Conformational Equilibration among 1,3-Dihalocyclobutanes[1]

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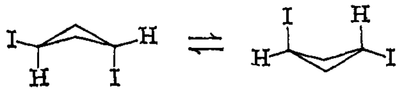
*Contribution from the Department of Chemistry, Yale University,
New Haven, Connecticut.* *Received May 25, 1966*

Abstract: The equilibrium constants for the *cis–trans* isomerization of 1,3-dichloro-, 1,3-dibromo-, and 1,3-diiodocyclobutanes have been determined. The dipole moments of the 1,3-dibromocyclobutanes permit an estimation of the geometry of the cyclobutane ring and give results in good accord with the structure of bromocyclobutane determined *via* the microwave spectrum. The factors responsible for the conformation of the cyclobutane ring and for the observed equilibrium constants are discussed.

The question of conformational equilibria among cyclobutane derivatives is of interest since the ring is known to be puckered by about 30°,[3] leading to both pseudo-axial and pseudo-equatorial positions which may be occupied by substituents. 1-Bromo-3-chlorocyclobutane was available from another investigation[4] and 1,3-diiodocyclobutane could easily be obtained by the reaction of bicyclobutane with iodine.[4] The availability of these compounds made a study of the *cis–trans* isomerization of 1,3-dihalocyclobutanes both practical and of interest.

The reaction of iodine with bicyclobutane led to a mixture of *cis-* and *trans*-diiodides, particularly when a small excess of iodine was used. The two isomers could be separated *via* gas chromatography, and the configurational assignment could be made *via* the nmr spectrum. The isomer with the shorter retention time was found to have a very simple spectrum: a triplet at τ 6.86 corresponding to the methylene protons and a pentuplet at τ 5.21 corresponding to the protons attached to the carbons bearing the iodines. This spectrum may be accounted for only by assuming the *trans* structure in which a rapid conformational flip makes all methylene protons and all coupling constants between the methylene and other protons equivalent during the time period of the measurement. The other possibility, that the ring is planar, is made unlikely by previous evidence and is ruled out by the dipole moment data to be presented below.



The isomer with the longer retention time was clearly the *cis* isomer since the nmr spectrum was complex showing the presence of several different types of hydrogens. This isomer would be expected to be largely in one conformation. The nmr spectrum could be used to distinguish between each of the isomeric pairs, and in each case the *trans* isomer had the shorter vpc retention time.

The equilibrium mixture of diiodides was established at 124.4° in acetone solution *via* the reaction with iodide ion. The same mixture was obtained starting with two different mixtures of the *cis-* or *trans*-diiodides and consisted of 68.6 ± 0.3% *cis* and 31.4 ± 0.3% *trans*. The equilibrium constant is then 2.18, giving $\Delta F = -0.62$ kcal/mole at 124.4°.

The dibromocyclobutanes were best prepared by the Cristol–Firth modification[5] of the Hunsdiecker reaction. In order to obtain a satisfactory yield of product, it was found necessary to modify the usual conditions for the reaction. By the simultaneous addition of bromine and 3-bromocyclobutanecarboxylic acid to a refluxing mixture of carbon tetrachloride and mercuric oxide,[6] about 50% of the dibromide was obtained. The isomers were separated and individually equilibrated using bromide ion in acetone at 124.4°; the equilibrium constant was found to be 2.07, again favoring the *cis* isomer.

Attempts to prepare 1,3-dichlorocyclobutane *via* the Hunsdiecker reaction on 3-chlorocyclobutanecarboxylic acid using a variety of conditions were not successful. The equilibrium constant was estimated by treating both *cis-* and *trans*-1-bromo-3-chlorocyclobutane with chloride ion in acetone at 124.4°. The mixtures of dichlorides obtained from the two chlorobromides were nearly identical giving an average equilibrium constant of 1.44, favoring the *cis* isomer. The equilibration data are summarized in Table I.

Table I. Equilibration Data for 1,3-Dihalocyclobutanes

Cyclobutane	*cis*/*trans*	$-\Delta F$ (124.4°), kcal/mole
Dichloro-	1.44 ± 0.01	0.29 ± 0.01
Dibromo-	2.07 ± 0.05	0.58 ± 0.02
Diiodo-	2.18 ± 0.03	0.62 ± 0.01

Having the equilibrium constants, it was of interest to determine the degree of puckering of the cyclobutane ring. In principle, one should be able to do this *via* a determination of the dipole moments of one of the isomeric pairs and of the corresponding monohalocyclobutane. The 2,2,4,4-tetramethylcyclobutane-1,3-dinitriles have been examined in this way.[7] The bromo isomers were chosen for this study and gave the data shown in Table II.

