The Ring-opening Reactions of Cyclobutylmethyl and Cyclobutenylmethyl Radicals

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Rate constants for the ring-opening reactions of cyclobutylmethyl, 1-cyclobutyl-1-methylethyl, and cyclobut-2-enylmethyl radicals have been determined over a range of temperatures by kinetic e.p.r. spectroscopy. The results can be represented by equations (i)—(iii), respectively. The results are compared with those for ring opening of other cycloalkylmethyl radicals. The rate constants for self-reaction of n-pentyl radicals in toluene solution have also been measured over a temperature range and found to fit relation (iv).

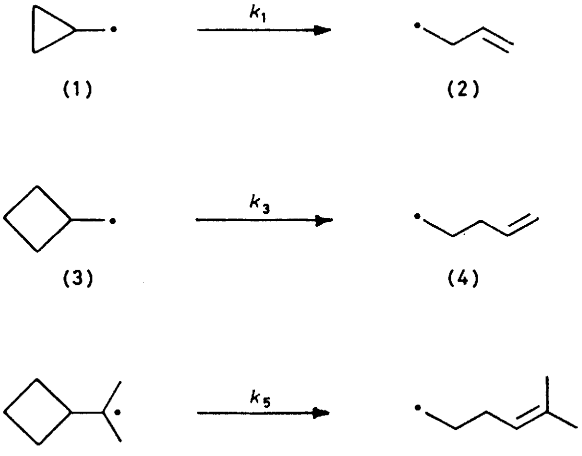
$$\log (k_3/\mathrm{s}^{-1}) = (13.1 \pm 1.4) - (49.8 \pm 7.5\ \mathrm{kJ\ mol}^{-1})/2.3RT \qquad \text{(i)}$$

$$\log (k_5/\mathrm{s}^{-1}) = (13.6 \pm 1.6) - (58.1 \pm 9.0\ \mathrm{kJ\ mol}^{-1})/2.3RT \qquad \text{(ii)}$$

$$\log (k_{10}/\mathrm{s}^{-1}) = (12.2 \pm 1.4) - (42.2 \pm 8.0\ \mathrm{kJ\ mol}^{-1})/2.3RT \qquad \text{(iii)}$$

$$\log (2k_t/\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}) = (12.3 \pm 0.7) - (10.5 \pm 3.0\ \mathrm{kJ\ mol}^{-1})/2.3RT \qquad \text{(iv)}$$

ALTHOUGH the rate constants for the cyclopropylmethyl (1) to but-3-enyl (2) rearrangement have been measured by kinetic e.p.r. spectroscopy,[1,2] and related reactions have been well studied by a variety of techniques,[3,4] the ring-opening reactions of cyclobutylmethyls have only recently begun to attract attention.[3-8] In a recent paper Beckwith and Moad reported relative rate constants for ring opening of a wide range of cyclobutylmethyl radicals, determined by treatment of cyclobutylalkyl chlorides with tri-n-butyltin hydride.[8] This prompts us to report our studies by kinetic e.p.r. spectroscopy of the ring-opening of cyclobutylmethyl (3), cyclobut-2-enylmethyl (10), and of 1-cyclobutyl-1-methylethyl (5), the latest being the first tertiary alkyl radical rearrangement to be studied by this well proven technique.[3,9]



(1) (2)

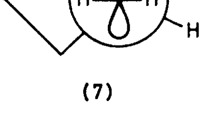
(3) (4)

(5) (6)

