

Investigations of Structure and Conformation. Part V.¹ Conformational Interconversion and Ring Shape in Five- and Six-membered Alicyclic Radicals

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A conformational analysis is presented of a variety of radicals generated by reaction of the hydroxyl radical with a number of cyclopentane and cyclohexane derivatives. The β -hydrogen splittings in their e.s.r. spectra are interpreted in terms of a $B\cos^2\theta$ dependence, where θ is the dihedral angle subtended by the β -C-H bond with the orbital of the unpaired electron. The results suggest that the cyclohexane-derived radicals prefer a twisted-chair geometry except for 2-oxocyclohexyl which exists as a half-chair. The cyclopentyl-type radicals exist in a half-chair conformation except for the planar 2-oxocyclopentyl. A kinetic analysis for the conformational interconversion of 4-ammoniocyclohexyl and 2-oxocyclohexyl is reported.

We have previously described the e.s.r. spectra of radicals derived from a variety of heterocyclic compounds by reaction with the hydroxyl radical in aqueous solution at room temperature.¹ In particular, we employed two approaches which enabled useful kinetic and thermodynamic information about conformational interconversion to be obtained: one approach involved the investigation of splittings and linewidths as a function of temperature (to assist assignment of splittings and to obtain kinetic parameters) and the other employed suitable ring substituents to create favourable weighting for certain conformations. For example, it was possible to demonstrate that the five-membered-ring radicals from pyrrolidine and its derivatives prefer a half-chair geometry and undergo rapid conformational interconversion; for six-membered-ring radicals, such as piperidinium-4-yl, chair-chair flipping in the range intermediate between fast and slow exchange was demonstrated.

Although the e.s.r. spectra of carbon-centred five- and six-membered alicyclic radicals have excited considerable interest (investigations of radicals in aqueous solution,²⁻⁶ non-aqueous solution,⁷⁻¹¹ and in the solid state¹²⁻¹⁵ have been described), variable temperature investigations have been comparatively rare and few examples of the effects of ring substituents have been reported (see, for example, refs. 12 and 14). Accordingly, we have extended our previous conformational study¹ to a variety of radicals from cyclopentane and cyclohexane derivatives and some closely related compounds. Observed substituent and temperature effects, when interpreted on the basis of the expected $B\cos^2\theta$ dependence of the splittings from β -hydrogens,

enable definite conclusions about ring shape and interconversion to be drawn.

EXPERIMENTAL

Radicals have been prepared by the reactions between a variety of alicyclic substrates and the hydroxyl radical (generated from the $Ti^{III}-H_2O_2$ couple) in rapid mixing flow systems. Details of the spectrometer, the flow systems, the procedure for measuring hyperfine splittings, and the spectrum simulation program, which incorporates an exchange routine, have been described previously.¹ In these experiments, radicals were generated in both three-way single-stage mixing systems (from amines) and two-way single-stage mixing systems (all other substrates). Reactants in the former system were typically as follows: the first solution contained 12.5% (w/v) titanium(III) chloride solution (10–15 ml l⁻¹) and concentrated sulphuric acid (5–10 ml l⁻¹), the second contained 100-volume hydrogen peroxide solution (ca. 5 ml l⁻¹) and concentrated sulphuric acid (5–10 ml l⁻¹), and the third solution contained the amine (30 ml l⁻¹) and sufficient concentrated sulphuric acid to give an effluent pH of ca. 1.5. The combined flow rate was typically 250 ml min⁻¹. For the experiments with the two-way flow system, one solution contained 12.5% (w/v) titanium(III) chloride solution (10 ml l⁻¹), concentrated sulphuric acid (ca. 5 ml l⁻¹), and the substrate (up to ca. 10 ml l⁻¹); the other contained 100-volume hydrogen peroxide solution (ca. 3 ml l⁻¹) and similar concentrations of acid and organic compound. The combined flow rate was typically 200 ml min⁻¹. All solutions were deoxygenated with a nitrogen purge prior to radical generation. Temperature variation was achieved with iced or hot water, and the mean values quoted ($\pm 2^\circ$) were measured with thermometers placed in each stream just before entry of the solutions to the cavity of the spectrometer.

¹ Part IV, B. C. Gilbert, M. Trenwith, and A. J. Dobbs, *J.C.S. Perkin II*, 1974, 1772.

² W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4850.

³ A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. (A)*, 1971, 124.

⁴ H. Taniguchi, *J. Phys. Chem.*, 1970, **74**, 3143.

⁵ C. Corvaja, M. Brustolon, and G. Giacometti, *Z. Phys. Chem. (Frankfurt)*, 1969, **66**, 279.

⁶ T. Shiga, A. Boukhors, and P. Douzou, *J. Phys. Chem.*, 1967, **71**, 4264.

⁷ I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, 1972, **28**, 867.

⁸ C. Corvaja, G. Giacometti, and M. Brustolon, *Z. Phys. Chem. (Frankfurt)*, 1972, **82**, 272.

⁹ C. Corvaja, G. Giacometti, and G. Sartori, *J.C.S. Faraday II*, 1974, 709.

¹⁰ A. Hudson and K. D. J. Root, *Tetrahedron*, 1969, **25**, 5311.

¹¹ E. A. C. Lucken and B. Poncioni, *Helv. Chim. Acta*, 1972, **55**, 2673.

