

# Cycloalkylmethyl Radicals. 6. The Unexpectedly High Barrier to the Rotation of Axial CH<sub>2</sub>· Groups in Cyclohexylmethyl Radicals<sup>1</sup>

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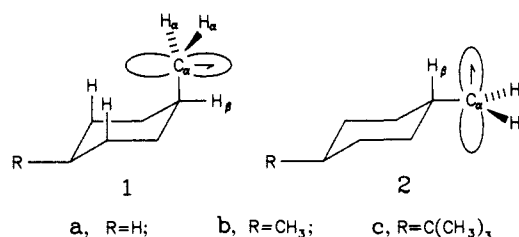
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**Abstract:** The EPR spectra of axial cyclohexylmethyl radicals show temperature-dependent line-broadening effects involving the hydrogen atoms responsible for "long-range" couplings. Since the H<sub>β</sub> hyperfine splittings (hfs) of axial cyclohexylmethyl radicals and of 2-adamantylmethyl (in which the CH<sub>2</sub>· moiety is necessarily axial to a chair cyclohexane ring) are of similar magnitude and show similar temperature dependencies, it is clear that the conformations of axial cyclohexylmethyl radicals have been correctly assigned. The observed line broadening must therefore be attributed to restricted rotation of the axial CH<sub>2</sub>·, the barrier to its rotation being ca. 6 kcal/mol. This barrier is enhanced relative to the barrier in equatorial cyclohexylmethyl radicals because of steric interactions with the syn axial hydrogens at positions 3 and 5. Moreover, this barrier is much greater than the ca. 1.5 kcal/mol calculated from the temperature dependence of H<sub>β</sub> hfs of the axial radicals by the "classical limit" procedure. This failure of the "classical limit" procedure is attributed to the fact that the rotational potential function for these radicals is not of the simple 2-fold type. There are no syn axial hydrogens at positions 3 and 5 in 4-*tert*-butyl-3,5-dioxanylmethyl radicals, and both the axial and equatorial radicals adopt "bisected" conformations, **8** and **9**, respectively, in which H<sub>β</sub> lies in the nodal plane of the C<sub>α</sub> 2p<sub>z</sub> orbital, whereas axial and equatorial cyclohexylmethyl radicals adopt a conformation, **3**, in which H<sub>β</sub> is eclipsed by this orbital. The cyclohexylmethyl radical was also investigated by semiempirical SCF MO calculations.

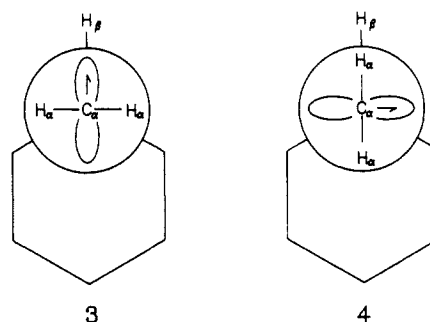
The substituent in all monosubstituted cyclohexanes, c-C<sub>6</sub>H<sub>11</sub>X, shows a distinct preference for the equatorial over the axial position because the former is sterically the less congested. Specifically, in the axial position there is a substantial steric repulsion between the substituent and the two axial hydrogens at positions 3 and 5. It would therefore be expected that the barrier to rotation about the C<sub>1</sub>-X bond would be greater for the axial than for the equatorial conformer. However, to our knowledge, the only attempt to measure rotation barriers for the same substituent in axial and equatorial positions was contained in our own earlier report<sup>4</sup> on the EPR spectroscopy and conformational preferences of cyclohexylmethyl radicals (i.e., for X = CH<sub>2</sub>·). An analysis of the temperature dependence of the β-hydrogen (C<sub>1</sub>-H) hyperfine splittings (hfs) for cyclohexylmethyl and for the 4-methyl and 4-*tert*-butyl substituted radicals by the "classical limit" procedure<sup>5-7</sup> yielded barriers in the range 0.35–0.43 kcal/mol for CH<sub>2</sub>· equatorial (equatorial radicals) and in the range 1.39–1.60 kcal/mol for CH<sub>2</sub>· axial (axial radicals).<sup>4</sup> In all three axial radicals there were, however, some unexpected line-broadening effects involving those hydrogen atoms that gave "long-range" couplings (i.e., small hfs from hydrogens remote from the singly occupied molecular orbital, SOMO). These line-broadening effects were absent in the equatorial radicals. Further exploration of these line-broadening effects has led us to conclude that the barrier for rotation of axial CH<sub>2</sub>· must be considerably greater than ca. 1.5 kcal/mol, which implies that the "classical limit" averaging procedure can yield misleading results when the rotational potential function is not of the simple 2-fold type.

## Results

The cyclohexylmethyl radicals, **1** (axial) and **2** (equatorial), were formed by bromine atom abstraction from the corresponding cyclohexylmethyl bromide with photochemically generated triethylsilyl or trimethyltin radicals in *tert*-butylbenzene at *T* > ca. 200 K and in cyclopropane at lower temperatures. The EPR



parameters of these radicals have been given previously.<sup>4</sup> For all these radicals the β-H hfs has a negative temperature coefficient.<sup>4</sup> This indicates that both axial and equatorial radicals prefer a conformation in which the C<sub>α</sub> 2p<sub>z</sub> orbital (i.e., the SOMO) eclipses the C<sub>β</sub>-H<sub>β</sub> bond, i.e., the "eclipsed" conformation **3** rather than the "bisected" conformation **4**.



The equatorial radicals, **2a-c**, showed a five line long-range splitting pattern which appears to arise from four equivalent hydrogens, probably the four H<sub>γ</sub> on C<sub>2</sub> and C<sub>6</sub>, vide infra [*a*<sup>H</sup>(4H) ≈ 1.0 G at 140 K].<sup>4</sup> In the case of **2a** the line width decreased with increasing temperature, and the multiplet was partly resolved at 230 K: *a*<sup>H</sup>(2H) ≈ 1.0 G and *a*<sup>H</sup>(2H) ≈ 1.5 G (see Supplementary Material).

The axial radicals, **1b** and **1c**, showed *six line* multiplets from long-range splittings, apparently in a binomial distribution, and therefore arising from *five* equivalent hydrogens at 140 K with *a*<sup>H</sup> ≈ 0.75 G. As the temperature was increased, the lines within each multiplet first broadened, coalesced at ca. 210 K, and finally sharpened up into an *eight line* pattern at 280 K and above (see Figure 1), again apparently in a binomial distribution and therefore arising from *seven* equivalent hydrogens with *a*<sup>H</sup> ≈ 0.65 G.

