mixture was cooled, 12 g of deuterium oxide added dropwise, the solid precipitate removed by filtration, and 100 ml of ether added to the filtrate. The ethereal solution was washed with two 100-ml portions of water and 100 ml of saturated salt solution, and dried over anhydrous potassium carbonate. The solvent was removed by distillation and the residue separated into two fractions by preparative scale vpc using a 9 ft × 3/8 in. 20% DEGS column at 150°. The nmr spectrum of the two fractions indicated that the first (29% of the mixture) was actually a mixture of compounds, while the second (71%) was pure cycloheptanol. The first vpc fraction showed a parent peak with *m/e* 112 in its mass spectrum which corresponds to a molecular formula of $C_7H_{12}O$. The mass spectrum of the second fraction (cycloheptanol) showed a parent peak with *m/e* 115 which corresponds to a molecular formula of $C_7H_{13}DO$. Analysis on a 30 ft × 3/8 in. 20% DEGS column at 150° indicated the presence of the following: spiro[2.4]heptan-4-ol (6.1%), *trans*-bicyclo[3.2.0]heptan-1-ol (20.8%), *cis*-bicyclo[3.2.0]heptan-1-ol (1.8%), and cycloheptanol (71.3%).

Reduction of 8-Oxatricyclo[3.2.1.0^{1,5}]octane with Lithium Aluminum Deuteride in 1,2-Dimethoxyethane. The reaction was carried out as described above using 1.13 g (27.2 mmoles) of lithium aluminum deuteride and 3.0 g (27.2 mmoles) of 8-oxatricyclo-[3.2.1.0^{1,5}]octane. Deuterium oxide was used to decompose the excess lithium aluminum deuteride. Vpc analysis on a 30 ft × 3/8 in. 20% DEGS column showed the products to be spiro[2.4]-heptan-4-ol (6.7%), *trans*-bicyclo[3.2.0]heptan-1-ol (45.5%), *cis*-bicyclo[3.2.0]heptan-1-ol (2.1%), and cycloheptanol (45.6%). The material was separated into a mixture of bicyclic components and cycloheptanol by preparative vpc. The mass spectrum of the first fraction containing the bicyclic compounds showed a parent peak *m/e* 113 which corresponds to a molecular formula of $C_7H_{11}DO$. The second component (cycloheptanol) had a parent peak with *m/e* 117, which corresponds to a molecular formula of $C_7H_{11}D_3O$.

Kinetic Method. Acetone was purified by distillation from potassium permanganate and degassed by boiling for several minutes. Distilled water was degassed in the same manner. The solvents and solutions were handled in an oxygen-free drybox in order to minimize oxidation of the solvent which occurs at higher temperatures. In all cases, the solvent was 80% (by volume) acetone.

In each case, 50 ml of a 0.01100 *M* solution of the 3,5-dinitrobenzoate was prepared, and 3.2-ml portions were sealed into ampoules. A set of ampoules was immersed in an oil bath at the appropriate temperature. After allowing 5–10 min for temperature equilibration, the zero point was taken. The ampoules were removed from the bath and plunged into ice–water to stop the solvolyses. After warming to room temperature, a 3.00-ml portion of the solution was removed and titrated with 0.0100 *M* sodium hydroxide solution to a brom thymol blue end point. Infinity titers were determined after 10 half-lives.

When the internal return products (if any) were unreactive, the rate constants were determined from

$$\ln (V - V_\infty) = -kt + b$$

and the slope was evaluated by the method of least squares. The rate constants thus obtained correspond to the sum of the rates of solvolysis and internal return. When the internal return product was reactive, its rate constant was determined, and the values of k_1 and k_3 (solvolysis and internal return) were obtained by minimizing the deviation between observed and calculated titers using a computer.

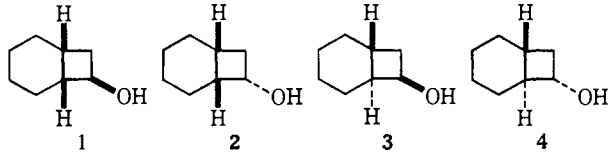
Solvolysis of *cis*- and *trans*-Fused Bicyclo[4.2.0]octyl 7-Tosylates[1]

Kenneth B. Wiberg and Joseph G. Pfeiffer[2]

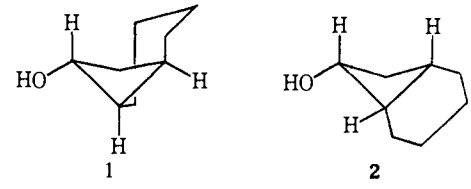
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received November 8, 1968*

Abstract: The synthesis of *trans*-fused bicyclo[4.2.0]octyl-7 derivatives is described. The solvolytic reactions of both *cis*- and *trans*-fused tosylates have been studied. It is concluded that a disrotatory cyclobutane ring opening is involved in those cases in which rate acceleration is found, and that the process proceeds so that maximum orbital overlap is maintained. The application of this type of process to the present data and to other data is considered. Evidence also is presented indicating that the symmetrical and unsymmetrical cyclopropylcarbinyl cations have only a small difference in energy.

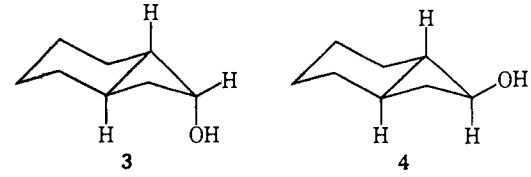
In a continuation of our work on *trans*-fused bicyclic cyclobutane derivatives, we have examined the reactions of derivatives of compounds **1–4**. A *cis* ring fu-



sion, as in **1** and **2**, leads to a flexible molecule since one bond from the attached ring must occupy an axial position and the other an equatorial position. Thus, a substituent in the 7 position may occupy an equatorial position in either **1** or **2**. On the other hand, a *trans* ring fusion leads to a rigid system in which a 7 substituent is



forced to occupy either an axial or an equatorial position.



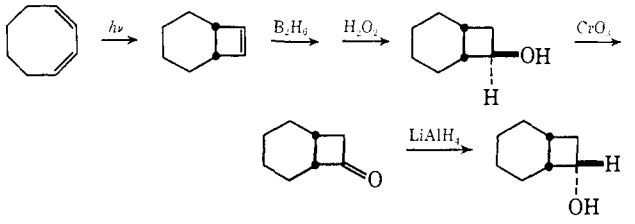
It was hoped that the variety of structural features found with **1–4** would permit a more detailed examination of the question of the nature of the species formed

(1) This investigation was supported by a Public Health Service Grant 12800 from the National Institutes of General Medical Science.
(2) Taken in part from the Ph.D. Thesis of J. G. P., 1968; NIH predoctoral fellow, 1965–1968.

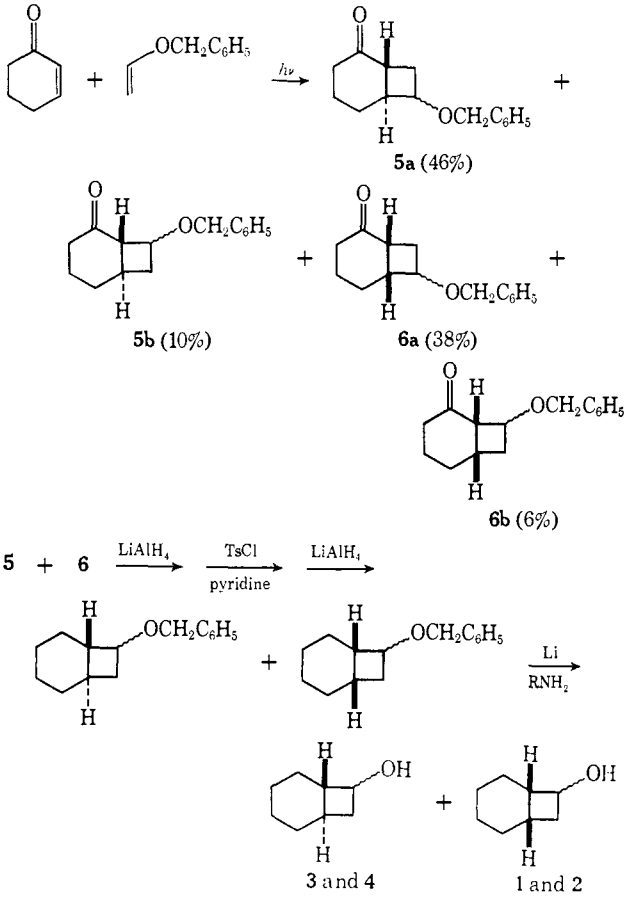
in the solvolysis of cyclobutane derivatives. The solvolysis of derivatives of **1** and **2** has been reported by Cope, *et al.*[3] However, the kinetics were not determined and the product studies did not differentiate between the initial products and those formed by solvolysis of the internal return products.

Synthesis

The *cis*-fused isomers were easily prepared by the procedures of Cope and Gleason.[4]

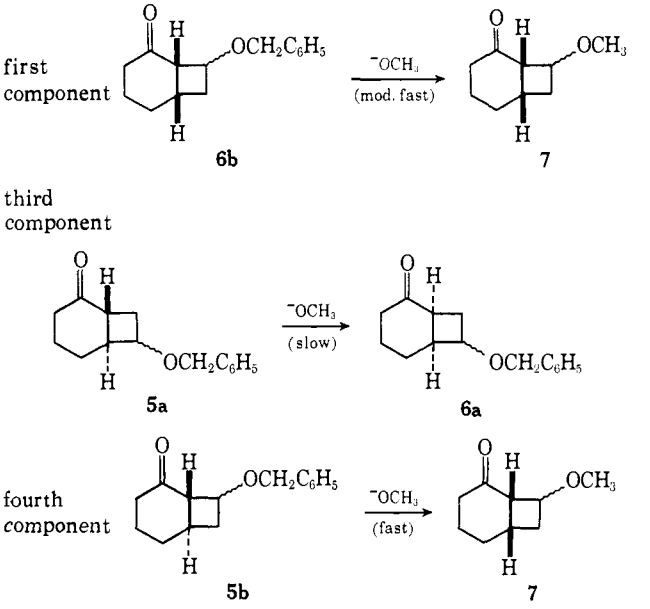


The preparation of the *trans*-fused derivatives made use of the observation of Corey, *et al.*,[5] that the light-catalyzed condensation of cyclohexenone with vinyl ethers led to *trans*-fused derivatives. We chose to use benzyl vinyl ether since the benzyl group could later be removed by hydrogenolysis.



The photolysis gave a mixture of four products in a 1:7:8:2 ratio in order of retention time as determined by vpc. In order to characterize the components small samples were treated with 20% methanolic potassium hydroxide at room temperature for 0.5, 1.5, 3, and 10 hr, respectively. After 0.5 hr, the first peak had decreased slightly and the fourth had disappeared and was replaced by a new component with a shorter retention time. The nmr spectrum of the new compound had a band for a methoxy group. After 1.5 hr, both the first and last peaks had been transformed into the new compound. After 3 hr, the third peak had decreased somewhat and the second had increased correspondingly. Finally, after 10 hr, the third component had been completely transformed into the second.

The transformations appear best to be formulated as shown. The compounds **5b** and **6b** are the only two in



which a benzyloxy group could readily be replaced by methoxy, and **5b** would be expected to be the more reactive of the two.[5] The transformation of **5a** to **6a** would be expected to occur more slowly. The final products of the reaction are then **6a** and **7**.

