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Conformations of Cycloalkenyl Radicals: a Dynamic EPR Study of the Cyclohept-4-enyl Radical

John C. Walton
Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK

Cyclopent-3-enyl, cyclohex-3-enyl and cyclohept-4-enyl radicals were generated and their EPR spectra obtained in solution over a range of temperatures. The spectral data were consistent with a fully planar conformation for cyclopent-3-enyl radicals and a slightly flattened half-chair conformation for cyclohex-3-enyl radicals. Cyclohept-4-enyl radicals showed exchange broadening in their EPR spectra which indicated inversion from one chair conformer to another with an Arrhenius activation barrier of 16.5 ± 0.3 kJ mol^{-1}.

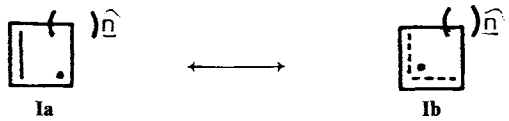
KEY WORDS EPR Radicals Cycloalkenyl radicals Ring conformations

INTRODUCTION

The ring motions of a number of cycloalkyl radicals have been studied by EPR spectroscopy. Thus, the cyclopentyl pseudo-rotation was followed in an adamantane matrix[1] and the ring inversion of cyclohexyl and some of its derivatives has been observed in fluid solution.[2,3] More recently, exchange broadening was observed in the EPR spectra of the cycloheptyl radical and attributed to the ring pseudo-rotation.[4] Comparison of the measured barriers in these cycloalkyl radicals with those of the corresponding parent cycloalkanes was very useful for charting the conformational changes caused by the introduction of the planar radical centre into each type of ring.

Cycloalkenes have been studied by a variety of techniques, including ^{1}H and ^{13}C NMR spectroscopy[5] and several different types of force field calculations have been applied,[6] so that a good understanding of their conformational preferences exists, particularly for five-, six- and seven-membered rings. The EPR spectra of some cycloalkenyl radicals have been observed, but little is known about their conformational behaviour. The conformations of cycloalkenyl radicals differ significantly from those of cycloalkyl radicals, so that spectroscopic study of the former seemed worthwhile. The stereodynamics of ring inversion in cycloalkenes are difficult to follow by NMR spectroscopy because the barriers are at the low end of the range accessible to this method. However, it was expected that the faster time scale of EPR spectroscopy would enable ring inversion of the corresponding radicals to be studied with ease. In practice this proved to be the case for only one radical, cyclohept-4-enyl.

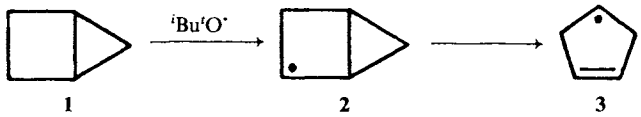
Cycloalk-2-enyl radicals (**Ia**) have been observed with a variety of ring sizes. Thus cyclopentenyl (**I**, $n = 2$),[7] cyclohexenyl (**I**, $n = 3$)[7,8] and cycloheptenyl (**I**, $n = 4$)[9] have been studied, but their EPR spectra are independent of temperature in fluid solution so that conformational motions could not be followed. The cyclohex-2-enyl radical (**I**, $n = 3$) was also studied in an adamantane matrix where conformational changes were apparent.[10] The allyl type of delocalization (**Ib**) which occurs in these species introduces a planar three-carbon unit into the ring which severely restricts their conformational options. A study of cycloalkenyl radicals, in which the radical centre is separated from the double bond by one or two methylene units, is reported in this paper.



Ia Ib

RESULTS AND DISCUSSION

The cyclopent-3-enyl radical (**3**) was generated by hydrogen abstraction from bicyclo[2.1.0]pentane (**1**).[11] The bicyclo[2.1.0]pent-2-yl radical (**2**) rearranged so rapidly that only (**3**) was detectable down to *ca* 110 K in solution.[11] The EPR spectrum of (**3**) showed hyperfine splitting (hfs) from four equivalent β-hydrogens (3.76 mT) which was essentially independent of temperature. The β-hydrogens remained equivalent at 110 K in propane solution, and the spectra showed no evidence of any intramolecular exchange process. Thus, if any ring motion occurs, its activation energy must be less than *ca* 10 kJ mol^{-1}. In radical **3** the hydrogen at C-1 is in the plane defined by C-2, C-1 and C-5, so that both angle and eclipsing strain are minimized if the whole ring remains planar with no pucker. Semi-empirical SCF MO calculations of the MINDO/3 and MNDO type on (**3**)[12] were in agreement with this. The optimized geometries indicated that the radical is com-



