N HCl (5 mL) for 24 h. The reaction mixture was diluted with water and the solution was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extract was dried (Na_2SO_4) and evaporated to dryness to yield 80 mg (85%) of **9a**, mp 234–236 °C, which was shown to be identical with material obtained below.

From 8b. Compound **8b** (150 mg, 0.43 mmol) was refluxed in 6 N HCl (2 mL) for 4 days. The separated solid was collected by filtration, washed with water, and dried. Recrystallization from acetone gave 45 mg (50%) of **9a** as colorless crystals: mp 234–236 °C (lit.[5a] mp 223 °C); IR (KBr) ν(max) 3490 (br), 1678 cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 1.40 (d, 3 H, J = 6.65 Hz), 2.8–3.2 (m, 2 H), 3.5 (br, 2 H), 4.63–4.76 (m, 1 H), 6.85 (d, 1 H, J = 8 Hz), 7.95 (d, 1 H, J = 8 Hz); ^{13}C NMR (Me$_2$SO-d_6) δ 20.2, 34.4, 74.7, 110.8, 115.7, 117.7, 136.4, 146.7, 161.8, 165.3, 168.8.

3-Methyl-5-chloro-7-carboxy-8-hydroxyisocoumarin (9b). *N,N*-Diethyl-2-methoxy-3-(diethylcarbamoyl)-5-chloro-6-allylbenzamide (**8c**) (155 mg, 0.41 mmol) was refluxed in 6 N HCl (2 mL) for 4 days. Workup as for **9a** followed by crystallization (acetone–methanol) fur-

nished 51 mg (49%) of **9b** as colorless crystals: mp 246 °C (lit.[5a] mp 229 °C, lit.[5b] mp 246–249 °C dec, lit.[5c] 246 °C); IR (KBr) ν(max) 3288, 1736, 1705, 1667 cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 1.43 (d, 3 H, J = 6.2 Hz), 2.49–3.23 (m, 2 H), 4.70–4.79 (m, 1 H), 7.98 (s, 1 H); ^{13}C NMR (Me$_2$SO-d_6) δ 20.1, 32.1, 74.4, 112.4, 117.7, 120.6, 136.0, 143.4, 160.2, 165.4, 167.1.

The ^{1}H and ^{13}C NMR spectra were found to be identical with those reported[5c] for **9b**. Its ^{13}C spectrum was directly compared with that kindly provided by Professor G. A. Kraus.

Cycloalkylmethyl Radicals. 2. Axial and Equatorial Cyclohexylmethyl and (4-Alkylcyclohexyl)methyl Radicals. First Determination of the Conformational Free Energy Difference of the CH$_2$· Group[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A OR6, Canada, and the Department of Chemistry, The University, St. Andrews, Fife, Scotland KY16 9ST, U.K. Received April 8, 1985. Revised Manuscript Received August 5, 1985

Abstract: At 140 K the EPR spectra of cyclohexylmethyl and (4-alkylcyclohexyl)methyl radicals in which the CH$_2$· group adopts the axial conformation have $a^{H_\beta} \sim$ 42–43 G, while those in which the CH$_2$· group adopts the equatorial conformation have a^{H_β} = 30–31 G. Both conformers can be observed over a range of temperatures for cyclohexylmethyl and for (*cis*-4-methylcyclohexyl)methyl. For the former radical, the relative conformer concentrations under conditions where ring inversion is rapid relative to radical lifetime can be described by log ([axial]/[equatorial]) = 0.79 – 1.79/θ (where θ = 2.3RT kcal/mol). At 300 K, therefore, the conformational free energy difference of the CH$_2$· group in the axial and equatorial positions is –$\Delta G°$ = 0.71 kcal/mol. The greater a^{H_β} value for the axial conformers is attributed to a higher barrier to rotation about the C_α–C_β bond.

We recently reported[4] that two conformers of the cyclo-undecylmethyl radical, $\overline{CH_2(CH_2)_9CHCH_2}$·, could be detected by EPR spectroscopy at temperatures below 230 K.[5] The main spectroscopic difference between the two conformers lay in the magnitudes of their β-H hyperfine splittings[6] (hfs); at 140 K one conformer had a^{H_β} = 31.1 G and the other had a^{H_β} = 38.3 G. The absolute magnitudes of these two β-H hfs,[7] as well as the fact that for both radicals a^{H_β} decreased with an increase in temperature, indicated that both of these radicals adopted an eclipsed conformation, **1**. It therefore seemed likely that in one conformer the CH$_2$· group was quasi-axial and in the other it was quasi-equatorial. This suggested to us that axial cyclohexylmethyl radicals, i.e., those with the CH$_2$· group axial, **2**, and equatorial cyclohexylmethyl radicals, i.e., those with the CH$_2$· group equatorial, **3**, should be distinguishable by EPR spectroscopy. Such is the case and have been able to make the first measurement of

