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

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

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

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

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

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

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

Acetolysis of Bridged Cyclobutylcarbinyl Tosylates[1]

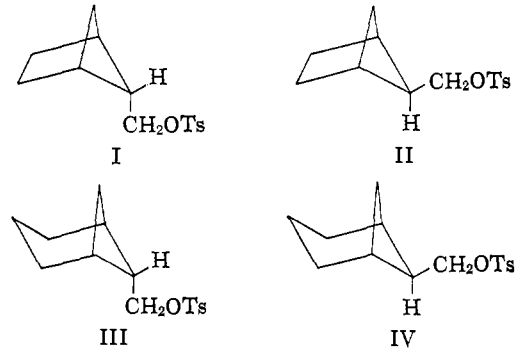
Kenneth B. Wiberg and B. Andes Hess, Jr.[2]

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

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

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

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



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

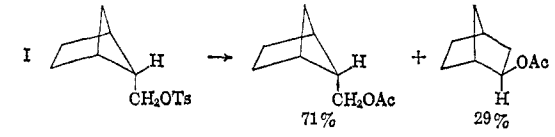
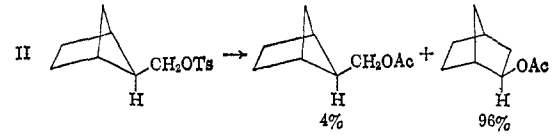
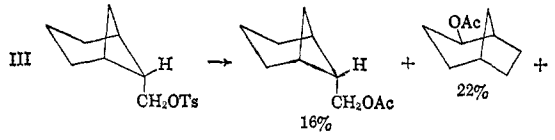
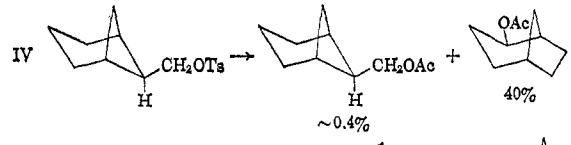
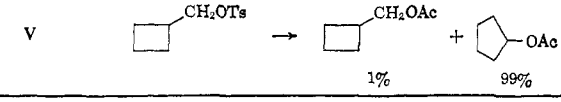
(1) This work was supported by the Army Research Office, Durham, and forms part of the Ph.D. thesis of B. A. H., 1966.
(2) National Institute of Health Predoctoral Fellow, 1963–1966.
(3) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).
(4) K. B. Wiberg and B. A. Hess, Jr., *J. Org. Chem.*, **31**, 2250 (1966).

Table I. Rates of Acetolysis of Cyclobutylcarbinyl Tosylates

Tosylate	Temp, °C	k, sec^{-1}	ΔH^*,[a] kcal/mole	ΔS^*, eu
endo-Bicyclo[2.1.1]hexane-5-methyl (I)	127.3	7.98×10^{-5}	23.8	−18
	144.6	2.87×10^{-4}		
	100.0	8.35×10^{-6} [b]		
exo-Bicyclo[2.1.1]hexane-5-methyl (II)	94.8	1.01×10^{-4}	26.1	−6
	107.8	3.54×10^{-4}		
	100.0	1.68×10^{-4} [b]		
endo-Bicyclo[3.1.1]heptane-6-methyl (III)	127.3	1.25×10^{-4}	28.3	−6
	140.0	3.85×10^{-4}		
	100.0	8.62×10^{-6} [b]		
exo-Bicyclo[3.1.1]heptane-6-methyl (IV)	85.1	1.11×10^{-4}	25.9	−5
	100.0	4.95×10^{-4}		
Cyclobutylcarbinyl (V)	89.9	1.63×10^{-4}	24.9	−8
	100.0	4.26×10^{-4}		
	75.0	3.57×10^{-5} [b,c]		

[a] The uncertainty in the ΔH^* values is approximately ±1.0 kcal/mole. [b] Extrapolated values. [c] This is in good agreement with the previously reported value of 3.56×10^{-5} at 75.0°: C. F. Wilcox, Jr., and M. E. Mesirov, *J. Am. Chem. Soc.*, **84**, 2757 (1962), attributed to J. Meinwald.

