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THE RELATIVE STABILITIES OF *cis-trans* ISOMERS OF BICYCLIC RING SYSTEMS WITH ANGULAR METHYL GROUPS. II

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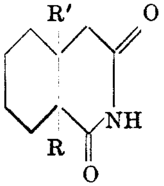
Received March 9, 1955

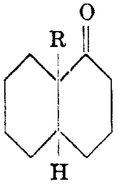
In a previous paper (1) it was demonstrated that decahydroisoquinoline-1,3-dione (hexahydrohomophthalimide), (I), exists predominantly in the *trans*-form when equilibrated over a palladium catalyst at 190°. When an angular methyl group was introduced in the 9 position (II), or in the 10 position (III), the point of equilibrium was shifted to favor the *cis*-form.



I, R = H, R′ = H
II, R = CH_3, R′ = H
III, R = H, R′ = CH_3

These latter results are contrary to the generalization emerging from the work of Hückel, Linstead, and others which holds that in an equilibrium system containing two fused six-membered rings the *trans*-form will be favored. An explanation for the role of the angular methyl group in determining the relative stabilities of *cis-trans*-isomers was presented, and it was predicted that the same effect would occur in a purely carbocyclic system. The present work confirms that prediction.

Hückel and Brinkmann (2) established that α-decalone (IV) was easily isomerized from the *cis*- to the *trans*-form. They estimated the equilibrium mixture to contain about 95% *trans*-isomer at the boiling point, 227°. We have now succeeded in isomerizing both *cis*- and *trans*-9-methyldecalone-1 (V) over palladium at 250° and find that in contrast to the unsubstituted compound, the point of equilibrium lies at about 60% for the *cis*- and 40% for the *trans*-form.



IV, R = H
V, R = CH_3

METHOD

Pure *cis*-9-methyldecalone-1 (V) was prepared by the method of Bachmann and Dreiding (3). We are indebted to Dr. W. S. Johnson for his courtesy in supplying the pure *trans*-isomer.

Since the angular methyl group replaces the active bridgehead hydrogen of α-decalone, the isomerization method of Hückel and Brinkmann could not be used. Instead, isomerization was accomplished by heating 50–75 mg. of the pure isomer with an excess of 5% palladium catalyst on charcoal (Baker & Co.) in the small stainless steel bomb previously described (1). The equilibrated mixture was dissolved in chloroform, the catalyst filtered off, and the solvent evaporated in a stream of dry air. To a weighed quantity of the residue (*ca.* 25 mg.) there was added a calculated volume of reagent chloroform to make a solution containing approximately 25 mg. of isomerized mixture/ml. of chloroform. This solution was then examined in a Baird Associates, double-beam infrared spectrometer with reagent-grade chloroform in the reference beam. The resulting spectra were then compared with the spectra of a series of standards which contained the same over-all concentration but with varying ratios of *cis-* to *trans*-isomer.

Results

The infrared spectra of pure *cis-* and pure *trans*-9-methyldecalone-1 are very similar, differing appreciably at only three frequencies. The *cis*-isomer has a unique band at 10.1 μ while the *trans*-form has a weak band at 9.6 μ and a fairly pronounced band at 10.7 μ. In the series of standards, the 10.1 μ and the 10.7 μ bands showed a regular variation of absorbance with concentration and were therefore selected for the quantitative estimation of the relative isomeric concentrations.