(1) Issued as N.R.C.C. No. 29466. For Part 5 see: Ingold, K. U.; Walton, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6937-6943.

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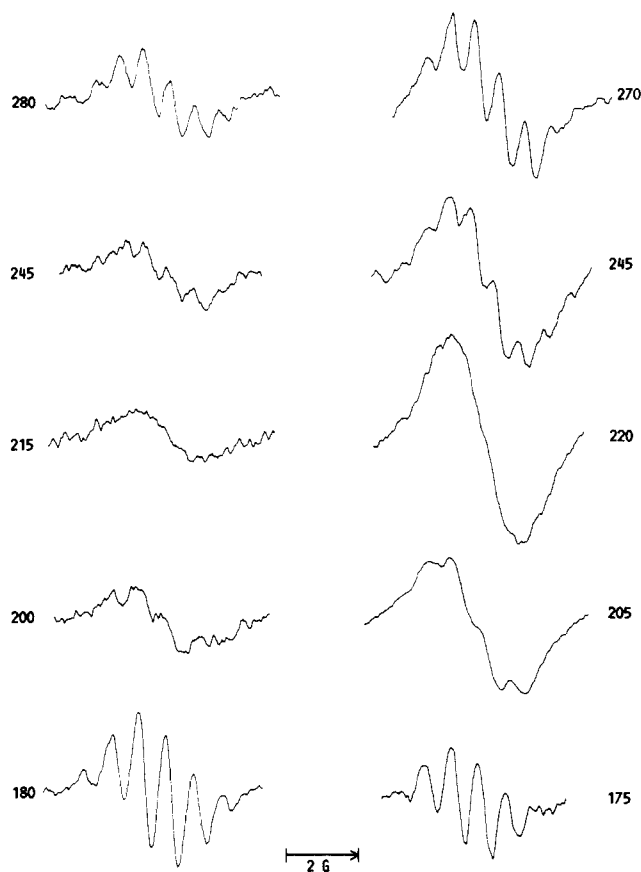
(3) St. Andrews.

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**Figure 1.** Exchange broadening of a single multiplet ( $m_\alpha = 0$ ,  $m_\beta = -1/2$ ) in the 9.4 GHz EPR spectra of axial 4-methylcyclohexylmethyl (**1b**, left-hand side) and 4-*tert*-butylcyclohexylmethyl (**1c**, right-hand side). The numbers by the multiplets refer to the temperature in degrees K.

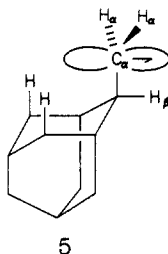
**Table I.** Hyperfine Splittings at 140 K for Some Cycloalkylmethyl and 3,5-Dioxanylmethyl Radicals

radical	conf <sup>a</sup>	Hfs (Gauss)		
		2H <sub>α</sub>	H <sub>β</sub>	other
<b>1c</b> <i>cis</i> -4- <i>tert</i> -butylcyclohexylmethyl <sup>b</sup>	Ax	22.1	41.9	0.75 (5 H)
<b>5</b> 2-adamantylmethyl	Ax	22.3	41.1	
<b>6</b> <i>cis</i> -4- <i>tert</i> -butyl-3,5-dioxanylmethyl <sup>c</sup>	Ax	22.2	19.8	2.8 (2 H), 0.8 (2 H)
<b>2c</b> <i>trans</i> -4- <i>tert</i> -butylcyclohexylmethyl <sup>b</sup>	Eq	22.1	29.9	0.95 (4 H)
<b>7</b> <i>trans</i> -4- <i>tert</i> -butyl-3,5-dioxanylmethyl <sup>d</sup>	Eq	22.2	16.5	1.15 (4 H)

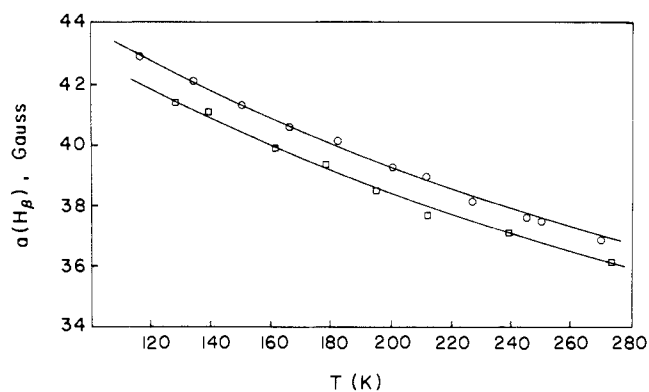
<sup>a</sup> Ax means the CH<sub>2</sub><sup>•</sup> group is axial with respect to the ring; Eq means the CH<sub>2</sub><sup>•</sup> group is in the equatorial position. <sup>b</sup> Data are from ref 4. <sup>c</sup> Measured *g* factor = 2.0028. <sup>d</sup> Measured *g* factor = 2.0027.

The axial cyclohexylmethyl radical, **1a**, is the minor radical formed from the bromide, and its proportion decreases with decreasing temperature.<sup>4</sup> For this reason, its EPR spectrum can be observed only at temperatures  $\geq 200$  K. At 280 K the multiplet from long-range splitting is essentially identical with that observed with **1b** and **1c**. On lowering the temperature broadening occurs (see Supplementary Material), but the spectra become too weak for the limiting slow exchange multiplet to be observed.

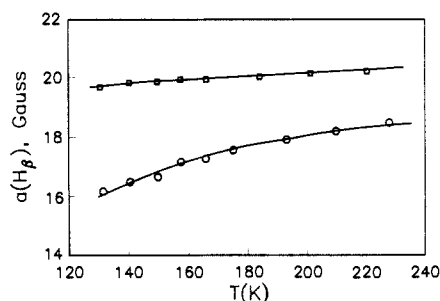
In the 2-adamantylmethyl radical, **5**, the CH<sub>2</sub><sup>•</sup> group is nec-



essarily axial with respect to the adjacent cyclohexane ring for



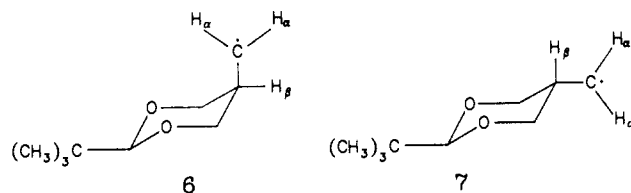
**Figure 2.** Magnitude of the H<sub>β</sub> hfs for axial 4-*tert*-butylcyclohexylmethyl, O (**1c**), and 2-adamantylmethyl, □ (**5**), radicals as a function of temperature.