Table II. Products of the Acetolysis of Cyclobutylcarbinyl Tosylates

Tosylate	Products
I	
II	
III	
IV	
V	

hyde-*d* was reduced with fermenting yeast[5] to give *endo*-bicyclo[2.1.1]hexane-5-methan-d_1-ol (αD −0.467°). The tosylate was prepared and solvolyzed. The products were reduced with lithium aluminum hydride and separated by vpc. The primary alcohol had a rotation αD +0.464°. The complete inversion of configuration provides strong evidence for the SN2 mode of formation of the unrearranged acetates.

In order to permit a more meaningful comparison of the solvolysis rates, the product data were used to separate the rates into SN2 and SN1 components. The constants thus obtained are given in Table III. It can be seen that SN2 rate constants vary over only a small range, and are similar to the rate constants for the acetolyses of *n*-butyl and isobutyl tosylates. The structural changes in going through the series I–IV would not be expected to have much effect on an SN2 displacement; thus the result provides support for the separation of the observed rate constants into two parts.

Table III. Rates of SN2 and SN1 Paths for the Acetolysis of Cyclobutylcarbinyl Tosylates at 100°

Tosylate	k, sec^{-1} SN2	k, sec^{-1} SN1
endo-Bicyclo[2.1.1]hexane-5-methyl (I)	5.8×10^{-6}	2.5×10^{-6}
exo-Bicyclo[2.1.1]hexane-5-methyl (II)	6.7×10^{-6}	1.6×10^{-4}
endo-Bicyclo[3.1.1]heptane-6-methyl (III)	1.4×10^{-6}	7.2×10^{-6}
exo-Bicyclo[3.1.1]heptane-6-methyl (IV)	2.0×10^{-6}	5.0×10^{-4}
Cyclobutylcarbinyl (V)	4.3×10^{-6}	4.2×10^{-4}
n-Butyl tosylate	4.8×10^{-6} [a]	
Isobutyl tosylate	3.8×10^{-6} [b]	

[a] Estimated from rate of acetolysis of the brosylate: A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **77**, 1117 (1955). [b] S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

On the other hand, SN1 rate constants vary considerably. The *exo* isomers react at about the same rate as cyclobutylcarbinyl tosylate. The *exo* isomers may then be considered as normal. No information is available on the nonassisted SN1 solvolysis of a primary tosylate. Since isobutyl tosylate leads largely to isobutyl acetate and only a small amount of *t*-butyl acetate, the SN1 rate must be at least an order of magnitude smaller than the observed rate for isobutyl tosylate. The normal cyclobutylcarbinyl tosylates then react at least 1000 times more rapidly than a nonassisted solvolysis as a result of carbon participation in the formation of the activated complex and the resultant relief of ring strain. In terms of free energy, the activated complex for these reactions is stabilized by over 5 kcal/mole as compared to the nonassisted case.

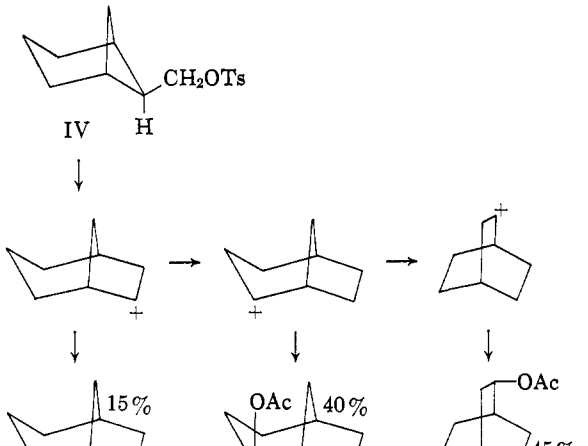
The two *endo* isomers react at less than 0.01 the rate of the corresponding *exo* isomer. Since the kinetic data indicate that rearrangement is involved in the rate-determining step, we may examine the geometry of the activated complexes derived from I and II (Figure 1). The structures are derived from the reactants by assuming that the reacting C_4–C_6–C_7–O atoms would remain in the plane which their coordinates describe, and by diminishing the C_4–C_6–C_7 angle to 90°. Of course, other geometrical reorganization will occur at the same time, but this simple model will suffice to indicate the nature of nonbonded interactions which will occur. In the *endo* isomer, the rearrangement forces one of the carbinyl hydrogens to move toward C_3 leading to repulsive nonbonded interactions.