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(1) This investigation was supported by the Army Research Office, Durham.

(2) Taken in part from the Ph.D. thesis of G. M. L., University of Washington, 1964.

(3) *Cf.* J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3884, 3891 (1965), for a summary of the evidence for a puckered conformation.

(4) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(5) S. J. Cristol and W. C. Firth, *J. Org. Chem.*, **26**, 280 (1961).

(6) *Cf.* J. S. Meek and D. T. Osuga, *Org. Syn.*, **43**, 9 (1963).

(7) F. Lautenschlaeger and G. F. Wright, *Can. J. Chem.*, **41**, 863 (1963).

Table II. Dipole Moments

Compound	μ, D.
Bromocyclobutane	2.03
cis-1,3-Dibromocyclobutane	2.02
trans-1,3-Dibromocyclobutane	1.10

Remembering that the observed dipole moment is the difference between the C–Br and C–H bond moments, and assuming that there will be no significant interaction between the two C–Br dipoles which would lead to a change in the magnitude of the moments, the angles between the C–Br bonds may be calculated from the dipole moments. Since the moment for the *cis* isomer is equal to that for bromocyclobutane, the angle must be 120°. Similarly, the angle for the *trans* isomer must be 149°. The relevant geometry is shown in Figure 1.

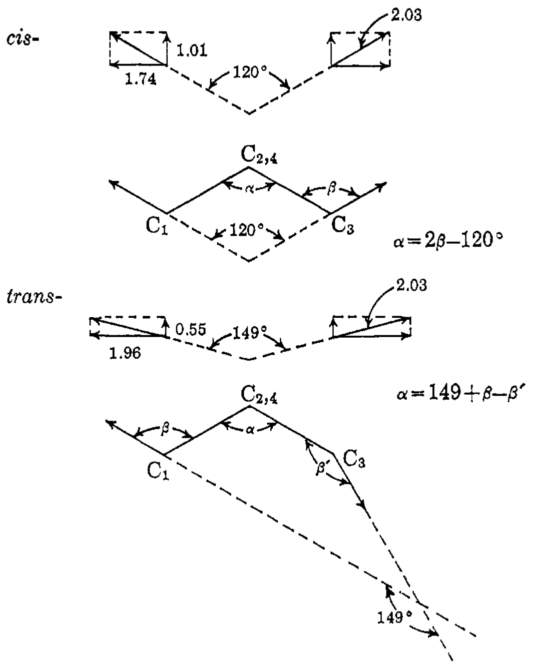

Figure 1. Geometry of the 1,3-dibromocyclobutanes.

If in the *trans* isomer the two angles β and β' were equal, the angle α would be 149°. The equality of the two angles would be a reasonable expectation, and the value of α which results is in excellent agreement with the corresponding value for cyclobutyl bromide as determined by microwave spectroscopy.[8] In the *cis* isomer, the value of β is required. It would be reasonable to expect β to be somewhat greater than 120° in order to minimize nonbonded repulsions. Rothschild and Dailey[8] found β to be 131° for cyclobutyl bromide; using this value, α is 142°. Considering the uncertainties in the estimation of the angle and the possibility that a small portion of the molecules may be present in a different conformation, this is also in satisfactory agreement with the value for cyclobutyl bromide. The data then show the *cis* isomer to be predominantly in the e,e conformation rather than a,a, and indicate the deviation from planarity of the cyclobutane ring to be 34 ± 4°.[9]

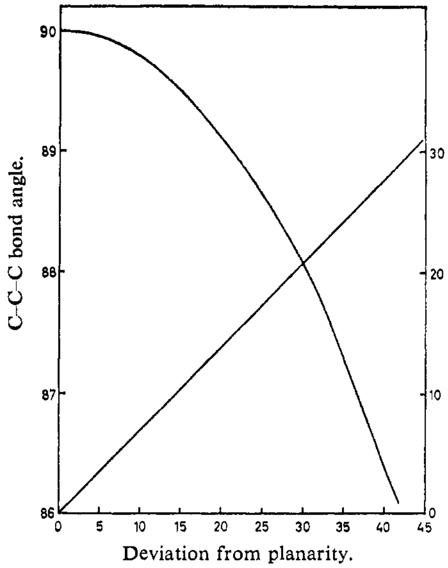

Figure 2. Relation between the bond angles, the torsional angles, and the deviation from planarity for the cyclobutane ring.

