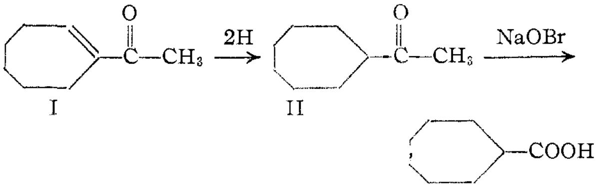
ence of aluminum chloride; it is the only defined product of the reaction and is obtained in 22% yield, isolated as the semicarbazone. (I) had been



previously prepared[1] by treatment of 1-ethinylcycloheptanol with formic acid; the reported ultraviolet spectrum of the product and the melting point of its semicarbazone are in good agreement with our observations. Friess and Pinson[2] have found that under the condition of Nenitzescu and Cioranescu[3] for the condensation between cycloheptene and acetyl chloride rearrangement and hydrogen transfer took place, and a mixture of acetylmethylcyclohexanes is obtained. The structure of (I) was, therefore, rigidly demonstrated. Hydrogenation led to acetylcycloheptane (II); the melting point of its semicarbazone agreed with that reported[2] for the product obtained through the reaction between cycloheptylmagnesium bromide and acetic anhydride.

Furthermore, hypobromite oxidation of (II) afforded cycloheptanecarboxylic acid which was characterized as its amide.

Experimental[4,5]

Cycloheptene was prepared by reduction of technical cycloheptanone[6] with aluminum isopropoxide,[7] and distillation at atmospheric pressure of the crude cycloheptanol over β-naphthalenesulfonic acid, b.p. 113–115° (756 mm.); yield 74%.

Acetylcycloheptene (I).—Aluminum chloride (166 g., 1.25 moles) was added in small portions over a period of 2.5 hours to a stirred solution of cycloheptene (120 g., 1.25 moles) and acetyl chloride (100 g., 1.27 moles) in 650 ml. of dry carbon disulfide. The temperature of the reaction mixture was maintained between -5 to 0°. Practically no hydrogen chloride was evolved. Stirring was continued for an additional hour at the same temperature; then the reaction mixture was poured into a vigorously stirred mixture of concentrated hydrochloric acid and crushed ice. The organic layer was washed with water and sodium bicarbonate solution and dried over calcium chloride. The solvent was evaporated and the residue distilled from 150 g. of anhydrous sodium carbonate at atmospheric pressure. The oil (75 g.) which came over at 208–215°, was distilled again from 50 g. of anhydrous sodium carbonate and yielded then 60 g. of a colorless liquid, b.p. 208–211° (756 mm.).

This product (57 g.) was treated with semicarbazide acetate and afforded 34 g. of a semicarbazone, melting at 194–195° (dec.) after two recrystallizations from ethanol; ultraviolet $\lambda_{\max}$ 264 mμ (log ϵ 4.39).

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.5; H, 8.8. Found: C, 61.5; H, 8.7.

A second crop of 17 g. (m.p. 188–190°) was isolated from the mother liquor.

Decomposition of the semicarbazone was carried out by refluxing with an aqueous solution of oxalic acid, b.p. 103.5° (20 mm.); ultraviolet $\lambda_{\max}$ 236 mμ (log ϵ 4.01); 308 mμ (log ϵ 1.66).

Anal. Calcd. for $C_9H_{14}O$: C, 78.3; H, 10.2. Found: C, 78.4; H, 9.9.

Acetylcycloheptane (II).—(I) (6.9 g.) was dissolved in 50 ml. of 95% ethanol and hydrogenated in the presence of 0.2 g. of 5% Pd–charcoal in an Adams hydrogenation apparatus. The theoretical amount of hydrogen was absorbed during 16 minutes. The mixture was filtered and concentrated to 10 ml. The semicarbazone was prepared as before; m.p. 177–178°; unchanged on recrystallization, yield 9.0 g. (97%).

Anal. Calcd. for $C_{10}H_{19}ON_3$: C, 60.9; H, 9.6. Found: C, 60.6; H, 9.3.

The semicarbazone (6.7 g.), oxalic acid (30 g.) and 150 ml. of water were refluxed for three hours, and the product worked up as usual. (II) (3.8 g., 80%) boiled at 101–102° (29 mm.).

Anal. Calcd. for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 77.3; H, 11.7.

