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THE BARRIER FOR THE INTERCONVERSION OF CIS-DECALIN

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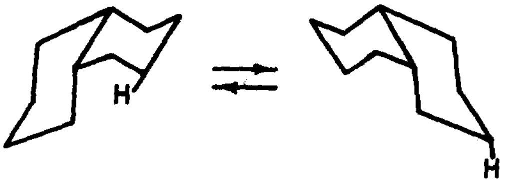
cis-Decalin molecules are expected to exist predominantly in chair-chair forms and to rapidly interconvert to their mirror image chair-chair counterparts (1,2). Nevertheless, conflicting reports have appeared in the literature regarding this interconversion as evidenced by changes in the NMR spectrum with changes in temperature.

Two groups (3,4) have reported no change occurs in the NMR spectrum when a sample of the material is cooled from room temperature to -100°, but two other groups (5,6) have claimed a transition is observed at about -20°. A transition in this region would be in accord with the observation that the NMR spectrum of cyclohexane (7) undergoes major changes below -66° since the barrier is expected to be smaller for cyclohexane than for the cis-decalin interconversion. The temperature dependence of the NMR spectrum of the deuterated cis-decalin has been examined, the interconversion confirmed, and the barrier measured.

An appropriate deuterated cis-decalin was prepared by the following reaction sequence: Perdeuterionaphthalene → 2-acetylperdeuterionaphthalene → β-perdeuterionaphthoic acid → cis-perdeuterio decalin-2-carboxylic acid (reduction with D_2 and

Rh/Al_2O_3 carried out in CF_3CO_2D) → 2-bromo-_cis_-perdeuterio perdeuterio decalin → 2-protio-_cis_-deuteriodecalin (I). This

STRUCTURE I



material was purified by preparative VPC. Unfortunately, the last step, carried out with lithium aluminum hydride, is not stereospecific. Even when utilizing the β-bromo isomer, a mixture of the α- and β-protio isomers was obtained. This mixture of isomers was therefore used in the NMR spectral studies.

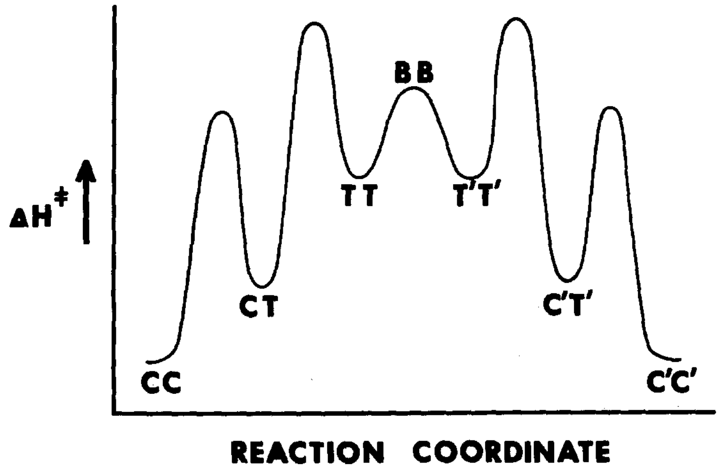
The room temperature NMR spectrum of a mixture of the α- and β-isomers of I consists of two peaks which are broadened somewhat by spin-spin coupling with the deuterium in the molecule (8). With heteronuclear spin decoupling the peaks become sharp (9), and the data reported here were obtained utilizing this technique.

Upon cooling the sample (20% by volume in CS_2 with TMS as an internal standard), the peak at δ 1.24 separates into two signals at δ 1.14 and 1.30 and the peak at δ 1.42 separates into separate resonances at δ 1.25 and 1.63 in the temperature interval -11 to -24°. However, the changes in the spectra with temperature are complicated by the proximity of the resonances and presence of trace amounts of hydrogen at the various positions. As a result, a very precise barrier was not obtained from the data. An approximate value is obtained by calculating maximum and minimum values at the temperature extremes. Rate constants and energy barriers for the chair-chair to chair'-chair' interconversion were calculated using the interconversion scheme given in Fig. 1, assuming that the twist-twist to twist'-twist' forms interconvert rapidly and have a 0.5 probability of becoming product (7). At -11° no separation for the signal which gives a maximum separation of 23 cps. has taken

FIG. 1

Energy Profile for the cis-Decalin Interconversion.