The small value of μ for the *cis* isomer indicates there is little if any a,a isomer present since this would have a dipole moment close to twice that for cyclobutyl bromide. It is not surprising that the *cis* isomer would prefer the e,e conformation since the dipole–dipole repulsion will be lower than for the a,a conformer. The *trans* isomer may assume only the a,e conformation.

The data obtained permits a consideration of two questions: (1) the reason for the puckered conformation of cyclobutane, and (2) the reason for the preference for the *cis* isomer at equilibrium. It has been suggested that a major factor responsible for the nonplanarity of the ring is the repulsion due to nonbonded substituents.[3,10] The present result which indicates the angle to be essentially the same for both dibromides makes this factor appear to be relatively unimportant. The only conclusion which appears to be in agreement with all of the available data is that the bent conformation results from an attempt to achieve more satisfactory torsional angles than those for the planar conformation.

The relationship between the deviation from planarity, the C–C–C bond angles, and the C–C–C–C torsional angles are indicated in Figure 2. The change in energy resulting from the change in torsional angle may be calculated from

$$v = 1.5(1 - \cos 3\phi) \text{ kcal/mole}$$

where ϕ is the torsional angle.[11] The change in energy as a function of the deviation from planarity is shown in Figure 3.

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(8) W. G. Rothschild and B. P. Dailey, *J. Chem. Phys.*, **36**, 2931 (1962).

(9) This conclusion has recently been confirmed by an electron diffraction study of these compounds by L. Walløe and O. Bastiansen (private communication from Professor Bastiansen) who found α to be 147° for the *cis* isomer and 148° for the *trans* isomer.

(10) This conclusion was based in part on the difference in degree of nonplanarity calculated for the *cis*- and *trans*-2,2,4,4-tetramethylcyclobutane-1,3-dinitriles.[7] The value for the *cis* isomer was calculated using $\beta = 125°$. Using the value derived from more recent structural studies,[8,9] the calculated angle for this isomer would be reduced by about 10°.

(11) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965), have shown that the barrier for substituted ethanes may be derived satisfactorily by summing the cos term given above and the nonbonded interaction terms for the six atoms attached to the two in question. The nonbonded terms will be taken into account separately.

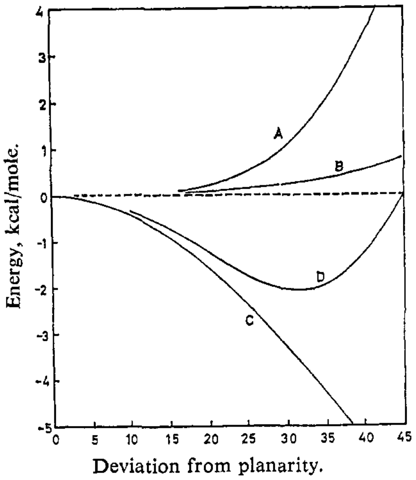

Figure 3. Energy terms for cyclobutane as a function of deviation from planarity. A is the C–C–C bond-bending term, B is the C–H nonbonded interaction term, C gives the change in the torsional energy, and D is the sum of A, B, and C.

The C–C–C bending force constant has been calculated by Rathjens, Freeman, Gwinn, and Pitzer[12] from an analysis of the vibrational spectrum of cyclobutane assuming D_{4h} symmetry. The interaction between bond bending and the torsional barrier was not considered in their treatment; it is probable that the inclusion of this interaction (which can be seen from Figure 3 to be large) will lead to a larger value for the force constant. In the absence of a detailed calculation, we shall guess that the true force constant will be about twice the observed constant. Thus, we shall use

$$v = 0.064(\Delta\theta)^2 \text{ kcal/mole}$$

where $\Delta\theta$ is the deviation from 90°. The energy as a function of the deviation from planarity is also indicated in Figure 3. For both curves, the values have been multiplied by a factor of four to take into account the four torsional angles in the first case and the four bond angles in the second.

The nonbonded interaction terms were estimated using the procedure described previously.[13] The H–H potential changed by only 0.1 kcal/mole over the whole range of angles examined and was neglected. The C–H potential changed somewhat more and is included in Figure 3. It, however, does not have much effect on the final result.