the conformational free energy difference (–$\Delta G°$ value)[8,9] of the CH$_2$· group in the axial and equatorial conformations.
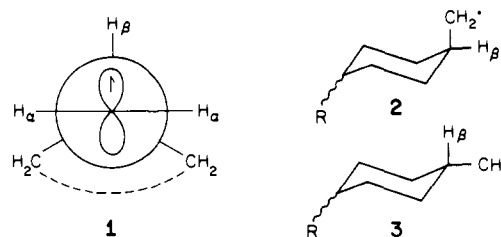
Results and Discussion

Initial experiments were designed to see whether or not axial, **2**, and equatorial, **3**, CH$_2$· groups could be unequivocally identified by their β-H hfs. Radicals were generated by bromine atom abstraction from the corresponding cyclohexylmethyl bromides with use of triethylsilyl radicals (formed by photolysis of di-*tert*-butyl peroxide in the presence of triethylsilane).[4] The radicals generated and their β-H hfs at 140 K are listed in Table I.

(*cis*-4-*tert*-Butylcyclohexyl)methyl bromide gave a single radical (a^{H_β} = 41.9 G) which must have CH$_2$· axial, **2a**. (*trans*-4-*tert*-

(1) Issued as N.R.C.C. No. 24876. For part 1 see ref 4.
(2) N.R.C.C.
(3) St. Andrews.
(4) Kemball, M. L.; Walton, J. C.; Ingold, K. U. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1017–1023.
(5) Above this temperature the lines due to the two radicals coalesce to give a single spectrum with a^{H_β} = 29.8 G at 270 K.
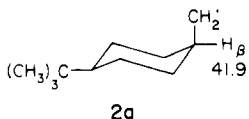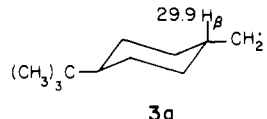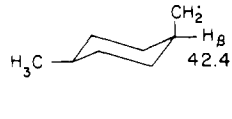(6) Throughout this article β-H refers to the tertiary H adjacent to the CH$_2$· group.
(7) The two conformers were referred to as cyclohexylmethyl-like and cyclooctylmethyl-like because their β-H hfs' resemble those of the named radicals, viz.[4] 30.4 and 40.1 G, respectively, at 140 K.
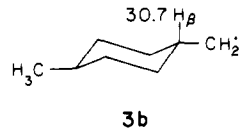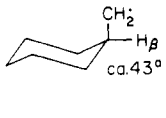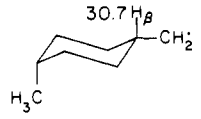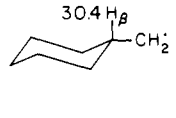
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Table I. Axial and Equatorial Cyclohexylmethyl Radicals (Magnitude of β-H hfs (in G) at 140 K in Cyclopropane as Solvent)

Axial	Equatorial
CH$_2^{\cdot}$ — H$_\beta$ 41.9 (CH$_3$)$_3$C **2a**	29.9 H$_\beta$ — CH$_2^{\cdot}$ (CH$_3$)$_3$C **3a**
	30.7 H$_\beta$ — CH$_2^{\cdot}$ H$_3$C **3b**
CH$_2^{\cdot}$ — H$_\beta$ 42.4 H$_3$C **2c**	30.7 H$_\beta$ — CH$_2^{\cdot}$ H$_3$C **3c**
CH$_2^{\cdot}$ — H$_\beta$ ca.43[a] **2d**	30.4 H$_\beta$ — CH$_2^{\cdot}$ **3d**

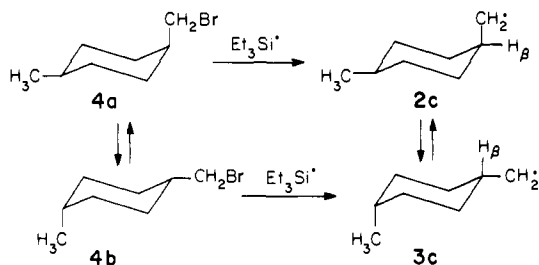[a]Estimated by extrapolation from measurements made over the temperature range 180–340 K.

