Homolytic Ring Fission Reactions of Bicyclo[*n*.1.0]alkanes and Bicyclo[*n*.1.0]alk-2-yl Radicals: Electron Spin Resonance Study of Cycloalkenylmethyl Radicals

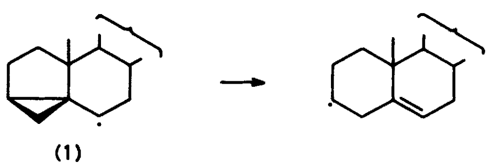
Charles Roberts and John C. Walton *
Department of Chemistry, The University, St. Andrews, Fife KY16 9ST

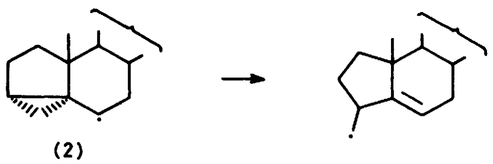
Hydrogen abstraction from bicyclo[*n*.1.0]alkanes (*n* = 3—6) by t-butoxyl radicals was examined by an e.s.r. technique. The main site of attack was C(2) giving bicyclo[*n*.1.0]alk-2-yl radicals which rearranged by β-scission of the outer cyclopropane bonds to give cycloalkenylmethyl radicals. This is in contrast to the bicyclo[*n*.1.0]alk-2-yl radicals (*n* = 1, 2) which rearranged by fission of the inter-ring bonds to give cycloalkenyl radicals. β-Scission in bicyclo[*n*.1.0]alk-2-yl radicals was examined by semi-empirical SCF MO calculations. The conformations and barriers to internal rotation of the cycloalkenylmethyl radicals were determined from the variation in the β-H hyperfine splitting constants with temperature. Photobromination of bicyclo[*n*.1.0]alkanes (*n* = 3, 4) was also investigated in CCl_4 solution. The main process was bimolecular homolytic substitution (S_H2) by bromine atoms at the cyclopropane carbons, but there was an increase in hydrogen abstraction with ring size. The S_H2 reactions parallel the β-scission reactions of the bicyclo[*n*.1.0]alk-2-yl radicals in that the main bond undergoing fission changes from the inter-ring bond to the outer cyclopropane bond as the ring size increases.

Ring opening by β-scission readily occurs in cycloalkyl radicals if the semi-occupied molecular orbital (SOMO) can asssume an eclipsed conformation with respect to the bond about to break, *i.e.* the β,γ-bond.[1] This stereoelectronic explanation accounts for the rapid β-scission of cyclopropylmethyl radicals [2] and the relatively reluctant ring opening of cyclopropyl radicals.[3,4] The stereoelectronic approach also rationalises the *selectivity* of β-scission in a number of bicycloalkyl radicals such as (1)—(3), where the β,γ-bond which cleaves is the one which overlaps most efficiently with the SOMO [5] even when this affords the thermodynamically less stable product radical.[1,5,6]

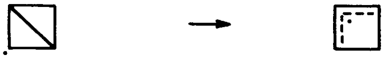
There are, however, several examples of homolytic ring fission reactions which occur in a contrastereoelectronic fashion. Bicyclo[1.1.0]but-2-yl radicals (4) and bicyclo[2.1.0]pent-2-yl radicals (5) undergo fission of the central inter-ring bond which is orthogonal to the SOMO,[7-9] probably because this leads to much greater relief of ring strain than does fission of the outer cyclopropane bonds.

The bicyclo[*n*.1.0]alkanes (6) and bicyclo[*n*.1.0]alk-2-yl radicals (7) derived from them provide a series of cyclopropylmethyl-type radicals in which ring strain and the extent of overlap of the SOMO with the β,γ-bonds varies in a systematic manner. Freeman *et al.* showed that there was very little rearrangement in the chlorination of bicyclo[3.1.0]hexane (6c) with t-butyl hypochlorite but that radical chloroformylation led to products derived from fission of both the inter-ring and outer cyclopropane bonds in approximately equal amounts.[10] Friedrich and Holmstead showed that the tri-n-butyltin hydride reductions of bicyclo[3.1.0]hex-2-yl and bicyclo[4.1.0]hept-2-yl chlorides yielded almost entirely products derived from outer cyclopropane bond fission.[11] In bicyclo[3.1.0]hexane hydrogen abstraction occurred mainly at C(2).[10] The results of a study of the ring fission reactions of the bicyclo[*n*.1.0]alk-2-yl radicals, generated by hydrogen abstraction from the corresponding hydrocarbons, are reported in this paper. Attempts to generate bicyclo[*n*.1.0]alk-2-yl radicals by chlorine abstraction from bicyclo[*n*.1.0]alk-2-yl chlorides with trialkyltin and trialkylsilyl radicals were unsuccessful.


(1)


(2)


(3)


(4)


(5)

Homolytic ring fission in cyclopropanes can also be brought about by displacement reactions (bimolecular homolytic substitution, S_H2) with halogens.[12,13] Iodination of (6a) produced exclusively 1,3-di-iodocyclobutane from fission of the inter-ring bond, but bromination and chlorination gave more complex product mixtures.[14] Bromination of (6b) gave products derived almost exclusively from fission of the inter-ring

