# Cycloalkylmethyl Radicals. Part 4.<sup>1</sup> Electron Spin Resonance Study of Conformational Equilibria in Cyclohexenylmethyl and 4-Alkylcyclohexenylmethyl Radicals

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For cyclohex-2-enylmethyl and 4-alkylcyclohex-2-enylmethyl radicals the quasi-axial and the quasiequatorial conformers can both be observed by e.s.r. spectroscopy. Similarly, the axial and equatorial conformers of cyclohex-3-enylmethyl radical can be distinguished by e.s.r. spectroscopy. The conformational free-energy difference of the CH<sub>2</sub><sup>\*</sup> group in the 2-position,  $-\Delta G_{300}^{*}$ , was found to be  $0.17 \pm 0.03$  kcal mol<sup>-1</sup> and in the 3-position  $-\Delta G_{300}^{*} = 0.0 \pm 0.1$  kcal mol<sup>-1</sup>. The Arrhenius parameters for inversion of the half-chair conformation of cyclohex-2-enylmethyl radical were determined by lineshape analysis of the exchange-broadened spectra and found to be:  $\log(k_f/s^{-1}) = 12.3 - (5.7 \text{ kcal} \text{ mol}^{-1})/2.3RT$  and  $\log(k_b/s^{-1}) = 12.0 - (5.5 \text{ kcal mol}^{-1})/2.3RT$ . The barrier to rotation about the  $C_{\alpha}-C_{\beta}$ bond in a cyclohexenylmethyl radical is much less than the barrier in a cyclohexylmethyl radical because the former radical has only one *syn*-axial hydrogen on C(5) to impede the rotation whereas the latter radical has two *syn*-axial hydrogens on C(3) and C(5).

We showed previously that for cyclohexylmethyl and 4-alkylcyclohexylmethyl radicals the conformers in which the  $CH_2^*$ group adopts the equatorial and axial positions can both be observed by e.s.r. spectroscopy.<sup>1,2</sup> Ring inversion interconverts these two conformers and, when the rate of ring inversion becomes fast on the e.s.r. timescale, exchange broadening will occur giving rise to a single average spectrum at sufficiently rapid rates. In practice, the temperature range where this exchange broadening occurs is too high for it to be detectable by e.s.r. spectroscopy in solution.<sup>1</sup>

The preferred conformation of the cyclohexene ring is the half-chair and this inverts much more rapidly than the chair conformation of cyclohexane. Substituents at the 1-position in cyclohex-2-ene can have quasi-axial (1) or quasi-equatorial (2) orientations whereas substituents at the 1-position in cyclohex-3-ene can occupy 'true' axial (3) or equatorial (4) orientations.<sup>3</sup> In the light of the rather large spectroscopic difference between axial and equatorial cyclohexylmethyl radicals, it seemed possible that radical (1) might be distinguishable from (2) by e.s.r. spectroscopy and that radical (3) might be distinguishable from (4).

The free energy of activation for cyclohexene inversion, ca. 5.3 kcal mol<sup>-1</sup>,\* as determined by n.m.r. measurements<sup>4,5</sup> is close to the lower limit that can be studied by that technique. Measurements have to be made at very low temperatures where experimental difficulties are considerable and relatively few quantitative results have been obtained. On the other hand activation barriers of this order fall in the middle of the range covered by e.s.r. spectroscopy. The study of the dynamics of cyclohexene inversion by e.s.r. spectroscopy using the CH<sub>2</sub><sup>•</sup> group as a 'spin probe' in the 1-position seemed to be an attractive possibility.

In this paper we show that (1) and (2) are spectroscopically distinguishable as are (3) and (4); the activation barrier for cyclohexene ring inversion was obtained from study of the  $(1) \rightleftharpoons (2)$  equilibrium. In addition, the 4-methyl- and 4-t-butyl-cyclohex-2-enylmethyl radicals were investigated.

