

wt., 82 (mass spectrum). Its structure was deduced from these observations: since the compound showed no evidence of unsaturation in its ultraviolet and infrared spectra, the formula demands the presence of two rings. Of the possible bicyclohexanes, bicyclo[2.2.0]hexane has already been made⁴ and bicyclo[3.1.0]hexane would show the presence of the cyclopropane ring in its spectra. The n.m.r. spectrum of the compound on hand (solvent: CCl₄, chloroform and tetramethylsilane as internal standards) consisted of 2 protons at 7.47 τ -broad, 6 protons at 8.41 τ -apparent singlet; 2 protons at 9.13 τ -quartet, which would fit only the bicyclo[2.1.1]structure. The spectrum agreed closely with that of authentic bicyclo[2.1.1]hexane which was synthesized by another route.⁵

Preliminary studies have shown that this photochemical method is also applicable to the synthesis of 1,5,5-trimethylbicyclo[2.1.1]hexane from *dl*-camphor. The yields of the bicyclohexanes obtained by this method ranged from 25% in the case of norcamphor using mercury photosensitization⁶ to 10% in the case of camphor using radiation from a medium pressure mercury arc. An increase in temperature generally decreased the yield. The improved yield as compared to the photochemical production of bicyclo[2.2.0]hexane by a similar process⁴ is understandable when the degree of strain involved in the two systems is considered.

Although the yields obtained are only fair, the ready availability of the starting materials and the simplicity of the process should make this an attractive path to the synthesis of certain bicyclo[2.1.1]hexanes. It is to be noted that the alternative route³ is also a photochemical reaction so that scaling up these methods should present similar problems.

Acknowledgment.—The author wishes to thank Professor W. Albert Noyes, Jr., for his advice and encouragement. He is grateful to Dr. Sheldon Cremer for helpful discussions.

(5) The author is deeply grateful to Professor K. Wiberg of the University of Washington for making this spectrum available to him for comparison.

(6) The photochemistry was more complex in this instance and led to derivatives of cyclopropane too.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK

R. SRINIVASAN

RECEIVED APRIL 26, 1961

RING CLOSURE TO THE NORBORNYL SYSTEM BY ANCHIMERICALLY ASSISTED SOLVOLYSIS OF 2-(Δ^3 -CYCLOPENTENYL)-ETHYL TOSYLATE*

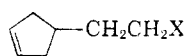
Sir:

2-(Δ^3 -Cyclopentenyl)-ethanol (I) has been prepared by the addition of ethylene oxide to the Grignard reagent prepared from Δ^3 -cyclopentenyl bromide.¹ Phenylurethan of I, m.p. 60°; calcd. for C₁₄H₁₇O₂N: C, 72.70; H, 7.41; N, 6.06; found: C, 72.53; H, 7.26; N, 6.06. The tosylate II was prepared by the method outlined by Tipson.² It was an oil down to -30°. The analytical

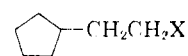
(*) Presented before the Organic Division of the American Chemical Society at St. Louis, Missouri, March 27, 1961.

(1) Marian R. Rice, Thesis, Radcliffe College, 1957.

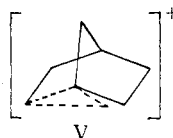
(2) R. S. Tipson, *J. Org. Chem.*, **9**, 238 (1944).



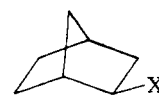
I, X = OH
II, X = OTs



III, X = OH
IV, X = OTs



V



VI, X = OH
VII, X = OAc

sample still contained alcohol. Calcd. for a mixture of 88.7% II and 11.3% I: C, 62.13; H, 6.47. Found: C, 62.13; H, 6.57. These compounds showed infrared spectra consistent with the assigned structures. The corresponding saturated alcohol³ III and its tosylate IV were prepared for comparative kinetic studies.

If the double bond does not participate anchimerically in the ionization of II, its rate of solvolysis in any given medium should differ inappreciably from that of IV, and would be expected to correspond to bimolecular displacement of tosylate ion by a solvent molecule and to increase in rate with the nucleophilic reactivity of the solvent. For the kinetic investigation three solvent mixtures were chosen with similar ionizing powers as reflected in their Grunwald-Winstein *Y* values (see Table I) but of widely different nucleophilic reactivities. Rates of appearance of *p*-toluenesulfonic acid in the solutions were followed conductimetrically.

