ALICYCLIC KETYLS

II. TEMPERATURE DEPENDENCE OF THE CONFORMATIONAL MOBILITY OF MEDIUM-SIZED RINGS[1]

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ABSTRACT

The electron paramagnetic resonance spectra of ketyls derived from alicyclic ketones containing from 6 to 12 carbons have been recorded in 1,2-dimethoxyethane or dimethoxymethane at temperatures from −96 to +87 °C. At −96° individual conformers of the cyclohexyl ketyl are observed with hyperfine couplings in close agreement with that of the conformationally 'frozen' 4-*tert*-butyl analogue at room temperature. The cycloheptyl ketyl conformational equilibrium between forms which have a plane of symmetry through the C—O bond axis is 'frozen' with respect to the spectrometer frequency at temperatures from −40 to +88 °C. Cyclooctyl ketyl equilibrates at ordinary temperatures between two conformers lacking a plane of symmetry through the C—O bond axis. The electron paramagnetic resonance spectra of the ketyls derived from 10- and 12-membered rings show dramatic temperature dependence, which is interpreted in terms of two or more simultaneous conformational equilibria. Values for the dihedral angles of the alpha protons and for the spin density on the sp^2 carbon are derived.

We recently demonstrated (1) that a study of the electron paramagnetic resonance (e.p.r.) spectra of alicyclic ketyls in 1,2-dimethoxyethane can give valuable information about the conformations adopted by these radical anions in solution. It was found that the predicted (2) angular dependence of hyperfine coupling from protons alpha to the carbonyl group was confirmed and that it could be used to deduce dihedral angles. Within a given ring system, *A* values (conformational free energy differences) determined from neutral molecules were found to have validity when applied to the conformational analysis of such ketyls. In view of increasing interest in the shapes of medium-sized rings (7 to 12 carbons (3–8)) it was decided to examine the e.p.r. of the corresponding ketyls. A study of the temperature dependence of the e.p.r. spectra afforded valuable information concerning the individual conformers in each case.

Six-Membered Rings

Cyclohexyl ketyl had been shown (1) to give a sharp quintet of lines (1:4:6:4:1; a_H = 10.4 oersteds (Oe)) when generated from the ketone by potassium in dimethoxyethane at room temperature.

The conformationally 'frozen' 4-*tert*-butylcyclohexyl ketyl gave a seven-line spectrum ($a_{H_{ax}}$ = 14.4 and $a_{H_{eq}}$ = 7.2 Oe). Because of the conformational freedom of the unsubstituted six-membered ring, one would anticipate very little change in the e.p.r. spectrum except at low temperatures. A solution of the ketyl in dimethoxymethane (m.p. −104°) gave a quintet at room temperature, but as the temperature was lowered broadening of alternate lines occurred as the rate of inversion became comparable with the difference in the hyperfine frequencies between the two conformers, in accordance with prediction (9), until at −96° seven distinct lines were observed (Fig. 1B). At this temperature the lines are still broad, and accurate intensity computation is not possible. If it were possible to achieve lower temperatures with another solvent, presumably the lines would become

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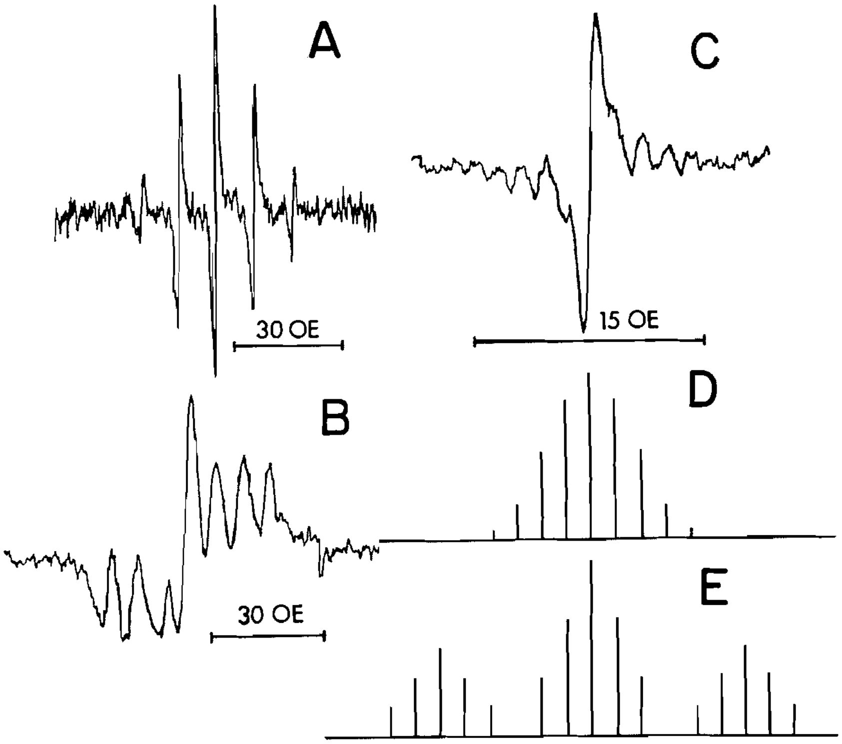


