intensity of the symmetrical absorption is equal to or stronger than the asymmetrical, while in the spectra of cyclohexane, polyethylene, and pentane the situation is reversed. The intensity of the symmetrical methylene stretching absorption seems to be related to the number of —CH_2O groups present in the molecule, as can be seen by comparing the spectra of tetrahydropyran, tetrahydrofuran, and 1,4-dioxane. However, in the more complex molecule, polypropylene glycol, this correlation cannot be applied.

The effect of ether oxygen on the methyl stretching vibration has been reported.[4,5] A similar effect appears to apply to the methylene group. It is believed that the C—H force constants are greater in the presence of the more electronegative oxygen, which causes the asymmetrical methylene stretching vibration to shift to higher frequencies. It may be concluded that a greater net dipole moment change occurs with the symmetrical methylene vibration than with the asymmetrical when oxygen of ether type is present and that, therefore, the intensity of the asymmetrical absorption band is enhanced.

All the samples were examined by Perkin-Elmer, Model 21 spectrophotometer with a calcium fluoride prism. Most of the samples were obtained from Eastman Kodak Co. and were used without further purification. Carbon tetrachloride was used as a solvent. The thickness of the cell was 0.2 mm.

(4) H. B. Henbest, G. D. Meakins, B. Nicholls, and A. A. Wagland, *J. Chem. Soc.*, 1462 (1957).

(5) F. Dalton, R. D. Mill, and G. D. Meakins, *ibid.*, 2927 (1960).

Quantitative Study of the Interconversion of Hydrindane Isomers by Aluminum Bromide

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Received August 13, 1962

In connection with investigations of aluminum halide isomerization of polycyclic hydrocarbons,[3] the development of quantitative techniques for studying the relative stabilities of isomers was desired.[4] The interconversion of *cis*- and *trans*- hydrindane was chosen as a model system, since the present study should complement nicely two recent investigations which employed different methods to obtain the same thermodynamic information. Allinger and Coke[5] equilibrated the two isomers at high temperatures by means of the hydrogenation–dehydrogenation action of a palladium-on-charcoal catalyst and studied the variation of the relative equilibrium concentrations with temperature. Browne and Rossini[6] determined the heats of combustion, isomerization, and formation of the pure isomers in both the liquid and gaseous states.

In the present investigation equilibration was carried out by aluminum bromide, which offers the advantage over aluminum chloride of being somewhat soluble in organic liquids. The catalyst, a powerful Lewis acid, effects equilibration by an ionic chain process[4]; abstraction of a hydride ion produces a carbonium ion which can react further by several paths, *e.g.*, fragmentation and rearrangement, in addition to reverting to one of the hydrindane isomers.[7] It was found that these undesired side reactions could be suppressed by the addition of small amounts of indane, which was more effective than benzene for this purpose.[4]

The relative equilibrium concentrations were determined at four different temperatures ranging from 251–320.3° K.[8] By gas chromatographic analysis identical compositions wereo btained approaching equilibrium from both the *cis* and *trans* sides. The results are shown in Table I.

TABLE I

EQUILIBRIUM COMPOSITION OF HYDRINDANE ISOMERS

T, °K.	K^a	% *trans*
251	1.926	65.8
277	1.728	63.3
300.0	1.586	61.3
320.3	1.482	59.7

[a] See ref. 8.

From these data a plot of ln K *vs.* $1/T$ was made and a straight line of best fit was calculated by the method of least squares; the slope of this line gave $-\Delta H/R$. The value of ln K at 298° from the graph was used to calculate $-\Delta F^{298}$ and $-\Delta S^{298}$ was estimated from the equation, $\Delta F = \Delta H - T\Delta S$. The thermodynamic values obtained are summarized in Table II, along with literature values.