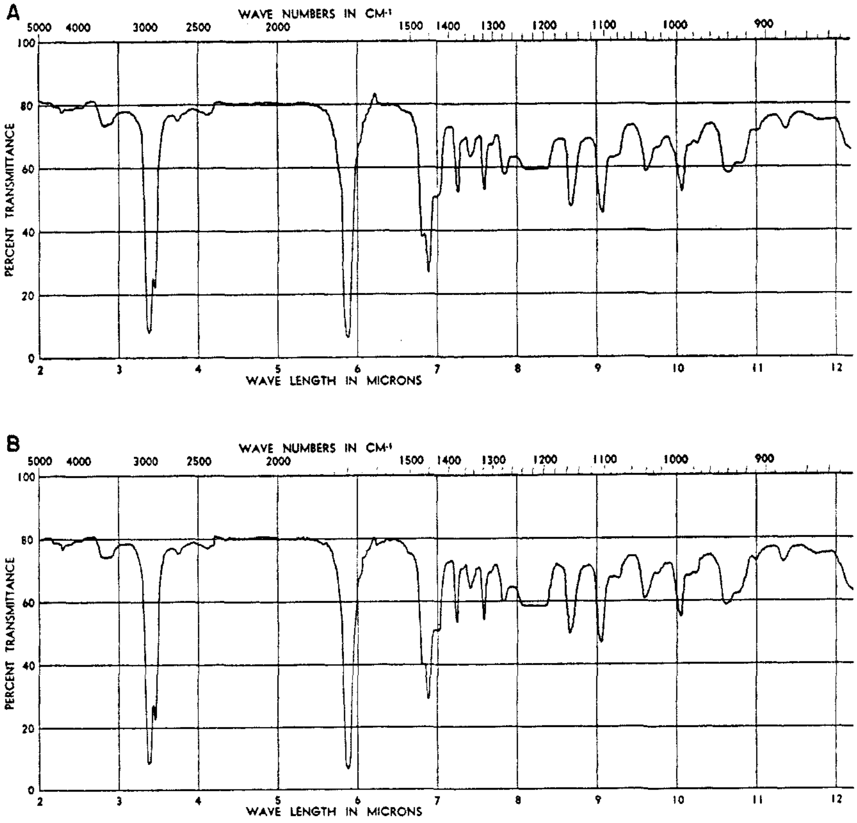


Figure 1. Infrared spectra of mixtures of cis- and trans-9-methyldecalone-1.

A. Standard containing 60% cis- and 40% trans-isomer.

B. Product of reaction at 250° for four hours starting with the pure cis-isomer.

TABLE I

INFRARED ABSORPTIONS OF STANDARDS AND ISOMERIZED PRODUCTS OF 9-METHYLDECALONE-1

Concentration of Standards (mg./ml. $CHCl_3$)		% Transmittance		Concentration of products from plot of conc. vs log 1/T (mg./ml. $CHCl_3$)		Relative Concentration (%)	
cis	*trans*	10.1 μ	10.7 μ	*cis*	*trans*	*cis*	*trans*
15	10	52.3	58.2	—	—	60	40
12.5	12.5	55.0	56.2	—	—	50	50
10	15	58.7	54.1	—	—	40	60
Product of *cis* isomerization		55.1	59.3	12.6	8.7	59	41
Product of *trans* isomerization		54.9	59.2	12.8	8.8	59	41

Initial isomerizations made at 300° showed excessive decomposition (broad diffuse bands in the infrared spectra). The runs made at 250° were more successful, showing no appreciable decomposition. Several four-hour runs at this temperature gave almost identical spectra whether starting with the *cis*- or the *trans*-ketone. In turn these spectra were practically identical to the spectrum of the standard containing 60% *cis*- and 40% *trans*-isomer (Figure 1).

Working plots of concentration *vs.* log 1/T were made from the spectra of the standards. From these plots the concentrations of the *cis*- and *trans*-isomers present in the equilibrated mixtures were obtained. These data are shown in Table I. Whether the starting material is the pure *cis*- or pure *trans*-ketone the equilibrated product is seen to contain approximately 59% *cis*- and 41% *trans*-isomer.

CONCLUSIONS

This work demonstrates that the introduction of a methyl group into the angular position of decalone-1 shifts the ratio of isomers present at equilibrium from about 95% of the *trans*-form for decalone-1 to only 40% for the 9-methyl homolog. Since these results are very similar to those obtained in comparable heterocyclic nitrogen compounds (1) and heterocyclic oxygen compounds (5), it may be concluded that this is a general effect of the angular methyl group in saturated bicyclic systems. This also constitutes evidence for the belief that $=CH_2$, $=NH$, and $=O$ are sterically very similar when incorporated into cyclic systems, a conclusion also reached recently by Brown, Brewster, and Schechter in a totally different study (6).

Although the *cis*-epimer was favored in this study, the equilibrium mixture contains fairly close to equal amounts of the *cis*- and *trans*-forms. These results lend support to the contention that Hibbit and Linstead (4) did not isomerize *cis*-9-methyldecalin to the *trans*-form as claimed. Our earlier suggestion that the product they obtained was probably the *cis*- rather than the *trans*-isomer they thought they had, must now be amended. It is more likely that a mixture of almost equal amounts of *cis*- and *trans*-isomers would be formed if 9-methyldecalin were equilibrated. This prediction still awaits experimental verification, however, since Dauben, Rogan, and Blanz (7) have recently shown that aluminum chloride, the only catalyst used by Hibbit and Linstead, effects a more deep-seated skeletal rearrangement.

It must be allowed that the compounds involved in this study differ from 9-methyldecalin in that they possess an oxygen attached to the No. 1 carbon rather than two hydrogens. The exact significance of this difference cannot be accurately estimated at the present time, but it is thought, on the basis of appearances of molecular models, to be relatively unimportant with respect to the relative stability of ring-fusion isomers.

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