A Kinetic Electron Spin Resonance Study of Ring Fission in Methyl-substituted Cyclobutylmethyl Radicals

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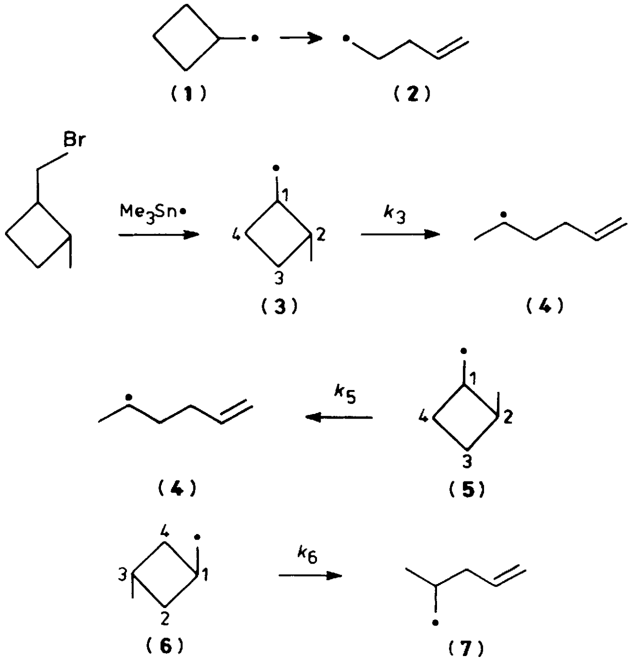
Rate constants for the ring-opening reactions of *cis*- and *trans*-2-methylcyclobutylmethyl, *cis*- and *trans*-3-methylcyclobutylmethyl, and 2,2-dimethylcyclobutylmethyl radicals have been determined over a range of temperatures by kinetic e.s.r. spectroscopy. For the limited series of cyclobutylmethyl radicals the activation energies for ring-opening show a linear correlation with the enthalpies of the rearrangements. Barriers to internal rotation of the *trans* methyl groups have been determined from exchange broadening in the e.s.r. spectra of *trans*-2-methylcyclobutylmethyl and 2,2-dimethylcyclobutylmethyl radicals.

The kinetics of the ring-opening of cyclobutylmethyl radicals (1) to pent-4-enyl radicals (2) has been studied by treatment of cyclobutylmethyl chloride with tri-n-butyltin hydride[1] and by kinetic e.s.r. spectroscopy.[2] The rate constant for ring fission (*ca.* 5×10^3 s^{-1} at 25 °C) is considerably less than that of the analogous ring-opening reaction of cyclopropylmethyl radicals for which the rate constant is *ca.* 1×10^8 s^{-1} at 25 °C.[3,4] These β-scission reactions are sensitive to stereoelectronic effects[1,5] and it is therefore of interest to know the quantitative effect of substituents on the rate of ring-opening. Alkyl-substituted cyclopropylmethyl radicals undergo ring-opening too rapidly for study by either the e.s.r. or the tin hydride methods, but the cyclobutylmethyl system enables the effect of alkyl substituents on the rearrangement to be investigated.[6]

The rates of ring fission of a number of substituted cyclobutylmethyl radicals, relative to the rate of hydrogen abstraction from tri-n-butyltin hydride by alkyl radicals (k_H), were measured by Beckwith and Moad.[1] The kinetic e.s.r. technique allows the determination of absolute rate constants for ring fission.

The alkyl-substituted cyclobutylmethyl radicals are reasonable models for more complex radicals derived from natural products, such as the radicals formed by addition to α- and β-pinene. Knowledge of the rates of rearrangement of the model radicals will enable the reaction mechanisms of the more complex natural products to be refined.



Results and Discussion

Kinetics of Ring-opening of Methyl-substituted Cyclobutylmethyl Radicals.—*trans*-2-Methylcyclobutylmethyl radicals (3) were generated by photolysis of the corresponding bromide and hexamethylditin in t-butylbenzene containing a trace of di-t-butyl peroxide at temperatures from 230 to 270 K directly in the cavity of the e.s.r. spectrometer. The e.s.r. parameters of (3) are recorded in Table 1. At temperatures above 240 K ring-opening of (3) by fission of the C(1)–C(2) bond was observed and radical (4) was detected (e.s.r. parameters in Table 2). At temperatures above *ca.* 265 K (4) becomes the only detectable radical. The measured concentrations of (3) and (4) in the temperature range 238—266 K are given in Table 3, together with the values of $k_3/2k_t^{44}$ derived by the usual kinetic treatment,[3,6] $2k_t^{44}$ being the rate constant for bimolecular self-reactions of (4). The alternative rearrangement, by fission of the C(1)–C(4) bond to give a primary alkyl radical, could not be detected.

The *cis*-2-methylcyclobutylmethyl radicals (5) were generated from the corresponding bromide in t-butylbenzene solution in a similar way. The e.s.r. parameters of (5) and the rearranged radical [identical with (4)] are given in Tables 1 and 2. The measured concentrations of the two radicals and the drived rate constant ratios are given in Table 4. Fission of the C(1)–C(4) bond to give a primary alkyl radical could not be observed.

Bromine abstraction from *trans*-3-methylcyclobutylmethyl bromide gave the corresponding *trans*-radical (6) (Table 1). The rearrangement by β-scission to give radical (7) (Table 2) was followed in the temperature range 250—280 K and the kinetic data are recorded in Table 5. Radical (7) actually consists of an enantiomeric pair; fission of C(1)–C(4) in radical (6) produces the *R*-enantiomer and fission of C(1)–C(2) produces the *S*-enantiomer. The two are, of course, indistinguishable by e.s.r. spectroscopy. The statistical factor of two (Table 5, right-hand column) has been introduced to allow for the fact that radical (7) can be formed in these two ways.