TABLE II

THERMODYNAMIC VALUES FOR HYDRINDANE ISOMERIZATION

State	T, °K.	$-\Delta H$, kcal./mole	$-\Delta S$, e.u.	$-\Delta F$, kcal./mole	Ref.
Liquid	298	0.74 ± 0.52	1.68 ± 0.10	0.24 ± 0.52	6
Gas	298	1.04 [illegible] 0.53			6
Liquid (?)	552	1.07 ± 0.09	2.30 ± 0.10	[a]	5
Liquid	298	0.58 ± 0.05	1.00 ± 0.06	0.28 ± 0.06	This work

[a] Extrapolation of Allinger and Coke's data[5] to 298° gives ln K = 0.642; $-\Delta F$ (298°) = 0.38 kcal./mole.

Agreement between our results and those of Browne and Rossini[6] is very good; however, if the relative heat capacities of the hydrindane isomers can be considered nearly constant over the range from 552–298° K., there is a small but significant difference between our values and those of Allinger and Coke.[5] The data of the latter authors correspond closely to that

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[1] National Science Foundation Predoctoral Fellow, 1962–1963.

[2] Alfred P. Sloan Research Fellow.

[3] P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960); P. von R. Schleyer and R. D. Nicholas, *Tetrahedron Letters*, No. **9**, 305 (1961).

[4] For a review, see H. Pines and J. M. Mavity, "The Chemistry of Petroleum Hydrocarbons," Vol. 3, B. T. Brooks, *et al.*, eds., Reinhold Publishing Corp., New York, N. Y., 1955, chap. 39, pp. 9-58.

[5] N. L. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **82**, 2553 (1960).

[6] C. C. Browne and F. D. Rossini, *J. Phys. Chem.*, **64**, 927 (1960).

[7] N. D. Zelinsky and M. B. Turowa-Pollak, *Ber.*, **62**, 1658 (1929), reported the treatment of hydrindane (mostly *cis* isomer from hydrogenation) with aluminum bromide at steam-bath temperature. They claimed that the product was *trans*-hydrindane, but it is clear from the properties of the material they reported and from our experience with this reaction that fragmentation, disproportionation, etc., are the main reactions under these conditions, rather than isomerization.

[8] In keeping with the convention used previously[5,6] the isomerization is regarded to proceed from *cis*- to *trans*-hydrindane; K (equil.) = (*trans*/*cis*).

reported for the *gaseous* state at 298° K.[6] The large experimental error precludes any definite conclusion, but the data do suggest that despite a concerted and seemingly effective effort to maintain their samples in the liquid state, Allinger and Coke may have had an appreciable fraction of their samples in the gaseous state at the temperatures used. Perhaps the high pressures developed during the equilibrations, when the samples were heated well above their boiling points, can account for some of the difference.

As predicted in the literature,[5,6] *trans*-hydrindane is the more stable isomer at room temperature, due to a more favorable enthalpy. At higher temperatures (above 466° K.[5]) the *cis* form is more stable because of a more favorable entropy. The conformational implications of these facts have been considered in detail.[5,6,9]

Experimental

Preparation of the Hydrindanes.—One liter of commercial indene and 40 g. of 5% palladium on charcoal were placed in a 4-l. bomb. Hydrogen pressure of 1000–2000 p.s.i. and a temperature of 160° were maintained for 24 hr. Distillation of the crude product through a 100-cm. column filled with Podbielniak "Heli-Pak" packing gave 600 g. of material boiling at 159–166°. The remainder of the product was primarily indane (b.p. 177°).

The hydrindane mixture obtained from the hydrogenation product, containing approximately 70% *cis* isomer, was used for approaching the equilibria from the *cis*-rich side. *trans*-Rich material was made by equilibrating a 100-g. portion of the hydrogenation product mixture with 10 g. of aluminum bromide at room temperature overnight. Distillation of this product through the 100-cm. packed column gave 75 g. of material containing more than 80% *trans* isomer.

The pure isomers were prepared only in small quantities. Two careful distillations of 50 g. of the hydrogenation mixture through the 100-cm. packed column gave 3 g. of material boiling at 166° (755 mm.), which was shown by gas chromatographic analysis to be greater than 99.5% pure *cis* isomer. Two similar distillations of 50 g. of the mixture containing 70% *trans*-hydrindane gave 2 g. of material boiling at 159° (760 mm.). Gas chromatographic analysis showed that this material was better than 98% pure *trans*-hydrindane.