RESULTS

Radical (3) was generated by photolysis of cyclobutylmethyl bromide and hexamethylditin in toluene at temperatures from 148 to 313 K directly in the cavity of the e.p.r. spectrometer. This procedure gave stronger e.p.r. signals at the higher temperatures than did photolysis of the appropriate diacyl peroxide or t-butyl perester. It should be added that hexabutylditin gives good signals with the bromide, but it cannot be utilised for kinetic purposes since on photolysis it yields some n-butyl radicals which cannot be distinguished spectroscopically from radicals (4). The e.p.r. parameters for (3) at 243 K are: g 2.0026, $a^{\mathrm{H}}{}_{\alpha}$ (2 H) 2.15, $a^{\mathrm{H}}{}_{\beta}$ (1 H) 1.403, $a^{\mathrm{H}}{}_{\gamma}$ (2 H) 0.143 mT. It should be noted that only *two* γ-H atoms are resolved. The hyperfine splitting by these γ-H atoms was not observed in the only previous e.p.r. study of (3).[6] The value of $a^{\mathrm{H}}{}_{\beta}$ is relatively small but increases substantially with increasing temperature: $\partial a^{\mathrm{H}}{}_{\beta}/\partial T = +3.3\ \mu\mathrm{T/K}$ (with some curvature) from 188 to 313 K. These facts indicate that (3), like (1) [10] and like cyclobut-2-enylmethyl,[10] adopts form (7) as its preferred conformation.[10] Stereoelectronic arguments [3,8] suggest that such conformations favour ring scission because the SOMO and the bond to be cleaved are relatively favourably oriented.

At temperatures above 250 K ring opening of (3) occurs and (4) [g 2.0027, $a^{\mathrm{H}}{}_{\alpha}$ (2 H) 2.19, $a^{\mathrm{H}}{}_{\beta}$ (2 H) 2.81 mT] is detected. At temperatures above *ca.* 315 K (4) becomes the only observable radical. The measured concentrations of (3) and (4) in the temperature range 268—297 K are given in Table 1. They give, by the usual kinetic treatment,[1,3,9] $\log (k_3/2k_t^{44}/\mathrm{mol\ dm}^{-3}) = (0.75 \pm 0.75) - (39.3 \pm 4.5\ \mathrm{kJ\ mol}^{-1})/2.3RT$ where $2k_t^{44}$ is the rate constant for the bimolecular self-reaction of (4) and the errors were estimated from the scatter on the plot. Values of $2k_t$ for the n-pentyl radical [a reasonable model for (4)], which was generated from n-pentyl bromide under comparable conditions, were measured by kinetic e.p.r. spectroscopy. The results are given in Table 2. They can be represented by $\log (2k_t/\mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{s}^{-1}) = (12.3 \pm 0.7)$ -- (10.5 ± 3.0



(7)

kJ mol^{-1})/2.3RT. Hence, log (k_3/s^{-1}) = (13.05 ± 1.4) − (49.8 ± 7.5 kJ mol^{-1})/2.3RT.

Some difficulties were encountered in synthesizing the bromide which would yield (5). Treatment of 2-cyclobutylpropan-2-ol with 48% hydrogen bromide and lithium bromide yielded mainly the ring-expanded 2,2-dimethylcyclopentyl bromide. Similar difficulties were experienced by Beckwith and Moad in the preparation of the analogous chloride.[8] This radical was therefore generated *via* the intermediate alkoxycarbonyl (8) which was formed by hydrogen-atom abstraction from the appropriate formate using photochemically generated t-butoxyl in di-t-butyl peroxide as solvent.[11] At temperatures from 234 (near the f.p. of the solvent) to 260 K, radical (8) is observed as a single e.p.r. line at g 2.001 25. Radical (5) [g 2.0029, a^{H} (6 H) 2.25 mT, a^{H} (1 H) 1.58 mT at 242 K] can also be detected in this temperature range indicating that (8) undergoes β-scission. The rate constant ratio, $k_8/2k_t^{55}$, was obtained from the absolute concentrations (given in Table 3) of (8) and (5). Our data are more limited than those obtained by Griller and Roberts [12] in the same solvent for the closely related decarboxylation of t-butoxycarbonyl (9).