TABLE I
SOLVOLYTIC RATE CONSTANTS (SEC.⁻¹ $\times 10^4$) IN ABSENCE OF ADDED REAGENTS

Solvent	50% Ethanol (70°)	50% Acetic Acid (60°)	98% Formic acid (60°)
<i>Y</i> value	1.66	1.94	2.10
<i>k</i> ₁ for IV	0.58	0.076	~0.003
<i>k</i> ₁ for II	3.36	3.8	5.7
<i>k</i> _{II} / <i>k</i> _{IV}	5.8	50	~1900

As seen from the table, the solvolysis rate of the saturated IV declines about 200-fold in going from 50% alcohol to formic acid, while the solvolysis rate of the unsaturated II increases by 70%. Since any inductive effect of the double bond can only be unfavorable to ionization, the ratio *k*_{II}/*k*_{IV} is a measure of anchimeric driving force from the double bond, and this quantity amounts to 5.8 in 50% alcohol and about 1900 in formic acid.

The product of heating 0.341 g. of II in 50% acetic acid at 72° for 7 hours was isolated by neutralization and ether extraction. Vapor chromatography showed that 92% of the total product was a 60-40 mixture of *exo*-norbornyl acetate (VII) and *exo*-norborneol (VI), confirmed by comparison with known mixtures of these compounds. The mixture was converted into *exo*-norborneol (VI) by saponification with potassium hydroxide; this alcohol was isolated by continuous extraction with petroleum ether, careful evaporation of the solvent and sublimation of the VI as white crystals having the infrared spectrum of norborneol, identical with

(3) V. N. Ipatieff, W. W. Thompson and H. Pines, *J. Am. Chem. Soc.*, **73**, 553 (1951).

that of a similarly purified authentic specimen. The tosylate II was recovered unchanged after 72 hours at 65° in nitromethane.

The strain energy (about 19 kcal.)⁵ of the norbornyl ring system is almost as great as the calculated standard heat of cyclization of an olefin. The near thermoneutrality of the conversion of I into VI offers in itself no basis for this greatly preferred course of the solvolysis. The drive toward ring closure must be related rather to the favorable electronic structure of the bridge ion V, already well recognized from evidence concerning the behavior of norbornyl sulfonates. We plan to extend this investigation to include the effects of substitution and of structural and stereochemical variations in the starting material.

The present ring closure has been investigated independently by R. G. Lawton⁴ of the University of Wisconsin. This work was supported by the National Science Foundation.

(4) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

(5) The much lower value of 9.49 kcal. has been estimated by Prof. H. J. Dauben, Jr. (private communication).

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS

PAUL D. BARTLETT
SHELTON BANK

RECEIVED APRIL 24, 1961

INTRAMOLECULAR HYDROGEN BONDING IN NON-CHAIR CONFORMATIONS OF CIS-1,4-CYCLOHEXANEDIOLS

Sir:

Examination of models of 1,4-cyclohexanediols suggests that intramolecular hydrogen bonding can occur only when the hydroxyl groups have the *cis* configuration, and then only in certain *non-chair* conformations.¹ Therefore, the observation of strong intramolecular hydrogen bonding in a *cis*-1,4-cyclohexanediol would provide compelling evidence for the presence of non-chair conformations. This communication presents such evidence, obtained by infrared spectroscopy, for a 2,5-di-*t*-butyl-1,4-cyclohexanediol.