**Figure 3.** Magnitude of the H<sub>β</sub> hfs for axial 4-*tert*-butyl-3,5-dioxanylmethyl, □ (**6**), and equatorial 4-*tert*-butyl-3,5-dioxanylmethyl, O (**7**), radicals as a function of temperature.

which H<sub>β</sub> is equatorial. This radical was generated from the corresponding bromide, and its EPR parameters are compared with those of the axial radical **1c** in Table I and in Figure 2. The similar magnitudes and temperature coefficients of the H<sub>β</sub> hfs for these two radicals show that they adopt similar conformations about their C<sub>β</sub>-C<sub>α</sub> bonds (i.e., the eclipsed conformation, **3**) and that the barriers for rotation about these bonds must also be similar. Unfortunately, **5** had such broad lines at all temperatures<sup>8</sup> (line width,  $\Delta H_{pp} \sim 2.0$  G) that no dynamic processes analogous to those exhibited by **1b** and **1c** could be observed.

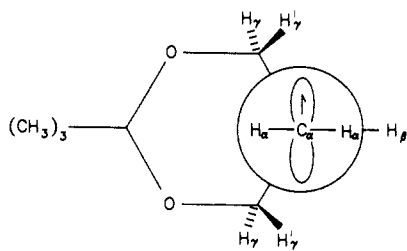
Axial, **6**, and equatorial, **7**, 4-*tert*-butyl-3,5-dioxanylmethyl radicals were generated from *cis*- and *trans*-2-*tert*-butyl-5-bromomethyl-1,3-dioxane, respectively, in order to learn more



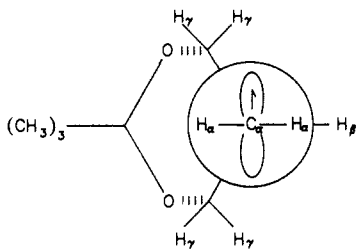
about the role of 1,3-axial steric interactions in cyclohexylmethyl radicals. Their EPR spectra were recorded at a series of temperatures, and the hfs are given at 140 K in Table I. The H<sub>α</sub> hfs are normal for a planar radical center, but the H<sub>β</sub> hfs for both **6** and **7** are lower than the "free rotation" limit of about 26.8 G.<sup>6</sup> Furthermore, both H<sub>β</sub> hfs increased with increasing temperature (see Figure 3) which indicates that radicals **6** and **7** prefer the bisected conformations, **8** and **9** respectively, with H<sub>β</sub> lying in the nodal plane of the SOMO.

The axial radical, **6**, has both a large (2.8 G) and a small (0.8 G), long-range hfs, each arising from a pair of hydrogens. The larger hfs can be assigned to the H<sub>γ</sub> pair in **8** since these are in an all *trans* position (W plan arrangement) with respect to the SOMO. The equatorial radical, **7**, shows one small long-range hfs (0.95 G) due to four equivalent  $\gamma$ -hydrogens. Spectra were

(8) This is probably due to a plethora of unresolved long-range interactions.



8



9

recorded from 130 to 230 K, with the lines remaining sharp and well resolved throughout this temperature range, there being no evidence of any exchange broadening.

### Discussion

**Axial Cyclohexylmethyl Radicals.** The outstanding feature of the foregoing results is the temperature dependence of the long range hfs of the axial radicals (see Figure 1). At first sight, this phenomenon would appear to be due to a simple exchange broadening in which some dynamic process makes hydrogen atoms that are inequivalent at low temperatures become magnetically equivalent at high temperatures. However, in this kind of exchange broadening there are always more EPR lines at low temperature than at high, while the overall spectral width at high temperatures is either the same or less than its width at low temperatures.<sup>9</sup> To our knowledge, axial cyclohexylmethyl radicals represent the first example of a dynamic process in which there are more EPR lines at high temperature (eight lines due to long-range hfs) than at low temperature (six lines due to long-range hfs) and in which the overall spectral width (due to long-range hfs) is slightly greater (by ca. 0.7–0.8 G) at high than at low temperature.

The simplest explanation for the unique behavior of axial cyclohexylmethyl radicals, insofar as the number of lines is concerned, is that in the ground state only five hydrogens<sup>10</sup> are "visible", i.e., have  $a^H > \Delta H_{pp}$ . As the temperature is raised dynamic processes alter the time-averaged conformation of the radicals as higher energy states become increasingly populated. In these higher energy states two "additional" hydrogens interact sufficiently strongly with the SOMO so as to become "visible" for a total of seven hydrogens.<sup>10</sup> However, the magnitudes of the hfs due to the "original" five hydrogens<sup>10</sup> are not much different in the higher energy states than are their magnitudes in the ground state. As a consequence, both the number of lines and the spectral width increase on going from low to high temperatures.

What is the nature of the dynamic process observed in axial cyclohexylmethyl radicals?

(9) Consider a radical with two H's that are nonequivalent at low temperatures and have hfs of +2.0 and +1.0 G. At low temperature the EPR spectrum will consist of four lines of equal intensity separated by 1.0 G, while at high temperatures where these hydrogens have become magnetically equivalent the spectrum will consist of a 1:2:1 triplet with a separation between the lines of 1.5 G, the total spectral width being 3.0 G both at low and at high temperatures. If the two H have hfs of +2.0 and -1.0 G, then the low-temperature spectrum will be unchanged, but at high temperatures it will consist of a 1:2:1 triplet with a separation of only 0.5 G between the lines and an overall width of just 1.0 G.

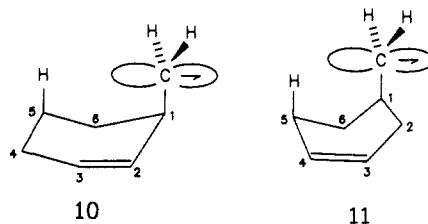
(10) This assumes that the observed long-range hfs pattern is binomial in intensity, i.e., that it is due to the stated number of hydrogens all of which have hfs that are equal or approximately equal.