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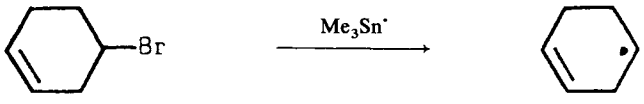
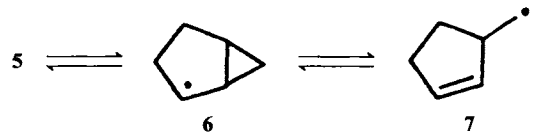
pletely planar with all five carbon atoms, and the hydrogens at C-1, C-3 and C-4, in the same plane. Thus the conformation of the cyclopent-3-enyl radical differs from that of cyclopentene and cyclopentane, both of which show sizeable ring puckers.[6]

The cyclohex-3-enyl radical (**5**) was generated by bromine abstraction from 4-bromocyclohexene (**4**) using trimethyltin radicals in *tert*-butylbenzene solution. The EPR hfs at 210 K were a(H-α) = 2.20, a(2H-β) = 2.56

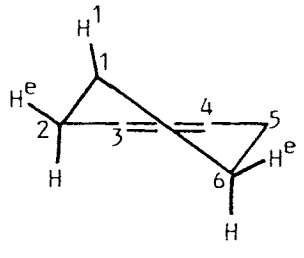


4 **5**

and a(2H-β) = 3.05 mT. The spectra were weak and broad and attempts to observe the radicals at low temperatures in cyclopropane solution were unsuccessful. The spectra also weakened rapidly at higher temperatures, possibly owing to exchange broadening, but the fast exchange limit could not be observed. The inversion barrier of the half-chair conformation of cyclohexene, $\Delta G^{\ddagger}$, is 22.6 kJ mol^{-1}.[13] If radical (**5**) has a similar inversion barrier, a coalescence temperature of about 220 K would be expected. The fact that the H-β hfs are non-equivalent indicates that the radical is below coalescence at 210 K. Hence the experimental observation of rapid spectral weakening above 210 K is consistent with the occurrence of a ring inversion with a barrier of the same magnitude as that of cyclohexene. It seems probable that cyclohex-3-enyl radicals (**5**) take part in a degenerate rearrangement to bicyclo[3.1.0]hex-2-yl radicals (**6**), which can further rearrange to cyclopent-2-enylmethyl radicals (**7**). The rearrangement of (**6** to **5**) has been observed,[14] as has the reversible rearrangement (**6** to **7**).[14,15] It is possible that radical (**5**) cyclizes to (**6**) sufficiently rapidly to lower the stationary concentration of (**5**) under EPR conditions. This would account for the weakness of the spectra at higher temperatures and the lack of success in observing the fast exchange spectra. In the half-chair conformation (**A**) the hydrogen at the radical centre, H-1, virtually eclipses both equatorial hydrogens (H^e) at C-2 and C-6. It is likely, therefore, that either the radical becomes slightly pyramidal or it has a shallower pucker than cyclohexene, in order to reduce this eclipsing strain. A MNDO study of (**5**) indicated that both of