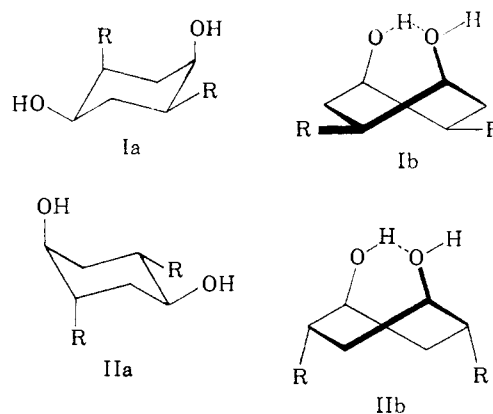
Four racemates and two *meso* stereoisomers are theoretically possible for 2,5-di-*t*-butyl-1,4-cyclohexanediol. Of these, only the two racemates, I and II, in which the hydroxyl groups are *cis* to one another and the *t*-butyl groups are *cis* to one another would be expected to exhibit intramolecular hydrogen bonding. The conformations of I present at equilibrium would include the chair conformation, Ia, destabilized by the crowding together of the axial *t*-butyl group, the abutting axial hydrogen, and the axial hydroxyl group, and the twist² conformation, Ib, in which the *t*-butyl groups can be positioned more comfortably,³ with possible additional stabilization through intramolecular hydrogen bonding.⁴ Similarly, but to a lesser degree, IIa is destabilized by its axial *t*-butyl group, while

(1) G. Hite, E. E. Smisman and R. West, *J. Am. Chem. Soc.*, **82**, 1207 (1960).

(2) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *ibid.*, **83**, 806 (1961).

(3) N. L. Allinger and L. A. Freiberg, *ibid.*, **82**, 2393 (1960).

(4) Partial relief of axial group repulsions in Ia by slight rotation and bond angle bending would be expected to give a distorted chair conformation corresponding to an energy minimum, with a structure intermediate between that drawn for Ia and the transition state leading to Ib.



R is *t*-Bu

IIb may be stabilized by intramolecular hydrogen bonding.

Addition of 3 moles of hydrogen to 2,5-di-*t*-butylhydroquinone in acetic acid solution with platinum oxide catalyst at 25° under 2–3 atm. pressure, yielded a white solid product mixture (from acetic acid–water). Fractional recrystallization effected isolation in 20% yield of a 2,5-di-*t*-butyl-1,4-cyclohexanediol (diol A), m.p. 157.5–158.5°, which exhibited intense absorption at 3480 cm.⁻¹ (C, 73.63; H, 12.11). The maximum amount of diol A present in the total hydrogenation products was about 40% (infrared analysis).

Spectral data for diol A, reproduced in Table I, show that in the concentration range 0.0005 to

TABLE I
CONCENTRATION DEPENDENCE OF INFRARED OH BANDS
FOR DIOL A

Concn., moles/l.	Relative ^a absorbance at cm. ⁻¹		
	3640	3619	3480
0.00054	1.0	1.0	1.0
.0011	2.0	1.9	2.0
.0022	4.1	4.0	3.9 ^b
.0043 ^c	7.9	7.8	7.3

^a The values tabulated are relative to the absorbances at the lowest concentration (0.0054 M): 0.036, 0.032 and 0.071 for peaks at 3640, 3619 and 3480 cm.⁻¹, respectively.

^b Band width at half maximum intensity ($\nu_{1/2}$): 71 cm.⁻¹.

^c At 0.0043 M, small but significant absorbance attributable to intermolecular hydrogen bonding is observed.

0.002 M where *intermolecular* hydrogen bonding is expected to be negligible, the absorption bands at 3640, 3619 and 3480 cm.⁻¹ exhibit the same concentration dependence.⁵ The three peaks were diminished by 2–3% and the frequencies were increased by 1, 3 and 10 cm.⁻¹, respectively, when a 0.002 M solution of diol A in carbon tetrachloride was heated from 20 to 70°. The replacement of the hydroxyl hydrogens by deuterium resulted in the replacement of the absorption bands at 3640, 3619 and 3480 cm.⁻¹ by new bands having similar relative intensities and appearing at 2687, 2672 and 2576 cm.⁻¹.

The slight temperature dependence, the concentration dependence and the results of deuterium

(5) A Perkin-Elmer Model 221G Infrared Spectrophotometer with a sodium chloride prism-grating interchange was employed to record spectra in the region 2500 to 4000 cm.⁻¹. Near-infrared silica cells of 1 cm. path length were used with solutions in carbon tetrachloride (dried "Spectro Grade") at about 30°. The accuracy of the frequencies reported is claimed to be within ± 4 cm.⁻¹.