¹² D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1973, **95**, 7978.

¹³ A. L. Blyumenfel'd and V. I. Trofima, *Zhur. strukt. Khim.*, 1973, **14**, 230.

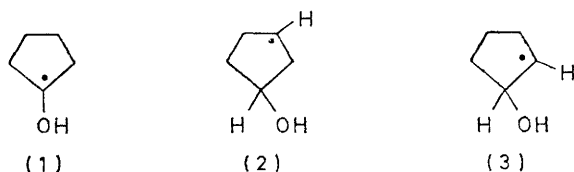
¹⁴ D. M. Camaioni and D. W. Pratt, *J. Amer. Chem. Soc.*, 1972, **94**, 9258.

¹⁵ D. M. Camaioni, H. F. Walter, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1973, **95**, 4057.

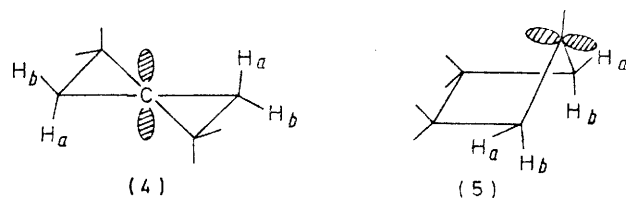
All compounds employed were commercial samples and were used without further purification.

RESULTS AND DISCUSSION

(a) *Radicals from Compounds with Five-membered Rings.*—(i) *Cyclopentanol.* The e.s.r. spectrum detected during the reaction of cyclopentanol with $\text{Ti}^{\text{III}}\text{-H}_2\text{O}_2$ is analysed in terms of species (1) and (2), present in the concentration ratio *ca.* 2:1. Their hyperfine parameters are presented in Table 1, and our assignments are justified in the analysis given below. The spectra also show the presence of some other broad resonances but there appear to be no signals definitely attributable to (3). Although e.s.r. spectroscopy has previously been employed^{2,5,9} in studies of the radical oxidation of this substrate, only radical (1) has been characterised [with, typically,⁹ $a(\beta\text{-H})$ 2.76 mT, *cf.* Table 1].



The observed 1:4:6:4:1 intensity ratio of the lines in the β -hydrogen multiplet of (1) and its insensitivity to changes in temperature are consistent either with a planar ring or with very rapid interconversion between non-planar isomers. To estimate the shape of this radical, the average β -hydrogen splittings expected for a planar conformation, a half-chair conformation (4), and an envelope conformation (5) were calculated. The pairs of dihedral angles (subtended by the β -C-H bonds with the orbital of the unpaired electron) which would characterise these model ring-shapes are 30 and 30°, 10 and 50°, and 10 and 70°, respectively. A $B\cos^{2\theta}$ dependence for $a(\beta\text{-H})$ was assumed: it was felt that the appropriate value of B is 3.96 mT [from the β -splitting for $\cdot\text{CMe}_2\text{OH}$ ¹⁶ in which $\langle\cos^{2\theta}\rangle$ is 1/2 and in which spin



is withdrawn on to the oxygen as in (1)]. The results for $a(\beta\text{-H})$ are as follows: 2.97 mT for a planar ring, an average value of 2.74 mT for a half-chair (*cf.* pyrrolidinium-3-yl¹), and an average value of 2.15 mT for an envelope conformation. The experimental value of 2.841 mT suggests that the geometry is probably a half-chair [*cf.* (4)], with some deviation from planarity,

¹⁶ A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 786.

in agreement with the conclusion of Corvaja *et al.*⁹ Angles of 15 and 45° for the two β -hydrogens (H_a and H_b , respectively) would give values of $a(\beta\text{-H}_a)$ and $a(\beta\text{-H}_b)$ which are then averaged to the observed

TABLE 1

Radical	$T/^\circ\text{C}$ ^c	$a(\alpha\text{-H})$	$a(\beta\text{-H})$ ^d	$a(\text{other H, N})$ ^d
(1)	18		2.841(4)	
	9	2.144	2.984(1) 3.231(1) 3.869(1) 3.991(1)	0.059 (3, $\gamma\text{-H}$)
(2)	24	2.128	3.025(1) 3.244(1) 3.813(1) 3.922(1)	0.056 (3, $\gamma\text{-H}$)
			38	
	(8) ^e	20	2.17	3.812(2) 3.566(2) 3.837(2) 3.92(1)
(9) ^f	20	2.20	2.84(1) 3.67(1) 3.92(1)	0.86 (1, $\beta\text{-N}$)
(10)	19	1.796	3.812(2)	0.454 (2, $\gamma\text{-H}$) ^g
(11)	19	2.186	3.566(2) 3.837(2) 2.857(2)	0.095 (2, $\gamma\text{-H}$)
(12)	8	1.229	3.55(4)	0.082 (2, $\gamma\text{-H}$)
			26	1.210
	40	1.203	2.835(2)	
(13) ^e	8	2.12	3.53(4)	<i>i</i>
	26	2.12	3.49(4)	<i>i</i>
	40	2.10		<i>i</i>
(14; X = OH)	18	1.247	2.570(1) 3.150(1)	0.069 (2, $\gamma\text{-H}$) 0.208 (1, $\gamma\text{-H}$) ⁱ
(14; X = NH ₂)	19	1.329	2.753(1) 3.087(1)	0.076 (2, $\gamma\text{-H}$) 0.171 (1, $\gamma\text{-H}$) ⁱ
(14; X = OAc)	18	1.292	2.589(1) 3.207(1)	0.082 (2, $\gamma\text{-H}$) 0.195 (1, $\gamma\text{-H}$) ⁱ