FIG. 1. First derivative e.p.r. spectra. LEGEND: A, cyclohexyl ketyl in 1,2-dimethoxyethane at +20°; B, cyclohexyl ketyl in dimethoxymethane at −96°; C, 2,2,6,6-tetradeuteriocyclohexyl ketyl in 1,2-dimethoxymethane at +20°; D, spectrum of C reconstructed from four equivalent deuterons (a_D = 1.6 Oe); E, spectrum of C reconstructed from one pair of equivalent deuterons (a_D = 1.6 Oe) and a pair of equivalent protons (a_H = 10.4 Oe).

sharp. However, the complete reversibility of the spectrum when the temperature is raised and lowered gives one confidence in assigning the seven-line spectrum to the conformationally 'frozen' ketyl. The fair agreement of the coupling constants 14.20 and 6.90 Oe with those of the 4-*tert*-butyl analogue is gratifying and confirms our previous prediction that distortion of the chair in the latter molecule is not serious (1).

Introduction of a ring substituent might be expected to slow down the rate of interconversion to the point where some temperature dependence could be observed at moderate temperatures. The e.p.r. spectra of the 3-methyl- and 4-methyl-cyclohexyl ketyls reported previously, while being well resolved, had lines appreciably broader than those of the unsubstituted ketyl, indicating some uncertainty broadening. Raising the temperature moderately (+60°) resulted in well-resolved spectra with accurate intensity distribution (Fig. 2A), whereas at temperatures of −35° extensive uncertainty broadening occurred.

The spectra retained their appearance up to +85°, a temperature approaching the boiling point of the solvent. This is consistent with our previous interpretation that inversion is rapid but that the equilibrium population favors the conformer which places the CH_3 group equatorial, so that complete averaging of the hyperfine couplings does not take place.

The increased resolution thus obtained allowed a more accurate determination of the coupling constants for these ketyls.

