acid, and 300 ml of methylene chloride was stirred at room temperature for 10 days. The excess peracid was destroyed by the cautious addition of saturated sodium sulfite solution. The mixture was filtered and the layers were separated. The organic layer was washed with 100 ml of saturated sodium carbonate solution and 100 ml of saturated sodium chloride solution. After drying over sodium sulfate, the solvent was removed by distillation through a 12-in. Vigreux column leaving 10.5 g of a slightly yellow oil. Vpc and ir analysis indicated the presence of less than 5% of recovered ethyl ketone.

Bicyclo[2.1.1]hexan-*exo*-5-*d*-*endo*-5-ol. A solution of 10.5 g (68 mmoles) of the bicyclo[2.1.1]hexyl 5-propionate in 25 ml of ether was slowly added to a suspension of 5.0 g of lithium aluminum hydride in 150 ml of ether. The mixture was then stirred at reflux for 45 min. The excess lithium aluminum hydride was destroyed by the careful addition of 15 ml of water. The mixture was filtered and the solids were washed with 50 ml of ether. After drying the solution over magnesium sulfate, the solution was concentrated to a volume of 15 ml by distillation through a 12-in. Vigreux column. The mixture was separated by vpc ($^3/_8$ in. × 10 ft 20% Carbowax 20M at 135°) and the alcohol was collected as 4.6 g (69%) of a volatile solid. Except for the hydrogen which had been replaced by deuterium, the nmr spectrum corresponded to that of an authentic sample of the alcohol.[5] The alcohol was converted to the tosylate as previously described.[5]

Solvolysis of Bicyclo[2.1.1]hexyl-*exo*-5-*d* *endo*-5-Tosylate in 70% Aqueous Ethanol. An ether solution of the tosylate derived from 1.68 g of the alcohol was added over 5 min to a solution of 2.0 g (51 mmoles) of sodium hydroxide in 500 ml of 70% aqueous ethanol. The mixture was stirred at room temperature for 2 hr and then was poured into 500 ml of ice water. The resulting solution was extracted eight times with 50 ml of pentane. The pentane solution was washed with 50 ml of saturated sodium chloride solution. After drying over potassium carbonate, the pentane was removed by distillation through a 12-in. Vigreux column. The residue was bulb-to-bulb distilled *in vacuo* at 0.05 mm (bath at 40°). The distillate was analyzed by vpc ($^3/_8$ in. × 15 ft 20% Carbowax 20M at 80°) showing four components with retention times of 30, 35, 60, and 70 min. The first and major component (55%) was identified as *exo*-2-ethoxybicyclo[3.1.0]hexane-1-d_1. The second component (35%) was a mixture of two ethyl ethers which could not be separated by vpc. Inspection of the nmr spectrum indicated that the collected peak was a 3:1 mixture of *endo*-2-ethoxybicyclo[3.1.0]hexane-1-d_1 and probably 4-ethoxycyclohexene-2-d_1. The remaining peaks corresponded to the epimeric northujyl alcohols.

The nmr spectrum of *exo*-2-ethoxybicyclo[3.1.0]hexane-d_1 showed absorption at τ 6.19 (one-proton doublet, $J = 5$ cps), 6.53 (two-proton quartet, $J = 7$ cps), 7.90–9.25 (eight-proton complex multiplet), 9.42–9.74 (one-proton multiplet), and 9.90–10.16 (one-proton multiplet).

The nmr spectra of the other components were not clearly definable, either because of an impure sample or because of a scarcity of sample.

From the nmr spectrum of the labeled *exo*-2-ethoxybicyclo[3.1.0]hexane, it can be concluded that no hydride shift occurs during the solvolysis process.

Reaction of *endo*-Bicyclo[2.1.1]hexyl 5-Tosylate with Tetra-*n*-butylammonium Chloride. An ethereal solution (50 ml) of 1.43 g (5.7 mmoles) of *endo*-bicyclo[2.1.1]hexyl 5-tosylate was added to an ice-cooled solution of 29.0 g (100 mmoles) of tetra-*n*-butylammonium chloride in 110 ml of acetone. The solution was allowed to stand in a refrigerator for 48 hr. The mixture was poured into 200 ml of ice water and the layers were separated. The aqueous layer was extracted five times with 50 ml of pentane. The combined organic extracts were washed with 50 ml of saturated sodium chloride solution. After drying over sodium sulfate, the solvent was removed by distillation through an 18-in. column packed with glass beads. The residue was bulb-to-bulb distilled *in vacuo* (1 mm, bath at 50–60°) into a Dry Ice–acetone cooled trap.

The nmr spectrum of the distillate indicated that the product was mainly a mixture of the *exo*- and *endo*-northujyl chlorides ($\sim$4:1). Attempted separation by vpc was unsuccessful, probably due to the decomposition of the chlorides on the column. No evidence for *endo*-5-chlorobicyclo[2.1.1]hexane was found in the nmr spectrum.

Kinetic Method. The kinetic method was the same as that described earlier.[4]

Acid-Catalyzed Solvolyses of Bicyclobutane Derivatives. Stereochemistry of the Cyclopropylcarbinyl–Cyclopropylcarbinyl and Related Rearrangements[1]

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Received November 8, 1968

Abstract: The stereochemistry of the acid-catalyzed addition of acetic acid, methanol, and water to bicyclobutane and tricyclo[4.1.0.0^{2,7}]octane has been determined. The proton addition proceeds with retention of configuration. Similar results have been obtained in the addition of chlorine to bicyclobutane. The cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement has been found to proceed in a stereoselective fashion. Similar results were obtained for the conversion of the allylcarbinyl ion to the cyclopropylcarbinyl ion. CNDO calculations, with parameters optimized for hydrocarbons, give results which are in accord with the observations, and suggest that the lower energy form of the cyclobutyl cation is puckered.

We have previously observed that bicyclobutane and its derivatives react rapidly with electrophiles.[3] It was of interest to us to determine whether or not the reactions were stereospecific, and to determine the direction from which the proton was transferred. In two previously reported cases, the stereochemistry was determined. Blanchard and Cairncross[4] reported that the reaction of 3-methylbicyclobutane-1-nitrile with water gave *cis* addition to the central C–C bond. Dauben and coworkers[5] found that the reaction with

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[1] This investigation was supported by the U. S. Army Research Office and the National Science Foundation. We also wish to acknowledge NSF Grant GP-6938 which enabled the purchase of a 100-MHz nmr spectrometer.

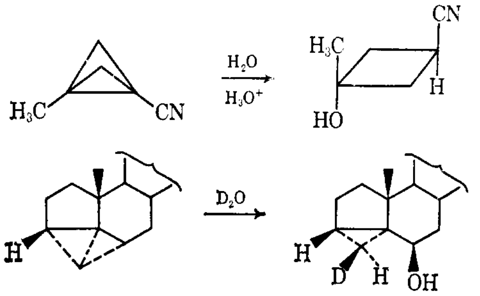
[2] Institute for Organic Chemistry, University of Munich.

