There was isolated from the distillation residue 4 g. of triphenylene, m.p. 199°, and 2 g. of tetraphenylene, m.p. 241–242°.

The infrared spectrum was in accord with the assigned structure for the major product and showed bands at 5.98 μ (C=C) stretching, and 10.33 μ *trans* out-of-plane (C—H) deformation. These bands have an extensive literature for characterizing *trans* double bonds of the type RCH=CHR. The ultraviolet spectrum showed λ_{max} 250 mμ (ϵ 660) indicating that the benzene ring and double bond are not in conjugation.

Catalytic hydrogenation of the phenyloctene using platinum oxide in ethanol at 33° required 105% of one mole of hydrogen. The product was purified by v.p.c. and had n^{25}D 1.4831 (lit.[32] n^{25}D 1.4831 for 1-phenyloctane). The infrared spectrum of the hydrogenation product was identical to that of an authentic sample of 1-phenyloctane. Oxidation of the phenyloctene with cold potassium permanganate solution led to the isolation of phenylacetic acid in 76% yield (identified as the amide).

Reaction of Benzyne with 1,3-Cyclohexadiene.—The reaction was carried out under the usual conditions employing *o*-fluorobromobenzene (10.0 g., 0.057 mole), magnesium (1.40 g., 0.058 mole), 1,3-cyclohexadiene (9.1 g., 0.11 mole) and tetrahydrofuran (20 ml.). There was obtained 4.1 g. (46%) of a mixture of 5,6-benzobicyclo[2.2.2]-octa-2,5-diene (XIII) and a second 1:1 adduct (XIV), b.p. 75–80° (1.3 mm.), n^{25}D 1.5677; v.p.c. analysis of the mixture showed the ratio of XIII:XIV was 65:35. A sample of pure XIII was obtained by preparative v.p.c. and had b.p. 79–80° (1 mm.), n^{25}D 1.5657.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 92.20; H, 8.04.

A pure sample of XIV could not be obtained by v.p.c. However, a sample of a mixture of XIII and XIV, in which the latter was enriched, was used for n.m.r. analysis. The lines of the spectrum attributable to XIV could be interpreted on the basis of the assigned structure, and a line

(32) A. W. Schmidt, *Ber.*, **75**, 1399 (1942).

of weight 2 at τ 6.51 indicated the presence of cyclobutane hydrogens in the benzocyclobutene structure.

Reaction of Benzyne with Cyclohexene.—The reaction was carried out under the usual conditions employing *o*-fluorobromobenzene (20.0 g., 0.114 mole), magnesium (2.80 g., 0.115 mole) and cyclohexene (32.0 g., 0.390 mole) in tetrahydrofuran (45 ml.). After workup, distillation afforded 5 g. of a fraction, b.p. 60–65° (0.6 mm.); v.p.c. analysis showed a complex mixture from which 3.3 g. (18%) of fairly pure 3-phenylcyclohexene, b.p. 64–65° (0.55 mm.), n^{25}D 1.5402 (lit.[33] b.p. 235°, n^{20}D 1.5440), was obtained. The infrared and ultraviolet spectra of the product indicated that the benzene ring and double bond are not in conjugation, and this is further confirmed by the low value of the refractive index.[33]

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.75; H, 9.17.

Catalytic hydrogenation of the phenylcyclohexene in ethanol at 33° over platinum oxide required 104% of one mole of hydrogen. The product of the hydrogenation had b.p. 67° (0.5 mm.), n^{25}D 1.5413 (lit.[34] n^{20}D 1.5429), and its infrared spectrum was identical with that of authentic phenylcyclohexane.

Reaction of Tetrafluoroethylene with *o*-Fluorobromobenzene and Magnesium.—*o*-Fluorobromobenzene (10.0 g. 0.057 mole), magnesium (1.40 g., 0.058 mole) and tetrahydrofuran (35 ml.) were sealed in a 100-ml. silver-lined pressure vessel. Tetrafluoroethylene (12.0 g., 0.12 mole) was introduced into the vessel which was then sealed and heated at 65° for 3 hours. After cooling and venting the vessel, the contents were worked up in the usual fashion. Distillation afforded 1.0 g. of *o*-fluoro-α,β,β-trifluorostyrene, b.p. 125°, n^{25}D 1.4441. The n.m.r. fluorine spectrum was entirely in accord with the assigned structure.