## **Results and Discussion**

The cyclohexenylmethyl radicals were generated by bromine abstraction from the corresponding bromomethyl compounds



using photochemically produced triethylsilyl radicals or, at T > ca. 200 K, trimethyltin radicals.<sup>6</sup> t-Butylbenzene was used as solvent for most of the experiments at T > ca. 200 K and cyclopropane or n-propane for lower temperatures. The bromomethylcyclohexanes were synthesised from the corresponding carboxylic acids by reduction with lithium aluminium hydride and conversion of the resulting cyclohexenylmethanols into the bromides by treatment of the mesylates with lithium bromide in dry acetone.<sup>7</sup> The carboxylic acids were obtained by double Birch-type reduction of the aromatic acid with lithium metal in liquid ammonia.<sup>8</sup>

Cyclohex-2-enylmethyl Radicals.—The e.s.r. spectra at 140 K showed the presence of two radicals each with two  $H_{a}$ , one  $H_{g}$ , and four small long-range hyperfine splittings (h.f.s.). The spectra overlapped considerably, but were successfully simulated using the h.f.s. given in Table 1. The main difference in the spectra lay in the  $\beta$ -hydrogen h.f.s., *i.e.* 30.6 and 32.6 G at 140 K. The spectrum with the smaller  $\beta$ -h.f.s. can be assigned to the quasi-equatorial conformer (2), and the spectrum with the larger  $\beta$ -h.f.s. to the quasi-axial conformer (1). The larger  $\beta$ -h.f.s. for (1) is a consequence of steric hindrance to the CH<sub>2</sub>' group rotation by the single axial hydrogen on C(5); this increases the

Radical	ation <sup>a</sup>	<i>T</i> /K	a(2H <sub>a</sub> )/G	<i>а</i> (Н <sub>в</sub> )/G	a(H other)/G
Cyclohex-2-enylmethyl (2)	qeq	140	22.5	30.6	0.72 (4H)
4-Methylcyclohex-2-enylmethyl	qeq	140	22.3	30.6	0.77 (4H)
4-t-Butylcyclohex-2-enylmethyl	qeq	140	22.3	27.1	0.75 (4H)
Cyclohex-3-enylmethyl	eq	140	22.3	28.8	0.75 (4H)
Cyclohexylmethyl	eq	140	21.5	30.4	0.96 (4H)
Cyclohex-2-enylmethyl (1)	qax	140	22.5	32.6	0.81 (4H)
4-Methylcyclohex-2-enylmethyl	qax	140	22.3	32.2	0.77 (4H)
4-t-Butylcyclohex-2-enylmethyl	qax	140	22.3	30.6	0.75 (4H)
Cyclohex-3-enylmethyl	ax	140	22.3	32.3	0.85 (4H)
Cyclohexylmethyl	ax	184	21.5	41.2	0.75 (5H)

Table 1. E.s.r. hyperfine splittings in cyclohexenylmethyl and related radicals

" Prefix q. indicates quasi-equatorial or quasi-axial.



CH<sub>2</sub><sup>•</sup> torsional barrier and hence the  $\beta$ -h.f.s. These assignments are also analogous to those found for the corresponding cyclohexylmethyl radicals.<sup>1</sup> An attempt to confirm the assignment by observation of *cis*-4-t-butylcyclohex-2-enylmethyl radicals was frustrated because it was not possible to separate the precursors of the *cis*- and *trans*-radical. Cyclohex-2-enylmethyl radicals were previously generated by hydrogen abstraction from bicyclo[4.1.0]heptane (5). The bicyclo[4.1.0]hept-2-yl radicals (6) were not observed because they rearrange too rapidly by  $\beta$ -scission to give cyclohex-2-enylmethyl radicals.<sup>9</sup> The e.s.r. spectra of the latter were essentially identical to those obtained in this work and the analysis in terms of conformers (1) and (2) explains the anomalous long-range h.f.s. noted before.<sup>9</sup>

The magnitude of the  $a(H_{\rm B})$  values of both (1) and (2), and the fact that both h.f.s. decreased with increasing temperature, shows <sup>10</sup> that they both adopt the eclipsed conformation (7) about the  $\dot{C}_{\alpha}$ - $C_{\beta}$  bond. Both radicals also showed long-range h.f.s. from four hydrogens. It is probable that these h.f.s. originate with the three  $\gamma$ -hydrogens and the unique  $\delta$ -hydrogen attached to the  $sp^2$  carbon atom of the double bond. Both (1) and (2) are therefore closely analogous to the acyclic but-3-enyl radical which also shows a resolved h.f.s. from one  $\delta$ -hydrogen attached to the double bond.<sup>11,12</sup>

The e.s.r. spectra of the mixture of (1) and (2) showed line broadening in the temperature range 180–270 K; above this range a single spectrum with, at 306 K,  $a(2H_a) 22.4$ ,  $a(H_B) 28.3$ , a(4H) 0.8 G was obtained. The line broadening is almost certainly due to inversion of the half-chair conformations of (1) and (2); at T > ca. 270 K the inversion is rapid on the e.s.r. timescale and only the average is observed. In order to determine the rates of ring inversion from the exchange broadening the relative concentrations of the two conformers must be



