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# RING OPENING OF OXIRANYLMETHYL AND 3-METHYL-3-OXETANYLMETHYL RADICALS

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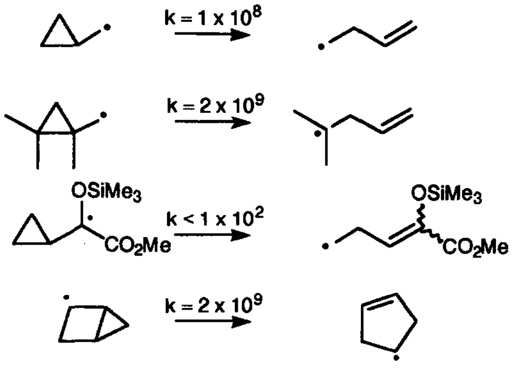
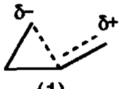
**Abstract:** Oxiranylmethyl and 3-methyl-3-oxetanylmethyl radicals were generated from the corresponding bromides and their rearrangements to allyloxyl and 2-methylprop-2-enyloxymethyl radicals respectively, were studied by kinetic EPR spectroscopy. The former radical was shown to ring open with a rate constant of > 4 x $10^8$ $s^{-1}$ at 25°C. The following kinetic parameters were measured for ring opening of the latter radical: k(25°C) = 8.9 x $10^2$ $s^{-1}$, log[A/$s^{-1}$] = 13.97, E/kJ $mol^{-1}$ = 63.3. Comparison of this data with that of related radicals supported the proposal that the transition state for β-scission of three-membered and four-membered cycloalkylmethyl radicals has dipolar character.

## INTRODUCTION

It has been shown by several methods that the cyclopropylmethyl radical ring opens to give the but-3-enyl radical with a rate constant of 1 x $10^8$ at 300 K.[1] The rates of ring opening of substituted cyclopropylmethyl radicals are accelerated by substituents which increase the stability of the rearranged radical[1,2] and decreased by substituents which enhance the stability of the initial radical.[3,4] The rate of ring opening of the bicyclo[2.1.0]pent-2-yl radical is greater than that of the cyclopropylmethyl radical due to release of ring strain.[1,5,6,7]



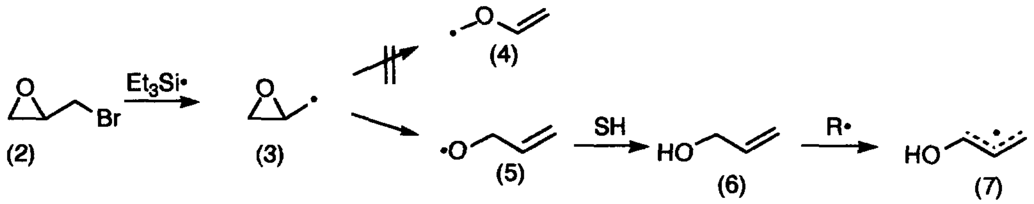
Beckwith *et al* [8,9] have also postulated that the ring-opening process proceeds *via* a dipolar transition state (1). If this is so, substituents which would increase the dipolar character of the transition state might be expected to increase the rate of ring opening of the radical and *vice versa*.



(1)

## RESULTS AND DISCUSSION

One test of this postulate would be to examine the rate of ring opening of the oxiranylmethyl radical (3). The electronegative oxygen would be expected to lower the energy of the transition state. A previous EPR study of (3) had shown that it was not possible to detect oxiranylmethyl radicals at 157 K in cyclopropane as solvent:[10] the only species which could be detected was the 2-hydroxyallyl radical (7), which was formed as depicted in the Scheme. We have repeated this experiment using propane as solvent in order to be able to study the reaction at a lower temperature and obtained the same result at 128 K. From the fact that (3) was fully ring opened at 128 K, under EPR conditions, we can estimate that the activation energy for rearrangement, $E_a < 6$ kcal mol$^{-1}$ (25 kJ mol$^{-1}$) and hence $k_r$ (25° C) $> 4 \times 10^8$ s$^{-1}$. The EPR parameters of radical (7) [*a*(1H, 1.27), *a*(2H, 1.38), *a*(1H, 0.33), *a*(1H, 0.08mT)] were very similar to those reported previously.[10] The rate of ring opening of oxiranylmethyl radical is thus at least an order of magnitude greater than that of cyclopropylmethyl radicals. The cyclopropylmethyl radical can be observed free of any of the ring-opened but-3-enyl radical at 133 K under EPR conditions and is only completely rearranged at 173 K.[11] It is also relevant to note that ring opening of (3) occurs by exclusive cleavage of the C-O bond to give initially (5) and not by cleavage of the C-C bond in the oxiranyl ring even though a C-O bond is generally stronger than a C-C bond by 4-20 kJ mol$^{-1}$.[12] Recent work of Murphy *et al* has shown that oxiranylmethyl radicals preferentially undergo cleavage of the C-O bond, except for 3-phenyl- and 3-vinyl-oxiranylmethyl radicals which undergo preferential C-C bond cleavage because this leads to the more thermodynamically stable radical $\bullet CH(Ph)OCH{=}CH_2$.[13-15]