[3] K. B. Wiberg, G. M. Lampmann, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

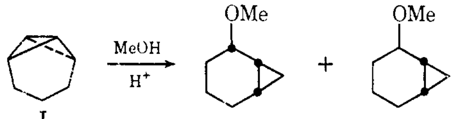
[4] E. P. Blanchard, Jr., and A. Cairncross, *J. Am. Chem. Soc.*, **88**, 487 (1966).

[5] W. G. Dauben and F. G. Willey, *Tetrahedron Lett.*, 893 (1962); W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

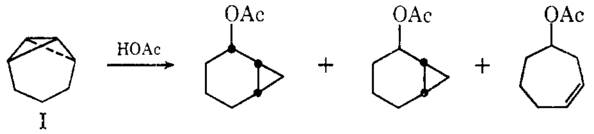
water of the bicyclobutane formed by the photolysis of 3,5-cholestadiene gave predominantly a cyclopropylcarbinyl derivative. Using deuterium oxide, they found the addition of the proton to occur with retention of configuration, whereas inversion was noted at the center bearing the hydroxyl function. The first of these reactions probably has its course largely governed by the methyl substituent, leading to the tertiary cyclobutyl cation. The second reaction might easily be atypical since the polycyclic bicyclobutane derivative has an unusually large amount of strain, and is unusually reactive, even for a bicyclobutane. Consequently, we have examined the addition of acetic acid and methanol to tricyclo[4.1.0.0^{2,7}]heptane (I) and to bicyclobutane.



The reaction of I was of particular interest since the substituents on the bicyclobutane ring facilitate the determination of the course of the reaction. The reaction of I with acidified methanol occurred rapidly and led to a mixture of *cis*- and *trans*-2-norcaranyl methyl ethers (IIa, IIb). The reaction of I with glacial acetic acid also occurred rapidly, and gave the norcaranyl acetates as well as 4-acetoxycycloheptene.

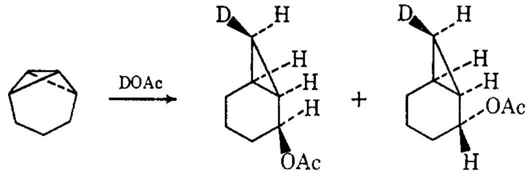


I IIa IIb

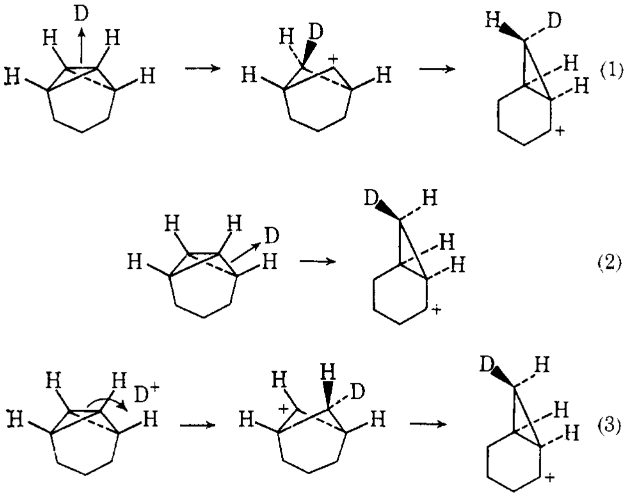


I

The nmr spectra of norcarane and of *cis*-2-norcaranol have been examined by Dauben and Wipke.[6] In each case, they found that the *endo* proton of the cyclopropane ring appeared upfield from all other protons. When the reaction was carried out in acetic acid-*d*, the nmr spectra of the norcaranyl acetates lacked the upfield band, indicating that the added proton appeared exclusively in the *endo* position. In the *cis* compound, the band for the *exo* proton is at τ 9.49 and appears as a complex multiplet in the unlabeled material. In the deuterium-labeled sample, the band collapses to a triplet at τ 9.48 with $J = 9.0$ Hz. This provides additional evidence for the assignment for only the *exo* proton could have this large a coupling constant with the bridgehead hydrogens. The reaction then proceeds as shown. This result corresponds to that of Dauben and Wipke,[4] and probably represents a general mode of reaction. The formation of the two epimeric acetates is characteristic of the bicyclo[4.1.0]heptyl-2 cation.[7]

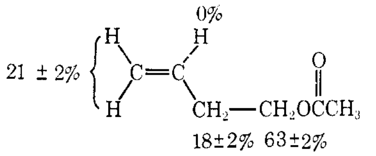


The reaction might proceed in any one of three ways. (1) The proton attacks the central bond giving a cyclobutyl cation which rearranges to the more stable secondary 2-norcaranyl cation. (2) One of the four outside bicyclobutane bonds is attacked and gives the 2-norcaranyl ion directly. (3) An S_E2-like attack of the proton at a bridgehead carbon cleaves the central bond and leads to the cyclobutyl cation. It is clear that process 1 would lead to the wrong isomer, and so it may be excluded. Both (2) and (3) lead to the correct product. These two processes will be discussed in more detail in a later section.



We may now consider the reactions of bicyclobutane itself. When bicyclobutane was allowed to react with acetic acid, a mixture of 67% cyclopropylcarbinyl acetate, 23% cyclobutyl acetate, and 10% allylcarbinyl acetate was formed. The product ratio corresponds closely to that found by Roberts in the acetolysis of cyclopropylcarbinyl tosylate.[8]

The reaction of bicyclobutane with acetic acid-*d* gave the same three products. The location of the deuterium was determined for each of the compounds by the use of the nmr spectrum. The spectrum of allylcarbinyl acetate was easily analyzed, giving the result shown. The



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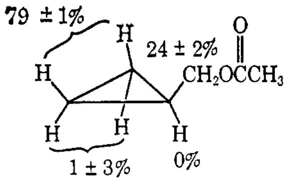
[6] W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, 32, 2976 (1967).

[7] K. B. Wiberg and B. A. Hess, Jr., *J. Am. Chem. Soc.*, **89**, 3015 (1967).

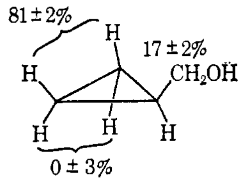
[8] It might be noted that D. D. Roberts [*J. Org. Chem.*, **30**, 23 (1965)] reports that the ethanolysis of cyclopropylcarbinyl tosylates gives only cyclopropylcarbinyl ethyl ether. If this were the case, it would be particularly significant. However, when we repeated this experiment, the products were found to be 75% cyclopropylcarbinyl ethyl ether and 25% cyclobutyl ethyl ether.

nmr spectrum of cyclopropylcarbinol has been analyzed in detail by Barth.[9] Using his assignments, the deuterium distribution was found to be

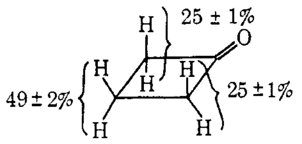


The nmr spectrum of cyclobutyl acetate was too complex to permit an analysis at this time.

