Solvolysis of 6-Bicyclo[3.1.1]heptyl Tosylates[1]

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

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut. *Received February 2, 1967*

Abstract: The acetolysis and ethanolysis of *exo*- and *endo*-6-bicyclo[3.1.1]heptyl tosylates have been studied. The tosyl group must occupy the pesudo equatorial position on a cyclobutane ring in order to permit a high degree of participation. The *endo*:*exo* ratio was about 10^6. Using the rate of borohydride reduction of the corresponding ketone as a model, both epimers appeared to react at an accelerated rate. The products of the reactions have been determined; the *endo* isomer gives mainly the 2-norcaranyl acetates, whereas the *exo* isomer gives a variety of products. The ratio of the products is not significantly solvent dependent.

We have previously shown that *endo*-5-bicyclo-[2.1.1]hexyl tosylate undergoes acetolysis at a rate 10^6 faster than the *exo* isomer.[3] The remarkably high *endo*:*exo* ratio has prompted us to investigate two series of isomeric cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives.[4] We now wish to report on the part of this investigation which deals with the bicyclo[3.1.1]heptanes. The syntheses of the compounds to be discussed are reported elsewhere.[5]

The rates of solvolysis of *endo*-6-bicyclo[3.1.1]heptyl tosylate (I) and of the *exo* isomer II were determined in glacial acetic acid and in two ethanol–water mixtures. In all cases, the reactions proceeded to completion; no internal return was noted. The data are summarized in Table I.

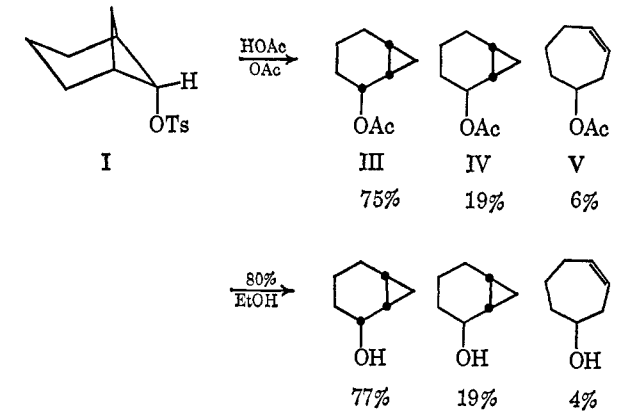
Table I. Rates of Solvolysis of 6-Bicyclo[3.1.1]heptyl Tosylates

Tosylate	Solvent	Temp, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
endo	HOAc	17.0	1.70×10^{-3}	20.1	+2
		32.0	9.90×10^{-3}		
		25.0	4.44×10^{-3} [a]		
	80% EtOH	25.0	2.40×10^{-2}		
	95% EtOH	25.0	4.61×10^{-3}		
	97.7% EtOH	25.0	2.92×10^{-3} [a]		
exo	HOAc	115.0	8.84×10^{-5}	28.5	+4
		130.0	3.61×10^{-4}		
		120.0	1.43×10^{-4} [a]		
		25.0	1.01×10^{-9} [a]		
	80% EtOH	120.0	2.47×10^{-4}		
	97.7% EtOH	120.0	2.73×10^{-5}		

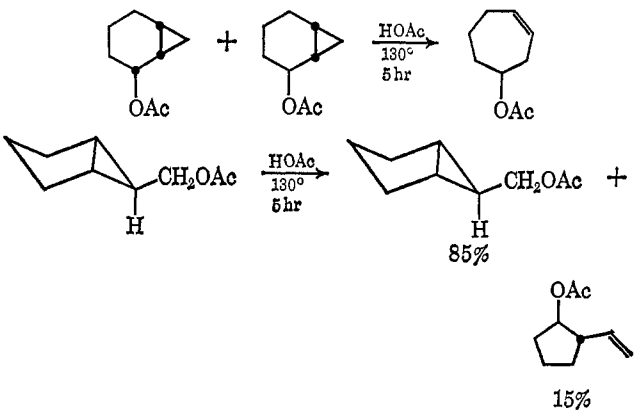
[a] Extrapolated values.

