

## Cycloalkylmethyl Radicals. Part 3.<sup>1</sup> Dynamic Stereochemistry of Axial and Equatorial Cyclohexylmethyl and 4-Alkylcyclohexylmethyl Radicals

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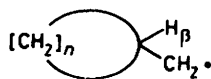
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For cyclohexylmethyl and 4-alkylcyclohexylmethyl radicals the conformer in which the  $\text{CH}_2^\bullet$  group adopts the axial position and that in which the  $\text{CH}_2^\bullet$  group adopts the equatorial position can both be observed by e.s.r. spectroscopy. At 140 K the axial conformers have  $a(\text{H}_\beta)$  ca. 42–43 G; the equatorial conformers have  $a(\text{H}_\beta)$  ca. 30–31 G. For *cis*-4-methylcyclohexylmethyl radicals the ratio of the concentrations of the two conformers was studied as a function of temperature and shown to depend on the rate of radical ring inversion vs. the radical lifetime; the rate constant for ring inversion was obtained. As a check on the e.s.r. results the conformational equilibrium of *cis*-4-methylcyclohexylmethyl bromide was studied by  $^1\text{H}$  n.m.r. spectroscopy, which gave  $-\Delta G_{300}^\circ(\text{CH}_2\text{Br}) = 1.91$  kcal mol<sup>-1</sup>. The relative conformer concentrations were also measured as a function of temperature for cyclohexylmethyl radicals and the conformational free energy difference of the  $\text{CH}_2^\bullet$  group ( $-\Delta G_{300}^\circ$ ) was found to be 0.71 kcal mol<sup>-1</sup>. The preponderance of the conformer of the *cis*-4-methylcyclohexylmethyl radical with the  $\text{CH}_3$  group axial at  $T < \text{ca. } 175$  K was attributed to the fact that the axial *non-rotating*  $\text{CH}_3$  group can adopt a staggered, minimum-energy conformation, whereas the axial *non-rotating*  $\text{CH}_2^\bullet$  group cannot because of its planarity. The barriers to rotation about the  $\text{C}_\alpha\text{--C}_\beta$  bonds in the axial radicals were found to be ca. 1.0 kcal mol<sup>-1</sup> greater than those of the equatorial radicals; this is responsible for the greater  $a(\text{H}_\beta)$  values of the axial radicals. The axial and equatorial conformers of cyclohexylmethyl radicals were investigated by semi-empirical SCF MO methods.

N.m.r. spectroscopy has proved a very effective method for the study of the conformations of alicyclic compounds and their rates of interconversion. E.s.r. spectroscopy has been far less exploited for conformational studies, although Russell showed the potential of the method in his pioneering work with mono- and bi-cyclic semidiones.<sup>2</sup> There have also been a number of e.s.r. studies of cyclohexyl and related radicals, and barriers to ring inversion have been determined in a few cases.<sup>3–7</sup> The disadvantage of e.s.r. studies of semidione and cycloalkyl radicals is that the introduction of the planar radical centre into the ring drastically alters the structure of the ring and so prevents investigation of the unperturbed conformations of alicyclic rings. Cycloalkylmethyl radicals (1) contain the small



(1)

non-polar  $\text{CH}_2^\bullet$  group attached to the ring as a 'spin probe'. Perturbation of the ring conformation(s) will be minimal and thus the possibility of studying them by e.s.r. spectroscopy is opened up. We have begun a systematic investigation of ring conformations using cycloalkylmethyl and related radicals.

In a previous paper we reported that two forms of the cycloundecylmethyl radical (1;  $n = 10$ ) could be detected at low temperatures ( $T < 230$  K).<sup>8</sup> As the temperature was increased the e.s.r. spectra exhibited exchange broadening, finally sharpening to give a single average spectrum at  $T > 260$  K. The main spectroscopic difference between the two radicals lay in

the  $\beta$ -hydrogen hyperfine splitting (h.f.s.); at 140 K one radical had  $a(\text{H}_\beta) = 38.3$  G<sup>†</sup> and the other had  $a(\text{H}_\beta) = 31.1$  G. The spectra were attributed to two conformers of (1;  $n = 10$ ) with the  $\text{CH}_2^\bullet$  group in quasiaxial and quasiequatorial orientations, but it was not possible to assign a given spectrum to one or other of these conformations. We reasoned that if our interpretation of the cycloundecylmethyl e.s.r. spectrum was correct, then axial cyclohexylmethyl radicals, *i.e.* those with the  $\text{CH}_2^\bullet$  group axial (2), and equatorial cyclohexylmethyl radicals, *i.e.* those with the  $\text{CH}_2^\bullet$  group equatorial (3), should be distinguishable by their e.s.r. spectra. That is, the  $\beta$ -hydrogen h.f.s. of (2) and (3) should be significantly different.



(2)



(3)

The free energy difference between the axial and equatorial conformers of methylcyclohexane is<sup>9</sup> 1.74 kcal mol<sup>-1</sup>; ‡ the ratio of the equatorial to axial conformers is 521:1 at 140 K or 18.5:1 at 300 K. If the equatorial preference of the  $\text{CH}_2^\bullet$  group is similar to that of the  $\text{CH}_3$  group then under equilibrium conditions the axial radical (2) would be very difficult to detect by e.s.r. spectroscopy in the accessible temperature range. In a previous e.s.r. study of cyclohexylmethyl radicals<sup>8</sup> we observed only a single spectrum with  $a(\text{H}_\beta) = 30.4$  G at 140 K, which can presumably be assigned to the equatorial radical (3). Axial cyclohexylmethyl radicals should be observable if the radicals

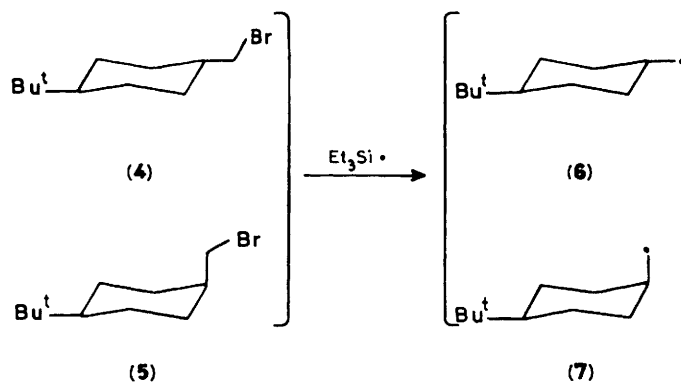
<sup>†</sup> 10 G = 1 mT.