Anal. Calcd. for $C_8H_4F_4$: C, 54.56; H, 2.29; F, 43.15. Found: C, 54.29; H, 2.38; F, 43.43.

(33) A. Berlande. *Bull. soc. chim. France*, [V] **9**, 942 (1942). 1-Phenylcyclohexene is reported to have n^{20}D 1.5718.

(34) O. Neunhoffer. *J. prakt. Chem.*, [II] **133**, 95 (1932).

Conformational Analysis. XIII. On the Geometry of the Cyclooctane Ring. The Relative Stabilities of the 1,3-Dimethylcyclooctanes[1,2]

BY NORMAN L. ALLINGER AND SHIH-EN HU

RECEIVED SEPTEMBER 22, 1960

Infrared studies confirm an earlier suggestion that cyclooctanone exists very largely in a single conformation in the liquid phase at 25°. The pure isomeric *cis*- and *trans*-1,3-dimethylcyclooctanes have been prepared and equilibrated in the presence of a palladium catalyst at 260°. The free energy of the reaction *trans*- ⇌ *cis*-1,3-dimethylcyclooctane was found to be +0.25 kcal./mole. It was concluded that the conformation of the cyclooctane ring which best fits this and other available data is the skewed crown.

Introduction

The conformations of the cyclooctane ring have been the subject of a number of recent papers.[3–8] Three separate conformational structures for cyclooctane have been proposed together with two

additional ones for certain cyclooctane derivatives including cyclooctanone.[9,10] The purpose of the present work is to furnish additional information which bears on this question, and to attempt to reach the correct conclusion as to the conformation of the eight membered ring.

The conformations of the medium rings became of interest as soon as the relative difficulty of their synthesis was noted.[11] In an effort to explain the variation of the carbonyl stretching frequency with ring size in the cyclanones, the "O-inside" and "O-outside" conformations were discussed,

(1) Paper XII, N. L. Allinger and V. Zalkow. *J. Am. Chem. Soc.*, **83**, 1144 (1961).

(2) This work was supported by a research grant from the National Science Foundation.

(3) (a) E. Billeter, T. Bürer and H. H. Günthard. *Helv. Chim. Acta*, **40**. 2046 (1957); (b) T. Bürer and H. H. Günthard, *ibid.*, **40**, 2054 (1957).

(4) R. Kolinski, H. Piotrowska and T. Urbanski. *J. Chem. Soc.*, 2319 (1958).

(5) G. Chiurdoglu, T. Doehaerd and B. Tursch. *Chemistry & Industry*, 1453 (1959).

(6) H. E. Bellis and E. J. Slowinski. Jr.. *Spectrochim. Acta*, 1103 (1959).

(7) N. L. Allinger. *J. Am. Chem. Soc.*, **81**, 5727 (1959).

(8) R. Pauncz and D. Ginsburg. *Tetrahedron*, **9**, 40 (1960).

(9) N. L. Allinger and S Greenberg. *J. Am. Chem. Soc.*, **81**, 5733 (1959).

(10) N. J. Leonard, T. W. Milligan and T. L. Brown, *ibid.*, **82**, 4075 (1960).

(11) For a summary of earlier work, see V. Prelog, *J. Chem. Soc.*, 420 (1950).

but otherwise little was done until recently on the detailed conformation of these rings[11] with the notable exception of cyclooctatetraene.[12]

Discussion

Recently two independent sets of theoretical calculations on the geometry of cyclooctane were published.[6,7] Because of the numerical complexity of exact calculations, in both cases approximations were used. The two sets of calculations led to different conclusions. The more empirical calculations[7] based on rotational barriers gave an energy for cyclooctane, relative to cyclohexane, of 10.4 kcal./mole (in good agreement with the experimental value[13] of 9.9 kcal./mole) with the stable form being the skewed crown (approximately[14] D_4), I. The more detailed calculations of Pauncz

I   II   III
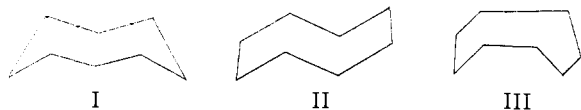
and Ginsburg[8] did not consider this form. For the regular crown (D_{4d}) they calculated an energy which on the above basis amounts to 17.3 kcal./mole, and for the regular forms II (C_{2h}) and III (D_{2d}), allowing for angular deformation, their calculations gave energies of 19.7 and 27.8 kcal./mole, respectively. They concluded that II is similar in energy to the regular crown, but they did not consider the effects of skewing the various forms.