The products of the solvolyses were determined by isolation of the product mixtures followed by vpc separation and identification of individual components by comparison of the nmr and infrared spectra with those of authentic samples. The result, in the case of the *endo* isomer, was fairly simple (see Scheme I). In the ethanolysis experiment, the alcohols were identified by treatment of the reaction mixture with acetyl chloride followed by separation of the acetates. The ethers were not separated and identified as such, but the vpc curve for the ether mixture was quite similar to that for the acetate mixture (except at shorter retention times) suggesting that the ethers were formed in about the same ratio. The ether:alcohol ratio was 88:12.

Scheme I



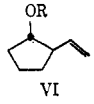
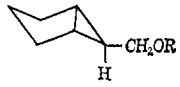
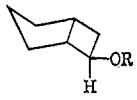
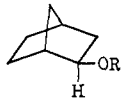
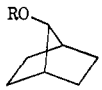
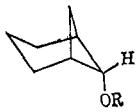
The solvolyses of the *exo* isomer led to more complex product mixtures. The data are summarized in Table II. Since the reaction conditions for acetolysis (5 hr, 130°) might lead to further reactions of the products initially formed, the stability of the products was investigated. A mixture of *cis*- and *trans*-2-norcaranyl acetates was found to isomerize to 4-cycloheptenyl acetate. *exo*-Bicyclo[3.1.0]hexane-6-methyl acetate (VII) was found to be partially converted to *trans*-2-vinylcyclopentyl acetate under the reaction conditions.



In the solvolysis in 80% ethanol, the ratio of ethers to alcohols was 30:70. In the absence of base, the 2-norcaranols were converted to 4-cycloheptenol, and

(1) This investigation was supported by the Army Research Office, Durham, and forms part of the Ph.D. Thesis of B. A. H., 1966.
(2) National Institutes of Health, Predoctoral Fellow, 1963–1966.
(3) K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, 1273 (1963).
(4) Some of the results of this investigation are given in K. B. Wiberg and B. R. Lowry, *J. Am. Chem. Soc.*, **85**, 3188 (1963); K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Letters*, 1553, 4245 (1965).
(5) K. B. Wiberg and B. A. Hess, Jr., *J. Org. Chem.*, **31**, 2250 (1966).

Table II. Products of the Solvolysis of *exo*-Bicyclo[3.1.1]heptyl Toysylate

Product	Obsd product compositions,[a] % HOAc OAc⁻ (R = Ac)	80% EtOH (R = H)	80% EtOH HO⁻ (R = H)	Cor compositions,[a] % HOAc	Cor compositions,[a] % 80% EtOH
 VI	17	36	14	15	15
 VII	14	..	23	16	25
 VIII	7	9	11	7	12
 IX	51	37	3	5	3
 X	4	6	8	4	9
 XI	7	10	8	7	9
 XII	1	2	8	..	..
 III	..	..	20	37	21
 IV	..	..	5	9	5

[a] Corrected for isomerization under the reaction conditions and for the SN2 reaction.

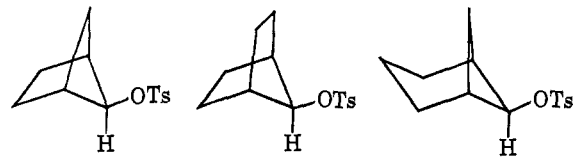
bicyclo[3.1.0]hexane-6-methanol was completely converted to *trans*-2-vinylcyclopentanol. The compounds were, however, stable under the reaction conditions when a slight excess of base was added to the solvent. When this was done, the SN2 product, *endo*-6-bicyclo[3.1.1]heptanol, increased in amount.

It is possible to correct the observed data to take into account the isomerization reactions, making only the assumption that most of the cycloheptenyl acetate found in the acetolysis experiments arose from the norcaranyl acetates. This does not appear unreasonable in view of the results of the ethanolysis experiments. The corrected data are included in Table II.

