Dynamics of Internal Rotation in 2-(Cycloalkenyl)ethyl Radicals

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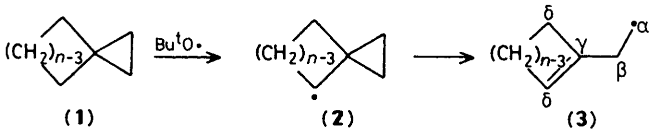
2-(Cycloalkenyl)ethyl radicals having C_4 to C_7 rings were observed by e.s.r. spectroscopy. The barriers to rotation about the $\dot{C}_\alpha$–C_β bonds were determined from the temperature variation of the β-hydrogen hyperfine splittings and shown to decrease with increasing ring size. In all cases, the preferred conformation about the C_β–C_γ bond was found to be the one in which the $\dot{C}_\alpha$–C_β bond makes an angle of 90° with the plane of the ring. Exchange broadening due to restricted rotation about the C_β–C_γ bond was observed and the rotation barriers were determined for the radicals with C_6 and C_7 rings. The radicals were studied using the semi-empirical MINDO/3 and MNDO methods and the corresponding hydrocarbons were investigated by the MM2 force field approach. The variations in the rotational barrier heights were attributed to steric effects.

In a previous paper[1] we reported that t-butoxyl radicals abstract hydrogen mainly at the 2-position of spiro[2.*n*]alkanes (**1**) to give spiro[2.*n*]alk-2-yl radicals (**2**).

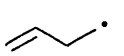


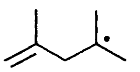
(**1**) (**2**) (**3**)

a; *n* = 4 **c**; *n* = 6
b; *n* = 5 **d**; *n* = 7

These latter radicals rearrange rapidly by β-scission to give 2-(cycloalkenyl)ethyl radicals (**3**). For *n* ⩾ 5 the rearrangement was so rapid that only (**3**) could be observed by e.s.r. spectroscopy. For spiro[2.3]hexane (**1a**) the rearrangement was spectroscopically observable between 140 and 170 K and clean spectra of the 2-(cyclobut-1-enyl)ethyl radical (**3a**) were obtainable at temperatures above the end of this range. The 2-(cycloalkenyl)ethyl radicals contain the but-3-enyl (homoallyl) unit. This method of formation provides an opportunity to study the stereodynamics of a series of but-3-enyl analogues.

The e.s.r. spectrum of the but-3-enyl radical itself[2,3] (**4**) [$a(2H_\alpha) = 22.2, a(2H_\beta) = 28.5, a(H_\gamma) = 0.6, a(2H_\delta) = 0.4$ G]* at 168 K showed that very little unpaired spin reaches the double bond. Radical (**4**) adopts the staggered conformation about the $\dot{C}_\alpha$–C_β bond, but no line broadening due to restricted rotation about the C_β–C_γ bond was observable.[4] However, the related 2,4-dimethylpent-4-en-2-yl radical (**5**) showed exchange broadening in its e.s.r. spectrum from the analogous rotation and the barrier was found to be[4] 3.5 kcal mol^{-1}.*


(**4**)


(**5**)

The very small spin densities associated with the double bonds, and the low barriers to rotation about the $\dot{C}_\alpha$–C_β and C_β–C_γ bonds, suggest that 'homoallylic conjugation'[4,5] is not important in these open-chain radicals. We have shown[6] that 'homoallylic conjugation' is negligible in methylenecyclobutyl and cyclopent-4-enyl radicals. The 2-(cycloalkenyl)ethyl radicals provided an opportunity to assess the extent of 'homoallylic conjugation' and to determine the preferred conformations and internal rotation barriers for a sequence of struturally related radicals. Results for radicals containing C_4—C_7 rings are reported in this paper.