Reduction with lithium aluminum hydride followed by conversion to the tosylate and a second lithium aluminum hydride reduction gave a mixture of benzyl ethers in good yield. Hydrogenolysis was effected using lithium in ethylamine and gave a mixture of **1**, **2**, **3**, and **4**. The *trans*-fused alcohols **3** and **4** could be separated from the *cis*-fused isomers **1** and **2** on a 13 ft × 0.75 in. 20% Carbowax column to give 62% of the *trans*-fused and 38% of the *cis*-fused alcohols. In order to separate **3** and **4**, the alcohol mixture was converted to the acetates, and the acetates were separated using the column previously employed for the *cis*-fused isomers. Reduction with lithium aluminum hydride provided pure samples of **3** and **4**.

The nomenclature used herein for the bicyclic isomers requires a note of explanation. The initial *cis* or *trans* will refer to the ring fusion and the later *cis* or *trans* will refer to the relationship between the substituent and the nearest bond of the bridging ring. Thus the tosylate derived from **1** is *cis*-bicyclo[4.2.0]octyl *trans*-7-tosylate and that derived from **4** is *trans*-bicyclo[4.2.0]octyl *trans*-7-tosylate.

(3) A. C. Cope, R. W. Gleason, S. Moon, and C. H. Park, *J. Org. Chem.*, 32, 942 (1967).
(4) A. C. Cope and R. W. Gleason, *J. Am. Chem. Soc.*, 84, 1928 (1962).
(5) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, 86, 5570 (1964).

Table I. Rates of Acetolysis of Bicyclo[4.2.0]octyl 7-Tosylates

Tosylate	T, °C	k, sec^{-1}	$\Delta H^{\pm}$, kcal/mole	$\Delta S^{\pm}$, eu
cis-Bicyclo[4.2.0]octyl *trans*-7-tosylate (**1a**)	17.0	$1.80 \pm 0.03 \times 10^{-5}$	23.1	−0.6
	37.0	$2.55 \pm 0.01 \times 10^{-4}$		
	50.0	1.21×10^{-3} [a]		
cis-Bicyclo[4.2.0]octyl *cis*-7-tosylate (**2a**)	30.0	$1.27 \pm 0.02 \times 10^{-5}$	25.3	2.5
	50.0	$1.83 \pm 0.01 \times 10^{-4}$		
trans-Bicyclo[4.2.0]octyl *cis*-7-tosylate (**3a**)	70.0	$3.62 \pm 0.03 \times 10^{-5}$	29.6	7.0
	80.0	$1.28 \pm 0.02 \times 10^{-4}$		
	90.0	$4.19 \pm 0.02 \times 10^{-4}$		
	50.0	2.30×10^{-6} [a]		
trans-Bicyclo[4.2.0]octyl *trans*-7-tosylate (**4a**)	70.0	$2.92 \pm 0.09 \times 10^{-5}$	29.3	5.9
	90.0	$3.31 \pm 0.02 \times 10^{-4}$		
	50.0	1.93×10^{-6} [a]		
3-Cyclooctenyl tosylate (**8a**)	17.0	$1.70 \pm 0.01 \times 10^{-5}$	25.5	7.6
	37.0	$3.15 \pm 0.01 \times 10^{-4}$		
	50.0	1.74×10^{-3} [a]		
trans-2-Vinylcyclohexyl tosylate (**9a**)	80.0	$3.70 \pm 0.09 \times 10^{-5}$	27.2	−2.0
	100.0	$3.13 \pm 0.04 \times 10^{-4}$		
	50.0	9.07×10^{-7} [a]		

[a] Extrapolated values.

Results and Discussion

The rates of acetolysis of the tosylates derived from compounds **1–4** were determined giving the data summarized in Table I. The *cis*-fused compounds gave *trans*-2-vinylcyclohexyl tosylate as an internal return product. The rate constants are the sum of those for acetate formation and internal return, and correspond to the apparent rates of ionization. The relative rates of reaction are summarized in Table II.

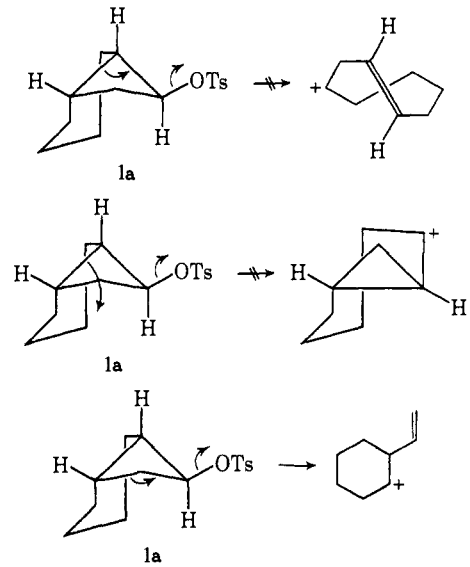
Table II. Relative Rates of Solvolysis at 50°

Tosylate	k_{rel}
cis-Bicyclo[4.2.0]octyl *trans*-7	627
cis-Bicyclo[4.2.0]octyl *cis*-7	95
trans-Bicyclo[4.2.0]octyl *cis*-7	1.19
trans-Bicyclo[4.2.0]octyl *trans*-7	1.00
3-Cyclooctenyl	902
trans-2-Vinylcyclohexyl	0.47
Cyclobutyl	18.4
cis-Bicyclo[3.2.0]heptyl *trans*-6[a]	1.36
cis-Bicyclo[3.2.0]heptyl *cis*-6[a]	622
Cyclohexyl	0.944

[a] H. L. Goering and F. F. Nelson, private communication.

The products were determined by isolating the acetates and separating them by vpc. The structures of the products were determined by comparison of the nmr spectra with those of authentic samples and by vpc retention times. The results are summarized in Table III.

We shall first consider the *cis*-fused isomers. The solvolysis of **1a** gave *trans*-2-vinylcyclohexyl tosylate and acetate as the initial products. On the other hand, the solvolysis of **2a** gave only a small amount of vinylcyclohexyl derivatives, and rather gave 3-cyclooctenyl acetate and bicyclo[5.1.0]octyl 2-acetate. The reaction of **1a** prefers not to give these products for the stereochemistry of a concerted reaction leading to the 3-cyclooctenyl cation would require the formation of a *trans* double bond, and similarly formation of the bicyclo[5.1.0]octyl-2 cation would require *trans* ring fusion.[6] As a result, the alternative path is taken.



If the 3-cyclooctenyl and bicyclo[5.1.0]octyl-2 cations are more stable than the vinylcyclohexyl cation, the preference for the former products in the solvolysis of **2a** could easily be explained.[7] If this is not the case, some other factor must be sought to explain why **2a** gives so little of the 2-vinylcyclohexyl derivatives.

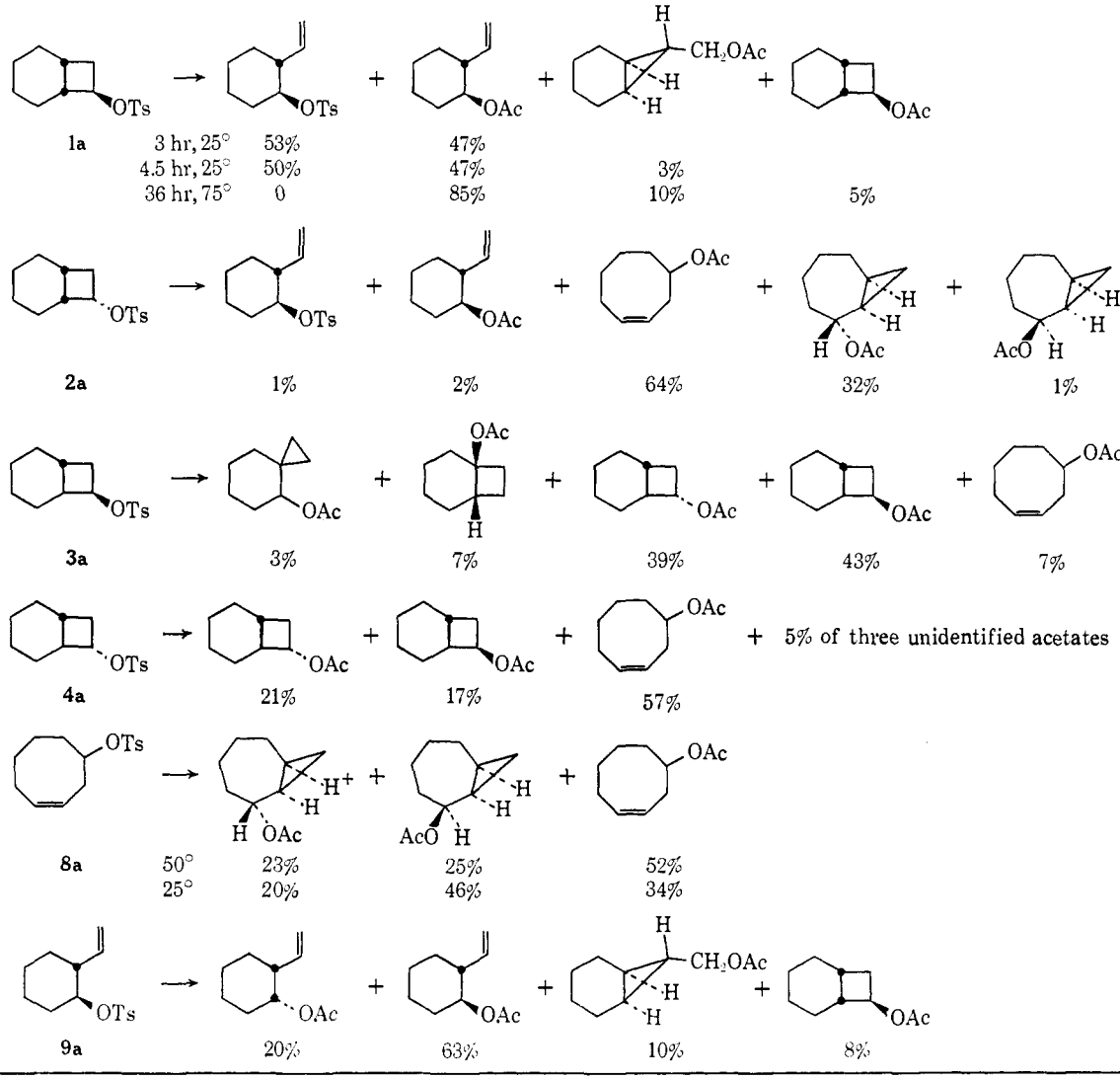
The behavior of **2a** and of the ions derived from it is interesting. 3-Cyclooctenyl tosylate (**8a**) gives cyclooctenyl and bicyclo[5.1.0]octyl-2 derivatives on solvolysis and the same is true with *cis*-bicyclo[4.2.0]octyl *cis*-7-tosylate. However, unlike the group of compounds which lead to the 2-norcaranyl ion,[7,8] the two sources of bicyclo[5.1.0]octyl-2 ions lead to different proportions of products. The solvolysis of **2a** gives essentially only the *exo* isomer. The solvolysis of **8a** gives both epimers, but the amount of the *endo* isomer increases with decreasing temperature. Of more importance, the solvolysis of **8a** in the more nucleophilic sol-

(6) This explanation has previously been applied by us to the solvolysis of bicyclo[3.2.0]heptan-6-ol derivatives [K. B. Wiberg and A. J. Ashe III, *Tetrahedron Lett.*, 1553 (1965)] and by Cope, *et al.* (ref 3), to the cyclopropylcarbinyl ion formation in the present case.