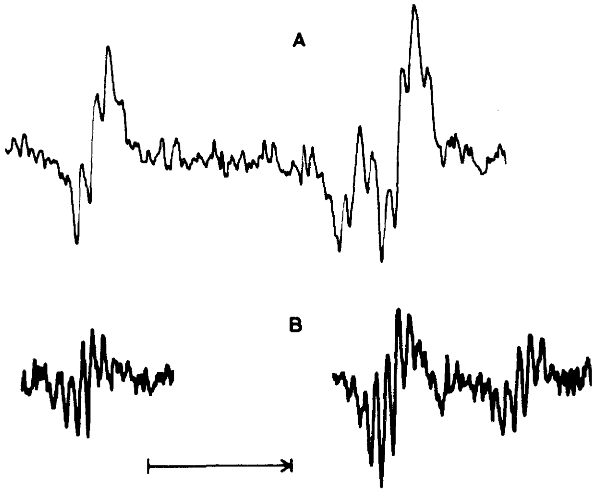


Figure 1. Low-field halves of the 9.4 GHz e.s.r. spectra of cycloalkenylmethyl radicals. Upper spectrum (A) cyclopentenylmethyl radicals at 220 K. Lower spectrum (B) cyclohexenylmethyl radicals at 150 K

bond.[8] We also report a study of the radical bromination of bicyclo[3.1.0]hexane and bicyclo[4.1.0]heptane which shows how far the S_H2 reaction of the bicycloalkanes parallels the homolytic fission of the bicycloalk-2-yl radicals (7).

Results and Discussion

E.s.r. Study of Hydrogen Abstraction from Bicyclo[n.1.0]*alkanes.*—Mixtures of the bicycloalkane and di-t-butyl peroxide were made up in cyclopropane, or other hydrocarbon solvent, degassed, and photolysed in the cavity of the e.s.r. spectrometer. Spectra were recorded at 9.4 GHz over a range of temperatures; neat di-t-butyl peroxide being used for temperatures above *ca.* 240 K.

With bicyclo[1.1.0]butane (6a) we observed the spectra of both the bicyclo[1.1.0]but-2-yl radical (7a) and the cyclobutenyl radical (8a) at low temperatures with e.s.r. parameters identical to those given by Krusic *et al.*[7] Attempts to measure the absolute concentrations of the two radicals over a range of temperatures, in order to determine the activation parameters for the rearrangement, were unsuccessful because the concentration of (7a) did not increase steadily as temperature was lowered along with a parallel decrease in the concentration of (8a). Instead the intensity of the cyclobutenyl radical (8a) spectrum increased with time of photolysis, almost independently of the solution temperature.

Examination of the contents of the e.s.r. tube after photolysis showed that cyclobutene was present in addition to unreacted (6a). The cyclobutenyl radicals abstract hydrogen from the solvent and substrate to give cyclobutene which builds up with time. Hydrogen abstraction will occur much more rapidly from the allylic positions in cyclobutene than from (6a) and therefore as soon as small quantities of cyclobutene are formed the spectrum of cyclobutenyl radicals begins to dominate. Similar behaviour was observed in other solvents and the system was abandoned as unsuitable for kinetic measurements. The fact that bicyclo[1.1.0]but-2-yl radicals can be observed at all under e.s.r. conditions implies that they rearrange appreciably more slowly than bicyclo[2.1.0]pent-2-yl radicals (7b) which cannot be detected under similar conditions because they are fully rearranged to cyclopent-3-enyl radicals at $T \geqslant 115$ K.[8] The activation energy for β-scission of radicals (7b) was estimated [8] to be $\leqslant 25$ kJ mol^{-1} and therefore the activation energy for ring fission of bicyclo[1.1.0]but-2-yl radicals must be greater than this.

Table 1. E.s.r. parameters for cycloalkenylmethyl radicals

Radical	T/K	H.f.s. (mT)
(9b)[a]	190	($2H_\alpha$) 2.10, (H_β) 0.99, (1H) 0.26, (1H) 0.11, (1H) 0.05
(9c)	225	($2H_\alpha$) 2.15, (H_β) 1.85, ($\geqslant$4H) 0.08
(9d)	150	($2H_\alpha$) 2.16, (H_β) 3.08, (>4H) 0.08
(9e)	240	($2H_\alpha$) 2.15, (H_β) 2.84
(9f)	230	($2H_\alpha$) 2.15, (H_β) 3.14

[a] From ref. 17.

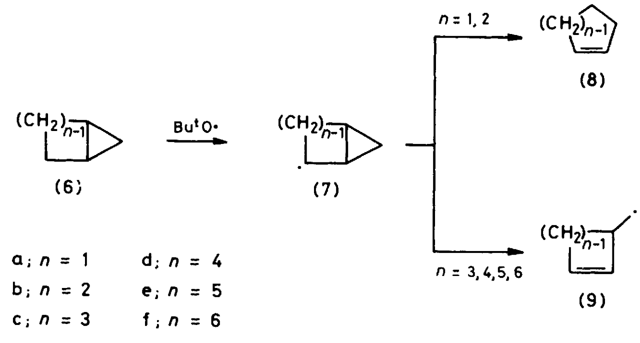
The spectrum shown in Figure 1 was obtained on hydrogen abstraction from bicyclo[3.1.0]hexane (6c). It shows a double triplet from hyperfine splittings (h.f.s.) by the two α- and one β-hydrogens, with further small h.f.s. from γ- and possibly δ-hydrogens; the e.s.r. parameters are given in Table 1. The h.f.s. of this radical are similar to those of cyclopentylmethyl radicals [15] and it can be identified as being due to cyclopentenylmethyl (9c). The spectra were very weak in cyclopropane solvent but (9c) was the only observable radical down to *ca.* 160 K below which no radicals were detectable.