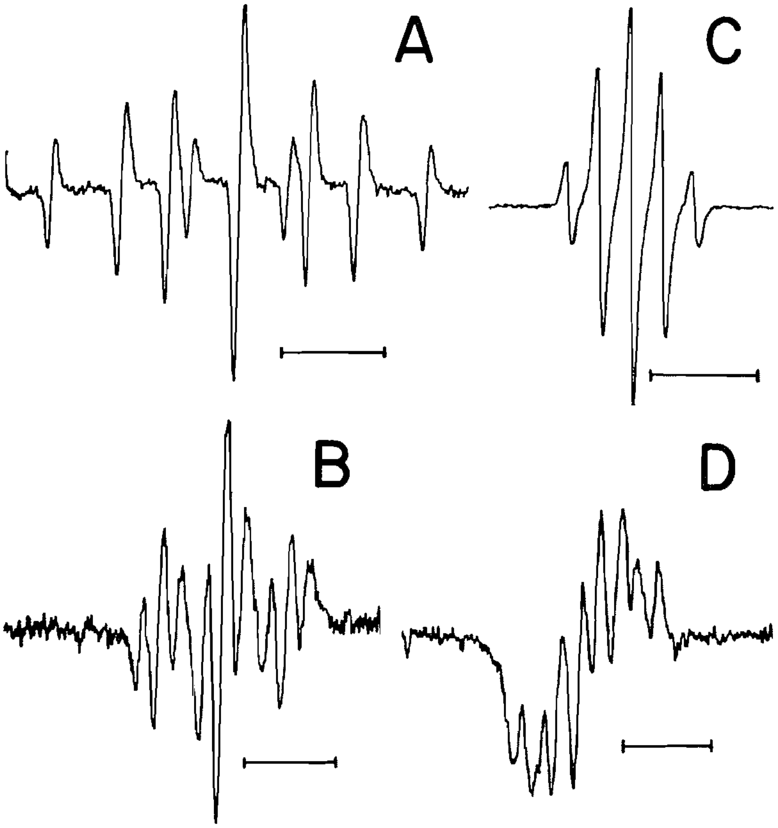


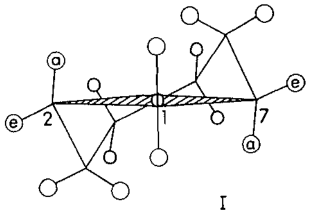
FIG. 2. First derivative e.p.r. spectra in 1,2-dimethoxyethane. LEGEND: A, 4-methylcyclohexyl ketyl at +61°; B, cycloheptyl ketyl at +72°; C, cyclooctyl ketyl at +24°; D, cyclooctyl ketyl at −35°. The bar in each case represents 10 Oe.

Care was taken to use excess potassium in the preparation of the samples to effect complete conversion of the ketone into the ketyl, so as to prevent broadening of the lines resulting from the electron exchange between ketyl and ketone (10). This more pronounced temperature dependence of the e.p.r. spectra of the substituted cyclohexyl ketyls indicates an appreciably larger energy barrier to inversion than exists in cyclohexyl ketyl itself.

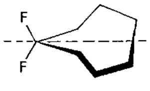
Seven-Membered Ring

Cycloheptyl ketyl gives a well-resolved spectrum consisting of 1:2:1 triplets of 1:2:1 triplets at room temperature with a_H = 7.02 and 2.08 Oe (Fig. 2B). This shows that the conformation of the radical ion is 'frozen' with respect to the difference in the hyperfine frequencies between the two conformers and indicates a lower frequency of conformational inversion than that which obtains in analogues having six-membered rings. The shape of the spectrum is unaltered when the temperature is lowered to −40°, showing that a conformational equilibration between only two forms is involved (see later discussion on 10- and 12-membered rings). The spectrum is unchanged up to +86°, at which temperature decomposition appears to take place. Clearly, the cycloheptyl ketyl interconverts between two conformational forms which have a plane of symmetry through the C—O bond axis at a rate much slower than that corresponding to the frequency difference of the two couplings (approximately 6×10^7 s^{-1}) up to a temperature of +86°.

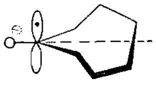
The most detailed calculation of the conformational energies of cycloheptane yet reported (3) predicts the 'chair' form to be more stable than the 'boat' form. (These conformers are analogues to the cyclohexane forms.) A particular arrangement of the cycloheptane chair, the 'twist-chair' (I), was considerably preferred over other alternatives.



I



II



III

The most comfortable positions for the carbonyl group in cycloheptanone have been predicted to be at C-1, C-2, or C-7 (11) of the 'twist-chair' form of cycloheptanone (I). Since placing the C—O$^{\ominus}$ group only at the C-1 position in I yields a molecular form with a plane of symmetry, we may speculate that III is the preferred conformation of the ketyl. Coupling from two pairs of equivalent protons at the C-2 and C-7 positions would be expected to give rise to couplings of the order of those observed, since the dihedral angles are substantially different. It is interesting to note that recent nuclear magnetic resonance studies (12) of 1,1-difluorocycloheptane (II) show that this molecule interconverts between two 'twist-chair' conformations which have a similar plane of symmetry through the C-1 position.

Eight-Membered Rings

In rings of more than seven carbons transannular interactions become increasingly important in conformational considerations until one reaches rings which are large enough to approximate open chain compounds. At room temperature the spectrum of cyclooctyl ketyl consists of five lines (1:4:6:4:1; $a_{\mathrm{H}} = 3.45$ Oe) clearly arising from four equivalent protons (Fig. 2C). This form of the spectrum is retained up to a temperature of +88°. At temperatures below +14° an additional fine structure makes its appearance until, at −35°, eight clearly resolved lines with an intensity pattern close to 1:1:3:3:3:3:1:1, $a_{\mathrm{H}_1} = 4.47$, $a_{\mathrm{H}_2} = 2.35$ Oe, are observed (Fig. 2D). This spectrum arises from coupling of the unpaired electron to *three* equivalent protons and a single proton, and represents a 'freezing out' of the conformation, i.e. rate $\ll 3 \times 10^7$ s^{-1}. These interesting observations show that at room temperature the eight-membered ketyl is inverting more rapidly than the seven-membered analogue, that as a result of its marked temperature dependence the energy barrier to inversion is greater than that for the six-membered ring, and that inversion takes place between two conformers which do *not* possess a plane of symmetry through the C—O bond.

