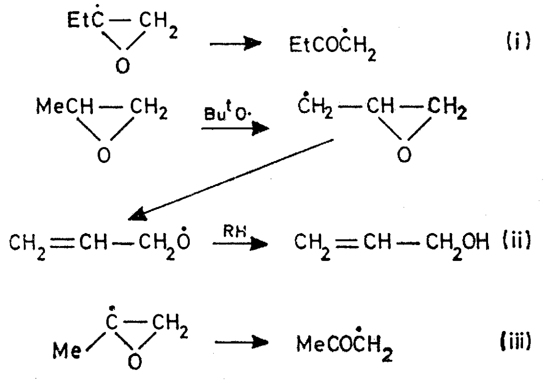
Electron Spin Resonance Studies. Part IL.[1] Radicals derived from Oxirans in Aqueous Solution

By **Anthony J. Dobbs, Bruce C. Gilbert,* Hugh A. H. Laue,** and **Richard O. C. Norman,** Department of Chemistry, The University of York, Heslington, York YO1 5DD

E.s.r. spectroscopy, in conjunction with a flow-system technique, has been used to study the reactions of the hydroxyl radical with some substituted oxirans, and the further transformations (notably ring-opening) of the resulting oxiranyl-substituted radicals. For example, there is evidence that propylene oxide yields, sequentially, the oxiranylmethyl, allyloxyl, and 1-hydroxyallyl radicals.

THERE is evidence that both oxiranyl and oxiranylalkyl radicals can undergo ring-opening reactions. For example, the occurrence of reactions (i) and (ii) has been inferred from product studies,[2,3] and the e.s.r. spectrum of the radical (1) (from propylene oxide and $Bu^tO\cdot$) is replaced by that of the radical (2) above −10 °C.[4] In contrast, e.s.r. evidence[5] indicates that the unsubstituted oxiranyl radical, prepared by reaction of hydroxyl with oxiran, does not undergo ring-opening at room temperature in aqueous solution.



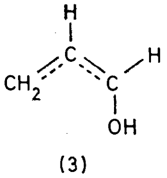
(1) (2)

We have studied the reactions between the hydroxyl radical and some substituted oxirans in order to establish the selectivity of the radical, to investigate the structures of derived radicals (the oxiranyl radical is thought[5] to be markedly bent at the radical centre), and to characterise features of possible ring-opening reactions.

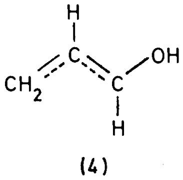
RESULTS AND DISCUSSION

The hydroxyl radical was generated from the titanium(III) ion–hydrogen peroxide couple in the presence of the oxiran, at both low and high pH (*ca.* 1 and 10); a flow system[6] was employed so that e.s.r. observations could be made shortly after mixing of the reagents. Some reactions were carried out in the presence of the nitromethane *aci*-anion, to take advantage of the propensity of this species to trap radicals and thereby give nitro radical-anions whose spectra can allow the addends to be identified.[7]

(a) *Reactions in the Absence of a Trap.—Propylene oxide.* Reaction with the hydroxyl radical at low pH (*ca.* 1) gave a complex spectrum (Figure) which was analysed as due to a mixture of the isomeric 1-hydroxyallyl radicals (3) and (4) (see Table 1), with g *ca.* 2.003 0. There was good agreement with the data previously obtained for these species,[8] and the spectrum was satisfactorily simulated (see Figure) by the sets of splitting constants in Table 1, a radical concentration ratio of 1 : 1, and a g-value difference[8] $[g(4) - g(3)]$ of 0.000 1; the assignment of a particular set of splittings to a particular isomer is tentative, and follows that for some substituted allyl radicals.[9]



(3)



(4)

Reaction at high pH gave a spectrum showing the presence of the anionic forms of the same two radicals.

---

[1] Part XLVIII, B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, preceding paper.

[2] T. J. Wallace and R. J. Gritter, *Tetrahedron*, 1963, **19**, 657.

[3] E. C. Sabatino and R. J. Gritter, *J. Org. Chem.*, 1963, **28**, 3437.

