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ACTIVATION ENERGY OF RING INVERSION IN 9,10-DISUBSTITUTED CIS-DECALINS

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The activation energy of ring inversion (E), may be measured by the nmr technique, provided that the relationship $10^{-2} \leq \tau\delta$ or $\tau J \leq 10$, approximately obtains.[1,2] The mean lifetime of a conformer is τ. δ or J are the appropriate chemical shift or spin-spin interaction, respectively.

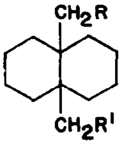
The value of δ in cis-decalin[3] is presumably too small to permit E to be measured but this problem was overcome by Gerig and Roberts[4] by introduction of fluorine substituents into the decalin system, thus achieving a considerable increase in δ. The values of E they obtained are about 14 kcal/mole for angularly unsubstituted cis-decalins and about 10 kcal/mole for cis-decalins angularly substituted either in the 9 or in the 10 position.

We report herein measurements of E in cis-decalins by observing the nmr spectra of the methylene hydrogens of CH_2R substituents (R=Br, CN, CO_2CH_3) in the 9 and 10 positions.[5] At low temperature the CH_2 hydrogens exhibit an AB type spectrum. As the temperature is raised the AB spectrum collapses into a singlet whilst showing the characteristic intramolecular AB exchange pattern.[6,7] The rates of inversion ($1/\tau$) were evaluated by comparing the experimental line-shapes to those calculated by using Alexander's equations.[6] At very high inversion rates the approximation formula for fast exchange was used.[1] It was assumed that the value of δ or J does not vary with temperature. Measurements at low temperature (down to $-20^{\circ}C$) justify this assumption.

The results are summarized in the Table.

TABLE

Nmr and Kinetic Parameters for 9,10-disubstituted *cis*-decalins [a)]



Compound [b)]	δ_{AB} [c)] (ppm)	J_{AB} [c)] (cps)	E [d)] (kcal/mole)	$\log_{10}K_0$ [d)]	$\Delta S^{\ddagger}$ [e)] (eu)	$\Delta G^{\ddagger}$ [e)] (kcal/mole)	Temp. Range (°C)
$R=R'=CO_2CH_3$	0.835	12.9	20.6±0.6	15.8±0.6	13.3	15.9	20–80
R=R'=Br	0.576	10.0	18.7±1.2	15.5±0.9	11.0	14.7	0–60
R=Br	0.670	10.1	18.0±1.4	14.9±1.0	7.9	15.0	0–60
R'=CN	0.502	16.7	18.5±0.7	15.2±0.4	9.3	15.1	0–60

a) All measurements were performed on a Varian A60 Spectrometer equipped with V-6040 temperature control. b) 10% solution in $CDCl_3$. c) Accuracy in δ is ± 0.006 ppm and in J is ± 0.2 cps. d) From Arrhenius plot. e) Calculated for 30°C.

Gerig and Roberts[4] have estimated that the barrier for inversion, using potential energy calculations and assuming a particular model for transition path and equilibrium, should be about 17 kcal/mole. Our results are in good agreement with their estimate and model. The changes in $\Delta S^{\ddagger}$ in going from the unsubstituted,[4] through the angularly (9- or 10-) monosubstituted,[4] to the 9,10-disubstituted *cis*-decalins, are worth noting. The value of $\Delta S^{\ddagger}$ changes sign and is negative in the angularly mono-substituted compounds. This may be understood in terms of the relative increase in symmetry of the angularly monosubstituted (low-symmetry) compounds whilst traversing their more symmetrical transition state. In the angularly unsubstituted or disubstituted compounds, the formation of a transition state appears to involve decrease in symmetry.

It is clear that we have not measured simply the hindered rotation of the angular substituents. Had there been hindered rotation of the CH_2R groups we would have expected to obtain superposition of an AB spectrum and a singlet. That the observed collapse of the AB spectrum be attributed merely to librations of the CH_2R groups is ruled out because the energy involved in such a process is much lower[8] than that found; because one would expect different energies, e.g. for the CH_2Br and CH_2CN groups (contrary to the results), and because complex changes with temperature (not reported herein) were concurrently observed in the resonances of the ring protons.

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