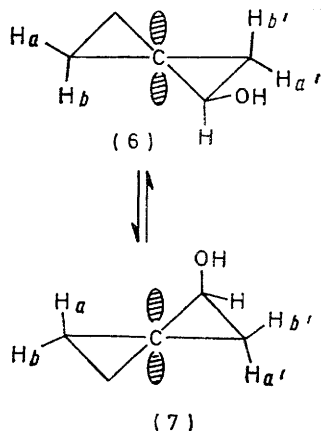
^a ± 0.005 mT, unless stated otherwise. ^b pH *ca.* 1.5. ^c $\pm 2^\circ$. ^d Number of nuclei indicated. ^e Splittings ± 0.01 mT. ^f Splittings ± 0.02 mT. ^g Hydrogens of the methylene group adjacent to the carbonyl function. ^h Hydrogens of the methylene group adjacent to the oxygen atom. ⁱ Other, small splittings incompletely resolved.

splitting. These angles concur with those (14 and 40°) estimated for cyclopentyl itself from data for the radical trapped in a solid matrix.¹³

The non-equivalence of the β -hydrogen splittings for (2) is clearly indicative of a non-planar ring: the individual splittings do not correspond to a single, fixed conformation but rather must be weighted averages of two or more conformations and, as such, are temperature dependent. We can assign the largest and smallest of the four values of $a(\beta\text{-H})$ at each temperature to the pseudo-axial and pseudo-equatorial hydrogens, respectively, attached to one of the β -carbon atoms, and the remaining two splittings similarly to the hydrogens attached to the other carbon [in this way the two values of $\Sigma a(\beta\text{-H})$, and hence their averages, are

more alike and vary little with temperature]. The sums of the pairs of β -hydrogen splittings for (2) (*ca.* 7.0 mT for the β -hydrogens on each side of the radical centre) enable an approximate geometry to be estimated as follows: assuming a $B\cos^2\theta$ dependence for $a(\beta\text{-H})$, with B now 5.0 mT (from the β -splitting for $\cdot\text{CHMe}_2$ ¹⁷

in which $\langle\cos^2\theta\rangle$ is again 1/2) and assuming that $\text{H}_a\widehat{\text{C}}\text{H}_b$ is 120° , then the dihedral angles θ and θ' (for H_a and H_b , respectively) required to give $\Sigma a(\beta\text{-H})$ 7.0 mT are 10 and 50° (splittings of 4.9 and 2.1 mT are calculated for pseudo-axial and pseudo-equatorial hydrogens, respectively), as found for the pyrrolidinium radicals reported previously.¹ We believe that the spectra from (2) are thus interpretable in terms of rapid interconversion between the two conformers (6) and (7), and it seems likely that (6), with the $\gamma\text{-OH}$ group disposed pseudo-equatorially is preferred.

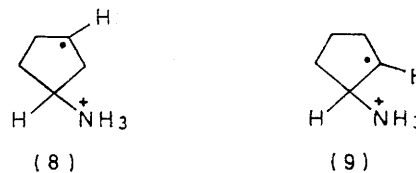


The apparent (averaged) pseudo-axial and pseudo-equatorial β -hydrogen splittings can be employed in conjunction with the values calculated for a fixed conformation to determine the weightings of (6) and (7) at each temperature. The results for conformation (6) are as follows: 64.0% at 9° , 63.1% at 24° , and 61.9% at 38° . We calculate that ΔH° for the interconversion is 2.4 ± 0.5 kJ mol⁻¹, and that ΔG° is 1.3 kJ mol⁻¹ at 24° . The latter value may be compared with that of 1.4 kJ mol⁻¹ at 23° for the related interchange of an *N*-methyl group in the pyrrolidinium-3-yl radical.¹

(ii) *Cyclopentylamine*. The predominant species observed when $\cdot\text{OH}$ reacts with cyclopentylamine at pH 1.9 is, as expected on the basis of the electrophilic nature of hydroxyl, the radical (8); a very much weaker signal assigned to (9) is also detected (see Table 1). Previously,² radical (8) was detected, but the degree of non-equivalence reported here was not resolved.

Radical (8) is an analogue of (2), but with a smaller difference between the splittings of non-equivalent hydrogens. The average β -hydrogen splitting in (8) is *ca.* 3.5 mT, as it is for radical (2), although for radical (8) the individual splittings are too close to each other for

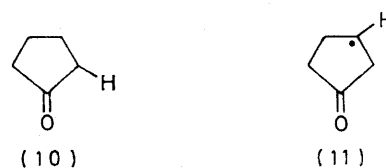
more detailed assignment [the hydrogen atoms with $a(\text{H})$ 3.67 mT are probably pseudo-axial]. Since $\Sigma a(\beta\text{-H})$ for the pair of hydrogens attached to each β -carbon atom in (8) is *ca.* 7.0 mT, the ring shape must



be essentially the same as for (2), *i.e.* a half-chair with $\beta\text{-C-H}$ dihedral angles of *ca.* 10 and 50° and hence corresponding individual splittings before weighted averaging. There must be less conformational fixing in the amine-derived radical than for (2) on account of the smaller extent of non-equivalence in the former.