The only detectable radical on H-abstraction from bicyclo[4.1.0]heptane (6d) had an e.s.r. spectrum consisting of a double triplet (Figure 1). At $T <$ *ca.* 160 K h.f.s. from γ- and δ-hydrogens were resolved. The e.s.r. parameters (Table 1) are similar to those of cyclohexylmethyl radicals [15] and we identify this radical as cyclohexenylmethyl (9d). The fact that a δ-hydrogen gives a resolvable splitting supports this identification because the structurally related but-3-enyl radicals also show a small h.f.s. from the δ-hydrogen.[16]

The cycloheptenylmethyl and cyclo-octenylmethyl radicals (9e) were the only identifiable radicals observed on hydrogen abstraction from bicyclo[5.1.0]octane (6e) and bicyclo[6.1.0]nonane (6f); the spectra were very weak and other radicals [though not (8e) or (9e)] were present. The e.s.r. parameters for (9e and f) are given in Table 1.

Our observation of radicals (9c and d) from the corresponding bicycloalkanes is in good accord with the results of Friedrich and Holmstead who obtained products mainly derived from (9c and d) on rearrangement of radicals (7c and d).[11] The participation of minor amounts of the cycloalkenyl radicals (8), as observed by Friedrich and Holmstead, is not excluded by our e.s.r. work because the signal to noise ratio was not good enough to allow minor component radicals to be detected.

There is a sharp division between radicals (7a and b) on the one hand in which the inter-ring bonds break to produce the thermodynamically more stable cycloalkenyl radicals (8), and radicals (7c—f) on the other hand in which the outer cyclopropane bonds break to give the primary cycloalkenylmethyl radicals (9) (see Scheme 1). The possibility that bicyclo[2.1.0]pent-2-yl radicals (7b) actually rearrange to give cyclobutenylmethyl radicals (9b) initially but that these rearrange to the more stable (8b) so rapidly that they are undetectable can be excluded. Radicals (9b) were previously generated from cyclobutenylmethyl bromide, detected by e.s.r. and shown not to rearrange to (8b).[17] Models indicate that for all the radicals (7a—f) the SOMO overlaps the outer cyclopropane bond more efficiently than the inter-ring bond. For the larger rings (7d—f) the SOMO can overlap the inter-ring bond when the ring adopts a boat conformation, but all other conformations favour overlap with the outer cyclopropane bond and boat conformations are unlikely to be important.[11] Therefore the stereoelectronic factor favours fission of the outer cyclopro-



Scheme 1.

Table 2. Relief of ring strain in homolytic fission of bicyclo[*n*.1.0]-alk-2-yl radicals[a]

Radical	RS(7) − RS(8)/kJ mol^{-1}	RS(7) − RS(9)/kJ mol^{-1}
(7a)	155	56
(7b)	206	107
(7c)	131	112
(7d)	98	115
(7e)	99	101
(7f)	89	105

[a] Ring strain energies (RS) of the radicals taken to be the same as in the corresponding hydrocarbons; values from ref. 18.

pane bond to give cycloalkenylmethyl radicals (9) for all members of this series (7).

The ring strain energies (RS) of radicals (7)—(9) are probably slightly less than those of the corresponding hydrocarbons which are all known.[18] Estimates of the relief of ring strain involved in the two modes of β-scission of radicals (7), based on the RS values of the hydrocarbons, are given in Table 2. For all the radicals in the series there is a large relief of strain involved in fission of either bond. The rearrangements are likely to be exothermic with the possible exception of (7a) ⟶ (9a). However, for both (7a and b) there is *ca.* 100 kJ mol^{-1} greater relief of ring strain on fission of the inter-ring bonds [(7) ⟶ (8)]. For radical (7c) there is *ca.* 20 kJ mol^{-1} greater relief of ring strain on fission of the inter-ring bond but for the rest of the radicals (7d—f) fission of the outer cyclopropane bonds leads to slightly greater relief of ring strain. Thus it seems that the much greater relief of ring strain involved in inter-ring bond fission of (7a and b) is able to outweigh the unfavourable stereoelectronic effect. In (7c) although fission of the inter-ring bond involves *ca.* 20 kJ mol^{-1} greater relief of ring strain, this is not able to outweigh the favourable stereoelectronic effect, because this radical mainly rearranges by fission of the outer cyclopropane bond. For the rest of the radicals (7d—f) both the stereoelectronic effect and the relief of ring strain favour fission of the outer cyclopropane bonds and thus the preferential formation of the thermodynamically less stable cycloalkenylmethyl radicals (9) can be explained.

Semi-empirical SCF MO Calculations.—Semi-empirical MO calculations cannot give a quantitative measure of the extent of overlap of the SOMO with the orbitals forming the β,γ-bonds. We have shown, however, that in cycloalkylmethyl and bicycloalkyl radicals the optimised geometries have increased β,γ-bond lengths and decreased α,β-bond lengths relative to the hydrocarbon precursors.[9] *Ab initio* calculations on simpler alkyl radicals show similar trends in the bond lengths.[19] This extension of the β,γ-bonds in the radicals gives an indication of the weakening of the individual bonds by overlap with the SOMO, and other factors. Furthermore, the enthalpies of reaction ($\Delta H^{\ominus}$) and enthalpies of activation ($\Delta H^{\ddagger}$) can be computed to reveal the relative importance of thermodynamic and kinetic factors in the rearrangements.

Table 3. Semi-empirical MNDO and MINDO/3[a] calculations for β-scission of bicyclo[*n*.1.0]alk-2-yl radicals

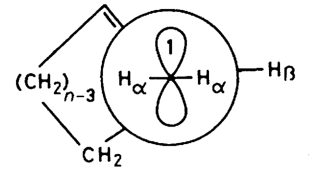
Reaction	Inter-ring bond[b]	Outer cyclopropane bond[c]	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}
(7a) ⟶ (8a)	0.08 (0.07)		−164 (−59)	
(7a) ⟶ (9a)		0.00 (0.00)	−35 (55.2)	
(7b) ⟶ (8b)	0.02 (0.03)		−152 (−123)	50 (21)
(7b) ⟶ (9b)		0.02 (0.02)	−30 (+2)	97 (84)
(7c) ⟶ (8c)	0.02		−66	87
(7c) ⟶ (9c)		0.02	−13	98
(7d) ⟶ (8d)	0.02		−32	94
(7d) ⟶ (9d)		0.02	−1	95

[a] MINDO/3 results in parentheses. [b] Increase in inter-ring bond length relative to hydrocarbon precursor. [c] Increase in outer cyclopropane bond length relative to the hydrocarbon precursor.

