# Homolytic Abstraction of Enolic Hydrogen

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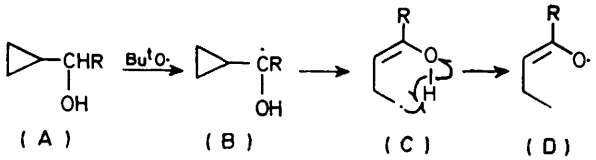
The e.s.r. spectrum of the homoallylic radical (C) is observed when a mixture of di-t-butyl peroxide and a cyclopropylcarbinol (A; R = H or alkyl) is photolysed at low temperature, but near room temperature the spectrum shows that the enolic hydrogen has been transferred to the alkyl radical to give the enoxyl radical (D). Studies of the thermolysis of di-t-butyl peroxide or of di-t-butyl hyponitrite in the presence of 1-cyclopropylethan[$^2$H]ol confirmed that deuterium was located in the 5-position of the pentan-2-one which was formed. The same sequence

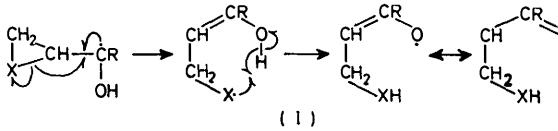



( A ) ( B ) ( C ) ( D )

of radicals (B) ⟶ (C) ⟶ (D) (R = Me) occurs when cyclopropyl methyl ketone is photolysed in the presence of 1-cyclopropylethanol. Aryl(cyclopropyl)methanols (A; R = Ar) yield only the radical (B), and no ring opening could be detected. 2-(Hydroxymethyl)oxiran shows the formation of the 3-hydroxyprop-2-enoxyl radical, consistent with the occurrence of ring opening and hydrogen transfer from enolic oxygen to oxygen, but no evidence could be found for transfer of hydrogen from lactim oxygen to carbon, or from enolic oxygen to nitrogen, in the reactions of 1- or 2-hydroxyalkylaziridines.

THE ability of phenols to donate their hydroxylic hydrogen to a variety of radicals is well known, and is exploited in, for example, the stabilisation of alkenes against polymerisation, or of hydrocarbons against autoxidation.[1] Alcohols, on the other hand, do not usually transfer hydroxylic hydrogen homolytically, although it has recently been shown[2,3] that such hydrogen transfer can occur from alcohols to alkoxyl radicals when the alcohols are not hydrogen bonded.† This difference in behaviour between phenols and alcohols is attributed to the thermodynamic and kinetic stabilisation of the phenoxyl radical which occurs when the unpaired electron is delocalised over the aromatic ring.

No comparable work appears to have been reported on the ability of simple enols to donate hydroxylic hydrogen, doubtless because the enols could not be prepared and handled uncontaminated by the corresponding keto-compounds. We have now made use of the ring-opening reactions of cyclopropylhydroxymethyl, (hydroxy)oxiranylmethyl, and aziridinylhydroxymethyl radicals (I; X = $CH_2$, O, or NR') to form the pure enols *in situ*, and have established by e.s.r. spectroscopy that, for the first two classes of compound, transfer of the hydroxylic hydrogen to the radical centre X· (X· = $CH_2$· or O·) does occur, in all probability by a 1,5-shift [equation (1)].[5]




( 1 ) (1)

Similar work on the cyclopropylhydroxylmethyl radicals (I; X· = $CH_2$·) has recently been carried out independently by Itzel and Fischer,[6] with very similar results and conclusions.

† The assumption that hydrogen bonding always reduces the hydrogen-donating ability of a hydroxy-group has recently been discounted.[4]

[1] K. U. Ingold, Chem. Soc. Special Publ., No. 24, 1970.
[2] D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 630.
[3] I. H. Elson and J. K. Kochi, *J. Org. Chem.*, 1974, **39**, 2091.
[4] M. Simonyi, J. Kerdos, I. Fitos, I. Kovács, and J. Pospišil, *J.C.S. Chem. Comm.*, 1975, 15.
[5] The ring opening of cycloalkylmethyl radicals, and the 1-5-hydrogen transfer of hydrogen atoms, are reviewed by J. W. Wilt in ' Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, 1973, ch. 8, vol. I.
[6] H. Itzel and H. Fischer, *Tetrahedron Letters*, 1975, 563.

EXPERIMENTAL

*Starting Materials.*—Cyclopropylmethanol, 1-cyclopropylethanol, cyclopropyl methyl ketone, the aryl(cyclopropyl)methanols, and 2-hydroxymethyloxiran were commercial materials. *trans*-1-(2-Methylcyclopropyl)ethanol was a gift from Drs. M. Pereyre and J.-C. Pommier, Bordeaux.

*N*-1-Hydroxybutylaziridine, b.p. 32° at 18 mmHg, was prepared from aziridine and butanal,[7] and 2-bromobutanal was made by the reaction of butanal with bromine in dichloromethane.[8] Dehydrodimerisation of pentan-2-one with lead dioxide [9] gave a mixture of *meso*- and ±-3,4-diethylhexane-2,5-dione, b.p. 85° at 0.1 mmHg.

3-Hydroxycyclohexene oxide [10] was prepared by oxidising cyclohex-2-enol in chloroform with *m*-chloroperbenzoic acid. The initial product, b.p. 106—108° at 14 mmHg, contained a trace of *m*-chlorobenzoic acid (i.r. and n.m.r.) which was removed by redistilling the oxiran from a trace of solid potassium hydroxide.

*Allyloxytributyltin.*—A mixture of bis(tributyltin) oxide (6.0 g) and allyl alcohol (1.17 g) in benzene was heated under reflux under a Dean and Stark water separator for 40 min. Distillation gave *allyloxytributyltin*, b.p. 108° at 0.01 mmHg (Found: C, 51.8; H, 9.4. $C_{15}H_{32}OSn$ requires C, 51.9; H, 9.3%).

*Tributyl*-[trans-1-(2-*methylcyclopropyl*)*ethoxy*]*tin.*—By a similar method, azeotropic dehydration of a mixture of the alcohol and bis(tributyltin) oxide gave the *alkoxytin compound*, b.p. 116° at 0.1 mmHg (Found: C, 55.0; H, 10.1. $C_{18}H_{38}OSn$ requires C, 55.5; H, 9.8%).

N-*Butyl*-2-*hydroxymethylaziridine.*—Butylamine (5.62 g) and triethylamine (15.5 g) in benzene (150 cm³) were added to a stirred solution of ethyl 2,3-dibromopropionate (20.0 g) in benzene (50 cm³) below 15°. The mixture was then heated under reflux for 3 h, cooled, filtered from the precipitated triethylammonium bromide, and passed down an alumina column (4 × 6 cm) to remove any residual salt, water, and acid. Distillation gave N-*butyl*-2-*ethoxycarbonylaziridine* (10.8 g, 82%), b.p. 66° at 0.1 mmHg, as an oil which developed a yellow colour after a few days (Found: C, 62.8; H, 9.9; N, 8.1. $C_9H_{17}NO_2$ requires C, 63.1; H, 10.0; N, 8.2%). If the treatment with alumina was omitted, only a high boiling polymer was obtained.