TABLE 1

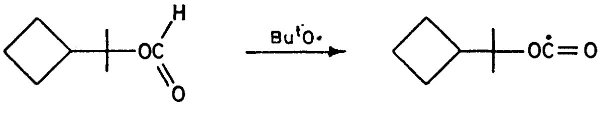
Ring-opening of cyclobutylmethyl radicals

T/K	10^8[(3)]/M	10^8[(4)]/M	$10^8k_3/2k_t^{44}$/ mol dm^{-3}
297	21.1	9.1	70.0
289	17.8	12.4	43.4
289	17.6	10.1	48.3
286	16.8	12.9	38.7
285	21.0	28.2	36.6
281	16.0	19.8	28.9
280	18.9	31.6	30.2
277	14.4	25.8	22.4
273	12.8	33.6	17.7
268	10.4	42.3	13.0

TABLE 2

Termination rate constants for n-pentyl radicals in toluene solution

T/K	$2k_t \times 10^{-9}$/ dm^3 mol^{-1} s^{-1}
292	23.8
272	21.2
247	10.4
222	7.0
192	2.56



(8)

$$(8) \xrightarrow{k_8} (5) + CO_2$$

TABLE 3

Decarboxylation of alkoxycarbonyl radicals (8)

T/K	10^8[(8)]/M	10^8[(5)]/M
234	3.29	9.61
239	1.64	15.4
241	1.21	16.2
249	0.80	21.8
260	0.54	27.6

For this reason we have made the same assumption as Griller and Roberts [12] regarding $2k_t$, *i.e.* that $2k_t = 2 \times 10^9$ mol^{-1} dm^3 s^{-1} at 303 K and that E_t 8.4 kJ mol^{-1}. (It has been suggested [13] that $2k_t$ should be increased by a factor of *ca.* 5, in which case k_9, and also k_8, would have to be increased by the same factor at each temperature.) On average, our values for k_8 were found to be *ca.* 50 times larger than Griller and Roberts' [12] values for k_9. Therefore since Griller and Roberts obtained equation (1) our data give equation (2).

$$(CH_3)_3CO\dot{C}O \xrightarrow{k_9} (CH_3)_3\dot{C} + CO_2 \quad (9)$$

$$\log(k_9/\mathrm{s}^{-1}) = (13.38 \pm 0.02) - (50.45 \pm 1.46\ \mathrm{kJ\ mol^{-1}})/2.3RT \quad (1)$$

$$\log(k_8/\mathrm{s}^{-1}) = (13.4 \pm 0.5) - (42.7 \pm 3.0\ \mathrm{kJ\ mol^{-1}})/2.3RT \quad (2)$$

At temperatures above 270 K when all (8) is gone, radical (6) starts to appear and is the only radical detectable above 310 K. The data, which are listed in Table 4, give equation (3).

$$\log(k_5/2k_t^{66}/\mathrm{mol\ dm^{-3}}) = (1.6 \pm 0.9) - (47.7 \pm 6.0\ \mathrm{kJ\ mol^{-1}})2.3RT \quad (3)$$

Values of $2k_t^{66}$ in di-t-butyl peroxide were estimated from the measured values for $2k_t$ (n-pentyl) in toluene (see Table 3) by multiplying by the measured ratio of the viscosities of toluene and di-t-butyl peroxide at 303 K.[14] At this temperature the viscosity of toluene is 0.518 cP,[15] and $\eta_{\text{toluene}}/\eta_{\text{di-t-butyl peroxide}} = 0.727$. This procedure yields equation (4).