<sup>‡</sup> 1 kcal = 4.184 kJ.

contain substituents in the 4-position which have equatorial preferences greater than, or similar to, that of  $\text{CH}_2^{\cdot}$ . In a preliminary report,<sup>1</sup> we showed that the axial and equatorial conformers of 4-alkylcycloalkylmethyl radicals can be distinguished by their e.s.r. spectra and that axial cyclohexylmethyl radicals (2) can also be observed at higher temperatures. We have now explored the thermodynamic relationship between the axial and equatorial conformers of 4-alkylcyclohexylmethyl radicals in greater detail; in addition the dynamics of ring inversion are reported in this paper together with a study by semi-empirical MO theory.

## Results and Discussion

**4-Alkylcyclohexylmethyl Radicals.**—A mixture containing 70% *trans*-4-*t*-butylcyclohexylmethyl bromide (4) and 30% of the *cis*-isomer (5) was prepared from commercial 4-*t*-butylcyclohexane carboxylic acid. The corresponding radicals were generated by photolysis of the mixture of bromides, triethylsilane (or, at higher temperatures, hexamethyldistannane) and di-*t*-butyl peroxide in the cavity of the e.s.r. spectrometer, with propane, cyclopropane, or *t*-butylbenzene as solvent. The spectrum shown in Figure 1 was obtained at 115 K in propane. It can be seen that two radicals are present, each of which has a basic double triplet splitting pattern from one  $\beta$ - and two  $\alpha$ -hydrogen atoms; each of these main lines is further split into a multiplet by long-range interactions. The long-range splitting was different for the two radicals; the nature of this effect will be described in a subsequent publication. The two spectra can be attributed to the equatorial radical (6) derived from the *trans*-diequatorial bromide (4) and the axial radical (7) derived from the *cis*-bromide (5) in which the *t*-butyl



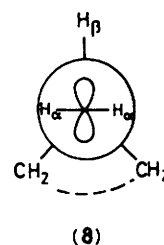
group monopolises the equatorial position. This experiment established that the equatorial and axial radicals have distinguishable spectra with very different  $a(\text{H}_\beta)$  values. However, the unequivocal assignment of each spectrum to a specific axial or equatorial radical required the preparation of a precursor which would yield only (6) or (7). Pure (4) and pure (5) were therefore synthesised from the corresponding acids (see Experimental section).



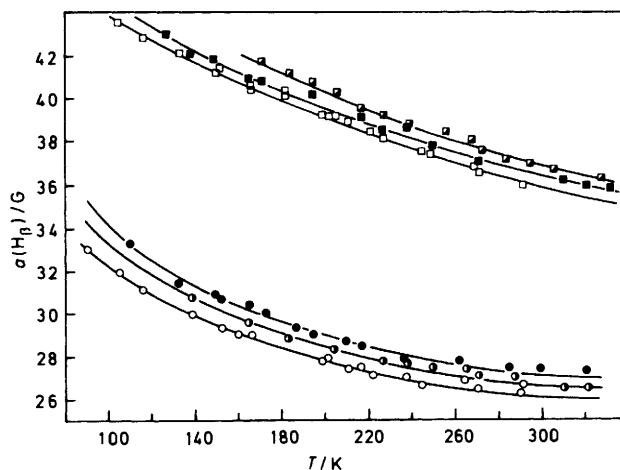
**Figure 1.** 9.4 GHz E.s.r. spectrum from a mixture of *cis*- and *trans*-4-*t*-butylcyclohexylmethyl bromides in propane at 115 K. Some lines from the isopropyl radical, derived from the solvent, can also be observed

The e.s.r. spectrum obtained by bromine abstraction from the *trans*-diequatorial bromide (4) showed only a single radical, with e.s.r. parameters identical with those of the 'inner' species in Figure 1. This must be the equatorial radical (6). Likewise, the *cis*-bromide (5) gave rise to the spectrum of a single radical with e.s.r. parameters identical with those of the 'outer' species in Figure 1; this must be the axial radical (7). The e.s.r. parameters are recorded in Table 1. The main spectroscopic difference between the two radicals lies in the  $\beta$ -hydrogen h.f.s.; the equatorial radical (6) has  $a(\text{H}_\beta)$  ca. 10 G, smaller than the axial radical (7) at 140 K. In this connection it should be noted that in the n.m.r. spectra of the bromides (4) and (5) the coupling constant between  $\text{H}_\beta$  and  $\text{CH}_2\text{Br}$  is smaller for (4) than for (5) ( $J$  6 vs. 8 Hz); the corresponding alcohols show a similar trend. This kind of correlation between radical h.f.s. and the n.m.r. coupling constants of their precursors has also been observed for other classes of alkyl radicals.<sup>10-13</sup>

The similarity of the  $a(\text{H}_\beta)$  values for the equatorial radical (6) and the cyclohexylmethyl radical<sup>8</sup> (Table 1) serves to confirm that the observed radical in the latter case was the equatorial radical (3). The magnitude of the  $a(\text{H}_\beta)$  values of radicals (6) and (7) and the fact that in both cases  $a(\text{H}_\beta)$  decreased with increasing temperature (see Figure 2) shows that both (6) and (7) prefer the eclipsed conformation (8) about the  $\text{C}_\alpha\text{-C}_\beta$  bond.