We have also investigated the rate of ring opening of the 3-methyl-3-oxetanylmethyl radical (8) for comparison with the rate of ring opening of the analogous hydrocarbon radical, i.e. the (1-methylcyclobutyl)methyl radical (10). There are no reports in the literature on the influence of substituents other than alkyl groups on the rate of ring opening of cyclobutylmethyl radicals. However, this evidence is consistent with the conclusion that the rate of ring opening is decreased by factors which stabilise the initial radical and enhanced by increased thermodynamic stability of the rearranged radical and also if the ring opening is accompanied by relief of strain.[16-20]

The rate constant for the rearrangement of (8) was obtained from a kinetic EPR study. The 3-methyl-3-oxetanylmethyl radical (8) was generated by photolysis of a solution containing 3-bromomethyl-3-methyloxetane and equimolar amounts of triethylsilane and di-t-butyl peroxide in cyclopropane in the cavity of an EPR spectrometer. Radical (8) was identified from its EPR spectrum (Table 1) which showed a triplet splitting similar to that of the cyclobutylmethyl radical and two distinct small splittings due to coupling with the exocyclic methyl protons and the γ-protons (α to the oxygen) in the ring. The EPR spectrum of (8) was observed at higher temperatures in similar samples in t-butylbenzene as solvent and containing hexamethylditin instead of triethylsilane. Above 290 K the spectrum of (8) weakened and a new spectrum attributed to the rearranged radical, 2-methylprop-2-enyloxymethyl (9), was observed: this dominated the spectrum at 330 K. The ring-opened radical showed, as expected, α and γ splittings similar to those of $CH_3CH_2OCH_2\bullet$.[21] There was no evidence of radical (9) undergoing loss of methanal to give the isopropenyl radical, $CH_2{=}C(CH_3)CH_2\bullet$. The measured concentrations of unrearranged (8) and rearranged radicals (9), within the temperature range 295-328 K, together with values $k_f/2k_t$ derived by the usual treatment[22] are recorded in Table 2; $k_f$ being the rate constant for ring opening and $2k_t$ the rate constant for bimolecular termination of (8).

**Table 1.** EPR Parameters of Initial and Ring-opened Radicals

| Radical | T/K | $a$ (H$_\alpha$) | $a$ (H$_\beta$) | $a$ (H$_\gamma$) |
|---|---|---|---|---|
| 3-Methyl-3-oxetanylmethyl (8) | 150 | 2.13 (2H) | | 0.17 (4H), 0.05 (3H) |
| Cyclobutylmethyl$^b$ | 240 | 2.15 (2H) | 1.40 (1H) | 0.14 (2H) |
| $CH_2{=}C(CH_3)CH_2OCH_2\bullet$ (9) | 340 | 1.62 (2H) | | 0.18 (2H) |
| $CH_2{=}CHCH_2CH_2CH_2\bullet^b$ | 270 | 2.19 (2H) | 2.81 (2H) | |

