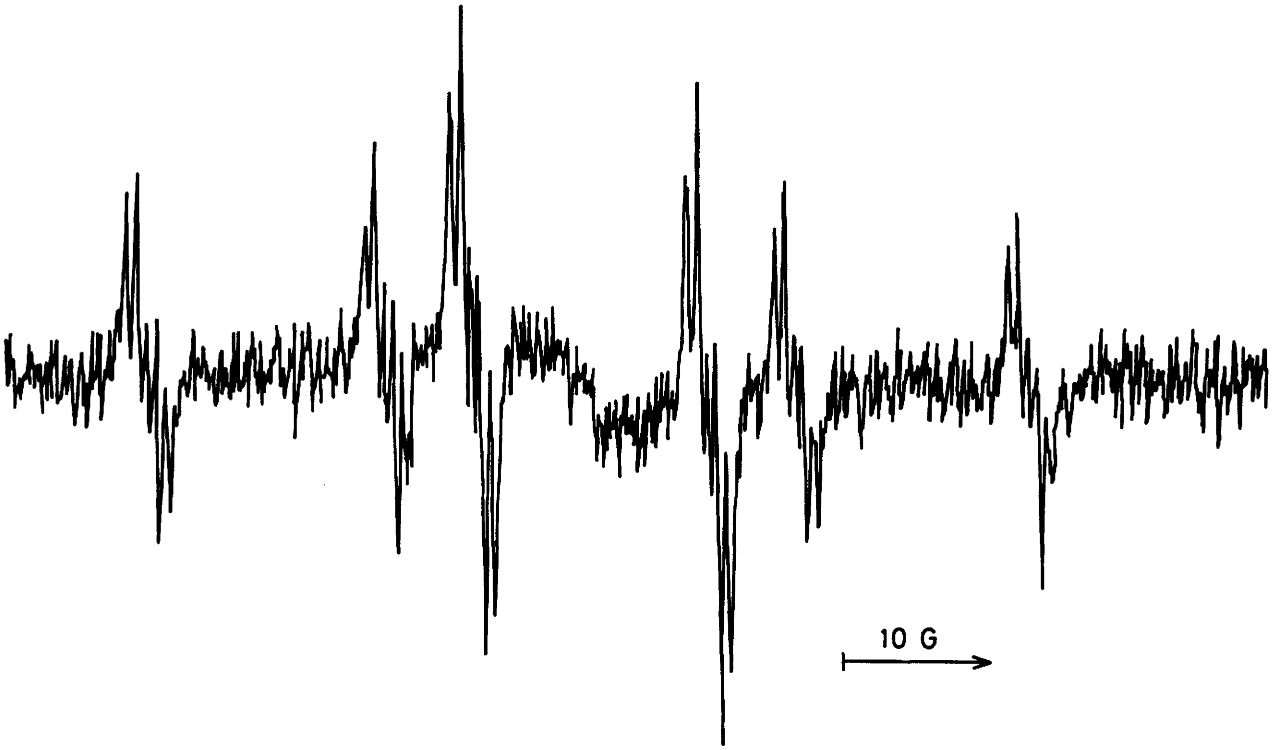
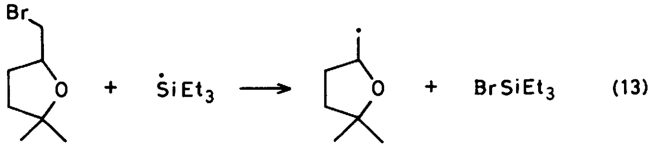


Figure 2. E.s.r. spectrum of the protonated (5,5-dimethyltetrahydrofuran-2-yl)methyl radical (**8b**) in cyclopropane containing trifluoroacetic acid at 165 K

$$\mathrm{Bu^tO{-}OBu^t \xrightarrow{h\nu} 2Bu^tO^{\bullet}} \qquad (11)$$

$$\mathrm{Bu^t\dot{O} + H{-}SiEt_3 \longrightarrow Bu^tOH + \dot{S}iEt_3} \qquad (12)$$