These dramatic changes, with temperature, of e.p.r. spectra from common intermediates show that consideration of conformational phenomena should be made in the interpretation of all e.p.r. spectra of cyclic radical species.

Ten- and Twelve-Membered Rings

Larger rings would be expected to show greater conformational freedom than six- or seven-membered rings. Consequently, the simple assumption of interconversion between only two conformational forms is no longer valid. The existence of two or more equilibria between different conformational forms, which do not necessarily occur at the same rate, is therefore to be anticipated. Such considerations apply in the cases of the 10- and 12-membered rings.

The room temperature spectrum of cyclododecyl ketyl consists of three lines (a_H = 9.25 Oe), with the central line appreciably broader and less intense than the outer lines (Fig. 3C). Raising the temperature causes a marked sharpening of the central resonance until, at +61°, a 1:2:1 triplet is observed (Fig. 3B). At +83° further splitting of each line can be seen and the spectrum consists of a 1:2:1 triplet of 1:2:1 triplets (a_{H_1} = 9.02, a_{H_2} = 1.67 Oe) showing coupling to two pairs of equivalent protons (Fig. 3A). As the temperature is lowered below 0° the central line becomes increasingly broad, until at −35° four distinct lines are observed, corresponding to coupling to *two* non-equivalent protons, a_H = 11.0 and 7.3 Oe, respectively (Fig. 3D). It is noteworthy that the overall splitting remains constant at ~18.3 Oe and that these dramatic changes are completely reversible, confirming that we are dealing with conformational forms. We interpreted these observations in terms of simultaneous conformational equilibria.

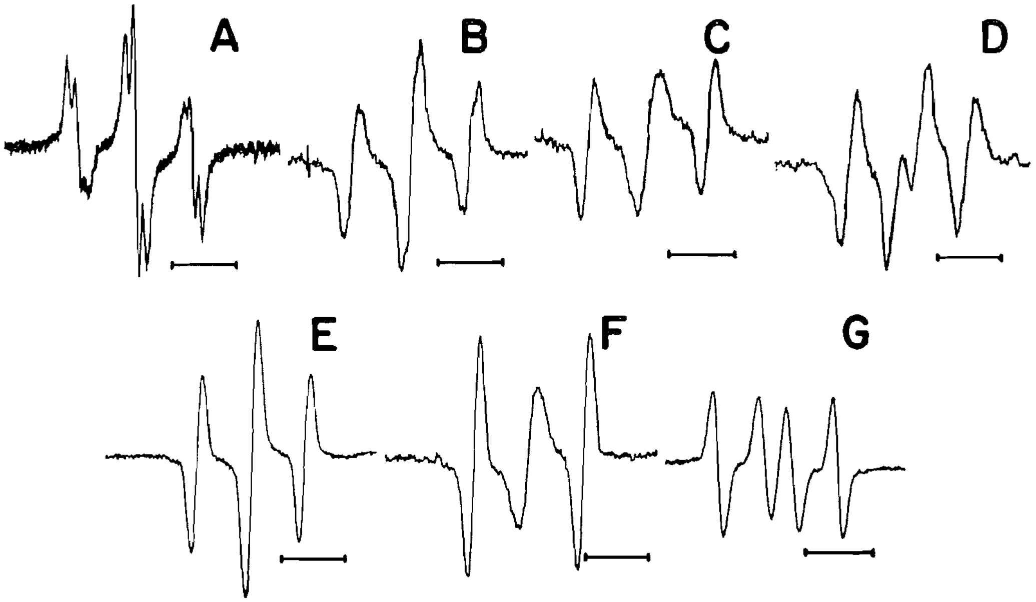


FIG. 3. First derivative e.p.r. spectra in 1,2-dimethoxyethane. LEGEND: A, cyclododecyl ketyl at +83°; B, cyclododecyl ketyl at +62°; C, cyclododecyl ketyl at +20°; D, cyclododecyl ketyl at −35°; E, cyclodecyl ketyl at +90°; F, cyclodecyl ketyl at +20°; G, cyclodecyl ketyl at −32°. The bar in each case represents 10 Oe.