The ring-opening of *cis*-3-methylcyclobutylmethyl radicals (8) gives the same pair of enantiomeric radicals (7) (e.s.r. parameters in Tables 1 and 2). In this case β-scission of C(1)–C(2) produces the *R*-enantiomer whereas scission of

Table 1. E.s.r. parameters of substituted cyclobutylmethyl radicals

Radical	T/K	Hyperfine splittings/G				
		$a(2H_\alpha)$	$a(H_\beta)$	$a(H_\gamma^{cis})$	$a(H_\delta)$	a(other)
Cyclobutylmethyl (**1**)[a]	140	22.1	9.0	1.43(2 H)		
trans-2-Me (**3**)	140	22.1	8.0	1.5(2 H)	0.73(3 H)	
	90	22.1	6.8	1.5(2 H)	2.0(1 H), 0.1(2 H)	
cis-2-Me (**5**)	140	21.8	12.9	1.5(1 H)		0.40(1 H)
cis-3-Me (**8**)	140	21.8	12.9	1.6(2 H)		0.40(2 H)
trans-3-Me (**6**)	140	22.3	9.7	1.6(2 H)		0.40(4 H)
2,2-diMe (**9**)	140	21.7	10.7	1.5(1 H)	0.73(3 H)	
	90	21.7	8.7	1.5(1 H)	2.0(1 H), 0.1(2 H)	

[a] From references 2, 7, and 8.

Table 2. E.s.r. parameters of rearranged radicals

Radical	T/K	Hyperfine splittings/G		
		$a(H_\alpha)$	$a(H_\beta)$	$a(H_\gamma)$
Hex-5-en-2-yl (**4**)	260	22.0(1 H)	25.1(5 H)	0.70(2 H)
2-Me-pent-5-enyl (**7**)	290	22.3(2 H)	29.1(1 H)	
2-Me-hex-5-en-2-yl (**10**)	235		17.7(2 H) 23.5(6 H)	

Table 3. Ring-opening of *trans*-2-methylcyclobutylmethyl radicals (**3**)[a]

T/K	10^8 [(**3**)]/M	10^8 [(**4**)]/M	$10^8\ k_3/2k_t^{44}$/mol dm^{-3}
243	19.5	4.29	5.23
249	21.5	6.23	8.04
252	23.7	6.34	8.04
255	14.0	7.53	11.58
257	16.9	7.60	11.02
261	19.4	10.74	16.69
263	15.6	13.27	24.56
266	12.8	12.15	23.68

[a] In t-butylbenzene solvent.

Table 4. Ring-opening of *cis*-2-methylcyclobutylmethyl radicals (**5**)[a]

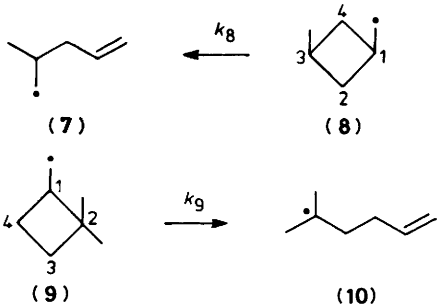
T/K	10^8 [(**5**)]/M	10^8 [(**4**)]/M	$10^8\ k_5/2k_t^{44}$/mol dm^{-3}
216	14.25	3.47	4.32
221	12.05	4.87	6.84
227	9.96	5.25	8.02
229	7.93	7.15	13.60
232	6.85	4.73	8.00
235	6.04	8.28	19.63
237	6.16	6.72	14.05
243	3.00	7.78	27.96
248	1.96	10.57	67.57

[a] In t-butylbenzene solvent.

Table 5. Ring-opening of *trans*-3-methylcyclobutylmethyl radicals (**6**)[a]

T/K	10^8 [(**6**)]/M	10^8 [(**7**)]/M	$10^8\ 2k_6/2k_t^{77}$/mol dm^{-3}
250	46.7	1.64	1.70
255	40.3	2.23	2.35
260	43.3	4.31	4.74
265	32.7	6.42	7.68
271	32.3	7.07	8.62
276	25.6	9.35	12.76
281	25.7	8.18	10.78

[a] In t-butylbenzene solvent.



C(1)–C(4) gives the *S*-enantiomer. The kinetics of the rearrangement was studied in t-butylbenzene solution in the temperature range 250—285 K and the data are given in Table 6.

In the rearrangement of 2,2-dimethylcyclobutylmethyl radicals (**9**) fission of the C(1)–C(2) bond to give radical (**10**) (see Tables 1 and 2) was the only observable process. This rearrangement occurred at temperatures too low for study in t-butylbenzene, and therefore cyclopropane was used as solvent. The kinetic data are recorded in Table 7.

The termination rates of small to moderately sized transient radicals are diffusion controlled in solution and do not depend to any significant degree on the structure at the radical centre, *i.e.*, primary, secondary, or tertiary, but rather on the solution viscosity.[9–13] In order to evaluate $2k_t^{44}$, $2k_t^{77}$, and $2k_t^{1010}$ we have used Fischer's accurate values for the self termination of t-butyl radicals in heptane.[10] At each temperature $2k_t$ was calculated for each radical from the Arrhenius equation, (1), given by Fischer: by correcting for the difference in viscosity of

$$\log\,[2k_t(\mathrm{Bu^t})/\mathrm{dm^3\ mol^{-1}\ s^{-1}}] = 11.63 - (2.30\ \mathrm{kcal\ mol^{-1}})/2.3\ RT^* \qquad (1)$$

the solvent from that of n-heptane at each temperature. The coefficients of viscosity of n-heptane,[10] cyclopropane,[14] di-t-butyl peroxide,[2] and toluene,[15] and their temperature dependencies, were taken from the literature. The temperature

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* 1 kcal mol^{-1} ≡ 4.18 kJ mol^{-1}.

Table 6. Ring-opening of *cis*-3-methylcyclobutylmethyl radicals (**8**)[a]

T/K	10^8 [(**8**)]/M	10^8 [(**7**)]/M	$10^8\ 2k_8/2k_t^{77}$/mol dm^{-3}
250	37.2	1.75	1.83
255	39.9	3.27	3.53
260	32.2	3.60	4.00
265	32.7	5.65	6.63
271	29.3	8.14	10.40
286	11.4	10.48	20.13

[a] In t-butylbenzene solvent.