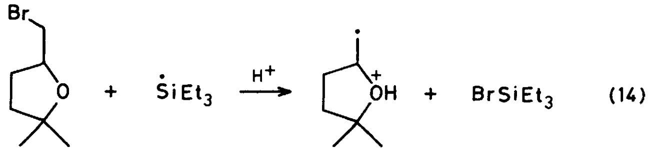


(13)

(**9b**) (**6b**)

Again, photolysis of a 1:20:2:1 mixture of bromide (**9b**), triethylsilane, di-t-butyl peroxide, and trifluoroacetic acid at 173 K [equations (11), (12), and (14)] gave a spectrum superimposable upon that from photolysis of peroxide (**2b**) in cyclopropane plus trifluoroacetic acid [equation (10)]. At this temperature and concentration the reaction of triethylsilane with trifluoroacetic acid was not a problem.

It could be argued that protonation occurs after cyclization and that observation of radical (**8b**) is not, therefore, conclusive

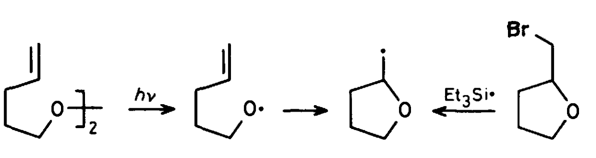


(14)

(**9b**) (**8b**)

proof of the intermediacy of the alcohol radical cation (**7b**). However, parallel experiments with the primary alkyl peroxide (**2a**) gave similar results but with one significant difference which supports the suggestion that protonation precedes cyclization. Thus, photolysis of a 1:4 mixture of peroxide (**2a**) and cyclopentane at 181 K and of a 1:20:2 mixture of tetrahydrofuran-2-ylmethyl bromide (**9a**), triethylsilane, and di-t-butyl peroxide gave identical e.s.r. spectra (see Table), which are assigned to radical (**6a**) [equation (15)].

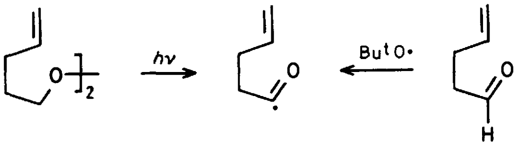
However, the spectrum from the peroxide route contained an additional strong broad singlet (ΔH_{pp} 1.6 G) with g 2.0006, indicating the acyl radical (**10**). The identity of this radical was confirmed by generating it independently by photolysis of a



(15)

(2a) (5a) (6a) (9a)

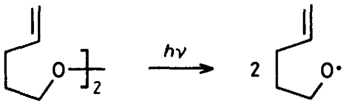
1:1:20 mixture of pent-4-enal (11), di-t-butyl peroxide, and cyclopentane [equation (16)].



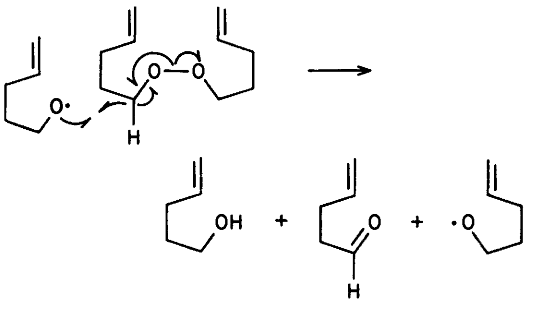
(16)

(2a) (10) (11)

Presumably the aldehyde (11) is formed during the photolysis of peroxide (2a) by induced decomposition[9] [equations (17) and (18)], for which there is no parallel with the tertiary peroxide (2b).