The reaction of bicyclobutane with water containing a trace of acid also was carried out. Cyclopropylcarbinol and cyclobutanol were found in equal amount, and only a trace of allylcarbinol was noted. The deuterium distribution in the cyclopropylcarbinol was

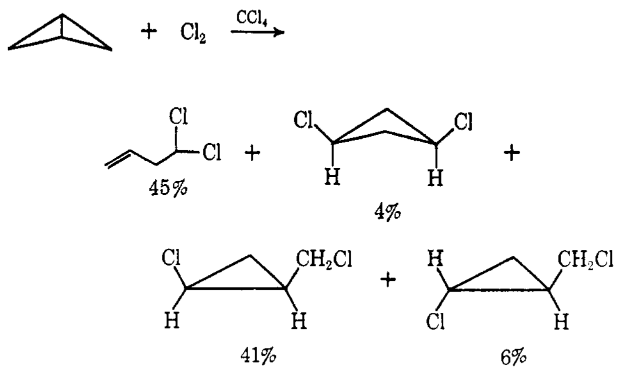


The deuterium distribution in the cyclobutanol could not be determined directly because of the complexity of its nmr spectrum. Cyclobutanol was oxidized to cyclobutanone with the pyridine–chromium trioxide complex.[10] The nmr spectrum indicated the following deuterium distribution.



The above results, in which essentially all of the ring deuterium appears *cis* to the carbinyl group, again indicates the stereochemistry of the ring opening reaction to involve retention of configuration at the carbon to which the proton is added.

It might be noted that the acid-catalyzed solvolysis of cyclopropanol also proceeds with retention of configuration at the carbon which accepts the proton.[11] It was interesting to note that the addition of chlorine proceeded with the inverse stereochemistry in this case.[11] In order to see if a corresponding change occurred with bicyclobutane, the stereochemistry of the addition of chlorine was examined. The reaction product was complex, and consisted of seven components. Four of these were formed in large enough amount to be separated by vpc and identified by their nmr spectra. Here again, the cyclopropylcarbinyl derivative was formed largely with retention of configuration. The other products are the corresponding cyclobutyl and allylcarbinyl derivatives. Thus, the chlorination proceeds in a fashion similar to the solvolysis, except for the lower degree of stereoselectivity.



Having presented the experimental data, we now wish to try to interpret them in the light of σ molecular orbital calculations. The problems to be considered are (1) the mechanism of addition of a proton to a bicyclobutane, (2) the nature of the process whereby ring deuterium is transferred to the carbinyl position in the cyclopropylcarbinyl ion, and (3) the nature of the cyclobutyl cation.

Protonation of Bicyclobutane. One may envision a number of different paths for the attack of a proton on bicyclobutane. The modes which were considered are as follows.

(1) The proton approaches the 1,3-central bond symmetrically from above.

(1′) The proton approaches the 1,3-central bond symmetrically from below.

(2) The proton approaches C_1 in an S_E2-like fashion. The line of approach lies in the plane which contains C_1 and C_3 and bisects the molecule, and forms a 43° angle with the C_1–C_3 line.

(3) The proton approaches the center of the C_1–C_2 bond on a line perpendicular to the $C_1C_3C_2$ plane.

(4) The proton approaches the center of the C_1–C_2 bond along a line that bisects the angle $C_1C_3C_2$.

The geometry of bicyclobutane was taken as that suggested by Haller and Srinivasan,[12] and the energy of the bicyclobutane–proton complex was calculated using the CNDO method[13] as a function of distance between the two starting at 3 Å. The results of the calculations are indicated in Figure 1.

In interpreting the results of the calculations, it must first be said that the energies were not minimized with respect to the carbon coordinates for each proton–bicyclobutane distance. Although this minimization procedure should be done, in the present case it was prohibitively expensive. Comparisons of two similar modes of reaction (such as 1 with 1′ or 3 with 4) should be reliable, but other comparisons are much less certain. It can be seen that mode 1 is calculated to be strongly favored over 1′, and that mode 4 is calculated to be favored over 3. Modes 1 and 4 appear to be the most likely paths for reaction.

The reaction modes which correspond to the predominant stereochemistry of the reaction are, as indicated above, 2, 3, and 4. Of the three, mode 4 is favored by the calculations, and corresponds to the mode of protolytic ring opening of cyclopropane suggested by Baird and Aboderin.[14] Mode 1 is actually very similar

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[9] K. B. Wiberg and D. Barth, unpublished results.

[10] M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

[11] C. H. DePuy, W. G. Arney, Jr., and D. H. Gibson, *J. Am. Chem. Soc.*, **90**, 1830 (1968).

[12] I. Haller and R. Srinivasan, *J. Chem. Phys.*, **41**, 2745 (1964).

[13] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); **43**, S136 (1965); **44**, 3289 (1966).

[14] R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964).

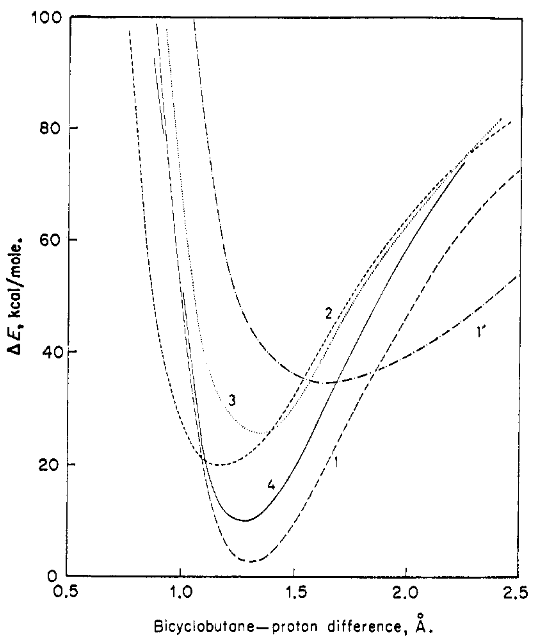
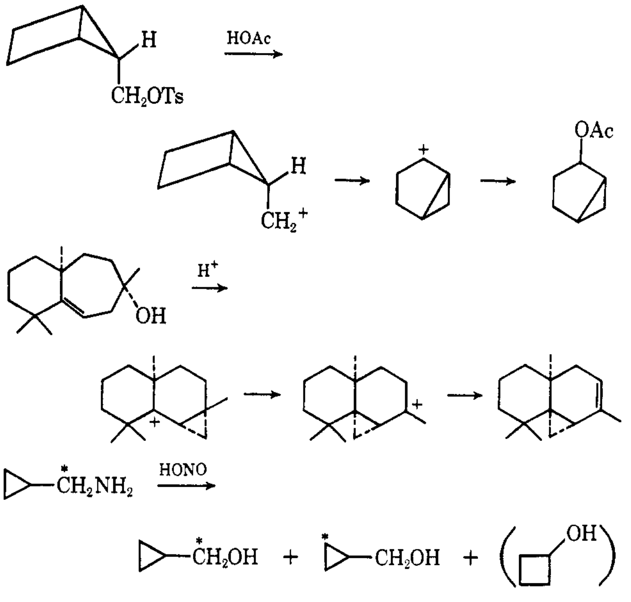
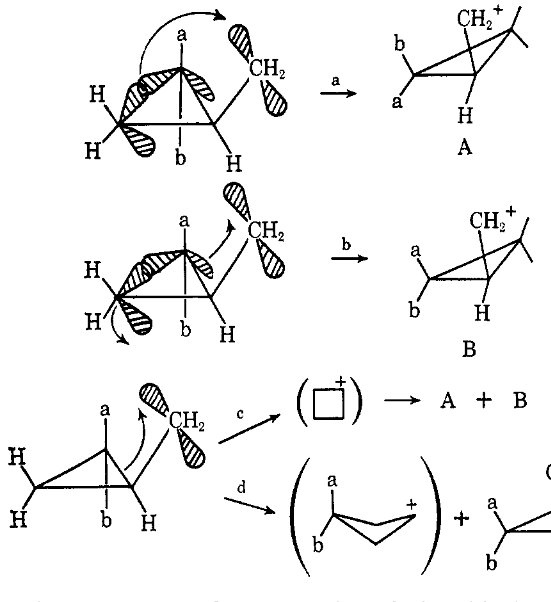


Figure 1. Energies for several models for protonation of bicyclobutane.