The spectrum from (9) is interpreted in a similar fashion. The splittings of 2.84 and 3.92 mT are assigned to the hydrogen atoms of the β -methylene group: their sum (6.76 mT) is then close to those of most of the cyclopentyl derivatives so far discussed. Their non-equivalence presumably reflects the weighting of a preferred conformation and since the splitting assigned to the β -methine hydrogen (3.67 mT) is greater than the average of the others it appears that this hydrogen is pseudo-axial in the preferred conformation (with, as expected, NH_3^+ pseudo-equatorial). The limited quantity of cyclopentylamine available precluded an investigation of the temperature dependence of the spectra from the derived radicals.

(iii) *Cyclopentanone*. The e.s.r. spectrum detected during the reaction of the hydroxyl radical with cyclopentanone at low pH consists of signals from two radicals, (10) and (11), in the concentration ratio 0.7 : 1 (see Table 1): radical (10) has not previously been detected in this system.



The very large $\Sigma a(\beta\text{-H})$ for (10) of *ca.* 7.6 mT is strongly suggestive of a planar structure for this radical. The value of $a(\beta\text{-H})$ which would result for this geometry can be calculated by employing a $B\cos^2\theta$ relationship with θ 30° and B 4.50 mT [from $a(\beta\text{-H})$ for $\cdot\text{CHMeCOEt}$,¹⁸ with a small correction applied to allow for slightly different α -carbon spin densities, as judged by $a(\alpha\text{-H})$]; the result is $a(\beta\text{-H})$ *ca.* 3.3 mT, which is close to but somewhat lower than the experimental value. It may be that the rigidity of the system, imposed presumably by the conjugation between the radical centre and the

¹⁷ R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

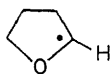
¹⁸ B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1973, 2174.

carbonyl group, causes the HC_βH angle to be greater than expected, so that the dihedral angles for the β -hydrogens become less than 30° . The radical (10) showed no temperature variation in its splittings or linewidths, as also reported for the same radical generated in the range 182–382 K by X-irradiation of cyclopentanone;¹² this provides support for the conclusion that a planar structure is adopted.

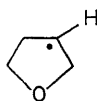
Radical (11) has a rather lower sum for $a(\beta\text{-H})$ than (10), even though there can be no spin withdrawal from the radical centre in the former case. The magnitude of $a(\beta\text{-H})$ for (11) nevertheless suggests that the ring is planar or only slightly distorted [calculated values of $\Sigma a(\beta\text{-H})$ for a pair of β -hydrogens are *ca.* 7.5 mT for a planar form and *ca.* 7.0 mT for a half-chair]. The non-equivalence of the β -splittings (not detected in the previous work⁵) is probably a consequence of the asymmetry introduced in the ring by the carbonyl substituent rather than a manifestation of the conformational preference of a $>\text{C}=\text{O}$ group in this system: there was no detectable variation in the magnitudes of $a(\beta\text{-H})$ with temperature, which supports this assertion and suggests an appropriate analysis in which the pair of hydrogens with a given splitting are those on the same side of the radical centre.

Our deductions about favoured geometries based on e.s.r. data for substituted cyclopentane-derived species indicate that attention must be paid to ring shape when hyperfine parameters for this type of radical are considered. For example, in a recent analysis¹⁹ of the splittings for 1-methylcyclopentyl [$a(\text{Me})$ 2.224, $a(4\beta\text{-H})$ 3.290 mT at -17°] it has been assumed that there is a *planar* geometry for the ring. The splittings were interpreted then in terms of a ($B_0 + B\cos\theta$) relationship for $a(\beta\text{-H})$, with B_0 0.092 and B 4.264 mT. We feel that these numbers are erroneous (in particular, B_0 appears considerably too large). However, if B_0 is taken as zero, and B set at 4.45 mT [from the value of $a(\beta\text{-H})$ for the freely rotating methyl group] then dihedral angles for the ring β -hydrogens are estimated as 17° (pseudo-axial) and 43° (pseudo-equatorial); rapid interconversion then accounts for the averaging of the individual $\beta\text{-H}$ splittings. These angles correspond closely with those calculated for various cyclopentyl-type radicals (see earlier, and refs. 1 and 13 for example).

(iv) *Tetrahydrofuran and some related compounds.* The reaction of the hydroxyl radical with tetrahydrofuran generates both (12) and (13) [see also refs. 5, 6,



(12)



(13)

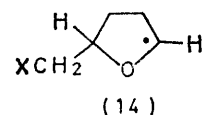
10, and 13; data are given in Table I]. Both these hyperfine data and the detection of temperature in-

¹⁹ H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575.

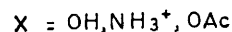
²⁰ W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.

dependent intensity patterns imply that each radical either is planar or is non-planar and undergoes rapid interconversion.