At −35° interconversion occurs between pairs of conformers (which have no plane of symmetry through the C—O bond axis) at a rate much slower than that corresponding to the difference in the hyperfine frequencies. At this temperature in these equivalent conformations, coupling of 11.0 and 7.3 Oe occurs with two protons at the C-2 and (or) C-12 positions, the remaining two protons having couplings close to 0. At room temperature the interconversion between these conformers takes place at a rate now comparable with the hyperfine frequency difference, thus accounting for the broadening of the central line of the triplet. The appearance of the spectrum under these conditions (~+20°) can be explained by an argument similar to that used by Dixon and Norman (13) to interpret the e.p.r. spectra of radicals derived from hydrogen abstraction from dioxane, cyclohexanol, and cyclohexylamine at room temperature.

TABLE I

Nuclear spin orientations in conformer A		Total spin interaction in:			
x	y	Conformer A	Conformer B	Difference	Average
+	+	$x+y$	$x+y$	0	$x+y$
+	−	$x-y$	$-x+y$	$+2x-2y$	0
−	+	$-x+y$	$x-y$	$-2x+2y$	0
−	−	$-x-y$	$-x-y$	0	$-x-y$

Since two of the protons at the C-2 and C-12 positions have 0 hyperfine couplings under these conditions, one need not consider their spin orientations in this discussion. x and y represent the positions adopted by the remaining (coupled) protons, analogous to axial and equatorial protons in cyclohexane. If an x proton changes places with a y proton of different spin in the conformational equilibria, a change in total nuclear spin interaction will result. Table I shows the difference and average spin interactions which result from the equilibration. The 'difference' column predicts that the two outer lines are not subject to change and therefore remain sharp, whereas there are two ways in which the central resonance will be changed, so that a broadened line equal to twice the intensity of the flanking lines is predicted. Examination of Fig. 3C shows that these predictions are confirmed.

As the temperature is raised to $\sim+62°$, interconversion is sufficiently rapid to produce an accurate 1:2:1 triplet ($a_H = 9.25$ Oe), indicating complete averaging of the two coupling constants 11.0 and 7.30 Oe. At this temperature the individual lines of the triplet are still broad enough to prevent resolution of the additional hyperfine splitting observed at +83°, thus revealing the presence of another conformational equilibration. At +62° this latter equilibration clearly takes place at a rate comparable with the hyperfine frequency difference, but at +83° is sufficiently rapid for clear resolution of the two hyperfine couplings of 9.02 and 1.67 Oe from two pairs of protons at the C-2 and C-12 positions in a conformer of cyclododecyl ketyl which possesses a plane of symmetry through the C—O bond axis. This latter conformational equilibrium does not make a significant contribution at −35°, as shown by the fact that couplings of 9.02 and 1.67 Oe are not involved at this temperature. This type of 'locking out' of a particular conformational equilibrium at low temperatures for energetic reasons has been postulated to account for the temperature variation of the nuclear magnetic resonance spectra of fluorinated cyclooctanes (12).

The spectrum at +87° resembles that of cycloheptyl ketyl, and presumably at a still higher temperature (provided the radical did not decompose) complete averaging of the couplings of the four equivalent protons would produce a 1:4:6:4:1 spectrum. In practice, the radical begins to disappear at $\sim+98°$.

Cyclodecyl ketyl exhibits similar behavior (cf. Fig. 3). The room temperature spectrum consists of three lines spacing 8.52 Oe, with the central line much broader and less intense than the outer lines (Fig. 3F). At lower temperatures the broadening of the central line increases until at −32° four lines (1:1:1:1; $a_{H_1} = 10.77$, $a_{H_2} = 6.50$ Oe) are observed, arising from coupling to *two* non-equivalent protons (Fig. 3G). As the temperature is raised above +20° the central line is seen to sharpen, until at +61° an accurate 1:2:1 triplet is obtained (a_H = 8.52 Oe) consistent with the rapid conformational averaging of the two couplings observed at lower temperatures. The lines are still noticeably broad, however, up to +89°, at which temperature the radical is unstable (Fig. 3E). Consequently, further splitting, which was anticipated in view of the results obtained with cyclododecanone, could not be obtained.