Having presented the experimental data, we may now consider their significance. The *endo* isomer I is over a million times as reactive as the *exo* isomer II, indicating that the rate acceleration characteristic of cyclobutyl derivatives requires that the leaving group occupy the pseudo equatorial position.[6] This conclusion had also been reached in our previous study of the 5-bicyclo[2.1.1]hexyl tosylates.[3]

A comparison of the kinetic data for acetic acid and for aqueous ethanol permits an estimation of the Winstein *m* and **N** values.[7] The **Y** value for 97.7% ethanol corresponds to that for glacial acetic acid. For the solvolysis of I, *m* was 0.56 and **N** was 0.66; whereas for II, *m* was 0.59 and **N** was 0.19. The last value is based on **Y** values determined at 25° whereas the rates of reaction were measured at 120°. The unusually low value of **N** is probably a result of not using **Y** values for 120°. The low values of **N** demonstrate that the reactions are limiting solvolyses, and the values of *m* are of a reasonable magnitude for such a process.

It is of interest to try to relate the rates of solvolysis with those of other compounds. At first, it appeared to us that 7-norbornyl derivatives would provide an adequate model in view of the similarity in structure.



(OTs) (OTs)

It is generally recognized that there is a correlation between the C–C–C bond angle at the reaction site and the rate of solvolysis.[8] The angle for 7-norbornyl derivatives is 94°,[9] whereas that for bicyclo[3.1.1]heptyl derivatives must be less than 88°.[10] Thus, on this basis one might expect the latter to react more slowly than 7-norbornyl.

However, Brown has suggested that 7-norbornyl derivatives may for some reason be abnormal, since the rate of solvolysis of the tosylate is less than that of any other tosylate which has been studied, and since the rate of borohydride reduction of 7-norbornanone is greater than that of any other ketone which has been studied.[11] We may ask if there should be any structural factor which would lead to anomalous rates of reaction.

The important factor in these reactions is the *difference* in destabilization due to bond angle deformation between the tetrahedral and trigonal structures. Here, 7-norbornyl derivatives would be anticipated to be significantly different from monocyclic compounds. With cyclobutyl derivatives, for example, the tetrahedral structure has a bond angle[6] of about 87.8°, whereas the trigonal structure (cyclobutanone)[12] has an angle of

(6) Cyclobutane deviates from planarity by 35° (P. N. Skanke, Thesis, Oslo, 1960) leading to positions for substituents which are analogous to axial and equatorial positions of a cyclohexane ring.

(7) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(8) H. C. Brown and M. Gerstein, *ibid.*, 72, 2926 (1950); P. von R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 182 (1961); *cf.* C. S. Foote, *ibid.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854 (1964), where the correlation was made with the infrared carbonyl frequencies rather than bond angles.

(9) Dr. G. Dallinga, private communication.

(10) The C–C–C bond angle in cyclobutane is 87.8°[6] and that in bicyclo[2.1.1]hexane is 84.5°.[9]

(11) H. C. Brown and J. Muzzio, *J. Am. Chem. Soc.*, **88**, 2811 (1966).

(12) A. Bauder, F. Tank, and H. H. Günthard, *Helv. Chim. Acta*, **46**, 1453 (1963).