TABLE 4

Ring-opening of 1-cyclobutyl-1-methylethyl radical

T/K	10^8[(5)]/M	10^8[(6)]/M	$10^8k_5/2k_t^{66}$/ mol dm^{-3}
309	5.7	12.2	38.4
304	6.7	10.8	28.0
301	9.8	11.1	23.7
298	10.0	6.4	10.6
295	13.0	5.8	8.30
290	11.8	7.7	12.7
288	11.7	5.8	8.68
285	11.8	6.5	9.98
281	14.0	4.0	5.18
276	16.9	5.6	7.38
276	16.5	4.4	5.6
271	17.1	1.0	1.1

$$\log(k_5/\mathrm{s}^{-1}) = (13.63 \pm 1.6) - (58.1 \pm 9.0\ \mathrm{kJ\ mol^{-1}})/2.3RT \quad (4)$$

We have previously reported that cyclobut-2-enylmethyl (10) and its trimethylsiloxy-derivative (11) undergo ring opening to form the corresponding *E,E*-pentadienyls (12) and (13) at *ca.* 230 and 270 K, respectively.[11]

(10) R = H

(11) R = OSiMe$_3$

(12) R = H

(13) R = OSiMe$_3$

We have now re-examined the ring-opening of (10) quantitatively. This radical was generated from the parent bromide using hexamethylditin in toluene as solvent. Both (10) and (12) could be detected in the temperature range 214—247 K. The measured concentrations of these two radicals (see Table 5) give equation (5). Values of

$$\log(k_{10}/2k_t^{12,12}/\text{mol dm}^{-3}) = (-0.07 \pm 0.7) - (31.9 \pm 5.0 \text{ kJ mol}^{-1})2.3RT \quad (5)$$

$2k_t^{12,12}$ were taken to be the same as those of the n-pentyl radical in toluene, given above, which yields equation (6).

$$\log(k_{10}/\text{s}^{-1}) = (12.23 \pm 1.4) - (42.2 \pm 8.0 \text{ kJ mol}^{-1})/2.3RT \quad (6)$$

Assuming that the pre-exponential factors for the ring-opening reactions of (10) and (11) are identical, then, from the temperature at which (11) undergoes ring-opening (*i.e.* 255 K) we estimate that the temperature dependence of k_{11} can be represented by equation (7).

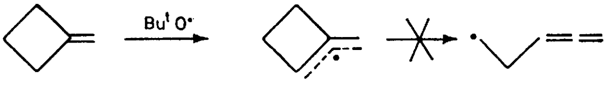
TABLE 5

Ring-opening of cyclobut-2-enylmethyl radicals

T/K	$10^8[(10)]$/M	$10^8[(12)]$/M	$10^8k_{10}/2k_t^{12,12}$/ mol dm^{-3}
214	14.6	1.26	1.37
219	11.2	1.66	1.91
222	8.96	2.41	3.06
229	11.5	3.00	3.78
230	11.6	2.97	3.73
236	5.14	3.81	7.60
241	6.47	4.89	8.59
247	2.58	5.79	18.8

$$\log(k_{11}/\text{s}^{-1}) = 12.23 - (45.1 \text{ kJ mol}^{-1})/2.3RT \quad (7)$$

The cyclobut-1-enylmethyl radical (14) was recently observed by Lunazzi *et al.*[16] We also generated (14) by hydrogen abstraction from methylenecyclobutane with t-butoxyl radicals. Our spectrum was somewhat better resolved than that of Lunazzi *et al.*, but yielded similar hyperfine splittings, *viz.* *a* (2 H) 0.410, *a* (1 H) 1.330, *a* (1 H) 1.370, *a* (1 H) 1.410, *a* (1 H) 2.380, *a* (1 H) 2.400 mT. This radical did not undergo ring-opening even at temperatures as high as 350 K, from which we estimate that $E_{14} \geqslant 70$ kJ mol^{-1}. The failure of (14) to ring-open is not surprising since both thermodynamic (allylic radical ⟶ primary alkyl radical) and stereoelectronic (the SOMO and the bond to be broken are orthogonal) factors militate against this reaction.