Butylcyclohexyl)methyl bromide also gave a single radical (a^{H_β} = 29.9 G) which must have CH$_2^{\cdot}$ equatorial, **3a**. Likewise, (*trans*-4-methylcyclohexyl)methyl bromide gave a single radical (a^{H_β} = 30.7 G) which must have CH$_2^{\cdot}$ equatorial, **3b**. However, (*cis*-4-methylcyclohexyl)methyl bromide exists as an equilibrium mixture of two conformers, in one of which the bromomethyl group is axial, **4a**, and in the other it is equatorial, **4b**. This compound gave two radicals, one of which had essentially the same EPR parameters as **3b** and, in particular, the same β-H hfs of 30.7 G. We assign this radical the equatorial structure **3c**. The other radical had a β-H hfs of 42.4 G and so we assign it to the axial conformer, **2c**.

H$_3$C — CH$_2$Br **4a** $\xrightarrow{\text{Et}_3\text{Si}^{\cdot}}$ H$_3$C — CH$_2^{\cdot}$ —H$_\beta$ **2c**

H$_3$C — CH$_2$Br **4b** $\xrightarrow{\text{Et}_3\text{Si}^{\cdot}}$ H$_3$C — CH$_2^{\cdot}$ H$_\beta$ **3c**

Although radicals **2c** and **3c** can interconvert by inversion of the cyclohexane ring, the fact that both radicals could be observed at temperatures as high as 400 K indicates that this process is slow *on the EPR time scale*.[10] However, the ring inversion rate for these two radicals does become fast in comparison with the

lifetimes of the individual radicals at temperatures > ca. 200 K. That is, at temperatures in the range 155–200 K the **[2c]/[3c]** concentration ratio was found to be essentially the same as the **[4a]/[4b]** concentration ratio at the same temperature. We determined the latter ratio by 360-MHz ^{1}H NMR spectroscopy and in the temperature range 155–290 K obtained log ([**4a**]/[**4b**]) = −0.23 + 0.15/θ (where θ = 2.3RT kcal/mol).[13] Rate constants for the formation of **2c** from **4a** and of **3c** from **4b** are expected to be essentially equal.[14] Furthermore, the rate constants for reactions which lead to destruction of **2c** and **3c** (i.e., the bimolecular self-reactions of these radicals) are also expected to be essentially equal.[15-17] Hence, the fact that [**2c**]/[**3c**] ≈ [**4a**]/[**4b**] implies that there is no significant interconversion of **2c** and **3c** within the lifetime of these radicals.[18] In contrast, at temperatures in the range 200–325 K [**2c**]/[**3c**] > [**4a**]/[**4b**], the difference becomes greater as the temperature increases and a plot of log ([**2c**]/[**3c**]) vs. 1/T is approximately linear. The [**2c**]/[**3c**] ratio is ca. 3.6 at 300 K and hence the difference in free energies between **2c** and **3c** is ca. 0.76 kcal/mol. Combining this value with the known[19,20] value of 1.74 kcal/mol for $-\Delta G^{\circ}_{300K}(CH_3)$ and assuming additivity in the effects of the two groups leads to $-\Delta G^{\circ}_{300K}(CH_2^{\cdot}) \approx 0.98$ kcal/mol.

We previously reported observing only a single conformer of the parent cyclohexylmethyl radical.[4] This must have the equatorial structure, **3d**, because a^{H_β} was 30.4 G at 140 K[4] (see Table I). The small magnitude found for $-\Delta G^{\circ}_{300K}(CH_2^{\cdot})$ from the **2c**/**3c** pair of radicals suggested that axial cyclohexylmethyl, **2d**, should be fairly readily observed. This proved to be the case. Over the temperature range 172–340 K the relative concentration of the two conformers could be described by log ([**2d**]/[**3d**]) = 0.79 − 1.79/θ, which correponds to [**2d**]/[**3d**] = 0.3 at 300 K and $-\Delta G^{\circ}_{300K}(CH_2^{\cdot}) = 0.71$ kcal/mol. This value will be more reliable than the value obtained from the *cis*-4-methyl-substituted radical. As might be expected, the CH$_2^{\cdot}$ group has a greater equatorial preference than OH ($-\Delta G^{\circ}_{300K} = 0.52$ kcal/mol in aprotic solvents)[9] and OCH$_3$($-\Delta G_3^{\circ}_{300K} = 0.60$ kcal/mol),[9] and a lower equatorial preference than CH$_3$ ($-\Delta G^{\circ}_{300K} = 1.74$ kcal/mol)[19,20] and other alkyl groups.[20] However, the CH$_2^{\cdot}$ group also has a considerably lower equatorial preference than NH$_2$ ($\Delta G^{\circ}_{300K} = 1.20$ kcal/mol in aprotic solvents)[9] which is rather surprising.