Cycloheptanecarboxylic Acid.—The hypobromite oxidation of (II) was carried out according to the known procedure.[8] The alkaline reaction mixture was steam distilled, acidified and extracted with ether. The ethereal solution was washed with water, dried on sodium sulfate and evaporated. The resulting oily acid was converted into the acid chloride with thionyl chloride and the latter treated, without further purification, with a concentrated aqueous ammonia solution. The crude amide, m.p. 150–165°, was recrystallized from boiling water, which left some brown, oily impurity undissolved. The amide crystallized in large colorless plates, m.p. 191–193.5°. After one further recrystallization from water it melted at 193.5–194.5°.[9]

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[1] I. Heilbron, E. R. H. Jones, J. B. Toogood and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1949).

[2] S. L. Friess and R. Pinson, Jr., This Journal, **73**, 3512 (1951).

[3] C. D. Nenitzescu and E. Cioranescu, *Ber.*, **69**, 1820 (1936).

[4] All melting points are uncorrected.

[5] The ultraviolet absorption spectra were determined by Dr. Y. Hirshberg, with a Beckman quartz spectrophotometer; 95% ethanol was employed as solvent.

[6] Courtesy of Messrs. J. R. Geigy, Ltd., Basle.

[7] H. Lund, *Ber.*, **70**, 1520 (1937).

[8] L. T. Sandborn and E. W. Bousquet in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 526.

[9] E. Buchner and A. Jacobi, *Ber.*, **31**, 2008 (1898); W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948); R. Willstaetter, *Ber.*, **31**, 2498 (1898).

WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL
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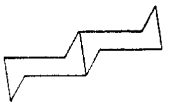
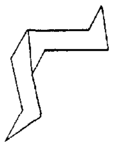
Energy Differences in the *cis*- and *trans*-Decalins

BY RICHARD B. TURNER

Barton's[1] semi-theoretical treatment of the non-bonded repulsive interactions in *trans*-decalin (I) and in the two constellations, II and III,[2] of *cis*-decalin gives I > II > III as the stability order of these forms. Uncertainties in van der Waals radius for hydrogen and in the magnitude of the repulsion term appearing in Barton's calculations, however, vitiate any quantitative estimate of the energy differences in this system, at least within an order of magnitude of ten. Thus, depending upon the choice of the above parameters, a series of values ranging from 0.52 to 8.23 kcal. was obtained for the energy difference between I and II. Estimation of the rotational barrier in ethane by the same procedure gave energy values, 0.09 to 0.39 kcal., appreciably lower than the gener-


I


II


III

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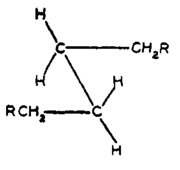
[1] D. H. R. Barton, *J. Chem. Soc.*, 340 (1948).

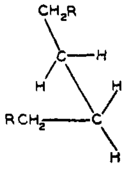
[2] Electron diffraction data of O. Bastiansen and O. Hassel, *Nature*, **157**, 765 (1946), verify II as the stable structure of *cis*-decalin. Structure III is therefore to be regarded as hypothetical.

ally accepted value of approximately 2.8 kcal., for which there is considerable support.[3,4]

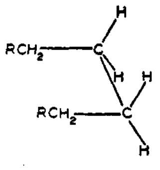
In calculating statistical entropies (gas phase, 25°) for *n*-butane and for a number of other hydrocarbons including cyclohexane and the alkylcyclohexanes, Pitzer[4,5] achieved a remarkable degree of correspondence with observed entropies by employing 0.8 kcal. for the steric energy of the skew form (V) of the *n*-butane structure as compared with the stable staggered constellation IV, and



IV



V



VI

3.6 kcal. for the barrier to rotation through the eclipsed form VI. Application of these values to the "boat" and "chair" constellations of cyclohexane (VII and VIII, respectively) led to an estimated energy difference (gas phase, 25°) of 5.6 kcal. in favor of the "chair" form (VIII), since this structure possesses 6 skew interactions of the *n*-butane type, whereas the "boat" form involves 4 skew and 2 eclipsed interactions.