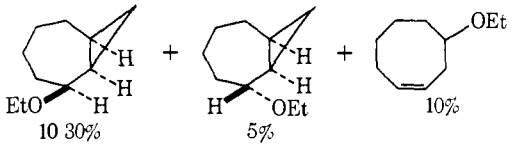
(7) This order of stability is almost certainly the case with the bicyclo[3.2.0]heptanol-6 derivatives [*cf.* K. B. Wiberg and A. J. Ashe III, *J. Am. Chem. Soc.*, **90**, 63 (1968)]. However, it is more difficult to estimate relative energies in the present case.

(8) K. B. Wiberg and B. A. Hess, Jr., *ibid.*, **89**, 3015 (1967).

Table III. Products of Acetolysis

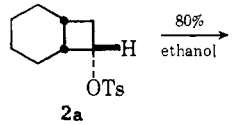


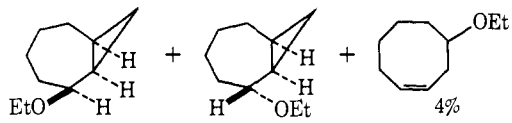
vent, aqueous ethanol, gives predominantly the *endo* isomer (**10**). The solvolysis of **2a** in aqueous ethanol



(and the corresponding alcohols)

gives the following product distribution.



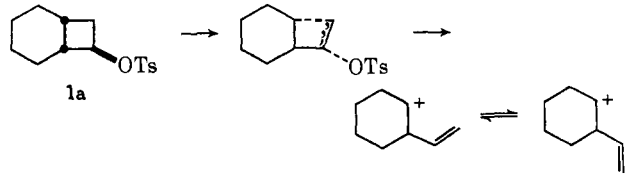


(and the corresponding alcohols)

These data suggest that the product ratio in the acetolysis of **2a** probably was determined by acid-catalyzed equilibration of the initially formed products to give the more stable *exo*-acetate. However, even in buffered aqueous ethanol, the product ratios are significantly different. This will be considered further after presenting the data on the *trans*-fused compounds.

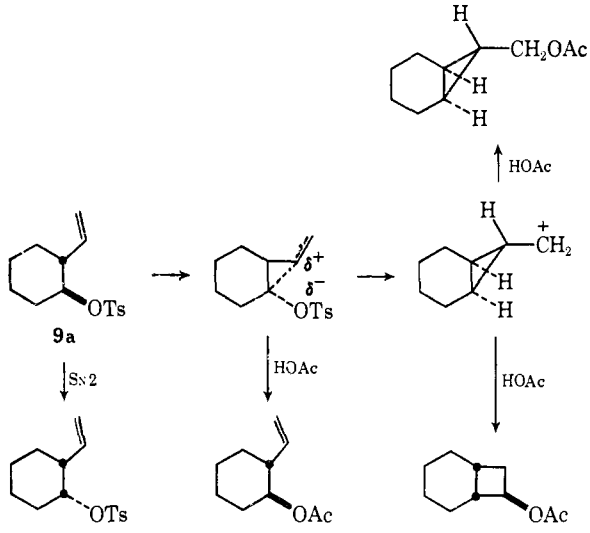
The solvolyses of **1a** and 2-vinylcyclohexyl tosylate (**9a**) raise an interesting problem. The only products derived from **1a** are 2-vinylcyclohexyl tosylate and acetate. However, the solvolysis of **9a** gives both bicyclo[4.1.0]heptane-7-methyl acetate and bicyclo[4.2.0]octyl 7-acetate. It seems clear that the latter is not formed from a cyclobutyl ion of the type which might be formed from **1a**.

The ionization of **1a** would lead to a vinylcyclohexyl

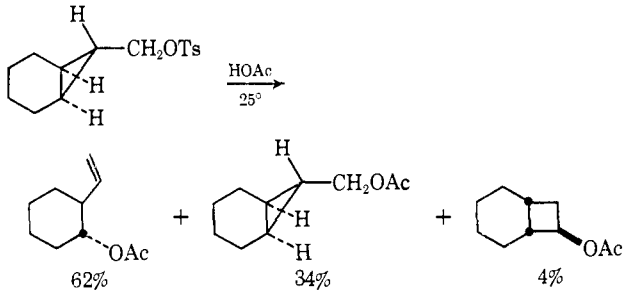


ion as shown. On the other hand, the formation of the cyclopropylcarbinyl product from **9a** requires that the

other end of the double bond be involved.

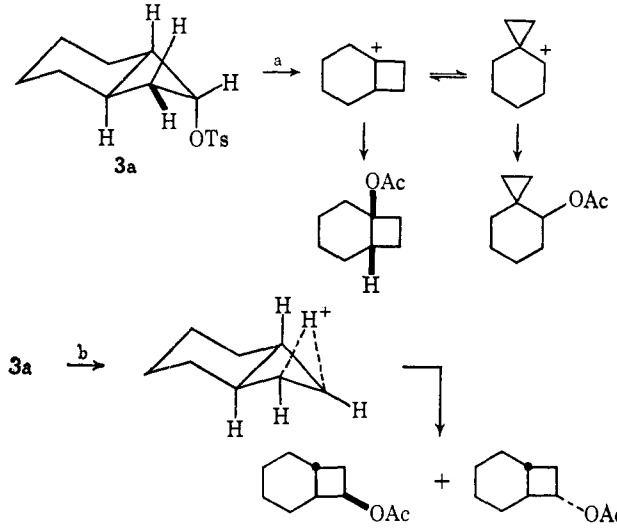


It would appear that the *cis*-bicyclo[4.2.0]octyl *trans*-7-acetate must also be formed from the above homoallylic or cyclopropylcarbinyl ion intermediate. The stereochemistry of the product is that required for such a process, and it may be noted that the solvolysis of *exo*-bicyclo[4.1.0]heptane-7-methyl tosylate also gives *cis*-bicyclo[4.2.0]octyl *trans*-7-acetate.[9] This appears to be

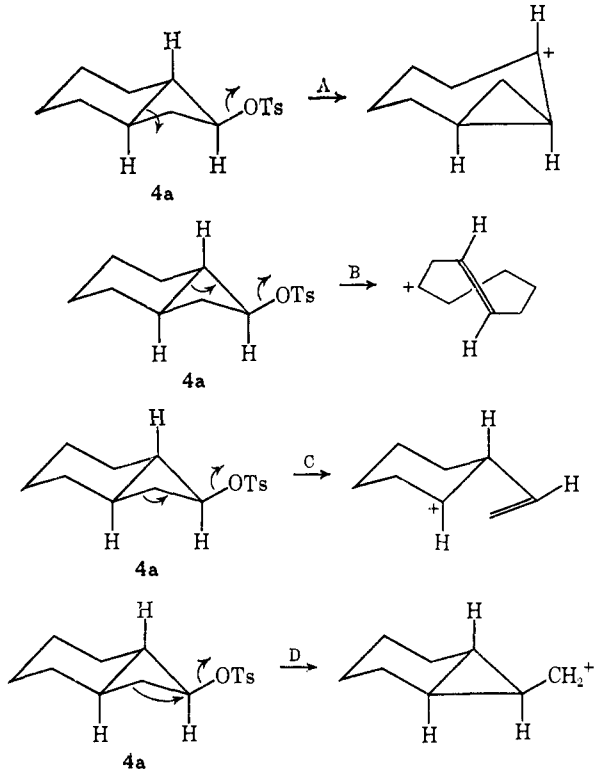


one of the first cases in which a cyclopropylcarbinyl cation or a closely related species can be shown to lead to a cyclobutyl product without the intervention of a cyclobutyl cation. This process may be more general, and this possibility is being explored.

We may now turn to the solvolysis of the *trans*-fused isomers. In **3a**, there are no carbon atoms in a *trans* position to the leaving group, and carbon participation would not be expected. On the other hand, two hydrogens occupy such positions. One is at the bridgehead, and its migration would lead to the bridgehead cation. The spiro[2.5]octyl 2-acetate and bicyclo[4.2.0]octyl 1-acetate are known to be products derived from this ion.[10] Migration of the methylene hydrogen to give a bridged ion or an equilibrating pair of ions would lead to the acetates corresponding to **3a** and **4a**.[11] A small amount of leakage to the 3-cyclooctenyl ion also occurs.



The reaction of **4a** is the least easily understood of this group. It should first be noted that it is relatively unreactive despite having somewhat more strain than **1a** or **2a**.[12] Let us examine the possible reactions of the tosylate. Process D would lead to a *trans*-fused cyclo-



propane ring, and reasonably, it should not occur. Processes A and C appear on these simple grounds to be satisfactory, but the compound does not choose these courses. The observed rearrangement product is predicted by these considerations to have a *trans*-double bond.

It is known that a *trans*-double bond in a cyclooctane ring will not survive the reaction conditions which are used for acetolysis.[13] Therefore, the solvolysis was

(9) J. A. Meschino, private communication. We wish to thank him for supplying us with his data prior to publication.

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

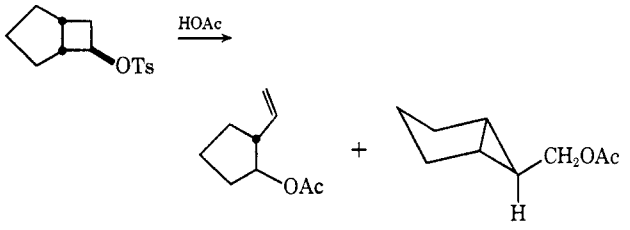
(11) Tracer experiments aimed at determining whether or not hydrogen migration accompanies the formation of the epimeric acetate are in progress.

(12) The difference in strain energy has been estimated to be on the order of 2 kcal/mole based on reactivity data (ref 10). Calorimetric experiments are in progress to determine the difference in energy between *cis*- and *trans*-fused cyclobutane derivatives.

(13) This was shown in an independent experiment. *Cf.* K. Ziegler and H. Wilms, *Ann.*, 567, 1 (1950), for the corresponding isomerization of *trans*-cyclononene.

carried out in aqueous dioxane using calcium carbonate as a base to remove the acid as it is formed. These conditions permit the isolation of *trans* 2-cycloocten-1-ol from the solvolysis of *endo*-8-bromobicyclo[5.1.0]-octane.[14] The cyclooctenol isolated from the reaction of **4a** was shown to contain a *trans* double bond by its rapid reaction with phenyl azide to give a triazoline. Under the same conditions, the corresponding alcohol with a *cis* double bond was found to be essentially inert.[15] It is clear that the reaction prefers path B despite the extra strain associated with a *trans* double bond in an eight-membered ring.[16]

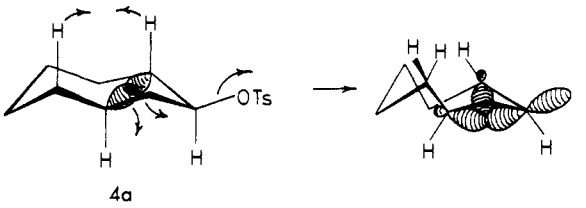
The Cyclobutyl Cation. In the previous section, we have attempted to treat the experimental data using a simple classical approach. In part, this was successful, but it failed completely when applied to *trans*-bicyclo-[4.2.0]octyl *trans*-7-tosylate (**4a**). Further, it does not readily account for the exclusive formation of *trans*-2-vinylcyclohexyl derivatives from **1a**, when bicyclo-[4.1.0]heptane-6-methyl derivatives might reasonably be expected, especially since the corresponding compound is formed in the solvolysis of *cis*-bicyclo[3.2.0]heptyl



trans-6-tosylate.[17] It seems clear that we must seek a more detailed explanation of the reactions of these compounds.