(5) The general procedure of V. E. Althouse, K. Ueda, and H. S. Mosher, *J. Am. Chem. Soc.*, **82**, 5938 (1960), was used.

These can be relieved only by some other distortion which will lead to an increased energy. On the other hand, with the *exo* isomer, the nonbonded interactions are much smaller and relatively little distortion will be required to relieve them. Thus, it is not surprising that the *exo* isomers behave in the same fashion as cyclobutylcarbinyl, and that the *endo* isomers react at a lower rate.

The variation in activation parameters may also be rationalized by the separation into SN1 and SN2 components. The activation enthalpy and entropy are essentially the same for the two *exo* isomers and cyclobutylcarbinyl tosylate. *endo*-Bicyclo[3.1.1]heptane-6-methyl tosylate reacts predominantly *via* the SN1 route, but at a lower rate than for the *exo* isomer. Correspondingly, the activation enthalpy has increased. *endo*-Bicyclo[2.1.1]hexane-5-methyl tosylate reacts predominantly *via* the SN2 route, and as a result there occurs the characteristic change to a lower activation enthalpy and a lower activation entropy.

Having considered the nature of the activated complex and the rate effects, we may turn to the observed products. It is interesting that the rearranged products from *exo*-bicyclo[3.1.1]heptane-6-methyl tosylate (IV) are the same, both in structure and quantity, as those obtained by Goering and Padmanathan[6] from the solvolysis of *exo*-bicyclo[3.2.1]octane-6-brosylate (VI). Regardless of the details of the solvolysis of the latter, it is probable that IV rearranges on ionization to the ion(s) derived from VI. The solvolysis of the *endo* isomer gives the same set of products, except that VII is now the main product (64%). A similar result was obtained by Goering and Padmanathan in the acetolysis of *endo*-bicyclo[3.2.1]octane-6 brosylate. The increased amount of VII obtained from the *endo* isomers is probably a result of the anion blocking the reaction site in



the *exo* isomers. This would decrease the rate of reaction with solvent and would favor further rearrangement. The anion is removed from the site of attack in the *endo* isomers which may lead to more facile capture of the cation.

The products of the solvolysis of the bicyclo[2.1.1]-hexane-5-methyl tosylates are unexceptional and require no elaboration.

(6) H. L. Goering and T. Padmanathan, private communication. We thank them for supplying us with their results prior to publication.

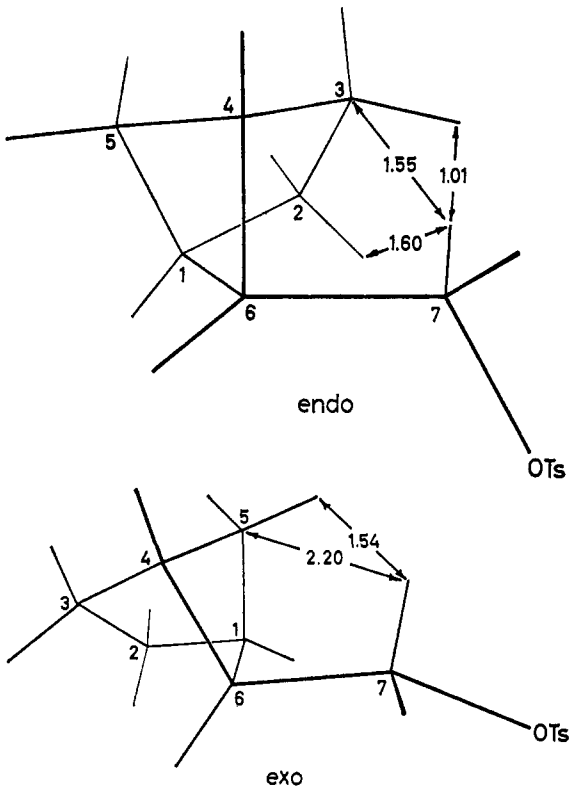


Figure 1. Geometry of a model for the activated complex for the reactions of *endo*- and *exo*-bicyclo[2.1.1]hexane-5-methyl tosylates.