The fact that essentially identical phenomena were observed for hydrogen (1a), methyl (1b), and *tert*-butyl (1c) attached to the 4-position rules out a dynamic process related to some motion (e.g., rotation) of the 4-substituent.

A motion involving a change in the conformation of the cyclohexane ring can also be ruled out. Thus, the barrier to the motion that produces line broadening can be estimated from the temperature of coalescence ( $\sim 210$  K) to be about 6 kcal/mol.<sup>11</sup> This is considerably lower than the 10.5 kcal/mol barrier to ring inversion of cyclohexane and alkyl-substituted cyclohexanes,<sup>13</sup> which serves to rule out a chair-to-chair ring inversion.<sup>14</sup> However, the pseudorotation which interconverts twist-boat forms of cyclohexane has a much lower energy barrier, and the twist-boat conformation lies ca. 6 kcal/mol above the chair form in energy.<sup>15–18</sup> If pseudorotation of the twist-boat conformer of cyclohexane were responsible for the observed line broadening, it would require that the supposed "axial" cyclohexylmethyl radicals actually had their cyclohexane ring in a twist-boat structure. This is almost inconceivable in view of the energy differences between twist-boat and chair,<sup>15–18</sup> but "to be on the safe side" we examined the 2-adamantylmethyl radical, 5, in which the  $\text{CH}_2^\bullet$  group is axial with respect to a chair cyclohexane, and twist-boat conformations are impossible. In 5 the hfs of  $\text{H}_\beta$  (which is equatorial with respect to the cyclohexane ring of interest) is only very slightly lower at all temperatures than the  $\text{H}_\beta$  hfs of axial 4-*tert*-butylcyclohexylmethyl (see Figure 2), and it is essentially identical at all temperatures with the  $\text{H}_\beta$  hfs of the axial cyclohexylmethyl radical itself.<sup>4</sup> This confirms our earlier deduction regarding the conformation of axial cyclohexylmethyl radicals<sup>4,19</sup> and rules out ring motion as a cause of line broadening.

The only remaining motion that could produce exchange broadening is rotation about the  $\text{C}_\beta\text{--C}_\alpha^\bullet$  bond. In axial cyclohexylmethyl radicals, 1a–c, the rotation barrier is enhanced relative to the barrier in the equatorial radicals, 2a–c, because of steric interactions with the syn axial hydrogens at positions 3 and 5. We reasoned, therefore, that axial radicals lacking one or both of these syn axial hydrogen atoms would have greatly reduced  $\text{C}_\beta\text{--C}_\alpha^\bullet$  rotation barriers and, hence, reduced  $\text{H}_\beta$  hfs.

The cyclohex-2-enylmethyl radical, 10, and the cyclohex-3-enylmethyl radical, 11, each have a single pseudoaxial hydrogen



at C-5, and their axial conformers have  $\text{H}_\beta$  hfs of 32.6 and 32.3

(11) The rate constant for exchange at the coalescence temperature is given by  $K = 6.22 \times 10^6 \Delta a \text{ s}^{-1}$ , where  $\Delta a$  is the difference in gauss of the hfs for the two hydrogens that are inequivalent at low but equivalent at high temperatures.<sup>12</sup> Assuming that  $\Delta a$  must be of the same order of magnitude as the long-range hfs, viz., ca. 0.8 G and assuming a "normal" Arrhenius preexponential factor of ca.  $10^{13} \text{ s}^{-1}$ , yields an activation energy for the exchange process of ca. 6 kcal/mol.

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(14) Such a process can also be ruled out because axial and equatorial cyclohexylmethyl radicals give distinct EPR spectra at temperatures well above 210 K.<sup>4</sup>

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G, respectively, at 140 K,<sup>20</sup> which indicates that the  $C_\beta-C_\alpha^*$  rotational barriers are much lower than those in axial cyclohexylmethyl radicals. Both **10** and **11** exhibited exchange broadening, but this was of a completely different type and involved broadening of the lines from *both* the axial and the equatorial conformers.<sup>20</sup> This indicates that the dynamic process being monitored involved ring inversion, the activation energy for ring inversion being only about 5.5 kcal/mol.<sup>13,18,20-22</sup>

The 4-*tert*-butyl-3,5-dioxanylmethyl radicals contain no syn axial hydrogens at positions 3 and 5. Both the axial, **6**, and the equatorial, **7**, radicals prefer bisected conformations, **8** and **9**, respectively. That **6** can adopt conformation **8** ( $\equiv$ **4**) certainly shows that syn axial interactions have a profound influence on the  $C_\beta-C_\alpha^*$  potential function. The analogous bisected conformation for the axial cyclohexylmethyl radicals, **4**, must be disfavored because it requires one of the  $C_\alpha^*H_2$  hydrogen atoms to be in close proximity to the syn axial hydrogens at positions 3 and 5. Of course, it does not follow that if these hydrogens were removed, the preferred conformation would automatically "switch" to **8** ( $\equiv$ **4**). However, in the absence of the steric repulsions from axial H-3 and H-5, the difference in energy between the eclipsed conformation and the bisected conformation will be very small,<sup>23</sup> and the controlling factors are therefore extremely difficult to pinpoint.<sup>24,25</sup>

It is worth noting that at 140 K the axial, bisected 3,5-dioxanylmethyl radical, **6**, has a greater spectral width due to long range couplings ( $2 \times 2.8 + 2 \times 0.8 = 7.2$  G, see Table I) than the equatorial conformer, **7** ( $4 \times 0.95 = 3.8$  G), and a greater width than axial (eclipsed) cyclohexylmethyl radicals at the same temperature (e.g., **1c**,  $5 \times 0.75 = 3.75$  G). This provides a rationale for the greater spectral width due to long range hfs of axial cyclohexylmethyl radicals at temperatures above 210 K. That is, once the temperature is such that the  $H_\alpha$ -axial  $H_3$  barrier can be surmounted, the axial cyclohexylmethyl radical will be able to populate the bisected conformation, **4**, which, by analogy with **6**, will have a greater spectral width than the eclipsed conformation, **3**. The spectral width for the time-averaged conformation at the higher temperature will therefore be increased relative to that for **3**.