The radical (13) has a β -splitting close to that of the pyrrolidinium-3-yl radical¹ and close to the average β -splittings for (2) and (8), so that a similar half-chair geometry may therefore be proposed for this species. The analysis for (12) may be complicated by a significant degree of bending at the trivalent carbon [in particular, this has been proposed³ to account for the radical's unusually low α -hydrogen splitting, but it may also affect the magnitude of B_0 and B in the customary relationship for $a(\beta\text{-H})$]. However, clear evidence that the ring itself is non-planar derives from the spectra of some ring-substituted radicals (see Table 1). Thus, when hydroxyl reacts at low pH with tetrahydrofurfuryl alcohol, amine, or acetate, the major species detected in each case can be characterised as a radical of the type (14), formed *via* hydrogen atom abstraction from the methylene group attached to the ether oxygen atom. The spectra also show the presence of a number of other, less intense resonances, the nature of which is discussed later.



(14)



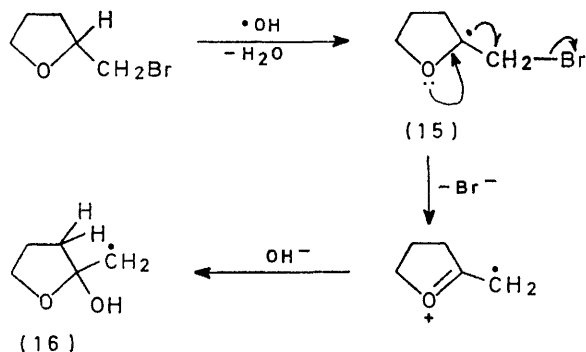
Radicals (14) are ring-substituted tetrahydrofuran-2-yl species and it is encouraging to find that the sums of the β -hydrogen splittings (5.720, 5.840, and 5.796 mT, respectively) are very similar to that for (12) (*e.g.* 5.696 mT at 26°). Moreover, the non-equivalence of the β -splittings detected for the substituted radicals provides support for the suggestion¹³ that the parent unsubstituted radical has a non-planar structure.

Employing a value for B in these radicals of 4.38 mT [from ²⁰ $a(\beta\text{-H})$ for $\cdot\text{CHMeOEt}$] together with values of θ appropriate to a half-chair conformation (10 and 50°), it is possible to calculate β -splittings for a fixed conformation and hence to determine the weighting of the predominant conformation of radicals (14), as outlined above. We find that the preferred conformation, presumably that with CH_2X pseudo-equatorial, has weightings of 59% ($\text{X} = \text{OH}$), 55% ($\text{X} = \text{NH}_3^+$), and 60% ($\text{X} = \text{OAc}$).

The spectrum observed from tetrahydrofurfuryl bromide under similar conditions is quite unlike that from the other derivatives: it has $a(2\text{H})$ 2.00, $a(2\text{H})$ 0.15 mT. The signal is ascribed to (16) formed *via* (15) by the fragmentation-addition pathway (*cf.* the oxidation of β -chloroethanol,²¹ for example) outlined in the Scheme. The minor signals in the spectra from tetrahydrofurfuryl alcohol, amine, and acetate may include those from (16) and the appropriate first formed oxygen-

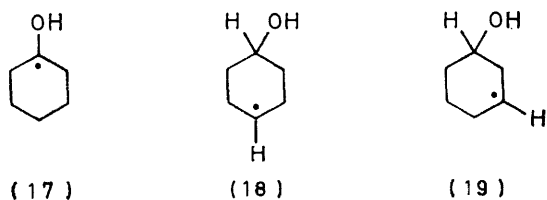
²¹ B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 794.

conjugated radicals (with, possibly, less ready fragmentation of the latter in these examples). That a radical of the type (14) is not observed from the bromo-compound may reflect an exclusive destruction pathway for (14; X = Br) or neighbouring group participation of bromine so that the formation of (15) is favoured.



SCHEME

(b) *Radicals from Compounds with Six-membered Rings.*—(i) *Cyclohexanol.* The spectra detected during the oxidation of cyclohexanol with $\cdot\text{OH}$ at pH 1.5 and 22° were similar to those previously reported:^{2,6} there are three dominant central lines (one, not exactly at the centre of the other two, is somewhat less sharp) with a number of broad, ill-defined wing-lines. A complete solution of the spectra proved impossible, and it seems likely that all four carbon-centred radicals produced by C-H abstraction are present. The following qualitative conclusions can, however, be drawn. The spectrum from (17) at room temperature is evidently a 1:4:1 pattern which derives from the occurrence of an interconversional exchange process in the range intermediate between fast exchange (expected ratios 1:4:6:4:1) and the slow-exchange limit (at low temperatures, the β -hydrogen splitting pattern of a triplet of triplets indicates two non-equivalent pairs of hydrogens, typical of a twist-chair conformation⁹).^{1,2} The spectra from (18) and (19) should be a doublet (1:1) of triplets (1:2:1) of triplets (1:2:1) which has similarly undergone line broadening so that a pair of sharp lines in the centre is detected (*cf.* the discussion

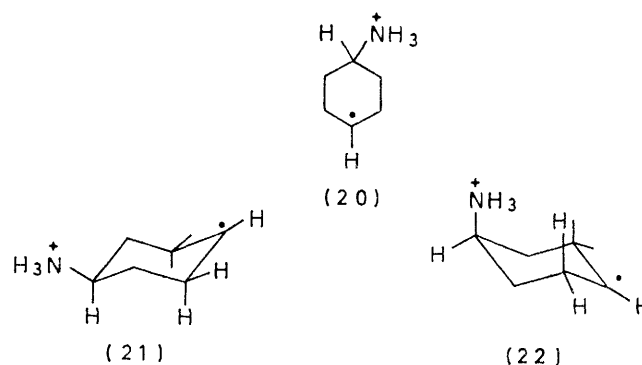


for the piperidiniumyl radicals¹ and for 4-ammonio-cyclohexyl, discussed below: see also Figure 1). The main features of the spectrum observed from cyclohexanol are then the doublet (a 2.10 ± 0.01 mT) from (18) and (19), together with the central peak from (17)

at slightly higher g -value (Δg *ca.* 0.0005, as expected). Overlapping resonances in the wings preclude further analysis.