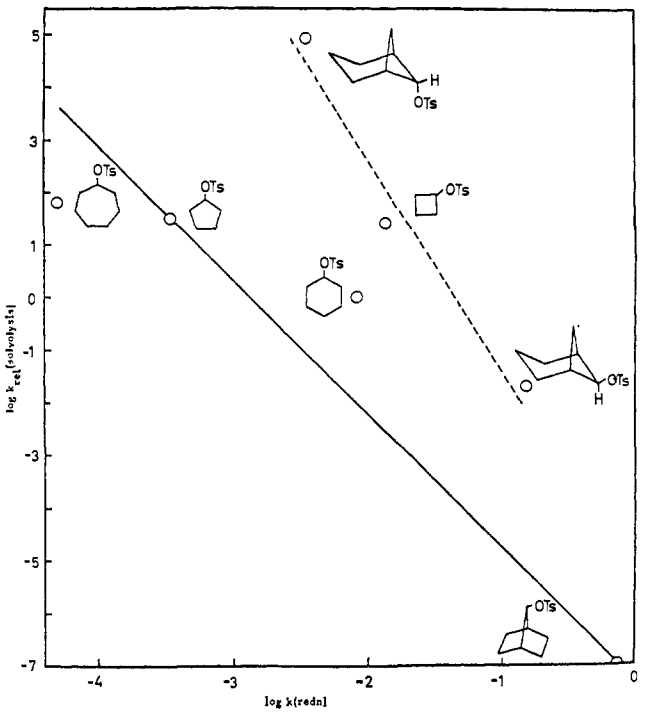


Figure 1. Relationship between rates of solvolysis and rates of borohydride reduction of the corresponding ketones. The solid line joins cyclopentyl with 7-norbornyl; the dashed line indicates the results with the cyclobutyl derivatives.

90.5°. Thus, the angle has increased significantly on going to the ketone, relieving some of the strain associated with the formation of a trigonal center. With norbornyl derivatives, however, the angle at the methylene bridge is constrained by the two-carbon wings and probably cannot change significantly on going from the alcohol to the ketone. Thus, despite the larger angles in 7-norbornanol and 7-norbornanone as compared to cyclobutanol and cyclobutanone, the increase in strain is probably greater for the former than for the latter.

The bicyclo[*n*.1.1]alkane derivatives would be expected to be intermediate in strain increase between cyclobutyl and 7-norbornyl compounds. This postulate could be tested if the heats of hydrogenation of the ketones to the alcohols were known. Unfortunately, these values are not as yet available. As a result, we have adopted the suggestion of Brown and Muzzio[11] that the rates of borohydride reduction of the ketones provide a model for the effect of converting a tetrahedral center to trigonal. The rate of reduction of bicyclo[3.1.1]heptanone-6 was determined giving a rate constant of 1.4×10^{-1} sec^{-1} at 0°. As expected, the rate is between those for cyclobutanone and 7-norbornanone. The reaction led to 97.5% of *endo*-6-bicyclo[3.1.1]heptanol and 2.5% of *exo*-6-bicyclo[3.1.1]heptanol, giving the partial rate factors for *endo* and *exo* attack of 3.5×10^{-3} and 1.5×10^{-1} sec^{-1}, respectively. The data required for a correlation with rates of solvolysis are summarized in Table III.

The rates of acetolysis are compared with the rates of borohydride reduction in Figure 1. Brown and Muzzio[11] have suggested that a line drawn through 7-norbornyl and cyclopentyl "would provide a reasonably satisfactory locus" for most of the compounds they examined. Such a line is drawn in the figure; the deviations (±2 log units) for cyclohexyl and cycloheptyl

Table III. Rates of Acetolysis and Borohydride Reduction

Ring	Solvolysis k, 25°	k_{rel}	Reduction[a] k, 0°
Cyclobutyl	3.0×10^{-6}	27[b]	1.33×10^{-2} [e]
Bicyclo[3.1.1]heptyl			
exo-6	1.0×10^{-9}	0.021	1.5×10^{-1}
endo-6	4.44×10^{-3}	91,000	3.5×10^{-3}
Norbornyl-7		10^{-7} [c]	7.5×10^{-1} [f]
Cyclohexyl	4.88×10^{-8}	1.00[d]	8.1×10^{-3} [e]
Cyclopentyl	1.58×10^{-6}	32.4[d]	3.5×10^{-4} [e]

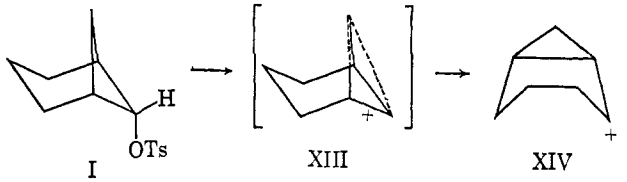
[a] Partial rate factors. [b] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951); H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956). [c] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955). [d] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, **74**, 1127 (1952). [e] H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957). [f] H. C. Brown and J. Muzzio, *J. Am. Chem. Soc.*, **88**, 2811 (1966).

derivatives perhaps suggest the uncertainty inherent in the correlation.