This ethoxycarbonylaziridine (5.0 g) in ether (27 cm³) was added to a stirred suspension of lithium aluminium hydride (1.33 g) in ether (40 cm³) at 0°. The mixture was heated under reflux for 4.5 h, then hydrolysed with water (1.3 cm³), 15% NaOH solution (1.3 cm³), and water (5.3 cm³). The aluminium hydroxide was filtered off, and the ethereal solution distilled to give N-*butyl*-2-(*hydroxymethyl*)*aziridine*, b.p. 46° at 0.02 mmHg (Found: C, 65.2; H, 11.4; N, 10.9. $C_7H_{15}NO$ requires C, 65.1; H, 11.7; N, 10.8%) {$CH^cCH^bH^aOH$: τ ($CCl_4$) 6.40 ($H^a$) and 6.82 ($H^b$) [*J* ($H^aH^b$) 12, *J* ($H^aH^c$) 6, and *J* ($H^bH^c$) 3.25 Hz]}.

N-*t-Butyl*-2-*hydroxymethylaziridine.*— *N*-t-Butyl-2-ethoxycarbonylaziridine, b.p. 44° at 0.06 mmHg, was prepared by a similar method in 57% yield, but contained a small amount of ethyl acrylate (n.m.r.); this might have been avoided if the reagents had been mixed at a lower temperature. Reduction with lithium aluminium hydride gave N-*t-butyl*-2-*hydroxymethylaziridine* in 88% yield, b.p. 50° at 1 mmHg, m.p. 38—40° (Found: C, 64.9; H, 12.0; N, 10.7. $C_7H_{15}NO$ requires C, 65.1; H, 11.7; N, 10.8%), τ ($CCl_4$) 6.72 ($CHCH_2OH$) and 8.25 ($CHCH_2OH$).

*E.s.r. Spectroscopy.*—E.s.r. experiments were carried out by photolysis in the cavity of a Varian E4 spectrometer of a degassed mixture of di-t-butyl peroxide and the appropriate substrate in cyclopropane or t-butyl alcohol, depending on the solubility. Photolysis was carried out with a Mazda 1000 W direct current ME/D or a Phillips 500 W alternating current SP 500 high pressure mercury arc.

$^{13}C$ *N.m.r. Spectroscopy.*—Spectra were recorded on a Varian CFT 20 instrument with benzene (δ 128.7 p.p.m.) as the solvent and internal standard. Relevant chemical shifts are given in Table 1.

TABLE 1

$^{13}C$ Chemical shifts (p.p.m. downfield from tetramethylsilane)

| | C-1 | C-2 | C-3 | C-4 | C-5 |
|---|---|---|---|---|---|
| $^{1}CH_3{}^{2}COCH_3$ | 30.5 | 208.0 | | | |
| $(^{1}CH_3)_3{}^{2}COH$ | 31.4 | 68.2 | | | |
| $(^{1}CH_3)_3{}^{2}CO_2C(CH_3)_3$ | 26.8 | 78.1 | | | |
| $^{1}CH_3{}^{2}CO{}^{3}CH_2{}^{4}CH_2{}^{5}CH_3$ | 29.2 | 206.4 | 45.2 | 17.3 | 13.6 |
| $^{1}CH_3{}^{2}COCH_2{}^{3}CH_2{}^{4}CH_2{}^{5}$ | 29.8 | 206.3 | 20.9 | 10.2 | 10.2 |
| $^{1}CH_3{}^{2}CH(OH){}^{3}CHCH_2{}^{4}CH_2{}^{5}$ | 30.2 | 7.18 | 19.6 | 2.4 | 3.2 |
| $^{1}CH_3{}^{2}CO{}^{3}CHCH_2{}^{4}CH_2{}^{5}CH_3$ | 30.7 | 193.5 | 55.5 | 23.9 | 11.5 |
| | 30.2 | | | | |
| *meso* and ± | 25.1 | 192.5 | 52.1 | 21.1 | 10.2 |
| $CH_3COCHCH_2CH_3$ | 24.5 | | | | |

*Mass Spectroscopy.*—Mass spectra were recorded at 70 eV on an AEI MS9 spectrometer, using a cold inlet system.

*Ring Opening of* 1-*Cyclopropylethan*[$^2$H]*ol.*—(i) *By di-t-butyl peroxide.* Cyclopropylethan[$^2$H]ol (0.855 g) and di-t-butyl peroxide (0.4608 g) were sealed in a glass tube and heated at 130 ± 5° for 6.5 h. The proton-decoupled $^{13}C$ n.m.r. spectrum of the product showed that all the peroxide had decomposed to give mainly t-butyl alcohol together with some acetone. Some of the initial alcohol remained and the rest had been converted into pentan-2-one, together with a trace of the *meso*- and ±-dehydrodimer (3,4-diethylhexane-2,5-dione). The three signals due to deuterium coupling were prominent about the signal due to the 3-$CH_2$ group of pentan-2-one, with a total intensity of *ca.* 60% of that of the main peak, and apparent, though less well defined, on the 5-$CH_3$ group. Pentan-2-one was separated by preparative g.l.c. on a Carbowax column; the $^{13}C$ n.m.r. spectrum then showed δ 45.4 (3-$CH_2$), 46.0, 45.0, and 44.1 (3-$CH_2D$), 13.9 (5-$CH_3$), and 14.5, 13.6, and 12.6 (5-$CH_2D$).

The intensities of the various peaks in the mass spectrum, corrected for $^{13}C$ and for the contribution of unlabelled ketone, are given in Table 2.

The fragment of *m/e* 58 arises from the McLafferty rearrangement of the 5-$CH_2D$ ketone, *m/e* 87: $CH_3COCH_2CH_2CH_2D \longrightarrow CH_3C(OH)=CH_2 + CH_2=CHD$. The percentage of 5-$CH_2D$ ketone is therefore given by 3/2 × 295/9 540 × 10 000/4 650 × 100 = 10%.

The fragment of *m/e* 73 arises from the loss of $CH_3$ from

[7] W. J. Raborn and W. L. Howard, *J. Org. Chem.*, 1962, **27**, 1039.

[8] J. J. Riehl, *Compt. rend.*, 1957, **245**, 1321.

[9] E. Wolthuis, B. Bossenbrock, G. DeWall, E. Greels, and A. Leegwater, *J. Org. Chem.*, 1963, **28**, 148.