[4] G. Behrens and D. Schulte-Frohlinde, *Angew. Chem. Internat. Edn.*, 1973, **12**, 932.

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

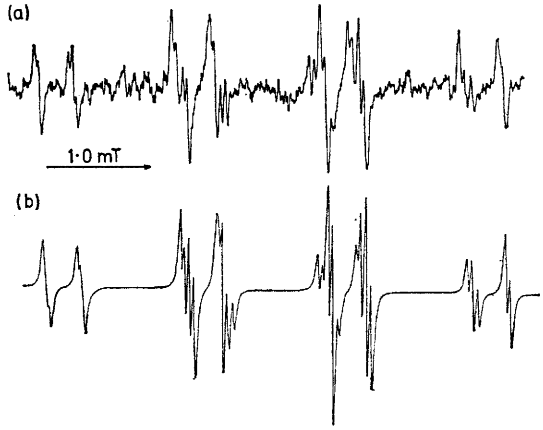
[6] R. O. C. Norman and B. C. Gilbert, *Adv. Phys. Org. Chem.*, 1967, **5**, 53.

[7] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

[8] R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245.

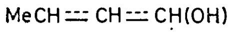
[9] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1968, **90**, 7157.

Both the splitting constants and relative concentrations ([*endo*-O$^-$] : [*exo*-O$^-$] *ca.* 1 : 1.5) are in close agreement with those previously reported by Simic *et al.*[10] who generated these species by reaction of O$^-$ (produced radiolytically) with allyl alcohol. At intermediate pH values (*ca.* 7, 8), the spectrum showed broad, unresolved lines, probably reflecting exchange between the neutral and ionised forms of the hydroxyallyl radicals. Under no conditions could spectra attributable to the radicals (1) or (2) be detected.

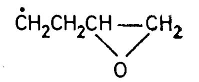


E.s.r. spectrum of a mixture of the radicals (3) and (4), (a) observed and (b) simulated with the parameters in the text and Table 1

But-1-*ene oxide.* The spectrum at low pH showed the presence of two radicals. One, with *g* 2.003 0, had splittings attributable to the 3-hydroxyl-1-methyallyl radical (5), but there was no basis for assigning the stereochemistry in this or subsequent examples of substituted allyl radicals. We attribute the second to the radical (6) on the basis of its alkyl-like *g*-factor (2.002 6), the magnitude of the triplet splitting for the protons at the tervalent carbon, and the inequivalence of the methylene protons adjacent to the ring which arises from the attachment of the methylene group to a chiral carbon atom (*cf.* ref. 7). Radical (6) is expected to be formed by hydrogen-atom abstraction and not to rearrange.


$\mathrm{MeCH \overset{\cdots}{-} CH \overset{\cdots}{-} \underset{\bullet}{C}H(OH)}$

(5)



(6)

3-*Isopropyloxypropylene oxide.* The spectrum at low pH showed the presence of a mixture of two substituted allyl radicals (*g ca.* 2.003 4) and the species formed by abstraction of hydrogen from the 2-position of the isopropyl group (*g* 2.003 3).

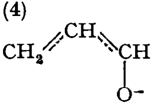
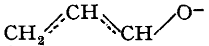
But-2-*ene oxide.* A mixture of the *cis*- and *trans*-isomers of this compound yielded a complex spectrum at low pH which is tentatively assigned to 1-hydroxy-1-methylallyl.

Epichlorohydrin. The spectrum at low pH showed the presence of two radicals which, on the basis of their proton splittings, are deduced to be of allylic type. One, which showed a chlorine splitting [$a(^{35}\mathrm{Cl})$ and $a(^{37}\mathrm{Cl})$ not resolved] as well as splitting from two protons of a magnitude characteristic of the terminal protons in an allylic system, is assigned the structure $\mathrm{CHCl \overset{\cdots}{-} CH \overset{\cdots}{-} CH(OH)}$. The other showed splittings from three such terminal protons, but no small splitting attributable to a C-2 substituent; we suggest it has the structure $\mathrm{CH_2 \overset{\cdots}{-} C(OH) \overset{\cdots}{-} CH(OH)}$ (its possible mode of formation is discussed later). The larger *g*-value for the former radical compared with the latter (Δg 0.001 2) is consistent with expectation [6] for a radical in which the unpaired electron is conjugated with the (α) chlorine substituent.