The three species of present interest, *endo*-6-bicyclo[3.1.1]heptyl, cyclobutyl, and *exo*-6-bicyclo[3.1.1]heptyl have acetolysis rates which are greater than expected by 6.0, 4.3, and 3.3 log units, respectively. Thus, using Brown's criterion, all appear to undergo solvolysis at accelerated rates.

The magnitude of the rate acceleration for cyclobutyl is in accord with other data. It has been found that the replacement of the α-hydrogen by methyl in secondary alcohol derivatives normally produces a rate increase by a factor of about 5×10^4.[13] In the case of cyclobutyl, methyl substitution increases the rate by only a factor of about 10^2.[14] If there were no special stabilization of the tertiary derivatives, the rate acceleration for cyclobutyl itself would be $\sim 5 \times 10^2$. This, of course, is a minimum value since 1-methylcyclobutyl derivatives may also react at a somewhat increased rate.[15]

The very large rate acceleration observed with *endo*-6-bicyclo[3.1.1]heptyl tosylate indicates a bridged activated complex. One may write the structure XIII and ask whether this represents the activated complex for a rearrangement to a more stable ion XIV, or whether it is an intermediate in the reaction and is stabilized by virtue of electron delocalization.



I XIII XIV

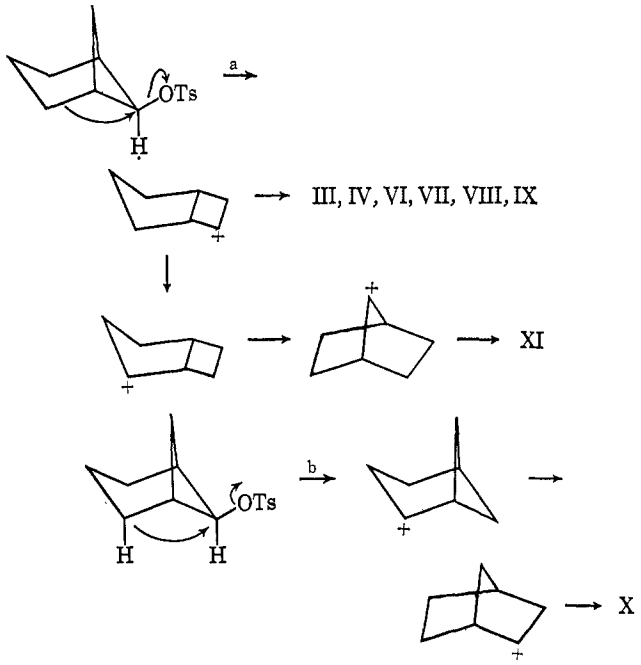
The 2-norcaranyl derivatives are very reactive in solvolytic reactions suggesting that the ion XIV is probably well stabilized in the fashion of cyclopropylcarbinyl cations.[16] The stabilization is particularly

(13) H. C. Brown and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 5008 (1964).
(14) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952); J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).
(15) The correlation of acetolysis rates with carbonyl frequencies[10] does not appear to be particularly useful with cyclobutyl derivatives because of the lack of correlation of vibrational frequency with bond angle. Thus: cyclobutanone, 1791 cm^{-1}; 6-methylbicyclo[3.2.0]-heptan-6-one, 1776 cm^{-1}; bicyclo[3.1.1]heptan-6-one, 1775 cm^{-1}.
(16) (a) Cyclopropylcarbinyl intermediates: Wiberg and Ashe, see ref 4; P. von R. Schleyer and G. van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966). (b) Stable cyclopropylcarbinyl ions: N. Deno H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *ibid.*, **84**, 2016 (1962); C. V. Pittman and G. Olah, *ibid.*, **87**, 2998 (1965); N. C. Deno, J. S. Liu, J. O. Turner, O. N. Lincoln, and R. E. Fruit, *ibid.*, **87**, 3000 (1965).

favorable since XIV is both cyclopropylcarbinyl and secondary. Since little thermochemical evidence is available concerning the relative energies of the classical cyclobutyl and the cyclopropylcarbinyl cations, it is not possible to estimate if the observed effect can be rationalized in terms of such a driving force. If the rate acceleration for *endo*-6-bicyclo[3.1.1]heptyl tosylate is taken as 10^6, this corresponds to a stabilization of the activated complex by about 8.3 kcal/mole. The driving force would have to be greater than this amount since the driving force cannot be fully realized in the activated complex.