All the evidence is consistent with the conclusion that the axial  $C_\alpha^*H_2$  substituent on a cyclohexane ring has an unusually high

Table II. INDO Calculated Long-Range Hfs for Cyclohexylmethyl Radicals<sup>a</sup>

radicals	$H_\beta$ - SOMO	Hfs (Gauss)					
		$H_{Ax}^{2,6}$	$H_{Eq}^{2,6}$	$H_{Ax}^{3,5}$	$H_{Eq}^{3,5}$	$H_{Ax}^4$	$H_{Eq}^4$
ax, <b>1a</b>	eclipsed, <b>3</b>	-2.0	-1.0	0.2	0.2	0.0	-0.3
ax, <b>1a</b>	bisected, <b>4</b>	1.6	-2.2	0.1	1.9	-0.1	-0.1
eq, <b>2a</b>	eclipsed, <b>3</b>	-3.2	-1.4	0.2	0.5	-0.1	0.0
eq, <b>2a</b>	bisected, <b>4</b>	-1.5	-1.8	0.1	2.5	-0.1	-0.1

<sup>a</sup> Data refer to MINDO/3-UHF geometries.

rotation barrier as a result of steric hindrance by the syn axial hydrogens at positions 3 and 5. A higher barrier for axial than for equatorial cyclohexylmethyl is perfectly reasonable, of course, but the apparent magnitude of the barrier (ca. 6 kcal/mol) is, unexpectedly, very much greater than the value of ca. 1.5 kcal/mol calculated from the variation in the  $\beta$ -H hfs with temperature by the "classical limit" method.<sup>4</sup> The derivation of the "classical limit" equation *assumes* a simple 2-fold barrier about the  $C_\beta-C_\alpha^*$  bond. In the axial radicals, **1**, the rotational potential is obviously more complex than this because of the syn axial interactions. The poor performance of the "classical limit" method for axial cyclohexylmethyl radicals can probably be traced to this cause.

**Semiempirical SCF MO Calculations.** We have previously shown<sup>4</sup> that the UHF versions of MINDO/3<sup>36</sup> and MNDO<sup>37</sup> are not successful in predicting the  $C_\beta-C_\alpha^*$  rotation barriers in cycloalkylmethyl radicals. The former method badly underestimated the barrier in both the axial, **1a**, and equatorial, **2a**, conformers, and the latter method predicted incorrect conformations, i.e., bisected rather than eclipsed.<sup>4</sup> Both methods gave optimized geometries in which the cyclohexane rings were too "flattened" (dihedral angles of 42° and 46°, respectively) which has the effect of placing the  $C_\alpha^*H_2$  group in the axial radical, **1a**, further from the axial hydrogen at positions 3 and 5 than is likely to be the case. INDO<sup>38</sup> calculations gave rotation barriers of 1.0 and 0.4 kcal/mol for **1a** and **2a**, respectively, when the optimum geometries from the MINDO/3-UHF computations were used.<sup>4</sup> In order to overcome the problem of ring flattening for axial cyclohexylmethyl in the MINDO/3-UHF geometry, INDO calculations were also carried out with a ring geometry taken from the electron diffraction geometry of cyclohexane<sup>32</sup> (ring dihedral angles = 55°),<sup>32</sup> with the MINDO/3-UHF geometry being retained at

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(21) Anet, F. A. L.; Haq, M. Z. *J. Am. Chem. Soc.* **1965**, *87*, 3147-3150.

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(23) These axial interactions are absent in the isobutyl and in the equatorial cyclohexylmethyl radicals for which the barriers to  $C_\beta-C_\alpha^*$  rotation are ca. 0.4 kcal/mol: see ref 7 and references cited.

(24) The equatorial-to-axial preference of alkyl groups in 5-alkyl-1,3-dioxanes has been shown by NMR spectroscopy to be dramatically less than for the comparable alkyl-substituted cyclohexanes. See: Ridell, F. G.; Robinson, M. J. T. *Tetrahedron* **1968**, *23*, 3417-3425. Eliel, E. L.; Knoeber, M. C. *J. Am. Chem. Soc.* **1968**, *90*, 3444-3458.

(25) We have previously reported that cycloalkylmethyl radicals<sup>7,26</sup> and cycloalkenylmethyl radicals<sup>27</sup> undergo a "switch" from the bisected conformation to the eclipsed conformation as the ring size is increased from five to six atoms. The conformational preferences of these radicals could be largely rationalized in terms of the main steric interactions between the hydrogens on the  $C_\alpha^*H_2$  moiety and the adjacent  $\beta$ ,  $\gamma$ , and  $\delta$  hydrogens on the ring.<sup>7,27</sup> In the bisected conformations the shortest H-H distance for these radicals is the unique (eclipsed)  $H_\alpha-H_\beta$ , and for equatorial cyclohexylmethyl and isobutyl this repulsive interaction dominates all others and causes these two radicals to adopt the eclipsed conformation.<sup>7</sup> However, for cyclopentylmethyl the bisected conformation is favored because repulsion due to the single  $H_\alpha-H_\beta$  interaction is outweighed by the repulsion due to the double  $H_\alpha-H_\gamma$  interaction in the eclipsed conformation.<sup>7</sup> The preference for the bisected conformation increases as the  $C_\gamma C_\beta C_\alpha$  angle decreases along the series cyclopentylmethyl to cyclobutylmethyl to cyclopropylmethyl. There is good evidence from electron diffraction,<sup>28</sup> X-ray crystallography,<sup>29</sup> and molecular mechanics calculations<sup>30</sup> that the CCC angle in 1,3-dioxanes is appreciably smaller than that in cyclohexane.<sup>31</sup> We therefore tentatively suggest that  $C_\alpha^*H_2-H$  repulsive interactions similar to those operating in cycloalkylmethyl radicals cause 3,5-dioxanylmethyl radicals to adopt a bisected conformation.<sup>33</sup> For 3,5-dioxanylmethyl, just as for cyclopentylmethyl, the smaller interior ring angle causes repulsion by the double  $H_\alpha-H_\gamma$  interaction to outweigh the single  $H_\alpha-H_\beta$  interaction.<sup>35</sup> The axial radical, **6**, adopts the same conformation as the equatorial radical, **7**, because of the absence of syn-axial hydrogens at positions 3 and 5.

(26) See also Part 5.<sup>1</sup>

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(35) Narrowing of the  $C_\gamma C_\beta C_\alpha$  angle may be accompanied by a widening of the  $C_\alpha C_\beta H_\beta$  angle which would reduce the  $H_\alpha-H_\beta$  repulsion.