Butadiene monoxide. The spectrum at low pH showed the presence of two radicals. One was inferred to be the allylic species (7) by the splitting of 1.31 (2H) and 0.30 mT (1H) which are characteristic of the terminal and C-2 protons respectively of an allylic radical, the splitting of 0.95 (2H) and 0.05 mT (1H) being ascribed to the methylene and allylic hydroxyl-protons, respectively.

TABLE 1

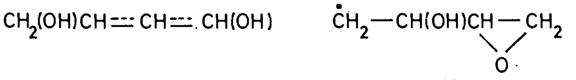
Radicals derived from oxirans and the hydroxyl radical

R,R′ in $\mathrm{R\overline{CH{-}CHR'\cdot O}}$		pH	Hyperfine splittings/mT	Radical
R	R′			
Me	H	1	1.39 (2 H), 1.33 (1 H), 0.32 (1 H), 0.05 (1 H) 1.42 (1 H), 1.33 (2 H), 0.37 (1 H), 0.04 (1 H)	(3) (4)
Me	H	10	1.28 (1 H), 1.24 (1 H), 1.19 (1 H), 0.19 (1 H)	
			1.33 (1 H), 1.28 (1 H), 1.12 (1 H), 0.26 (1 H)	
Et	H	1	1.58 (3 H), 1.34 (2 H), 0.39 (1 H) 2.18 (2 H), 2.80 (1 H), 2.65 (1 H)	(5) (6)
$\mathrm{Me_2CHOCH_2}$	H	1	1.34 (2 H), 0.35 (1 H) 1.35 (2 H), 0.34 (1 H) 2.01 (6 H), 0.13 (2 H)	$\mathrm{Pr^iOCH\ CH \overset{\cdots}{-} CH \overset{\cdots}{-} (OH)}$ $\mathrm{\cdot CMe_2OCH_2\overline{CH{-}CH_2\cdot O}}$
Me	Me	1	1.40 (4 H), 1.33 (1 H), 0.30 (1 H)	$\mathrm{CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CMe(OH)}$
$\mathrm{CH_2Cl}$	H	1	1.47 (1 H), 1.33 (1 H), 1.29 (1 H) 1.47 (1 H), 1.335 (1 H), 0.355 (1 H), 0.065 (1 Cl)	$\mathrm{CH_2 \overset{\cdots}{-} C(OH) \overset{\cdots}{-} CH(OH)}$ $\mathrm{CHCl \overset{\cdots}{-} CH \overset{\cdots}{-} CH(OH)}$
$\mathrm{CH_2{:}CH}$	H	1	1.31 (2 H), 0.95 (2 H), 0.30 (1 H), 0.05 (1 H) 2.40 (1 H), 2.20 (2 H)	(7) (8)

---

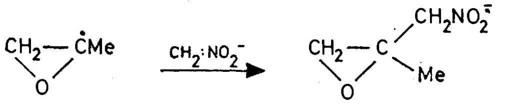
[10] M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 1973, **77**, 2662.

The other is evidently the adduct (8), having an α-proton splitting typical of alkyl-type radicals, a lower *g*-value than that for (7) (Δ*g* 0.000 4), and the expected single β-proton splitting.



(7) (8)

Reactions in the Presence of a Trap.—When propylene oxide was oxidised by the Ti^{III}–H_2O_2 system in the presence of nitromethane at *ca.* pH 9, two radicals in addition to $HO\cdot CH_2NO_2^{-\cdot}$ [11] and $CH_3NO_2^{-\cdot}$ [12] were detected. One had *a*(N) characteristic of aliphatic nitro radical-anions and inequivalent *a*(β-H), implying the proximity of a chiral carbon atom; [7] we suggest that it is the species (10), formed by addition of the radical (9) to the *aci*-anion. The other species had *a*(N) in the region for nitro radical-anions with a β-oxygen substituent,[1,7] equivalent *a*(β-H), and no further splitting (the line-width was 0.04 mT; a splitting greater than this would have been detected); we believe it to be $CH_2{:}CH\cdot CH_2\cdot OCH_2NO_2^{-\cdot}$, and describe further examples of this type of radical later.[13]