Table 1. E.s.r. parameters of 2-(cycloalkenyl)ethyl radicals

		H.f.s. (G)	
Radical	*T*/K	$a(H_\alpha)$(2H)	$a(H_\beta)$
2-(Cyclobut-1-enyl)ethyl (**3a**)	240	21.6	28.7 (2H)
2-(Cyclopent-1-enyl)ethyl (**3b**)	240	21.6	27.9 (2H)
2-(Cyclohex-1-enyl)ethyl (**3c**)	240	22.5	27.7 (2H)
2-(Cyclohex-1-enyl)ethyl (**3c**)	140	22.5	27.4 (1H), 29.5 (1H)
2-(Cyclohept-1-enyl)ethyl (**3d**)	230	22.4	26.7 (2H)
2-(Cyclohept-1-enyl)ethyl (**3d**)	140	22.4	26.3 (1H), 28.5 (1H)

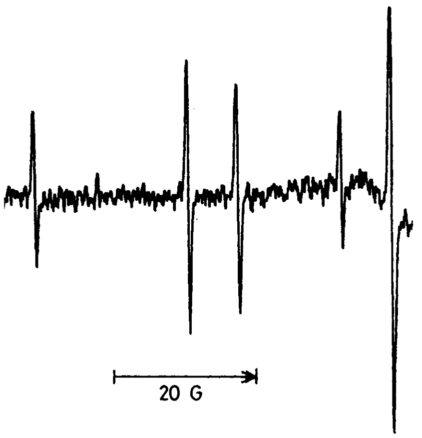


Figure 1. Low-field half of the 9.4 GHz e.s.r. spectrum of 2-(cyclobut-1-enyl)ethyl radicals (**3a**) in cyclopropane at 172 K

Results and Discussion

Dynamic E.s.r. Study of 2-(Cycloalkenyl)ethyl Radicals.—All four radicals (**3a**—**d**) gave e.s.r. spectra at 240 K which consisted of a basic triple triplet from $2H_\alpha$ and $2H_\beta$. The e.s.r. parameters are in Table 1.

The spectrum of the 2-(cyclobut-1-enyl)ethyl radical (**3a**) is shown in Figure 1. The H_α hyperfine splittings (h.f.s.) were close to the normal value of 22 G for all four radicals.

The temperature dependencies of the H_β h.f.s. are shown in

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* 1 cal ≡ 4.18 J, 1 G ≡ 0.1 mT.

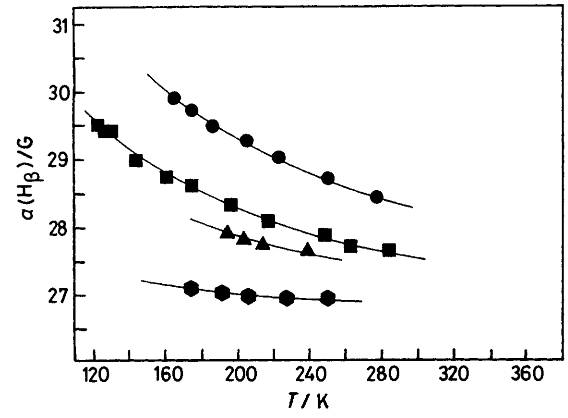
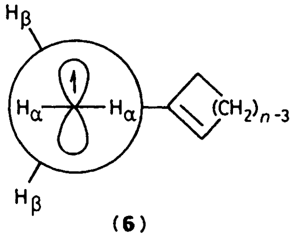


Figure 2. Temperature dependence of β-h.f.s. from radicals (**3a**—**d**). Experimental points: circles; 2-(cyclobut-1-enyl)ethyl (**3a**), squares; 2-(cyclopent-1-enyl)ethyl (**3b**), triangles; 2-(cyclohex-1-enyl)ethyl (**3c**), hexagons; 2-(cyclohept-1-ethyl)ethyl (**3d**). Full lines are results calculated from equation (1)

Figure 2. The magnitudes of the $a(H_\beta)$ h.f.s. and their negative temperature coefficients prove[4] that, as expected, all four radicals adopt (**6**) as their preferred conformation about the $\dot{C}_\alpha$–C_β bond.



(**6**)

This is similar to the conformation adopted by but-3-enyl radicals (**4**) and n-alkyl radicals in general.