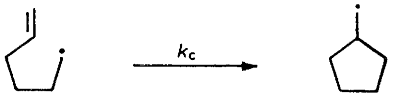
(14)

DISCUSSION

The Arrhenius parameters for the ring fission of cyclobutylmethyl obtained in the present work by e.p.r. spectroscopy enable the reliability of the tin hydride method used by other workers [8] to be assessed and, more importantly, allow it to be further refined. That is, Arrhenius parameters for primary alkyl radical rearrangements obtained by the tin hydride method depend on estimated Arrhenius parameters for the reaction of primary alkyls with the tin hydride.

$$\text{RCH}_2\cdot + \text{Bu}^n{}_3\text{SnH} \xrightarrow{k_H} \text{RCH}_3 + \text{Bu}^n{}_3\text{Sn}\cdot$$

The value of k_H has been determined at 298 K [17] but the Arrhenius parameters must be obtained indirectly from the Arrhenius equation for cyclization of hex-5-enyl [18,19] and from the results of a study of this reaction by the tin hydride method.[20]



(15) (16)

The temperature dependence of k_c has twice been measured by e.p.r. spectroscopy in our laboratory.[18,19] Although the second measurement [19] *should* have been the more accurate, it gave, after a ' correction ' to the measured radical concentration, an almost unacceptably low pre-exponential factor, A_c, of $10^{9.5}$ s^{-1}. We have now re-examined this work and conclude that not only was the correction incorrectly applied, but that it should not have been applied in any case. Without this ' correction ' A_c decreases to the totally unacceptable value of $10^{9.1}$ s^{-1}. These results should therefore be ignored. The first set of measurements [18] gave equation

$$\log(k_c/\text{s}^{-1}) = (10.7 \pm 1.0) - (32.6 \pm 4.2 \text{ kJ mol}^{-1})/2.3RT \quad (8)$$

(8). Combining this equation with values of k_c/k_H [20] yields equation (9). Combining this Arrhenius equation

$$\log(k_H/\text{s}^{-1})\ 9.5 - (20.1 \text{ kJ mol}^{-1})/2.3RT \quad (9)$$

with Beckwith and Moad's results [8] for the cyclobutylcarbinyl ring fission yields equation (10). This pre-

$$\log(k_3/\text{s}^{-1}) = 13.15 - (58.1 \text{ kJ mol}^{-1})/2.3RT \quad (10)$$

exponential factor is in good agreement with the value measured in this work, *i.e.* $10^{13.05}$ s^{-1}, but the activation energy is somewhat larger than the 49.8 kJ mol^{-1} found by e.p.r. spectroscopy.

At 333 K the tin hydride method gives $k_5 = 0.55k_3$,[8] while our own data, extrapolated to this temperature, give $k_5 = 0.16k_3$. It is perhaps worth noting that the rearrangement of (5) is the first clock reaction for the t-alkyl ' horlogerie ' which can be used over a range of temperatures.[9]

The activation energies measured by kinetic e.p.r. spectroscopy for the ring fission of a number of cycloalkylmethyl radicals are listed in Table 6 together with some thermodynamic and structural data. It is immediately obvious that the activation energies for ring fission do not correlate with ring strain,[21] nor do they correlate with the reaction enthalpies, ΔH^0, calculated by the group contribution method.[21] That this method is fairly accurate is indicated by the fact that the calculated ΔH^0 for cyclopropylmethyl (−24.6 kJ mol^{-1}) is in satisfactory agreement with an experimental value derived from the measured activation energies for ring fission[2] and for the reverse reaction, *i.e.*,[3] —13.4 kJ mol^{-1}. Errors in other calculated ΔH^0 values are probably no greater than this difference.

TABLE 6

Cycloalkylmethyl ring-opening reactions

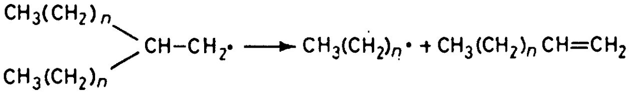
Reaction	T_f [a]/ K	E_f [b]/ kJ mol^{-1}	$a(H_\beta)$ [c]/ mT	R.S.[d]/ kJ mol^{-1}	ΔH^0 [e]/ kJ mol^{-1}
(1) →(2)	133	24.7 [f]	0.26	115.4	−24.7
(10) →(12)	240	42.2	1.11	124.6	−95.3
(3) →(4)	285	49.7	1.54	109.5	−18.8
(5) →(6)	300	58.1	1.73	109.5	−10.9
(16) →(15)		(97.6) [g]	(2.13) [h]	26.3	+64.8