[10] H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 1957, 4608.

the [$^2H_2$]ketone, *m/e* 88. The percentage of [$^2H_2$]ketone that loses $CH_3$ is therefore 457/1 155 × 10 000/5 650 × 100 = 70%, and the remaining 30% must lose $CH_2D$ (or $CHD_2$). Godet [11] has shown that the ketone (5-$CH_2D$) loses methyl from the C-1 and C-5 in the ratio of 3 : 2

TABLE 2

Peak intensities in mass spectra of labelled and unlabelled pentan-2-one formed by ring opening of 1-cyclopropylethan[$^2$H]ol with di-t-butyl peroxide

| | | Intensity [a] | |
|---|---|---|---|
| *m/e* | Fragment | Unlabelled MeCOPr | Deuteriated MeCOPr [b] |
| 88 | [$^2H_2$]-[*M*]$^{+\cdot}$ | | 1 155 |
| 87 | [$^2H_1$]-[*M*]$^{+\cdot}$ | | 9 540 |
| 86 | [*M*]$^{+\cdot}$ | 10 000 | |
| 73 | [$^2H_2$]-]*M*(−Me)]$^+$ | | 457 |
| 72 | [$^2H_1$]-[*M*(−Me)]$^+$ | | 4 930 |
| 71 | [*M*(−Me)]$^+$ | 5 650 | 500 |
| 60 | [$^2H_2$]-[$CH_2$=CMeOH]$^{+\cdot}$ | | 505 |
| 59 | [$^2H_1$]-[$CH_2$=CMeOH]$^{+\cdot}$ | | 3 875 |
| 58 | [$CH_2$=CMeOH]$^{+\cdot}$ | 4 650 | 295 |

[a] Corrected for contribution by $^{13}C$ molecules. [b] Corrected for contribution by undeuteriated material.

TABLE 3

Peak intensities in mass spectra of labelled and unlabelled pentan-2-one formed by ring opening of 1-cyclopentylethan[$^2$H]ol with di-t-butyl hyponitrite

| | | Intensity | |
|---|---|---|---|
| *m/e* | Fragment | Unlabelled MeCOPr | Deuteriated MeCOPr |
| 88 | [$^2H_2$]-[*M*]$^{+\cdot}$ | | 120 |
| 87 | [$^2H_1$]-[*M*]$^{+\cdot}$ | | 350 |
| 86 | [*M*]$^{+\cdot}$ | 865 | |
| 73 | [$^2H_2$]-[*M*(−Me)]$^+$ | | 80 |
| 72 | [$^2H_1$]-[*M*(−Me)]$^+$ | | 355 |
| 71 | [*M*(−Me)]$^+$ | 855 | 125 |

although this may vary from instrument to instrument. Our results would therefore be compatible with essentially all the dilabelled ketone, constituting 12% of labelled material, being $CH_3COCHDCH_2CH_2D$.

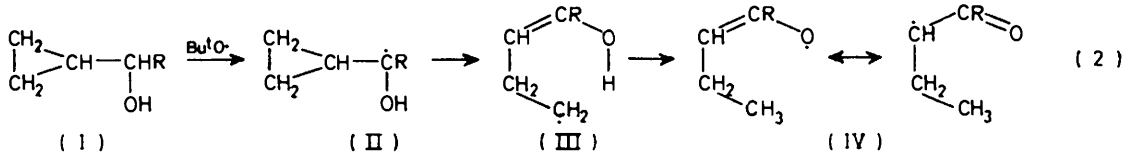
(ii) *By di-t-butyl hyponitrite.* 1-Cyclopropylethan[$^2$H]ol (0.10 cm$^3$) and di-t-butyl hyponitrite (0.032 g) were sealed under vacuum and heated at 70—73° for 3 h. The pentan-2-one which was formed was purified by g.l.c. (*ca.* 10 mg) but, because of the small scale of the reaction, it could not be separated from an impurity. The mass spectrum, however, showed again that, from the fragment in [$^2H_2$]-[*M*]$^{+\cdot}$ ⟶ [$^2H_2$]-[*M*(−Me)]$^+$, the [$^2H_2$]ketone had one label in the 5-position.

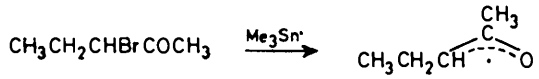
The percentage of [$^2H_1$]ketone that loses $CH_3$ is 80/120 × 865/855 × 100 = 67%, and the remaining 33% must lose $CH_2D$ (or $CHD_2$). If methyl is lost from C-1 and C-5 in the ratio 3 : 2 the bulk of the second label must again be in the 5-position. The presence of the impurity rendered impossible any calculations based on the cluster *m/e* 58—60.

RESULTS

*Cyclopropylcarbinols.*—Photolysis of di-t-butyl peroxide with cyclopropylmethanol (I; R = H) in cyclopropane solvent at −80° gives the e.s.r. spectrum of the 4-hydroxybut-3-enyl radical (III; R = H) resulting from the ring opening (β-scission) of the cyclopropylhydroxymethyl radical (II; R = H).[12,*] At higher temperatures, the spectrum of a second radical with a higher *g* value (Δ*g* *ca.* 0.0025) becomes apparent at the expense of the first. We assign this spectrum to the *cis*-form of the but-1-enoxyl radical $CH_3CH_2CH$=C(H)O· (IV; R = H), because the same spectrum [together with a second, similar spectrum, which is assigned to the *trans*-form of (IV)], can be obtained by photolysing a mixture of di-t-butyl peroxide and hexamethylditin in the presence of 3-bromopentanal [equation (3)]. Details of the spectra of these and other radicals are given in Table 4.

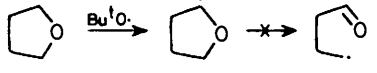
When the cyclopropylmethanol system is photolysed above −30°, the spectrum of the radical (IV) is apparent immediately, and at each temperature the relative intensities of the spectra of (III) and (IV) remain approximately constant throughout the period of the photolysis. The enoxyl radical (IV) is therefore not a secondary product of the reaction, but is derived directly from the radical (III), in all probability by a 1,5-intramolecular transfer of hydrogen from oxygen to carbon.




1-Cyclopropylethanol (I; R = Me) behaves similarly. At low temperatures the spectrum of the 4-hydroxypent-3-enyl radical † (III; R = Me) is observed, which gives way to the spectrum of the 1-methylbut-1-enoxyl radical (IV; R = Me) at higher temperature; this radical was also prepared independently by abstraction of hydrogen by the t-butoxyl radical from pentan-2-one [equation (4)].

* For the purposes of comparison we attempted to obtain the isomeric keto form of the radical (III; R = H) by ring opening of the radical derived from tetrahydrofuran. Although there is




chemical evidence [13] that this ring opening does occur at higher temperatures, we could observe by e.s.r. only the cyclic radical up to 100°.

† The isomeric keto-form of the radical has been generated by photolysis of the peroxide ($MeCO[CH_2]_3CO_2)_2$: *a* ($H_\alpha$) 22.18; *a* ($H_\beta$) 29.69; *a* ($H_\gamma$) 0.32 G at −106°.[14]

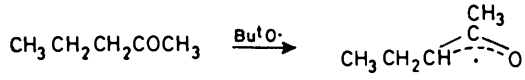
[11] J.-Y. Godet, Thesis, Bordeaux, 1974.

[12] J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, 1969, **91**, 1877, 1879.