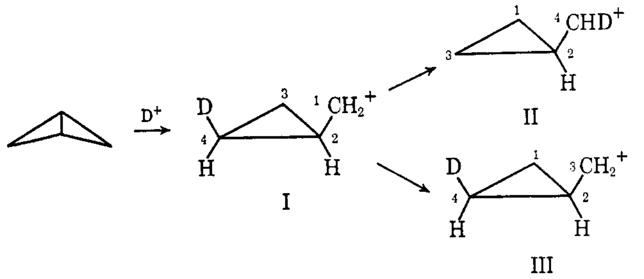
to mode 4 except it involves a different bond. The 1,3-dihalocyclobutanes found in the addition of halogens to bicyclobutane may well originate from such an attack. In summary, both the experimental data and the calculations are in accord with a mechanism involving attack of a proton on a cyclopropane C–C bond with the approach of the proton being in the plane of the cyclopropane ring.

Cyclopropylcarbinyl-Cyclopropylcarbinyl Rearrangement. The transfer of ring deuterium to the carbinyl position of the cyclopropylcarbinyl cation involves the rearrangement of one cyclopropylcarbinyl ion to another. This type of process has been observed previously, as in the rearrangement of bicyclo[2.1.0]pentane-5-carbinyl ion to the bicyclo[3.1.0]hexyl-2 cation,[15] the rearrangement of widdrol to thujopsene,[16a] the rearrangement of the dehydroadamantyl cation,[16b] and the ^{14}C-label scrambling process of the cyclopropylcarbinyl cation itself.[17] Three courses are possible for the reaction. First, the 2,3 bond may be involved, leading to rotation of the methylene group in the process. Second, the backside of the orbital forming the 2,3 bond may be involved, leading to no rotation of the methylene group. Finally, the rearrangement may proceed *via* a cyclobutyl cation as an intermediate or activated complex. Here, different stereochemical results would be obtained if the ring is planar or if it is puckered. In the first case, the relationship between a and the carbinyl carbon is inverted, whereas in the second it is retained. In the third, a mixture of A and B would be obtained if the cyclobutane ring were planar, and B should be obtained if it is not.





The path of the solvolysis of bicyclobutane may be described as shown. The first intermediate is I, and this may rearrange to II or III. Because of the symmetry of the molecule, the two species must be formed in equal amounts. Since essentially all of the deuterium is in the position *cis* to the carbinyl group, III must have been formed with the stereochemistry shown. Thus, paths b and d are the two which are allowed by the experimental results.



The amount of the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement which occurred in this case was relatively small. In order to examine a case in which the degree of rearrangement was larger, and in which we

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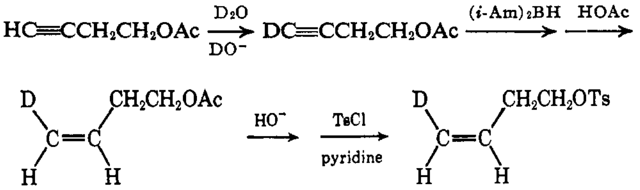
[15] K. B. Wiberg and A. J. Ashe III, *Tetrahedron Lett.*, 4245 (1965); *J. Am. Chem. Soc.*, **90**, 63 (1968).

[16] (a) W. G. Dauben and L. E. Friedrich, *Tetrahedron Lett.*, 1735 (1967); (b) J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4303 (1968).

[17] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951).

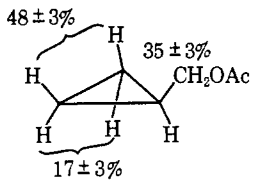
may see how the allylcarbinyl cation is converted to the cyclopropylcarbinyl cation, we have examined the solvolysis of a deuterium-labeled allylcarbinyl tosylate. The reactant was prepared as shown. The allylcarbinyl



$$HC{\equiv}CCH_2CH_2OAc \xrightarrow[DO^-]{D_2O} DC{\equiv}CCH_2CH_2OAc \xrightarrow{(i\text{-}Am)_2BH} \xrightarrow{HOAc}$$

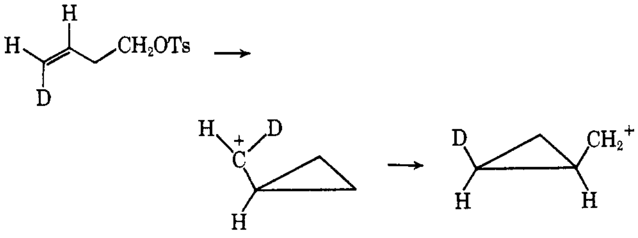
acetate was shown to have the stereochemistry shown above by its nmr spectrum, and contained 95% of one deuterium. Solvolysis in acetic acid gave allylcarbinyl acetate, cyclopropylcarbinyl acetate, and cyclobutyl acetate. The allylcarbinyl acetate had the same nmr spectrum as that formed in the synthetic sequence, and thus was formed without isomerization about the double bond or carbon rearrangement. It is probably the product of an S_N2-type displacement reaction.

The cyclopropylcarbinyl acetate had the following deuterium distribution



It can be seen that the deuterium is essentially statistically distributed between the ring and the carbinyl position. This in good agreement with the results of Servis and Roberts,[18] who solvolyzed allylcarbinyl-1,1-d_2 tosylate. The ring deuterium is still predominantly in the *cis* position.

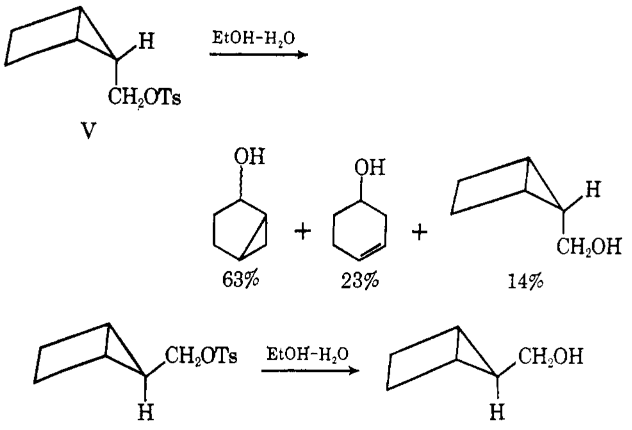
The cyclopropylcarbinyl acetate may be formed as shown. Since the deuterium is *cis* to the carbinyl group



IV

in the reactant, the first step would almost certainly lead to a cyclopropylcarbinyl cation in which the deuterium lies over the cyclopropane ring. Rearrangement of this ion by either path b or d (above) would lead to an ion having the deuterium *cis* to the carbinyl carbon. However, it is clear that in this case, in which the rearrangement steps must have occurred several times so as to give the statistical deuterium distribution, there is a process by which some deuterium appears in the *trans* position. This could easily occur by one or both of the following. First, the barrier to rotation of the methylene group in IV may be low enough so that rotation may compete with rearrangement. The species in which the deuterium is away from the ring will lead to a cyclopropylcarbinyl ion having the deuterium *trans* to the carbinyl carbon. Second, if path d represents the correct process, the intermediate puckered cyclobutyl cation may (and probably does) have a low enough barrier to ring inversion to permit this to compete with rearrangement.