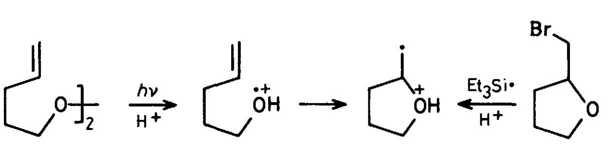
(17)



(18)

(11)

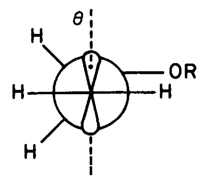
Significantly, the corresponding photolysis of a 1:1:4 mixture of peroxide (2a), trifluoroacetic acid, and cyclopentane at 184 K gave only one spectrum consisting of a doublet of triplets, with g 2.0025 (see Table). This suggests that the pent-4-en-1-ol radical cation (7a) is formed and undergoes cyclization to the distonic radical cation (8a) [equation (19)] rather than reaction with the parent dialkyl peroxide. If significant amounts of the unprotonated alkoxyl radical (5a) were present, then formation of acyl radical (10) would be observed [equations (17) and (18)]. The identity of radical (8a) was confirmed by generating it independently from tetrahydrofuran-2-ylmethyl bromide (9a) [equation (19)].*



(19)

(2a) (7a) (8a) (9a)

E.S.R. Spectra of Protonated β-Alkoxyalkyl Radicals.—The e.s.r. spectra of β-hydroxyethyl,[10] β-alkoxyethyl, and β-trimethylsiloxyethyl[9] radicals have been reported previously. All show large values of $a(2H_\beta)$ (usually 30—35 G) with a negative temperature coefficient, and this is interpreted to imply that at low temperatures the radicals adopt the staggered conformations (12) in which the time-averaged value of dihedral angle θ is *ca.* 30° and there is effective hyperconjugative interaction between the β-CH bonds and the singly occupied $2p$ orbital.



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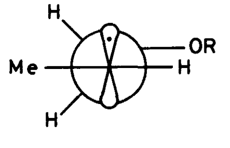

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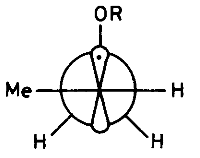

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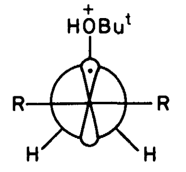

(15)

In β-alkoxypropyl radicals the energies of the staggered (13) and the eclipsed (14) conformations are more nearly balanced.[11] When R = H or Me, the conformation (13) is still preferred, but when R = CF_3 (or Me_3Si), $a(H_\beta)$ = 16.56 at 173 K, with a negative temperature coefficient, arguing for the eclipsed conformation (14). It was suggested that the dominant factor in determining the conformation was the relative homoconjugative interactions between the p-orbitals on oxygen and on the radical centre in (13) and (14), and that electronegative groups R (*e.g.*, acyl or CF_3) favoured the eclipsed conformation (14).[12]

The outstanding feature which distinguishes between the neutral and the protonated β-alkoxyalkyl radicals in the Table is the values of $a(H_\beta)$.† On protonation of the oxygen $a(H_\beta)$ drops by some 5 G, suggesting that the radical changes on protonation from a staggered to an eclipsed conformation (15). This would be compatible with Kochi's[12] suggestion that the more electronegative groups tend to adopt an eclipsing conformation.

Our results refer to primary alkyl radicals with substituents $R\overset{+}{O}H$ in the β-position. Marti, Paul, and Roberts[13] have reported the e.s.r. spectra of some tertiary alkyl radicals carrying the group $Bu^t\overset{+}{O}H$ in the β-position, namely $Me_2\dot{C}CH_2\overset{+}{O}(H)Bu^t$, $\overline{CH_2CH_2CH_2\dot{C}}CH_2\overset{+}{O}(H)Bu^t$, and $\overline{CH_2CH_2CH_2CH_2\dot{C}}CH_2\overset{+}{O}$(H)Bu^t, which show similar low values of $a(2H_\beta)$ (13.7, 13.3, and 12.8 G respectively). They concluded that both steric and polar factors probably combined in imposing the preferred conformation (15)

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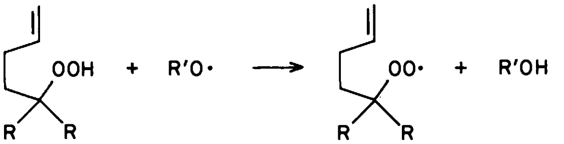
* Similarly photolysis of ethyl t-butyl peroxide in propene at 164 K shows only a weak spectrum of the allyl radical, together with signals resulting from the decomposition of the peroxide. If trifluoroacetic acid is present, strong spectra of the radicals $Et\overset{+}{O}(H)CH_2\dot{C}HMe$ and $Bu^t\overset{+}{O}(H)CH_2\dot{C}HMe$ are observed. Again, it appears that protonation of the alkoxyl radicals precedes their addition to the double work (A. J. Bloodworth, A. G. Davies, and R. Hay-Motherwell, unpublished work).