These phenomena can be explained in a similar way in terms of the existence of two or more simultaneous conformational equilibria.

Angular Dependence of Hyperfine Couplings in Medium-Sized Ketyls

The coupling of protons attached to a carbon atom adjacent to a carbon bearing a free electron has been predicted (2) to satisfy an equation of the type

$$a_H = B\rho \cos^2 \theta, \tag{1}$$

where θ is the dihedral angle between the H—C_α—C_π and the C_α—C_π—$2p_\pi$ orbital planes, and ρ is the spin density on C_π.

Refinements of eq. [1] have been attempted by including a second parameter (13–15)

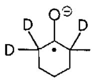
$$a_H = B_0 + B\rho \cos^2 \theta. \tag{2}$$

We derived (1) an equation of the form shown in eq. [2] which satisfactorily interpreted the observed couplings and conformational averaging for six-membered rings. It was found, not unexpectedly, that the derived equation could not be applied indiscriminately to different ring systems, because of substantial differences in unpaired spin density at the ketyl carbon in different rings.

In the discussion of the geometry of the wide range of ring sizes examined here it is preferable to use the simpler original McConnell equation because of uncertainty in the magnitude and signs (15) of the parameters required by eq. [2]. This approach, requiring the minimum of assumptions, has been employed recently in a discussion of the geometry of alicyclic semiquinones (16).

A value of B = 58.5 Oe derived from the $CH_3CH_2\cdot$ radical is used, and substitution in two equations of the type shown in eq. [1] for the two observed couplings (related by $\theta_{\text{equat. H}} = \theta_{\text{axial H}} + 120°$ for tetrahedral alpha carbon) allows derivation of the values for the angles and spin density shown in Table II.

The solution of equations of the type shown in eq. [2] lead to two values of $B\rho$ and of θ (except where $\cos^2 \theta_{\text{equat. H}} = 0$). In accordance with previous practice (16), unrealistic solutions ($B\rho > 58.5/2$) have not been listed.



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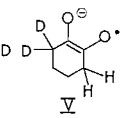
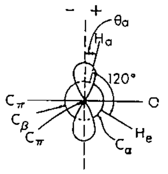


V



VI

The relationship of the dihedral angles considered is illustrated in VI. This type of analysis could not be carried out on the cyclodecyl ketyl at −35°, or the cyclododecyl ketyl at −32°, since coupling from only two protons was observed in both these cases. Therefore it is impossible to decide if these couplings arise from protons on the same carbon or not, and the relationship $\theta_{\text{equat. H}} = \theta_{\text{axial H}} + 120°$ cannot be applied in these cases.

TABLE II

Conformation of cycloalkyl ketyls*

Ketyl radical anion	Temp. (°C)	Hyperfine coupling ($a_{\text{axial H}}$ (Oe))†							
		Axial	Equatorial	$\theta_{\text{axial H}}$	$B\rho$	ρ‡	$\theta_{\text{axial H}}$§	$B\rho$§	ρ§
Cyclohexyl	+20	10.40 (4)		+34°	15.0	0.25	(+43°)	13.8	0.24
	−96‖	14.20 (2)	6.90 (2)	+13°	15.0	0.25			
4-Methylcyclohexyl	+60	13.20 (2)	7.60 (2)	+17°	14.4	0.25			
3-Methylcyclohexyl	+58	13.20 (2)	7.60 (2)	+17°	14.4	0.25			
Cycloheptyl	+51	7.02 (2)	2.08 (2)	+3° or −50°	7.04 or 17.2	0.12 or 0.29	+3° or −50°	6.7 or 16.7	0.11 or 0.29
Cyclooctyl	+26	3.45 (4)		+31° or −60°	4.77 or 13.4	0.08 or 0.23	+30° or −60°	4.4 or 13.3	0.08 or 0.23
	−35	4.47 (3)	2.35 (1)	+15° or −55°	4.77 or 13.4	0.08 or 0.23			
Cyclodecyl	−35	10.78 (1) 6.30 (1)		¶					
	+84	8.52 (2)	~0 (2)	−30°	11.4	0.19	−30°	11.1	0.19
Cyclododecyl	−32	11.02 (1) 7.30 (4)		¶					
	+61	9.27 (2)					−30°	10.5	0.18
	+87	9.02 (2)	1.63 (2)	+5° or −47°	9.11 or 19.3	0.16 or 0.33			

*Except where otherwise stated, the solvent was 1,2-dimethoxyethane.
†The number of equivalent protons is shown in parentheses in each case.
‡B = 58.5 Oe.
§Values for the cycloalkanedione radical anions (see ref. 16) in dimethylsulfoxide (80%) – *tert*-butyl alcohol (20%) at room temperature.
‖Solvent was dimethoxymethane.
¶Angles cannot be assigned; see text.