If the important terms leading to the difference in energy between planar and bent cyclobutane have been correctly estimated, the sum of the three terms will give the energy difference as a function of the deviation from planarity. This is indicated as curve D in Figure 3. The curve has a minimum at about 33°, which is in good accord with the experimental data.[8,9,14] The maximum stabilization of the bent conformation is calculated to be about 2 kcal/mole. This is in good accord with the data on the infrared spectrum,[12] and suggests that it is unlikely that the rate of inversion can be slowed sufficiently that it may be studied by low-temperature nmr spectroscopy. It can be seen that our simple approximation adequately accounts for the conformation of cyclobutane.

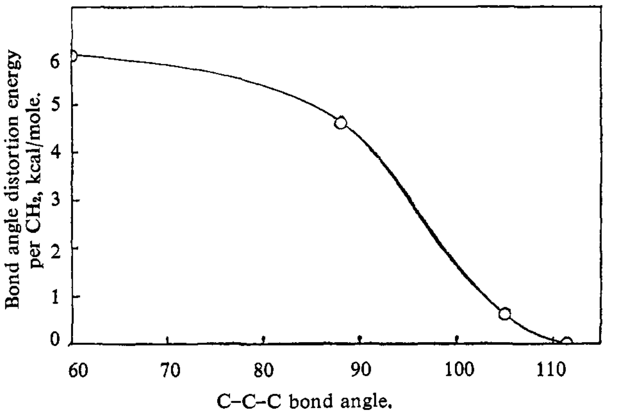

Figure 4. Energy required to bend a C–C–C bond angle from its equilibrium value to a smaller angle.

One difficulty with cyclobutane is that the application of the bond-bending potential function using a reasonable force constant and the deviation from tetrahedral angles gives a calculated thermochemical destabilization which is higher than the observed value. The addition of the term due to the torsional angles makes the calculated value even worse. It seems not unlikely that the difficulty results from the type of potential function used. Whereas the quadratic term is undoubtedly important at angles near the equilibrium angle, there appears to be no good reason to believe that this will also apply for relatively large changes in angle.

The approach used above may also give information concerning the potential due to large angle deformations. The "strain energy" of cyclobutane is 26 kcal/mole.[15] The destabilization due to the torsional angles (about 24°) will be 1.3 × 1.5 kcal/mole per torsional angle, or 7.7 kcal/mole for the four angles. Subtracting this from the strain energy and dividing by four gives a bond-bending energy of 4.6 kcal/mole per bond angle. With cyclopropane, having a strain energy of 27 kcal/mole,[16] the destabilization due to the torsional angles (0°) will be about 3.0 kcal/mole per angle or 9.0 kcal/mole for the molecule. Subtracting this from the strain energy and dividing by three gives a bond angle bending energy of 6.0 kcal/mole. A plot of these values against the C–C–C angles is shown in Figure 4 which also includes cyclohexane and cyclopentane. Cyclohexane is considered to be the normal "unstrained" alkane. The total strain energy for cyclopentane (6.5 kcal/mole)[15] was assumed to result from a balance between the energy terms due to bond angle distortion and torsional angles. The bond angle term is then about 3.25 kcal/mole or 0.65 kcal/bond angle mole. This would correspond to a C–C–C bond angle of about 106°.

The curve does not correspond to a quadratic potential function except for a small change in angle. A curve of this type may prove useful in semiempirical

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(12) G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953).

(13) K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

(14) P. N. Skanke, Thesis, University of Oslo, 1960, found the angle for cyclobutane to be 35°.

(15) S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **71**, 261 (1952).

(16) J. W. Knowlton and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **43**, 113 (1949).

estimates of strain energies.[17] One might at first think that it would be more satisfactory to consider interorbital angles rather than internuclear angles. The former have been estimated for some cycloalkanes by Coulson and Moffitt.[18] However, there is no reason to believe that the bond-bending potential results solely from the behavior of the electrons associated with the bond.[19] Repulsion between nuclei must also play an important (and perhaps dominant) role, and the distance between nuclei is associated with the simple C–C–C bond angle.