Figure 1. Arrhenius plots of the conformer ratios from cyclohexenylmethyl radicals:  $\bigoplus$ , [(1)]:[(2)] as determined from equation (1);  $\triangle$ , [(1)]:[(2)] as determined by simulation;  $\bigcirc$ , [(3)]:[(4)] as determined from the  $\beta$ -h.f.s.;  $\triangle$ , [(3)]:[(4)] as determined by simulation. The vertical bar gives an estimate of the error limits on the simulation experiments

known. In the temperature range 128-160 K, where separate spectra were obtained for (1) and (2), the relative concentrations were determined by simulation of the spectra. Unfortunately, this method was rather inaccurate because of the extensive overlap of the two spectra.

In order to overcome this problem we attempted to prepare 2,3,4,5,6-pentadeuterio-1-bromomethylcyclohex-2-ene (8). The radical derived from this bromide, *i.e.* (9), would have only one  $\gamma$ -hydrogen to give long-range h.f.s. and hence the spectra of the two conformers might be separated. In practice it was only possible to prepare a mixture of (8) together with the tetra- and tri-deuterio-compound (see Experimental section). The e.s.r. spectrum from this mixture showed no resolved long-range h.f.s. at all  $[a(2H_{\alpha}) 22.3, a(H_{\beta}) 31.6 \text{ G}$  at 140 K] but the lines were so broad ( $\Delta H_{pp}$  ca. 1.8 G) that the spectra of conformers (1) and (2) were not resolved either. In this case the  $\beta$ -h.f.s. is a weighted mean of the values from the two conformers and hence we have equation (1) where X(Ax) is the mol fraction of the quasi-axial

$$X(\mathbf{A}\mathbf{x}) = [a(\mathbf{H}^{\mathbf{D}}_{\beta}) - a(\mathbf{H}^{\mathbf{A}\mathbf{x}}_{\beta})]/[a(\mathbf{H}^{\mathbf{A}\mathbf{x}}_{\beta}) - a(\mathbf{H}^{\mathbf{E}\mathbf{q}}_{\beta})] \quad (1)$$

conformer (1) and  $a(H_{\beta}^{D})$  is the  $\beta$ -h.f.s. from the deuteriated radical (9). The  $a(H_{\beta}^{D})$  were measured at a series of temperatures; the  $a(H_{\beta}^{Ax})$  and  $a(H_{\beta}^{Eq})$  values were measured directly from the spectra of (1) and (2) in the temperature range 128— 180 K and extrapolated values were used at higher temperatures. An Arrhenius plot of the ratio [(1)]:[(2)] (Figure 1)



**Figure 2.** Left-hand side: experimental 9.4 GHz e.s.r. spectra (low-field multiplet only) from cyclohex-2-enylmethyl radicals in t-butylbenzene; from the top, 184, 223, 273 K. Right-hand side: simulated spectra with, from the top,  $k 4.0 \times 10^5$ ,  $4.5 \times 10^6$ , and  $6.0 \times 10^7$  s<sup>-1</sup>



Figure 3. A, One multiplet from the 9.4 GHz e.s.r. spectrum of 4methylcyclohex-2-enylmethyl radicals at 139 K. B, One multiplet from the 9.4 GHz e.s.r. spectrum of 4-t-butylcyclohex-2-enylmethyl radicals at 133 K

shows that satisfactory agreement between the two methods of concentration measurement was obtained.

We showed previously<sup>1</sup> that the ratio of the axial and equatorial radical concentrations as measured by e.s.r. spectroscopy will only represent the *equilibrium* ratio if the rate of ring inversion is fast in comparison with the radical lifetimes, *i.e.* with the rate of destruction of the radicals in bimolecular termination processes. For cyclohexylmethyl radicals this condition was not fulfilled throughout the whole temperature range and the concentration ratio was dependent on the termination rate constant, the total radical concentration, and the concentrations of the bromide precursors.<sup>1</sup> For cyclohex-2-enylmethyl radicals the ring inversion rate is much faster and the linearity of the



**Table 2.** Rate constants for half chair ring inversion in cyclohex-2-enylmethyl radicals (1) and  $(2)^a$ 

T/K	$10^{-7} k_{\rm f}/{\rm s}^{-1}$	$10^{-7} k_{\rm b}/{\rm s}^{-1}$
172	0.0102	0.0098
184	0.0414	0.0385
200	0.158	0.141
211	0.268	0.233
223	0.487	0.413
228	0.653	0.547
239	1.099	0.902
250	2.21	1.79
262	3.35	2.65
273	6.73	5.27