However, since further resolution is obtained at higher temperatures, as has been noted, values for dihedral angles and parameters $B\rho$ and ρ could be obtained.

The results obtained are in good general agreement with the studies reported on the cycloalkyldione radical anions (16), which were, however, restricted to observations at room temperature. The close parallel with these latter results, also tabulated in Table II for comparison, necessitates a proof of the structure of our cycloalkyl ketyls to eliminate the possibility that our method of generation inadvertently has produced the cycloalkyldione radical anions. 2,2,6,6-Tetradeuteriocyclohexanone was prepared and treated with potassium in 1,2-dimethoxyethane, and the e.p.r. spectrum is shown in Fig. 1C. If oxidation to the radical anion V accounted for the signal, one would anticipate a nine-line spectrum similar to that shown in Fig. 1E. The much closer resemblance to that predicted for IV in Fig. 1D confirms the structure of the ketyls.

Some exchange of the deuterium is to be anticipated under the strongly basic conditions used to generate the ketyl, thereby accounting for the weak outer lines caused by traces of partially exchanged ketyl. The reduction in hyperfine coupling on deuteration equals the theoretically predicted value of 6.5.

In view of the complexity of the possible conformational forms of the medium-sized ring (3–5), it is idle to speculate about the actual shapes at this stage. An examination of the behavior of suitably substituted ketyls could, however, be expected to yield more precise information about ring geometry. Work along these lines is continuing.

In principle, it is possible to deduce conformational energy barriers from a consideration of line broadening of the e.p.r. spectra of the ketyls at different temperatures. This is very similar to problems encountered in the theory of nuclear resonance line widths when the environment of the nucleus is undergoing rapid fluctuations which change the resonance frequency. Such treatments based on the Bloch equations are commonly used (17–20). The same principles apply to e.p.r. line-width phenomena, and a theory accounting for the alternation in line widths as a result of rapid isomerization effects in the e.p.r. of radicals has been described (9). It is hoped that a computer program based on this theory will allow the derivation of energy barrier values by a comparison of observed and predicted e.p.r. line shapes.

EXPERIMENTAL

Materials

All liquid ketones, which were commercially available, were fractionated and gave single peaks on gas–liquid chromatographic analysis. The solvents used, 1,2-dimethoxyethane, dimethoxymethane, and bis-(2-methoxyethyl) ether, were refluxed over sodium metal for 12 h and fractionated.

The procedures used for the generation of the ketyls, and the recording and calibration of their e.p.r. spectra, have been described previously (1).

Temperature Control and Measurements

The temperature of the samples in the V-4532 dual cavity was controlled by passing cold dry nitrogen gas through the temperature variable unit of the Varian V-2503 spectrometer. The temperature inside the sample cavity was measured with a copper constantan thermocouple with the reference junction cooled to 0 °C. Temperature readings are estimated to have an accuracy of ±2°.

2,2,6,6-Tetradeuteriocyclohexanone

A solution of 5.06 g of cyclohexanone and 0.333 g of anhydrous potassium carbonate in 7 ml of 99.7% deuterium oxide and 10 ml of sodium-dried dioxane was refluxed for 12 h, cooled, and extracted with light petroleum (b.p. 30–60°). The extract was evaporated to a small volume *in vacuo* and the residual oil subjected to a second similar exchange. The 2,2,6,6-tetradeuteriocyclohexanone was isolated by extraction with light petroleum and fractionation *in vacuo* (b.p. 55° at 20 mm), yield 4.3 g. The nuclear magnetic resonance spectrum of the product showed removal of a band at 7.5 to 7.9 τ characteristic of the four protons alpha to the carbonyl group, with the required reduction in intensity.

The corresponding ketyl was generated with clean potassium and freshly dried, distilled 1,2-dimethoxyethane, and the e.p.r. spectrum was examined as rapidly as possible to minimize exchange.

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