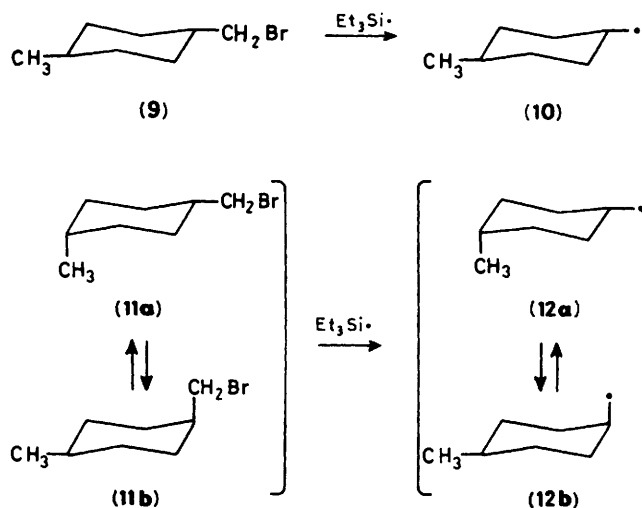
E.s.r. spectra of the 4-methylcyclohexylmethyl radicals were examined by generation of the radicals from *trans*-4-methylcyclohexylmethyl bromide (9) and *cis*-4-methylcyclohexylmethyl bromide (11a and b). The spectrum obtained from (9) showed the expected equatorial radical (10) with  $a(\text{H}_\beta)$  similar to that obtained from the analogous *t*-butyl-substituted radical (Table 1). The spectrum showed a decrease in  $a(\text{H}_\beta)$  with increasing temperature (Figure 2) which indicates that the radical (10) also prefers conformation (8).



**Figure 2.** Temperature dependence of  $a(\text{H}_\beta)$  from cyclohexylmethyl radicals; full lines calculated from equation (12) with parameters listed in Table 5;  $\circ$ , radical (6);  $\bullet$ , radical (10);  $\bullet$ , radical (3);  $\square$ , radical (7);  $\blacksquare$ , radical (12b);  $\blacksquare$ , radical (2)

**Table 1.** E.s.r. parameters of axial and equatorial cyclohexylmethyl radicals

Radical	Conf.	T/K	g Factor	$a(2 H_a)$	$a(H_\beta)$	$a(H \text{ other})/$ G
Cyclohexylmethyl (3)	eq	140		21.5	30.4	0.96 (4 H)
<i>trans</i> -4-Bu <sup>-</sup> (6)	eq	140	2.0026	22.1	29.9	0.95 (4 H)
<i>trans</i> -4-Me- (10)	eq	140		22.2	30.7	0.95 (4 H)
<i>cis</i> -4-Me- (12a)	eq	140		22.2	30.7	0.95 (4 H)
Cyclohexylmethyl (2)	ax	184		21.5	41.2	
<i>cis</i> -4-Bu <sup>-</sup> (7)	ax	140	2.0027	22.1	41.9	0.75 (5 H)
<i>cis</i> -4-Me- (12b)	ax	140		22.1	42.4	0.75 (5 H)



The *cis*-bromide (11) consists of a mixture of two conformers in which the bromomethyl group occupies an equatorial (11a) or an axial (11b) position. The e.s.r. spectra showed the presence of two radicals, one with essentially the same h.f.s. as (10), and the other with a larger  $a(H_\beta)$  characteristic of an axial radical (Table 1). We attribute these spectra to the equatorial radical (12a) and the axial radical (12b). For both these radicals  $a(H_\beta)$  decreases with temperature (Figure 2), which indicates that they also prefer conformation (8).

The radicals (12a) and (12b) can interconvert by inversion of the cyclohexane ring, and the fact that separate spectra could be observed for the two species at temperatures as high as 400 K indicates that this process is slow on the e.s.r. timescale. At these elevated temperatures the signal intensities were too weak for precise measurements. Inversion of the cyclohexane ring should cause broadening of the signals and coalescence when the temperature is high enough to make ring inversion rapid on the e.s.r. timescale. However, the weakness of the spectra made it impossible to study the dynamics of ring inversion by the exchange-broadening technique.

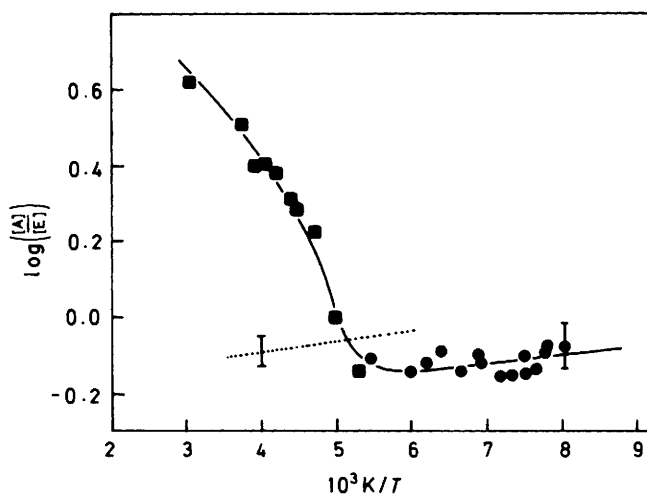
The absolute concentrations of (12a) and (12b) were measured at a series of temperatures by double integration of the  $m_x = 1$ ,  $m_\beta = -\frac{1}{2}$  lines from the e.s.r. spectra of each radical; the results are given in Table 2. A plot of the logarithm of the ratio  $[(12b)]/[(12a)]$  vs. reciprocal temperature is distinctly non-linear (see Figure 3). At higher temperatures the axial radical (12b) predominates. At lower temperatures the concentration of the axial isomer is greater than would be expected from extrapolation of the high-temperature data.

The ratio of the radical concentrations  $[(12b)]:[(12a)]$  measured by e.s.r. will represent the equilibrium ratio only if ring inversion is fast in comparison with the radical lifetimes, i.e. with the destruction of the radicals in bimolecular termination

**Table 2.** E.s.r. study of the conformational equilibrium of 4-methylcyclohexylmethyl radicals (12a) and (12b)

T/K	M <sup>a</sup>	$10^7 \times$ [(12b)] <sup>b</sup>	$10^7 \times$ [(12a)] <sup>b</sup>	[(12b)]/ [(12a)]
124	Si <sup>•</sup>			0.822
128	Si <sup>•</sup>			0.83
128	Si <sup>•</sup>			0.80
131	Si <sup>•</sup>			0.72
133	Si <sup>•</sup>	1.38	1.74	0.79
133	Si <sup>•</sup>			0.71
136	Si <sup>•</sup>			0.71
139	Si <sup>•</sup>	1.02	1.45	0.70
139	Si <sup>•</sup>			0.79
144	Si <sup>•</sup>			0.77
145	Si <sup>•</sup>	1.84	2.33	0.79
150	Si <sup>•</sup>	1.59	2.20	0.72
156	Si <sup>•</sup>	2.18	2.65	0.82
161	Si <sup>•</sup>	1.62	2.12	0.76
167	Si <sup>•</sup>	1.49	2.08	0.71
184	Si <sup>•</sup>	1.86	2.35	0.79
189	Sn <sup>•</sup>	2.18	3.04	0.72
200	Sn <sup>•</sup>	4.94	4.88	1.01
211	Sn <sup>•</sup>	7.20	4.30	1.67
223	Sn <sup>•</sup>	7.25	3.75	1.93
228	Sn <sup>•</sup>			2.01
234	Sn <sup>•</sup>	6.70	2.80	2.39
239	Sn <sup>•</sup>			2.38
245	Sn <sup>•</sup>	6.50	2.60	2.50
256	Sn <sup>•</sup>	4.90	1.95	2.51
267	Sn <sup>•</sup>	5.30	1.65	3.21
328	Sn <sup>•</sup>			4.12