From a consideration of the methylene scissoring frequencies in the infrared spectrum of a number of medium ring compounds, Chiurdoglu, Doehaerd and Tursch concluded a crown structure was most probable.[5] Bellis and Slowinski made a very detailed study of the infrared and Raman spectra of cyclooctane and concluded that III (D_{2d}) was most consistent with the data, but structure I in the skewed form (D_4) was also possible.[6] Their work appears to eliminate II in either regular (C_{2h}) or skewed (C_2 or lower) form, as well as the skewed form of III (D_2). All of the spectral data are consistent with there being only a single conformation for cyclooctane itself.[3,5,6]

The chemical evidence is clear cut. Hydride is transferred to carbon 1 from carbon 5 and probably from 3 but not from 4.[15] Such transfers are characteristic of only structure I. While this does not prove that I is the only, or even the principal species in solution, it seems likely that this is the case. From the chemist's point of view, it does indicate that I is the form to be considered in understanding most chemical reactions.

While cyclooctane itself appears to exist almost exclusively in a single conformation, it was con-

(12) O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

(13) S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952).

(14) Since fairly small distortions may seriously change the symmetry class without significantly affecting the shape or energy of the molecule (which are more important for present purposes), the symmetry notation is used here with the reservation that the actual symmetry of the molecule may be lower than indicated.

(15) (a) A. C. Cope, S. Moon and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1650 (1959); (b) S. Greenberg, Ph.D. thesis, Wayne State University, November, 1959.

cluded[9] from the dipole moment of 5-(p-chlorophenyl)-cyclooctanone that that molecule, and cyclooctanones in general, existed in solution as a mixture of conformations IV and X. This possibility has now been further examined. The

IV   X
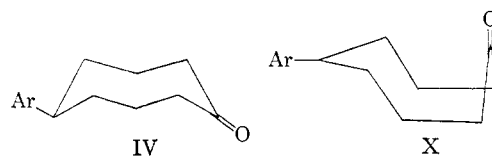
infrared spectra of cyclooctanone as a liquid and as a solid have been reported[3] and seem to be very similar. In the present work the spectra of the liquid at 62 and 102°, and the solid at 25° were obtained. No bands in the 7–12μ region disappear when the liquid is frozen and there is no significant difference in the ratios of the band areas in the three spectra, which indicates that in the liquid one conformation is present to the virtual exclusion of other possible ones. Confirmation of this conclusion comes from a comparison of the infrared spectra of 5-(p-chlorophenyl)-cyclooctanone in solution in carbon disulfide, and in the solid phase (potassium bromide pellet). Again the spectra are virtually identical, showing the presence of only one conformation for this molecule in solution.

Since the spectral evidence seemed to indicate a single conformation for cyclooctanone, a reconsideration of the dipole moment data was deemed necessary. Since X has little flexibility, it is likely that its moment is close to that calculated earlier (4.17 D.)[9,16] and this is considerably greater than the experimental value (3.39 D). This evidence excludes this form as the sole conformation of the molecule. It was earlier thought that this form would have a stability comparable to that of the crown if it could be assumed that the C=O system would not seriously interfere with hydrogens on carbons 4 and 6. Subsequent studies have shown that this assumption probably is not correct,[17,18] and it now seems likely that these interactions may be large enough to keep the molecules from assuming conformation X.

In contrast to X which is fairly rigid, form IV is quite flexible (in models), and the angle between the dipoles can vary from 90 to 150°. The two extremes correspond approximately to the two ways of skewing the structure and the corresponding values for the dipole moments vary from 3.52 to 1.58 D. Previously an average value for the moment was assigned to the conformation. However, if a certain definite angle is to be preferred, any value in this range is possible. It is noted that the range includes the experimental value. Hence the dipole moment of the 5-(p-chlorophenyl) derivative is consistent with conformation IV, but not with X. There are also distorted forms

(16) This value was obtained using the value μ = 1.95 D. for p-chlorotoluene (unpublished results of M. A. DaRooge), and differs slightly from that given in ref. 9.