Table 7. Ring-opening of 2,2-dimethylcyclobutylmethyl radicals (**9**)[a]

T/K	10^8 [(**9**)]/M	10^8 [(**10**)]/M	$10^8\ k_9/2k_t^{1010}$/mol dm^{-3}
194	5.20	1.52	1.96
196	4.57	1.84	2.58
199	3.95	2.09	3.20
201	2.95	2.55	4.81
205	3.50	2.82	5.09
207	2.54	3.45	8.14
210	2.41	3.36	8.04
212	1.78	4.33	14.86
215	1.16	4.20	17.38
221	1.28	4.86	23.3

[a] In cyclopropane solvent.

Table 8. Rate constants and Arrhenius parameters for ring-opening of cyclobutylmethyl radicals[a]

Radical		$10^{-3}\ k$/s^{-1} (25 °C)	log A/s^{-1}	E/kcal mol^{-1}
Cyclobutylmethyl	(1)	4.7	12.26 ± 1.0	11.7 ± 0.3
1-Cyclobutyl-1-methylethyl	(11)	0.67	13.21 ± 1.5	14.1 ± 1.8
trans-2-Methylcyclobutylmethyl	(**3**)	5.7	12.51 ± 1.0	11.9 ± 0.6
cis-2-Methylcyclobutylmethyl	(**5**)	17.8	12.41 ± 1.0	11.1 ± 1.3
trans-3-Methylcyclobutylmethyl	(**6**)	1.6	12.6 ± 1.0	12.8 ± 1.2
cis-3-Methylcyclobutylmethyl	(**8**)	1.8	12.7 ± 1.5	12.8 ± 0.9
2,2-Dimethylcyclobutylmethyl	(**9**)	870	12.4 ± 1.0	8.8 ± 0.5

[a] The rate constants and A-factors refer to the *total* rate, and have *not* been adjusted by the statistical factor of 2.

dependence of the coefficient of viscosity of t-butylbenzene has not been published; the data for isobutylbenzene,[16] which should be very similar, have been used. The rate constants of the ring-opening reactions derived in this way are shown in the form of Arrhenius plots in Figure 1; the Arrhenius parameters are listed in Table 8. We have previously determined the rate constants for ring-opening of cyclobutylmethyl (**1**) and 1-cyclobutyl-1-methylethyl radicals[2] (**11**). In Table 8 we also list Arrhenius parameters for β-scission of these two radicals which have been recalculated using $2k_t$ values evaluated as outlined above. We believe this procedure gives more accurate results than that used previously.

The relative rate constants for ring-opening of cyclobutylmethyl radicals, determined by Beckwith and Moad at 60 °C using the tin hydride method, can be converted into absolute rate constants by use of the value of k_H obtained recently by Ingold and co-workers[17] from laser flash photolysis experiments, *i.e.*, equation (2). The rearrangement rate constants

$$\log\,[k_H(\mathrm{Pr^i})/\mathrm{dm^3\ mol^{-1}\ s^{-1}}] = 9.07 - (3.69\ \mathrm{kcal\ mol^{-1}})/2.3RT \qquad (2)$$

derived in this way are shown on the Arrhenius plots in Figure 1. A slightly lower k_H value was found for t-alkyl radicals,[17] and this has been used in conjunction with Beckwith's data on the tertiary radical (**11**). The 3-methylcyclobutylmethyl radicals were not examined by Beckwith and Moad, but their data for 3,3-dimethylcyclobutylmethyl radicals, which should be virtually identical, are plotted in Figure 1. Examination of Figure 1 shows that in each case the rate constants derived from the tin hydride work lie close to the Arrhenius lines drawn through our corresponding kinetic e.s.r. data; the two methods give a gratifyingly consistent picture.

Good Arrhenius pre-exponential factors cannot be obtained from the kinetic e.s.r. experiments because of the short range of temperatures over which experiments can be made. Table 8 shows that the measured A-factors are all within range of 10^{13} s^{-1}, which is normal for unimolecular processes of this type.

The kinetic results (Table 8) indicate that methyl substituents at C(3) have a relatively small effect on the rate and activation energy of ring-opening, as does a *trans*-2-methyl substituent, but a *cis*-2-methyl substituent causes a significant increase in rate. A very pronounced increase in rate, with consequent lowering of the activation energy, is observed for the 2,2-dimethyl case.

Methyl substituents at the radical centre, as in the α,α-dimethyl radical (**11**), retard the rate of ring fission. The fact that substituents at C(2) have the greatest effect on the rate of β-scission suggests that the strength of the bond being broken and/or the stabilisation of the rearranged radical have the most important influence on the reaction, *i.e.*, that the transition state resembles the product radical. For radicals (**3**) and (**5**) this would mean the transition states would be very similar, both resembling radical (**4**). The higher activation energy for rearrangement of radical (**3**) therefore implies that the *trans*-2-methyl group stabilises the cyclobutylmethyl radical. The rearrangements of radicals (**1**) and (**3**) have essentially the same activation energy, even though (**1**) gives a primary radical (**2**), and (**3**) gives the more stabilised secondary radical (**4**). This is also consistent with a stabilisation of radical (**3**) by the *trans*-2-methyl group. Radicals (**1**), (**6**), and (**8**) rearrange to primary radicals (**2**) and (**7**) which should be stabilised to about the same extent. The higher activation energies for rearrangement of (**6**) and (**8**) (Table 8) imply that methyl substituents at C(3) also increase the stabilisation of the cyclobutylmethyl radical. Similar comparison of the activation energies for the rearrangements of (**1**) with (**5**) and of (**6**) with (**9**) suggests that *cis*-2-methyl substituents decrease the stabilisation of cyclobutylmethyl radicals.