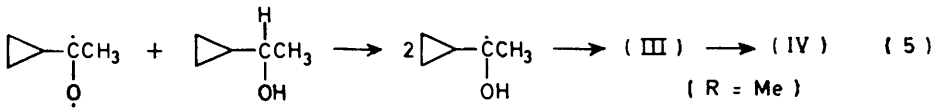
[13] T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, 1961, **26**, 5256.

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

The same temperature-dependent effects are observed when the radicals (III) and (IV; R = Me) are generated instead by photolysing cyclopropyl methyl ketone in the presence of 1-cyclopropylethanol. In this reaction, the ketone in its triplet state abstracts hydrogen from the α-carbon of the alcohol [equation (5)].



(4)



(5)

TABLE 4

E.s.r. parameters of homoallyl, enoxyl, allyl, and related radicals

| | Radical | Source | $T$/°C | $a(H_\alpha)$ | $a(H_\beta)$ | $a(H_\gamma)$ | $a$(H) | Notes[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | $\dot{C}H_2CH_2CH{=}CHOH$ (III; R = H) | $CH_2CH_2CHCH_2OH$ + $Bu^tOOBu^t$ | −45 | 22.2(2) | 30.0(2) | 0.8(1) | 0.8(1) | *b* |
| 2 | *cis*-$CH_3CH_2\dot{C}H{=}O$ (IV; R = H) | $CH_2CH_2CHCH_2OH$ + $Bu^tOOBu^t$ | +16 | 18.4(1) | 19.8(2) | | 1.3(1) | |
| 3 | *cis*- and | $CH_3CH_2CHBrCH{=}O$ + $Bu^tOOBu^t$ + | −98 | 17.8(1) | 20.5(2) | | 1.8(1) | *c* |
| 4 | *trans*-$CH_3CH_2\dot{C}H{=}O$ (IV; R = H) | $Me_6Sn_2$ | | 17.0(1) | 21.3(2) | | 1.8(1) | *c* |
| 5 | $\dot{C}H_2CH_2CH{=}CMeOH$ (III; R = Me) | $CH_2CH_2CHCMeOH$ + $Bu^tOOBu^t$ | −111 | 22.0(2) | 31.25(2) | | | *d* |
| 6 | $\dot{C}H_2CH_2CH{=}CMeOH$ (III; R = Me) | $CH_2CH_2CHCHMeOH$ + $CH_2CH_2CHCMe{=}O$ | | 22.0(2) | 31.25(2) | | | |
| 7 | $CH_3CH_2\dot{C}HCMe{=}O$ (IV; R = Me) | $CH_2CH_2CHCHMeOH$ + $Bu^tOOBu^t$ | −34 | 18.9(1) | 20.8(2) | | 1.0 (3; $COCH_3$) | *e* |
| 8 | $CH_3CH_2\dot{C}HCMe{=}O$ (IV; R = Me) | $CH_2CH_2CHCHMeOH$ + $CH_2CH_2CHCMe{=}O$ | | 18.9(1) | 20.8(2) | | 1.0 (3; $COCH_3$) | |
| 9 | $CH_3CH_2\dot{C}HCMe{=}O$ (IV; R = Me) | $CH_3CH_2CH_2CMe{=}O$ + $Bu^tOOBu^t$ | −35 | 18.9(1) | 20.5(2) | | 0.9 (3; $COCH_3$) | *f* |
| 10 | $\dot{C}H_2CHMeCH{=}CMeOH$ (VII) | *trans*-$MeCHCH_2CHCHMeOH$ + $Bu^tOOBu^t$ | −86 | 21.9(2) | 27.8(1) | | | |
| 11 | $Me_2CH\dot{C}HCMe{=}O$ (VIII) | *trans*-$MeCHCH_2CHCHMeOH$ + $Bu^tOOBu^t$ | −9 | 9.6(1) | 18.8(1) | 0.8(6) | | |
| 12 | $Me_2CH\dot{C}HCMe{=}O$ (VIII) | $Me_2CHCH_2CMe{=}O$ + $Bu^tOOBu^t$ | −16 | 9.5(1) | 18.7(1) | 0.8(6) | | |
| 13 | $CH_2{=}CH\dot{C}HOH$ (XII) | $OCH_2CHCH_2Br$ + $Bu^tOOBu^t$ + $Et_3SiH$ | −110 | 13.5(1) | 3.0(1) | 13.5(1) and 12.6(1) | 1.2 (1; OH) | *g* |
| 14 | $CH_2{=}CH\dot{C}HOSnMe_3$ | $OCH_2CHCH_2Br$ + $Bu^tOOBu^t$ + $Me_6Sn_2$ | −51 | 13.1(1) | 3.0(1) | 13.1(1) and 12.0(1) | | |
| 15 | $CH_2{=}CH\dot{C}HOSnBu_3$ (*cis* and *trans*) | $CH_2{=}CHCH_2OSnBu_3$ + $Bu^tOOBu^t$ | −77 | 13.2(1) | 2.6(1) | 13.2(1) and 12.7(1) | | |
| 16 | | | | 13.7(1) | 3.0(1) | 13.7(1) and 12.2(1) | | |
| 17 | $HOCH_2\dot{C}HCH{=}O$ (XIV) | $OCH_2CHCH_2OH$ + $Bu^tOOBu^t$ | −30 | 18.3(1) | 26.9(2) | | 1.25(1) | *h*, *i* |
| 18 | $HOCH_2\dot{C}HCH{=}O$ (XIV) | $HOCH_2CH(OH)CH_2OH$ + $Bu^tOOBu^t$ + $CF_3CO_2H$ | −12 | 18.4(1) | 26.4(2) | | 1.25(1) | *i* |
| 19 | $HO\dot{C}HCH(OH)CH_2OH$ | $HOCH_2CH(OH)CH_2OH$ + $Bu^tOOBu^t$ | −6 | 16.5(1) | 11.8(1) | | | *i* |
| 20 | $HO\dot{C}HCHCOCH_2CH_2CH_2$ (XVI) | $HOCHCHOCHCH_2CH_2CH_2$ | −53 | 17.5(1) | 32.5(1) | | | |
| 21 | $\dot{C}H_2CH_2N{=}CPrOH$ (XIX) | $CH_2CH_2NCHPrOH$ | −82 | 22.0(2) | 31.4(2) | | *a*(N) 2.75 | |