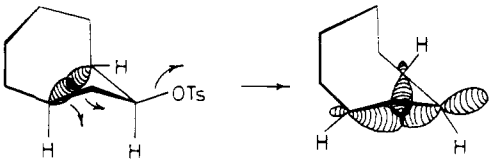
We have previously reported σ molecular orbital calculations on models for the activated complex in the solvolysis of cyclobutyl derivatives.[18] When the leaving group was in the equatorial position a significant cross-ring interaction was calculated. With the *cis*-fused bicyclo[4.2.0]octane derivatives, we have noted a significant rate acceleration over that for cyclobutyl itself, and it is probable that rearrangement accompanied the ionization step. Thus, rather than the symmetrical activated complex one might write for the unsubstituted cyclobutyl case, the present compounds require an unsymmetrical species.

In the ionization step, it will be necessary to maintain maximum bonding throughout. Otherwise, a rate slower than that for cyclobutyl might be expected. In accord with this, we propose that the orbitals forming the bond which is involved in the ionization step rotate in such a way as to give maximum overlap with the developing empty p orbital.[19] Let us apply this to the anomalous tosylate, **4a**. Ionization accompanied by



4a

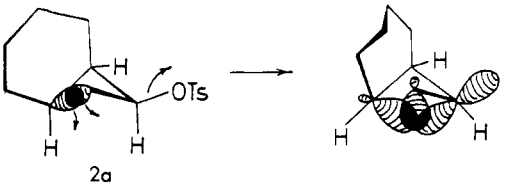
participation of the bridging bond would require the formation of a much deformed cyclohexane ring and marked interference between two of the axial hydrogens. Such an activated complex seems most improbable. As a consequence, a bicyclo[5.1.0]octyl-2 cation is not formed. This may be contrasted with the *cis*-fused isomer **2a**. The cyclobutane ring would tend to flatten the cyclohexane ring at the ring junction. The mode of rotation suggested above will tend to restore the cyclohexane bond angles to their normal values. As a result, strain relief should accompany the ionization process leading to the observed rate enhancement.



2a

The ionization of **4a** proceeds *via* an energetically less favorable route to *trans*-cyclooctenyl 3-acetate and gives about 40% of the unrearranged products with a rate one-tenth that of cyclobutyl tosylate. Thus there is relatively little stabilization of the activated complex and the reaction may proceed through a species resembling a cyclobutyl cation.

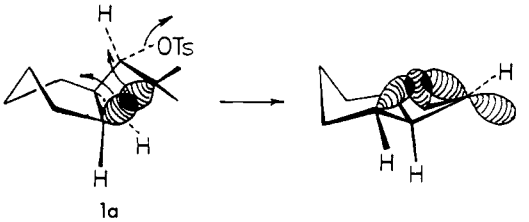
The ionization of **2a** leads to very little vinylcyclohexyl acetate. If one considers the process which would lead to this product, the mode of rotation shown above



2a

will tend to convert the cyclohexane ring from a chair form to a boat form. This should be less favorable than the route shown above, and agrees with observed results.

It now remains to explain why **1a** gives only vinylcyclohexyl derivatives. The formation of the vinylcyclohexyl ion will lead to a change of the flattened cyclo-



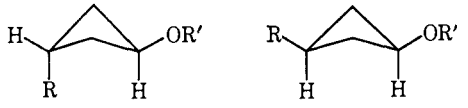
1a

hexane ring into its normal chair form, and should be an energetically favorable process. The other possible process leads to a much less satisfactory activated complex.

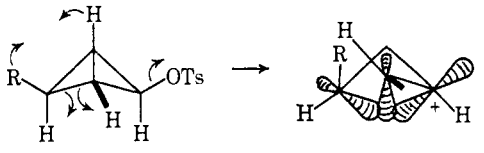
(14) G. H. Whitham and M. Wright, *Chem. Commun.*, 294 (1967).
(15) K. Ziegler and H. Wilms [*Ann.*, **567**, 1 (1950)] found that *trans*-cyclooctene reacts rapidly with phenyl azide. On the other hand, K. Alder and G. Stein [*ibid.*, **501**, 41 (1933)] found *cis*-cyclooctene to react only very slowly with this reagent.
(16) R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957).
(17) H. L. Goering and F. F. Nelson, private communication. F. F. Nelson, Ph.D. Thesis, University of Wisconsin, 1960.
(18) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).
(19) This idea has been reported in a preliminary communication: K. B. Wiberg and J. G. Pfeiffer, *J. Am. Chem. Soc.*, **90**, 5324 (1968); *cf.* C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968). Only a disrotatory ring opening is electronically allowed [K. B. Wiberg and G. Szeimies, *J. Am. Chem. Soc.*, **92**, 571 (1970)].

The ideas presented above also accommodate the difference in products between the *cis*-bicyclo[4.2.0]octyl 7-tosylates and the *cis*-bicyclo[3.2.0]heptyl 6-tosylates. The main factor which operates is the smaller dihedral angles for a five-membered ring than a cyclohexane ring. Thus, whereas **1a** prefers a reaction path which leads to an increase in the dihedral angles for the attached ring, this path may be opposed by the corresponding bicyclo[3.2.0]heptyl 6-tosylate.

The results of Lillien, Reynolds, and Handloser[20] appear to be in accord with the proposed mode of ring opening. They found *trans*-3-isopropylcyclobutyl derivatives to be more reactive than the corresponding *cis* derivatives. Similar results have been obtained with other alkyl groups,[21] and also with the *cis*- and *trans*-3-hydroxycyclobutyl derivatives.[22] If one assumes that participation is possible only when the leaving group is equatorial, the reacting conformations will be

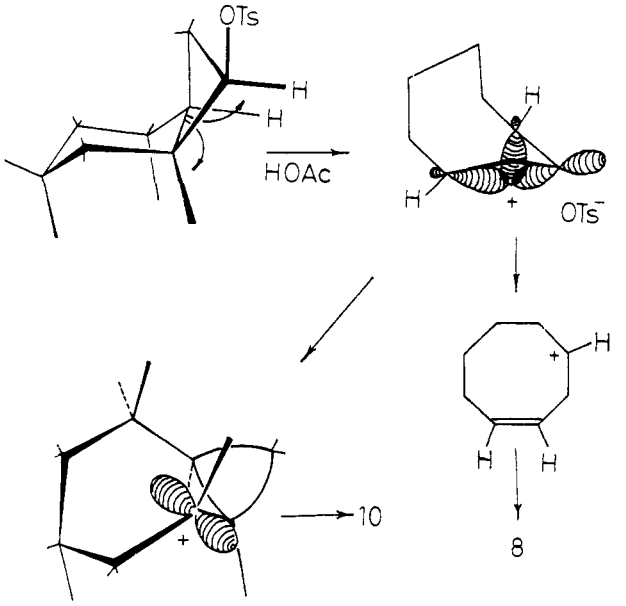


A disrotatory ring opening of the *trans* isomer is not opposed by any steric factors. However, the corresponding reaction of the *cis* isomer should lead to a marked interaction between the 3 substituent and the partially opened cyclobutane ring. Such an interaction will re-



tard the reaction and leads to the observed rate reduction.

Scheme I



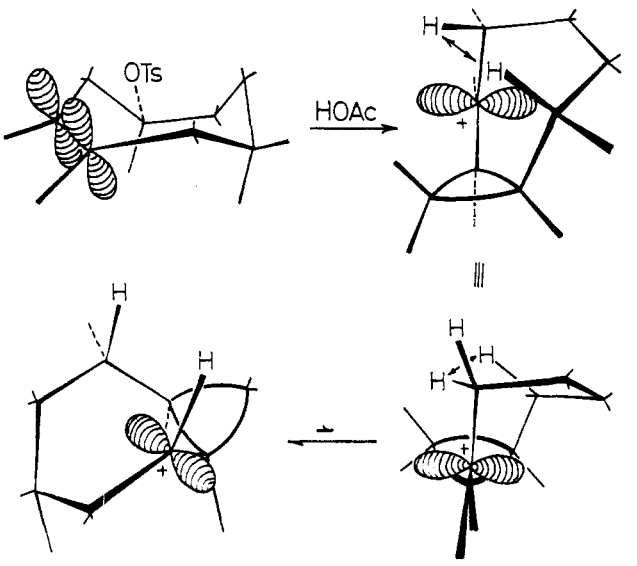
(20) I. Lillien, G. F. Reynolds, and L. Handloser, *Tetrahedron Lett.*, 3475 (1968).

(21) Professors P. v. R. Schleyer and Y. Rhodes, private communications.

(22) C. F. Wilcox, Jr., and D. L. Nealy, *J. Org. Chem.*, **28**, 3450 (1963).

Geometry of the Cyclopropylcarbinyl Cation. The observation that the ethanolyses of **2a** and cyclooctenyl tosylates gave different proportions of the *exo*- and *endo*-bicyclo[5.1.0]octyl-2 derivatives suggest the possibility that there may be two bicyclo[5.1.0]octyl-2 cations and that solvent capture may compete with the equilibration of the ions. If we examine the nature of the geometrical changes which occur during each of these reactions, we find that the initial ions are indeed different. Thus, starting with **2a**, we find the mechanism shown in Scheme I. Here, the cyclopropylcarbinyl cation will have the empty p orbital lying over one of the cyclopropane C–C bonds. This may be contrasted with the reaction of

Scheme II



cyclooctenyl tosylate (see Scheme II). In this case, the cyclopropylcarbinyl ion has its empty p orbital symmetrically disposed with respect to the cyclopropane ring. This conformation suffers from a H–H nonbonded repulsion in the bridging ring.

If the ion originally derived from **8a** were to react primarily from the less hindered side, it would give the *endo* derivatives. Conversely, the ion initially derived from **2a** would give the *exo* derivatives. This is in accord with the difference in observed product ratios. Thus, we may ask whether the two ions could have similar energies, and whether there may be a significant energy barrier to their interconversion.

It is first necessary to know approximately the difference in energy between symmetrical and unsymmetrical cyclopropylcarbinyl cations. This was calculated *via* the CNDO method[23] using parameters which have been optimized for hydrocarbons.[24] The change in energy on rotating the methylene group from the symmetrical conformation is shown in Figure 1, and the corresponding changes in the bond indices[18] are shown in Figure 2.

The energy change approximates a cosine curve, and leads to an estimate of 20 kcal/mole as the difference in energy between the extreme conformations. However, after a 30° rotation from the more stable conformation, the energy is calculated to increase by only about 4 kcal/mole. This energy difference is on the order of a torsional interaction or some nonbonded interactions

(23) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, 5136 (1965); **44**, 3289 (1966).

(24) K. B. Wiberg, *J. Am. Chem. Soc.*, **90**, 59 (1968).

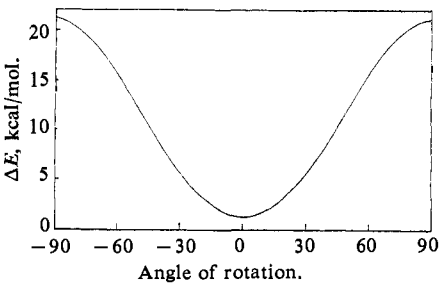


Figure 1. Change in energy of the cyclopropylcarbinyl cation as the cationic center is rotated.