Experimental Section

exo-**Bicyclo[2.1.1]hexane-5-methanol.** A mixture of methyl *exo*- and *endo*-bicyclo[2.1.1]hexane-5 carboxylates was prepared as previously described,[8] and the *exo* isomer (~10% of the mixture) was separated by preparative vpc. Using a 20 ft × 3/8 in. didecyl phthalate column at 145° the *endo* isomer (45 min) was separated from a mixture of the *exo* isomer and nortricyclanone (50 min). The latter mixture was separated into its components using a 10 ft × 3/8 in. diethylene glycol succinate column at 130°. The *exo* ester could be identified by its nmr spectrum: τ 6.38 (s), 7.27 (d), 7.70 (b), 8.32 (s), and 9.20 (t).

Anal. Calcd for $C_7H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.7, 68.7; H, 8.6, 8.8.

A solution of 4.5 g (32 mmoles) of methyl *exo*-bicyclo[2.1.1]-hexane-5-carboxylate in 25 ml of anhydrous ether was added to a slurry of 0.90 g (24 mmoles) of lithium aluminum hydride in 50 ml of ether over a period of 20 min. The mixture was heated at reflux and stirred for another 30 min. A 30% Rochelle salt solution was added cautiously with ice cooling until a white solid collected at the bottom of the flask. The ether layer was decanted, and the solid was washed with two 50-ml portions of ether. The ether solution was dried, and the solvent removed by distillation to give 3.0 g (83%) of *exo*-bicyclo[2.1.1]hexane-5-methanol. Analysis by vpc indicated that it was probably 99+% pure.

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 74.8, 74.6; H, 10.4, 10.5.

exo-**Bicyclo[2.1.1]hexane-5-methyl Tosylate.** A solution of 3.0 g (27 mmoles) of *exo*-bicyclo[2.1.1]hexane-5-methanol in 30 ml of dry pyridine was cooled in an ice–salt bath and 5.67 g (30 mmoles) of *p*-toluenesulfonyl chloride was added. The stoppered mixture was swirled and cooled until all of the tosyl chloride had dissolved, and then was placed in a refrigerator. After 24 hr, 20 g of ice was added followed by 30 ml of water. The mixture was extracted with three 100-ml portions of ether. The ether solution was washed with two 250-ml portions of 1 *N* sulfuric acid, two 250-ml portions of water, and two 250-ml portions of saturated sodium bicarbonate solution. After drying, distillation of the ether gave 6.3 g (88%) of a white solid. Recrystallization from pentane gave pure tosylate with mp 48–48.5°.

Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.1; H, 6.8; S, 12.0. Found: C, 62.8, 62.9; H, 6.7, 6.8; S, 11.5, 11.5.

Acetolysis of *exo*-Bicyclo[2.1.1]hexane-5-methyl Tosylate. A solution of 1.0 g (4 mmoles) of the tosylate in 150 ml of anhydrous acetic acid was heated in a sealed flask at 108° for 6 hr. The mixture was cooled, diluted with 300 ml of water, and extracted with four 175-ml portions of pentane. The pentane solution was washed with three 250-ml portions of 2.5% sodium bicarbonate solution and once with water, and then dried. Distillation gave 0.5 g (86%) of an acetate mixture, bp 60–65° at 9 mm. The acetate mixture had an nmr spectrum identical with that of a mixture of 95% *exo*-norbornyl acetate and 5% *exo*-bicyclo[2.1.1]hexane-5-methyl acetate. The mixture was reduced with lithium aluminum hydride to give a mixture of alcohols. The latter was separated by vpc using a 10 ft × 3/8 in. Carbowax column at 150° into *exo*-norborneol (16.9 min, 93%) and *exo*-bicyclo[2.1.1]hexane-5-methanol (19.6 min, 7%).