The magnitudes of the β-H hfs for all cyclohexylmethyl radicals as well as the fact that these hfs decrease with an increase in temperature shows[21] that both the axial and equatorial conformers prefer the eclipsed structure, **1**. The characteristically greater β-H hfs of the axial radicals implies that the barrier to rotation about the C$_\alpha$–C$_\beta$ bond is higher in axial than in equatorial radicals. This must be due to the interaction between the α-hydrogens and the axial hydrogens at positions 3 and 5 (see **5**).

In summary, EPR spectra of axial and equatorial cyclohexylmethyl radicals can be readily distinguished by the magnitudes of their β-H hfs. Future publications will provide additional details on these radicals and on cycloalkylmethyl radicals with ring sizes up to 15 carbon atoms, for most of which both axial and equatorial conformers can be observed. We believe that the CH$_2^{\cdot}$ group will be a useful spin probe for studying conformational

(10) At 420 K the signal was too weak to decide whether the disappearance of the spectrum was due to exchange broadening or to low signal to noise. At 400 K, a^{H_β}(**2c**) − a^{H_β}(**3c**) = 4.0 G, and since k/s^{-1} = (6.22 × 10^6)(Δa^{H_β})[11] the activation energy for ring inversion is ≥10 kcal/mol (assuming a preexponential factor of 10^{13} s^{-1}). The barrier for *cis*-1,4-dimethylcyclohexane is 11.0 ± 0.7 kcal/mol.[12]

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(13) At 300 K the free energy difference favoring an equatorial CH$_2$Br over an equatorial CH$_3$ is, therefore, 0.17 kcal/mol. With the usual assumptions (vide infra) this yields $-\Delta G^{\circ}$(CH$_2$Br) = 1.91 kcal/mol. A value of 1.79 kcal/mol has been obtained by ^{13}C NMR. See: Kitching, W.; Olszowy, H.; Adcock, W. *Org. Mag. Reson.* **1981**, *15*, 230–237.

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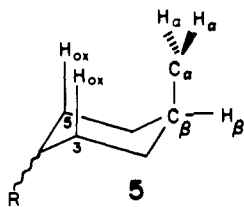
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(18) See, e.g.: Griller, D.; Ingold, K. U.; Walton, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 758–759. Davies, A. G.; Griller, D.; Ingold, K. U.; Lindsay, D. A.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 633–641.

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(21) Kochi, J. K. *Adv. Free Radical Chem.* **1974**, *5*, 189–317.

5

equilibria in cycloalkanes and will serve as a reference group for determining the equatorial and quasi-equatorial preferences of other substituents.

Experimental Section

(*cis*- and *trans*-4-alkylcyclohexyl)methyl bromides were prepared by literature methods.[12,22] EPR spectra were obtained by photolysis of

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(22) Kitching, W.; Olszowy, H.; Adcock, W. *Org. Mag. Reson.* **1981**, *15*, 230–237.

solutions of the bromide (10%), triethylsilane (10%), and di-*tert*-butyl peroxide (10%) in cyclopropane, with light from a 500-W super-pressure Hg arc. At temperatures above ca. 200 K, hexamethylditin was used in place of the silane and *tert*-butylbenzene was the solvent. Spectra were recorded with a Bruker ER 200 D spectrometer. The ratio of the concentrations of the axial and equatorial (4-methylcyclohexyl)methyl bromides [**4a**]/[**4b**] was obtained from the 360-MHz ¹H NMR signals for the bromomethyl groups. At temperatures below coalescence the separate signals were integrated both instrumentally and by planimetry. Above coalescence the ratio was determined from the average value of the chemical shift, the chemical shifts of the axial and equatorial groups being extrapolated from the low-temperature data.[20,22]

Reactivities of Rotameric *ap*- and *sp*-3,5-Dimethyl-2-(9-fluorenyl)phenylnitrenes

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Contribution from the Division of Applied Molecular Science, Institute for Molecular Science, Okazaki 444, Japan. Received February 5, 1985