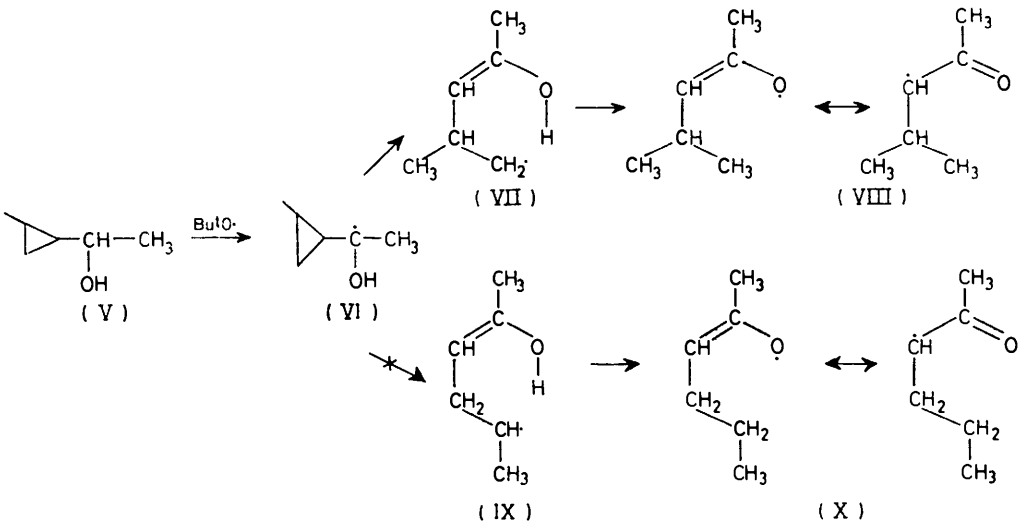
[a] In cyclopropane solvent unless otherwise stated. Number of protons coupling are indicated in parentheses after the coupling constants. [b] Kochi *et al.*[12] report that at −48°, for the *trans*-radical (the principal species) $a(H_\alpha)$ 21.96; $a(H_\beta)$ 28.26; $a(H_\gamma)$ 0.69, and, for the *cis*-radical $a(H_\alpha)$ 21.9; $a(H_\beta)$ 29.6; $a(H_\gamma)$ 0.6 G. In our spectrum, the presence of two radical species was apparent, but the resolution was not sufficient for accurate hyperfine splittings to be assigned to the weaker isomer. [c] Relative concentration *ca.* 1 : 3. [d] Itzel and Fischer [6] report $a(H_\alpha)$ 22.14; $a(H_\beta)$ 30.76; $a(H_\gamma)$ 0.64 G at −60° in hexane or $C_2Cl_3F_3$, $g$ 2.002 69. [e] Itzel and Fischer [6] report $a(H_\alpha)$ 18.84; $a(H_\beta)$ 20.55; $a(H_\gamma)$ 0.12; $a$ 0.12 ($COCH_3$) G at −33°, $g$ = 2.0042. [f] H. Paul and H. Fischer (*Chem. Comm.*, 1971, 1038) report $a(H_\alpha)$ 18.8; $a(H_\beta)$ 19.2; $a(H_\gamma)$ 0.9 G (in $CCl_3F$ at −4°); See also D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1973, **95**, 7978. [g] R. Livingstone and H. Zeldes (*J. Chem. Phys.*, 1966, **44**, 1245) report $a$(H) 13.86, 13.86, and 13.33(1); $a(H_\beta)$ 3.16; $a$(OH) 0.46 for the isomer giving the stronger spectrum from the photolysis of $H_2O_2$ in allyl alcohol at 29°. The presence of an isomeric radical in lower concentration was also apparent in our spectrum. [h] Norman [27] reports $a(H_\alpha)$ 18.1; $a(H_\gamma)$ 25.6; $a$(CHO) 1.4; $g$ 2.0043 in water at room temperature. [i] In $Bu^tOH$–$Bu^t_2O_2$ as solvent.

Neckers *et al.*[15] reported that when a mixture of 1-cyclopropylethan[$^2$H]ol and di-t-butyl peroxide (*ca.* 10%) was kept at 130° for 12 h, analysis by mass spectrometry of the pentan-2-one which was formed showed that it contained deuterium only at the 3- and not at the 5-position. This result would not permit the hydrogen transfer (III) ⟶ (IV; R = Me), which we propose, and implies that the radical (III; R = Me) abstracts hydrogen from some other donor site, presumably the α-CH group of a second molecule of the alcohol.

We therefore carried out the ring opening reaction of 1-cyclopropylethan[$^2$H]ol with t-butoxyl radicals generated from di-t-butyl peroxide at 130°, and from di-t-butyl hyponitrite at 70°. Both reactions gave pentan-2-one in good yield, and the location of deuterium in the molecule was determined by mass spectrometry, and, for the former reaction, also by $^{13}$C n.m.r. spectroscopy. Both products were labelled to the extent of *ca.* 60% in the 3-position, and *ca.* 10% in the 5-position, which is consistent with the occurrence of the transfer of hydrogen from the enolic hydroxy-group to the C-5 radical, which we propose.

The behaviour of the aryl(cyclopropyl)carbinols (I; R = aryl) is different from that described above [equation (2)] for the alkyl(cyclopropyl)carbinols (I; R = alkyl). Cyclopropylphenylmethanol (I; R = Ph), cyclopropyl-4-methylphenylmethanol (I; R = 4-Me$C_6H_4$), and cyclopropyl-4-fluorophenylmethanol (I; R = 4-F$C_6H_4$) reacted with t-butoxyl radicals to give the corresponding aryl(cyclopropyl)hydroxymethyl radicals (II) which now could be observed by e.s.r., and which gave no evidence of the formation of the ring opened radicals (III) or of their products of hydrogen transfer (IV) over the temperature range which was studied (−100 to −20°). Apparently stabilisation by benzylic resonance of the radicals (II) which are initially formed is enough to make the ring-opening process at best a slow reaction.

The behaviour of one ring-substituted cyclopropylcarbinol, *viz.*, *trans*-1-(2-methylcyclopropyl)ethanol (V) was also studied [equation (6)].




Ring opening of the first formed radical (VI) could in principle lead to the formation of the primary alkyl radical (VII) and thence the enoxyl radical (VIII), or it could give the secondary alkyl radical (IX) and the alternative enoxyl radical (X).*

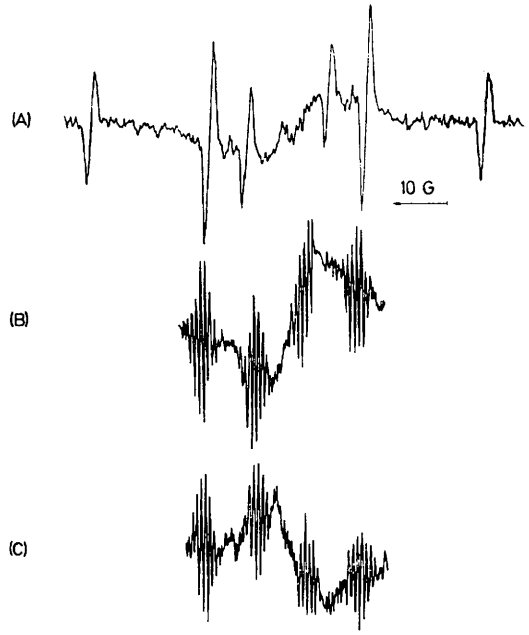
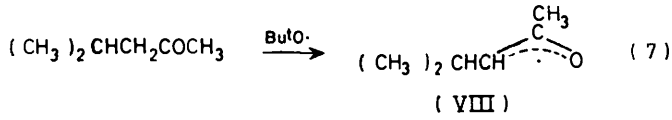