† The fact that Gilbert and Norman[3] observed a lower value of $a(H\beta)$ (18.5 G) for the radical (6a) in aqueous solution at room temperature than we do (22.51 G) in cyclopropane at 181 K may in part be ascribed to a solvent effect but may also represent a greater population of the staggered conformation at lower temperatures.

Radicals Derived from Unsaturated Alkyl Hydroperoxides (**1a**) *and* (**1b**).—In the hope of observing similar behaviour with alkyl peroxyl ($\mathrm{RO\dot{O}}$) and protonated alkyl peroxyl ($\mathrm{R\dot{O}\overset{+}{O}H}$) radicals, we have carried out similar experiments with the alkyl hydroperoxides (**1a**) and (**1b**). However, over a wide range of conditions the only signals observed by e.s.r. spectroscopy corresponded to the alkyl peroxyl radicals (**16a, b**). Thus, photolysis of a 1:4 mixture of the t-alkyl hydroperoxide (**1b**) and cyclopentane at 201 K showed a singlet with *g* 2.0151 (ΔH_{pp} 2 G), typical for an alkylperoxyl radical. The spectrum was observed over the temperature range 196—322 K but no other signals appeared. Inclusion of di-t-butyl peroxide in the solution resulted in a stronger signal for radical (**16b**), but again no other signals were seen over a temperature range of 183—299 K. Thirdly, a solution of hydroperoxide (**1b**) in cyclopentane containing di-t-butyl peroxyoxalate as a thermal source of t-butoxyl radical was observed over the temperature range from 304—317 K, but once more the singlet for peroxyl radical (**16b**) was all that was detected [equation (20)].



(20)

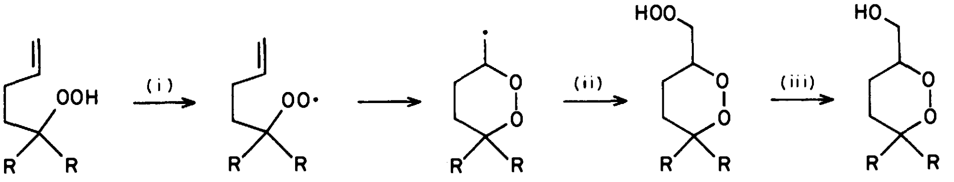
(**1**) (**16**)

a; R = H

b; R = Me

Similarly, photolysis of a 4:1:16 mixture of the primary alkyl hydroperoxide (**1a**), di-t-butyl peroxide, and cyclopentane at 184 K produced a weak triplet [*g* 2.0137, *a*(2H) 5.97 G, ΔH_{pp} 2.48 G] which is assigned to peroxyl radical (**16a**) [equation (20)]; no signals were observed in the absence of the di-t-butyl peroxide.

Porter's product studies [equation (3)] have indicated that unsaturated alkylperoxyl radicals similar to (**16a,b**) do undergo 6-*exo*-cyclization.^{5} Using Porter's conditions for trapping the cyclized radical (**17**) with oxygen, and reducing the hydroperoxide with triphenylphosphine, we were able to isolate the corresponding (1,2-dioxan-3-yl)methanols (**4a**) (10%) and (**4b**) (24%) [equation (21)], confirming Porter's observation.