[a] Temperature at which the cycloalkylmethyl radical and the ring-opened radical are equal in concentration in a typical e.s.r. experiment. [b] Activation energy for ring fission measured by e.p.r. spectroscopy. [c] Hyperfine splitting at the temperature of rearrangement (T_f). [d] Conventional ring strain from ref. 21. [e] Reaction enthalpies calculated by the group contributions method of ref. 21. [f] Result from ref. 21. [g] Calculated value from the computed ΔH^0 and the known activation energy for hex-5-enyl cyclization.[18] [h] Hyperfine splitting at 183 K;[29] value at T_f will be greater.

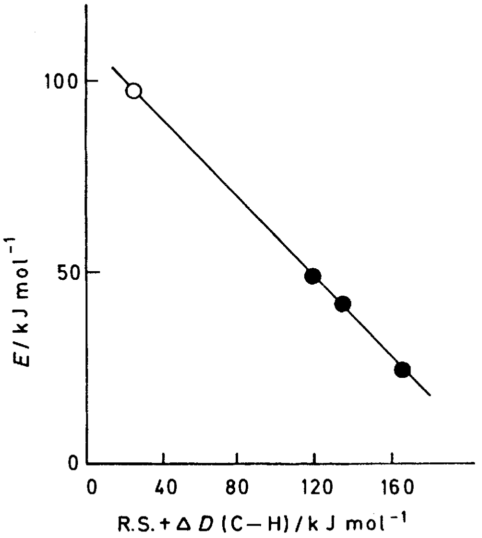
Although the activation energies for ring fission do not correlate with ΔH^0 for all the radicals listed in Table 6, it is worth noting that for the two structurally similar radicals (3) and (5) the difference in the ΔH^0 values and the difference in the activation energies are almost the same.

In cyclopropane the C–H bonds have more *s*-character and are stronger than secondary C–H bonds in n-alkanes, while the C–C bonds have more π-character and are weaker than C–C bonds in n-alkanes. The C–C bond weakening in cyclopropane is a consequence of the combined effects of conventional ring strain[21] (R. S.) and C–H bond strengthening. The extent of C–H bond strengthening in the cycloalkanes is given by the difference in C–H bond strengths for the cycloalkane and a secondary C–H in an n-alkane [ΔD(C–H)]. The activation energy for ring-opening in cycloalkylmethyl radicals might therefore be a function of the sum of ΔD(C–H) and the ring strain, *i.e.* $E = f[\text{R.S.} + \Delta D(\text{C–H})]$. The bond strength of a secondary C–H bond in an n-alkane is 395 kJ mol^{-1},[21,22] the C–H bond strength in cyclopropane was recently[23] found to be 444 kJ mol^{-1}, and the C–H bond strengths in cyclobutane and cyclopentane are 403 and 394 kJ mol^{-1} respectively.[24] On combining these values with the ring strain energies given in Table 6 the correlation shown in the Figure is obtained. There is a good straight line with a correlation coefficient of 0.9998 and it suggests that the strength of the C–C bond being broken in the cycloalkylmethyl radical is the dominant factor which controls the activation energy and hence rate of ring fission. It is unlikely, however, that all the ring strain has been released in the transition state for ring-opening.