FIGURE 1 E.s.r. spectra of (A) the radical $\dot{C}H_2CHMeCH{=}CMeOH$ at −86°, and of (B) the radical $Me_2CH\dot{C}HCOMe$ at −90°, both derived from 1-(*trans*-2-methylcyclopropyl)ethanol [equation (6)]. Spectrum (C) is of the radical $Me_2CH\dot{C}HCOMe$ at −16°, derived from 4-methylpentan-2-one [equation (7)]

* Godet and Pereyre [16] have shown that, in the addition of tributyltin hydride to *trans*-2-methylcyclopropyl methyl ketone, initiated by azobisisobutyronitrile at 80°, the intermediate radical $\overline{MeCHCH_2CHC}(OSnBu_3)Me$ undergoes ring opening to give 15% n-butyl methyl ketone *via* the radical $CH_3\dot{C}HCH_2CH{=}C(OSnBu_3)Me$ and 85% isobutyl methyl ketone *via* the radical $\cdot CH_2CH(CH_3)CH{=}C(OSnBu_3)Me$. The factors influencing the direction of ring opening will be discussed in a subsequent publication.

[15] D. C. Neckers, A. P. Schaap, and J. Hardy, *J. Amer. Chem. Soc.*, 1966, **88**, 1265.
[16] J.-V. Godet and M. Pereyre, *Compt. rend.*, 1973, **277**, 211.

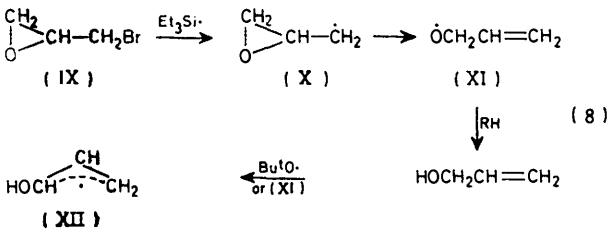
The e.s.r. spectra unambiguously endorse the former route [(VI) ⟶ (VII) ⟶ (VIII)]: at low temperatures the radical (VII) shows its presence as a doublet of triplets,



(7)

(VIII)

and this at higher temperature gives way to a basic doublet of doublets with some further hyperfine splitting by the



(8)

(IX) (X) (XI) (XII)

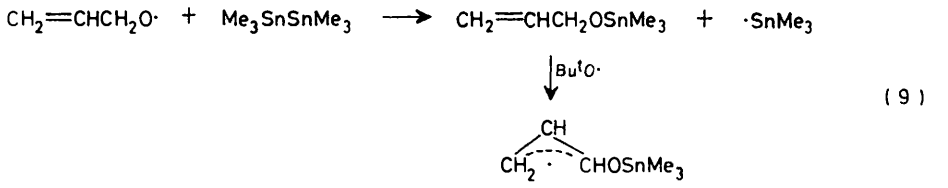
methyl groups. These spectra are illustrated in Figure 1. The assignment of the high temperature spectrum to the radical (VIII) was confirmed by generating the same spectrum by treating 4-methylpentan-2-one with t-butoxyl radicals [equation (7)].

We have examined three such systems which incorporated the oxiran-2-yl-, aziridin-1-yl-, and aziridin-2-yl-carbinol structures.

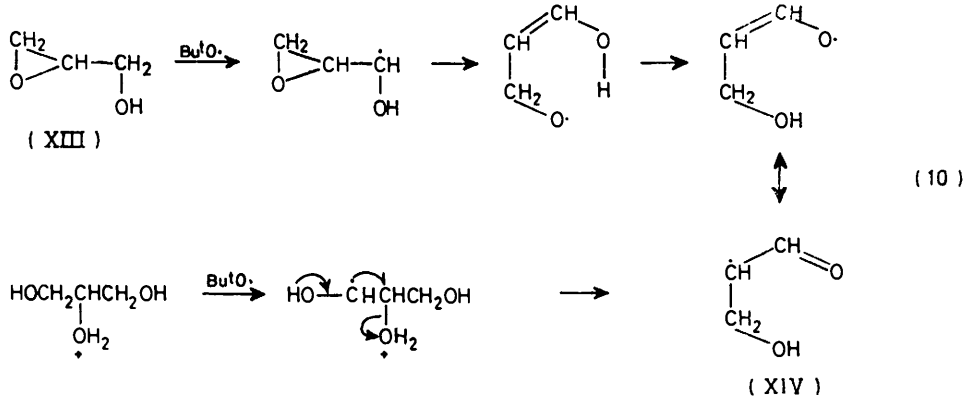
*Oxiranylcarbinols.*—The ring opening of oxiran-2-ylmethyl radicals, with cleavage of a C–O bond, has been reported from product studies of various reactions,* but apparently has not been studied previously by e.s.r. spectroscopy. We therefore examined first the behaviour of epibromohydrin which is readily available.

When di-t-butyl peroxide is photolysed in the presence of triethylsilane and epibromohydrin (IX) the triethylsilyl radical which is formed abstracts bromine. The e.s.r. spectrum of the oxiran-2-ylmethyl radical (X) is not detected, because it rapidly undergoes ring opening at −116° to give the allyloxyl radical (XI). Further, like all alkoxyl radicals, species (XI) has an orbitally degenerate ground state, and so its e.s.r. spectrum cannot be observed.[19] The spectrum that is detected is that of the 1-hydroxyallyl radical (XII) which is probably formed by abstraction of allylic hydrogen from the allyl alcohol derived from (XI).

A similar reaction with hexamethylditin in place of the silane gave the spectrum (with OH coupling absent) of the corresponding trimethyltin derivative of (XII) which is presumably formed by reaction of the allyloxyl radical (XI) with the hexamethylditin [equation (9)]. The spectrum was similar to that which was observed when di-t-butyl



(9)



(XIII) (10) (XIV)

It might be expected that intramolecular transfer of enolic hydrogen should also occur where the precursor of the enol is a heterocyclic analogue of a cyclopropylcarbinol.

peroxide was photolysed in the presence of allyloxytributyltin.

Next, the photoinitiated reaction of 2-hydroxymethyloxiran (XIII) with di-t-butyl peroxide was studied. It was found that, between −38° (when the sample froze) and −12°, a strong spectrum of the 3-hydroxyprop-1-enoxyl radical (XIV) was visible.† This would be consistent with the occurrence of a 1,5-transfer of the enolic hydrogen from oxygen to oxygen [equation (10)].

* *E.g.* epibromohydrin is reduced by trialkyltin hydrides to give allyl alcohol,[17] and the reaction of alkyl radicals with vinyl (ethylene) oxide gives 3-alkylallyl alcohols.[18]

† The spectrum of the radical (XIV) was accompanied by that of a second species which apparently consisted of a simple doublet, $a$ 19.5 G, $g$ *ca.* 2.0005. The same spectrum was obtained from redistilled 2-hydroxymethyloxiran (which showed the absence of any carbonyl group in the i.r. spectrum), but no such complication was apparent when the same radical (XIV) was generated from glycerol. The very low $g$ value might be taken to indicate an acyl radical such as $\dot{C}H_2$–O–$\dot{C}$H–C=O.