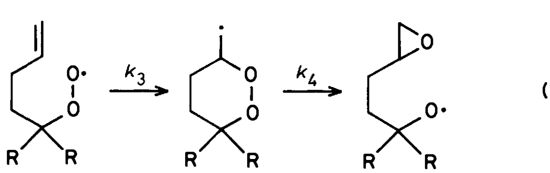
(21)

(**1**) (**16**) (**17**) (**4**)

Reagents: (i) $(\mathrm{Bu^tOOCO})_2$, PhH, 25 °C; (ii) $\mathrm{O_2}$; (iii) $\mathrm{Ph_3P}$

Our failure to observe the expected cyclized radicals (**17a,b**) by e.s.r. spectroscopy cannot therefore be because they are not formed. Neither is there any evidence that the addition of the peroxyl radical to the alkene is reversible, even in acyclic systems where elimination might be expected to occur more readily.^{14,15} Rather, the rate of cyclization (k_3) must be slower than that of destruction (k_4) by subsequent γ-scission to afford the unobservable alkoxyl radicals (**18a,b**) [equation (22)].

This mode of reaction in the absence of oxygen has been confirmed for related radicals by product analysis studies,^{14,15}



(22)

(**16**) (**17**) (**18**)

and k_4 is expected^{14,15} to have a value of between 10^4 and 10^5 $\mathrm{s^{-1}}$ at 298 K.

Search for Alkyl Hydroperoxide Radical Cations.—To date we have been unable to find e.s.r. evidence to support the existence of alkyl hydroperoxide radical cations ($\mathrm{R\dot{O}\overset{+}{O}H}$). Thus, photolysis of a 1:1:4 mixture of hydroperoxide (**1b**), trifluoroacetic acid, and cyclopentane at 206 K gave a strong singlet (*g* 2.0136, ΔH_{pp} 2.4 G) which seems likely to be due to the unprotonated peroxyl radical (**16b**) (*vide supra*). Similarly, photolysis of a mixture of t-butyl hydroperoxide, trifluoroacetic acid, ethylene, and cyclopropane showed only a signal attributable to the t-butyl peroxyl radical. Further, the decay kinetics of the t-butyl peroxyl radical were unchanged when the reaction was carried out in trifluoroacetic acid.

Again, photolysis at 196 K of a 1:4 mixture of cyclopentyl hydroperoxide and cyclopentane showed a spectrum of the cyclopentyl peroxyl radical^{16} *a*(1H) 7.10 G, *g* 2.0151, ΔH_{pp} 3.6 G. Under the same conditions, a 1:4:0.25 or 1:4:1 mixture of the cyclopentyl hydroperoxide, and trifluoroacetic acid showed similar spectra, *a*(1H) 6.97 G, *g* 2.0146, and *a*(1H) 7.4, *g* 2.0147 respectively, providing no evidence for protonation of the radical.

It seems likely that our failure to find evidence for protonated alkylperoxyl radicals, $\mathrm{R\dot{O}\overset{+}{O}H}$, under conditions where protonated alkoxyl radicals, $\mathrm{R\overset{\bullet +}{O}H}$, are formed, is a consequence of the greater acidity of the former species.

The parent hydroperoxides, ROOH, are stronger acids than the alcohols, ROH, and are closer to the phenols ArOH. E.s.r. spectroscopy shows that phenoxyl radicals are not protonated in trifluoroacetic acid, but they are in trifluoroacetic acid containing sulphuric acid.^{17} It may yet prove possible to generate protonated peroxyl radicals under strongly acid conditions, provided that concomitant acid-induced decomposition of the hydroperoxide can be avoided.

Experimental

Instrumental Methods.—N.m.r. spectra were recorded using a Varian XL200 spectrometer with $\mathrm{CDCl_3}$ solvent. Mass spectroscopic data were obtained using a VG 707OH spectrometer fitted with a Finnigan Incos data system.

E.s.r. spectra were recorded with a Varian E109 instrument. Samples were photolysed in the cavity using an Osram HBO-500 W/2 mercury discharge lamp. Solutions in cyclopropane were degassed by freeze–thaw cycles on a vacuum line, and solutions in higher-boiling solvents were degassed with a stream of argon. The concentrations used were (v/v) peroxide:solvent, 1:4; peroxide:trifluoroacetic acid:solvent, 1:1:4 or 2:1:4. In reactions involving bromides, the substrate, triethylsilane, and di-t-butyl peroxide were taken in the ratio 1:20:2, trifluoroacetic acid being added as required.