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the radical center. The calculated rotation barrier was now 2.3 rather than 1.0 kcal/mol, which serves to demonstrate the sensitivity of this barrier to ring structure.

The results of INDO calculations of long-range hfs for **1a** and **2a** in both their preferred, eclipsed conformations, **3**, and in their disfavored, bisected conformations, **4**, using the MINDO/3-UHF geometries are given in Table II. For the axial radical in its eclipsed conformation the INDO calculations imply that four out of the five hydrogens observed at low temperatures are the axial and equatorial hydrogens at positions 2 and 6. However, the calculations fail to predict a significant hfs for the axial hydrogen at position 4, yet a splitting by this (unique) hydrogen would certainly appear to be required by the observation of a six line spectrum at low temperatures (see Figure 1). At higher temperatures some of the bisected conformation will become mixed with the eclipsed conformation, and the INDO calculations suggest that the two "new" hydrogens that become "visible" (seven hydrogens total<sup>10</sup> yielding an eight line spectrum, see Figure 1) are the equatorial hydrogens at positions 3 and 5. However, these calculations also indicate that an admixture of the bisected conformation to the eclipsed would reduce the spectral line width due to long-range hfs (which is  $-5.5$  G for **1a** eclipsed and  $+2.6$  G for **1a** bisected), rather than increase the width as is actually observed.

For the equatorial, eclipsed cyclohexylmethyl, **2a**, INDO predicts sizeable long-range hfs by four hydrogens which agrees with the observation of a five line spectrum. However, at higher temperatures increased mixing with the bisected conformation would be expected to lead to additional hfs from the equatorial hydrogens at positions 3 and 5, which is contrary to experiment.

In conclusion, INDO calculations fail to predict the patterns of long-range hfs obtained with axial and equatorial cyclohexylmethyl radicals. A definitive identification of the ring hydrogens responsible for the long-range hfs will require either high level ab initio calculations or specific deuterium labeling. Nevertheless, whichever ring hydrogens are actually responsible for the long-range hfs, the experimental observations with axial cyclohexylmethyl radicals leave little doubt that the barrier to rotation about the  $C_\beta-C_\alpha$  bond is considerably greater than that calculated from the temperature dependence of the  $H_\beta$  hfs.

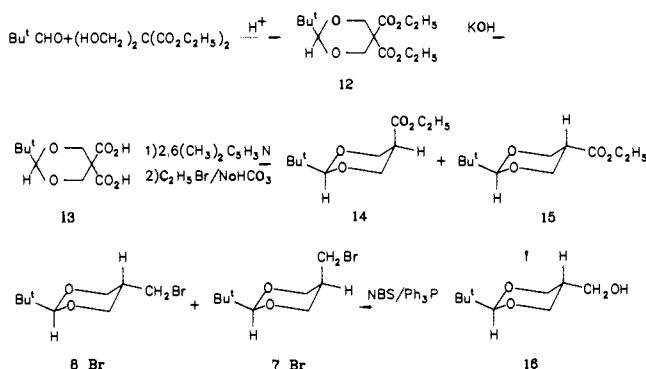
## Experimental Section

**General Methods.** EPR spectra were recorded on Bruker ER 200D and Varian E104 spectrometers with samples that had been degassed by several freeze-pump-thaw cycles. These samples were sealed in 4 mm o.d. spectroil tubes and were then irradiated in the cavity of the EPR spectrometer with light from a 500-W high-pressure mercury lamp. <sup>1</sup>H NMR spectra were recorded on a 60 MHz Varian EM 360 and <sup>13</sup>C NMR spectra on a 400 MHz Bruker instrument in CDCl<sub>3</sub> as solvent with tetramethylsilane as internal standard, unless otherwise noted. Mass spectra were recorded on a Hewlett-Packard 5970 A Mass Selective Detector with an HP-Ultra I fused silica capillary GC column (10 m × 0.2 mm i.d., OV-101 type, cross-linked, bonded phase). Preparative GC separations were carried out on a Varian 920 instrument equipped with a 10 ft, 30% carbowax (20 M) column (injector at 210 °C, column at 190 °C, detector at 220 °C). Thin-layer chromatography was performed on BDH silica gel plates (60F-254) and developed with ethyl acetate/hexane. Spots were visualized with iodine vapor. Column chromatographic purifications used Merck grade 60 silica gel (230–400 mesh, 60 Å, Aldrich). Unless otherwise noted all reactions were carried out under a nitrogen atmosphere.

**Materials.** Cyclohexylmethyl bromide, *trans*- and *cis*-4-methylcyclohexylmethyl bromide, and *trans*- and *cis*-4-*tert*-butylcyclohexylmethyl bromide were available from previous work.<sup>4</sup>

**2-Bromomethyladamantane** was prepared from 2-adamantanone as follows: To *n*-butyllithium (63 mL of a 1.6 M solution in benzene, 100 mmol) in dry ether under N<sub>2</sub> was added methyltriphenylphosphonium bromide (26.1 g, 73 mmol), the solution was stirred (1 h), and then 2-adamantanone (Aldrich 7.3 g, 49 mmol) in dry ether (50 mL) was added dropwise, followed by refluxing for 7 h. The ether was then decanted, and water (100 mL) was added to the residue which was extracted with additional ether (2 × 100 mL). The combined ethereal solutions were dried over Na<sub>2</sub>SO<sub>4</sub> and distilled to give 2-methyleneadamantane (4.4 g, 61%), bp 155 °C at 20 Torr, which solidified on cooling: <sup>1</sup>H NMR,  $\delta$  1.8 (brs, 12 H), 2.5 (brs, 2 H), 4.5 (s, 2 H). This compound (4.2 g, 28 mmol) in dry THF (50 mL) was cooled in ice, and