(17) (a) E. L. Eliel, *J. Chem. Ed.*, **37**, 126 (1960); (b) N. L. Allinger and R. J. Curby, *J. Org. Chem.*, **26**, 933 (1961).

(18) (a) E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960); (b) J. Allinger and M. A. DaRooge, unpublished.

of II and III which could explain the observed moment.

Leonard, Milligan and Brown have described[10] a related compound, 1-oxacyclooctan-5-one, and have reported its dipole moment as 4.09 D. Since the moments for ketone and ether groupings are 2.93 and 1.22 D., respectively, it is clear the angle between the dipoles is quite small. They suggest a conformation (folded form) in which the ring atoms have approximately D_{2d} symmetry. Although this form explains the dipole moment, there are objections to it. The hydrogens around the ring are all eclipsed, which will destabilize this conformation. Since no stability is gained by transannular interaction, this form seems unlikely.[19]

Since the skewed crown form seems to fit the other cyclooctanone derivatives, it was examined here. This form is flexible in models and the potential minimum can only be estimated to perhaps 10°. Nevertheless, when the oxa compound in the crown form (XII) is skewed in the same way as was found to yield the experimental moment with 5-(p-chlorophenyl)-cyclooctanone, it was seen that the angle between the dipole was indeed small, approximately 24°. The calculated value for the resultant moment was 4.0 D. In XII hydrogens are staggered as well as possible, and this form seems to be a more likely alternative than XI.

XI   XII
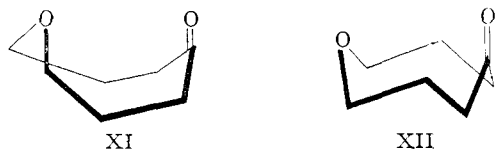
The available data on the cyclooctane ring therefore can all be interpreted as consistent with a single conformation, which appears to be either the skewed crown (I) or the tub form (III).[20]

Examination of a scale model of III shows that every carbon is identical in having a "hindered" and an "unhindered" hydrogen. It can also be seen that a methyl group in one of the "hindered" positions would be of exceedingly high energy. Further examination shows that 1,3-dimethyl-cyclooctane can exist in form III about as well as can cyclooctane itself if the methyl groups are trans, but if the groups are cis one of them must occupy a "hindered" position. Consequently the trans isomer of 1,3-dimethylcyclooctane must be

(19) N. J. Leonard (personal communication) has made the following comment on this point: "The authors are indeed correct in pointing out that another conformation of 1-oxacyclooctan-5-one, possibly preferred to XI, will account for the observed dipole moment. In our article,[10] we wished to focus attention on the geometrical relation of the ether and ketone dipoles, and, in stressing their near-parallel orientation, we were not intentionally directing a decision between conforma-

tions in which the 3- and 7-methylene groups occupied different relative positions. We have made such amplification in our talks on the subject and are grateful to the present authors for the opportunity of clarification here."

(20) The 1-thia- and 1-azacyclooctan-5-ones are specifically excluded from this generalization, since they do show transannular interaction which may lead to atypical geometry.[10]

of much lower heat content than the cis if the ring has the "tub" form.

The predicted stability relationship is reversed if the ring is in the skewed crown form. In this case the cis isomer has both methyls in comfortable "equatorial" positions, while in the trans one methyl must be "axial." Models indicate that the "axial" position here is about as crowded as the corresponding position in the cyclohexane system In the eight-membered ring though, the methyl can bend out away from the interior of the ring more easily, since along with this bending will go an improved dihedral angle. A 10° bending for example is unfavorable by 1.8 kcal.,[21] but 1.1 kcal. is regained through the more favorable dihedral angles,[7] leaving a net energy increase of only 0.7 kcal. How these effects will balance out is not easy to predict, but it seems that the cis isomer will be only slightly more favorable if the ring is in the skewed crown form. For structure II, the cis isomer looks more comfortable, but the difference appears small.