<sup>2</sup> See structures (	1)	and (	(2)	for	definition	of k	f and	$k_{i}$	ь.
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Arrhenius plot in Figure 1 confirms that this is so. The inversion rate of the half-chair comfortably exceeds the rate of radical destruction over the accessible temperature range and therefore  $[(1)]:[(2)] = k_f/k_b$ . Least-squares analysis of the data gave equation (2). Extrapolation to 300 K gives [(1)]:[(2)] = 0.75

$$\log\{[(1)]\}:[(2)] = -0.27 \pm 0.02 + (0.20 + 0.01 \text{ kcal mol}^{-1})/2.3RT \quad (2)$$

and hence the conformational free-energy difference of the CH<sub>2</sub>' group,  $-\Delta G_{300}^{\circ} = 0.17 \pm 0.03$  kcal mol<sup>-1</sup>.

The relative concentrations of (1) and (2) calculated from equation (2) were used in the simulations of the exchange broadening. A modified version of Heinzer's program<sup>13</sup> was employed, the exchange rate being varied to give best fit of the calculated spectrum to the experimental spectrum at a given temperature. Figure 2 shows a comparison of some of the experimental and simulated spectra; satisfactory agreement was obtained over the whole temperature range. The rate constants derived from the simulations are given in Table 2; the corresponding Arrhenius parameters are:  $\log(k_f/s^{-1}) = 12.3 \pm 0.2 - (5.7 \pm 0.2 \text{ kcal mol}^{-1})/2.3RT$  and  $\log(k_b/s^{-1}) = 12.0 \pm 0.2 - (5.5 \pm 0.2 \text{ kcal mol}^{-1})/2.3RT$ .

The free energies of activation of ring inversion have been determined by n.m.r. line-shape analysis for cyclohexene ( $\Delta G^{\ddagger}$  5.3 kcal mol<sup>-1</sup>),<sup>4.5</sup> some 4-halogenocyclohexenes ( $\Delta G^{\ddagger}$  5.3 for 4-fluoro to 6.5 kcal mol<sup>-1</sup> for 4-iodo),<sup>5</sup> for 3,3-dimethylcyclohexene ( $\Delta G^{\ddagger}$  6.3 kcal mol<sup>-1</sup>),<sup>14</sup> and for a few other derivatives.<sup>15</sup> The inversion barriers do not lie outside the range given above except in 3,6-disubstituted cyclohexenes where 'prow-prow' interactions occur in the boat transition state.<sup>14</sup> The entropy of activation is small<sup>4.5</sup> and therefore the free energies of activation or the Arrhenius activation energies in this case. The results for  $E_f$  and  $E_b$  fall in the range defined above and this confirms the usefulness of the CH<sub>2</sub> group as a 'spin probe' for ring inversions of this type.

At high temperatures there is a preponderance of the quasiequatorial conformer (2), (see Figure 1), as might have been expected. However, at T < ca. 170 K the quasi-axial conformer (1) predominates. The free-energy difference between the two conformers is so small that it would be fruitless to speculate on the origin of this effect. The small size of  $-\Delta G_{300}^{\circ}$  does, however, show that any homoallyl type of interaction between the unpaired electron and the double bond must be extremely small because this would favour the quasi-equatorial conformer. Similar inversions in the axial:equatorial ratios were discovered by Booth and Everett in their n.m.r. study of *cis*-1,4-dialkylcyclohexanes.<sup>16</sup> The cyclohexylmethyl radical also



shows a changeover, but in the opposite sense, *i.e.* the axial conformer predominates at T > ca. 495 K.<sup>1</sup>

4-Alkylcyclohex-2-enylmethyl Radicals.—4-Methyl- and 4-tbutyl-cyclohex-2-enylmethyl bromides were obtained as mixtures of *trans*- and *cis*-isomer. Efforts to separate these isomers by g.l.c. were unsuccessful; no significant resolution was obtained with any stationary phase. The e.s.r. spectrum of the 4methylcyclohex-2-enylmethyl radical showed the basic double triplet expected for a cycloalkylmethyl radical. One multiplet from the spectrum is shown in Figure 3A. The six-line fine structure is due to the overlap of two pentets, each originating from long-range h.f.s. from four hydrogens, but displaced from each other by exactly the value of one long-range h.f.s. This displacement is due to the different  $\beta$ -h.f.s. of the quasi-axial (10a) and quasi-equatorial (11a), (12a) conformers. The spectrum with the larger  $\beta$ -h.f.s. can be assigned to radical (10a) with the quasi-axial CH<sub>2</sub><sup>\*</sup> group.