<sup>a</sup> M<sup>•</sup> in  $\text{R}_3\text{M}^{\cdot}$ , the agent for bromine abstraction ( $\text{Et}_3\text{Si}^{\cdot}$  or  $\text{Me}_3\text{Sn}^{\cdot}$ ).  
<sup>b</sup> Mol dm<sup>-3</sup>.



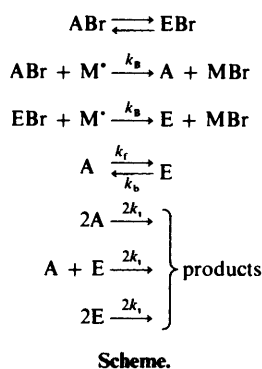
**Figure 3.** Plot of  $\log[(12b)]/[(12a)]$  vs.  $10^3 K/T$ ; ●, experimental results with  $\text{Et}_3\text{Si}^{\cdot}$  abstraction; ■, experimental results with  $\text{Me}_3\text{Sn}^{\cdot}$  abstraction; the vertical bars give the estimated error limits. Full line calculated from equation (4) (see text); dotted line n.m.r. results for  $\log[(11a)]/[(11b)]$  according to equation (10)

processes. The termination rates of radicals (12a) and (12b) will be diffusion-controlled and essentially identical.<sup>14,15</sup> They can be approximated after correction for the difference in solvent viscosities by the Arrhenius equation (1) given by Fischer

$$\log(2k_t/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 11.63 - (2.3 \text{ kcal mol}^{-1}/2.3RT) \quad (1)$$

for *t*-butyl radicals in *n*-heptane.<sup>14</sup> The concentrations of photochemically generated alkyl radicals under e.s.r. conditions are normally<sup>16</sup> *ca.*  $10^{-7}$  mol dm<sup>-3</sup> and the ring inversion is expected to have an activation energy of 10 kcal mol<sup>-1</sup> and a pre-exponential factor of  $10^{13}$  s<sup>-1</sup>. From these estimates the temperature at which ring inversion will equal the rate of termination is found to be *ca.* 200 K. Figure 3 shows that the curvature on the plot becomes pronounced at temperatures immediately below this. In this low-temperature region therefore ring inversion is slow in comparison with bimolecular termination and the measured concentration ratio is not the equilibrium concentration ratio.

The mechanism of the process can be generalised for cycloalkylmethyl and related radicals as in the Scheme. Here ABr



represents the axial bromide [*e.g.* (11b)] and A the corresponding axial radical [*e.g.* (12b)]. Similarly, EBr and E are the equatorial bromide and corresponding radical. M\* represents either the triethylsilyl radical or the trimethylstannyl radical. Because both ABr and EBr are primary bromides the rate constants for bromine abstractions are expected to be essentially equal<sup>17</sup> and both reactions have been assigned the same rate constant  $k_B$ . Similarly, the termination reactions are all assigned the same rate constant  $2k_t$ . Making the usual steady-state approximation, expressions for the rates of change of the axial and equatorial radical concentrations can be derived. Substituting from one to the other leads to equation (2). Using the

$$k_B[\text{M}^*] \left( \frac{[\text{ABr}]}{[\text{A}]} - \frac{[\text{EBr}]}{[\text{E}]} \right) + k_b \left( 1 + \frac{[\text{E}]}{[\text{A}]} \right) - k_f \left( 1 + \frac{[\text{A}]}{[\text{E}]} \right) = 0 \quad (2)$$

fact that in the steady state the total rate of initiation equals the total rate of termination, *i.e.*  $k_B[\text{M}^*]([\text{ABr}] + [\text{EBr}]) = 2k_t([\text{A}] + [\text{E}])$ ,<sup>2</sup> and rearranging we obtain equation (3),

$$2k_t([\text{E}] + [\text{A}]) (X_{\text{ABr}} - X_{\text{EBr}}[\text{A}]/[\text{E}]) = k_f[\text{A}]/[\text{E}] - k_b \quad (3)$$

where  $X_{\text{ABr}}$  and  $X_{\text{EBr}}$  are the mol fractions of the axial and equatorial bromides. In principle equation (3) can be used for a direct experimental determination of  $k_f$  and  $k_b$ . A plot of the left-hand side against  $[\text{A}]/[\text{E}]$  will have gradient  $k_f$  and intercept  $-k_b$ . We attempted to apply this method by varying the total radical concentration ( $[\text{A}] + [\text{E}]$ ) in the e.s.r. tube by placing metal gauzes of known, but different, transmittance in the light beam, thus restricting the intensity of the incident light and so reducing the initiation rate. In this way the total radical concentration could be varied by about a factor of three. However,

the change in  $[\text{A}]/[\text{E}]$  which this produced was simply too small to be useful.