The potential barrier to rotation about the $\dot{C}_\alpha$–C_β bond, V_α, can be estimated by fitting the observed temperature dependence of $a(H_\beta)$ with calculated values using the classicial limit method,[4,7–9] equation (1). In equation (1) $\lambda = V_\alpha/RT$, θ_0

$$a(H_\beta) = A + \tfrac{1}{2}B + \tfrac{1}{2}B\cos 2\theta_0[I_1(\lambda)/I_0(\lambda)] \qquad (1)$$

is the dihedral angle between the SOMO and the $\dot{C}_\alpha$–C_β bond, *i.e.* $\theta_0 = 30°$ for conformation (**6**); the other quantities have their usual meanings.[9] The full lines in Figure 2 were calculated using equation (1) with $A = 1$ G, $B = 50$ G, and the V_α values given in Table 2. These A and B values are similar to those found previously for other alkyl radicals.[9,10] The fits were somewhat 'soft' so that the calculated potential barriers must only be regarded as approximate; the relative order is much more reliable.

The interesting feature of these barriers is the decrease in V_α as the ring size increases (Table 2). The V_α value for the 2-(cyclobut-1-enyl)ethyl radical (**3a**) is comparable to that found for the $\dot{C}_\alpha$–C_β rotation in n-propyl radicals (*ca.* 0.4 kcal mol^{-1}).[4,11] Similarly, the V_α values for (**3b**) and (**3c**) are comparable with the barrier of 0.2 kcal mol^{-1} found for but-3-enyl,[4] the analogous open-chain radical. In the 2-(cyclohept-1-enyl)ethyl radical (**3d**) there is virtually free rotation about the $\dot{C}_\alpha$–C_β bond. In the series (**3a**—**d**) the interior ring angle at C_γ opens up and hence the *s*-character of the orbitals forming the C_β–C_γ bond decreases from the C_4 to the C_7 ring. This will cause an increase in the C_β–C_γ bond length along the series so that C_γ will be closest to the α-hydrogens in (**3a**) and furthest away in (**3d**). Semi-empirical MO calculations supported this suggestion (see below). The decrease in V_α may therefore be a consequence of decreased steric hindrance from C_γ as the ring size increases.

Table 2. Barriers to rotation about the $\dot{C}_\alpha$–C_β bonds in 2-(cycloalkenyl)ethyl radicals[a]

Radical	$V_\alpha{}^b$/kcal mol^{-1}
2-(Cyclobut-1-enyl)ethyl (**3a**)	0.40 ± 0.06
2-(Cyclopent-1-enyl)ethyl (**3b**)	0.26 ± 0.05
2-(Cyclohex-1-enyl)ethyl (**3c**)	0.24 ± 0.10
2-(Cyclohept-1-enyl)ethyl (**3d**)	0.12 ± 0.10

[a] Potential barriers obtained from equation (1) with $A = 1$ G, $B = 50$ G, $\theta_0 = 30°$. [b] The error limits were estimated from the fits.

Table 3. Dynamics of C_β–C_γ bond rotation in 2-(cyclohex-1-enyl)ethyl (**3c**) and 2-(cyclohept-1-enyl)ethyl (**3d**) radicals

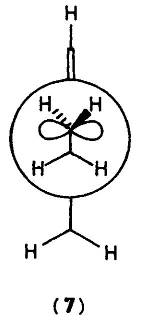
Radical (**3c**)		Radical (**3d**)	
T/K	10^{-7} *k*/s^{-1}	*T*/K	10^{-7} k/s^{-1}
161	0.15	150	0.05
177	0.60	184	1.0
183	0.80	195	1.8
188	1.0	206	3.5
194	1.7	223	7.0
200	3.5	239	10.0
206	5.5	262	20.0
217	8.5	284	60.0
239	20.0		

The spectrum of (**3a**) showed a small amount of selective line broadening. Figure 1 shows that the $M_\beta = 0$ peak heights are reduced, relative to the others, at 172 K. The effect could not be followed to lower temperatures because only unrearranged spiro-[2.3]hex-2-yl radicals could be observed. However, the spectra of the 2-(cyclopent-1-enyl)ethyl radicals (**3b**) were examined down to 120 K in CF_2Cl_2 and propane solution. The line broadening was not significantly greater than that observed for (**3a**) at 172 K. In contrast to this, the spectra of both (**3c**) and (**3d**) showed extensive line broadening (Figure 3) in the accessible temperature range.