The spectrum with the smaller  $\beta$ -h.f.s. can be assigned to both radicals (11a) and (12a) which have quasi-equatorial CH<sub>2</sub><sup>-</sup> groups and will be spectroscopically indistinguishable. This indistinguishability of (11a) and (12a) is analogous to that of the corresponding *cis*- and *trans*-equatorial isomers of the 4methylcyclohexylmethyl radicals which were also found to have identical e.s.r. spectra.<sup>1</sup> The e.s.r. parameters are given in Table 1. The magnitude of the  $\beta$ -h.f.s. and the decrease in the  $\beta$ -h.f.s. of both (10a) and (11a) with increasing temperature indicates that they adopt (7) as their preferred conformation about the  $\dot{C}_{\alpha}$ -C<sub> $\beta$ </sub> bond.

The e.s.r. spectra from the 4-t-butylcyclohex-2-enylmethyl radicals were similar to those from the 4-methyl derivative except that each multiplet in the spectrum showed a seven-line fine structure (Figure 3B). In this case the spectrum is an overlap of conformers (10b)—(12b) but the spectra are displaced from each other by twice the value of the long-range h.f.s. The correctness of this analysis was confirmed by the observation of partial resolution within the multiplet at 140 K. The e.s.r. h.f.s. are recorded in Table 1. Interestingly, the  $\beta$ -h.f.s. of the quasiaxial radicals show a decrease as the 4-substituent changes from H to Me to Bu<sup>t</sup>. A similar decrease was observed for the analogous series of cyclohexylmethyl radicals.<sup>1</sup> These changes are too small for present theory to interpret but it is likely that they arise from small changes in the ring geometries brought about by the substituents.

The relative concentrations of (10) and (11) could not be determined because of the presence of the *trans*-isomers (12); this also prevented analysis of the exchange broadening at higher temperatures.

Cyclohex-3-enylmethyl Radicals.—The e.s.r. spectrum showed the presence of two radicals (h.f.s. in Table 1). To the radical with the larger  $\beta$ -h.f.s. (32.3 G at 140 K) we assign the axial conformation (3) and to the radical with the small  $\beta$ -h.f.s. (28.8 G) the equatorial conformation (4). The magnitude of the  $\beta$ h.f.s. of both (3) and (4) and the fact that both  $\beta$ -h.f.s. decreased with increasing temperature shows that both adopt (7) as their preferred conformation about the  $\dot{C}_{\alpha}$ - $C_{\beta}$  bond. Both radicals showed fine structure from four equivalent  $\gamma$ -hydrogens, as would be expected by analogy with cyclohexylmethyl radicals.

The relative concentrations of (3) and (4) were difficult to determine because of overlap of the spectra and changes in the overlap pattern with the variation in the  $\beta$ -h.f.s. with temperature. In the temperature range 94-150 K the [(3)]: [(4)] ratio was determined by simulation of the spectra. It was found that to within the (large) experimental error the concentrations of (3)and (4) were equal in this range. In the range 270-320 K only the average spectrum was observable and hence the relative concentrations could be determined from the  $\beta$ -h.f.s. by use of an equation similar to (1). The Arrhenius plot of the two sets of data (Figure 1) shows that the [(3)]: [(4)] ratio differs from unity by less than the experimental error limit throughout the entire temperature range. It follows that  $-\Delta G^{\circ}_{300} = 0.0 \pm 0.1$  kcal mol<sup>-1</sup> and the equatorial preference of the CH<sub>2</sub> group is negligible in the 3-position of cyclohexene. It is surprising that the equatorial preference of the CH<sub>2</sub> group is less in the cyclohex-3-enylmethyl radical, where it can adopt 'true' axial and equatorial positions, than in the cyclohex-2-enylmethyl radical where the choice is between quasi-axial and quasiequatorial positions. However, the difference is very small and the main observation, *i.e.* that the  $-\Delta G^{\circ}_{300}$  values for both types of cyclohexenylmethyl radical are much less than the  $-\Delta G^{\circ}_{300}$  value for cyclohexylmethyl (0.71 kcal mol<sup>-1</sup>), is in accord with expectation.