For a series of closely related reactions involving bond fission Evans–Polanyi-type relations between the activation energy E and the over-all reaction enthalpy ΔH° are often found, equation (3), where α and C are constants and $0 < \alpha < 1$. A

$$E = \alpha\Delta H^\circ + C \qquad (3)$$

number of such relations have been demonstrated for H-abstraction reactions.[18,19] We have shown previously that the

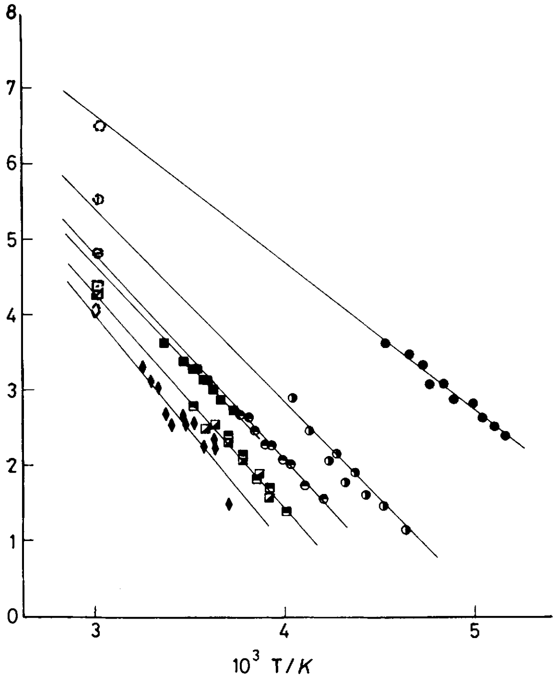
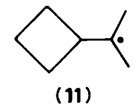


Figure 1. Arrhenius plots for ring-opening of cyclobutylmethyl radicals. Radical (**1**) ■, radical (**3**) ⊖, radical (**5**) ◑, radicals (**6**) and (**8**) ⊟ and ◪, radical (**9**) ●, radical (**11**) ◆. Data from Beckwith and Moad[1] (see text) shown dotted



(**11**)

activation energies for ring-opening of cyclopropylmethyl, cyclobutylmethyl, cyclobutenylmethyl, and cyclopentylmethyl radicals do *not* correlate with the over-all enthalpies of the rearrangements.[2] This is probably because the transition-state configurations are too dissimilar in this series. For the cyclobutylmethyl radical derivatives studied in this work the release of ring strain is the same in each case and the transition-state geometries are expected to be similar. We estimated the ΔH° values using Benson's group contributions (GC)[20] and the Evans–Polanyi plot is shown in Figure 2. The result is a reasonably straight line (r = 0.981) which can be represented by equation (4). The high value of α provides additional support

$$E/\text{kcal mol}^{-1} = (0.94 \pm 0.08)\,\Delta H^\circ + 16.2 \pm 0.4 \qquad (4)$$

for the view that the transition state is late and resembles the rearranged radicals.

The tin hydride results[1] when plotted in the same manner all lie reasonably close to the correlation line given above except for two points from ring-opening of cyclobutylmethyl radicals with methyl substituents at C(1). Beckwith has previously suggested that the anomalous nature of these results may be a consequence of the 1-methyl groups preventing efficient overlap of the SOMO with orbitals of the C(1)–C(2) bond.

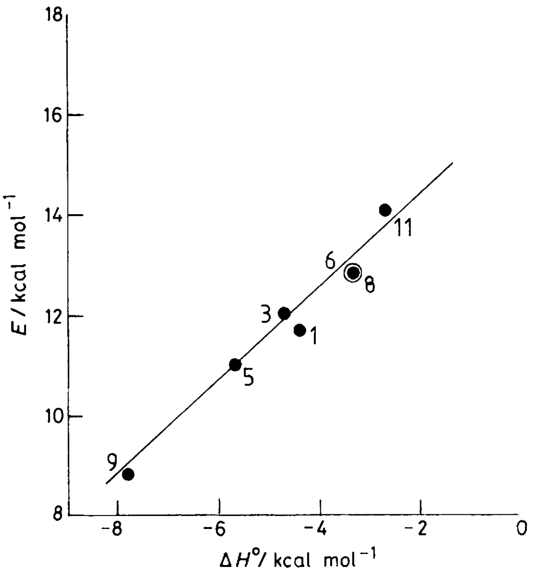


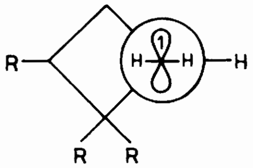
Figure 2. Correlation of activation energy for ring-opening, E, with reaction enthalpy ΔH°. The numbers on the correlation refer to the structure number of each radical

In the addition reaction of free radicals with alkenes both experimental and theoretical studies suggest an early transition state, resembling the reactants.[21] Similarly, in the intramolecular addition (cyclisation) of hexenyl and related radicals, *i.e.*, the reverse of ring-opening, the transition state is early.[5] Thus a late transition state for ring-opening is in accord with expectation. A study of the ring-opening of cyclobutylmethyl radicals using the semi-empirical MINDO/3 SCF MO method[22] indicated that the C(1)–C(2) bond lengthens from 1.56 Å in (**1**) to 2.05 Å in the transition state and the double bond is predicted to be almost fully formed in the transition state. The MINDO/3 predictions are therefore in full accord with a late transition state in which C(1) and C(2) are well on the way to full sp^2 hybridisation.