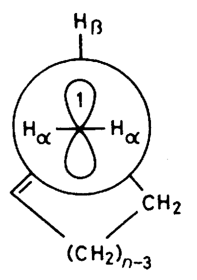
SCF MO calculations were carried out for the rearrangements of the first four bicycloalkyl radicals in the series *i.e.* (7a—d) using the MNDO procedure of Dewar and Thiel;[20,21] some calculations were also made using the earlier MINDO/3 method[22,23] which has some advantages for free radicals.[9,20] Geometries were fully optimised with respect to all bond lengths, bond angles, and dihedral angles. Enthalpies of activation were calculated by taking a series of increasing values of each β,γ-bond in turn and optimising the geometry with respect to all other variables. The calculated extensions of the β,γ-bonds in the radicals (7) as compared with the bicycloalkanes (6) are given in columns 2 and 3 of Table 3. Both the MNDO and MINDO/3 calculations predict a large extension of the inter-ring bond in the bicyclo[1.1.0]but-2-yl radical (7a) but negligible extension of the outer cyclopropane bond. This extension, and hence weakening, of the inter-ring bond is almost certainly not due to overlap with the SOMO. In (7a) there is flattening at the radical centre; although this does not go so far that the SOMO becomes a pure *p* orbital. Both MNDO and MINDO/3 predict a non-planar radical centre for (7a), the calculated deviations from planarity being 8 and 20° by the two methods, respectively. These predicted values span the out-of-plane angle (15°) deduced by comparing the experimental e.s.r. h.f.s. with those calculated by the INDO method for a range of out-of-plane angles.[16] This flattening causes (or is accompanied by) opening up of the $C\dot{C}C$ angle and hence a lengthening of the opposite inter-ring bond. The calculations suggest therefore that radical (7a) rearranges by fission of the inter-ring bond because this is weakened to a much greater extent than the outer cyclopropane bond.

The calculations predict radicals (7b—d) to be essentially planar at the radical centre. However, the opening up of the $C\dot{C}C$ angle which is associated with this flattening is not so great for any of these radicals as for (7a) because of the larger rings. Hence there are only small extensions of the β,γ-bonds, comparable with those in cycloalkylmethyl radicals,[9] and the inter-ring bonds and outer cyclopropane bonds show about the same extension (Table 3). The predicted bond extensions do not provide a good indicator of which β,γ-bond will break, except when large extensions are found as in (7a).

The calculated enthalpies of activation are given in Table 3 for radicals (7b—d). Neither the MNDO nor MINDO/3 methods were successful in calculating the reaction co-ordin-



(10)



(11)

ate for β-scission of bicyclo[1.1.0]but-2-yl radicals (7a). Extending the β,γ-bonds led to catastrophic descents in the energy or failure to converge; the use of other geometrical parameters, such as the inter-ring angle, was equally unsuccessful. It appears that the rearrangement involves crossing from one potential energy surface to another, or across a fold in the potential energy surface and configuration interaction will be required to handle this situation. Similar difficulties were encountered with the computation of β-scission in the structurally related cyclopropyl radicals.[9] Both the MNDO and MINDO/3 calculations correctly predict much lower $\Delta H^\ddagger$ values for β-scission of the inter-ring bond in (7b) and the MNDO results also show that $\Delta H^\ddagger$ for inter-ring bond scission increases with the size of the ring containing the radical centre, *i.e.* from (7b) to (7d). For radicals (7c and d) the calculations show inter-ring bond fission to be more exothermic, as would be expected. However, little difference in the $\Delta H^\ddagger$ values for the two modes of β-scission was found, whereas the experimental results indicate virtually exclusive scission of the outer cyclopropane bonds. The experimental activation energies for β-scission of (7b—d) were <25 kJ mol^{-1} and thus the computations overestimate the barriers in each case.

Conformations of Cycloalkenylmethyl Radicals and Barriers to Internal Rotation.—The absolute magnitude of the β-H h.f.s. and the fact that $\partial a(H_\beta)/\partial T$ has a positive sign (see Figure 2) for cyclobutenylmethyl and cyclopentenylmethyl radicals proves [16] that these radicals prefer the bisected conformation (10). For cyclohexenylmethyl radicals the absolute magnitude of $a(H_\beta)$ and the negative sign of $\partial a(H_\beta)/\partial T$ prove that these radicals prefer the eclipsed conformation (11). The absolute magnitudes of the β-h.f.s. for the cycloheptenylmethyl and cyclo-octenylmethyl radicals suggest that they too prefer the eclipsed conformation (11). Therefore the cycloalkenylmethyl radicals show an exact parallel to the cycloalkylmethyl radicals which exhibit the same change in preferred conformation between the radicals with five- and six-member rings,[15] and the change can be accounted for in similar terms.