## Scheme I



BH<sub>3</sub>·THF (20 mL of a 1 M solution) was added slowly, and the mixture was stirred for 30 min. Water (3 mL) was added, the solution was heated to 45 °C, and NaOH (15 mL of a 3 M solution) was then added, followed by H<sub>2</sub>O<sub>2</sub> (7 mL of a 9 M solution). The mixture was stirred at 45 °C for 1 h and cooled, and ether (100 mL) was added. The ether layer was separated, and the aqueous layer was saturated with NaCl and extracted with ether (2 × 50 mL). The combined organic solvents were washed with saturated NaCl, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to give 4.4 g (94%) of crude 2-adamantylmethanol. To this crude alcohol (4.4 g, 26 mmol) was added Et<sub>3</sub>N (2.7 g, 27 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (170 mL), the solution was cooled in ice, and methanesulfonyl chloride (3.4 g, 29 mmol) was added followed by stirring for 30 min, addition of water (100 mL), and separation of the CH<sub>2</sub>Cl<sub>2</sub> layer. The last named layer was washed with 2 M HCl (100 mL), 5% NaCl in water (100 mL), and saturated NaHCO<sub>3</sub> solution (100 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. The CH<sub>2</sub>Cl<sub>2</sub> was removed at room temperature on a rotary evaporator. The involatile mesylate was added to refluxing, dry acetone (85 mL) containing LiBr (7 g, 80 mmol). After 10 h the solution was filtered, the solvent was evaporated, and the residue was dissolved in light petroleum (bp 40–60 °C) and chromatographed on silica to yield 0.8 g (13%) of 2-bromomethyladamantane: <sup>1</sup>H NMR,  $\delta$  1.5–2.1 (m, 15 H), 3.55 (d,  $J = 8$  Hz, 2 H); MS (on an AEI MS 902 instrument), M<sup>+</sup> (obsd) 228.0505, calcd for C<sub>11</sub>H<sub>17</sub><sup>79</sup>Br 228.0514.

*cis*- and *trans*-2-*tert*-butyl-5-bromomethyl-1,3-dioxane (**7 Br** and **8 Br**, respectively) were synthesized according to Scheme I. To 30 g (348 mmol) of trimethylacetaldehyde (Aldrich) in 250 mL of petroleum ether (bp, 30–60 °C) were added 75.5 g (343 mmol) of diethyl bis(hydroxymethyl)malonate (Aldrich) and 4.0 g (21 mmol) of *p*-toluenesulfonic acid. The solution was refluxed 2 h with a Dean and Stark water trap connected to the reflux condenser. The solution was then cooled to 25 °C, 3.5 g of sodium acetate was added, and the mixture was stirred for 20 min. Ether (300 mL) was added, and the ether layer was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated in vacuo, and distilled to give 76 g (76%) of 2-*tert*-butyl-5,5-dicarboxy-1,3-dioxane, **12**, bp 93–98 °C at 0.25 Torr [<sup>1</sup>H NMR,  $\delta$  0.9 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.1–1.5 (m, 6 H, (CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 3.7–4.7 (m, 9 H, (CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>, ring H); GC/MS,  $m/e$  (rel intensity) 287 (M – 1, 27), 273 (20), 231 (100), 173 (31)]. This compound (76 g, 264 mmol) was converted to the corresponding dicarboxylic acid by dissolving in 520 mL of 95% ethanol, adding 63.1 g (1.12 mmol) of KOH, and refluxing for 1 h. The thick reaction mixture was cooled, and ca. 125 mL of solvent was removed by distillation under reduced pressure, this was replaced by 125 mL of H<sub>2</sub>O, and a procedure involving distillation followed by a further addition of water was applied repeatedly until ca. 500 mL of distillate had been collected. The mixture was then cooled to 0 °C, stirred, treated dropwise with 108 mL of concentrated HCl (to pH = 1), and extracted with ether (2 × 500 mL), and the organic phase was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated in vacuo to give 2-*tert*-butyl-5,5-dicarboxy-1,3-dioxane, **13**, 59.1 g (96.4%), mp 70–71 °C: <sup>1</sup>H NMR  $\delta$  0.9 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 3.6–4.8 (m, 5 H, ring H). This material (59.1 g, 255 mmol) was then dissolved in 60 mL of 2,6-lutidine, refluxed 1.5 h, and cooled to 0 °C, and 295 mL of 20% HCl was added dropwise with stirring. An ether extract (3 × 300 mL) was washed with 300 mL of 20% HCl, 300 mL of water, and 300 mL of brine, then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated in vacuo to give a mixture of *cis*- and *trans*-2-*tert*-butyl-5-carboxy-1,3-dioxane (38.0 g, 85.1%) mp = 175.5–176.5. This monocarboxylic acid (38 g, 202 mmol) was dissolved in 527 mL of DMF and treated with 34 g (404 mmol) of NaHCO<sub>3</sub>, followed by 75.3 mL (976 mmol) of ethyl bromide. The resultant mixture was stirred 18 h at room temperature, followed by the addition of water (500 mL) and extraction into ether (2 × 500 mL). The ether extract was washed with bicarbonate and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated in vacuo to give 38 g of a mixture which, by <sup>1</sup>H NMR analysis, consisted of ca. 34% *cis*-

and ca. 66% *trans*-2-*tert*-butyl-5-carbomethoxy-1,3-dioxane, **14** and **15**, respectively. This isomeric mixture was separated by column chromatography (3% ethyl acetate/hexane) to give two oils as products: 16.8 g (30.6%) of the pure *trans* isomer, **15**, and 4.7 g (8.6%) of the pure *cis* isomer, **14** (yields are based on the starting dicarboxylic acid). For the *trans* isomer, **15**:  $^1\text{H NMR}$   $\delta$  0.9 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.1–1.4 (t,  $J$  = 7 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.6–1.7 (m, 1 H, CHCO<sub>2</sub>), 3.4–4.5 (m, 7 H, CH<sub>2</sub>-CH<sub>3</sub> and remaining ring H). For the *cis* isomer, **14**:  $^1\text{H NMR}$   $\delta$  0.9 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.2–1.4 (t,  $J$  = 7 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 2.1–2.3 (m, 1 H, CHCO<sub>2</sub>), 3.5–4.6 (m, 7 H, CH<sub>2</sub>CH<sub>3</sub> and remaining ring H). The *trans* isomer, **15** (6.8 g, 31.6 mmol), was dissolved in 100 mL of anhydrous ether, and this solution was added dropwise to a suspension of 3.0 g (79 mmol) of LiAlH<sub>4</sub> in 150 mL of anhydrous ether. After the suspension was stirred at room temperature for 2 h, it was carefully poured onto ice containing 0.3 g of solid NaOH, extracted with ether (2 × 75 mL), washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to give 3.8 g (69%) of *trans*-2-*tert*-butyl-5-hydroxymethyl-1,3-dioxane, **16**, mp 59.0–60.5 °C:  $^1\text{H NMR}$   $\delta$  0.9 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.9–2.6 (m, 1 H, CHCH<sub>2</sub>OH), 3.2–4.3 (m, 7 H, CH<sub>2</sub>OH and remaining ring H). To 1.0 g (5.7 mmol) of this compound dissolved in 16 mL of CH<sub>2</sub>Cl<sub>2</sub> and cooled to –10 °C was added 1.5 g (5.7 mmol) of triphenylphosphine followed by 1.0 g (5.6 mmol) of *N*-bromosuccinimide. The mixture was stirred 10 min at –10 °C and then at room temperature for a further 30 min. Analysis by GC indicated the presence of *cis*- and *trans*-2-*tert*-butyl-5-bromomethyl-1,3-dioxane, **7 Br** and **8 Br**, respectively, in yields of 16.4% and 73.1%, respectively, together with unreacted starting material (3.6%) and the isomerized, i.e., *cis*, starting alcohol (6.9%). Evaporation of the