Evans–Polanyi relationships are useful for estimating bond dissociation energies from activation energies,[18] especially when high α values are obtained. For β-scission of cycloalkylmethyl radicals we can write equation (5) where RS is

$$\Delta H^\circ = DH^\circ[\mathrm{C(1)–C(2)}] - D_\pi^\circ(\mathrm{C{=}C}) - RS \qquad (5)$$

the ring strain and D_π°(C=C) is the π-bond dissociation energy in the rearranged radicals. Perhaps it is somewhat artificial to separate the ring strain from the bond dissociation energies of the ring C–C bonds as is done in equation (5). However, all the ring strain is released when only one of the ring C–C bonds is broken and hence if RS were not separated from DH°[C(1)–C(2)] as in equation (5) it would all appear as a lowering of the energy of one bond, which would be equally misleading. Equations (4) and (5) can, in principle, be used for determining DH°(C–C) values in rings because D°(C=C) is essentially the same for all the rearranged radicals [except that from (**11**)]. At present only order of magnitude estimates are possible because the ΔH° values used in constructing equation (4) are only approximations obtained from the GC method. The following estimate can be made for cyclobutylmethyl radicals (**1**). The activation energy for ring fission is 11.7 kcal mol^{-1} (Table 8), ΔH° can be obtained from equation (4) or by the GC method and is *ca.* −4.4 kcal mol^{-1}, the RS is 26.2 kcal mol^{-1} for the cyclobutane ring,[20] D°(C=C) is 58.6 kcal mol^{-1} for ethylene[23,24] and hence DH°[C(1)–C(2)] = 80.4 kcal mol^{-1}. This is very close to the C–C bond dissociation energy in the analogous open-chain compound, *i.e.*, DH°(Et–Pr^i) = 81 kcal mol^{-1}.[25] The 'average' C–C bond-dissociation energy in a cyclobutane ring, obtained by combining this with one quarter of the ring strain, is therefore *ca.* 74 kcal mol^{-1}. This value lies between DH°(Pr^i–Pr^i) and DH°(Bu^t–Bu^t) which are 79 and 71 kcal mol^{-1}, respectively.[25] Of course, the cyclobutane bonds appear much weaker than this because all the ring strain is released when the first bond breaks.



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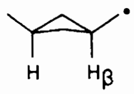

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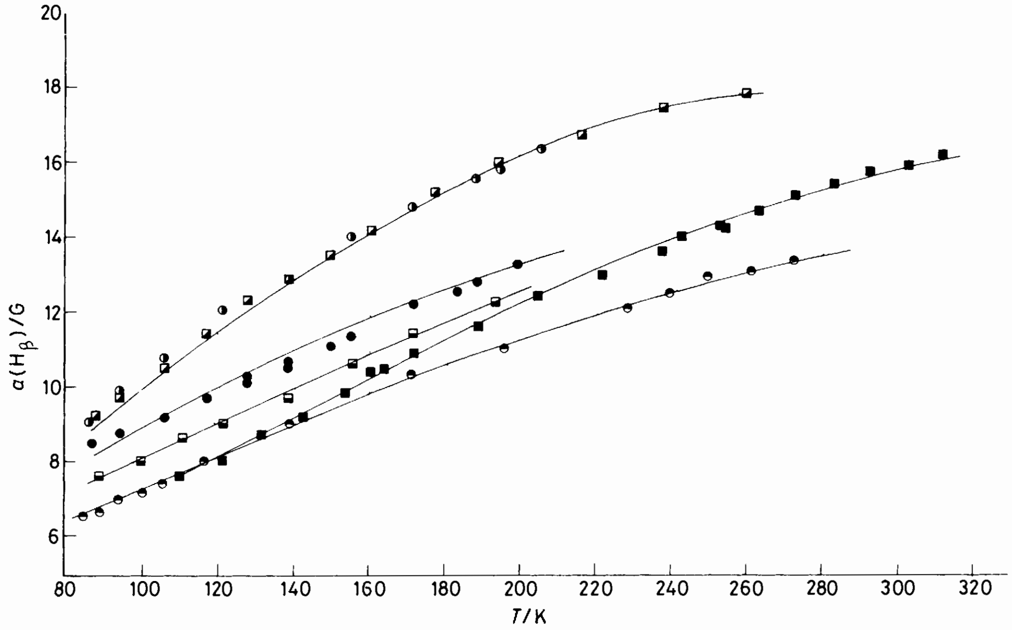


Figure 3. Temperature variation of $a(H_\beta)$ of cyclobutylmethyl radicals. Symbols have the same meaning as in Figure 1. Full lines calculated from equation (6) with parameters given in Table 9

Table 9. Barriers to rotation about $\dot{C}_\alpha$–C_1 in cyclobutylmethyl radicals

Radical		θ_0	A/G	B/G	V_0/kcal mol^{-1}
Cyclobutylmethyl-	(1)[a]	90	2	50	1.2
trans-2-Me-	**(3)**	90	3	35	1.0
cis-2-Me-	**(5)**	90	2	50	0.8
trans-3-Me-	**(6)**	90	3	35	0.8
cis-3-Me-	**(8)**	90	2	50	0.8
2,2-diMe-	**(9)**	90	3	35	0.7

[a] From reference 8.

Conformations and Barriers to Internal Rotation.—The substituted cyclobutylmethyl radicals were also studied at low temperatures in propane solution; photochemically generated triethylsilyl radicals being used in place of the trimethyltin radicals. For all the cyclobutylmethyl radicals reported in Table 1 the $a(H_\beta)$ values are relatively small but increase substantially with increasing temperature. This indicates that they, like cyclobutylmethyl itself,[2,7] adopt the bisected form **(12)** as their preferred conformation. Stereoelectronic arguments[1,5] suggest that such conformations favour ring scission because the SOMO and the bond to be broken are relatively favourably oriented. The potential barrier to rotation about the $\dot{C}_\alpha$–C_1 bond, V_0, can be estimated by fitting the observed temperature dependence of $a(H_\beta)$ with calculated values. The 'classical limit' approach leads to expression (6),[8,26] where A and B are

$$[a(H_\beta)] = A + \tfrac{1}{2}B + \tfrac{1}{2}B\cos 2\theta_0\left[\frac{I_1(\lambda)}{I_0(\lambda)}\right] \qquad (6)$$