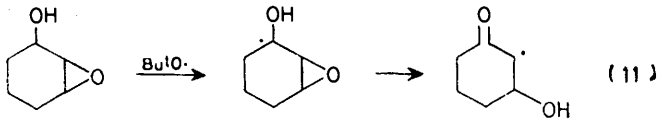
[17] H. G. Kuivila, *Accounts Chem. Res.*, 1968, 1299.

[18] E. S. Huyser and L. P. Munson, *J. Org. Chem.*, 1965, **30**, 1436.

[19] M. C. R. Symons, *J. Amer. Chem. Soc.*, 1969, **91**, 5924.

The radical (XIV) was identified by generating it also by photolysing di-t-butyl peroxide in glycerol containing a trace of trifluoroacetic acid [equation (10)].

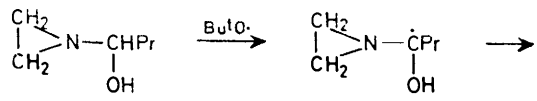
To obtain further information about the origin of the enoxyl radical (XIV) from 2-hydroxymethyloxiran, the epoxide (XV) derived from cyclohex-2-enol was treated with t-butoxyl radicals. The oxiran, as it was prepared, gave a strong spectrum consisting of a doublet of doublets, which we assign to the enoxyl radical (XVI), but when acid impurities were removed from the oxiran by distilling it from potassium hydroxide, the intensity of the spectrum was reduced. The implication of these observations is discussed later.




(11)

(XV) (XVI)

*Aziridinylcarbinols.*—Danen and West [20] photolysed di-t-butyl peroxide in the presence of *N*-methylaziridine and showed that the e.s.r. spectrum of the aziridin-1-ylmethyl radical could be observed at −136°; above that temperature ring opening occurred to give the radical

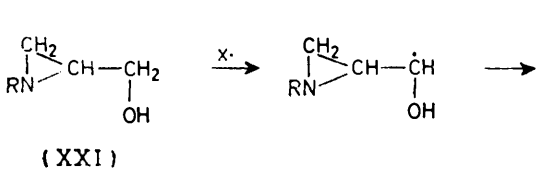



(XVII) (XVIII)

$CH_2CH_2N{=}CH_2$. Even at −160°, however, *N*-ethylaziridine showed only the spectrum of the ring-opened radical.

Similarly we found that photolysis of di-t-butyl peroxide in the presence of 1-(aziridin-1-yl)butanol (XVII) gave no sign of the exocyclic radical (XVIII) but only the ring-opened species (XIX).

No spectrum with a high $g$ value corresponding to that which would be expected for the predicted product (XX) [21] of 1,5-hydrogen transfer, could be observed, although the probable overlap of the line positions of the radicals (XIX) and (XX) might preclude the observation of a small amount of the radical (XX).




(XXI)

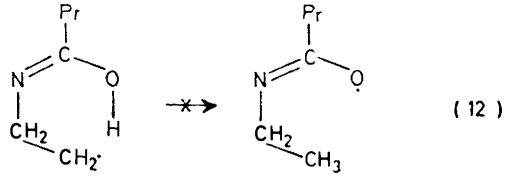
The behaviour of aziridin-2-ylalkyl radicals has not been reported previously. *N*-Butylaziridin-2-ylmethanol (XXI; R = Bu$^n$) was therefore synthesised to investigate whether it would behave in the same way as oxiran-2-ylmethanol [equation (13)].

Generation of t-butoxyl radicals or of acetone triplets in the presence of the aziridine, however, gave only a broad spectrum with some weak superimposed fine structure which could not be interpreted. To avoid any complication which might arise from abstraction of hydrogen from the α-methylene of the n-butyl group, *N*-t-butylaziridin-2-ylmethanol was also prepared and treated similarly, but again no interpretable spectrum could be obtained.

## DISCUSSION

Our experiments with 1-cyclopropylethan[$^2$H]ol establish that the hydroxylic hydrogen is abstracted by the homoallylic radical (III). Itzel and Fischer reported that only the *cis*-form of (III; R = H), and not the *trans*-form, takes part in this reaction, and our experiments on the reaction of cyclopropylmethanol show that only one form of the enoxyl radical (IV) (presumably the *cis*-form) is produced [reaction (3; R = H)]. It therefore seems highly probable that the enoxyl radical is formed by an intramolecular 1,5-transfer of hydrogen.*

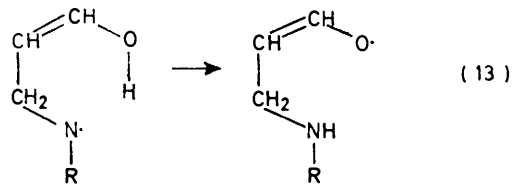
The enthalpy changes which are involved in extracting




(12)

(XIX) (XX)

hydrogen from enol- and keto-tautomers are illustrated in Figure 2. Considering first the keto-form, the C–H bond dissociation energy will be that of a normal C–H bond (*ca.* 98 kcal mol$^{-1}$), less any stabilisation energy of the radical Ċ–C=O arising from delocalisation of the unpaired electron onto the oxygen atom. By the iodine abstraction method, Golden and Benson [22] estimated this stabilisation energy to be 0 ± 1 kcal mol$^{-1}$, but studies by Cocks and Egger [23] on the pyrolysis of cyclopropyl methyl ketone suggest a higher value of *ca.* 7 kcal mol$^{-1}$. This would correlate better with the rotational barrier about the Ċ–CO bond of *ca.* 9 kcal




(13)

mol$^{-1}$, which has been determined by e.s.r. spectroscopy, from which it was concluded that the radicals are largely

* In collaboration with M. Pereyre and J.-C. Pommier, Bordeaux, we have investigated the behaviour of the corresponding trialkyltin derivatives of the cyclopropylcarbinols and have shown that the equivalent 1,5-transfer of the $R_3Sn$ group does not occur. This work supports the conclusions which we draw in the present paper and will be published separately.

[20] W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, 1974, **96**, 2447.

[21] *Cf.* W. C. Danen and R. W. Gellert, *J. Amer. Chem. Soc.*, 1972, **94**, 6853.

[22] D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125.

[23] A. T. Cocks and K. W. Egger, *J.C.S. Perkin II*, 1973, 197.

alkyl in character, but are stabilised by delocalisation to a small but chemically significant extent (*ca.* 15%).[24]

If this value of 7 kcal mol$^{-1}$ be accepted, the C–H bond dissociation energy, $D$(C–H) will be 91 kcal mol$^{-1}$.