The e.s.r. spectrum of the mixture of conformers (3) and (4) showed line broadening above *ca.* 230 K which is attributable to the exchange between (3) and (4). Spectra at 300 K showed a single radical with  $a(2H_{\alpha}) 22.3$ ,  $a(H_{\beta}) 27.5$  G, but the  $\gamma$ -h.f.s. were unresolved even at 320 K. The poor resolution and weak spectra in the fast-exchange limit prevented satisfactory analysis of the dynamics of the half-chair inversion in this system.

Calculation of Barriers to Rotation about  $\dot{C}_{\alpha}-C_{\beta}$  Bonds in Cyclohexenylmethyl Radicals.—We showed previously<sup>7</sup> that the potential barrier to rotation about the  $\dot{C}_{\alpha}-C_{\beta}$  bond,  $V_{o}$ , in primary alkyl radicals can be determined by comparing the experimental temperature dependence of  $a(H_{\beta})$  with values calculated from equation (3) where  $I_1(\lambda)$  and  $I_o(\lambda)$  are modified

$$a(\mathbf{H}_{\mathbf{B}}) = A + \frac{1}{2}B + \frac{1}{2}B\cos 2\theta_{\mathbf{o}}[I_{1}(\lambda)/I_{\mathbf{o}}(\lambda)]$$
(3)

Bessel functions,  $\lambda = V_o/kT$ , and  $\theta_o$  is the value of the dihedral angle between the SOMO and the  $C_{\beta}$ -H bond at the potential minimum; for (1)—(4)  $\theta_o 0^\circ$  [see (7)]. The  $a(H_{\beta})$  values were calculated using equation (3) and compared with experiment for each of (1)—(4). In each case the experimental trend could be satisfactorily represented by a suitable choice of the parameters in equation (3). The A and B values and the calculated rotation barriers are given in Table 3. The equatorial radicals have rotation barriers of 0.2—0.4 kcal mol<sup>-1</sup> which are similar in magnitude to those of acyclic radicals such as isobutyl ( $V_o$  0.44 kcal mol<sup>-1</sup>).<sup>7,10</sup> In each case the calculated  $V_o$  for the axial conformer exceeded that of the corresponding equatorial con-

Table 3. Barriers to rotation about  $\dot{C}_{\alpha}$ - $C_{\beta}$  bonds in cyclohexenylmethyl and related radicals"

Radicals	Conform- ation	A/G	<i>B</i> /G	V₀/kcal mol <sup>-1</sup>
Cyclohex-2-enylmethyl (2)	qeq	1.8	46	0.29
Cyclohex-3-envlmethyl (4)	eq	0.5	46	0.25
Cyclohexylmethyl <sup>b</sup>	eq	0.0	46	0.43
Cyclohex-2-envlmethyl (1)	qax	3.0	46	0.33
Cyclohex-3-envlmethyl (3)	ax	3.0	46	0.31
Cyclohexylmethyl <sup>b</sup>	ax	1.2	46	1.60
<i>4</i> <b>0 · · 1</b> · ·	1	c	c .	

<sup>a</sup>  $\theta_o$  was taken as zero in each case. <sup>b</sup> Data from ref. 1.

former as expected. However, the striking feature of Table 3 is that the  $V_0$  values of the axial conformers are only marginally above those of the equatorial conformers and are very much less than the rotation barrier in axial cyclohexylmethyl and related radicals (see Table 3). This observation provides excellent corroboration for the explanation of the high  $V_0$  value in axial cyclohexylmethyl radicals which we gave previously,<sup>1</sup> viz. that the high barrier arises because of syn-axial interactions of the hydrogens on the  $CH_2$  group with the axial hydrogens at C(3)and C(5) [see (13)]. The axial conformations of both cyclohexenvimethyl radicals, *i.e.* (14) and (15) have only one axial hydrogen [on C(5)] so that syn-axial interaction is greatly reduced and the lower observed barriers are entirely consistent with this explanation. In turn the comparatively low barriers in (14) and (15) ensure that the SOMO on the CH<sub>2</sub> group spends relatively little of its time eclipsing the  $C_{\beta}$ -H bond and thus the  $\beta$ -h.f.s. in (14) and (15), though larger than those of the equatorial conformers, are not nearly so large as the  $\beta$ -h.f.s. of axial cyclohexylmethyl radicals such as (13) (Table 1).