(iv)

(9) (10)

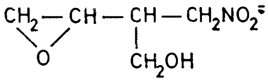
The only radical detected from epichlorohydrin had inequivalent β-proton splittings, signifying the presence of an adjacent chiral carbon, and no further proton splitting; the ascription in Table 2 follows. Likewise, butadiene monoxide gave a radical with inequivalent β-proton-splittings, but in this case there was a triplet splitting (0.055 mT) from two further protons; since these cannot both be γ-protons (for the β-protons would then almost certainly be equivalent), we suggest that they are single γ- and δ-protons, fortuitously equivalent. The most probable species with these characteristics is (11); the single (oxiranyl) δ-proton could well have the observed splitting [*cf. e.g.* $\cdot CH(OH)CH_2CH_2CHO$ [14] and $^{-\cdot}O_2NCH_2CH_2CHO$ [7]], whereas the splitting for the δ-protons in the CH_2OH group could well be much smaller.[7]

TABLE 2

Radicals detected in the presence of the nitromethane *aci*-anion [a]

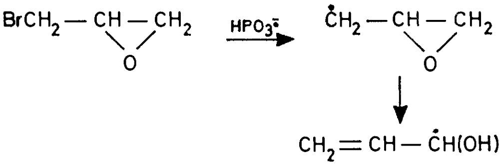
Reactant	Hyperfine splittings /mT	Radical
$MeCH{-}CH_2\cdot O$	2.42 (1 N), 0.94 (2 H)	$CH_2{:}CH\cdot CH_2OCH_2NO_2^{-\cdot}$
	2.54 (1 N), 1.15 (1 H), 0.86 (1 H)	(10)
$ClCH_2\cdot CH{-}CH_2\cdot O$	2.50 (1 N), 1.20 (1 H), 0.90 (1 H)	$O\cdot CH_2{-}C(CH_2Cl){-}CH_2NO_2^{-\cdot}$
$CH_2{:}CH\cdot CH{-}CH_2\cdot O$	2.56 (1 N), 1.17 (1 H), 0.86 (1 H), 0.055 (2 H)	$O\cdot CH_2{-}CH{-}CH(CH_2OH){-}CH_2NO_2^{-\cdot}$

[a] The radicals $CH_2(OH)NO_2^{-\cdot}$ and $^{-\cdot}MeNO_2$ were detected in each case.



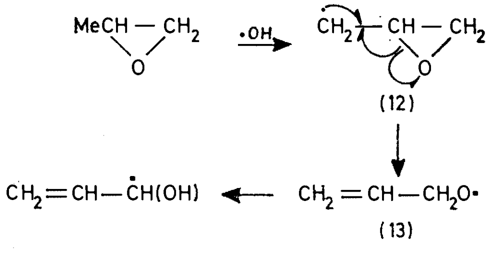
(11)

Reaction Mechanisms.—The isomeric forms of the 1-hydroxyallyl radical which are detected during the oxidation of propylene oxide cannot be formed *via* allyl alcohol, since this predominantly undergoes addition of the hydroxyl radical, rather than abstraction of a hydrogen atom, under our conditions.[15] Nor can they be formed by way of propane-1,2-diol (were hydrolysis of the epoxide to be rapid enough), since this behaves differently towards ·OH.[16] Further, when epibromohydrin was treated with the Ti^{III}–H_2O_2 couple in the presence of phosphorus acid, the spectra of the isomeric forms of the hydroxyallyl radical were again observed; under these conditions the radical-anion $HPO_3^{-\cdot}$, which is an efficient bromine-atom abstractor, is formed,[17] so that we can infer the occurrence of reaction (v). Thus, the hydroxyl radical is not itself material to the formation of the hydroxyallyl radical.



(v)

We suggest that the 1-hydroxyallyl radical is formed from propylene oxide by way of the radicals (12) and (13) as in reaction (vi); analogous paths would apply to the substituted hydroxyallyl radicals in Table 1. This is compatible with the evidence that the allyloxyl radical is



(vi)

---

[11] D. J. Edge and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 182.