(ii) *Cyclohexylamine.* In contrast, the e.s.r. spectrum observed during oxidation of cyclohexylamine at low pH can be clearly identified as that of the radical (20), formed by reaction of the electrophilic hydroxyl radical at the position remote from the positive charge. Although resonances previously detected² during this reaction were attributed to a mixture of radicals, it now seems clear that the positions and shapes of all the lines can be accounted for in terms of a rapid interchange between the two non-equivalent chair forms of (20), *i.e.* (21) and (22).

The widths of certain lines and also the apparent β -hydrogen splittings prove to be markedly temperature dependent; in particular, specific lines sharpen and the measured β -splittings become less non-equivalent (see Table 2) with increasing temperature. It has proved



possible to simulate the observed spectrum, including the linewidth effects, at each temperature by employing

TABLE 2

Hyperfine splittings (in mT^a) for radicals derived from compounds with six-membered rings^b

Radical	$T/^\circ\text{C}$ ^c	$a(\alpha\text{-H})$	$a(\beta\text{-H})$ ^d	$a(\text{other H})$ ^e
(20) ^e	8	2.14	3.98(1) 0.88(1)	
	18	2.12	3.97(1) 0.91(1)	
	31	2.10	3.93(1) 0.96(1)	
(25)	13	1.74	6.85 ^f	0.19 (2, $\gamma\text{-H}$) ^g
(23)	13	2.16 ^h	2.78(4) ^h	
(24)	13	2.16 ^h	2.76(4) ^h	
2-Oxo-5-t-butylcyclohexyl	32	1.75	2.51(1) 4.34(1)	0.33 (1, $\gamma\text{-H}$) ^g

^a ± 0.01 mT, unless stated otherwise. ^b pH *ca.* 1.5. ^c $\pm 2^\circ$. ^d Number of nuclei indicated. ^e Splittings ± 0.02 mT. ^f Sum of the two β -hydrogen splittings, see text. ^g Attributed to the hydrogen(s) of the methylene group adjacent to the carbonyl function. ^h See also ref. 18.

suitable conformational weightings and exchange rates for the two conformers.

In order to calculate these weightings in the equilibrating mixtures, the individual (fixed) β -hydrogen

splittings for the unsubstituted cyclohexyl radical were employed (suitably adjusted to give the correct sum). These splittings have been measured²² as 4.00 and 0.55 mT at 186 K in an adamantane matrix: the β -splittings measured here are then obtained if the predominant conformation (21) is favoured to the extent of 92.1% (at 8°), 91.3% (at 18°), and 90.1% (at 31°). At 18°, we calculate that ΔG^0 for the interconversion is 5.7 kJ mol⁻¹, a value comparable with that (6.5–7.8 kJ mol⁻¹) estimated²³ for the parent molecule at room temperature.

These weightings were next used in the simulation program and the interconversion rates were varied to obtain best fits to the experimental traces (see Figure 1

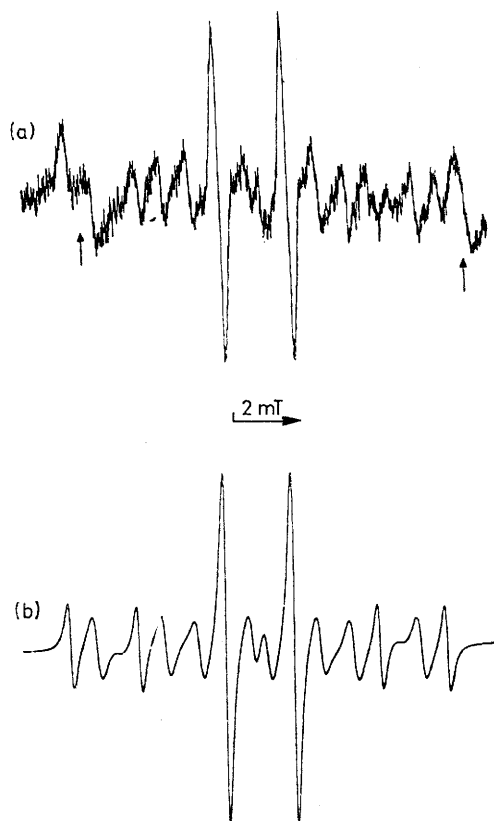


FIGURE 1 (a) E.s.r. spectrum of the radical (20) at 8° (the arrowed signals are spurious). (b) Simulated spectrum, with $a(\alpha\text{-H})$ 2.14, $a(2\beta\text{-H})$ 4.27, $a(2\beta\text{-H}')$ 0.59 mT, $\Delta H = 0.2$ mT, and rate constants for conversion from the more to the less favoured conformation and the reverse process of 1.0×10^8 and 1.2×10^9 s⁻¹, respectively

for example): the optimum exchange rate constants thus obtained are given in Table 3. We believe that the reasonable agreement achieved between observed and simulated spectra indicates the appropriateness of the method and of the choice of individual β -hydrogen splittings. We note, in particular, that the small sums of the β -hydrogen splittings for cyclohexyl (4.55 mT) and 4-ammoniocyclohexyl (4.9 mT) are in contrast with