The more important steric effects are revealed by calculating the distances between the α-hydrogens and the β- and γ-hydrogens for the cycloalkenylmethyl radicals in the bisected (10) and eclipsed (11) conformations. There are, however, a number of imponderables which introduce uncertainty into the results. These include the $\dot{C}$–C_β bond lengths,* the degree of puckering in the rings, the precise configurations (planarity or otherwise) of the radical centres in the eclipsed conformations,[24,25] *etc.* We report in Table 4 the more important (*i.e.* shorter) H–H inter-atomic separations we have calculated using 'rationalised' geometries,[15] *viz.* a planar conformation for all radical centres with $\dot{C}$–H_α 1.08, $\dot{C}$–C_β 1.48, C_β–H 1.12 Å, and $H_\alpha\dot{C}H_\alpha$ 120°. The rest of the radical structures were taken from the optimised MNDO geometries.

Table 4. Calculated H–H distances (Å) for cycloalkenylmethyl radicals [a]

	Cyclobutenyl-methyl		Cyclopentenyl-methyl		Cyclohexenyl-methyl	
	E(11)	B(10)	E(11)	B(10)	E(11)	B(10)
H_α–H_β	2.79	2.41	2.77	2.38	2.76	2.34
H_α–H_β	2.79	3.12	2.77	3.11	2.76	3.08
H_α–$H_{\gamma'}$	4.18	3.90	3.99	3.54	3.77	3.29
H_α–H_γ	2.72	3.67	2.42	3.40	2.67	3.35
H_α–H_γ	3.57	4.07	3.36	3.84	2.73	3.64
H_α–$H_{\gamma'}$	3.10	3.45	2.70	3.32	2.48	3.04
H_α–H_γ	3.74	2.81	3.61	2.70	3.60	2.68
H_α–H_γ	4.39	3.93	4.27	3.84	3.90	3.34

[a] For structural parameters and assumptions see text. γ′ represents the alkenyl γ-hydrogens.

An examination of Table 4 shows that except for one factor the steric situation in a given cycloalkenylmethyl radical closely resembles that in the analogous cycloalkylmethyl radical.[15] In the bisected conformations (10) the shortest H–H distance for all radicals is the unique (eclipsed) H_α–H_β separation at 2.34—2.41 Å. For cyclohexenylmethyl radicals (and probably larger cycloalkenylmethyl radicals) this repulsive H_α–H_β interaction dominates all others and causes these radicals to adopt the eclipsed conformation (11). In the cyclopentenylmethyl radical steric factors are quite similar for the two conformations but evidently the H_α–H_γ repulsions of 2.42 and 2.70 Å together with the two H_α–H_β interactions at 2.77 Å in the eclipsed conformation (11) outweigh the H_α–H_β interaction (2.38 Å) and the H_α–H_γ interaction of 2.70 Å in the bisected form and the radical adopts the bisected conformation (10). The main difference between the cycloalkenylmethyl and the cycloalkylmethyl radicals comes from the alkenic γ′-hydrogens. These $H_{\gamma'}$ lie close to an α-hydrogen in the eclipsed conformations of cyclohexenylmethyl and cyclopentenylmethyl radicals and although this steric factor does not cause any change in the preferred conformations it may contribute to the higher barriers to rotation about the $\dot{C}$–C_β bonds.

For cyclobutenylmethyl radicals, as for cyclobutylmethyl radicals,[15] simple steric arguments break down because they predict that the eclipsed conformation should be preferred. Following our earlier suggestion,[15] we propose that the conformation of the cyclobutenylmethyl radical is determined by electronic effects: specifically by C–C hyperconjugation involving $\dot{C}$ and the C_β–C_γ bonds.

The potential barrier to rotation about the $\dot{C}$–C_β bond, V_0, can be estimated by fitting the observed temperature dependence of $a(H_\beta)$ with calculated values. A classical limit approach [16,26] has been shown to give essentially the same results for small primary alkyl radicals as a more cumbersome quantum mechanical procedure.[27] We have shown [15] that the integrals involved in the classical limit procedure can be evaluated to give the analytical expression (1) for $a(H_\beta)$ where

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

$I_1(\lambda)$ and $I_0(\lambda)$ are modified (hyperbolic) Bessel functions, $\lambda = V_0/kT$, θ_0 is the value of the dihedral angle θ at the potential

---

* MNDO calculations predict $\dot{C}$–C_β bond lengths increasing from (9b) to (9d).

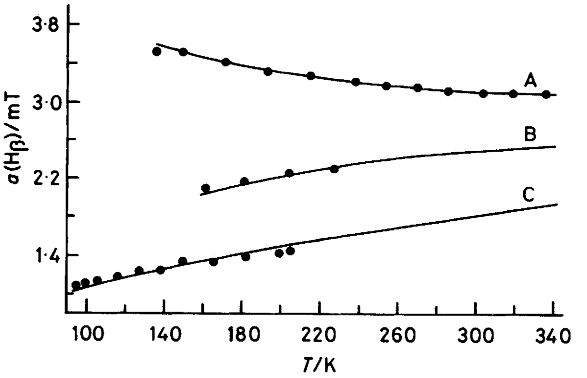


Figure 2. Variation of $a(\mathrm{H}_\beta)$ with temperature; curve A, cyclohexenylmethyl radicals; curve B, cyclopentenylmethyl radicals; curve C, cyclobutenylmethyl radicals. Filled circles, experimental data, full curves calculated from the equation given in the text

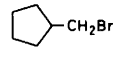
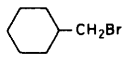
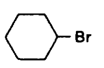
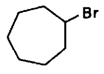
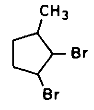
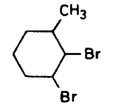
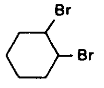
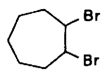
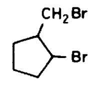
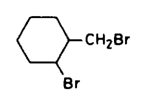
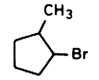
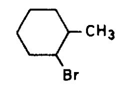
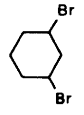
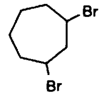
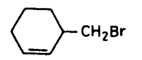
Table 5. Barriers to rotation about the $\dot{C}_\alpha$–C_β bonds in cycloalkenylmethyl radicals