## Experimental

<sup>1</sup>H N.m.r. spectra were recorded on a Bruker WP 80 instrument and <sup>13</sup>C n.m.r. spectra were obtained with a Varian CFT 20 instrument for  $CDCl_3$  solutions at ambient temperature with tetramethylsilane as internal standard. Mass spectra were obtained with an A.E.I. MS 902 spectrometer. Preparative g.l.c. was carried out with a Pye 105 chromatograph. E.s.r. spectra were obtained with a Bruker ER 200D spectrometer, samples being degassed, sealed in Spectrosil tubes and irradiated in the cavity of the spectrometer by light from a 500 W super pressure mercury arc.

Cyclohex-2-ene-1-carboxylic Acid.—To benzoic acid (29.3 g) in liquid NH<sub>3</sub> (800 cm<sup>3</sup>) and dry ether (250 cm<sup>3</sup>) was added lithium metal (6.6 g) in small pieces. The blue solution was stirred for 1 h and then anhydrous ethanol (40 cm<sup>3</sup>) was added dropwise. The mixture was stirred overnight and liquid NH<sub>3</sub> (700 cm<sup>3</sup>) was added followed by lithium metal (5.0 g). The blue solution was stirred for 0.5 h and then anhydrous ethanol (44 cm<sup>3</sup>) was added dropwise. After a further 15 min NH<sub>4</sub>Cl (90 g) was added and NH<sub>3</sub> allowed to evaporate. The mixture was acidified with 6M-HCl, extracted with ether (3 × 300 cm<sup>3</sup>), and the ether extracts were washed with saturated NaCl solution (3 × 200 cm<sup>3</sup>), dried (Na<sub>2</sub>SO<sub>4</sub>), and distilled to give the acid (30.2 g, 84%), b.p. 85–90 °C at 0.8 Torr;  $\delta_{\rm H}$  1.6–2.2 (6 H, m), 3.2 (1 H, s), 5.95 (2 H, br s), and 10.3 (1 H, br s).

#### 1-Bromomethylcyclohex-2-ene.--Cyclohex-2-ene-1-car-

boxylic acid was reduced with LiAlH<sub>4</sub> using standard conditions to give cyclohex-2-enylmethanol (71%), b.p. 51–54 °C at 1.3 Torr;  $\delta_H$  1.3–2.5 (8 H, m), 3.62 (2 H, d, J 7 Hz), and 5.85

(2 H, br AB). The alcohol (4.5 g) and triethylamine (4.0 g) were dissolved in  $CH_2Cl_2$  (30 cm<sup>3</sup>), cooled in ice, and methanesulphonyl chloride (4.7 g) was added dropwise over 15 min. After 0.5 h water was added, the organic layer was separated, washed with 2M-HCl, saturated NaCl solution, NaHCO<sub>3</sub> solution, and CH<sub>2</sub>Cl<sub>2</sub> removed under reduced pressure. The mesylate was added to LiBr (10.4 g) in dry acetone (105 cm<sup>3</sup>) and the mixture was refluxed for 16 h. The solution was filtered, the acetone was removed on a rotary evaporator, water was added, and the aqueous phase was extracted with ether. The ether solution was dried (Na2SO4) and distilled giving the bromide (57%), b.p. 36—40 °C at 1.8 Torr; δ<sub>H</sub> 1.2—2.2 (6 H, m), 2.3-2.7 (1 H, m), 3.52 (2 H, d, J 7 Hz), and 5.82 (2 H, AB + additional splitting);  $\delta_{C}$  20.7, 25.2, 27.7 [C(4), C(5), and C(6)] 36.1 [C(1)], 37.7 (CH<sub>2</sub>Br), 128.3, and 129.7 p.p.m. [C(2) and C(3)] (Found: m/z, 174.0039. Calc. for C<sub>7</sub>H<sub>11</sub><sup>79</sup>Br: M, 174.0045).

#### 2,3,4,5,6-Pentadeuterio-1-bromomethylcyclohex-2-ene.

Pentadeuteriobenzoic acid was reduced with lithium metal in liquid ammonia as described above to give pentadeuteriocyclohex-2-ene-1-carboxylic acid together with tetra- and trideuteriated material. The acid was reduced with LiAlH<sub>4</sub> and converted into the bromomethyl derivative as described above, b.p. 71–72 °C at 20 Torr, yield 49% (Found: m/z 181.0330.  $C_7H_6D_5^{81}Br$  requires M, 181.0339). The mass spectrum indicated the presence of the pentadeuterio compound (15%), the tetradeuterio compound (47%), the trideuterio compound (30%), and the dideuterio compound (ca. 8%). The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra were consistent with this analysis and showed that the additional hydrogen atoms in the tetra- and tri-deuterio material were distributed approximately randomly amongst C(2)—C(6). The bromide was purified by preparative g.l.c. using a 5 m column packed with 20% Embaphase silicone oil.