Equation (3) may be rearranged to give equation (4). In the limit of fast inversion, equation (4) simplifies to  $[\text{A}]/[\text{E}] =$

$$\frac{[\text{A}]}{[\text{E}]} = \frac{k_b + 2k_t([\text{A}] + [\text{E}])X_{\text{ABr}}}{k_f + 2k_t([\text{A}] + [\text{E}])X_{\text{EBr}}} \quad (4)$$

$k_b/k_f$ . Thus, the linear portion of Figure 3 for  $T > 200$  K ( $10^3 \text{ K}/T < 5.0$ ) corresponds to this fast-inversion region, and least-squares treatment of the data gives equation (5). In the limit

$$\log(k_b/k_f) = 1.35 \pm 0.05 - (1.07 \pm 0.08 \text{ kcal mol}^{-1})/2.3RT \quad (5)$$

of slow ring inversion equation (4) simplifies to  $[\text{A}]/[\text{E}] = X_{\text{ABr}}/X_{\text{EBr}} = [\text{ABr}]/[\text{EBr}]$ . Least-squares treatment of the low-temperature data,  $T < 150$  K ( $10^3 \text{ K}/T > 6.67$ ), gives equation (6).

$$\log[\text{ABr}]/[\text{EBr}] = -0.32 \pm 0.04 + (0.13 \pm 0.1 \text{ kcal mol}^{-1})/2.3RT \quad (6)$$

In equation (4) ( $[\text{A}] + [\text{E}]$ ) is known from the e.s.r. radical concentration measurements, the  $2k_t$  values can be calculated at each temperature from equation (1), correcting for the difference in viscosities of cyclopropane (the solvent used here) and *n*-heptane,<sup>16</sup> and both  $X_{\text{ABr}}$  and  $X_{\text{EBr}}$  can be directly deduced at any temperature from equation (6). Thus the only unknowns in equation (4) are  $k_b$  and  $k_f$  and these are, of course, linked by equation (5). The values of  $[\text{A}]/[\text{E}]$  were therefore calculated over the whole temperature range using equation (4) with various assumed values of  $k_f$  and  $k_b$ . Best fit to the experimental points was obtained for the Arrhenius parameters in equations (7) and (8). The good fit obtained with equation (4)

$$\log k_b = 14.65 \pm 1.0 - (10.1 \pm 1.0 \text{ kcal mol}^{-1})/2.3RT \quad (7)$$

$$\log k_f = 13.30 \pm 1.0 - (9.0 \pm 1.0 \text{ kcal mol}^{-1})/2.3RT \quad (8)$$

using these rate constants is shown as the full line in Figure 3; the error limits were estimated from the fits.

The value of  $[(12b)]/[(12a)]$  is 3.69 at 300 K [from equation (5)]; hence the difference in free energies between (12b) and (12a) is 0.78 kcal mol<sup>-1</sup>. Combining this value with the known<sup>9,18</sup> value of 1.74 kcal mol<sup>-1</sup> for  $-\Delta G_{300}^\circ(\text{CH}_3)$ , and assuming additivity in the effects of the two groups leads to  $-\Delta G_{300}^\circ(\text{CH}_2^*) = 0.96 \text{ kcal mol}^{-1}$ .\*

The equilibrium radical concentration ratio can be calculated at low temperatures from the foregoing Arrhenius parameters. Interestingly, it is found that in the equilibrium situation ( $T > 200$  K) the axial radical predominates as expected, but at lower temperatures the equatorial radical (12a) predominates, *i.e.* the CH<sub>2</sub>\* group has a greater equatorial preference than the CH<sub>3</sub> group below *ca.* 175 K. This changeover is due to the entropy and enthalpy terms, which underlie the equilibrium constant, counteracting each other. The preponderance of (12a) at low temperatures may be due to the fact that the non-rotating CH<sub>3</sub> group in the axial position actually involves less steric hindrance than does a non-rotating CH<sub>2</sub>\* group. The CH<sub>3</sub> group can adopt a perfectly staggered, minimum-energy, conformation in which the torsion angles between the C-H bonds of the CH<sub>3</sub> group and the ring C-C bonds are optimum at 60°.

\* This value differs slightly from that given previously<sup>1</sup> because additional experimental results have been included.

For the planar  $\text{CH}_2^{\cdot}$  group on the other hand the favourable staggered conformation is not possible; the torsion angles between the C–H bonds of the  $\text{CH}_2^{\cdot}$  group and the ring C–C bonds ( $30^\circ$ ) will be unfavourable.

The error limits on the Arrhenius parameters for  $k_b$  and  $k_f$  are large because of the softness of the fit of the calculated [equation (4)] to experimental results. *cis*-1,4-Dimethylcyclohexane is closely similar to (12) in structure. For this molecule Dalling *et al.*<sup>19</sup> determined activation parameters of  $\Delta H^\ddagger = 11.0 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = 4.1 \text{ cal K}^{-1} \text{ mol}^{-1}$  for the ring inversion by  $^{13}\text{C}$  n.m.r. lineshape analysis. These parameters are equivalent to an activation energy of  $11.4 \text{ kcal mol}^{-1}$  and a pre-exponential factor  $\log(A/s^{-1})$  of 13.70. These values would be expected to be close to the Arrhenius parameters for ring inversion of the radicals (12a) and (12b). The  $A$  factors are in excellent agreement and the activation energies agree to within the combined experimental error, although the e.s.r. results [equations (7) and (8)] suggest slightly lower activation energies. The satisfactory agreement of the e.s.r. results for the radicals (12) with the n.m.r. results for *cis*-1,4-dimethylcyclohexane builds confidence in the use of equation (4) to explain the e.s.r. results and derive  $k_b$  and  $k_f$  values.

At low temperatures, in the limit of slow exchange,  $[A]/[E]$  determined by e.s.r. spectroscopy equals the ratio of the bromide precursors  $[(11b)]/[(11a)] = [A\text{Br}]/[E\text{Br}]$ . The bromide concentrations can be independently determined by n.m.r. spectroscopy. The chemical shift difference between the  $^1\text{H}$  n.m.r. signals of the axial and equatorial  $\text{CH}_2\text{Br}$  groups in (11b) and (11a) was comparatively large (*i.e.* 0.23 p.p.m. at 360 MHz) and hence the conformational equilibrium could be adequately monitored by 360 MHz n.m.r. spectroscopy. The *cis*-bromide (11) showed separate  $^1\text{H}$  resonance doublets for the axial and equatorial  $\text{CH}_2\text{Br}$  groups of (11b) and (11a) in the temperature range 159–200 K. The coalescence temperature was 208 K and above this the average doublet signal was observed. At coalescence the concentrations of the two conformers were approximately equal so the rate of inversion was estimated using the simple expression  $k = \pi\delta\nu/2^\ddagger$ . The measured  $\delta\nu$  value at coalescence was 79.5 Hz; hence, assuming a 'normal' pre-exponential factor of  $10^{13} \text{ s}^{-1}$ , an activation energy for ring inversion of  $10.2 \text{ kcal mol}^{-1}$  was obtained. This compares favourably with the inversion barriers found for other 1,4-disubstituted cyclohexanes<sup>16,19,20</sup> and for radicals (12) (see before).