[12] M. McMillan and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 590.

[13] B. C. Gilbert, R. G. G. Holmes, H. A. H. Laue, and R. O. C. Norman, following paper.

[14] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 794.

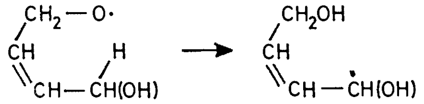
[15] P. Smith and P. B. Wood, *Canad. J. Chem.*, 1967, **45**, 649.

[16] A. L. Buley, R. O. C. Norman, and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1966, 849.

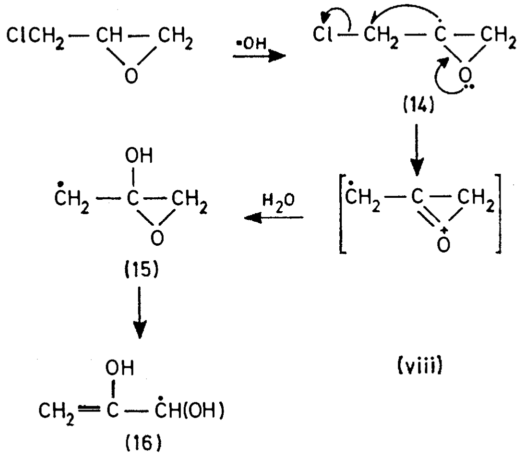
[17] A. L. J. Beckwith, *Austral. J. Chem.*, 1972, **25**, 1887.

trapped by the nitromethane *aci*-anion, and with our evidence[1,13] that alkoxyl radicals rearrange in aqueous solution to hydroxyalkyl radicals. It is interesting to note that hydroxyl radicals react preferentially at the acyclic alkyl group to give (12) and related species, in contrast to t-butoxyl which preferentially abstracts an alicyclic C–H hydrogen atom.[4]

It is notable that, whereas the allyloxyl radical is trapped when propylene oxide is oxidised in the presence of $CH_2{:}NO_2^-$, neither substituted allyloxyl radicals nor their precursors are trapped during oxidation of the other two epoxides in Table 2, although their mediation is inferred from the formation of substituted hydroxyallyl radicals in the absence of the trap. In the case of butadiene monoxide, this may be because there is an especially rapid intramolecular pathway available for rearrangement of the allyloxyl to the hydroxyallyl radical, as shown in reaction (vii). In neither case would we necessarily expect to trap the hydroxyallyl radicals, assuming they are formed, since both should have low ionisation potentials and may preferentially react by transferring an electron to nitromethane,[12] to yield $MeNO_2^{-\cdot}$.


(vii)

There remains as so far unaccountable the formation from epichlorohydrin of the species believed to be (16). A possible mechanism is shown in reaction (viii). Radical (14) is of a type which readily undergoes heterolysis, aided by the $+M$ effect of oxygen, providing a path for formation of radical (15); an analogy is the reaction of chlorohydrin with ·OH, where there is evidence that the radical $\cdot CH(OH)\cdot CH_2Cl$ yields $\cdot CH_2CH(OH)_2$.[14] Reaction of (15) as for the other oxiranylmethyl radicals we have discussed would then give radical (16).


(viii)

EXPERIMENTAL

All materials were available commercially and were used without further purification. The spectrometer, flow system, calibration methods, and oxidation procedure were as described in the previous paper,[1] with the following exceptions. (i) To minimise the possibility of hydrolysis, oxirans were dissolved in cold water shortly before flowing and only the Ti^{III} and H_2O_2 solutions were acidified or basified. (ii) Propylene oxide was sufficiently water-soluble for concentrations up to *ca.* 4M to be used; this upper limit was found necessary for obtaining spectra at high pH. The other oxirans were used in concentrations between 0.02 and 0.06M; this was insufficient for reactions at high pH, where the spectra from oxirans were obscured by that from EDTA. (iii) For the reaction with epibromohydrin, the hydrogen peroxide stream contained $0.12M-H_3PO_3$.

We thank the S.R.C. for their support.

[5/1802 *Received*, 18*th September*, 1975]