reaction mixture, treatment with 50 mL of 5% ethyl acetate/hexane, filtration, and column chromatography (5% ethyl acetate/hexane) gave 0.8 g of a mixture consisting of ca. 20% of the *cis*, **7 Br** and ca. 80% of the *trans*, **8 Br**, bromomethyl compounds. Preparative GC gave the pure (>95%) isomers. *Cis*-2-*tert*-butyl-5-bromomethyl-1,3-dioxane, **7 Br**, mp 35.2–36.1 °C:  $^1\text{H NMR}$  (400 MHz)  $\delta$  0.89 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.70–1.74 (br t,  $J$  = 7.3 Hz, 1 H, CHCH<sub>2</sub>Br), 3.72–3.74 (d,  $J$  = 7.3 Hz, 2 H, CH<sub>2</sub>Br), 3.89–3.91 (d,  $J$  = 11.2 Hz, 2 H, (H<sub>ax</sub>CH<sub>eq</sub>)<sub>2</sub>), 4.10 (s, 1 H, CHC(CH<sub>3</sub>)<sub>3</sub>), 4.13–4.16 (d,  $J$  = 11.2 Hz, 2 H, (H<sub>ax</sub>CH<sub>eq</sub>)<sub>2</sub>);  $^{13}\text{C NMR}$   $\delta$  24.50, 30.00, 33.64, 37.83, 68.39; GC/MS,  $m/e$  (rel intensity) 237 (M – 1 <sup>81</sup>Br, 1.8), 235 (M – 1 <sup>79</sup>Br, 2.06), 181 (96.0), 179 (100), 135 (12.5), 133 (12.2). *Trans*-2-*tert*-butyl-5-bromomethyl-1,3-dioxane, **8 Br**, mp 27.7–28.4 °C:  $^1\text{H NMR}$  (400 MHz)  $\delta$  0.90 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.26–2.31 (m, 1 H, CHCH<sub>2</sub>Br), 3.09–3.11 (d,  $J$  = 6.2 Hz, 2 H, CH<sub>2</sub>Br), 3.38–3.44 (t,  $J$  = 11.5 Hz, 2 H, (H<sub>ax</sub>CH<sub>eq</sub>)<sub>2</sub>), 4.00 (s, 1 H, CHC(CH<sub>3</sub>)<sub>3</sub>), 4.18–4.22 (dd,  $J$  = 11.5 Hz and 4.4 Hz, 2H, (H<sub>ax</sub>CH<sub>eq</sub>)<sub>2</sub>).  $^{13}\text{C NMR}$ ,  $\delta$  24.76, 29.63, 34.74, 36.10, 70.71; GC/MS,  $m/e$  (rel intensity) 237 (M – 1 <sup>81</sup>Br, 2.15), 235 (M – 1 <sup>79</sup>Br, 2.22), 181 (93.9), 179 (100), 135 (10.5), 133 (13.0).

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**Supplementary Material Available:** Figure 4 showing one main line of the EPR spectrum of **1a** and **2a** (1 page). Ordering information is given on any current masthead page.

## Chemical Reactivity of the Three-Sulfur Ring in Norbornanetrithiolanes. The S<sub>3</sub> Transfer Reaction

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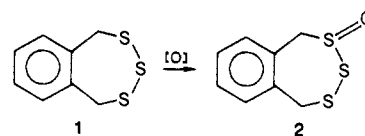
Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129. Received March 7, 1988

**Abstract:** The oxidation of norbornanetrithiolanes with *m*-chloroperbenzoic acid and with ozone has been studied in detail. The trithiolane 1- and 2-oxides are formed, their ratio depending on the substitution at C<sub>2</sub> of the norbornane framework. In some cases it has been possible to separate the exo and endo isomers of these oxides. Heating *endo*-2-phenyl-*exo*-3,4,5-trithiatriacyclo[5.2.1.0<sup>2,6</sup>]decane (**8**) with norbornene at 100 °C gives *exo*-3,4,5-trithiatriacyclo[5.2.1.0<sup>2,6</sup>]decane (**3**) and 2-phenylnorbornene. Thus, for the first time an S<sub>3</sub>-transfer reaction has been observed. A thorough kinetic analysis of this reaction has been carried out, and the results indicate a bimolecular concerted mechanism.

In a recent study<sup>1</sup> we have shown that a variety of norbornene double bonds react with elemental sulfur to give norbornanetrithiolanes and -pentathiepanes. Here we report on (i) oxidation of norbornanetrithiolanes with different oxidizing reagents and (ii) the capability of some of the trithiolanes to act as donors of the "S<sub>3</sub>" unit.

### Introduction

Oxidation of monosulfides to sulfoxides and sulfones is an actively researched branch of organosulfur chemistry. In recent years the oxidation of disulfides has also received considerable interest.<sup>2,3</sup> Feher et al.<sup>4</sup> have shown that oxidation of linear trisulfides with excess of peroxides gives symmetrical disulfonyl sulfides, suggesting that the middle sulfur is least prone to attack. This observation has also been found to be true in the oxidation of the benzotrithiepane (**1**).<sup>5</sup>



We have carried out a systematic study of the oxidation of norbornanetrithiolanes by different oxidizing agents. This study has revealed that the norbornane framework exerts some unique control on the regio- and stereochemistry of oxidation.

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