Pure cis- and trans-1,3-dimethylcyclooctane were prepared as outlined on the flow sheet. The reaction sequence is straightforward. The known dicarboxylic acids V, meso and dl, were prepared as described earlier.[22] Each diacid was reduced with lithium aluminum hydride to the diol, which was converted via the iodide into the dinitrile VII. The Ziegler ring closure[23] gave, after hydrolysis and decarboxylation, the corresponding ketone. It is noteworthy that the yield of the cyclizations is so high. The cis isomer appears to give nothing but the cyclic product, no polymer was detected and the yield was determined by only mechanical considerations. The yield of the trans compound was nearly as good, and these yields are to be contrasted with that obtained in forming the parent cyclooctanone under the same conditions (30%).[24] This is an example of what has been called the "gem-dimethyl effect."[25]

The ketones were then reduced to the hydrocarbons by the Wolff–Kishner method.[26]
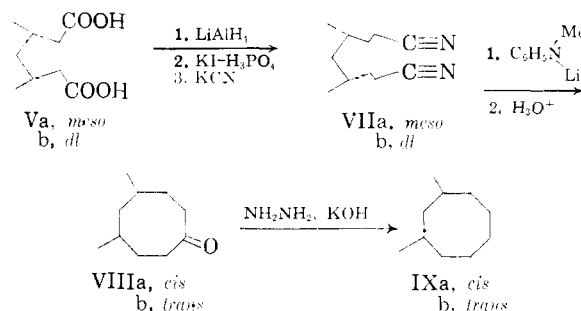
Pure samples of the cis- and trans-1,3-dimethyl-cyclooctanes were then available for study, and it was known which was which by the method of synthesis. A comparison of the physical properties of the compounds was of interest.

(21) A. C. Evans. Trans. Faraday Soc., 42, 719 (1946).

(22) N. L. Allinger, J. Am. Chem. Soc., 81, 232 (1959).

(23) N. L. Allinger, M. Nakazaki and V. Zalkow, ibid., 81, 4074 (1959).

(24) S. Greenberg, unpublished.

(25) N. L. Allinger and V. Zalkow, J. Org. Chem., 25, 701 (1960).

(26) Huang-Minlon, J. Am. Chem. Soc., 68, 2487 (1946).

For the *trans* compound the following constants were found: b.p. 181.5–182°, $n^{25}D$ 1.4564, d^{25} 0.8192. The corresponding constants for the *cis* isomer were: b.p. 181–181.5°, $n^{25}D$ 1.4520, d^{25} 0.8175. It is seen that the refractive indices and densities show small but consistent differences, and the numerical values are greater for the *trans* isomer. Application of the Conformational rule[27] predicts the *trans* isomer will have the higher heat content.

Of the various ways for determining relative heat contents of *cis* and *trans* isomers, the equilibration method[28] has proved to be quite reliable, and it has the advantage of requiring only small amounts of material. The method was therefore applied in the present case.

It was found that heating either of the 1,3-dimethylcyclooctanes in a sealed tube with palladium-on-carbon catalyst at 260° for 2 weeks gave the same mixture of the two isomers. At higher temperatures considerable decomposition occurred, while at lower temperature the equilibration was incomplete.

Usually the most accurate method of analyzing mixtures of the above type is by vapor phase chromatography.[28] In the present case it did not prove possible to effect a separation of the isomers by this method. The less accurate infrared method[1] was therefore used for the analysis. There are no really ideal bands in the infrared for this purpose. At every frequency at which one isomer has a relatively strong band, the other also has a band. There are however three reasonably good bands for the *trans* isomer, and four for the *cis*. The analytical results from these bands indicate that the equilibrium mixture contains 56% *trans* and 44% *cis*, with a probable error of 3%. For the reaction *trans-* $\rightleftarrows$ *cis-*1,3-dimethylcyclooctane, ΔF_{533} + 0.25 kcal./mole. To find ΔH, the value for ΔS must be known. The *cis* isomer is *meso* while the *trans* is *dl*, and consequently an entropy of mixing of $R \ln 2$ is predicted for the latter. The $T\Delta S$ term consequently favors the *trans* isomer by 0.75 kcal./mole, and hence for the reaction, ΔH_{533} −0.50 kcal./mole. While use of a calculated rather than an experimental value for the entropy may introduce some error,[29] it is clear that ΔH for the reaction is not far from zero, and it appears to favor the *cis* isomer. It seems that structure III for the 1,3-dimethylcyclooctanes can therefore definitely be excluded. Of the various possibilities it is concluded that the skewed crown structure (probably D_4) best fits all of the known experimental facts as well as the theoretical calculations.