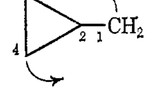
It should be noted that the type of process described above is required to explain the results of some solvolyses, such as that of the bicyclo[2.1.0]pentane-5-methyl



VI

tosylates.[15] If the reaction occurs *via* paths b and d, only V is able to rearrange to the bicyclo[3.1.0]hexyl-2 cation. The corresponding rearrangement of VI would lead to a cation having a *trans*-ring fusion.

It is difficult to find a definitive experimental test which would distinguish between paths b and d. For this reason, we have attempted to calculate energies for reasonable models of the activated complexes using the CNDO procedure. As a model for path b we considered C_1 approaching C_3 from the backside as the C_3C_4 bond was broken. In the process, C_1 and C_4 were



allowed to move on a circle with C_2 at its center, and defined by C_1, C_3, and C_4. The total angle of rotation to give the rearranged ion is 76.9°. The coordinates of C_2 and C_3 remained fixed. The activated complex is reached when the angle α is 76.9/2 and $C_1C_3 = C_3C_4$. The energy as a function of α is given in Table I.

Table I. Calculated Energies for Path b as a Function of the Angle of Rotation

α	ΔE, kcal/mole[a]	$R(C_1C_3)$	$R(C_3C_4)$
0.0	0	2.603	1.540
7.69	10	2.545	1.686
2 × 7.69	23	2.475	1.826
4 × 7.69	45	2.297	2.079
5 × 7.69	49	2.195	2.195

[a] The energies are based on the empirical energy conversion factor of K. B. Wiberg, *J. Am. Chem. Soc.*, **90**, 59 (1968).

It should be noted that this rearrangement does not go through a species of C_{3v} symmetry (tricyclobutonium ion) where the highest occupied and lowest occupied orbitals are expected to be degenerate. The calculated

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(18) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 3773 (1964); **87**, 1331 (1965).

Table II. Calculated Energies of the Cyclobutyl Cation as a Function of Geometry

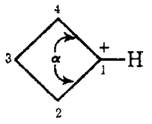
β, deg	α, deg 60	70	80	90	100	110	120
0	−31.9596 (2.677) [0.112]	−31.9953 (2.523) [0.066]	−32.0097 (2.359) [0.039]	−32.0136 (2.178) [0.037]	−32.0043 (1.980) [0.079]	−31.9807 (1.767) [0.205]	−31.9549 (1.540) [0.455]
20			−32.0080 (2.324) [0.048]	−32.0152 (2.144) [0.062]	−32.0133 (1.950) [0.145]		
40	−31.9007 (2.310) [0.092]	−31.9767 (2.371) [0.080]	−32.0055 (2.216) [0.089]	−32.0239 (2.047) [0.148]	−32.0414 (1.860) [0.278]	−32.0551 (1.660) [0.434]	−32.0120 (1.447) [0.583]
60			−32.0147 (2.043) [0.195]	−32.0523 (1.886) [0.288]	−32.0818 (1.715) [0.399]	−32.0753 (1.530) [0.516]	
80		−31.9825 (1.933) [0.281]	−32.0538 (1.807) [0.349]	−32.0940 (1.668) [0.426]	−32.0938 (1.517) [0.513]		
90	−31.8203 (1.886) [0.308]	−32.0033 (1.783) [0.368]	−32.0742 (1.668) [0.429]	−32.0944 (1.540) [0.496]	−32.0506 (1.400) [0.579]	−31.8926 (1.249) [0.693]	
100			−32.0657 (1.516) [0.511]	−32.0416 (1.400) [0.576]			
110	−31.7767 (1.530) [0.506]		−31.9728 (1.353) [0.615]	−31.8710 (1.249) [0.688]			
120		−31.7691 (1.261) [0.708]					

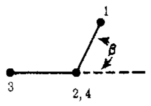
[a] The first number in each entry is the energy in atomic units, the number in parentheses is the C_1–C_3 distance, and the number in brackets is the C_1–C_3 bond index.

activation energy for this process (~50 kcal/mole) appears rather high. Apparently, the stretching of the C_3C_4 bond from 1.54 to 2.195 Å is not compensated by the formation of the C_1C_3 bond in this region of weak bonding. A more appropriate model might be one in which C_1 approaches C_3 on the same circle without moving C_4. This model is quite similar to that considered next.

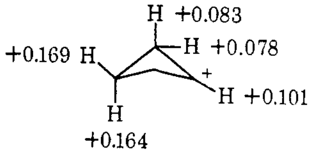
The Cyclobutyl Cation. In order to consider the second possible path for the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement, it is first necessary to consider the intermediate cyclobutyl cation. Our CNDO calculations[19] suggested that the species formed by the ionization of an equatorial leaving group was of lower energy than that formed by ionization of an axial leaving group. The primary stabilization in the former case arose from a 1,3 interaction leading to species which may be described as a symmetrical bicyclobutonium ion. Subsequently, the extended Hückel method was applied to the problem by Davis and Ohno[20a] and by Baldwin and Foglesong.[20b] Davis and Ohno concluded that the most stable species was a planar cyclobutyl cation whereas Baldwin and Foglesong found the lowest energy species to be puckered.

We wish to present the results of more detailed CNDO calculations using parameters which are optimized for hydrocarbons and which appear to give satisfactory results for carbonium ions.[21] The energies of several conformations of the cyclobutyl cation were calculated as a function of the angles α and β. In all the calculations, R(C–C) = 1.54 Å, R(CH) = 1.10 Å, the HCH angles were 110°, and the hydrogen attached to C_1 was in the $C_1C_2C_4$ plane. The results are summarized in Table II.

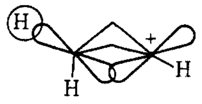




It can be seen that there is a rather deep and broad energy minimum at $\alpha \approx 90°$ and β = 80–90°. The structure with a minimum energy could be regarded as a symmetrical bicyclobutonium ion. The primary stabilization of this species is *via* a 1,3-cross ring interaction having a bond index[20] of 0.5. The calculated charge distribution for the favored conformation is



It can be seen that considerable charge is transferred to the equatorial hydrogen at C_3. As indicated previously,[20] this results from an interaction between the empty p orbital and the p component of the orbital which bonds to the C_3 equatorial hydrogen. Similarly,



considerable charge is transferred from the axial C_3 carbon as a result of overlap of the hydrogen s orbital with the empty p orbital. This description of the cyclobutyl cation as a puckered species is in accord with our observations on the bridgehead bicyclo[4.2.0]octyl and bicyclo[3.2.0]heptyl derivatives,[22] and generally is in accord with all of our observations on cyclobutyl species.