Abstract: The *ap*- and *sp*-3,5-dimethyl-2-(9-fluorenyl)phenyl azides (**4ap** and **4sp**) have been obtained separately from the corresponding amines **6ap** and **6sp** which in turn were obtained as a mixture by the AlCl₃-catalyzed isomerization of *N*-(9-fluorenyl)-3,5-xylidine and separated by chromatography. Isomerization **4ap → 4sp** was studied at 40–69 °C to give the kinetic and thermodynamic parameters: $\Delta H^{\ddagger} = 22.5$ kcal/mol, $\Delta S^{\ddagger} = -7.6$ eu, $\Delta G^{\ddagger}_{300} = 24.8$ kcal/mol; $\Delta H^{\circ} = -1.70$ kcal/mol, $\Delta S^{\circ} = -0.42$ eu, $\Delta G^{\circ}_{300} = -1.57$ kcal/mol. Conformationally fixed nitrenes **5ap** and **5sp** were generated independently from **4ap** and **4sp**, respectively, and their spectroscopic and chemical behaviors were scrutinized. When generated in an ESR cavity, **5ap** in the ground triplet state showed the X,Y transition at 6722 G. The resonance field characteristic of the *sp*-nitrene (6745 G) was obtained on the 9-*d* derivative **4'sp** of azide **4sp**. The INDO–UHF MO spin-density calculations have been performed on the *ap* and *sp* rotamers of *o*-(9-fluorenyl)phenylnitrene and other model nitrenes. The effect of the *o*-(9-fluorenyl) substitution and its conformation was found to be very small, although the order of the calculated nitrogen spin densities is in parallel with the observed zfs parameters. When photolyzed in an EPA glass, **4ap** showed absorptions at 309 and 340 nm due to **5ap** and azanorcaradiene **8**, respectively. Absorptions at 367, 426, and 554 nm were obtained from **4sp**. These were assigned to dihydroindenoacridine **12** and *o*-quinoid imine **11** from which 10,12-dimethylindeno[*k,l*]acridine (**13**) was isolated after warming up of the matrix, aeration, and chromatography. In fluid solutions of methanol in the presence of a small amount of NaOMe, methoxyamine **14**, 3H-azepine **15** and azepine **16** were obtained in different ratios from **4ap** and **4sp**. The loss of stereospecificity in these reactions was ascribed to the conformational isomerization in the benzazirine intermediate **17**. The rate constants for the formation of **8** and **11** and the decay of **11** were determined by the laser-flash photolysis experiments to be 7.1 × 10⁵, >10⁸, and 2.6 × 10³ s⁻¹, respectively. The deuterium isotope effect for the hydrogen 1,4-migration in **5sp** was obtained as 1.84 at 25 °C. In diethylamine, **4ap** gave **6ap** and diamine **21**, while **4sp** gave both isomers of **6**, diamine **20** and **21**. Benzazirine **22** is considered to be responsible for the *sp* to *ap* isomerization. Tetracyanoethylene trapped the intermediates to give adducts **24** and **25**. The contrasting spectroscopic and chemical properties of the conformationally restricted nitrenes **5ap** and **5sp** are consistent with the hypothesis that 2-(9-fluorenyl)phenylnitrenes generated from 1-azatriptycene and 2-(9-fluorenyl)phenyl azide by photolysis have the *ap* and *sp* forms, respectively.

We have been interested for some years in the photochemistry of triptycenes in which three benzene rings are fixed at a 120° angle to each other in the molecules of threefold symmetry.[1] In particular we studied in detail the photorearrangement of 1-azatriptycene (**1**) and found a cleavage of the two carbon–nitrogen bonds resulting in the formation of *o*-(9-fluorenyl)phenylnitrene (**2**).[2] The phenylnitrene derivative **2** was independently generated by the photolysis of *o*-(9-fluorenyl)phenyl azide (**3**), and thus the

intermediacy of **2** in the photolysis of **1** was unambiguously established.
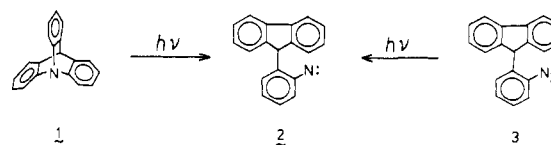
We noted, however, a slight difference in the behavior of the nitrenes **2** generated from the photolysis of **1** and **3**.[2] For example, the field positions of the X,Y transition of the triplet nitrenes were slightly different in the ESR spectra obtained at cryogenic temperature. The product distributions in the photoreactions of **1** and **3** in fluid solutions were significantly different. We explained

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(2) (a) Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1980**, *102*, 7134. (b) Sugawara, T.; Nakashima, N.; Yoshihara, K.; Iwamura, H. *Ibid.* **1983**, *105*, 859. (c) Sugawara, T.; Iwamura, H. *Ibid.* **1985**, *107*, 1329.