Equilibration.—Sample mixtures were prepared by stirring 15 ml. of either *cis*- or *trans*-rich hydrindane with freshly powdered aluminum bromide at room temperature for 5 min. Aliquots (2–3 ml.) of this aluminum bromide-saturated hydrindane solution were then pipetted into 5-ml. Pyrex ampoules and sealed. The samples were then placed in the desired temperature-controlled environment for the equilibration period, which ranged from 1 day at the higher temperatures to several weeks at the lower temperatures. The concentration of indane necessary to retard fragmentation and yet allow equilibration at a reasonable rate was a very critical factor in carrying out these equilibrations. This had to be determined by trial and error for each temperature, which ultimately required the preparation and analysis of approximately 200 samples. The concentrations of indane required varied from zero for the 251° K. sample to 6–7% for the 320° K. sample. Equilibrations at 251 and 277° K. were carried out in rooms closely regulated at those temperatures. Although fluctuations of 2° occurred, the equilibrations were so slow that the average temperatures can be used. At 300.0 and 320.3° K., the samples were immersed in oil baths regulated to ±0.05°. Individual samples were removed and analyzed regularly to follow the progress of each group of *cis*- or *trans*-rich samples toward equilibrium. This assured that the equilibrium was approached from both sides at each temperature. When an ampoule was opened, the sample was pipetted immediately into a test tube containing 10 ml. of cold water and mixed thoroughly to destroy the catalyst. The hydrindane layer was then pipetted off, dried with 0.5 g. of anhydrous potassium carbonate, and centrifuged.

Analysis.—The gas chromatographic analyses were carried out on a Perkin–Elmer Vapor Fractometer using a 300-ft. Golay "R" column at a temperature of 100° and helium pressure of 20 p.s.i. The separation was complete, and the retention times were 8.4 min. (*trans*) and 9.3 min. (*cis*). The product of the retention time and the peak height was taken as the measure of each peak. The number thus obtained for the *trans* peak was then divided by the corresponding number for the *cis* peak to get the ratio of *trans*- to *cis*-hydrindane. Two standard samples were carefully prepared and analyzed ten times each. These data showed that a correction factor of 0.942 for the *trans*- to *cis*-hydrindane ratio was required. This factor was applied to the results of all analyses.

Acknowledgment.—We wish to thank Dr. B. Franko and Mr. W. McCarthy of the Food Machinery and Chemical Corporation for carrying out the hydrogenation of indene. The gas chromatographic apparatus was purchased with a Grant-In-Aid from the Food Machinery and Chemical Corporation.

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Azasteroids. III.[1] 3-Aza-A-homo Androgens

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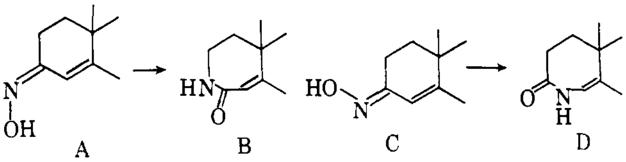
Received August 26, 1962

The continuing search for modified steroids with hormonal or antihormonal activity is currently emphasizing structures with hetero atoms incorporated in the polycyclic nucleus.[2–4] Our own interest has been in azasteroids[1,5] which are particularly attractive since they are potentially available from any ketosteroid *via* oxime and Beckmann rearrangement. The present report concerns work leading to A-homo derivatives of testosterone and 17α-methyltestosterone.

Beckmann rearrangement of an α,β-unsaturated ketoxime may give either an α,β-unsaturated lactam or an enamine lactam depending on the stereochemistry of the starting oxime. Thus, *syn*-oxime A leads to lactam B while *anti*-oxime C should give lactam D assuming no change in configuration of the oxime during the reaction.



A B C D

The structure of the lactam may be determined by the position of the ultraviolet maximum,[6] lactams of type B showing a maximum around 220 mμ while those of type D absorb maximally around 240 mμ. Some steroid A-homolactams derived from Δ^4-3-ketones have been described[7–9] and all seem to be of type B. It would also be useful to have a simple method for distinguishing between *syn*- and *anti*-α,β-unsaturated oximes both for purposes of structure assignment and for determination of homogeneity. We felt that nu-

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