In order to examine the possibility that the minimum energy structure had a different hydrogen geometry than that used above, the following modes of distortion were examined: (1) bending the hydrogen attached to C_1 out of the $C_2C_1C_4$ plane, (2) rotation of the methylene group at C_3 around an axis through C_3 and perpendicular to the plane defined by the methylene group, (3) rotation of the methylene group at C_3 around an axis through C_3 which bisects the methylene group, and (4)

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(19) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(20) (a) R. E. Davis and A. Ohno, *ibid.*, **24**, 2063 (1968); (b) J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4311 (1968).

(21) See Table I, footnote *a*.

(22) K. B. Wiberg and J. E. Hiatt, *J. Am. Chem. Soc.*, **92**, 544 (1970).

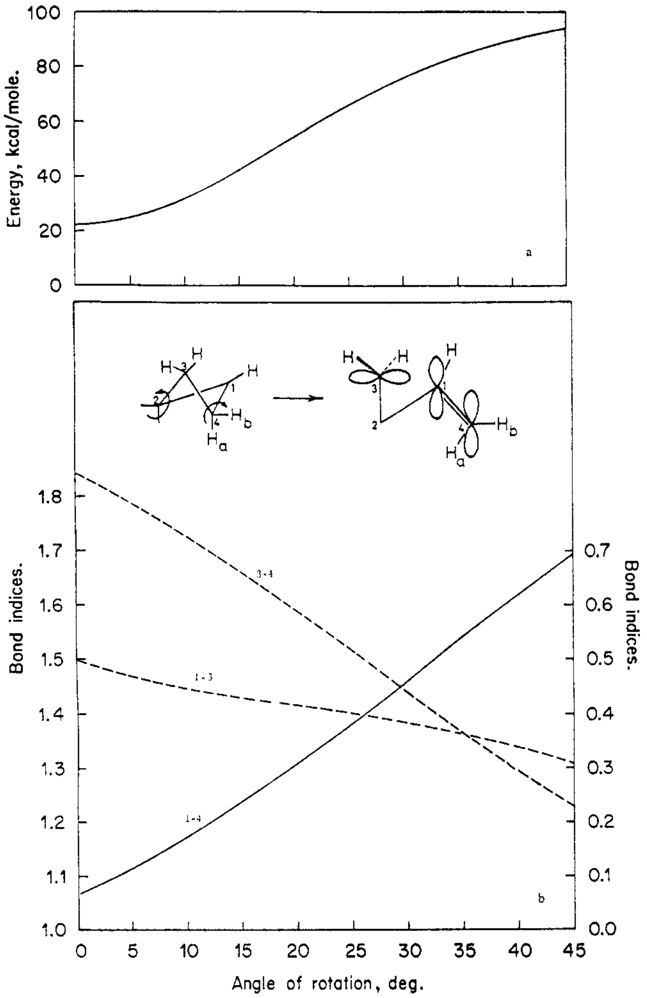

Figure 2. (a) Disrotatory opening of a cyclobutyl cation; (b) disrotatory opening of a cyclobutyl cation. The dashed lines refer to the right-hand scale and the solid line refers to the left-hand scale.

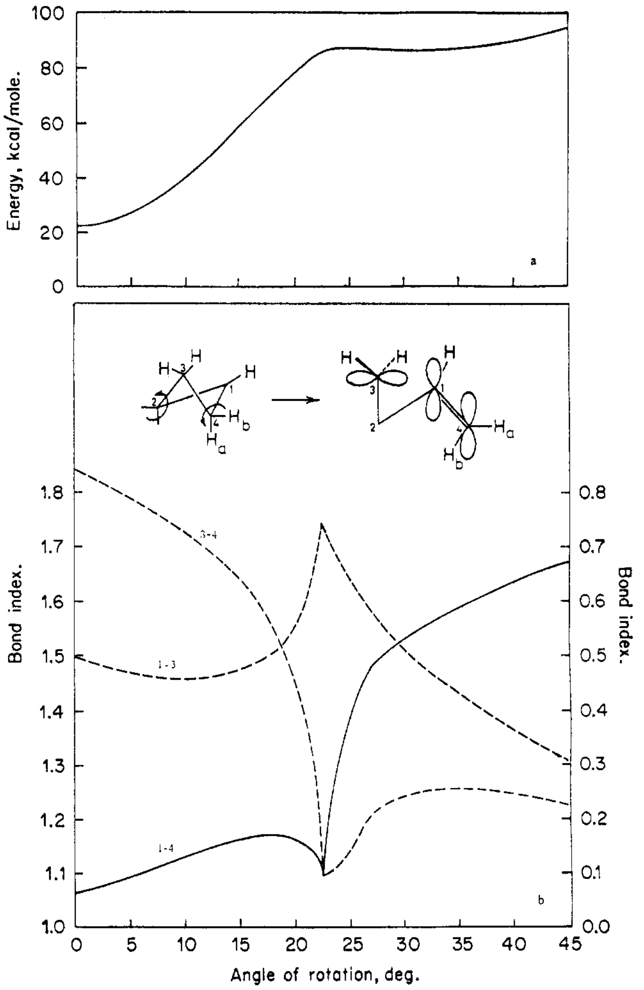

Figure 3. (a) Conrotatory opening of a cyclobutyl cation; (b) conrotatory opening of a cyclobutyl cation. The dashed lines refer to the right-hand scale and the solid line refers to the left-hand scale.

rotation of the methylene groups at C_2 and C_4 inward toward the center of the molecule. Mode 2 led to a comparatively small increase in energy. However, the other three modes led to considerable increases in the calculated energy and none of them appear to be favored.

With these results in hand, the rearrangement of the cyclopropylcarbinyl cation to the minimum energy geometry of the cyclobutyl cation was examined. Here, C_1 was rotated toward C_3 in the proper plane (total angle of rotation, γ, is 55.7°). Simultaneously, a gradual change of the geometry of the hydrogens at C_1, C_2, and C_3 was taken into account. The results are summarized in Table III.

Table III. Rearrangement of Cyclopropylcarbinyl Cation to a Cyclobutyl Cation

γ, deg	ΔE, kcal/mole[a]	$R(C_1C_3)$, Å
0	0	2.603
55.7–40	5	2.357
55.7–30	0	2.176
55.7–20	−14	1.978
55.7	−31	1.540

[a] The energies are based on the empirical energy conversion factor given in Table I, footnote *a*.

It is clear that the activation energy for this route will be relatively small and it is a much more probable process than the one described previously. Thus, we believe that the puckered cyclobutyl cation is the species through which the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement occurs. One may be concerned that the calculated energy of the cyclobutyl cation is significantly lower than that of the cyclopropylcarbinyl cation. We have found that the CNDO method underestimates angle strain. If this were included, the minimum energy geometry would have a somewhat smaller degree of puckering and a larger calculated energy. This would make the energies of the two ions comparable.