Radical	θ_0(°)	A	B	V_0/kJ mol^{-1}
c–$C_6H_9CH_2\cdot$	0	0	46	1.9
c–$C_5H_7CH_2\cdot$	90	2	50	2.5
c–$C_4H_5CH_2\cdot$	90	3	48	6.0

minimum, and A and B are constants. The experimental $a(\mathrm{H}_\beta)$ values have been fitted to the calculated values using this expression and adjusting A, B, and V_0 for best fit. The full curves in Figure 2 were calculated using the parameters listed in Table 5 and excellent fits to the experimental results were obtained. The optimum values of A and B for the cyclohexenylmethyl and cyclopentenylmethyl radicals were identical to those found for cyclohexylmethyl and cyclopentylmethyl radicals, respectively, and the optimum constants for cyclobutenylmethyl radicals were only slightly different from those of cyclobutylmethyl radicals. In each case, however, the barrier to rotation, V_0, was found to be greater in the cycloalkenylmethyl radical than in the corresponding cycloalkylmethyl radical. The increase may be partly due to steric effects and partly to electronic factors. The V_0 value for cyclobutenylmethyl radicals is appreciably greater than the V_0 values of other cycloalkenylmethyl radicals. This radical should have the least steric hindrance to rotation about the $\dot{C}$–C_β bond (see Table 4), hence it is clear that other factors (probably the C–C hyperconjugation referred to above) are operative in this radical.

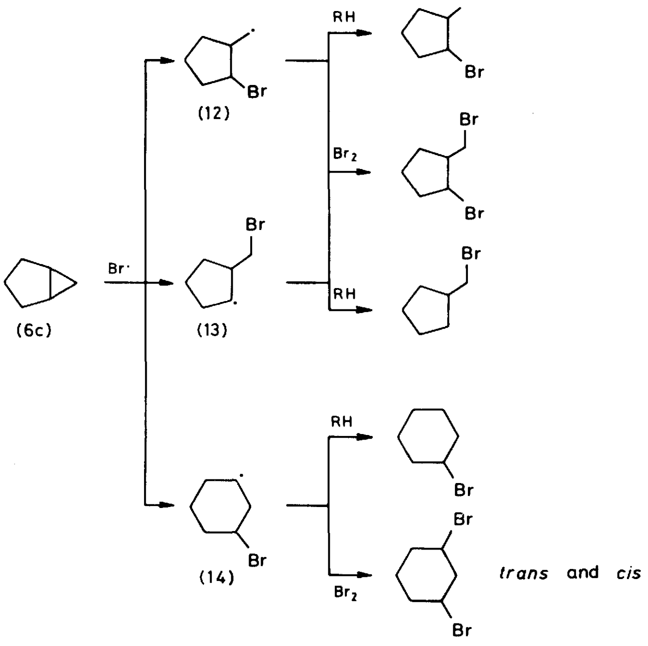
We showed previously that MNDO calculations were not successful at predicting the preferred conformations in cycloalkylmethyl radicals although INDO [28] calculations were.[15] We find that neither MNDO nor INDO calculations correctly predict the preferred conformations for the cycloalkenylmethyl radicals (9b—d). Barriers of approximately the right magnitude are calculated, but the energy differences between conformers (10) and (11) are very small and it is beyond the power of these techniques to correctly identify the preferred type.

Table 6. Products and yields in the photobromination of bicyclo[3.1.0]hexane (6c) and bicyclo[4.1.0]heptane (6d) in CCl_4 at 20 °C

(6c) Product	Yield[a]	(6d) Product	Yield[a]
	9·0		8·1
	17·7		1·4
	4·1[b]		42·5[b]
	3·7[c]		5·6[c]
	17·8[b]		17·0[b]
	8·7[b]		18·8[b]
	*trans* 20·0 *cis* 18·7		5·6[b]
			0·9

[a] Yields are mol % relative to the total products. [b] Mixture of isomers. [c] *trans*-Isomer.

Photobromination of Bicyclo[3.1.0]*hexane and Bicyclo*[4.1.0]*heptane*.—Reaction of bicyclo[3.1.0]hexane (6c) with molecular bromine in CCl_4 solution at 20 °C proceeded rapidly and was complete in a few minutes; rather longer was required for conversion of (6d). The main products together with their yields are given in Table 6. The product distribution from (6c) was quite different from that found in the electrophilic bromination,[29] but the small amounts of *trans*-1,2-dibromides can probably be attributed to electrophilic processes concurrent with the main radical reaction.[15,30] The main products were formed by bimolecular substitution reactions ($S_{\mathrm{H}}2$) of bromine atoms and the bicycloalkanes. Scheme 2 shows the main reaction sequences for (6c) and analogous processes are operative with (6d). Bromine atoms attack at the methylene carbon of the cyclopropane ring to give intermediate radicals (13) and at the bridgehead carbon atoms to give radicals (12), by fission of the outer cyclopropane bond, and (14) by fission of the inter-ring bond. The intermediate radicals then abstract bromine from molecular bromine or abstract hydrogen from more substrate (or from HBr produced in solution) to give the observed products. The ratio of *trans*- to *cis*-1,3-dibromocyclohexanes formed from (14) was 1.1. Direct photobromination of bromocyclohexane was shown to give 1,3-dibromocyclohexanes by reaction of the same radical (14) with molecular bromine.[31] The observed *trans* : *cis* ratio (1.3) [31] was close to the ratio found from bromination of (6c) and this lends support to the proposed mechanism. The presence of 2,3-dibromo-1-methylcycloalkanes and 3-(bromomethyl)cyclohexene amongst the products indicates that some hydrogen abstraction occurs at C(2) to give bicyclo[*n*.1.0]alk-2-yl radicals (7) which rearrange by fission of the outer cyclopropane bonds giving cycloalkenyl-