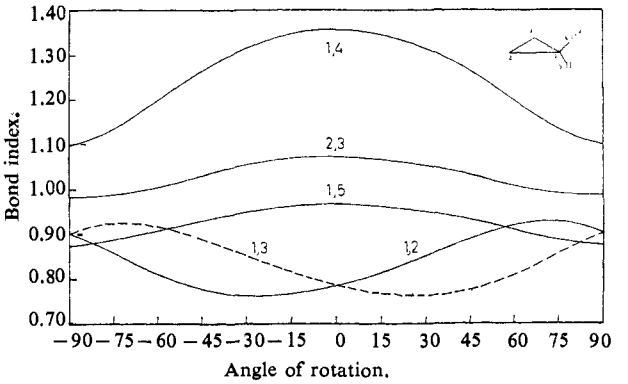


Figure 2. Change in bond indices with rotation of the cationic center in the cyclopropylcarbinyl cation.

and thus in some cases the unsymmetrical ion may have an energy comparable to the symmetrical species. The cyclopropylcarbinyl ions initially derived from **2a** and **8a** may then have similar energies, and if equilibration does not occur as rapidly as reaction with solvent, this may account for the observed differences in products. However, it is clear that other explanations are possible.

The bond index changes (Figure 2) are of some interest. In the symmetrical structure ($\alpha = 0°$), the 1,4-bond index is maximum and decreases steadily as the methylene group is rotated. The value at 90° rotation is however, still greater than unity. This results from the hyperconjugative interaction between the empty p orbital and the C_1–H_5 bond. Correspondingly, the 1,5-bond index decreases by 0.1 on going from 0.90°. The 2,3-bond order is largest at 0° corresponding to the relatively low values of the 1,2 and 1,3 indices. As the methylene group is rotated, the 1,2 and 1,3 indices change so that the bond more directly involved with the empty orbital has the lower bond index.

Experimental Section[25]

cis-**Bicyclo[4.2.0]octan-7-ols.** A solution of 125 ml (106 g, 0.98 mole) of *cis,cis*-$\Delta^{1,3}$-cyclooctadiene in 10 l. of dry ether contained in a 12-l. three-necked flask equipped with a reflux condenser connected at the top to a U tube partially filled with mercury, a gas inlet tube, a magnetic stirring bar, and a quartz immersion well was flushed with dry nitrogen for 1 hr and irradiated with stirring for 340–350 hr with a 450-W Hanovia high-pressure mercury arc lamp while maintaining a slight positive pressure of nitrogen on the system.[26] The reaction was followed by monitoring the disappearance of the diene absorption in the ultraviolet. After removal of the ether by distillation through a 15-cm Vigreux column, the yellow residue was further distilled through a Nester-Faust 2-ft spinning band column collecting the material with bp 134–135°. Contrary to published observations, this did not afford pure *cis*-Δ^7-bicyclo[4.2.0]octene. The nmr spectrum of the desired fraction showed the presence of up to 50% of the starting diene. By increasing the rate of distillation, the starting material contaminant could be reduced to approximately 30% but not lower. Therefore, the following work-up procedure was used. After the removal of the ether the yellow residue, in an appropriately sized flask, was connected to a vacuum line and a bulb-to-bulb distillation was performed, with the receiver cooled in Dry Ice–acetone. The first fraction, bp 23° (20 mm), consisted of 26 ml (21%) of a clear colorless liquid, shown by its nmr spectrum to be 83% pure *cis*-Δ^7-bicyclo[4.2.0]octene. During numerous subsequent runs the yield of 80–85% pure bicyclic product varied between 20 and 30%. The nmr spectrum had bands at τ 3.95 (s, 2 H), 7.00–7.39 (m, 2 H), and 8.10–9.06 (m, 6 H).

A solution of 17.9 g of 85% pure (0.14 mole) *cis*-Δ^7-bicyclo[4.2.0]-octene in 1 l. of dry ether was treated with diborane formed from 5.7 g (0.16 mole) of sodium borohydride and 28.4 g (0.2 mole) of boron trifluoride ethyl etherate. During the reaction the temperature was maintained at 0–4° and after the 2.5-hr reaction period, the solution was allowed to warm to room temperature for 1 hr. The reaction solution was stirred, cooled to 0–4°, and small pieces of ice were carefully added until the excess diborane had been hydrolyzed.

After the hydrolysis had been effected, the flask containing the now milky white ethereal solution was fitted with a 100-ml pressure-equalizing addition funnel containing 50 ml of ice-cold 3 *M* sodium hydroxide solution which was slowly added to the stirred and cooled contents of the flask. This was followed by the dropwise addition of 30 ml of ice-cold 33% hydrogen peroxide solution. After all reaction had ceased, stirring was stopped and the reaction mixture was left standing until it had warmed to room temperature. The ether layer was decanted and the bottom aqueous layer was extracted with three 50-ml portions of fresh ether and the combined ether extract was dried over anhydrous magnesium sulfate for 10 hr. The ether was removed on a steam bath and the residue distilled giving 13.4 g (76%) of a dense clear liquid, bp 205–206°. The product was further purified by preparative vpc on a 12 ft × 0.75 in. 20% Carbowax 20M on 50/60 mesh Anakrom U column at 175°. At a helium flow of 600 ml/min the alcohols appeared as one peak with an elution time of 37 min. Attempts to separate the *cis* and *trans* epimers of *cis*-bicyclo[4.2.0]octan-7-ol were unsuccessful. The nmr spectrum of the mixture showed absorption at τ 5.38 (s, moves on dilution, 1 H), 5.61–6.50 (superimposed multiplets from *exo* and *endo* epimers, 1 H), and 7.50–9.16 (m, 12 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.1; H, 11.3.

cis-**Bicyclo[4.2.0]octyl** *cis*- **and** *trans*-**7-Acetates.** To an ice-cold solution of 1.0 g (7.9 mmoles) of the mixture of *cis*-bicyclo-[4.2.0]octan-*cis*- and *trans*-7-ol in 15 ml of ice-cold, dry pyridine contained in a 50-ml round-bottomed flask was added with stirring 0.64 g (8.2 mmoles) of ice-cold acetyl chloride. After the acetyl chloride addition was complete, approximately 10 ml of ice water was added carefully to the reaction mixture to dissolve the pyridinium chloride precipitate. The solution was then extracted with three 25-ml portions of cold ether and the combined ether extracts washed with four 20-ml portions of 1 *N* hydrochloric acid, four 20-ml portions of ice water, and three 20-ml portions of 5% sodium bicarbonate solution, and dried for 6 hr over anhydrous magnesium sulfate. Careful removal of the ether over a steam bath and fractional distillation of the residue gave 1.21 g (91%) of a mixture of bicyclo[4.2.0]octyl *cis*- and *trans*-7-acetates, bp 97–99° (18–19 mm). Analysis of the product and subsequent preparative vpc separation using a 20 ft × 3/8 in. 20% FS 1265 on on 50/60 mesh Diatoport S column at 140° with a helium flow rate of 200 ml/min showed two components in a ratio of 5:1 which were characterized as *cis*-bicyclo[4.2.0]octyl *trans*-7-acetate (84%), retention time 20 min, and *cis*-bicyclo[4.2.0]octyl *cis*-7-acetate (16%), with a retention time of 23 min.

The nmr spectrum of the *trans* isomer showed bands at τ 4.75–5.20 (m, 1 H) and 7.30–9.15 (m, including an acetate CH_3 singlet centered at τ 8.05, 15 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.4; H, 9.5.

The nmr spectrum of the *cis* isomer had bands at τ 5.00–5.46 (m, 1 H) and 7.16–9.23 (m, broad absorption of ring protons and an acetate CH_3 singlet centered at τ 8.06, 15 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.5; H, 9.6.

(25) Nmr spectra were taken in carbon tetrachloride with TMS as an internal standard, and infrared spectra were taken in carbon tetrachloride solution.

(26) W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, 27, 1910 (1962).

cis-**Bicyclo[4.2.0]octan-7-one.** A 107.4-g sample of approximately 80% pure (0.79 mole) *cis*-Δ^7-bicyclo[4.2.0]octene was dissolved in 1 l. of dry ether contained in a 3-l. three-necked flask and was treated with diborane generated from 37.8 g (1 mole) of sodium borohydride and 142 g (1 mole) of boron trifluoride ethyl etherate. After hydrolysis of the excess diborane by the dropwise addition of 250 ml of ice water, the reaction flask was equipped with a refluxed condenser and a 1-l. addition funnel containing part of a previously prepared solution of 298 g (1 mole) of sodium dichromate dihydrate and 290 g (2.96 moles) of 96% sulfuric acid dissolved in 1 l. of water. All of this oxidizing solution was then added to the stirred, hydroborated solution at such a rate as to keep the ether solvent just below its reflux temperature. After the addition was complete (about 1 hr), the reaction mixture was stirred at room temperature for 1 hr and then left standing without stirring for an additional 30 min to allow separation of the two layers. The ether layer was decanted and the water layer extracted with four 150-ml portions of fresh ether. The combined ether extract was concentrated over a steam bath and after cooling to room temperature was washed with 100-ml portions of saturated sodium bicarbonate solution until a neutral test was obtained. The neutral ether solution was then dried over anhydrous magnesium sulfate and after careful removal of the ether over a steam bath the residue was subjected to vpc analysis using a 20 ft × 3/8 in. 20% DEGS on 50/60 mesh Anakrom U column at 140°. With a helium flow of 175 ml/min and a 1.5-μl sample injection, six major product peaks in a ratio of 40.0:28.2:7.4:21.3:2.7:3.5 were obtained with retention times of 17, 20, 22, 24, 30, and 34 min, respectively. The peak with 17-min elution time was identified as the desired *cis*-bicyclo[4.2.0]octan-7-one. The residue was distilled giving 46.4 g of the crude ketone, bp 48–51° (0.17 mm), which was then further purified by preparative vpc using a 12 ft × 0.75 in. 20% Carbowax 20M on 50/60 mesh Anakrom U column at 135° with a helium flow of 600 ml/min. With a 2-ml sample injection, the retention time of the ketone was 45 min, while with a 200-μl sample injection under identical conditions the retention time was 25 min. The yield of vpc pure *cis*-bicyclo[4.2.0]octan-7-one was 44.6 g (46%). The other products were not further investigated. The infrared spectrum of *cis*-bicyclo[4.2.0]octan-7-one had a band at 1775 cm^{-1} (C=O stretching characteristic of cyclobutanones), and the nmr spectrum showed absorption at τ 6.59–7.25 (m, 2 H) and 7.25–9.29 (m, 10 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.4; H, 9.8. Found: C, 77.4; H, 10.0.

Reduction of *cis*-Bicyclo[4.2.0]octan-7-one. A solution of 11.9 g (0.096 mole) of the ketone in 50 ml of dry ether was added dropwise to a stirred slurry of 7.4 g (0.19 mole) of lithium aluminum hydride in 200 ml of dry ether contained in a 500-ml flask. The rate of addition was controlled so as to maintain the ether solvent at reflux temperature. After the addition was complete, the reaction mixture was heated to reflux for 1 hr. After cooling to room temperature, 7.4 g of ice water, 7.4 g of ice-cold 15% potassium hydroxide solution, and 22 g of ice-water were carefully added to the reaction mixture in that order. The white granular precipitate formed was filtered off and washed with three 25-ml portions of fresh ether. The combined ethereal solution was then washed with two 75-ml portions of a saturated sodium chloride solution and dried over anhydrous magnesium sulfate for 5 hr. Careful removal of ether over a steam bath and fractional distillation of the residue gave 11.3 g (93%) of a mixture of *cis*-bicyclo[4.2.0]octan-*cis*- and *trans*-7-ol, bp 111–114° (21–23 mm). The product was characterized by its infrared and nmr spectra which corresponded to those found for the mixture of epimeric alcohols described above.

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.2; H, 11.3.