(C = chair, T = twist, B = boat) In cis-decalin, gauche-butane interactions are relieved in going from the chair-chair to the chair-twist form and therefore the C-C → C-T transition is expected to be about 1.5 kcal/mole lower than for the C → T transition for cyclohexane.



place, but assuming that the separation is half-complete, a minimum rate constant at this temperature of 86 sec^{-1} and a maximum $\Delta F^{\ddagger}$ = 13.0 kcal/mole are obtained. Similarly, at -24° the peaks are largely separated for the signal which separates a maximum of 10 cps, but assuming that the separation is only half-complete, a maximum rate constant of 38 sec^{-1} at this temperature and a minimum barrier for the process of $\Delta F^{\ddagger} = 12.7$ kcal/mole are obtained. Thus (for small $\Delta S^{\ddagger}$) an experimental value of $\Delta F^{\ddagger} = 12.85 \pm 0.2$ kcal/mole at -18° is obtained, assuming an intermediate occurs having a 0.5 probability of becoming product.* Utilizing the same theoretical considerations as in the case of cyclohexane (7) the entropy of activation can very likely be estimated much more accurately than it can be measured.** For cis-decalin, assuming chair-twist to twist-twist entirely rate-controlling, there are three different paths which appear to be of comparable energy for a chair-twist form to convert to the twist-twist form, giving a total of six pathways for the chair-chair to the twist-twist transformation (Fig. 2). If all of these pathways are of equal energy, the theoretical entropy for this reaction is R ln 6 or 3.6 eu. At the other extreme, if one of the three

* A less likely possibility is that the maximum barrier occurs at the center of the reaction coordinate, for example, if the twist-twist to twist'-twist' conversion is rate controlling (boat-boat as the transition state) the value of $\Delta F^{\ddagger}$ would be 13.2 kcal/mole. Also, from the same considerations as are given in the text, the number of reaction paths would be one and hence $\Delta S^{\ddagger} \sim 0$ and $\Delta H^{\ddagger} \sim \Delta F^{\ddagger} = 13.2$ kcal/mole.

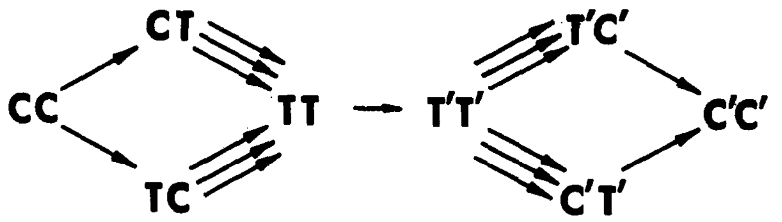
** The correction applied to our data in ref. 7 for cyclohexane by A. Allerhand, Fu-Ming Chen, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3440 (1965), is invalid. Furthermore, in ref. 7 it is explicitly stated that our results were obtained in a different manner than that reported by these workers and that a calculation of the type done by them would not be valid for our data.

The barrier for cyclohexane has been redetermined several times in our group, and in our opinion the best values for cyclohexane (-65.5°) are $\Delta F^{\ddagger} = 10.3$ kcal/mole, $\Delta S^{\ddagger} = 3.6$ eu (Six reaction paths, the transition state a perfect half-chair. Previously, in ref. 7 a preference for twelve reaction paths to form a twisted half-chair transition state was given.) and $\Delta H^{\ddagger} = \Delta F^{\ddagger} - T\Delta S^{\ddagger} = 11.1$ kcal/mole, in the solvent system used in ref. 7.

paths for the chair-twist to twist-twist conversion is of much lower energy than the other two, there would be only two main pathways for the transformation and $\Delta S^{\ddagger}$ would be R ln 2 (1.4 eu). If the paths are of similar but not equal energy the

FIG. 2

Intermediates for the Chair-Chair to Chair'-Chair'



entropy will have a value intermediate between that of the two extremes. Therefore, for deuterated cis-decalin (chair-twist to twist-twist rate controlling) the experimental $\Delta F^{\ddagger}$ is 12.8 ± 0.2 kcal/mole, the theoretical $\Delta S^{\ddagger}$ = 2.5 ± 1.1 eu, and $\Delta H^{\ddagger}$ = 13.4 - 0.5 kcal/mole (calculated from the experimental $\Delta F^{\ddagger}$ and the theoretical $\Delta S^{\ddagger}$).

In our work with the undeuterated cis-decalin, it was estimated that the center of the shift occurs at -15° to -20° and the major movement is on the order of 15 to 25 cps (6). Thus, the barriers for the deuterated and nondeuterated cis-decalins are similar.

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8. Other very small C-H resonances due to traces of protium at other sites appear in the spectrum.

9. Spectra were obtained on a Varian HR-60 NMR spectrometer. Deuterium decoupling was accomplished by means of a SD-60 spin decoupler manufactured by NMR Specialities Company, New Kensington, Pennsylvania.