constants, θ_0 is the value of the dihedral angle between the SOMO and the C_1–H_β bond at the potential minimum [*i.e.*, $\theta_0 = 90°$ for conformation **(12)**], and $I_1(\lambda)$ and $I_0(\lambda)$ are modified Bessel functions with $\lambda = V_0/kT$. We showed previously[8] that the temperature dependence of $a(H_\beta)$ for cyclobutylmethyl radicals **(1)** can be satisfactorily fitted by taking $A = 2$, $B = 50$, and $V_0 = 1.2$ kcal mol^{-1}. The experimental data for the methyl-substituted analogues are shown in Figure 3. Methyl substitution leads to some surprisingly large differences in the magnitude of the $a(H_\beta)$ values and in the curvature of the plots. The *cis*-2-methyl **(5)** and *cis*-3-methyl **(8)** radicals have very similar $a(H_\beta)$ values which lie above those for the *trans*-2-methyl **(3)** and *trans*-3-methyl **(6)** radicals; the 2,2-dimethyl radical **(9)** shows intermediate behaviour. We tentatively attribute these differences to changes in the average ring conformation with methyl substitution. Although the cyclobutane ring is puckered, the barrier to ring inversion is very low so that an average conformation will be registered in e.s.r. experiments. In the *cis*-3-methyl radical **(8)** steric repulsion between the methyl and methylene substituents will favour conformation **(13)** in which H_β has pseudo-axial character. Axial and equatorial β-hydrogens are known to have very different hyperfine splittings.[8] The higher $a(H_\beta)$ in **(8)** may

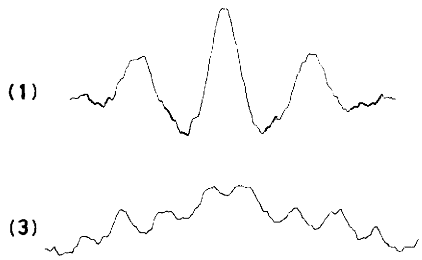
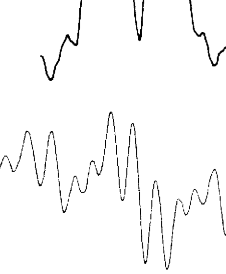


Figure 4. Fine structure on central component of the low-field triplet in the e.s.r. spectra of cyclobutylmethyl radicals. From the top: (1) at 90 K, (3) at 111 K, (5) at 122 K, (6) at 145 K, (8) at 90 K. All second harmonic presentation except (6)



(14)

therefore be a consequence of its greater axial character. The relatively high $a(H_\beta)$ in (**5**) may also be a consequence of axial character in H_β. In the *trans*-2-methyl (**3**) and *trans*-3-methyl (**6**) radicals the methyl and methylene groups are well separated and their average conformations should not be greatly different from that of (**1**). Figure 3 shows that the $a(H_\beta)$ values for (**3**) and (**6**) are indeed much closer to those of (**1**).

The V_0 values obtained by use of equation (6) are listed in Table 9. Radicals (**5**) and (**8**) have essentially the same $a(H_\beta)$ values, which show a similar rate of increase with temperature to that of $a(H_\beta)$ in (**1**). The same A and B values as were previously determined for (**1**)[8] enable good fits to the experimental data for (**5**) and (**8**) to be obtained (see Figure 3). However, in the *trans*-radicals (**3**) and (**6**) and in (**9**) the $a(H_\beta)$ values increase more slowly with temperature and lower B values coupled with higher A values are needed to reproduce the experimental trend. The fits are somewhat 'soft' and a range of A, B, and V_0 values give acceptable agreement with experiment. It is not at all obvious why different B values should be needed for the different radicals. Possibly the conformational changes suggested above lead to slightly different hybridisation at C(1) in the different radicals. This would then significantly affect the hyperconjugative interaction of the SOMO with the C_1–H_β bond and hence lead to differing A and B values. The V_0 barriers cannot be regarded as much more than order of magnitude estimates, but they do show that the barriers for all the cyclobutylmethyl radicals are significantly higher than the analogous barriers in cyclopentylmethyl and cyclohexylmethyl radicals (V_0 *ca.* 0.5 kcal mol^{-1}).[8] This lends support to our earlier suggestion[2,8] that C–C hyperconjugation involving the SOMO and the two C_1–C_γ bonds is important in determining the preferred conformations of cyclobutylmethyl radicals.

Long-range H.f.s. and Methyl Rotations.—Each of the cyclobutylmethyl radicals shows a basic triplet of doublets pattern from two α and one β hydrogen as its e.s.r. spectrum. These basic resonance lines are further split into mutliplets by long-range h.f.s. The central components of the low-field triplet from each radical are shown under high resolution in Figures 4 and 5. The unsubstituted radical (**1**) shows a triplet fine structure [a(2H) = 1.43 G] with no other splittings resolved. Similar triplet splittings are observed in radicals (**3**), (**6**), and (**8**) but not in the radicals with *cis*-methyl groups, *i.e.*, (**5**) and (**9**), which show a doublet of about the same magnitude. This splitting can therefore be attributed to the γ-hydrogens at C(2) and C(4) *cis* to the methylene radical centre. INDO calculations also indicate that the γ-*cis*-hydrogens should have appreciable h.f.s. but that the h.f.s. from the γ-*trans*-hydrogens should be negligible.[8] The *cis*-2-methyl radical (**5**) shows a double doublet structure (Figure 4) from the one *cis*-γ-hydrogen and another hydrogen which is most probably one of the δ-hydrogens at C(3) in the ring. The *trans*-3-methyl radical (**6**) shows a triplet h.f.s. from the two *cis*-γ-hydrogens and an additional quintet structure at temperatures above *ca.* 115 K. This splitting arises from the three equivalent ε-hydrogens of the *trans*-methyl group plus one other hydrogen, probably the δ-hydrogen at C(3). At lower temperatures the lines broaden because of restricted rotation of the methyl group. Unfortunately, the h.f.s. of the hydrogens in this radical at the slow exchange limit are not resolved at the lowest accessible temperature (*ca.* 90 K) and the barrier to rotation could not be determined. The *cis*-3-methyl radical (**8**) shows a triplet h.f.s. from two *cis*-γ-hydrogens and an additional triplet h.f.s. is partly resolved at the lowest temperatures (Figure 4). This additional triplet could be due to the two *trans*-γ-hydrogens, but it is more likely that it arises from one δ-hydrogen and one ε-hydrogen of the methyl group (which would be in a 'locked' conformation at 90 K). At higher temperatures this triplet h.f.s. is not resolvable, probably because rotation of the methyl group becomes appreciable. The observation of such a variety of long-range splitting in the substituted radicals supports our conclusion that subtle changes in ring conformation occur from one derivative to another.