***endo*-Bicyclo[2.1.1]hexane-5-carboxaldehyde-*d*.** A solution of 7.37 g (84 mmoles) of ethyl acetate in 80 ml of anhydrous ether was added dropwise over 1.5 hr to a stirred slurry of 3.17 g (84 mmoles) of lithium aluminum deuteride in 60 ml of anhydrous ether cooled to 0°. The resulting slurry was added dropwise over 45 min to a solution of 19.1 g (125 mmoles) of N,N-dimethyl-*endo*-bicyclo-[2.1.1]hexane-5-carboxamide[3] in 78 ml of anhydrous ether cooled to 0°. The mixture was stirred for an additional 30 min at 0° and 5 *N* sulfuric acid was added at a rate which permitted the temperature to remain under 8°. Approximately 100 ml of acid was added. The ether layer was separated, and the aqueous layer was extracted with four 100-ml portions of ether. The combined ether solution was washed with 60 ml of water, 70 ml of 1% sodium bicarbonate solution, and 60 ml of water. After drying, distillation gave 6.3 g (46%) of the aldehyde, bp 50–55° at 11 mm. The infrared spectrum showed a strong C–D band at 4.9 μ. The nmr spectrum showed no absorption at τ 0.71 where the aldehyde proton would normally appear in the unlabeled compound.

Reduction[5] of *endo*-Bicyclo[2.1.1]hexane-5-carboxaldehyde-*d*. To a solution of 223 g of dextrose in 686 ml of water was added a slurry of 220 g of Fleischman Baker's yeast and 264 ml of water. The slurry was stirred in a constant temperature bath at 33°. After 15 min, carbon dioxide evolution became vigorous, and 6.3 g (57 mmoles) of *endo*-bicyclo[2.1.1.1]hexene-5-carboxaldehyde-*d* in 2.5 ml of absolute ethanol was added over a period of 33 min. After 5 hr carbon dioxide evolution had ceased. The mixture was allowed to stand overnight and then steam distilled. Three fractions were collected having volumes of 400, 400, and 800 ml, respectively. Fraction 1 was extracted with four 100-ml portions of ether, fraction 2 was extracted with four 100-ml portions of ether, and fraction 3 was extracted with four 150-ml portions of ether. All of the aqueous phases were combined, saturated with sodium chloride, and extracted with two 200-ml portions of ether. This extract was combined with that from fractions 2 and 3, dried, and concentrated to 50 ml through a 30-in. Helipak column. The residue was combined with the dried extract from fraction 1, and the ether was removed through the column. Distillation of the residue gave 5.4 g (84%) of the crude alcohol, bp 85–92° at 23 mm. The alcohol was further purified by vpc using a Carbowax column with 95% recovery giving the pure alcohol having $\alpha^{25}D$ −0.467 ± 0.002°.

Acetolysis of *endo*-Bicyclo[2.1.1]hexane-5-methyl Tosylate. The alcohol (1.0 g) was converted to the tosylate (2.1 g, 89%) as described for the *exo* epimer. The tosylate was heated in acetic acid at reflux for 52 hr. The acetate mixture was isolated as above to give 1.2 g (98%) of product. Reduction with lithium aluminum hydride gave a mixture of *exo*-norborneol (29%) and *endo*-bicyclo-[2.1.1]hexane-5-methanol (71%) which was separated by vpc using a 10 ft × 3/8 in. Carbowax column. The alcohol had $\alpha^{25}D$ +0.464 ± 0.002°.

Acetolysis of *endo*-Bicyclo[3.1.1]heptane-6-methyl Tosylate. A solution of 1.0 g (3.6 mmoles) of *endo*-bicyclo[3.1.1]heptane-6-methyl tosylate in 150 ml of anhydrous acetic acid was heated in a sealed flask for 18 hr at 127°. The mixture was cooled, diluted with 150 ml of water, and extracted with four 175-ml portions of pentane. The pentane solution was washed with three 250-ml portions of 2.5% sodium bicarbonate solution and once with water, and dried. Distillation of the solvent gave 0.6 g (100%) of crude acetates. The mixture was reduced with lithium aluminum hydride to give an alcoholic mixture. Analysis by vpc at 152° using a 10 ft × 3/8 in. Carbowax column indicated two major peaks. The larger had a retention time of 20 min with a shoulder at 19 min. The smaller peak came at 25.5 min and represented 16% of the alcohol products. The retention time corresponds to that of *endo*-bicyclo-[3.1.1]heptane-6-methanol; it was collected and its nmr spectrum also corresponded to that of this alcohol.