The mixture of alcohols was converted to the acetates as described above. Vpc analysis and separation of the products as discussed above showed two components in the ratio of 1:6 which were identified as *cis*-bicyclo[42.0]octyl *trans*-7-acetate (14%) and *cis*-bicyclo[4.2.0]octyl *cis*-7-acetate (86%). The nmr and infrared spectra were compared and found to be identical with those of the bicyclic acetates obtained by the first method described.

cis-**Bicyclo[4.2.0]octan-*trans*-7-ol.** A 2.95-g (0.018 mole) sample of vpc pure *cis*-bicyclo[4.2.0]octyl *trans*-7-acetate dissolved in 10 ml of dry ether was added dropwise to a stirred slurry of 0.71 g (0.0185 mole) of lithium aluminum hydride in 20 ml of dry ether contained in a 250-ml three-necked round-bottomed flask. The rate of addition was controlled so as to maintain the solvent at its reflux temperature. After the addition was complete the reaction mixture was stirred at room temperature for 30 min and was treated with 0.70 g of ice water, 0.70 g of 15% ice-cold potassium hydroxide solution, and 2 g of ice water. The granular, white precipitate was filtered off, the solution was dried over anhydrous magnesium sulfate for 3 hr, and the ether removed by distillation. The residue was further distilled to give 2.21 g (97%) of pure *cis*-bicyclo[4.2.0]octan-*trans*-7-ol, bp 112–114° (21–23 mm). The nmr spectrum showed bands at τ 5.30 (s, moves on dilution, 1 H), 5.64–6.08 (m, 1 H), and 7.50–9.20 (m, 12 H).

The *cis* isomer was obtained in the same fashion from 2.50 g of *cis*-bicyclo[4.2.0]octyl *cis*-7-acetate and gave 1.82 g (96%) of the pure alcohol, bp 112–113.5° (22 mm). The nmr spectrum had bands at τ 6.83 (s, moves on dilution, 1 H), 5.80–6.22 (m, 1 H), and 7.50–9.34 (m, 12 H).

cis-**Bicyclo[4.2.0]octyl *trans*-7-Tosylate.** To a magnetically stirred ice-cold solution of 5.72 g (30 mmoles) of *p*-toluenesulfonyl chloride in 15 ml of dry pyridine was added with swirling 2.0 g (15.9 mmoles) of *cis*-bicyclo[4.2.0]octan-*trans*-7-ol. The solution was stored for 27 hr at −10°. To the reaction mixture was then added 40 ml of ice water and the solution extracted with three 25-ml portions of ice-cold ether. The combined extracts were washed with three 10-ml portions of ice-cold 1 *N* hydrochloric acid, three 10-ml portions of ice water, four 10-ml portions of 5% sodium bicarbonate solution, and three 10-ml portions of ice water, respectively, and dried over anhydrous sodium sulfate. Removal of the ether in the cold using a rotary evaporator gave 3.78 g (85%) of a slightly yellow oil. Two recrystallizations from ether–pentane at −78° afforded white crystals, mp 43–44.5° (lit.[8] mp 44.5–46.5°). The *cis* isomer was prepared in the same fashion and recrystallization from ether–pentane at −78° gave white crystals, mp 41.5–42.5° (lit.[8] mp 40.0–41.5°).

trans-**2-Vinylcyclohexanol.** A Grignard reagent was prepared from 24.3 g (1 g-atom) of magnesium turnings, 106.9 g (1 mole) of vinyl bromide, and 750 ml of dry tetrahydrofuran. To this solution was added 98.2 g (1 mole) of cyclohexene oxide with stirring and ice bath cooling. The mixture was stirred at room temperature for 10 hr and during this time changed to a semisolid brown sludge. Enough cold saturated ammonium chloride solution was carefully added to dissolve all solid and the two layers were separated. The water layer was extracted with three 250-ml portions of ether and the combined ether and tetrahydrofuran was dried for 5 hr over anhydrous magnesium sulfate. Removal of the solvent and distillation gave 95 g of a colorless oil, bp 35–37.5° (0.35–0.40 mm). Vpc analysis showed the material to consist of four components in a ratio of 2.4:1.0:22.5:9.8. The first component, retention time 4.3 min, was readily identified as cyclohexanol (6.3%) while component two (2.7%), with retention time 6 min, remained unidentified. The third component (59.9%) with a retention time of 6.5 min was the major product and appeared from its nmr spectra to be vinylcyclopentylcarbinol. The fourth component (26.1%) with a retention time of 7 min proved to be the desired *trans*-2-vinylcyclohexanol. The nmr spectrum showed bands at τ 3.90–4.60 (m, 1 H), 4.70–5.13 (m, 2 H), 6.60–7.14 (m, 1 H), 7.54 (s, moves on dilution, 1 H), and 7.60–9.27 (m, 9 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.2; H, 11.3.

trans-**2-Vinylcyclohexyl Tosylate.** A solution of 3.44 g (18 mmoles) of *p*-toluenesulfonyl chloride, 1.04 g (8.24 mmoles) of *trans*-2-vinylcyclohexanol, and 15 ml of dry pyridine was stored in a freezer at −10° for 20 hr. The reaction mixture was then treated with 45 ml of ice water and extracted with three 20-ml portions of cold ether. The combined ether extract was washed with several 5-ml portions of cold 1 *N* hydrochloric acid, ice water, cold 5% sodium bicarbonate solution, and ice water and dried over anhydrous sodium sulfate for 5 hr. Removal of the ether using a rotary evaporator gave 2.03 g (88%) of the crude tosylate. The slightly yellow oil was recrystallized from pentane at −78° to give white crystals, mp 42–43°. The nmr spectrum had bands at τ 2.00–2.75 (A_2B_2, 4 H), 4.07–4.72 (m, 1 H), 4.80–5.22 (m, 2 H), 7.55 (s, 3 H), and 7.65–9.25 (m, 9 H).

3,4-Epoxycyclooctene. To a vigorously stirred solution of 60 g (0.56 mole) of *cis,cis*-$\Delta^{1,5}$-cyclooctadiene in 1 l. of dry methylene chloride contained in a 3-l. three-necked flask equipped with a reflux condenser, mechanical stirrer, and dropping funnel was added dropwise 96 g (0.64 mole) of 40% peracetic acid solution. The rate of addition was controlled so as to maintain the solvent at its reflux temperature. After the addition was complete the reaction mixture was stirred at room temperature for 2 hr and then cooled to 0–4° with an ice bath. Enough anhydrous sodium sulfite was added to destroy the remaining peracid (as indicated by a negative iodine paper test) and the emulsion which had formed was separated by adding 1 l. of cold water. Enough anhydrous sodium carbonate

was then added barely to saturate the solution and the two layers were separated. The water layer was extracted with three 500-ml portions of fresh methylene chloride and the combined solution was dried over anhydrous sodium sulfate for 6 hr. Removal of the solvent and fractional distillation of the slightly yellow residue gave 55.9 g (81%) of 3,4-epoxycyclooctene, bp 76–78° (18 mm). Vpc analysis using a 20 ft × 3/8 in. 20% FS 1265 on 50/60 mesh Diatoport S column at 165° with a helium flow of 180 ml/min gave one peak with a retention time of 19 min. The nmr spectrum had bands at τ 3.90–4.50 (m, 2 H), 6.56–6.80 (m, 1 H), 6.82–7.30 (m, 1 H), and 7.50–9.00 (m, 8 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.4; H, 9.7.

3-Cycloocten-1-ol. A 50.0-g (0.403 mole) sample of 3,4-epoxycyclooctene was reduced in the usual fashion with 7.6 g (0.20 mole) of lithium aluminium hydride and 13.5 g (0.1 mole) of aluminum chloride in 550 ml of dry ether. Removal of the solvent after work-up and distillation of the residue gave 43.0 g (85%) of 3-cycloocten-1-ol, bp 102–103.5° (17–18 mm). Vpc analysis using a 20 ft × 3/8 in. 20% Dow 710 on 50/60 mesh Anakrome U column at 185° with a helium flow of 150 ml/min showed one component with a retention time of 18 min. The nmr spectrum gave bands at τ 4.33–4.70 (m, 2 H), 6.13–6.65 (m, 1 H), 6.88 (s, 1 H), 7.59–8.10 (m, 4 H), and 8.10–9.16 (m, 6 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.2, 76.1; H, 11.2, 11.2.

3-Cycloocten-1-yl Tosylate. To an ice-cold solution of 60.6 g (0.32 mole) of *p*-toluenesulfonyl chloride in 150 ml of dry pyridine was added dropwise with swirling 20.0 g (0.16 mole) of 3-cycloocten-1-ol and the solution was stored at −10° for 15 hr. The mixture was then poured into 250 ml of cold water and extracted with three 100-ml portions of cold ether. The combined extracts were washed successively with small portions of ice water, 1 *N* hydrochloric acid, 5% sodium bicarbonate solution, saturated sodium chloride solution, and ice water. After drying for 6 hr over anhydrous sodium sulfate, the ether was removed using a rotary evaporator to give 41.7 g (94%) of 3-cycloocten-1-yl tosylate as a slightly yellow oil which resisted all attempts at crystallization. The nmr spectrum had bands at τ 2.06–2.81 (A_2B_2, 4 H), 3.99–4.76 (m, 2 H), 5.20–5.66 (m, 1 H), 5.78 (s, 3 H), and 5.80–9.21 (m, 10 H).

Photochemical Cycloaddition of 2-Cyclohexen-1-one and Benzyl Vinyl Ether. A magnetically stirred, Dry Ice cooled solution of 34.0 g (0.35 mole) of 2-cyclohexen-1-one and 310 g (2.31 moles) of benzyl vinyl ether in 1890 ml of dry pentane was irradiated under a nitrogen atmosphere for 29.5 hr using a 450-W Hanovia high-pressure mercury arc lamp and a Corex filter.[5] The reaction was followed by removing small aliquots with a syringe and measuring the infrared absorption. Irradiation was stopped when the conjugated carbonyl peak of 2-cyclohexen-1-one (1685 cm^{-1}, pentane) had completely disappeared and had been replaced by the non-conjugated carbonyl absorption of the photoadducts (1715, 1720 cm^{-1}, pentane). Solvent was removed and 163.7 g of unreacted benzyl vinyl ether, bp 47–48° (3 mm), was recovered by distillation. Distillation of the residue through a 6-in. Vigreux column gave 61.3 g (76%) of a light yellow liquid, bp 123–135° (0.6 mm).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.2; H, 7.9. Found: C, 78.1, 78.2; H, 7.8, 7.8.