We may now turn to the second problem, the reason for the lower energy of the *cis* isomer as compared to the *trans* isomer. One possible factor is the interaction of the C–Br dipoles. Knowing the geometry of the two isomers, it is possible to estimate the magnitude of the Coulombic interactions of the dipoles in each. A simple approach is to consider each dipole as two point charges of appropriate magnitude separated by a distance equal to the C–Br bond length. The bond lengths, dipole moments, and related data are summarized in Table III. In making these calculations, the 1,3 C–C distance was taken as 2.15 A, and the geometry indicated in Figure 1 was used.

Table III. Dipole Moments and Bond Lengths

Type of bond	Bond length,[a] A	Dipole moment,[a] D.	Charge, esu × 10^{10}
C–Cl	1.78	2.05	1.15
C–Br	1.94	2.02	1.04
C–I	2.14	1.90	0.89

[a] Data from G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp 166, 213. The dipole moments are those for ethyl halides; cyclobutyl bromide and ethyl bromide have the same dipole moment.

In each case, the net Coulombic interaction was repulsive. The interaction was found to be largest with the chloride and least with the iodide. However, in each case there was no significant difference between the *cis* and *trans* isomers. One important factor which has been neglected is the effective dielectric constant of the medium.[20] It should be different for the two isomers since the hydrocarbon portion of the molecule is directly between the two dipoles in the *cis* isomer, whereas this is not the case for the *trans* isomer. It does not appear possible to make a quantitative estimate for this factor at the present time. Even though the contribution from the Coulombic interaction cannot be specified, it does not appear to be a major factor.

The increase in equilibrium constant favoring the *cis* isomer with increasing halogen size suggests that the main factor is the cross-ring halogen–carbon and halogen–hydrogen nonbonded interaction. An increase in size of the halogen would make the *trans* isomer, with relatively short cross-ring C–Br and H–Br distances from the axial halogen, less favored.

The H–C–C–H dihedral angles for cyclobutane approach those for cyclohexane; therefore, we might anticipate a similarity between the 1,3-dihalocyclobutanes and the 1,3-dihalocyclohexanes. The 1,3-dibromo- and -dichlorocyclohexanes have been investigated.[21] The *cis* isomers were found to have the e,e conformation and the *trans* isomers were found to have the a,e conformation. These results parallel those for the cyclobutanes. Unfortunately, the equilibrium constants for *cis–trans* interconversion were not determined and so the equilibrium constants for the cyclobutanes and cyclohexanes cannot be compared.

Experimental Section

3-Bromocyclobutanecarboxylic Acid. To a mixture of 73.2 g (0.38 mole) of methyl 3-bromocyclobutanecarboxylate[4] and 76 ml of 0.5 *N* sodium hydroxide was added with stirring 76 ml of 5 *N* sodium hydroxide, keeping the temperature between 4 and 11° (time required, 8 min). Stirring was continued for an additional 30 min at 14°, and then the mixture was stirred at room temperature for 2.5 hr. The solution was cooled in ice, and 37 ml of concentrated hydrochloric acid was added over a 5-min period, keeping the temperature below 15°. The oil was separated and the aqueous solution was extracted three times with ether. The combined organic solution was dried over magnesium sulfate, the ether was removed, and the residue was distilled to give 61 g (90 %) of 3-bromocyclobutanecarboxylic acid, bp 103–111° (0.2–0.8 mm). It partially solidified at room temperature. The nmr spectrum had bands at τ 7.10 (m, 4), 6.68 (m, 1), 5.53 (m, 1), −1.95 (s, 1).

1,3-Dibromocyclobutane. A 2-l. three-necked flask, wrapped with aluminum foil to exclude light, was equipped with a reflux condenser, stirrer, and a Y-tube containing two addition funnels. Into the flask was added 37.0 g (0.171 mole) of red mercuric oxide and 152 ml of reagent grade carbon tetrachloride. The solvent was brought to the reflux temperature with stirring, and 30.5 g (0.17 mole) of 3-bromocyclobutanecarboxylic acid in 152 ml of carbon tetrachloride was added simultaneously with 10 ml (0.188 mole) of bromine in 152 ml of carbon tetrachloride. The addition required 30 min. The mixture was cooled in ice and filtered, and the solids were washed with fresh solvent. The carbon tetrachloride was removed by distillation giving a residue which was distilled under reduced pressure to give 17.9 g (47%) of 1,3-dibromocyclobutane, bp 65–72° (14 mm). Analysis by vpc using diethylene glycol succinate indicated two components. The first, having a retention time of 7 min, was the *trans* isomer as indicated by its nmr spectrum: τ 6.92 (t, 4), 5.20 (p, 2).