The intercept on the activation energy axis of the correlation in the Figure (*i.e.* 111 kJ mol^{-1}) should give an estimate of the activation energy for β(C–C) bond fission in an alkyl radical such as isobutyl, where there is no ring strain and ΔD(C–H) is zero. The measured activation energy for β-scission of isobutyl radicals in the gas phase is[25] 136.5 kJ mol^{-1}, and for the similar decompositions of n-propyl[26] and n-butyl[27] radicals the measured activation energies are 136.3 and 120 kJ mol^{-1}, respectively. These values are in satisfactory agreement with the predicted value, considering the experimental errors and that the isobutyl and n-propyl radicals lose methyl rather than an n-alkyl radical.



$$\mathrm{(CH_3(CH_2)_n)_2CH{-}CH_2\cdot \longrightarrow CH_3(CH_2)_n\cdot + CH_3(CH_2)_nCH{=}CH_2}$$



Correlation of the sum of ring strain and ΔD(C–H) with the activation energies for ring fission in cycloalkylmethyl radicals. The activation energy for cyclopentylmethyl radicals (open circle) was estimated as described in the text.

The magnitudes of the $a(H_\beta)$ values for cyclopropyl-, cyclobutyl-, and cyclobut-2-enyl-methyl radicals (see Table 6) and their positive temperature coefficients indicate that the radicals have preferred conformations of type (7). This contrasts with the analogous open-chain radical, isobutyl (which adopts the alternative conformation), in which there is eclipsing between the SOMO and the β-hydrogen.[28] One reason for this difference in conformation may be that in acyclic alkyl radicals C–H hyperconjugation is better than C–C, whereas in small ring cycloalkylmethyls there is better C–C than C–H hyperconjugation. This too would stem from the weaker C–C bond with its greater π-character, which favours C–C hyperconjugation, while the stronger C–H bonds disfavour C–H hyperconjugation. These e.p.r. $a(H_\beta)$ values may in fact also reflect the weakening of the C–C bonds in the cycloalkanes, since there is a monotonic relationship between $a(H_\beta)$ at the temperature of ring scission and the experimental activation energies for the ring scission (see Table 6).

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Varian EM 360 instrument in $CDCl_3$ solutions at room temperature with tetramethylsilane as internal standard. Mass spectra were obtained with an A.E.I. MS 902 spectrometer.

The kinetic e.p.r. methods which were used to measure the rates of ring-opening and the termination rate have been described previously.[9] Varian E 104 and Bruker ER 200D instruments were employed.

Cyclobutylacetyl peroxide and the corresponding t-butyl perester were synthesised from cyclobutylacetic acid by the carbonyldi-imidazole route of Staab.[30] Photolysis of each of these peroxides in cyclopropane or toluene solutions gave rise to good e.s.r. spectra of the cyclobutylmethyl radical at low temperatures. At higher temperatures the signal to noise ratio decreased and the ring-opened radical could not be clearly identified.

Cyclobutylmethyl Bromide.—Cyclobutylmethanol (4.25 g, 0.05 mol) and triethylamine (7.6 g, 0.05 mol) in dry CH_2Cl_2 (150 ml) was stirred at −10 °C and methanesulphonyl chloride (6.3 g, 0.055 mol) added over 15 min under nitrogen. After a further 20 min, water was added and the CH_2Cl_2 layer separated, washed with 2M-HCl, 5% brine, and saturated $NaHCO_3$ solution, and dried (Na_2SO_4). The CH_2Cl_2 was removed on a rotary evaporator at room temperature. The mesylate and dry lithium bromide (7.0 g) were then refluxed in acetone (150 ml) for 5 h. The precipitate was filtered off and the acetone removed by distillation through a Vigreux column at atmospheric pressure. Water and then ether were added to the residue; the organic layer was separated and dried (Na_2SO_4) and the ether removed on a rotary evaporator at room temperature. Distillation of the resulting oil in a Vigreux flask gave cyclobutylmethyl bromide (2.0 g, 27%), b.p. 41 °C at 15 mmHg (lit.,[31] 123 °C at 710 mmHg), δ 1.5—2.3 (6 H, m), 2.3—2.9 (1 H, m), and 3.4 (2 H, d, *J* 7 Hz).