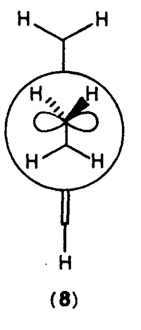
The spectrum from (**3c**) was a triple triplet similar to that shown in Figure 1 at 240 K, but the $M_\beta = 0$ lines broadened at lower temperatures, passed through coalescence at *ca.* 190 K, and sharpened up to give a spectrum showing two non-equivalent β-hydrogens at 160 K (Figure 3). A similar sequence of events was observed for radicals (**3d**) except that coalescence occurred at a lower temperature (*ca.* 170 K). The h.f.s. of the low-temperature radicals are given in Table 1.

Three conformations about the C_β–C_γ bond of radicals (**3**) may be considered.

In conformations (**7**) and (**8**) the two H_β are essentially



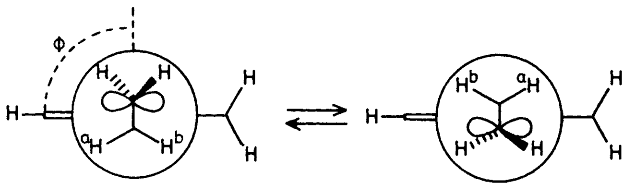
(**7**)



(**8**)

Figure 3. Exchange broadening in the e.s.r. spectra of 2-(cyclohex-1-enyl)ethyl radicals (**3c**). Left-hand side; experimental spectra, from the top; 161, 188, 239 K. Right-hand side, simulations with, from the top, (10^{-7} k/s^{-1}) 0.15, 1.0, 35.0

equivalent and therefore neither of them can explain the limiting low-temperature spectra obtained from (**3c**) and (**3d**), nor the type of exchange broadening. In conformation (**9**) the two H_β are inequivalent, as observed experimentally, and we attribute the line broadening to exchange between (**9a**) and (**9b**) in which the two β-hydrogens interchange positions.



(**9a**) (**9b**)

The exchange broadening was simulated with a two-jump model using Heinzer's program.[12] The good correspondence between simulated and experimental spectra is illustrated in Figure 3 for radical (**3c**). The best-fit rate constants for the two radicals are given in Table 3.

The Arrhenius pre-exponential factors calculated from these rate constants were 8.5×10^{12} s^{-1} and 1.0×10^{12} s^{-1} for (**3c**) and (**3d**) respectively. These values are within the range considered 'normal' for a bond rotation and this increases confidence in the reliability of the results. The calculated activation energies (E_β) are given in Table 4, along with an estimated upper limit for radical (**3b**).

Table 4. Experimental and calculated barriers for C_β–C_γ rotation in 2-(cycloalkenyl)ethyl radicals[a]

Radical	Ring size	E_β exptl.	$\Delta H^\ddagger$ MINDO/3[c]	$\Delta H^\ddagger$ MNDO[d]	V_β MM2[e]
(**3a**)	C_4		0.7	0.3	2.1
(**3b**)	C_5	<3.2[b]	1.3	1.0	2.2
(**3c**)	C_6	5.0 ± 0.4	2.0	1.6	2.1
(**3d**)	C_7	4.3 ± 0.7	1.8	2.3	2.0

[a] In kcal mol^{-1}. [b] Estimated from the coalescence temperature (< 120 K) and assumed values for $\Delta a(H_\beta)$ [2 G] and log A [13.0]. [c] UHF version. [d] RHF version. [e] For the corresponding ethylcycloalkenes. Rigid rotor approximation.