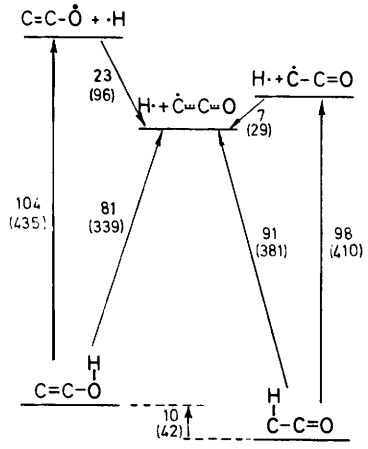



FIGURE 2 Enthalpy diagram for the homolysis of enol and keto tautomers; figures in kcal mol$^{-1}$ (kJ mol$^{-1}$ in parentheses)

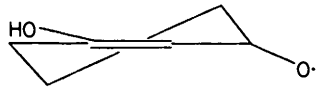
The difference in the enthalpy of formation of the keto and enol tautomers has similarly been a matter of some dispute,[25] but the best current estimate appears to be that, for simple acyclic ketones, the value of $\Delta H$ of enolisation at 25° is *ca.* 10 kcal mol$^{-1}$ in the vapour phase, or 7 kcal mol$^{-1}$ in the liquid phase.

The value of $D$(O–H) in the enol in the vapour phase will therefore be *ca.* 81 kcal mol$^{-1}$ (339 kJ mol$^{-1}$). This is much weaker than the corresponding bond in an alcohol (*ca.* 104 kcal mol$^{-1}$), but is comparable with that of a phenol (*ca.* 88 kcal mol$^{-1}$).[26] The enols and phenols both owe their propensity to donate hydrogen to the fact that the radicals which are formed from each are not oxygen-centred, but are essentially the much more stable carbon-centred species.

Abstraction of enolic hydrogen by an alkyl radical should therefore be exothermic by *ca.* 17 kcal mol$^{-1}$. From an analysis of the relative concentrations of the homoallylic and enoxyl radicals (III and IV; R = Me) derived from 1-cyclopropylethanol, Itzel and Fischer estimated the activation energy of the hydrogen transfer to be 4.8 ± 1 kcal mol$^{-1}$, with a frequency factor of $10^8$ s$^{-1}$.

The evidence for the mechanism of the formation of the enoxyl radical (XIV) from 2-hydroxymethyloxiran is less convincing. The experiments with epibromohydrin (IX) confirm that ring opening of the oxiranylmethyl radical (X) to give the allyloxyl radical (XI) does occur very readily. Intramolecular hydrogen transfer from enol to alkoxyl should be more exothermic than that to an alkyl radical,* and therefore the mechanism for the formation of enoxyl radical (XIV) from 2-hydroxymethyloxiran (XIII) *via* ring opening and 1,5-hydrogen transfer [equation (10)] is probably that which conforms best with the limited evidence.

The radical derived from 2,3-epoxycyclohexanol (XV), however, would have the structure (XXII) in which

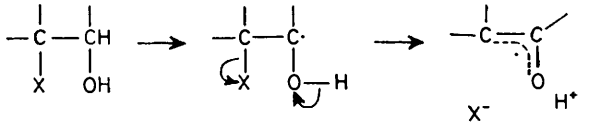



( XXII )

1,5-intramolecular transfer of hydrogen is impossible, yet it gives the spectrum of the enoxyl radical (XVI) strongly under acidic conditions but only weakly if the acid is removed. It is possible that this weak residual radical is formed by intermolecular hydrogen abstraction by the oxygen radical centre and from the hydroxy-group, but there is also a special heterolytic mechanism which could apply to the ring opening of the epoxides derived from allyl alcohols.

Norman and his colleagues [27] have shown that radicals derived from alcohols with electronegative substituents in the β-position can give enoxyl radicals by the heterolytic process illustrated in equation (14).

The leaving group X can be $H_2O$ (though, as far as is known, not $HO^-$), and we made use of this principle in preparing the radical (XIV) from glycerol under acid conditions [equation (10)]. A heterolytic mechanism of



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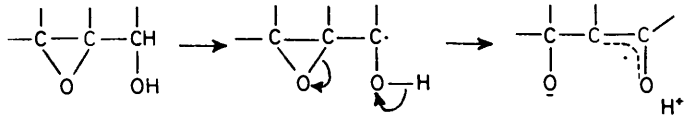


( 15 )

this type is probably responsible for the radical which we observed when acid was present [equation (15)], and the residual reaction of the purified oxiran may still indicate catalysis by adventitious acid: in some other

* Abstraction of enolic hydrogen by RS· radicals should also be exothermic, and hydroxymethylthiirans would be expected to take part in the sulphur analogue of reaction (10).

[24] D. M. Camaioni, H. F. Walker, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1973, **95**, 7978.

[25] Reviewed by S. Forsén and M. Nilsson in ' The Chemistry of the Carbonyl Group,' ed. J. Zabisky, Wiley, New York, 1970, ch. 3.

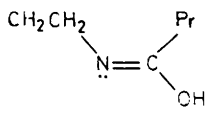
[26] K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, 1973, **56**, 1516.

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

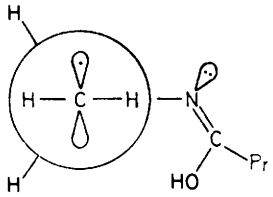
(acyclic) systems which give these rearrangements very readily, we have found that the results may be irreproducible unless very careful precautions are taken to avoid the presence of acids.

Such a process of course cannot govern the ring-opening reactions of the cyclopropylhydroxymethyl radicals because there the e.s.r. spectra of the homoallylic radicals can be observed.

Our inability to observe 1,5-hydrogen transfer in the radical derived from 1-(aziridin-1-yl)butanol [equation (12)] may in part be due to possible overlap of the e.s.r. signals in the radicals (XIX) and (XX),* but it is clear that at best this reaction can occur to only a relatively limited degree. Insufficient data appear to be available to allow a diagram equivalent to Figure 1 to be constructed for the tautomers N=C–OH and HN–C=O, and it is possible that the hydrogen transfer (XIX) ⟶ (XX) may be endothermic. A second factor could be that the structure of the ring-opened radical (XIX) is not conducive to hydrogen transfer. Ring opening may occur to place the alkyl group and the OH in a *trans*-sense about the N=C double bond (XXIII), or, as suggested by Danen and West,[20] a 1,3-interaction between the unpaired electron and the lone pair of electrons on the nitrogen atom may hold the molecule in the non-planar conformation (XXIV).




(XXIII)




(XXIV)

The reason why no specific radicals could be identified from the 2-hydroxymethylaziridines (XXI) is not apparent, and before the question of hydrogen transfer can be investigated, the basic reaction of ring opening must be established.

We thank Mrs. M. Maher for recording the $^{13}C$ n.m.r. spectra, Dr. A. G. Loudon for assistance and advice with the mass spectrometry, and Dr. B. P. Roberts for much valuable discussion. The award of a Research Fellowship to B. M. by the International Tin Research Council is gratefully acknowledged.

[5/1358 *Received*, 9*th July*, 1975]

* Radicals similar to (XX) have been observed by e.s.r. by photolysing *N*-chloroamides in cyclopropane solution.[21]