1-*Cyclobutyl*-1-*methylethyl Formate*.—2-Cyclobutylpropan-2-ol was prepared from cyclobutyl methyl ketone and methyl iodide by a standard Grignard reaction. Formic acid (95%, 0.92 g, 0.020 mol) was added to *NN'*-carbonyldi-imidazole (0.023 mol) in tetrahydrofuran and stirred at room temperature for 1 h. The alcohol (2.28 g, 0.020 mol) was then added and the solution refluxed for 5 h. The mixture was washed with water several times and residual tetrahydrofuran removed with a vacuum pump. The residual oil was distilled and examined by g.l.c. on an OV 101 column at 75 °C. This showed two peaks in the ratio 26 : 73, the former being unchanged alcohol. The larger peak was separated by preparative g.l.c. and shown to be the formate, δ 1.43 (6 H, s), 1.83 (2 H, m), 1.93 (2 H, s), 2.40 (1 H, m), and 8.03 (1 H, s).

Cyclobut-2-enylmethyl bromide and cyclobut-2-enylmethyl trimethylsilyl ether were prepared as described previously.[32]

[1/129 *Received*, 28*th January*, 1981]

REFERENCES

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

[2] A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, and A. K. Serelis, *J. Am. Chem. Soc.*, 1980, **102**, 1734.

[3] For a comprehensive review of free-radical rearrangements see 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, ch. 4.

[4] P. S. Mariano and E. Bay, *J. Org. Chem.*, 1980, **45**, 1763.

[5] M. Castaing, Thesis, Université de Bordeaux I, 1979.

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

[7] M. Castaing, M. Pereyre, M. Ratier, P. M. Blum, and A. G. Davies, *J. Chem. Soc., Perkin Trans. 2*, 1979, 287.

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

[9] D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317.

[10] J. K. Kochi, *Adv. Free-Radical Chem.*, 1975, **5**, 189.

[11] K. U. Ingold and J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1980, 604.

[12] D. Griller and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1972, 747.

[13] M. J. Perkins and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1975, 77 (see footnote on p. 81).

[14] For justification of this procedure see *e.g.* H. Schuh and H. Fischer, *Int. J. Chem. Kinet.*, 1976, **8**, 341; *Helv. Chim. Acta*, 1978, **61**, 2130, 2463; M. Lehni, H. Schuh, and H. Fischer, *Int. J. Chem. Kinet.*, 1979, **11**, 705.

[15] E. B. Evans, *J. Inst. Petrol. Tech.*, 1938, **24**, 537.

[16] L. Lunazzi, G. Placucci, and L. Grossi, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1063.

[17] D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, 1968, **90**, 7047.

[18] D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 6355.

[19] P. Schmid, D. Griller, and K. U. Ingold, *Int. J. Chem. Kinet.*, 1979, **11**, 333.

[20] See ref. 26 in ref. 8.

[21] S. W. Benson, ' Thermochemical Kinetics,' Wiley, New York, 1976, 2nd edn.

[22] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

[23] M. H. Beghal-Vayjooee and S. W. Benson, *J. Am. Chem. Soc.*, 1979, **101**, 2838.

[24] K. C. Ferguson and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2618.

[25] G. McKay and J. M. C. Turner, *Int. J. Chem. Kinet.*, 1978, **10**, 589.

[26] M. M. Papic and K. J. Laidler, *Can. J. Chem.*, 1971, **49**, 549.

[27] W. E. Morganroth and J. G. Calvert, *J. Am. Chem. Soc.*, 1966, **88**, 5387.

[28] Ref. 10, p. 235.

[29] J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, 1969, **91**, 3940.

[30] H. A. Staab, *Angew. Chem. Int. Edn. Engl.*, 1962, **1**, 351.

[31] R. C. Krug, L. W. Smith, and C. E. Fry, *J. Am. Chem. Soc.*, 1954, **76**, 3222.

[32] A. G. Davies, D. Griller, K. U. Ingold, D. Lindsay, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1981, 633.