$^a$ Hfs in mT, all $g$-factors 2.003 ± 0.001 $^b$Data from ref. 16

**Table 2.** Kinetic EPR Data for Ring Opening of 3-Methyl-3-oxetanymethyl Radicals.$^a$

| T/K | $10^{-7}$[8] mol dm$^{-3}$ | $10^{-7}$[9] mol dm$^{-3}$ | $10^7k_f/2k_t$ mol dm$^{-3}$ |
|---|---|---|---|
| 328 | 0.38 | 1.24 | 5.25 |
| 323 | 0.56 | 0.78 | 1.89 |
| 318 | 1.52 | 1.19 | 2.10 |
| 315 | 0.81 | 0.66 | 1.20 |
| 310 | 1.63 | 0.68 | 0.96 |
| 305 | 2.88 | 0.53 | 0.62 |
| 300 | 2.46 | 0.47 | 0.55 |
| 295 | 1.90 | 0.27 | 0.31 |

$^a$ In t-butylbenzene

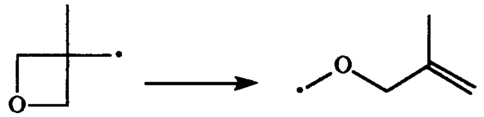
**Table 3.** Rate Constants and Arrhenius Parameters for Ring Opening of 3-Methyloxiranylmethyl and Cyclobutylmethyl radicals

| Radical | k/s$^{-1}$ (300 K) | log[A/s$^{-1}$] | E/kJ mol$^{-1}$ |
|---|---|---|---|
| Cyclopropylmethyl$^a$ | $1 \times 10^8$ | 13.15 | 29.5 |
| Oxiranylmethyl | $> 4 \times 10^8$ | [13.0] | < 25 |
| 3-Methyl-3-oxetanylmethyl (8) | 890 | 13.97 | 63.3 |
| Cyclobutylmethyl$^b$ | 4700 | 12.26 | 49.8 |
| (1-Methylcyclobutyl)methyl$^b$ (10) | 2500 | 12.6 | 56.8 |

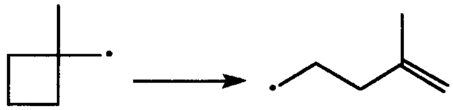
$^a$Data from ref. 1 $^b$Data from ref. 16

Termination rates of small transient radicals in solution are mainly controlled by the viscosity. As is usual we employed Fischer's accurate values for the self-termination of t-butyl radicals in heptane[23], correcting for the difference in viscosity between heptane and t-butylbenzene as described previously.[16] The $k_f$ values derived by this procedure are also recorded in Table 2.

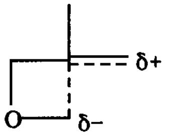
The results indicated that the radical (8) undergoes ring opening less rapidly than the 1-methyl-1-cyclobutylmethyl radical (10) (see Table 3). This result was unexpected as the ring-opened radical (9) should be more stabilised than its carbon analogue (11). Alkoxymethyl radicals have been shown to be thermodynamically more stabilised than the corresponding alkyl radicals because of electron delocalisation onto oxygen.[21] Consideration was given to the possibility that the initial radical could possibly have been stabilized by interaction of the lone pair on oxygen and the radical centre. This is most improbable particularly as studies indicate that the oxetane ring is much less puckered than the cyclobutane ring making any non-bonded interaction much less feasible.[24,25] The slower rate of ring opening could be explained if the ring-opening process, like that of the oxiranylmethyl radical, proceeds via a dipolar transition state (12). The electron withdrawing influence of the oxygen would destabilise this transition state thereby accounting for the slower rate of ring opening.



(8) (9)



(10) (11)



(12)

## Experimental.

EPR spectra were recorded with a Bruker ER 200D spectrometer operating with 100 kHz modulation. Samples were prepared in Spectrosil tubes, degassed, and photolysed in the cavity by light from a 500W super pressure mercury lamp. Radical concentrations were determined by double integration of suitable peaks from the spectra of the initial and rearranged radicals. Signal areas were converted to concentrations by comparison with the double integral of the signal from a known concentration of DPPH. All signals were normalised with repect to the constant signal from a ruby disc.

**Bromomethyloxirane.** A commercial sample was distilled using a spinning band column and the fraction, b.p. 134-136°C used.

**3-Bromomethyl-3-methyloxetane.** This was obtained by conversion of 3-hydroxymethyl-3-methyloxetan[26], into its mesylate and reacting the mesylate with lithium bromide in anhydrous acetone[16], and was obtained as a colourless liquid, b.p. 55-58°C/ 12 mm.(lit., [27] b.p. 62-64°C/14 mm).

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