At temperatures above *ca.* 110 K the *trans*-2-methyl radical (**3**) shows a triplet of quartets fine structure (Figure 4), which arises from the two *cis*-γ-hydrogens and the three equivalent δ-hydrogens of the methyl group. At *ca.* 90 K rotation of the methyl group is effectively 'frozen' and the e.s.r. spectrum consists of a triplet of doublets. One of the δ-hydrogens [H_δ in (**14**)] of the methyl group now occupies an all *trans*-conformation (**W**-plan) with respect to the radical centre and is responsible for the doublet splitting; the other two hydrogens [$H_{\delta'}$ in (**14**)] give negligible splitting. This situation is analogous to the 'locked' conformation of the n-propyl radical observed by Fessenden and Schuler at low temperatures,[27] except that δ-

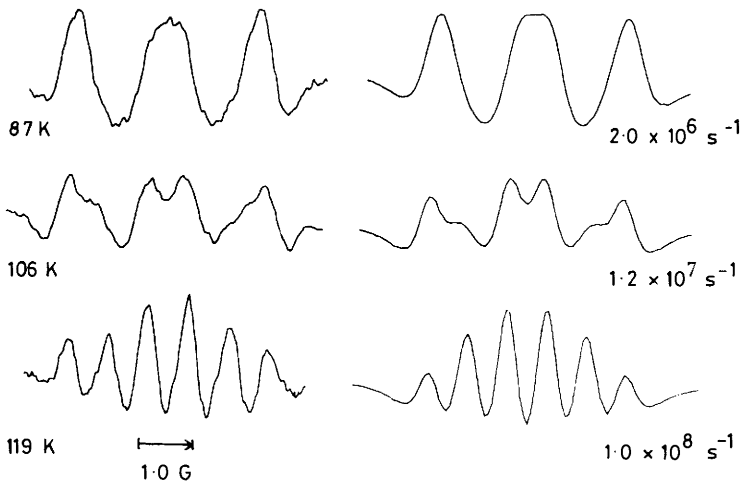


Figure 5. Exchange-broadened spectra of radical (**9**). Left: experimental. Right: computer simulations

rather than γ-hydrogens are under observation in (**3**). The e.s.r. spectrum of the 2,2-dimethyl radical (**9**) shows similar behaviour except that one of the *cis*-γ-hydrogens is absent so the spectrum changes from a double quartet at higher temperatures to a double doublet at *ca.* 90 K (Figure 5). The h.f.s. from H_δ in the 'frozen' conformations of (**3**) and (**9**) were not resolvable, but were calculated from $a(H_\delta)$ and the *average* h.f.s. of the methyl hydrogens in the fast exchange limit (see Table 1). Interestingly, all the δ-hydrogens of the methyl group in the slow exchange limit have the same sign (probably positive); opposite signs for $a(H_\delta)$ and $a(H_\delta')$ lead to the wrong type of exchange broadening. The exchange-broadened spectra from radicals (**3**) and (**9**) were simulated using a modified version of Heinzer's program.[28] Some of the simulations are shown in Figure 5. Good correspondence between the experimental and simulated spectra was obtained; the calculated Arrhenius parameters were expression (7) for (**3**) and (8) for (**9**).

$$\log(k/\mathrm{s}^{-1}) = (12.8 \pm 0.5) - (2.5 \pm 0.1 \text{ kcal mol}^{-1})/2.3\,RT \qquad (7)$$

$$\log(k/\mathrm{s}^{-1}) = (12.7 \pm 0.5) - (2.7 \pm 0.1 \text{ kcal mol}^{-1})/2.3\,RT \qquad (8)$$

As far as we know this is the first time the barrier to rotation of a methyl group has been determined for hydrocarbon radicals with δ-methyl hydrogens. The pre-exponential factors are close to 10^{13} s^{-1}, as expected for bond rotation. The methyl rotation barrier in (**3**) is slightly less than that of (**9**) as would be expected; the hydrogens of the extra methyl in (**9**) would provide greater steric hindrance. The measured barriers in (**3**) and (**9**) are less than the methyl rotation barrier in Me–CHMe$_2$, *i.e.*, 3.9 ± 0.75 kcal mol^{-1}.[29] In (**3**) and (**9**) the two adjacent carbons [C(1) and C(3)] form part of the cyclobutyl ring and will be 'tied back', thus opening up the C(1)–C(2)–Me and C(3)–C(2)–Me angles. This should lead to a lower barrier to rotation. The barriers in (**3**) and (**9**) can be compared with the methyl rotation barriers[30] in Me–CH=CH$_2$ (1.995 kcal mol^{-1}), methylcyclopropane (2.86 kcal mol^{-1}), and 2,2-difluoromethylcyclopropane (2.26 kcal mol^{-1}).

Experimental

^{1}H N.m.r. spectra were recorded on a Bruker WP80 instrument in CDCl$_3$ solutions at room temperature with Me$_4$Si as internal standard. Mass spectra were obtained with an AEI MS902 spectrometer.