Cyclobutyl–Allylcarbinyl Rearrangement. A process related to the ones described above is the conversion of a cyclobutyl cation to an allylcarbinyl cation. This could occur *via* a cyclopropylcarbinyl cation, but in some cases the conversion (forward or backward) may proceed directly.[23] There are four modes by which the reaction could occur, two disrotatory and two conrotatory. Only two of the processes, a (disrotatory) and c (conrotatory), were considered. Mode b appeared unlikely from steric considerations, and in the symmetrical case, mode d is equivalent to mode c.

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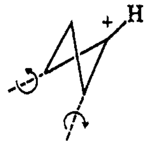
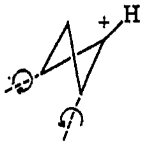
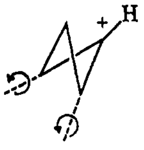
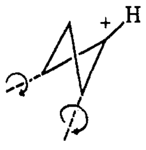
(23) *Cf.* K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *J. Am. Chem. Soc.*, **90**, 564 (1968).


a


b


c


d

In order to keep the problem relatively simple, the angle $C_2C_1C_4$ was kept 90°. The C_2–C_3 bond was maintained, and the C_3–C_4 bond was broken. The hydrogens at C_4 were rotated about the C_1–C_4 bond, and simultaneously, the carbon centers C_3 and C_4 were changed from tetrahedral to trigonal. The results for the disrotatory process (a) are shown in Figure 2a and b, and those for the conrotatory process (c) are shown in Figure 3a and b. The disrotatory process involves a continuous change in bond indices indicating an allowed process.[20] On the other hand, the conrotatory process involves a discontinuous change in bond indices, indicating a crossing of orbital energy levels, and an electronically forbidden process. It may be recognized that the bond angles in the product allyl cation formed by the process described above are considerably distorted. This is the reason for the relatively high calculated activation energy. This does not, however, affect the conclusions concerning the mode of ring opening.

Experimental Section

Methanolysis of Tricyclo[4.2.0.0^{2,7}]heptane. A solution of 1.71 g of tricyclo[4.2.0.0^{2,7}]heptane in 20 ml of methanol was treated with one drop of sulfuric acid. An exothermic reaction occurred. After 20 min, the acid was neutralized with potassium carbonate, the solvent was removed by distillation, and the residue was distilled giving 1.89 g of a liquid with bp 55–62° (25 mm). The nmr spectrum indicated the material to be a 20:80 mixture of *trans*- and *cis*-2-methoxynorcarane.[24]

Acetolysis of Tricyclo[4.2.0.0^{2,7}]heptane. To 3.51 g of the hydrocarbon cooled in a Dry Ice–acetone bath was added 4 ml of glacial acetic acid. The mixture was allowed to warm to room temperature and then allowed to stand for 1 hr. Distillation gave 4.92 g of a liquid, bp 60–65°(9 mm). Analysis by vpc (35-ft DEGS column at 160°) gave three peaks in a 26:62:12 ratio. The first component was mainly 4-acetoxycycloheptene contaminated with a small amount of an unidentified impurity. The second and third compounds were *cis*- and *trans*-2-acetoxynorcarane. The compounds were identified by comparison of their nmr spectra with those of authentic samples.

The reaction with acetic acid-*d* was carried out in the same way as described above. In both the *cis* and *trans* isomers the upfield *endo*-7 proton band completely disappeared. The effect of deuterium on the spectrum of the *cis* isomer was particularly marked. The unlabeled acetate has a ten-line pattern for the two cyclopropane methylene protons. In the deuterium-containing derivative, this portion of the spectrum collapsed to a triplet with $J = 9.0$ Hz corresponding to the coupling of the *exo* proton with the two bridgehead protons.

Acetolysis of Bicyclobutane. To 600 mg of acetic acid which had been cooled in Dry Ice–acetone was added an excess of bicyclobutane. The reaction vessel was allowed to warm in an ice bath. After a short time a vigorous reaction occurred. The excess bicyclobutane was allowed to evaporate giving 1.13 g (99%) of a colorless liquid. Separation by vpc (35 ft DEGS column at 115°) gave 10% allylcarbinyl acetate, 23% cyclobutyl acetate, and 67% cyclopropylcarbinyl acetate.

The reaction was repeated using acetic acid-*d*. The components were separated by vpc and their deuterium content was determined by repeated integration of their nmr spectra. The results for allylcarbinyl acetate were α-hydrogens, 1.77, 1.81; β-hydrogens, 1.82, 1.83; γ-hydrogens, 1.39, 1.34; δ-hydrogens, 1.02, 1.04. The two values correspond to two separate runs. These values lead to the deuterium distribution given in the text. It was not possible to determine the relative amounts of deuterium in the *cis* and *trans* δ positions.

The spectrum of cyclobutyl-d_1 acetate was too complex to be interpreted. A comparison of labeled with unlabeled material did not indicate much difference, suggesting that the deuterium may be fairly well distributed over the available positions.

The spectrum of cyclopropylcarbinyl acetate was of particular importance. It was found that the most reproducible integrals were obtained using a HA-100 spectrometer in the field sweep mode. The average of 40 integrations gave 1.21 ± 0.03 for the *cis*-β protons, 1.99 ± 0.03 for the *trans*-β protons, and 1.76 ± 0.03 for the carbinyl protons. These values lead to the deuterium distribution given in the text.

Hydrolysis of Bicyclobutane. To 10 ml of deuterium oxide containing 24 mg of sulfuric acid was added 5 g of bicyclobutane with ice bath cooling. The solution was extracted four times with ether. The ether solution was dried over magnesium sulfate and distilled giving 4.9 g of a liquid, bp 120–128°. Analysis by vpc gave a very small peak for allylcarbinol followed by two peaks of equal size for cyclobutanol and cyclopropylcarbinol. The two major components were separated by vpc and the deuterium content was determined by nmr. The *cis*-β position gave a relative integral of 1.19 ± 0.03, the *trans*-β position gave 1.98 ± 0.03, and the carbinyl position gave 1.83 ± 0.03.

The oxidation of 1 g of the labeled cyclobutanol was effected using the chromium trioxide–pyridine complex.[25] When the reaction was complete, all volatile products were distilled under vacuum into a Dry Ice–acetone-cooled trap. The distillate was redistilled through a 20-in. packed column collecting the fraction boiling between 85 and 105°. Final purification was effected by vpc using a 30-ft DEGS column at 95°. The α positions were found by nmr to contain 0.52 ± 0.02 deuterium, and the β position was found to contain 0.49 ± 0.02 deuterium.