Anal. Calcd for $C_4H_6Br_2$: C, 22.5; H, 2.8; Br, 74.7. Found: C, 22.4; H, 2.7; Br, 74.6.

The second component, having a retention time of 9 min, was the *cis* isomer. Its nmr spectrum had bands at τ 6.87 (m, 4) and 5.78 (m, 2).

Anal. Calcd for $C_4H_6Br_2$: C, 22.5; H, 2.8; Br, 74.7. Found: C, 22.4; H, 2.6; Br, 74.7.

Equilibration of *cis*- and *trans*- 1,3-Diiodocyclobutanes. To a tube containing 72 mg (0.23 mmole) of 1,3-diiodocyclobutane[4] containing 42% of the *trans* isomer was added 30 mg (0.22 mmole) of lithium iodide (Aldrich Chemical Co.) in 0.5 ml of reagent grade acetone. The tube was evacuated, degassed, and sealed under

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[17] As an example, we might consider norbornane. Here, the bridge C–C–C angle is 94° and the bridgehead C–C–C angles are 104° whereas the other angles are almost normal (*cf.* C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960); G. Dallinga, private communication). From the curve in Figure 4, the destabilization arising from a 94° angle is 3.3 kcal, and that from 104° is 0.8 kcal (and there are four such angles). The torsional angles for the two $-CH_2-CH_2-$ bridges are 0° giving twice 3-kcal destabilization, and the torsional angle between the bridgehead hydrogen and the methylene hydrogens is about 30° giving 1.5-kcal destabilization for each of the four angles. The sum is 18.5 kcal/mole which agrees well with the experimental value (18.5 kcal/mole: A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963)). This simple approach is also in agreement with the observations that except for bicyclo[1.1.0]butane, the strain energy for 1,2-fused bicyclic molecules may be estimated by summing the strain energies of the constituent rings: K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Conner, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave, and J. L. Franklin, *J. Am. Chem. Soc.*, **88**, 626 (1966).

[18] C. A. Coulson and W. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).

[19] L. S. Bartell, *Tetrahedron*, **17**, 177 (1962).

[20] J. G. Kirwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

[21] B. Franzus and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 2238 (1963); H. M. van Dort and T. J. Sekuur, *Tetrahedron Letters*, 1301 (1963).

vacuum. Another tube was made up in the same way except that diiodide containing 38% of the *trans* isomer was used. The tubes were placed in a bath at 124.4 ± 0.1° for 12 hr. Analysis of the products by vpc using diethylene glycol succinate indicated *cis*, 68.3 and 68.9%; *trans*, 31.7 and 31.1%. The average values were: *cis*, 68.6 ± 0.3%; *trans*, 31.4 ± 0.3%.

Equilibration of *cis*- and *trans*-1,3-Dibromocyclobutanes. To a tube containing 51 mg (0.23 mmole) of *trans*-1,3-dibromocyclobutane was added 20.2 mg (0.23 mmole) of lithium bromide (Matheson Coleman and Bell) in 0.5 ml of reagent grade acetone. Another tube was made up in the same fashion except that 50 mg of *cis*-1,3-dibromocyclobutane was used. The tubes were evacuated, degassed, and sealed under vacuum. After heating at 124.4 ± 0.1° for 23 hr, the contents were analyzed by vpc and indicated *cis*, 66.9 and 68.0%; *trans*, 33.1 and 32.0%. The average values were *cis*, 67.4 ± 0.6%; *trans*, 32.6 ± 0.6%.

Reaction of *cis*- and *trans*-1-Bromo-3-chlorocyclobutane with Lithium Chloride. To a tube containing 88 mg (0.52 mmole) of *trans*-1-bromo-3-chlorocyclobutane[4] was added 41 mg (0.96 mmole) of lithium chloride and 0.5 ml of reagent grade acetone. Another tube was made up in the same fashion except that 87 mg of *cis*-1-bromo-3-chlorocyclobutane was used. The tubes were sealed as above and heated at 124.4 ± 0.1° for 11.5 days. The contents were analyzed by vpc using GESF-96 and indicated mesityl oxide (4.5 min), *trans*-1,3-dichlorocyclobutane (5.5 min), *cis*-1,3-dichlorocyclobutane (6.0 min), *trans*-1-bromo-3-chlorocyclobutane (9 min), and *cis*-1-bromo-3-chlorocyclobutane (10 min). The dichlorides represented 67% of the dihalides. The dichloride peaks indicated *cis*, 59.1 and 58.9%; *trans*, 40.9 and 41.1%. The average values were: *cis*, 59.0 ± 0.1%; *trans*, 41.0 ± 0.1%.