Experimental

*meso-***3,5-Dimethyl-1,7-heptanediol** (VIa).—Twenty-five grams of *meso-β,β'*-dimethylpimelic acid[22] was added *via* a Soxhlet extractor to a suspension of 12 g. of lithium aluminum hydride in 500 ml. of ether. The solution was then heated under reflux overnight, and then in turn there was added dropwise 10 ml. of ethyl acetate, 150 ml. of water and 200 ml. of 6 N hydrochloric acid. The solution was extracted with five 100-ml. portions of ether, and the combined ether extracts were dried over anhydrous magnesium sulfate. After evaporation of the ether the product was distilled; b.p. 144–145° (5 mm.), $n^{25}D$ 1.4592, wt. 18 g. (88%).

Anal. Calcd. for $C_9H_{20}O_2$: C, 67.38; H, 12.52. Found: C, 67.05; H, 13.15.

*meso-***3,5-Dimethyl-1,7-dicyanoheptane** (VIIa).—Diol VIa, 18 g., was dissolved in a cold solution prepared by dissolving 22 g. of phosphorus pentoxide in 46 ml. of 85% phosphoric acid. After the addition of 113 g. of potassium iodide the mixture was stirred at 120° for 7 hours.[30] The cooled mixture was poured into 75 ml. of water and the solution was extracted with ether. The combined ether extracts were washed with sodium thiosulfate solution, then with water. After drying the solution, the ether was evaporated. The residual crude diiodide, 65 g., was added to 33.5 g. of potassium cyanide in 260 ml. of 70% ethanol. The resulting mixture was heated under reflux for 120 hours, and 80 ml. of ethanol was removed by distillation. The residue was diluted with water and the resulting solution was extracted with ether. The combined ether extracts were washed and dried and the solvent was removed. Distillation gave the product, b.p. 153–154° (2 mm.), $n^{25}D$ 1.4516, wt. 11 g. (68% from diol).

Anal. Calcd. for $C_{11}H_{18}N_2$: C, 74.10; H, 10.24. Found: C, 74.10; H, 10.34.

*cis-***4,6-Dimethylcyclooctanone** (VIIIa).—Bromobenzene, 78 g., was added with stirring during 2 hours to 7 g. of lithium in 1.5 liters of refluxing dry ether under a nitrogen atmosphere in a high-dilution apparatus.[23] To the resulting solution of phenyllithium was then added 68 g. of N-methylaniline. A solution of 11 g. of VIIa in 0.9 l. of dry ether was then added during 2 days. Water was then added to the cooled mixture. After stirring briefly, the aqueous layer was separated and discarded and the solvent was evaporated. The residue was combined with the residues from two similar runs and heated under reflux with 400 ml. of 33% sulfuric acid for 30 hours. The ketone formed was steam distilled during this time, the aqueous phase being constantly returned to the hydrolysis flask. The crude cyclooctanone was separated; wt. 30 g. (100%).

One gram of the crude ketone was converted to its semicarbazone derivative, yield 1.1 g., m.p. 196–197°. For analysis a sample was twice recrystallized and gave white needles, m.p. 197.5–198°.

Anal. Calcd. for $C_{11}H_{21}N_3O$: C, 62.52; H, 10.01. Found: C, 62.55; H, 10.24.

Two grams of the above semicarbazone (m.p. 197.5–198°) was hydrolyzed by refluxing with 20 ml. of 3 N hydrochloric acid for 3 hours. The solution was extracted with ether, the ether extracts were washed with water, dilute bicarbonate solution and water. The ether layer was dried, the solvent was evaporated and the ketone was distilled under vacuum; wt. 1.2 g., $n^{25}D$ 1.4624. For analysis a sample was redistilled; $n^{25}D$ 1.4622.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.80; H, 11.76. Found: C, 77.56; H, 11.40.