The major component of the mixture was also collected and was converted back to acetates with acetyl chloride and pyridine. The nmr spectrum of the mixture was very similar to that of the acetate products from the acetolysis of *exo*-6-bicyclo[3.2.1]octyl tosylate with only the relative intensities being different. Both nmr spectra had sharp singlets at τ 8.04, 8.06, and 8.09. The singlet at τ 8.09 corresponds to that of *exo*-6-bicyclo[3.2.1]octyl acetate. The relative intensities of the τ 8.04 and 8.06 bands were the same in both product mixtures. *exo*-6-Bicyclo[3.2.1]octyl brosylate is known to give as solvolysis products 40% *exo*-2-bicyclo-[3.2.1]octyl acetate, 45% 2-bicyclo[2.2.2]octyl acetate, and 15% *exo*-6-bicyclo[3.2.1]octyl acetate.[6] Knowing this product distribution, the nmr bands could be identified, and the product distribution for the present case could be determined: 16% *endo*-bicyclo-[3.1.1]heptane-6-methyl acetate; 22% *exo*-2-bicyclo[3.2.1]octyl acetate; 25% 2-bicyclo[2.2.2]octyl acetate; and 37% *exo*-6-bicyclo-[3.2.1]octyl acetate.

Acetolysis of *exo*-Bicyclo[3.1.1]heptane-6-methyl Tosylate. A solution of 2 g (7.1 mmoles) of *exo*-bicyclo[3.1.1]heptane-6-methyl tosylate in 225 ml of anhydrous acetic acid was heated in a sealed tube at 107° for 20 hr. The mixture was cooled, diluted with 300 ml of water, and extracted with four 300-ml portions of pentane. The pentane solution was washed with three 400-ml portions of 2.5% sodium bicarbonate solution and once with 400 ml of water and dried. Distillation of the solvent gave 1.2 g (100%) of the crude esters. A small portion of this was reduced with lithium aluminum hydride to give an alcoholic mixture. Analysis by vpc at 152° using a 10 ft × 3/8 in. Carbowax column indicated one major peak (20 min), and a shoulder (19 min) and a very small peak at 25.5 min. The latter was shown to correspond to 0.4% of *exo*-bicyclo[3.1.1]heptane-6-methanol. The nmr spectrum of the acetate mixture was identical with that from *exo*-6-bicyclo[3.2.1]-octyl tosylate.

Acetolysis of Cyclobutylcarbinyl Tosylate. Cyclobutylcarbinyl tosylate (1.2 g, 5 mmoles) was dissolved in 200 ml of anhydrous acetic acid and heated in a sealed tube at 100° for 6 hr. The mixture was cooled, diluted with 300 ml of water, and extracted with four 175-ml portions of pentane. The combined pentane solution was washed with two portions of 2.5% sodium bicarbonate solution and one 250-ml portion of water. Distillation gave 0.5 g (78%) of acetates, bp 42° at 11 mm. Reduction with lithium aluminum hydride followed by vpc on a 10 ft × 3/8 in. Carbowax column showed two peaks, one at 17 min (99%) and one at 19 min (1%). The first was cyclopentanol and the second was cyclobutylcarbinol.

Kinetic Measurements. Solutions of the tosylates were prepared by weighing the tosylates into a volumetric flask and diluting to 50 ml with glacial acetic acid containing approximately 1% acetic anhydride. Portions (3.3 ml) of this solution were placed in ampoules which were sealed. The set of ampoules for any run was allowed to equilibrate at least 15 min in the constant temperature bath before the first point was taken. Each tube, when removed, was cooled immediately to room temperature in a water bath and broken open, and 3.0 ml of the solution was pipetted into a 25-ml erlenmeyer flask. Titration was effected using a solution of sodium acetate in acetic acid prepared by dissolving an accurately weighed sample of sodium carbonate in acetic acid and diluting to the desired volume. Bromophenol blue was used as the indicator. The rate constants were obtained from plots of ln $(a - x)$ against time.