²² L. Bonazzola, N. Leray, and R. Marx, *Chem. Phys. Letters*, 1974, **24**, 88.

those for the half-chair and planar cyclopentyl-type radicals discussed earlier. The smaller values for the former are as expected for *chair*-type conformations:

TABLE 3

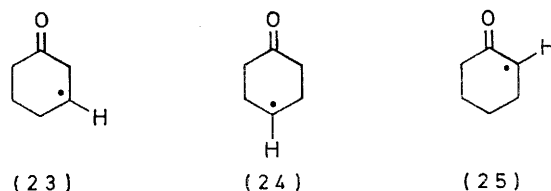
Rate constants for conformational interconversion of six-membered alicyclic radicals at various temperatures

Radical	$T/^\circ\text{C}$ ^a	$10^{-8}k/\text{s}^{-1}$	
(20)	8	1.0 ± 0.1 ^b	12 ± 1 ^c
	18	1.9 ± 0.2 ^b	20 ± 2 ^c
	31	3.2 ± 0.4 ^b	29 ± 4 ^c
(25)	7		14 ± 1
	11		15 ± 1
	23		25 ± 2
	33		35 ± 3
	43		39 ± 3

^a $\pm 2^\circ$. ^b Conversion from the more favoured conformer to the less favoured conformer. ^c The reverse process of b.

for a perfect chair we would expect dihedral angles of 30 and 90° for the β -axial and -equatorial C-H bonds, respectively, and hydrogen splittings of *ca.* 3.7 and *ca.* 0 mT [from B *ca.* 5.0 mT, from 17 $a(\beta\text{-H})$ from $\cdot\text{CHMe}_2$]. The higher sums observed than that calculated on this basis, and, in particular, the non-zero value for the equatorial β -hydrogen splitting, are consistent with some degree of distortion from a perfect chair. More appropriate values for θ in (20), calculated from the $B\cos^2\theta$ relationship, are 15 and 75°.

(iii) *Cyclohexanone and some alkylated derivatives.* Spectra from the radicals (23)–(25) are detected when the hydroxyl radical reacts with cyclohexanone at room temperature in aqueous solution: the splittings have been previously assigned and a kinetic analysis of the reaction scheme has been presented.¹⁸ We note that the sums of the β -splittings for radicals (23) and (24), 5.56 and 5.52 mT, respectively, are significantly greater than those for the cyclohexyl radical and for 4-ammoniocyclohexyl, which suggests¹⁸ that there is a greater deviation from the perfect chair geometry in the cyclohexanone-derived species (*i.e.* there is a greater extent of flattening of the ring, with calculated values θ of 10 and 70°).



The intensities of the lines in the β -hydrogen triplet pattern in (25) show a marked dependence on temperature (see also ref. 14). The ratio of the peak heights of the central to the outer resonances is 0.5 : 1 at 7° and 1.2 : 1 at 43°. This evidently arises because of interconversion, with rates in the intermediate region, between conformations in which the β -hydrogens exhibit different

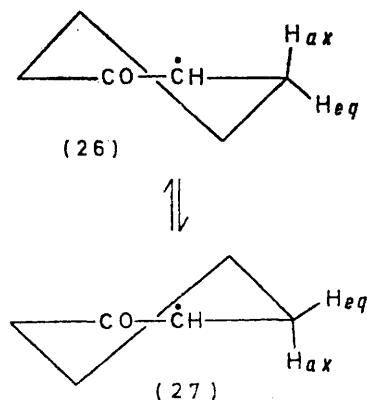
²³ E. L. Eliel, E. W. Della, and T. H. Williams, *Tetrahedron Letters*, 1963, 831.

dihedral angles and hence different splittings: the high temperature fast-exchange limit would then give a peak-height ratio of 2 : 1, which is clearly approached in the present study.

The very high $\Sigma a(\beta\text{-H})$ for 2-oxocyclohexyl [which is higher than the maximum sum predicted using a $B\cos^2\theta$ relationship (*cf.* the discussion for 2-oxocyclopentyl above)] is indicative of a coplanar configuration of the $-\text{CH}_2-\text{CO}-\dot{\text{C}}\text{H}-\text{CH}_2-$ fragment, presumably dictated by the conjugation between radical centre and the carbonyl group.

The spectra from (25) may then be interpreted, as previously suggested,^{14,18} in terms of interchange between the two equivalent half-chair geometries (26) and (27).

In order to simulate the observed degree of line-broadening, the individual β -splittings in the fixed conformations must be known. The analogous radical from 4-*t*-butylcyclohexanone was therefore generated (splittings are given in Table 2: these signals dominated the spectrum, evidently because the bulk of the *t*-butyl group hinders the abstraction of other hydrogen atoms from the ring). The two separate β -splittings detected (the sum of which coincides with that of the unsubstituted analogue) are similar in magnitude to those measured¹⁴ for 2-oxocyclohexyl in an adamantane matrix at 93 K (2.35 and 4.34 mT). This suggests that, as expected, the *t*-butyl substituent effectively locks the radical in one of the two possible geometries (*i.e.* with *t*-butyl pseudo-equatorial). The single γ -hydrogen



coupling is also indicative of a high degree of conformational fixing.