The mixture of photoadducts was subjected to vpc analysis using a 20 ft × 3/8 in. 20% FS 1265 on Diataport S column at 245° with a helium flow of 300 ml/min. A singular property of the Diataport S support is that it does not effect the isomerization of *trans*- to *cis*-fused adduct, which was observed with all other columns tried. The product mixture showed four components in the ratio 1:7:8:2, with 14-, 15-, 17-, and 18-min retention times, respectively. In order to characterize these components better, four 200-mg samples of the product mixture were treated with 20% methanolic potassium hydroxide solution at room temperature for 0.5, 1.5, 3, and 10 hr, respectively. A stream of carbon dioxide was bubbled through the solutions to decompose potassium methoxide and the mixtures were evaporated to dryness under reduced pressure. The residue from each sample was extracted with small portions of ether and the combined extracts dried over anhydrous magnesium sulfate. Removal of the ether by distillation and vpc analysis of the remaining oils led to the following observations. After 30 min of base treatment the area of the 14-min peak had decreased slightly while the 18-min peak had completely disappeared. Instead a new product peak appeared with a retention time of 11 min and a shoulder at 11.5 min. After 1.5-hr base treatment, both the 18-min as well as the 14-min peak had been transformed into new products with 11-min and 11.5-min retention times. Analysis of the products produced after 3 hr of base treatment showed that the 17-min peak had appreciably decreased in area while that of the 15-min peak had increased correspondingly. The 11-min and the 11.5-min peak remained unchanged. After 10 hr of treatment with methoxide only three product peaks were seen with 11-, 11.5-, and 15-min retention times, respectively. A micro nmr spectrum of the two-component new product mixture with 11- and 11.5-min retention times referred to above was informative only in that it showed the absence of aromatic absorption and two singlets at τ 6.85 and 6.80 (two methoxy methyl groups, presumably two epimers). Thus, chemical evidence permits the conclusion that the four products obtained from the irradiation of 2-cyclohexen-1-one and benzyl vinyl ether are as follows: *cis*-8-benzyloxybicyclo[4.2.0]octan-2-one (6%), retention time 14 min and nmr bands at τ 2.79 (s, 5 H), 5.65 (s, 2 H), 5.76–6.14 (m, 1 H), and 6.69–8.91 (m, 10 H); *cis*-7-benzyloxybicyclo[4.2.0]octan-2-one (38%), retention time 15 min and an nmr spectrum with bands at τ 2.80 (s, 5 H), 5.69 (s, 2 H), 6.06–6.54 (m, 1 H), and 6.90–8.61 (m, 10 H); *trans*-7-benzyloxybicyclo[4.2.0]octan-2-one (46%), with a retention time of 17 min and an nmr spectrum showing absorption bands at τ 2.78 (s, 5 H), 5.56–5.78 (d, J = 5 cps, 2 H), 5.78–6.50 (m), and 6.75–8.75 (m, 10 H); and *trans*-8-benzyloxybicyclo[4.2.0]octan-2-one (10%), retention time 18 min with an nmr spectra showing absorption at τ 2.78 (s, 5 H), 5.54–5.74 (d, J = 2 cps, 2 H), 6.03–6.53 (m), 7.29–8.83 (m, 10 H).

***cis*- and *trans*-7-Benzyloxybicyclo[4.2.0]octan-2-ol.** To a stirred slurry of 8.28 g (0.22 mole) of lithium aluminum hydride in 800 ml of dry ether was added dropwise with stirring 49.2 g (0.214 mole) of *cis*- and *trans*-7-benzyloxybicyclo[4.2.0]octan-2-one containing approximately 16% *cis*- and *trans*-8-benzyloxybicyclo[4.2.0]octan-2-one dissolved in 250 ml of dry ether. The rate of addition was controlled so as to maintain the ether solvent at reflux temperature. The reaction mixture was then heated to reflux for an additional 30 min and cooled to 0–4° in an ice bath. The excess hydride was hydrolyzed by the careful addition of 8 ml of ice water, 8 ml of 15% potassium hydroxide solution, and 24 ml of ice water in that order. The white granular precipitate was filtered off and washed with several small portions of fresh ether, and the combined extracts were then dried for 5 hr over anhydrous magnesium sulfate. Removal of the solvent over a steam bath and distillation of the residue afforded 49.0 g (99%) of a light yellow oil, bp 109–121° (0.8 mm), characterized as *cis*- and *trans*-7-benzyloxybicyclo[4.2.0]octan-2-ol, presumably still containing *cis*- and *trans*-8-benzyloxybicyclo[4.2.0]-octan-2-ol as minor products. Again, attempts to effect a better separation of the product mixture by distillation or by preparative vpc proved unsuccessful and an analytical sample was prepared by collecting a few drops of material with bp 115–116° (0.8 mm). The nmr spectrum had bands at τ 2.81 (s, 5 H). 5.00–6.35 (a complex of superimposed multiplets), 7.00 (s, moves on dilution), and 7.35–9.34 (broad, complex absorption).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.6; H, 8.7. Found: C, 77.7, 77.6; H, 8.6, 8.7.

***cis*- and *trans*-7-Benzyloxybicyclo[4.2.0]octane.** A solution of 60.8 g (0.26 mole) of *cis*- and *trans*-7-benzyloxybicyclo[4.2.0]octan-2-ol containing minor amounts of the 8 isomer in 300 ml of dry pyridine contained in a 1-l. flask was cooled to 0–4° with an ice bath. To the cold solution was added with swirling 55.5 g (0.29 mole) of *p*-toluenesulfonyl chloride and the reaction mixture was stored at −10° for 4 days. To the mixture was added 800 ml of ice water and the solution was extracted with four 250-ml portions of ether. The combined extracts were washed with four 250-ml portions each of 1 *N* hydrochloric acid, ice water, 5% sodium bicarbonate solution, and ice water, and dried over anhydrous potassium carbonate for 6 hr. Removal of the ether using a rotary evaporator left 82.1 g (81%) of the tosylates as a yellow oil. Attempts to crystallize a small portion of the product from pentane at −78° were unsuccessful and the tosylate was used for further reaction in the form of the oil.

To a stirred slurry of 25.8 g (0.68 mole) of lithium aluminum hydride in 800 ml of dry ether contained in a 3-l. three-necked flask equipped with reflux condenser, addition funnel, and mechanical stirrer was added a solution of 500 ml of dry ether and 250 g (0.65 mole) of *cis*- and *trans*-7-benzyloxybicyclo[4.2.0]octyl-2 tosylate. The rate of addition was adjusted so as to maintain gentle refluxing of the solvent. The reaction mixture was heated to reflux for 50 hr and then cooled to 0–4° with an ice bath. The excess hydride was destroyed by the addition of 26 g of ice water, 26 g of cold 15% potassium hydroxide solution, and 80 g of ice water in that order. The white granular precipitate was filtered off and washed with several small portions of fresh ether. The com-

bined ether extract was washed with 1 *N* hydrochloric acid solution and with several small portions of saturated sodium chloride solution and then dried over anhydrous magnesium sulfate for 6 hr. Removal of the solvent over a steam bath and distillation of the residue gave 138 g (98%) of *cis*- and *trans*-7-benzyloxybicyclo[4.2.0]-octane, bp 106–115° (0.4 mm). The nmr spectrum had bands at τ 2.64 (s, 5 H), at least four peaks in the region 5.37–5.70 (nonequivalent methylene hydrogens of the benzyl group), 5.70–6.70 (complex of superimposed multiplets), and broad absorption in the region 6.92–9.25.

Treatment of *cis*- and *trans*-7-Benzyloxybicyclo[4.2.0]octane with Lithium in Ethylamine. Approximately 1 l. of ethylamine was distilled into a Dry Ice cooled, 3-l. three-necked flask, equipped with a nitrogen inlet tube, addition funnel, a mechanical stirrer, and a Dry Ice condenser. Small pieces of freshly cut lithium wire were then added to the stirred ethylamine until a permanently blue solution was obtained, and then 14 g (2 g-atoms) of lithium was added. After warming the mixture to 0–4° with an ice bath, 184 g (0.850 mole) of *cis*- and *trans*-7-benzyloxybicyclo[4.2.0]octane was added in small portions. After the addition was complete, the reaction mixture was stirred for 5 hr at 0–4° and then at room temperature for 2 additional hr, with a brisk stream of nitrogen flowing through the apparatus to sweep out the evaporating ethylamine. The excess lithium was removed mechanically and ice water was carefully added to the mixture until all reaction had ceased, leaving a semisolid sludge. An additional 1 l. of water was added and the mixture repeatedly extracted with ether. The combined extract was washed with six 250-ml portions of water and six 250-ml portions of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the solvent and distillation of the residue afforded 100 g (94%) of impure *cis*- and *trans*-bicyclo-[4.2.0]octan-7-ol. The crude mixture was separated by preparative vpc using a 13 ft × 3/4 in., 20% Carbowax 20M column at 190° with a helium flow rate of 600 ml/min. The two major peaks, in a ratio of 62:38, were collected and identified as epimeric mixtures of *trans*-bicyclo[4.2.0]octan-7-ol, retention time 20 min, and *cis*-bicyclo[4.2.0]octan-7-ol, retention time 25 min, respectively. In this fashion 55.8 g of the *trans*-fused and 34.2 g of the *cis*-fused bicyclic alcohols were obtained. It proved impossible to separate the epimers of *trans*-bicyclo[4.2.0]octan-7-ol by vpc.

***trans*-Bicyclo[4.2.0]octyl *cis*- and *trans*-7-Acetate.** To an ice-cold solution of 10.3 g (0.082 mole) of epimeric *trans*-bicyclo[4.2.0]-octan-7-ols in 100 ml of dry pyridine was added dropwise with swirling 7.46 g (0.095 mole) of acetyl chloride. Enough ice water was added to the reaction mixture to dissolve the white pyridinium chloride precipitate and the solution was extracted with several small portions of cold ether. The combined ether extract was washed with four cold 50-ml portions each of 1 *N* hydrochloric acid, water, 5% sodium bicarbonate solution, and water, and then dried over anhydrous magnesium sulfate. Removal of the solvent by distillation left 13.7 g (~100%) of crude *trans*-bicyclo[4.2.0]octyl *cis*- and *trans*-7-acetates. The epimers were separated by preparative vpc using a 20 ft × 3/8 in., 20% FS 1265 on 50/60 mesh Diatoport S column at 150° to give 8.2 g (60%) of *trans*-bicyclo[4.2.0]-octyl *cis*-7-acetate and 5.5 g (40%) of *trans*-bicyclo[4.2.0]octyl *trans*-7-acetate. With a helium flow rate of 200 ml/min and a 2.0-μl sample injection, the retention times of the major and minor epimers were 11 and 12 min, respectively.

The nmr spectrum of the *trans,cis* epimer had bands at τ 4.81–5.20 (m, 1 H) and 7.17–9.00 (m, broad absorption of ring protons and an acetate CH_3 singlet centered at τ 8.05, 15 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.3; H, 9.6.

The nmr of the *trans,trans* epimer showed absorption at τ 5.33–5.76 (m, 1 H) and 7.30–9.16 (m, complex absorption of ring protons including an acetate CH_3 singlet centered at τ 8.07, 15 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.5; H, 9.6.

***trans*-Bicyclo[4.2.0]octanols.** The acetates were reduced to the alcohols with lithium aluminum hydride as described above. *trans*-Bicyclo[4.2.0]octan-*cis*-7-ol had bp 92–93.5° (14–15 mm), and its nmr spectrum had bands at τ 5.67–6.05 (m, 1 H), 6.55 (s, moves on dilution, 1 H), and 7.32–9.0 (m, 12 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.1; H, 11.3.

trans-Bicyclo[4.2.0]octan-*trans*-7-ol had bp 93–94° (15 mm), and its nmr spectrum had bands at τ 6.07–6.57 (m, 1 H), 7.05 (s, moves on dilution, 1 H), and 7.52–9.45 (m, 12 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.2; H, 11.3.

The alcohols were converted to tosylates with *p*-toluenesulfonyl chloride in pyridine at −10°. Both tosylates were found to melt somewhat below 0°.

Acetolysis of *cis*-Bicyclo[4.2.0]octyl *trans*-7-Tosylate. A 0.25-g sample of *cis*-bicyclo[4.2.0]octyl *trans*-7-tosylate was dissolved in 50 ml of a 0.0475 *N* solution of sodium acetate in anhydrous acetic acid. The solution was kept at 25° for 3 hr, poured into 150 ml of ice water, and repeatedly extracted with small portions of ether. The combined ether extract was washed with five 25-ml portions of ice water, ten 50-ml portions of cold 5% sodium bicarbonate solution, and five 25-ml portions of ice water. After drying over anhydrous magnesium sulfate, the ether was removed to give 0.204 g of residue. The nmr spectrum corresponded to a mixture of 53% *trans*-2-vinylcyclohexyl tosylate and 47% *trans*-2-vinylcyclohexyl acetate. The acetate was separated by bulb-to-bulb distillation at 0.5 mm giving 0.07 g of acetate and 0.13 g of tosylate. The tosylate was recrystallized from ether–pentane to give pure tosylate, mp 42–43.5°, identical with *trans*-2-vinylcyclohexyl tosylate. The acetate was examined by vpc and was found to be homogeneous.