*cis-***1,3-Dimethylcyclooctane** (IXa).—Two grams of ketone VIIIa was added to a solution of 2.2 g. of potassium hydroxide and 1.6 g. of 95% hydrazine in 10 ml. of diethylene glycol.[26] The mixture was heated under reflux for 1.5 hours, the water and excess hydrazine were removed until the temperature of the solution reached 180°, and refluxing was continued until nitrogen evolution ceased. Water then was added and the mixture was steam distilled. The product was taken up in pure pentane and the pentane layer was washed in turn with dilute acid, bicarbonate and water. After removal of the pentane from the dried solution, the product was distilled; b.p. 181–181.5°, wt. 0.9 g. (50%), $n^{25}D$ 1.4520, d^{25} 0.8175. Vapor phase chromatography showed the compound to be quite pure.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.62; H, 14.22. Found: C, 85.39; H, 14.13.

(27) N. L. Allinger. *J. Am. Chem. Soc.*, **79**, 3443 (1957).

(28) N. L. Allinger and J. L. Coke, *ibid.*, **81**, 4080 (1959); **82**, 2553 (1960).

(29) There are entropy differences known for quite a number of epimeric hydrocarbons. These differences are in general within 0.5 e.u. of the calculated values. The only exceptions seem to be compounds in which there are gross structural differences, for example the *cis* and *trans*-1,3-di-*t*-butylcyclohexanes (N. L. Allinger and L. Freiberg. *ibid.*, **82**, 2393 (1960)).

(30) H. Stone and H. Schechte. *J. Org. Chem.*, **15**, 491 (1950).

dl-3,5-Dimethyl-1,7-dicyanoheptane (VIIb).—From 22.3 g. of *dl*-β,β'-dimethylpimelic acid, by the method described for the preparation of VIa, 12 g. of *dl*-isomer VIb was obtained; b.p. 138–139° (2 mm.), n^{25}D 1.4582. This material was converted to the dinitrile in an over-all yield of 57% by the procedure described for the preparation of VIIa; b.p. 173–174° (3 mm.), n^{25}D 1.4550.

Anal. Calcd. for $C_{11}H_{18}N_2$: C, 74.10; H, 10.24. Found: C, 74.07; H, 10.18.

trans-4,6-Dimethylcyclooctanone (VIIIb).—From 6.5 g. of dinitrile VIIb was obtained 5.0 g. of crude VIIIb by the cyclization method described for the synthesis of VIIIa. One gram of this material was converted to its semicarbazone derivative, which after two crystallizations from aqueous alcohol gave 0.6 g. of white plates, m.p. 176–178°.

Anal. Calcd. for $C_{11}H_{21}NO_3$: C, 62.52; H, 10.01. Found: C, 62.64; H, 9.90.

Two grams of purified semicarbazone was hydrolyzed by the method described for the *cis* isomer, and after distillation under vacuum the product was obtained; wt. 0.6 g., n^{25}D 1.4631.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.80; H, 11.76. Found: C, 78.20; H, 11.59.

trans-1,3-Dimethylcyclooctane (IXb).—Ketone VIIIb was converted to the hydrocarbon as described for the *cis* isomer. From 1.5 g. of pure ketone there was obtained 0.8 g. (59%) of the pure hydrocarbon, b.p. 181.5–182.0°, n^{25}D 1.4564, d^{25} 0.8192.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.62; H, 14.22. Found: C, 85.57; H, 13.99.

Equilibration Experiments.—Samples of about 100 mg. of the isomeric hydrocarbons IX were sealed in small tubes with about 20 mg. of palladium-on-carbon catalyst. The tubes were heated in a furnace at the desired temperature for 2 weeks. At 260° it was found that equilibration had occurred since the same mixture (by infrared analysis) was obtained from both isomers. At 299° extra bands appeared in the infrared spectrum, and it was clear that a reaction other than equilibration was taking place. At 230° the equilibration was incomplete.