We have assumed that the individual β -hydrogen splittings in (25) are 2.51 ($\beta\text{-H}_{eq}$) and 4.34 mT ($\beta\text{-H}_{ax}$) and, using these and the other parameters for (25) we have been able to simulate accurately the spectra at different temperatures with different rates of interconversion (see, *e.g.*, Figure 2). The optimum values for the rate constant for interconversion are given in Table 3; from them we calculate E_a 22.8 ± 2.1 kJ mol⁻¹ and $\log_{10} A$ 13.4 ± 0.4 . This activation energy barrier may be compared with the value for ΔG^* of 21.3 kJ mol⁻¹ at -164° for ²⁴ *cis*-3,3,4,5,6,6-hexadeuteriocyclohexene

[similar geometries for this species and for radical (25) might be expected], but it is rather higher than might

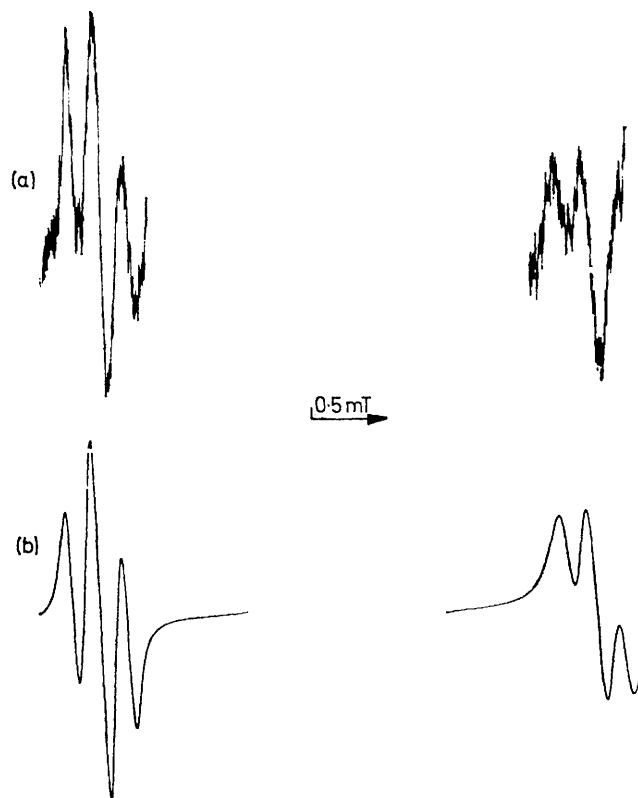


FIGURE 2 (a) Low field and central resonance in the $\Delta \tilde{M}(\alpha\text{-H}) + \frac{1}{2}$ group of lines in the e.s.r. spectrum of the radical (25) at 11° . (b) Simulated spectrum, with $a(\alpha\text{-H})$ 1.75, $a(\beta\text{-H})$ 4.34, $a(\beta\text{-H}')$ 2.51, $a(2\gamma\text{-H})$ 0.19 mT, ΔH 0.05 mT, and a rate constant for interconversion between equivalent conformations of 1.5×10^9 s⁻¹

have been anticipated from the value of ΔH^* (12.2 ± 1.3 kJ mol⁻¹) estimated¹⁴ for 2-oxocyclohexyl, trapped in an adamantane matrix, over the range 213–333 K.

The individual β -splittings of 4.34 and 2.51 mT can be used in conjunction with a suitable B value and the expected $B\cos^2\theta$ dependence to yield approximate dihedral angles for the $\beta\text{-C-H}_{ax}$ and $\beta\text{-C-H}_{eq}$ bonds of *ca.* 17 and 43° (the calculated values are 4.5 and 2.4 mT, respectively). This is consistent with a half-chair cyclohexene-like structure.

Attempts were made to study in similar fashion 5-methyl-2-oxocyclohexyl, but the complexity of the spectra precluded an analysis.

Conclusions.—Finally, it is interesting to compare the sums of the β -hydrogen splittings for the variety of non-conjugated radicals from substituted cyclopentane and cyclohexane compounds studied here. The sums vary from the lowest value, for 4-ammoniocyclohexyl (4.9 mT, interpretable in terms of a slightly twisted chair, with dihedral angles 15 and 75°) through those for 3- and

²⁴ F. A. L. Anet and M. Z. Haq, *J. Amer. Chem. Soc.*, 1965, **87**, 3147.

4-oxocyclohexyl (5.5 mT, indicative of a more twisted chair, θ 10 and 70°) and 3-hydroxycyclopentyl, 3-ammoniocyclopentyl, and tetrahydrofuran-3-yl (*ca.* 7.0 mT, for half-chair conformations with θ 10 and 50°) to the highest value, for 3-oxocyclopentyl (7.4 mT, probably planar, with both dihedral angles 30°).

2-Oxocyclopentyl appears to have a planar conform-

ation (the sum of the β -splittings is 7.6 mT, indicative of two angles of *ca.* 30°) and 2-oxocyclohexyl exists in a half-chair conformation (sum of the splittings 6.8 mT, with dihedral angles 17 and 43°).

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