Samples were prepared for e.s.r. examination sealed in Spectrosil tubes after degassing by three freeze–pump–thaw cycles. They were irradiated with light from a 500 W Wotan super pressure mercury lamp. The kinetic e.s.r. methods which were used to measure the rates of ring-opening have been described previously.[6] E.s.r. spectra were recorded with a Bruker ER200D spectrometer.

cis- *and* trans-2-*Methylcyclobutylmethyl Bromide*.—A mixture of the *cis*- and *trans*-alcohol was prepared by the method of Beckwith[1] and converted into a mixture of the bromides by reaction with PBr$_3$ under standard conditions. The mixture of bromides (b.p. 55—56 °C at 25 mmHg) was separated by preparative g.l.c. using a 15 ft. column packed with 10% FFAP on Chromosorb W at 100 °C. *trans:* δ_H 1.15 (3 H, d, *J* 6 Hz), 1.3—2.4 (6 H, m), and 3.47 (2 H, d, *J* 7 Hz); δ_C 20.9, 24.3, 25.3, 36.7, 38.3, and 45.3 p.p.m. *cis:* δ_H 1.10 (3 H, d, *J* 7 Hz), 1.25—2.25 (4 H, m), 2.25—3.0 (2 H, m), and 3.50 (2 H, dd partly resolved, *J ca.* 7 Hz, 2 Hz); δ_C 14.7, 24.7, 25.2, 31.9, 34.8, and 39.6 p.p.m.

cis- *and* trans-3-*Methylcyclobutylmethyl Bromide*.—A mixture of *cis*- and *trans*-3-methylcyclobutanecarboxylic acids was prepared from 1-bromo-2-methyl-3-chloropropane and diethyl malonate using a procedure analogous to that of Cason and Allen for cyclobutanecarboxylic acid.[31] The acid mixture was reduced to the alcohol with LiAH$_4$ and then converted into the bromide with PBr$_3$ using standard procedures. The bromide mixture (b.p. 42 °C at 15 mmHg) was separated by preparative g.l.c. on a 15 ft. column packed with 20% FFAP on Chromosorb WAW at 110 °C. *trans:* δ_H 1.04 (3 H, d, *J* 7 Hz), 1.2—1.6 (2 H, m), 2.0—2.7 (4 H, m), and 3.38 (2 H, d, *J* 8 Hz); δ_C 22.2, 25.5, 33.7, 35.6 (× 2), and 39.6 p.p.m. *cis:* δ_H 1.14 (3 H, d, *J* 7 Hz), 1.5—3.0 (6 H, m), and 3.55 (2 H, d, *J* 10 Hz); δ_C 21.8, 25.4, 33.8 (× 3), and 39.7 p.p.m.

2,2-*Dimethylcyclobutylmethyl Bromide*.—2,2-Dimethylcyclobutylmethanol was prepared by the method of Beckwith and Moad.[32] The alcohol was converted into the bromide using the method described previously.[1,2] The crude product was purified by preparative g.l.c. on a 15 ft. column packed with 10% Carbowax 20M at 120 °C. δ_H 1.08 (3 H, s), 1.15 (3 H, s), 1.5—2.7 (5 H, m), and 3.42 (2 H, dd, *J ca.* 8 Hz, 2 Hz); δ_C 21.5, 22.5, 30.3, 31.9, 34.5, 38.7, and 46.3 p.p.m.

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References

1 A. L. J. Beckwith and G. Moad, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1083.

2 K. U. Ingold, B. Maillard, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1981, 970.

3 B. Maillard, D. Forrest, and K. U. Ingold, *J. Am. Chem. Soc.*, 1976, **98**, 7024.

4 A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, and A. K. Seralis, *J. Am. Chem. Soc.*, 1980, **102**, 1734.

5 A. L. J. Beckwith and K. U. Ingold, in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, vol. 1, p. 162.

6 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317; M. Castaing, M. Ratier, P. Blum, and A. G. Davies, *J. Chem. Soc., Perkin Trans. 2*, 1979, 287.

7 P. M. Blum, A. G. Davies, and R. A. Henderson, *J. Chem. Soc., Chem. Commun.*, 1978, 569.

8 M. L. Kemball, J. C. Walton, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1017.

9 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 193.

10 H. Schuh and H. Fischer, *Int. J. Chem. Kinet.*, 1976, **8**, 341.

11 C. Huggenberger and H. Fischer, *Helv. Chim. Acta*, 1981, **64**, 338.

12 H. Schuh and H. Fischer, *Helv. Chim. Acta*, 1978, **61**, 2463.

13 H. Schuh and H. Fischer, *Helv. Chim. Acta*, 1978, **61**, 2130.

14 R. W. Gallant, *Hydrocarbon Process.*, 1970, **49**, 137.

15 E. B. Evans, *J. Inst. Pet. Technol.*, 1938, **24**, 537.

16 Landolt-Bornstein, ed. K. Schafer, Springer-Verlag, Berlin, 1969, vol. 59, p. 160 *et seq.*

17 C. Chatgilialoglu, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1981, **103**, 7739.

18 J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

19 D. C. Nonhebel and J. C. Walton, in 'Free-radical Chemistry,' Cambridge University Press, Cambridge, 1974, chs. 7 and 8.

20 S. W. Benson, in 'Thermochemical Kinetics,' 2nd edn., Wiley, New York, 1976.

21 J. M. Tedder and J. C. Walton, *Adv. Phys. Org. Chem.*, 1978, **16**, 51.

22 J. R. Bews, C. Glidewell, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1447.

23 S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502.

24 J. M. Pickard and A. S. Rodgers, *J. Am. Chem. Soc.*, 1977, **99**, 695.

25 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.

26 R. W. Fessenden, *J. Chim. Phys. Phys. Chim. Biol.*, 1964, **61**, 1570.

27 R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 7147.

28 J. Heinzer, Quantum Chemistry Program Exchange, No. 209, University of Indiana, Indiana, 1972.

29 D. R. Lide and D. E. Mann, *J. Chem. Phys.*, 1958, **29**, 914.

30 J. P. Lowe, *Prog. Phys. Org. Chem.*, 1968, **6**, 1, and references cited therein.

31 J. Cason and C. F. Allen, *J. Org. Chem.*, 1949, **14**, 1036.

32 A. L. J. Beckwith and G. Moad, *Aust. J. Chem.*, 1977, **30**, 2733.

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