Below the coalescence temperature the ratio of the concentration of (11b) to that of (11a) was determined by integration of the separate signals of the  $\text{CH}_2\text{Br}$  groups. Above coalescence  $[(11b)]/[(11a)]$  was determined from the average chemical shift of the  $\text{CH}_2\text{Br}$  signal using equation (9), where  $\bar{\delta}$  is the mean

$$[(11b)]/[(11a)] = \bar{\delta} - \delta_E/\delta_A - \bar{\delta} \quad (9)$$

chemical shift and  $\delta_E$  and  $\delta_A$  are the shifts of the equatorial and axial  $\text{CH}_2\text{Br}$  groups, respectively. At each temperature  $\delta_E$  and  $\delta_A$  were obtained by linear extrapolation of the values measured below coalescence. The measured concentration ratios are listed in Table 3. Least-squares treatment gave equation (10).

$$\log[(11b)]/[(11a)] = -0.23 \pm 0.15 + (0.15 \pm 0.03 \text{ kcal mol}^{-1})/2.3RT \quad (10)$$

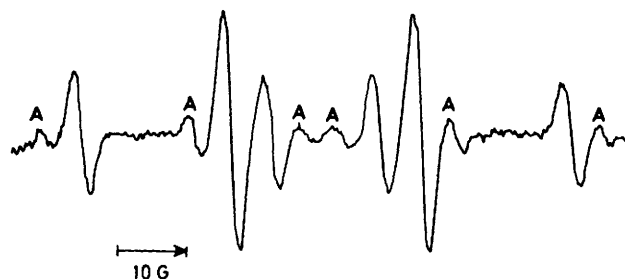
Comparison of these activation parameters with the corresponding values derived from the e.s.r. data [equation (6)] shows that they agree in sign and magnitude to within the experimental error. The best fit line from equation (10) is indicated by the dashed line in Figure 3. It shows that the n.m.r.

**Table 3.** 360 MHz  $^1\text{H}$  N.m.r. study of the conformational equilibrium of *cis*-4-methylcyclohexylmethyl bromide (11)<sup>a</sup>

T/K	[(11b)]/[(11a)]
159	0.894
164	0.879
169	0.919
175	0.919
180	0.905
190	0.855
195	0.886
221	0.859 <sup>b</sup>
237	0.838 <sup>b</sup>
251	0.802 <sup>b</sup>
265	0.776 <sup>b</sup>
290	0.695 <sup>b</sup>

<sup>a</sup> Concentrations determined by integration of separate signals.

<sup>b</sup> Concentration ratio obtained from the average chemical shift (see text).



**Figure 4.** 9.4 GHz E.s.r. spectrum of axial (2) and equatorial (3) cyclohexylmethyl radicals in *t*-butylbenzene at 240 K; axial radical (2) features marked with an A

data lie close to the e.s.r. data at low temperatures. Although the agreement is surprisingly good, the n.m.r. and e.s.r. data do not coincide precisely at low temperatures. This may be due to a small solvent effect on the equilibrium; the n.m.r. results were obtained in  $\text{CD}_2\text{Cl}_2$  as solvent and the e.s.r. results in liquid cyclopropane.

From equation (10) the free energy difference at 300 K is  $0.17 \text{ kcal mol}^{-1}$ , which leads to a value of the conformational free energy  $-\Delta G_{300}^\circ(\text{CH}_2\text{Br})$  of  $1.91 \text{ kcal mol}^{-1}$ , assuming additivity in the effects of the  $\text{CH}_3$  and  $\text{CH}_2\text{Br}$  groups. The conformational preference of the  $\text{CH}_2\text{Br}$  group was examined recently by Kitching *et al.* using  $^{13}\text{C}$  n.m.r. spectroscopy.<sup>21</sup> They found  $-\Delta G_{300}^\circ(\text{CH}_2\text{Br}) = 1.79 \text{ kcal mol}^{-1}$ , somewhat lower than our result but, as expected, both methods show that the  $\text{CH}_2\text{Br}$  group has a greater equatorial preference than the  $\text{CH}_3$  group.

From the foregoing  $-\Delta G_{300}^\circ(\text{CH}_2^{\cdot})$  value it follows that the ratio of equatorial to axial cyclohexylmethyl radicals [(3)]:[(2)] is *ca.* 5:1 at 300 K. This proportion of the axial radical (2) should be detectable under optimum e.s.r. conditions. The precursor, cyclohexylmethyl bromide, was purified by preparative g.l.c. and the spectra were re-examined in the high-temperature range. Spectra run at temperatures above *ca.* 180 K did indeed show the presence of a second radical with a large  $\beta$ -hydrogen h.f.s.; see Figure 4. The e.s.r. parameters of this minor radical are similar to those of the other axial radicals (Table 1) and it can be assigned conformation (2). The linewidths of radicals (2) and (3) were identical to within experimental error and therefore [(2)]:[(3)] was determined in the temperature range 172–340 K by measurement of peak heights; the results

**Table 4.** E.s.r. study of the conformational equilibrium of cyclohexylmethyl radicals (2) and (3)

T/K	[(2)]/[(3)]
172	0.032
184	0.044
195	0.061
206	0.082
217	0.106
228	0.107
239	0.135
245	0.158
250	0.196
256	0.179
262	0.218
267	0.215
278	0.229
284	0.231
295	0.278
306	0.353
317	0.390
328	0.372
340	0.444

are given in Table 4. Least-squares treatment of the data gave the Arrhenius parameters in equation (11), from which

$$\log[(2)]/[(3)] = 0.79 \pm 0.1 - (1.79 \pm 0.04 \text{ kcal mol}^{-1})/2.3RT \quad (11)$$