Chlorination of Bicyclobutane. Approximately 2 g of bicyclobutane was dissolved in carbon tetrachloride. The solution was kept in the dark and cooled in a Dry Ice–acetone bath. A small excess of chlorine in carbon tetrachloride was added over 10 min. The solvent and the excess of chlorine were removed immediately under vacuum. The remaining oil was analyzed by vpc (20-ft Carbowax at 135°) and seven components were found in the following proportions (increasing retention time): 45%, 0.5%, 2.4%, 3.8%, 0.9%, 6.4%, 41%. The first component was shown by its nmr spectrum (τ 7.11, 2 H), 4.35 (t, 1 H) and typical vinyl absorption) to be 1,1-dichlorobutene-3. The fourth component had a spectrum corresponding to *cis*-1,3-dibromocyclobutane.[26] Components 6 and 7 were cyclopropyl derivatives as shown by their upfield proton bands. In one isomer, the band for the proton attached to the cyclopropane carbon bonded to chlorine was at τ 6.8 whereas in the other isomer it was at τ 7.13. In analogy with cyclopropylcarbinol and its acetate,[9] the proton *cis* to the carbinyl group was assumed to absorb at higher field than the *trans* proton. Thus the major component has the chlorine *cis* to the carbinyl group. The same conclusion may be reached by considering the magnitudes of the coupling constants to the tertiary hydrogens.

Allylcarbinyl-*cis*-4-*d* Tosylate. The acetylenic proton of 3-butyn-1-yl acetate was replaced by deuterium by shaking it vigorously with sodium deuteroxide in deuterium oxide. Exchange was more rapid than esterification. The ester had 95 ± 3% deuterium as determined from the nmr spectrum.

To 57 g (0.4 mole) of boron trifluoride etherate in 100 ml of diglyme was added 11.5 g of sodium borohydride in 600 ml of diglyme. The diborane which was formed was swept with nitrogen into a flask containing 200 ml of dry tetrahydrofuran and 65 g (0.9 mole) of 2-methyl-2-butene. Then 35 g (0.31 mole) of 3-butyn-4-*d*-1-yl acetate was added. After 3 hr at room temperature, an excess of acetic acid was added to effect protolysis of the carbon–boron bonds. The solution was allowed to stand for 12 hr and then poured into water. Extraction with ether was followed by washing the ether solution with sodium carbonate solution, drying over magnesium sulfate, and distillation giving 24.2 g (68%) of allylcarbinyl-*cis*-4-*d* acetate, bp 45–60° (50 mm).

A mixture of 23.0 g of the ester, 24.0 g of potassium hydroxide,

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[24] W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).

[25] M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

[26] K. B. Wiberg and G. M. Lampman, *J. Am. Chem. Soc.*, **88**, 4429 (1966).

and 100 g of methanol was heated to reflux for 3 hr. Methanol (75 g) was removed by distillation and the cooled residue was added to water. The solution was extracted repeatedly with ether. The ether solution was dried with magnesium sulfate and distilled giving 8.1 g (68%) of allylcarbinol-*cis*-4-*d*, bp 112–114°.

The allylcarbinol was converted to the tosylate with *p*-toluenesulfonyl chloride in pyridine in the usual fashion. The nmr spectrum of the allylcarbinyl acetate indicated the deuterium to be located in the *cis* position, and showed the presence of 95 ± 3% of one deuterium.

Solvolysis of Allylcarbinyl-*cis*-4-*d* Tosylate. A solution containing 14 g of the tosylate, 200 ml of glacial acetic acid, and 5.5 g of dry sodium acetate was heated to reflux for 96 hr. The cooled solution was poured into ice water and extracted five times with pentane. The pentane solution was washed with sodium carbonate solution and dried over magnesium sulfate. After removal of the pentane, the residue was analyzed by vpc (30-ft DEGS column at 125°). There was found 80% allylcarbinyl acetate, 8% cyclobutyl acetate, and 12% cyclopropylcarbinyl acetate. The mixture was separated by preparative vpc. The 100-MHz spectrum of the allylcarbinyl acetate was identical with that of the acetate prepared in the synthetic sequence indicating no deuterium scrambling. The deuterium content of the cyclopropylcarbinyl acetate was determined by averaging the results of 60 integrations using an HA-100 spectrometer in the field sweep mode. The deuterium distribution was given earlier in the paper.

Organic Quantum Chemistry. XXIV. A Theoretical Study of the Stereochemistry of SE2 and SN2 Reactions[1,2]

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Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received June 16, 1969*

Abstract: The transition states which result when methane undergoes an SN2 or an SE2 reaction, when attacked by hydride ion or by a proton, respectively, have been studied by an SCF method, similar to the PNDO method of Pople. The energies of the transition states have been minimized with respect to all bond lengths and angles, and the results indicate that for the simple (gas phase) reactions, the SN2 reaction prefers an inversion to a retention mechanism by about 0.64 eV, while for the SE2 reaction, the inversion mechanism is preferred by only 0.23 eV.

The Walden inversion mechanism (SN2) has been known for a good many years, and it involves the attack of a Lewis base on a molecule to displace another Lewis base. More often than not, these bases are anions, although other charge types are possible. The transition states have the general structure $CR_1R_2R_3YZ^-$, where the R groups can be hydrogen, alkyl, or various other things, and where Y and Z are the attacking and leaving nucleophiles. Of the hundreds of examples of this reaction type which are known, no evidence has ever been forthcoming to show that any stereochemistry other than inversion occurs during the course of this reaction.[4,5] Certainly, inversion of configuration in the SN2 reactions is one of the most unqualified and absolutely dependable phenomena ever observed in the field of organic stereochemistry. Naturally, many chemists have been led to a consideration of the reasons behind the highly specific stereochemistry of this type of reaction.[6–8] Meer and Polanyi pointed out that the dipole field of a bond such as C–Cl would preferentially direct an anionic reagent like OH^- to the position leading to inversion of configuration. Thus they concluded that this electrostatic effect was sufficient to explain why inversion, rather than retention of configuration, was observed in reactions of this general type. That the situation is actually more complicated than they pictured was shown by the experiments of Read and Walker,[9] who showed that even when hydroxide ion is displacing a trimethylammonium group, and the dipole effects would presumably work in the opposite direction, inversion of configuration was still observed.

Hughes, Ingold, and coworkers[8] looked at these experiments qualitatively from a quantum mechanical point of view, and considered that the conditions which would "minimize the repulsive, exchange energy integrals" would lead to the transition state of lower energy. They considered that this was an effect arising from the exclusion principle; however, this conclusion seems to have been based mainly on intuition. Since one must consider the electronic repulsion integrals, not only between the entering and leaving groups, but between all of the electrons in the molecule, in addition to the nuclear repulsion and the attraction integrals, it is certainly not at all clear in a qualitative way why inversion of configuration is to be preferred. As far as the present authors are able to ascertain, no detailed theoretical study has ever indicated that the SN2 reaction should proceed by inversion of configuration, in spite of the fact that this is a simple fundamental reaction, and the experimental results are not affected by solvent, tem-

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[1] Paper XXIII: J. C. Tai and N. L. Allinger, *Theor. Chim. Acta*, **15**, 133 (1969).

[2] This research was supported by Grant No. GP 6763 from the National Science Foundation.

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[6] A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933); A. R. Olson and F. A. Long, *J. Amer. Chem. Soc.*, **56**, 1294 (1934); **58**, 393 (1936).

[7] N. Meer and M. Polanyi, *Z. Phys. Chem.*, **B19**, 164 (1932).

[8] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

[9] J. Read and J. Walker, *ibid.*, 308 (1934); *cf.* J. Read, "A Chapter in the Chemistry of Essential Oil," Institute of Chemistry, 1936, p 21.