The experiment was repeated keeping the solution at 25° for 4.5 hr, and in another case, keeping the solution at 75° for 36 hr. The mixtures were worked up as described above. The 25° reaction mixture gave an acetate mixture which could be separated into two components by vpc using a 20% FS 1265 on Diatoport S column at 160° and a helium flow of 130 ml/min. The components, found in a 93.1:6.9 ratio, were identified by nmr spectroscopy and by coinjection with authentic samples to be *trans*-2-vinylcyclohexyl acetate and *cis*-bicyclo[4.1.0]heptane *trans*-7-methyl acetate. The 75° reaction mixture contained no tosylate, and the acetate was shown by vpc to be a mixture of *trans*-2-vinylcyclohexyl acetate (84.9%, 8 min), *cis*-bicyclo[4.2.0]octyl *trans*-7-acetate (5.0%, 12 min), and *exo*-bicyclo[4.1.0]heptane 7-methyl acetate (10.1%, 13.5 min).

Acetolysis of *cis*-Bicyclo[4.2.0]octyl *cis*-7-Tosylate. A solution of 1 0 g of the tosylate in 100 ml of 0.0475 *N* sodium acetate in acetic acid was heated at 50.0° for 30 hr. The reaction mixture was worked up as described above. The acetates were separated from the residue by bulb-to-bulb distillation, and were analyzed by vpc under the conditions described above. The products were found to be *trans*-2-vinylcyclohexyl acetate (1.5%, 8 min), *exo*-bicyclo-[5.1.0]octyl 2-acetate (32%, 9.8 min), 3-cyclooctenyl acetate (64.5%, 12 min), and *endo*-bicyclo[5.1.0]octyl 2-acetate (1%, 13 min). The products were identified by comparison of their nmr spectra with those of authentic samples, and by coinjection with authentic samples. The nonvolatile material consisted of about 1% of 2-vinylcyclohexyl tosylate.

Acetolysis of *trans*-2-Vinylcyclohexyl Tosylate. A 0.64-g sample of *trans*-2-vinylcyclohexyl tosylate in 50 ml of 0.0475 *N* sodium acetate in acetic acid was heated at 100° for 2 hr. The reaction mixture was worked up as described above and gave only acetate products. Vpc analysis indicated *trans*-2-vinylcyclohexyl acetate (62.7%, 10.5 min), *cis*-2-vinylcyclohexyl acetate (20% 11.9 min), *cis*-bicyclo[4.2.0]octyl *trans*-7-acetate (7.8%, 15 min), and *exo*-bicyclo[4.1.0]heptane-7-methyl acetate (9.5%, 16.5 min).

Acetolysis of 3-Cycloocten-1-yl Tosylate. A solution of 1.5 g of the tosylate in 200 ml of 0.0475 *N* sodium acetate in acetic acid was heated at 50.0° for 5.0 hr. The normal work-up procedure gave a mixture of acetates. Separation by vpc gave *exo*-bicyclo[5.1.0]-octyl 2-acetate (22.9%, 9.8 min), 3-cycloocten-1-yl acetate (52.2%, 12 min), and *endo*-bicyclo[5.1.0]octyl 2-acetate (24.9%, 13 min). The experiment was repeated, keeping the solution at 25° for 13 hr. The same products were obtained and in the order given above the percentages were 20, 34, and 46%.

Acetolysis of *trans*-Bicyclo[4.2.0]octyl *cis*-7-Tosylate. A solution of 0.42 g of the tosylate in 200 ml of a 0.0475 *N* solution of sodium acetate in acetic acid was heated at 90.0° for 12 hr. After normal work-up, the residue was found by vpc to be a mixture of acetates. The products were identified by comparison of their nmr spectra with those of authentic samples and were spiro[2.5]octyl 4-acetate (2.7%, 23 min), *cis*-bicyclo[4.2.0]octyl 1-acetate (6.6%, 25 min), 1.8% of an unidentified compound, 28 min retention time, *trans*-bicyclo[4.2.0]octyl *cis*-7-acetate (39.4%, 31 min), *trans*-bicyclo-[4.2.0]octyl *trans*-7-acetate (42.9%, 34 min), and 3-cycloocten-1-yl acetate (6.7%, 37 min).

Acetolysis of *trans*-Bicyclo[4.2.0]octyl *trans*-7-Tosylate. A solution of 0.23 g of the tosylate in 250 ml of 0.0475 *N* sodium acetate in acetic acid was heated at 90.0° for 10 hr. After usual work-up, a mixture of acetates was found. Vpc analysis indicated *trans*-

bicyclo[4.2.0]octyl *cis*-7-acetate (21%), *trans*-bicyclo[4.2.0]octyl *trans*-7-acetate (17%), and 3-cycloocten-1-yl acetate (57%).

Reaction of *trans*-2-Cycloocten-1-ol with Phenyl Azide. The *trans*-2-cycloocten-1-ol was prepared by the solvolysis of *exo*-8-bromobicyclo[5.1.0]octane in aqueous dioxane as described by Whitham and Wright. In order to obtain reproducible results, it was found necessary to add calcium carbonate as a buffer. The alcohol obtained from 0.46 g of the bromide was allowed to react with 0.29 g of phenyl azide in 25 ml of ether at 25° for 30 min. The solvent was removed using a rotary evaporator and all volatile material was removed by maintaining the residue at 0.1 mm pressure for 20 hr. The red semisolid was characterized as the triazoline adduct of the *trans* double bond. The nmr spectrum had bands at τ 2.65–3.34 (aromatic protons), 5.35–6.27 (unresolved multiplet), 6.27–7.09 (unresolved multiplet), 7.18–9.40 (broad, complex band). The ultraviolet spectrum in hexane showed weak absorption at 310 mμ ($n \rightarrow \pi^*$) and an intense band at 239 mμ ($\pi \rightarrow \pi^*$ band of the phenyl substituent). The infrared spectrum showed the absence of phenyl azide. The mass spectrum had its high mass peak at *m/e* 217 ($P-N_2$). Other characteristic peaks were at *m/e* 200 ($P - N_2 - OH$), 126 ($P - N_2 - C_6H_5N$), 93 ($C_6H_5NH_2$), and 91 (C_6H_5N).

Solvolysis of *trans*-Bicyclo[4.2.0]octyl *trans*-7-Tosylate in Buffered Aqueous Dioxane. A solution of 0.22 g of the tosylate in 25 ml of 2:1 dioxane–water (by volume) containing 0.08 g of calcium carbonate was heated to reflux for 32 hr. The solution was diluted with 50 ml of cold water, and repeatedly extracted with small portions of ether. The combined ether extract was dried over anhydrous magnesium sulfate and then concentrated using a rotary evaporator. To the residue was added 15 ml of fresh dry ether containing 0.29 g of phenyl azide. After 15 min at 25°, the solvent was removed under reduced pressure and volatile materials were removed by keeping the residue at 0.1 mm for 25 hr. The red semisolid which remained was characterized as the triazoline adduct of *trans*-3-cycloocten-1-ol. The ultraviolet spectrum in hexane showed weak absorption at 310 mμ and an intense band at 239 mμ. The nmr spectrum showed bands at τ 2.69–3.60, 5.10–6.13, 6.15–7.03, and 7.40–9.40. The mass spectrum was quite similar to that of the previously described adduct and had the characteristic bands listed above.

Solvolysis of Bicyclo[2.1.0]pentyl 2-(3,5-Dinitrobenzoates)[1]

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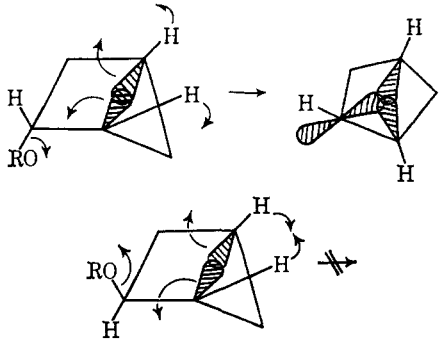
Abstract: The rates of solvolysis of *exo*- and *endo*-bicyclo[2.1.0]pentyl 2-(3,5-dinitrobenzoates) have been determined. The *endo*/*exo* rate ratio is 10^7, and the difference in activation enthalpy is 12 kcal/mole. The results are in accord with an assumption that maximum overlap is required between the developing empty p orbital and the orbitals of the bond being broken for a concerted accelerated solvolysis of a cyclobutyl derivative. The results are compared with those for the series of bicyclo[*m*.2.0]alkyl derivatives.

As a result of our study of the solvolyses of *cis*- and *trans*-bicyclo[4.2.0]octan-7-ol derivatives,[3] it became clear that the opening of the cyclobutyl ring required a specific mode of orbital motion, similar to that required with cyclopropyl derivatives.[4] In an effort to obtain a definitive test of this hypothesis, we have examined the solvolyses of *exo*- and *endo*-bicyclo[2.1.0]-pentyl 2-(3,5-dinitrobenzoates). In the *endo* isomer, the required orbital motion would lead to a decrease in strain and a markedly enhanced rate of reaction should be found. In the *exo* isomer, the same type of rotation would lead to an increase in strain. Thus, this isomer should have only a reactivity corresponding to a cyclopropylcarbinyl derivative.



Several routes were explored in an effort to obtain the required alcohols. Attempts were made to prepare cyclobutenone ketals by converting 2-bromocyclobutanone to a ketal followed by elimination of hydrogen bromide. The reaction of the bromo ketone with ethylene glycol gave both the dioxolane derivative and the ethylene glycol monoester of cyclopropanecarboxylic acid.[5] Elimination of hydrogen bromide from the dioxolane could not be effected.

Cyclobutenone dimethyl ketal could be prepared by the procedure of Vogel and Hasse[6] which involves the conversion of the Diels–Alder adduct of cyclooctatrienone and dimethyl acetylenedicarboxylate[7] to the dimethyl ketal followed by thermal elimination of the desired ketal. The reaction with diazomethane catalyzed by cuprous bromide proceeded satisfactorily giving the dimethyl ketal of bicyclo[2.1.0]pentan-2-one. Many attempts were made to effect the acid-catalyzed hydrolysis of the ketal. However, in each case the only product was cyclopentenone.[8]

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(2) (a) Taken in part from the Ph.D. Thesis of V. Z. W., 1968; Proctor and Gamble Fellow, 1966–1967; Heyl Fellow, 1967–1968. (b) National Science Foundation Postdoctoral Fellow, 1966–1967.

(3) K. B. Wiberg and J. G. Pfeiffer, *J. Am. Chem. Soc.*, **92**, 553 (1970).

(4) *Cf.* C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(5) These experiments were performed by Dr. R. Cottingham. We wish to thank him for his assistance. The formation of a Favorskii rearrangement product is not too surprising in view of the ease with which 2-bromocyclobutanone undergoes this rearrangement (J. M. Conia and J. L. Ripoll, *Bull. Soc. Chim. France*, 755 (1963)).

(6) E. Vogel and K. Hasse, *Ann.*, **615**, 22 (1958).

(7) A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *J. Am. Chem. Soc.*, **76**, 1096 (1954).