Preparation of Materials.—Cyclopentyl hydroperoxide,[5] (5,5-dimethyltetrahydrofuran-2-yl)methanol (**3b**),[18] tetrahydrofuran-2-ylmethyl bromide (**9a**),[19] pent-4-enal (**11**),[20] and di-t-butyl peroxyoxalate[21] were each prepared by the published route.

2-*Methylhex*-5-*en*-2-*yl Hydroperoxide* (**1b**) *and Bis*-(2-*methylhex*-5-*en*-2-*yl*) *Peroxide* (**2b**).—*Method* 1. Ethyl acetoacetate was treated with allyl bromide and ethanolic sodium ethoxide, and the product was hydrolysed with 15% aqueous NaOH to give a distillate of hex-5-en-2-one. This ketone was treated with methylmagnesium iodide in diethyl ether affording 2-methylhex-5-en-2-ol, b.p. 57 °C at 14 mmHg (lit.,[22] 58—59 °C at 17 mmHg). A mixture of this alcohol (1.0 g, 8.8 mmol) and 30% hydrogen peroxide (2.33 cm^3, 22.9 mmol) was stirred and cooled to -10 °C. Concentrated sulphuric acid (1.37 cm^3) was added dropwise so that the temperature did not exceed -5 °C.

After a further 2 h stirring, the mixture was saturated with ammonium sulphate and extracted with diethyl ether, yielding a crude product (h.p.l.c.) containing the starting alcohol (65%) and the desired *hydroperoxide* (**1b**) (35%).

If the temperature of the reaction mixture was allowed to rise to 10 °C the crude product (65%) was found to consist of the hydroperoxide (**1b**) and *peroxide* (**2b**), (5,5-dimethyltetrahydrofuran-2-yl)methanol (**3b**), and (6,6-dimethyl-1,2-dioxan-3-yl)methanol (**4b**) in the ratio 9:6:2 (by comparison with authentic samples).

When this reaction was carried out with pent-4-en-1-ol, no hydroperoxide was obtained although tetrahydrofurfuryl alcohol (**3a**) was identified by ^{1}H and ^{13}C n.m.r.

Method 2. In this preferred method, 2-methylhex-5-en-2-ol was treated with phosphorus tribromide and pyridine giving 2-bromo-2-methylhex-5-ene, b.p. 48 °C at 7 mmHg (lit.,[23] 65—66 °C at 20 mmHg). To a stirred solution of the bromide (3.77 g, 21 mmol) and 85% hydrogen peroxide (1.266 g, 26.3 mmol) in diethyl ether (40 cm^3) at 178 °C was added, in a single portion, silver tetrafluoroborate (4.96 g, 25 mmol). The mixture was stirred at -78 °C for 1 h, when t.l.c. showed that none of the bromide remained. The solution was neutralized with saturated sodium hydrogen carbonate. The ethereal layer was subjected to preparative h.p.l.c. to give 2-*methylhex*-5-*en*-2-*yl hydroperoxide* (**1b**) (1.34 g, 47%); δ_H 1.24 (6 H, s, Me), 1.66 (2 H, m,), 2.1 (2 H, m), 5.0 (2 H, m, CH$_2$=), 5.86 (1 H, m, CH=), and 7.58 (1 H, br s, OOH); δ_C 24.15, 28.68, 37.95, 81.84, 114.45, and 139.31 p.p.m. (Found: C, 63.9; H, 10.5. $C_7H_{14}O_2$ requires C, 64.6; H, 10.8%). *Bis*-(2-*methylhex*-5-*en*-2-*yl*) *peroxide* (**2b**) (0.80 g, 32%); δ_H 1.18 (6 H, s, Me), 1.6 (2 H, m), 2.06 (2 H, m), 4.95 (2 H, m, CH$_2$=), and 5.82 (1 H, m, CH=); δ_C 24.97, 28.90, 38.87, 80.01, 114.28, and 139.52 p.p.m. (Found: C, 74.4; H, 11.5. $C_{14}H_{26}O_2$ requires C, 74.3; H, 11.6%).