[(2)]/[(3)] = 0.3 at 300 K and  $-\Delta G_{300}^{\circ}(\text{CH}_2^{\bullet}) = 0.71 \text{ kcal mol}^{-1}$ . This value will be more reliable than the value obtained from the *cis*-4-methyl-substituted radical. As might be expected the  $\text{CH}_2^{\bullet}$  group has a greater equatorial preference than OH ( $-\Delta G_{300}^{\circ} = 0.52 \text{ kcal mol}^{-1}$  in aprotic solvents)<sup>22</sup> and  $\text{OCH}_3$  ( $-\Delta G_{300}^{\circ} = 0.60 \text{ kcal mol}^{-1}$ )<sup>22</sup> and a lower equatorial preference than  $\text{CH}_3$  ( $-\Delta G_{300}^{\circ} = 1.74 \text{ kcal mol}^{-1}$ )<sup>9,18</sup> and other alkyl groups.<sup>18</sup> However, the  $\text{CH}_2^{\bullet}$  group also has a considerably lower equatorial preference than  $\text{NH}_2$  ( $-\Delta G_{300}^{\circ} = 1.20 \text{ kcal mol}^{-1}$  in aprotic solvents),<sup>22</sup> which is rather surprising.

At very high temperatures both cyclohexylmethyl and 4-methylcyclohexylmethyl radicals prefer the conformation in which the  $\text{CH}_2^{\bullet}$  group adopts the axial position; this is owing to the favourable entropy factors [see equations (5) and (11)]. We tentatively attribute this effect to two factors, as follows. (i) The barrier to rotation about the  $\text{C}_{\alpha}\text{-C}_{\beta}$  bond is significantly greater in the axial radical than in the equatorial radical (see later). The freeing of this rotation at higher temperatures will lead to a more favourable entropy factor for the axial radical. (ii) The greater hyperconjugative interaction in the axial radicals (note the much larger  $\beta$ -h.f.s.) leads to a loosening of the  $\text{C}_{\beta}\text{-H}$  bonds with consequent favourable entropy effect.

**Calculation of Barriers to Rotation about the  $\text{C}_{\alpha}\text{-C}_{\beta}$  Bonds in 4-Alkylcyclohexylmethyl Radicals.**—The angular dependence of  $a(\text{H}_{\beta})$  can be represented by<sup>23</sup>  $a(\text{H}_{\beta}) = A + B\cos^2\theta$  where  $\theta$  is the torsion angle between the  $\text{C}_{\alpha} 2p_z$  orbital and the  $\text{C}_{\beta}\text{-H}$  bond. For cyclohexylmethyl radicals  $\theta = 0$  is the preferred conformation [*i.e.* conformation (8)] but the population of (8) varies with temperature, thereby making  $a(\text{H}_{\beta})$  temperature-dependent. We showed previously<sup>8</sup> that the potential barrier to rotation about the  $\text{C}_{\alpha}\text{-C}_{\beta}$  bond,  $V_0$ , can be determined by comparing the experimental temperature dependence of  $a(\text{H}_{\beta})$  with values calculated from equation (12), where  $I_1(\lambda)$  and  $I_0(\lambda)$

$$a(\text{H}_{\beta}) = A + \frac{1}{2}B + \frac{1}{2}B\cos 2\theta_0 [I_1(\lambda)/I_0(\lambda)] \quad (12)$$

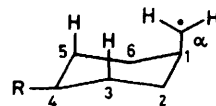
**Table 5.** Barriers to rotation about the  $\text{C}_{\alpha}\text{-C}_{\beta}$  bonds in cyclohexylmethyl radicals calculated with equation (12)<sup>a</sup>

	A <sup>b</sup> /G	B <sup>b</sup> /G	$V_0$ /kcal mol <sup>-1</sup>
Equatorial radicals			
Cyclohexylmethyl (3) <sup>c</sup>	0.0	46	0.43
<i>trans</i> -4-Me- (10)	0.0	46	0.39
<i>cis</i> -4-Me- (12a)	0.0	46	0.39
<i>trans</i> -4-Bu <sup>1</sup> - (6)	0.0	46	0.35
Axial radicals			
Cyclohexylmethyl (2)	1.2	46	1.60
<i>cis</i> -4-Me- (12b)	1.2	46	1.53
<i>cis</i> -4-Bu <sup>1</sup> - (7)	1.2	46	1.39

<sup>a</sup>  $\theta_0 = 0$  was used for all radicals. <sup>b</sup> Parameters used in the construction of the curves shown in Figure 2. <sup>c</sup> Data from ref. 8: the barrier given here differs slightly from that reported previously because additional experimental data have been included.

are modified (hyperbolic) Bessel functions,  $\lambda = V_0/kT$ , and  $\theta_0$  is the value of  $\theta$  at the potential minimum (*i.e.*  $\theta_0 = 0$  for 4-alkylcyclohexylmethyl radicals).

The experimental and calculated  $a(\text{H}_{\beta})$  values of the 4-methyl- and 4-*t*-butyl-cyclohexylmethyl radicals are compared in Figure 2. In each case the experimental trend could be well represented by a suitable choice of the parameters in equation (12). The values of A and B and the calculated rotation barriers are given in Table 5. The  $\beta$ -h.f.s. values of the equatorial radicals were all well represented using the same A and B values as were used previously for cyclohexylmethyl radicals.<sup>8</sup> A slight modification in the A values was required for good fit with the axial radicals. The equatorial radicals have rotation barriers of 0.35–0.45 kcal mol<sup>-1</sup> which are similar in magnitude to those found for acyclic radicals such as isobutyl ( $V_0 = 0.44 \text{ kcal mol}^{-1}$ ).<sup>8,23</sup> There is an intriguing increase in  $V_0$  as the 4-substituent changes from Bu<sup>1</sup> to Me to H. The differences are too small for present theory to interpret, but it is likely that they are due to minor changes in the ring geometry brought about by the different substituents. The most striking feature of Table 5 is the very large difference in the  $V_0$  values for axial and equatorial radicals; the axial radicals have rotation barriers about four times greater than those of equatorial radicals. It is, of course, these high barriers which lead to the large  $a(\text{H}_{\beta})$  values for the axial radicals and this in turn leads to clearly distinguishable e.s.r. spectra for the axial and equatorial species. The large barriers in the axial radicals almost certainly arise because *syn*-axial interactions of the hydrogen atoms on the  $\text{CH}_2^{\bullet}$  group with the axial hydrogen atoms at C(3) and C(5) [see (13)] will increase the potential



(13)

energy for rotation. *syn*-Axial interactions of this type have often been postulated to account for the behaviour of cyclohexanes; the  $V_0$  values give a quantitative measure of this effect.