Vapor phase chromatography of the pure hydrocarbons IX and synthetic mixtures of them on various columns gave no separation. The analysis was therefore done by the infrared method. The *trans* isomer gave bands at 8.45, 10.4 and 11.1μ which were suitable for analysis. The *cis* isomer likewise gave suitable bands at 8.56, 9.1, 10.3 and 11.35μ. From these bands the *trans* isomer in the equilibrated mixture was found to be 53, 55 and 51%. Similarly, the *cis* was 42, 36, 49 and 40%. After normalization the composition of the mixture is 56% *trans* and 44% *cis*, with a probable error of about ±3%. From the equilibrium constant and temperature (533°K.) it was found that for the reaction *trans* ⇌ *cis*-1,3-dimethylcyclooctane, $\Delta F = +0.25$ kcal./mole.
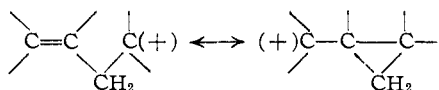

The Solvolysis of *exo*- and *endo*-7-Isopropylidene-dehydronorbornyl Tosylates

By C. H. DePuy, I. A. Ogawa and J. C. McDaniel

The tosylates of *exo*- and *endo*-7-isopropylidene-dehydronorborneol have been solvolyzed in glacial acetic acid containing sodium acetate. Both isomers solvolyzed with anchimeric assistance of the appropriate homoallylic unsaturation, the *exo* isomer with the 5,6- and the *endo* isomer with the 7,8-double bond. *Despite the fact that in both reactions a carbonium ion is generated at position 2, the two homoallylic ions are completely independent*, the ion from the *endo*-tosylate giving exclusively *endo*-acetate, the ion from the *exo*-tosylate giving exclusively rearranged acetate. Similar results were obtained on solvolysis of the dihydro compounds *exo*- and *endo*-7-isopropylidene-norborneol. The limits which these results place on the structure of homoallylic cations are discussed.

It is now well established that resonance interaction may take place between an electron-deficient center and a double bond not directly attached to the same carbon. When the site of unsaturation and the carbonium ion are separated by a single, saturated carbon atom, the system is known as "homoallylic," and the interaction as "homoallylic resonance." The interaction was first noted for cholesteryl cations,[1] and has been extensively investigated there, in the dehydronorbornyl system,[2] and with cyclopropylcarbinol compounds.[1b] Reactions involving such homoallylic participation are often characterized by an abnormally rapid rate of solvolysis relative to the

$$\overset{\displaystyle \diagdown}{\underset{\diagup}{C}}=\overset{\displaystyle \diagup}{\underset{\diagdown}{C}}\ \overset{\mid}{\underset{\diagdown}{\underset{CH_2}{C(+)}}} \longleftrightarrow (+)\overset{\mid}{\underset{\diagup}{\underset{CH_2}{C}}}\overset{\mid}{-C}\overset{\mid}{-C-}$$

corresponding dihydro compound,[3] by the isolation of products containing a cyclopropane ring, and by stereochemical criteria (*e.g.*, solvolyses

occurring with retention of configuration). Despite the extensive amount of work which has been published on homoallylic systems, a number of important problems dealing with the nature of the intermediate ions remain unsettled.[1] In particular, the type of bonding involved in these ions is unclear, as well as the possible participation of classical carbonium ions in some of their reactions. In this paper we report studies which place important restrictions on the type of bonding in some homoallylic ions, and which also demonstrate, in a convincing manner, that classical ions cannot be involved in their reactions.

We recently reported methods for the synthesis of *endo*-7-isopropylidene-dehydronorborneol (Ia) from 6,6-dimethylfulvene and α-acetoxyacrylonitrile.[4] The alcohol group in this interesting molecule is dihomoallylic, being separated from both the 7,8- and 5,6-double bonds by a single saturated carbon atom. Participation is then possible, at least in theory, with either of the two double bonds. On stereochemical grounds, interaction with the 5,6-double bond would not be expected to be detectable kinetically in this system but, if important, could be demonstrated by the nature of the products resulting from the reaction. At the

(1) For recent, comprehensive discussions see (a) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959), and (b) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(2) S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **73**, 5795 (1950).

(3) If the participation makes itself felt in the rate-determining step.

(4) C. H. DePuy and P. R. Story, *J. Am. Chem. Soc.*, **82**, 627 (1960).