Pent-4-*enyl hydroperoxide* (**1a**) *and di*(*pent*-4-*enyl*) *peroxide* (**2a**). These compounds were prepared from pent-4-enyl methanesulphonate as described by Porter *et al.*[5] The first extraction of the neutralized reaction mixture contained the crude peroxide, which was purified by flash chromatography on silica gel with diethyl ether–pentane (1:9) as eluant to give di(pent-4-enyl) peroxide (**2a**) (12%); δ_H 1.75 (2 H, m), 2.15 (2 H, m), 3.99 (2 H, t), 5.0 (2 H, t, CH$_2$=), and 5.8 (1 H, m, CH=); δ_C 27.60, 30.58, 73.42, 115.15, and 138.26 p.p.m. (Found: C, 70.5; H, 10.4. Calc. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.7%).

The final extraction yielded pent-4-enyl hydroperoxide (**1a**) (30%), with ^{1}H n.m.r. spectrum similar to that reported by Surzur and co-workers[4] and δ_C 27.18, 30.32, 76.24, 115.18, and 138.24 p.p.m.

(5,5-*Dimethyltetrahydrofuran*-2-*yl*)*methyl Bromide* (**9b**).—A mixture of 2-methylhex-5-en-2-ol (1.72 g, 15.1 mmol) and recrystallized *N*-bromosuccinimide (2.82 g, 15.9 mmol) in carbon tetrachloride (22.7 cm^3) was stirred at room temperature for 48 h. Pentane (30 cm^3) was added, and the mixture was filtered, and the residue washed (pentane). Sodium acetate (16 mg) was added to the filtrate which was then concentrated under reduced pressure at room temperature. Distillation gave (5,5-*dimethyltetrahydrofuran*-2-*yl*)*methyl bromide* (**9b**) (1.9 g, 65%), b.p. 47—48 °C at 4 mmHg; δ_H 1.24 (3 H, s, Me), 1.29 (3 H, s, Me), 1.79 (3 H, m), 2.25 (1 H, m), 3.38 (2 H, *ABX*, CH$_2$Br), and 4.2 (1 H, m, OCH); δ_C 28.06, 29.18, 30.96, 36.65, 38.28, 77.9, and 81.85 p.p.m. (Found: C, 43.5; H, 6.6; Br, 41.2. $C_7H_{13}BrO$ requires C, 43.5; H, 6.8; Br, 41.4%).

(6,6-*Dimethyl*-1,2-*dioxan*-3-*yl*)*methanol* (**4b**). A solution of di-t-butyl peroxyoxalate (0.475 g, 2.03 mmol) and 2-methylhex-5-en-2-ol (0.68 g, 5.2 mmol) in benzene (500 cm^3) was stirred vigorously in contact with air for 48 h. Triphenylphosphine (1.014 g, 3.8 mmol) was then added at 5—10 °C, and the mixture was stirred at this temperature for 30 min. The solvent was removed under reduced pressure at room temperature. The residue was extracted with cold diethyl ether (10 cm^3); the ether was removed under vacuum, and the residue was flash chromatographed on silica with 10—25% ethyl acetate–hexane. The product was rechromatographed to give (6,6-*dimethyl*-1,2-*dioxan*-3-*yl*)*methanol* (**4b**) (180 mg, 24%); δ_H 1.21 (3 H, s, Me), 1.33 (3 H, s, Me), 1.66 [4 H, m, (CH$_2$)$_2$], 1.85 (1 H, m, OH, exchangeable with D$_2$O), 3.65 (2 H, m, CH$_2$OH), and 4.17 (1 H, m, OCH); δ_C 22.15, 23.25, 26.97, 33.53, 63.80, 77.72, and 81.78 p.p.m. (Found: *m/z* 128.0834. $M - H_2O$ requires 128.08366. Found: C, 56.8; H, 9.7. $C_7H_{14}O_3$ requires C, 57.5; H, 9.7%).

Acknowledgements

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