Dipole Moments. A. Materials. Reagent grade benzene was dried by removal of the benzene–water azeotrope, and then a center cut was collected in a receiver protected from moisture. Cyclobutyl bromide was prepared by the method described above for 1,3-dibromocyclobutane except that water was removed as formed. Allylcarbinyl bromide was removed by the addition of bromine, and cyclopropylcarbinyl bromide was separated by preparative vpc on Ucon Polar. The *cis*- and *trans*-1,3-dibromocyclobutanes were also separated by preparative vpc and appeared to be at least 99% pure.

B. Apparatus. A Dipolemeter DM01 (Wissenschaftlich-Technische Werkstätten, Germany) was used for the determination of the dielectric constants. The instrument was calibrated by Dr. M. H. Krackov of the Department of Pharmacology, Yale University, and was made available by Professor H. G. Mautner of that department. We thank them for their invaluable assistance.

C. Calculations. The method of Halverstadt and Kumler[22] was employed in calculating the dipole moments from the dielectric constants of the benzene solutions of the compounds. Six solutions having weight fractions of solute from 0.0005 to 0.016 were used, and the dipole moments were calculated using the method of least squares. The experimental data are given in the thesis of G. M. L. (available through University Microfilms) and the results are summarized in Table II.

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[22] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

Acetolysis of Bridged Cyclobutylcarbinyl Tosylates[1]

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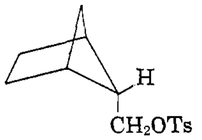
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut. *Received June 4, 1966*

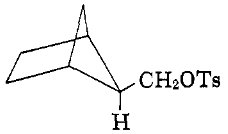
Abstract: The anomalously small degree of rearrangement in the acetolysis of *endo*-bicyclo[2.1.1]hexane-5-methyl tosylate has been investigated. The unrearranged product was shown probably to arise *via* an SN2 displacement since complete inversion of configuration was found. The SN1 rate for the *endo* isomer was 0.01 times as great as that for the *exo* isomer; the difference probably results from a steric effect. The solvolysis of the bicyclo[3.1.1]heptyl-5-methyl tosylates was also studied.

Our earlier observation that the acetolysis of *endo*-bicyclo[2.1.1]hexane-5-methyl tosylate gives largely the unrearranged acetate and only a small amount of norbornyl acetate[3] has led us to examine the acetolysis of several cyclobutycarbinyl tosylates. The compounds studied were the *endo*- and *exo*-bicyclo[2.1.1]hexane-5-methyl tosylates (I and II), the *endo*- and *exo*-bicyclo[3.1.1]heptane-6-methyl tosylates (III and IV), and cyclobutylcarbinyl tosylate itself. The syntheses of the four parent alcohols have been described.[3,4]

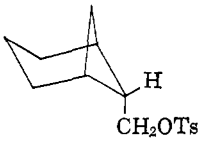
The rates of acetolysis were determined in the usual fashion and in each case the theoretical infinity titer was obtained. The rate constants are summarized in Table I. The product studies were carried out by running the reaction through 10 half-lives, diluting with water, and extracting with pentane, followed by vpc analysis of the concentrated solution. The products of the reactions are summarized in Table II.



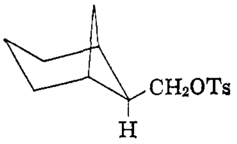
I



II



III



IV

The unrearranged acetate obtained from I, as well as the other tosylates, could arise either *via* a direct SN2 solvolytic displacement by acetic acid or *via* attack on some intermediate ion. The former route would be expected to give complete inversion of configuration, whereas the latter might be expected to give at least partial racemization or possibly retention of configuration. In order to eliminate one of these possibilities, *endo*-bicyclo[2.1.1]hexane-5-carboxalde-

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[1] This work was supported by the Army Research Office, Durham, and forms part of the Ph.D. thesis of B. A. H., 1966.

[2] National Institute of Health Predoctoral Fellow, 1963–1966.

[3] K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

[4] K. B. Wiberg and B. A. Hess, Jr., *J. Org. Chem.*, **31**, 2250 (1966).