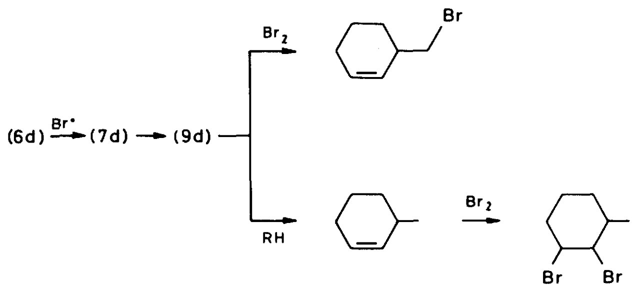
Scheme 2.

methyl radicals (9). These radicals then abstract bromine or hydrogen and finally the methylcycloalkenes add bromine (Scheme 3). The high proportion of 2,3-dibromo-1-methylcyclohexanes obtained from (6d) indicates that the importance of hydrogen abstraction increases with the ring size of the bicycloalkane. Chlorination of (6d) gave rise to a very complex mixture of products [32] but the main reactions were analogous to those found in bromination.

The extent of bromine atom attack at the bridgehead carbon relative to attack at the cyclopropane methylene carbon cannot be determined, because the 1-bromo-2-(bromomethyl)cycloalkanes could be formed by either route (see Scheme 2). Bromine atoms induce exclusive fission of the inter-ring bond in bicyclo[2.1.0]pentane, fission of both the inter-ring bond and the outer cyclopropane bond in bicyclo[3.1.0]hexane, and predominant fission of the outer cyclopropane bond in bicyclo[4.1.0]heptane. The ratio of the amount of outer cyclopropane bond fission to the amount of inter-ring bond fission can be determined from the relative amounts of the products formed by the two routes and values of 0.0, 0.6, and 6.3 are found for (6b, c, and d), respectively. This changeover from inter-ring bond fission to outer cyclopropane bond fission with increasing ring size of the bicycloalkanes parallels the same changeover which was observed in the β-scission of the bicyclo[*n*.1.0]alk-2-yl radicals but the change is less abrupt. The changeover in the S_H2 reactions can also be accounted for in terms of relief of ring strain. The ring strain released by inter-ring bond fission decreases very sharply from (6b) to (6d) but the ring strain released by outer cyclopropane bond fission increases slightly (*cf.* Table 2).

Experimental

^{1}H N.m.r. spectra were recorded on a Bruker WP 80 instrument in CCl$_4$ solutions at room temperature with tetramethylsilane as internal standard. Mass spectra were obtained with an A.E.I. MS 902 spectrometer. G.l.c. analyses were carried out with a modified Griffin and George D6 gas density balance chromatograph and a Pye 105 instrument. Columns packed with 10% SE 30 and TTP on Chromosorb G as solid support were employed. E.s.r. spectra were obtained with a



Scheme 3.

Bruker ER 200D spectrometer, samples being degassed, sealed in Spectrosil quartz tubes, and photolysed directly in the cavity with light from a 500-W medium-pressure mercury arc.

Bicyclo[1.1.0]butane (6a) was prepared from 1-bromo-3-chlorobutane by the method of Lampman and Aumiller.[33] Final purification was achieved by preparative g.l.c. using a 20 ft column packed with 12% ββ'-oxydipropiononitrile at 25 °C. The product was >99.5% pure and the ^{1}H n.m.r. spectrum agreed with the literature.

Bicyclo[3.1.0]hexane, bicyclo[4.1.0]heptane, bicyclo[5.1.0]octane, and bicyclo[6.1.0]nonane (6c—f) were prepared by Simmons–Smith reaction [34,35] of cyclopentene, cyclohexene, cycloheptene, and cyclo-octene, respectively. The products were purified by preparative g.l.c. using the ββ'-oxydipropiononitrile column; final purity was >99%. The ^{1}H n.m.r. spectra agreed with the literature.[35–37]

Bromination of Bicyclo[3.1.0]*hexane.*—Bromine (60 μl) in deaerated CCl$_4$ (250 μl) was added dropwise to a deaerated solution of (6c) (0.2 g) in CCl$_4$ (250 μl) maintained at 20 °C. On illumination with a tungsten lamp a vigorous reaction occurred and the bromine colour disappeared immediately. G.l.c. analysis on the TTP column showed eight main products, some of which were incompletely resolved. The components were separated by preparative g.l.c. and examined by ^{1}H n.m.r. spectroscopy. Peak 1 gave bromomethylcyclopentane; the n.m.r. spectrum was identical to that of authentic material; [15] peak 2 gave bromocyclohexane; peak 3, δ_H 1.0—1.2 (3 H, two d, J 6 Hz), 2.5—3.6 (5 H, m), and 4.2—4.7 (2 H, m), was a mixture of 1,2-dibromo-3-methylcyclopentane isomers; peak 4 was *trans*-1,2-dibromocyclohexane with n.m.r. spectrum identical to that given in the literature; [31] peak 5, δ_H 1.5—2.5 (7 H, m), 3.55 (2 H, d, J 7 Hz), and 3.9 (1 H, m), was 1-bromo-2-(bromomethyl)cyclopentane; peak 6, δ_H 1.05 (3 H, d, J 7 Hz), 1.3—2.2 (8 H, m), and 4.0—4.4 (1 H, m), was 2-(bromomethyl)cyclopentane; peaks 7 and 8 were *trans*- and *cis*-1,3-dibromocyclohexane with n.m.r. spectra the same as those in the literature.[31] The peaks were also examined by g.l.c.–mass spectrometry which provided corroborating evidence. The identities of peaks 1, 2, 4, 7, and 8 were confirmed by retention time comparisons with authentic materials. The proportions of the various products are shown in Table 6.