The E_β values for C_β–C_γ rotation (Table 4) show an increase as the ring size increases, *i.e.* they move in the opposite direction to the $\dot{C}_\alpha$–C_β rotation barriers (V_α). The explanations of these two effects are probably linked. The increase in the ring angle at C_γ with increasing ring size places the δ-hydrogens closer to the β-hydrogens. Thus, although the C_β–C_γ bond length increases from (**3a**—**d**) which lowers the rotation barriers, this is more than offset around C_β–C_γ by the increase in steric hindrance from the closer proximity of the δ-hydrogens and δ-carbons to the β-hydrogens. The net effect on E_β is an increase along the series. There is a small decrease in the barrier for (**3d**) (Table 4). Because C_γ forms part of a double bond, very little difference is expected in the ring angle at C_γ in (**3d**) as compared with (**3c**). The steric interaction of the δ-hydrogens with the β-hydrogens will be rather similar in these two radicals and roughly equal E_β values would be predicted. The actual decrease in E_β from (**3c**—**d**) is difficult to account for.

Intuitively, we expect that the C_β–C_γ rotations in (**3a**—**d**) are approximately six-fold in character and therefore barriers less than that of the three-fold ethane barrier (*ca.* 3 kcal mol^{-1}) would be expected.[13] It appears, therefore, that the barriers in (**3a**) and (**3b**), and but-3-enyl are normal while those for (**3c**) and (**3d**) are abnormally high. Because of their larger ring sizes these latter two radicals will have much greater steric hindrance from the δ-hydrogens to the C_β–C_γ rotation. The conformation which minimises this interaction is (**9**) and hence the rotation will have a deep minimum at this point and be roughly two-fold in character with a greatly increased barrier; just as is observed experimentally.

Any homoallylic stabilisation in radicals (**3**) would manifest itself as an increase in the magnitude of the $\dot{C}_\alpha$–C_β and C_β–C_γ bond rotation barriers. We find that the V_α values are <0.5 kcal mol^{-1} for all four radicals (Table 2) and that the E_β values are $\leqslant 5$ kcal mol^{-1} for all four radicals. This latter figure puts an upper limit on any homoallylic stabilisation in (**3**). However, the true homoallylic stabilisation is probably much less than this

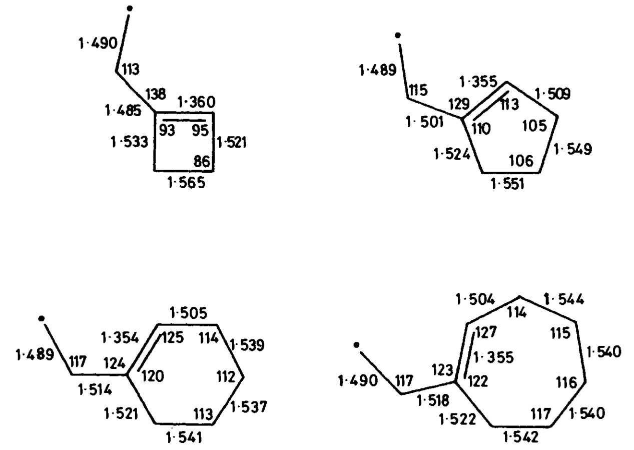


Figure 4. Partial MNDO-optimised structures for radicals (**3a**—**d**)

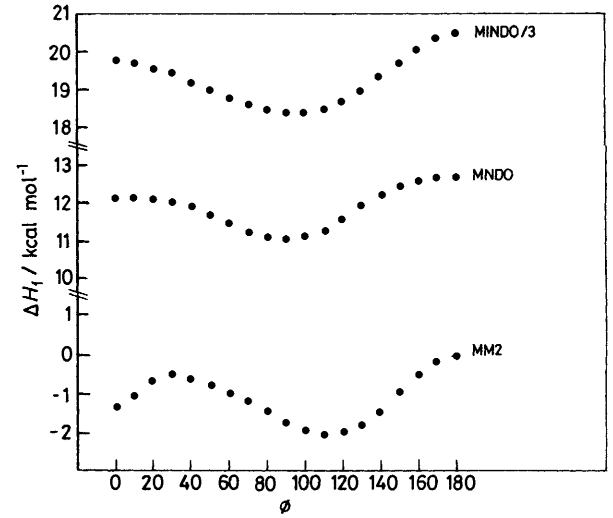


Figure 5. Calculated C_β–C_γ rotational energy functions for 2-(cyclohex-1-enyl)ethyl radicals (**3c**). Top; MINDO/3 result, centre, MNDO result. Bottom MM2 potential function for ethylcyclohexene. Note that the functions are symmetrical about $\varphi = 0°$

in all the radicals because both V_α and E_β seem to be mainly determined by steric factors. Thus, the present results are consistent with the negligible homoallylic stabilisation which has been found for other but-3-enyl-type radicals.[6]