6 **7**



A

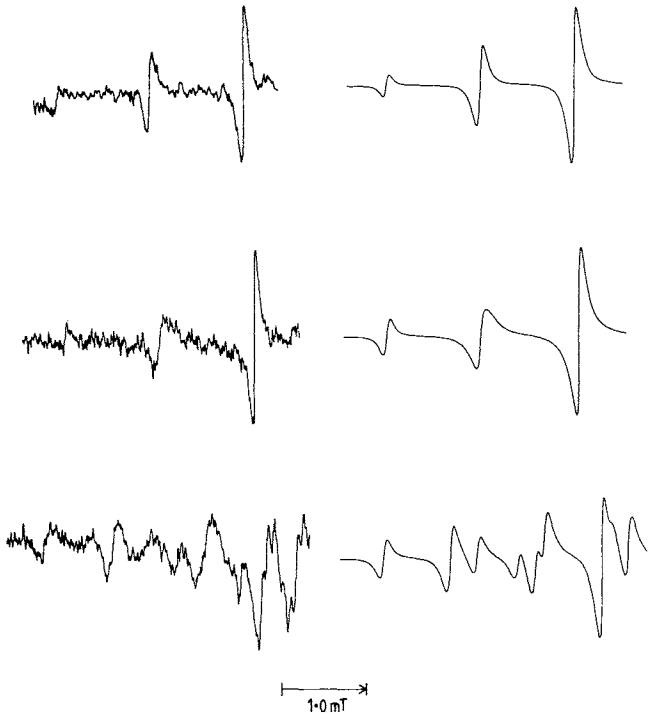


Figure 1. Low-field half of the 9.4 GHz EPR spectra of cyclopent-4-enyl radicals (**8**) in cyclopropane solution. Left: experimental spectra at, from the bottom, 139, 228 and 273 K. Right: simulations with, from the bottom, 10^{-7} k (s^{-1}) of 0.2, 50, 300.

these effects come into play; the minimum energy structure (ΔH_f = 68 kJ mol^{-1}) showed slight bending at the radical centre (*ca* 2° from planar) together with a very flat ring.

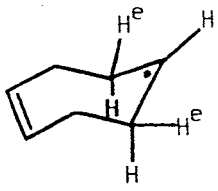
The cyclohept-4-enyl radical (**8**) was generated by bromine abstraction from 5-bromocycloheptene with trimethyltin radicals and, at low temperatures, with triethylsilyl radicals. At 150 K in cyclopropane solvent the spectrum showed two pairs of non-equivalent β-hydrogens (Fig. 1). As the temperature was raised, exchange broadening was observed; the spectra finally sharpened to show four equivalent β-hydrogens with hfs which, by chance, were equal to that of the α-hydrogen at 275 K. The EPR hfs are compared with those of the cycloheptyl radical in Table 1. The most interesting feature of these results is the large difference in magnitude of the β-hfs. The average β-hfs is much smaller for (**8**) at 275 K and one pair of β-hydrogens in (**8**) has a much smaller hfs in the 'frozen' conformation. By analogy with cycloheptene,[6] the preferred conformation of the cyclohept-4-enyl radical is probably the chair (**8**). In this conformation the two quasi-equatorial hydrogens (H^e) lie close to the nodal plane of the p-orbital

Table 1. EPR hyperfine splittings (mT) of cycloheptyl and cyclohept-4-enyl radicals

Radical	Temperature	H-α	H-β
Cycloheptyl (**9**)[a]	275	2.2	2.9 (4H)
	117	2.10	3.14 (2H), 2.1 (2H)
Cyclohept-4-enyl (**8**)	275	2.23	2.23 (4H)
	150	2.20	3.21 (2H), 1.23 (2H)

[a] Data from Ref. 4.

containing the unpaired electron (SOMO) and should therefore give rise to a small hfs, whereas the other pair of quasi-axial hydrogens lie at about 60° to this plane and so should give sizeable hfs. Experimentally, one pair of β-hydrogens were indeed found to have a small hfs (1.23 mT) and the other pair a moderately large hfs. Hence the EPR results support (**8**) as the preferred conformation. For the cycloheptyl radical the preferred conformation is the twist-chair (**9**).[4,6] Models show that the quasi-equatorial hydrogens are decidedly further from the nodal plane of the SOMO, and therefore the significantly larger β-hfs observed for (**9**) is readily understood in terms of the two different conformations.



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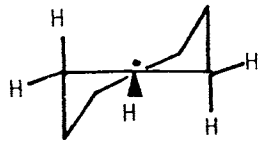

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The exchange broadening from (**8**) was simulated using Heinzer's program[16] assuming a two-jump model; satisfactory agreement between the simulated and experimental spectra was obtained throughout the whole temperature range. The best fit rate constants are given in Table 2; linear regression gave Arrhenius parameters of $\log[A(s^{-1})] = 12.4 \pm 0.3$, E(kJ mol^{-1}) $= 16.5 \pm 0.3$ (error limits twice the standard deviation). The experimental A factor is close to the normal value ($\log A = 13.0$) for this type of process, which is good evidence of the reliability of the results.