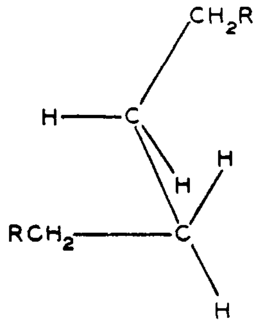
VII

VIII

Extension of these ideas to the *cis*- and *trans*-decalins gives a stability order, I > II > III, with an energy difference of 2.4 kcal. between I (6 staggered, 12 skew) and II (3 staggered, 15 skew). The heat of isomerization, I → II, determined by careful measurement of the heats of combustion (liquid phase, 25°) of pure samples of *cis*- and of *trans*-decalin is 2.12 kcal.[6]

For the purpose of direct comparison the calculated value (2.4 kcal.) must be corrected by a small factor for the difference in heats of vaporization of the two isomers at 25°. Such a correction could be derived from a knowledge of vapor pressure–temperature relationships by use of the Clausius–Clapeyron equation. Unfortunately, although the requisite data have been reported,[7] their validity, particularly at temperatures below 50° is doubtful.[8] The correction factor has therefore been approximated from an empirical equation, $\lambda_{25} = 5.4 + 0.036t_{\text{normal b.p.}}$, employed for a similar purpose by Klages.[9] Using the boiling points of *cis*- and of *trans*-decalin, 194.6 and 185.5°, respectively, the energy difference between I and II, corrected to the liquid phase at 25°, is estimated to be 2.07 kcal. Correspondence between the calculated and observed values is considerably better than could reasonably be expected of such a method of approximation.

The energy difference between II and III is more difficult to estimate. The "2-boat" form III possesses, in addition to 4 staggered, 8 skew, and 4 eclipsed *n*-butane interactions, 2 interactions of type IX, produced by a rotation of 60° from the stable staggered configuration (IV). The magnitude of this interaction cannot be evaluated in a simple way, owing to discontinuities in the rotational potential barrier curve of the Pitzer treatment. Neglecting these interactions, however, it is possible to arrive at a minimum value for the energy difference between II and III of 8.8 kcal.



Introduction of an angular methyl group (*cf.* the steroids) into *cis*- and *trans*-decalin (II and I, respectively) has the interesting consequence of lowering the energy difference between these structures from 2.4 to 0.8 kcal. In *trans*-decalin (I) the angular methyl group, being polar with respect to both rings, gives rise to 4 additional skew interactions, whereas in *cis*-decalin (II), in which the angular methyl group is polar with respect to one ring and equatorial with respect to the other, only 2 additional skew interactions result.

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(3) G. B. Kistiakowsky, J. R. Lacher and F. Stitt, *J. Chem. Phys.*, **7**, 289 (1939).

(4) K. S. Pitzer, *Chem. Revs.*, **27**, 39 (1940).

(5) C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

(6) G. F. Davies and E. C. Gilbert, *ibid.*, **63**, 1585 (1941).

(7) W. F. Seyer and C. W. Mann, *ibid.*, **67**, 328 (1945).

(8) W. F. Seyer, *ibid.*, **67**, 2281 (1945) (correction). In this connection it should be noted that in reference 7 the constants A, B and C (Table II) of the equation $\ln P = AT^{-1} + B \ln T + C$ do not correspond to the data of Table I, nor to the heats of vaporization, *cis*, 10210 cal.; *trans*, 9960 cal., calculated for these substances at their respective boiling points.

(9) F. Klages, *Ber.*, **82**, 358 (1949). Application of the above expression to the analogous case of the *cis*- and *trans*-1,2-dimethylcyclohexanes gives an estimated difference between the heats of vaporization of these substances at 25° of 227 cal. The experimentally determined value (A.P.I. Reports) is 325 cal.

DEPARTMENT OF CHEMISTRY
THE RICE INSTITUTE
HOUSTON 1, TEXAS

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NEW COMPOUNDS

N-Methyl-di-β-propionyloxyethylamine[1]

To 59.6 g. (0.5 mole) of N-methyldiethanolamine was added dropwise with rapid stirring 65.1 g. (0.5 mole) of propionic anhydride. After 2 hours, when the mixture had cooled, 65.1 g. of additional propionic anhydride was added. Saturated K_2CO_3 solution was then added to the cooled reaction mixture until evolution of CO_2 had ceased. The mixture was extracted twice with ether and the ethereal solution was dried over sodium sulfate. After removal of the ether, the yellowish fluid was distilled twice under reduced pressure; distilling range, 114.8 to 115.2° (1 mm.); yield 91.5 g. (79%). The product was water-clear; $d^{29.3}_4$ 1.0072; $n^{29.1}_D$ 1.4367; *R*D calcd. 60.25 cc., *R*D exptl. 60.12; pK'_a 6.62 (37°).

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[1] This compound was prepared in the course of work under a contract, recommended by the National Defense Research Committee between the Office of Scientific Research and Development and the Johns Hopkins University.