Semi-empirical MO and Force Field Study.—The structures, conformations, and energetics of radicals (**3a**—**d**) were examined using the MNDO(RHF) and MINDO/3(UHF) methods.[14] All geometries were initially fully optimised and the C_β–C_γ rotational energy function was then calculated for a series of values of the $C_\alpha C_\beta C_\gamma C_\delta$ dihedral angle (φ). In these reaction co-ordinate calculations for (**3c**) and (**3d**) the bond lengths and angles of all hydrogen atoms further than C_δ from the rotor were kept constant at the values found in the initial optimisations. Force field calculations were carried out for the ethylcycloalkenes corresponding to (**3a**—**d**) using the MM2 program.[15,16] The spin densities and h.f.s. of the radicals were calculated using the INDO method[17] with the optimum geometries from the MNDO calculations.

Partial MNDO-optimised structures are shown in Figure 4. As expected[18,19] the calculated $\dot{C}_\alpha$–C_β bonds are shorter and the C_β–C_γ bonds longer in all four radicals as compared with analogous bonds in hydrocarbons. The calculated structures show a progressive increase, with ring size, in the ring angle at C_γ and in the C_β–C_γ bond length. This agrees well with expectation (see above). The structures also illustrate how the δ-hydrogens approach the β-hydrogens more closely as the ring size increases. Although there were differences in detail, the MINDO/3 results showed these same trends. The semi-empirical calculations agree with the idea that the variations in V_α and E_β should be attributed to steric effects.

Previous work[9] has shown that the semi-empirical methods are not successful at calculating the very low barriers about the $\dot{C}_\alpha$–C_β bonds (V_α). Attention was therefore focused on the larger barriers about the C_β–C_γ bonds (E_β). The rotational energy functions for the 2-(cyclohex-1-enyl)ethyl radicals (**3c**) calculated by the three methods are plotted in Figure 5. The MNDO and MINDO/3 calculations show energy minima at $\varphi = 90°$ and 270°; *i.e.* they predict that (**9a**) and (**9b**) are the preferred conformations, in agreement with experiment. The MM2 results suggest larger values of φ (*ca.* 110° and 290°) at the minima together with a smaller energy minimum at $\varphi = 0°$. This latter value corresponds to conformation (**7**). All three methods predict that conformation (**8**) ($\varphi = 180°$) will be a maximum. Rather similar results were obtained for the other three radicals, the only significant difference being that the MNDO and MINDO/3 methods gave very 'flat' functions for (**3a**) and (**3b**) with only weak minima at $\varphi = 90°$. Thus the rotational functions for the radicals with the smaller rings are more like the expected six-fold rotational functions. The calculated enthalpies of activation ($\Delta H^\ddagger$) *i.e.* the difference in energy between the maximum at $\varphi = 180°$ and the minimum at $\varphi = 90°$ are given in Table 4 together with the rotational barrier calculated by the MM2 method with the rigid rotor approximation. The MNDO and MINDO/3 results successfully reproduce the increase in barrier height as the ring size increases, although they underestimate the magnitude of the barriers. The MINDO/3 method even predicts a decrease in the barrier for (**3d**), in agreement with experiment, but this was not confirmed by the MNDO calculations. The MM2 method calculates roughly equal barriers for all four species and fails to reproduce either the trend or the magnitude of the experimental results. The h.f.s. calculated by the INDO method for conformation (**9**) showed non-equivalence in the β-hydrogens, as expected, with the larger $a(H_\beta)$ value corresponding to the H *cis* to the double bond, *i.e.* H^a in structure (**9**).

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