Table 2. Best-fit exchange rate constants for cyclohept-4-enyl radicals

T (K)	$10^{-7}k$ (s^{-1})	T (K)	$10^{-7}k$ (s^{-1})
139	0.2	206	10.0
150	0.6	217	20.0
161	1.0	228	50.0
172	2.5	250	100.0
184	4.0	273	300.0
195	8.0		

The chair conformation inverts via boat forms similar to (**8b**), which may also be shallow minima on the potential energy surface.[6] The analogous ring inversion for cycloheptene has[17] $\Delta G^{\ddagger} = 21.0$ kJ mol^{-1}. The similarity to this of the observed barrier in (**8**) supports the conclusion that the dynamic process observed by EPR is the ring inversion (**8a** → **8c**). The activation barrier in the radical is slightly lower, possibly because the eclipsing strain is less in the transition state for inversion of (**8**) because it has only a single hydrogen at C-1. This inversion could also be made easier in the radical, compared with the hydrocarbon, if the radical centre is non-planar and inverts concurrently with the ring, as was suggested for the cyclohexyl[18] and cycloheptyl[4] radicals. The observed barrier for cycloheptyl radicals (14.2 kJ mol^{-1})[4] is lower than that for (**8**) because radical (**9**) can interconvert to a new twist-chair conformation via a low-energy pseudo-rotation pathway.[4]

EXPERIMENTAL

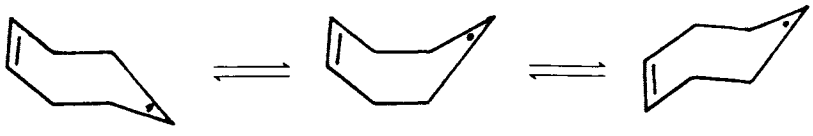
EPR spectra were recorded with a Bruker ER 200D spectrometer operating at 9.4 GHz with 100 kHz modulation. Solutions were prepared in Spectrosil tubes, degassed by several freeze–pump–thaw cycles and irradiated with light from a 500 W super pressure Hg arc.

Bicyclo[2.1.0]pentane (**1**) was prepared as described previously.[11]

4-Bromocyclohexene (**4**) was synthesized from cyclohexane-1,4-diol by the method of Fish and Broline;[19] b.p. 53–55 °C/25 Torr (lit.,[19] 49–52 °C/28 Torr); δ_H 1.9–2.2 (4H, m), 2.5 (2H, broad s), 4.4 (1H, m), 5.4–5.9 (2H, m).

To prepare cycloheptene-5-carbonyl chloride, cycloheptene-5-carboxylic acid[20] (1.0 g) in diethyl ether (5 ml) was added to thionyl chloride (1.2 g) in diethyl ether (10 ml) and the solution was refluxed for 7 h. The ether was removed and the product distilled to give the acyl chloride (51%); b.p. 150 °C/15 Torr; δ_H 1.5–2.5 (8H, m), 2.8–3.4 (1H, m), 5.9 (2H, b s).

5-Bromocycloheptene was prepared via the 2-mercaptopyridine N-oxide ester.[21] To the sodium salt of 2-mercaptopyridine N-oxide (1.72 g) and dimethylaminopryridine (0.05 g) in tetrahydrofuron (THF) (70 ml) was added the acyl chloride (1.85 g) in THF (20 ml) at room temperature. The yellow solution was filtered, the THF removed on a rotary evaporator and the ester used without purification. The crude ester was dissolved in bromotrichloromethane (10 ml) and the solution stirred at 90 °C for 1.5 h. The mixture was filtered and distilled, giving 0.7 g of oil, b.p. 120 °C/15 mmHg. Pure 5-bromocycloheptene was obtained by preparative GLC (3 m column packed with 10% MS 200/50, at 150 °C); M^+(obs) 174.0036, $C_7H_{11}{}^{79}Br$ requires 174.0044; δ_H 1.1–2.2 (8H, m), 4.0 (1H, m), 5.3 (2H, b s); δ_C 25.76 (C-3, 7), 37.35 (C-4, 6), 57.81 (C-5), 131.78 (C-1, 2).



8a **8b** **8c**

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