1-Bromomethylcyclohex-3-ene.—Tetrahydrobenzaldehyde was reduced with LiAlH<sub>4</sub> under standard conditions to give cyclohex-3-enylmethanol (87%), b.p. 95 °C at 20 Torr;  $\delta_{\rm H}$  1.0— 1.5 (1 H, m), 1.5—2.3 (6 H, m), 2.62 (1 H, s), 3.45 (2 H, d, J 5 Hz), and 5.65 (2 H, d, J 2 Hz). The alcohol was converted into the bromomethyl derivative via the mesylate as described above, yield 72%, b.p. 95—96 °C at 20 Torr. Traces of unchanged alcohol were removed by chromatography on alumina (Found: m/z, 174.0036. Calc. for C<sub>7</sub>H<sup>79</sup><sub>19</sub>Br: *M*, 174.0045);  $\delta_{\rm H}$  1.1—2.4 (7 H, m), 3.36 (2 H, d, J 6 Hz), and 5.65 (2 H, d, J ~ 2 Hz);  $\delta_{\rm C}$  24.7, 27.4, 30.4, 36.1, 39.6, 125.5, and 126.9 p.m.

4-Methylcyclohex-2-ene-1-carboxylic Acid.—p-Toluic acid was reduced with lithium metal in liquid ammonia, using the method described above, to give 4-methylcyclohex-2-ene-1carboxylic acid in 63% yield, b.p. 94—96 °C at 0.8 Torr;  $\delta_{\rm H}$  0.96 (3 H, d, J 7 Hz), 1.1—2.5 (5 H, m), 3.13 (1 H, m), 5.80 (2 H, s), and 11.4 (1 H, br s).

1-Bromomethyl-4-methylcyclohex-2-ene.—The 4-methylcyclohex-2-ene-1-carboxylic acid was reduced with LiAlH<sub>4</sub> under standard conditions to give 4-methylcyclohex-2-enylmethanol (79%), b.p. 77—78 °C at 3 Torr;  $\delta_{\rm H}$  0.93 (3 H, d, J 7 Hz), 1.1—2.5 (6 H, m), 3.55 (2 H, d, J 7 Hz), 4.00 (1 H, s), and 5.80 (2 H, br s). The alcohol was converted into the bromomethyl derivative by treatment of the mesylate with LiBr as described above, yield 49%, b.p. 52—53 °C at 0.4 Torr. The compound was purified by preparative g.l.c. on a 5 m column packed with 15% Embaphase silicone oil and operated at 150 °C;  $\delta_{\rm H}$  0.97 (3 H, d, J 7 Hz), 1.1—2.6 (6 H, m), 3.37 (2 H, d, J Hz), and 5.69 (2 H, s). The <sup>13</sup>C n.m.r. spectrum showed the presence of both the *trans*- and *cis*-isomers in roughly equal proportions; 14 of the expected 16 resonance lines being resolved,  $\delta_C 21.1$ , 21.5, 24.7, 27.7, 27.9, 30.0, 30.6, 37.4, 38.0, 39.1, 127.1, 127.5, 135.9, and 136.0 p.p.m. (Found: m/z, 188.0188. Calc. for C<sub>8</sub>H<sub>19</sub><sup>19</sup>Br: *M*, 188.0201).

1-Bromomethyl-4-t-butylcyclohex-2-ene was synthesised from 4-t-butylbenzoic acid using the same sequence of reactions as for the 4-methyl compound, yield 57%, b.p. 130 °C at 1.0 Torr. The compound was purified by preparative g.l.c. on an Embaphase silicone oil column operated at 150 °C;  $\delta_{\rm H}$  1.20 (9 H, s), 1.5—2.4 (6 H, m), 3.40 (2 H, d, J 7 Hz), and 5.6 (2 H, m). The <sup>13</sup>C n.m.r. spectrum showed the presence of both *cis*- and *trans*isomer, but the individual resonances were not so well resolved,  $\delta_{\rm C}$  24.0, 27.0, 27.2, 27.4, 28.3, 28.6, 29.1, 30.8, 36.1, 39.5, 39.8, 127.1, and 133.9 p.p.m.

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