**Semi-empirical SCF MO Calculations.**—The cyclohexylmethyl radicals (2) and (3) were chosen as models of equatorial and axial radicals and investigated by using the UHF versions of the MINDO/3<sup>24</sup> and MNDO methods.<sup>25</sup> Geometries were

fully optimised with respect to all bond lengths, bond angles, and torsion angles in preliminary calculations. It was found that the C-H bond lengths and HCC bond angles of atoms further from the radical centre than C<sub>β</sub> were not sensitive to the torsion angle about C<sub>α</sub>-C<sub>β</sub> and they were subsequently held constant. The enthalpies of formation of the radicals were then calculated for a series of values of the torsion angle about the C<sub>α</sub>-C<sub>β</sub> bond. Unfortunately, both methods gave ring structures which were too flattened; thus the MINDO/3 calculations predicted the torsion angle between the ring carbons to be 42° and the MNDO calculations predicted 46°. Both these predictions are considerably below the experimental electron diffraction value of 55° for cyclohexane.<sup>26</sup> This flattening of the cyclohexane ring in the computed structures has the effect of placing the CH<sub>2</sub>· group considerably further from the axial hydrogen atoms at C(3) and C(5) than is really the case and thus the computed barrier to rotation in the axial radical will be underestimated. In fact values of 0.7 and 0.5 kcal mol<sup>-1</sup> were obtained for V<sub>o</sub> in the axial and equatorial radicals respectively using the MINDO/3 method. The MNDO-UHF calculations predicted the wrong stable conformation for both (2) and (3), *i.e.* conformation (8) appeared as a maximum instead of a minimum in the rotational potential energy function. The MINDO/3-UHF calculations gave minimum ΔH<sub>f</sub> values of 3.4 and 2.1 kcal mol<sup>-1</sup> for the radicals (2) and (3), respectively, *i.e.* the equatorial conformation was correctly predicted to be lower in energy. The MNDO-UHF results were -5.8 and -6.6 kcal mol<sup>-1</sup>.

Because the MINDO/3-UHF method gave predictions in the right sense for both V<sub>o</sub> and ΔH<sub>f</sub> values of (2) and (3), the MINDO/3-UHF-optimised geometries were used in INDO calculations.<sup>27</sup> The INDO calculations correctly predicted (8) as the preferred conformation for both (2) and (3) and gave rotation barriers of 1.0 and 0.43 kcal mol<sup>-1</sup>, respectively; also in the same order as the experimental results. The INDO h.f.s. values must be obtained by a Boltzmann-type average of the h.f.s. values computed for each value of θ using the rotational potential function also obtained from the INDO calculations.<sup>8</sup> The average a(H<sub>β</sub>) values obtained in this way were 67.4 G for (2) and 50.8 G for (3). Thus the INDO method correctly predicts a much larger a(H<sub>β</sub>) value for the axial radical, but overestimates the magnitude of both β-h.f.s. values (*cf.* Table 1). Lower average a(H<sub>β</sub>) values would be obtained for both (2) and (3) if deeper rotational potential functions were used in the Boltzmann averages.

### Experimental

Routine <sup>1</sup>H n.m.r. spectra were obtained with a Bruker WP 80 instrument for CDCl<sub>3</sub> solutions at room temperature, with tetramethylsilane as internal standard. The quantitative measurements on *cis*-4-methylcyclohexylmethyl bromide [(11a) + (11b)], including the exchange-broadened spectra, were made with a Bruker 360 MHz spectrometer operated for <sup>1</sup>H on CD<sub>2</sub>Cl<sub>2</sub> solutions. The separate resonance doublets of the axial and equatorial groups (δ 3.47 and 3.24, respectively, at 159 K) below coalescence were integrated both instrumentally and by planimetry. E.s.r. spectra were recorded with a Bruker ER200D spectrometer for samples degassed by three freeze-pump-thaw cycles and sealed in Spectrosil quartz tubes.

*cis*-4-*t*-Butylcyclohexylmethyl Bromide (5).—4-*t*-Butylbenzoic acid was hydrogenated over 5% rhodium-alumina as described by Jensen *et al.*<sup>28</sup> The *cis*-4-*t*-butylcyclohexanecarboxylic acid obtained was reduced to the corresponding methanol with lithium aluminium hydride, and the alcohol was then converted into the bromide *via* the mesylate, using the procedure described previously.<sup>8</sup> The product showed δ<sub>H</sub> 0.84 (9 H, s), 1.0–2.2 (10

H, m), and 3.5 (2 H, d, *J* 8 Hz); δ<sub>C</sub> 21.54, 27.46, 29.40, 35.58, 36.67, and 48.40; the spectra also showed the presence of *ca.* 5% of the *trans*-isomer.

*trans*-4-*t*-Butylcyclohexylmethyl Bromide (4).—*cis*-4-*t*-Butylcyclohexanecarboxylic acid was esterified with ethanol and isomerised to the *trans*-acid with potassium *t*-butoxide and Me<sub>2</sub>SO.<sup>28</sup> The ester was then reduced with LiAlH<sub>4</sub> and the resulting methanol converted into the bromide as before; δ<sub>H</sub> 0.83 (9 H, s), 1.0–2.2 (10 H, m), and 3.3 (2 H, d, *J* 6 Hz); δ<sub>C</sub> 26.87, 27.58, 32.21, 40.28, 40.57, and 47.94. No *cis*-bromide (5) was detectable in the n.m.r. spectra.

*cis*- and *trans*-4-Methylcyclohexylmethyl Bromides (11) and (9).—*p*-Toluic acid was hydrogenated over 5% rhodium-alumina and the resulting acids were converted as before into a mixture which g.l.c. analysis indicated contained 22% (9) and 78% (11). The *cis*- (11) and the *trans*-bromide (9) were separated by preparative g.l.c. (15 ft column packed with 10% Carbowax 20 M on Chromosorb W maintained at 140 °C). The <sup>1</sup>H and <sup>13</sup>C spectra of the purified isomers were identical with those given in the literature.<sup>21</sup>

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