Bromination of Bicyclo[4.1.0]*heptane.*—Bromine (60 μl) in deaerated CCl$_4$ (250 μl) was added slowly to a solution of (6d) (0.2 g) in deaerated CCl$_4$ (250 μl) at 20 °C. The mixture was irradiated with light from a tungsten lamp and all the bromine colour was discharged in *ca.* 20 min. G.l.c. analysis showed eight main products, some of which were incompletely resolved. The components were separated by preparative g.l.c. and examined by ^{1}H n.m.r. spectroscopy. Peak 1 was bromomethylcyclohexane; the n.m.r. spectrum was similar to that of authentic material; [15] peak 2 was bromocycloheptane;

peak 3 δ_H 1.22 (3 H, d, J 7 Hz), 1.3—2.5 (9 H m), and 3.73 (1 H, dq), was bromo-2-methylcyclohexane; peak 4, δ_H 1.6—2.4 (m), 3.35 (d, J 7 Hz), and 5.6—6.0 (m), was 3-(bromomethyl)cyclohexene; peak 5, *trans*-1,2-dibromocycloheptane; peak 6, δ_H 1.05 (3 H, d, J 7 Hz), 1.4—2.6 (7 H, m), 4.5—4.9 (2 H, m) and δ_H 1.30 (3 H, d, J 7 Hz), 1.4—2.6 (7 H, m), and 3.6—4.2 (2 H, m), contained two isomers of 1,2-dibromo-3-methylcyclohexane; peak 7, δ_H 1.2—2.3 (m), 3.70 (d, J 7 Hz), and 4.1—4.8 (m), was 1-bromo-2-(bromomethyl)cyclohexane; peak 8 gave *trans*- and *cis*-1,3-dibromocycloheptane.[31] The components were also examined by g.l.c.–mass spectrometry which provided supporting evidence of the structures. The identities of peaks 1,2, 5, and 9 were confirmed by retention time comparisons with authentic samples. The proportions of the various products are given in Table 6.

References

1 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. 161.
2 B. Maillard, D. Forrest, and K. U. Ingold, *J. Am. Chem. Soc.*, 1976, **98**, 7024.
3 J. T. Groves and K. W. Ma, *J. Am. Chem. Soc.*, 1974, **96**, 6527.
4 K. Herwig, P. Lorenz, and C. Rüchardt, *Chem. Ber.*, 1975, **108**, 1421.
5 A. L. J. Beckwith and G. Phillipou, *Aust. J. Chem.*, 1976, **29**, 123.
6 A. L. J. Beckwith and G. Moad, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1083.
7 P. J. Krusic, J. P. Jesson, and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 4566.
8 C. Jamieson, J. C. Walton, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1366.
9 J. Bews, C. Glidewell, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1282, 1447.
10 P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, 1968, **33**, 1448.
11 E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, 1972, **37**, 2550.
12 C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, 1962, **84**, 3326.
13 J. M. Tedder and J. C. Walton, *Adv. Free-Radical Chem.*, 1980, **6**, 155.
14 K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 1965, **21**, 2749.
15 K. U. Ingold, M. J. Kemball, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1017.
16 J. K. Kochi, *Adv. Free-Radical Chem.*, 1975, **5**, 189.
17 K. U. Ingold and J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1980, 604.
18 S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1976, 2nd edn., p. 273.
19 J. Pacansky and M. Dupuis, *J. Chem. Phys.*, 1978, **68**, 4276; 1979, **71**, 2095.
20. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899, 4907.
21 W. Thiel, Quantum Chemistry Program Exchange, No. 353, University of Indiana, Indiana, 1978.
22 R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285.
23 M. J. S. Dewar, Quantum Chemistry Program Exchange, No. 309, University of Indiana, Indiana, 1976.
24 J. Pacansky and M. Dupuis, *J. Chem. Phys.*, 1980, **73**, 1867.
25 J. Pacansky and W. Schubert, *J. Chem. Phys.*, 1982, **76**, 1459.
26 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1971, **93**, 846.
27 R. W. Fessenden, *J. Chim. Phys. Phys. Chim. Biol.*, 1964, **61**, 1570.
28 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
29 J. B. Lambert, R. D. H. Black, J. H. Shaw, and J. J. Papay, *J. Org. Chem.*, 1970, **35**, 3214.
30 K. J. Shea and P. S. Skell, *J. Am. Chem. Soc.*, 1973, **95**, 6728.
31 D. S. Ashton, J. M. Tedder, M. D. Walker, and J. C. Walton, *J. Chem. Soc., Perkin Trans 2*, 1973, 1346.
32 R. S. Boikess, M. MacKay, and D. Blithe, *Tetrahedron Lett.*, 1971, 401.
33 G. M. Lampman and J. C. Aumiller, *Org. Synth.*, 1971, **51**, 55.
34 H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, 1959, **81**, 4256.
35 F. LeGoff, *J. Org. Chem.*, 1964, **29**, 2048.
36 D. I. Shuster and F.-T. Lee, *Tetrahedron Lett.*, 1965, 4119.
37 H. Blancou and E. Casadevall, *Tetrahedron*, 1976, **32**, 2907.

Received 6th *September* 1982; *Paper* 2/1533