One possible way in which to obtain evidence dealing with the above question is to examine the possibility of trapping an intermediate using an ion in solution. In some cases, this has been accomplished using halide ion,[17] azide ion,[18] and methoxide ion.[19] An attempt was made to capture an intermediate ion using azide ion in acetic acid, and chloride ion in acetone. No chloride or azide corresponding to I was obtained[20] and olefin was the major product in acetone solution. Thus, the question remains unresolved at the present time. We shall, however, return to this question at a later time.

The solvolytic behavior of the *exo*-tosylate II is also of some interest in view of its apparent higher than expected reactivity. The products of the reaction may be derived *via* a series of carbonium ion reactions.



The carbon participation path, a, might be expected to give a modest rate acceleration since a 1,3-bridged cyclobutane is probably somewhat destabilized in comparison to a 1,2-bridged cyclobutane.[21] In the absence of thermochemical data, it is difficult to estimate the magnitude of the possible rate factor.

(17) S. Winstein, A. Ledwith, and M. Hojo, *Tetrahedron Letters*, 341 (1961).
(18) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **86**, 120 (1964).
(19) H. Tanida, T. Teruji, and T. Irie, *ibid.*, **88**, 864 (1966).
(20) See, however, the reaction of *endo*-5-bicyclo[2.1.1]hexyl tosylate with chloride ion[4] in which unrearranged *endo*-chloride was the major product.
(21) This conclusion is not at all certain and is in the process of being tested. If the conclusion is incorrect, there would be no apparent driving force for rearrangement to XV.

The products of the reaction are, however, not in accord with the above formulation. First, the acetolyses of *exo*- and *endo*-bicyclo[3.2.0]heptyl-6 tosylates have been investigated[22] and neither gives bicyclo-[3.2.0]heptyl-6 acetate or 7-norbornyl acetate as a product. However, both are formed in the present case. It seems likely that they are not formed *via* the 6-bicyclo[3.2.0]heptyl cation. Second, it is difficult to see why the product composition should be essentially unchanged on going from acetic acid to aqueous ethanol as solvent if the reaction involves a series of rearrangement steps. In these cases, one usually intercepts the ions at an earlier stage with the more nucleophilic aqueous ethanol as compared to acetic acid.

The simplest explanation for the rate acceleration and for the solvolysis products suggests that the products are derived from one principal intermediate which is stabilized in part by electron delocalization and in part by some strain relief resulting from the longer bonds in the "nonclassical" intermediate. The reactions may be formulated as in Scheme II. It can be seen that this intermediate provides a reasonable path for the formation of both bicyclo[3.2.0]heptyl-6 and 7-norbornyl derivatives. We do not consider that the data are such that they force one to accept a "nonclassical" intermediate. However, such an intermediate provides a simple, economical explanation for all of the data.

Experimental Section

Acetolysis of *endo*-Bicyclo[3.1.1]heptyl-6 Tosylate. Into a set of about 15 test tubes was accurately measured increasing amounts of standard sodium acetate in acetic acid. The final volume in each was adjusted to 10 ml with anhydrous acetic acid. Several drops of brom phenol blue in acetic acid was added to each tube as an indicator. The test tubes were stoppered, placed in a constant temperature bath, and allowed to equilibrate for 15 min. *endo*-Bicyclo[3.1.1]heptane-6 tosylate (300 mg) was dissolved in approximately 3 ml of carbon tetrachloride. A 200-μl portion of this solution was transferred with stirring to a test tube using a Hamilton 250-μl syringe. Zero time was taken at the completion of addition, and the time for the indicator change was recorded. The process was repeated for each test tube, covering a range of 10–90% reaction. This method eliminated the problem of the time required to dissolve the tosylate in the reaction solvent, and permitted reactions with a half-life as short as 30 sec to be studied.

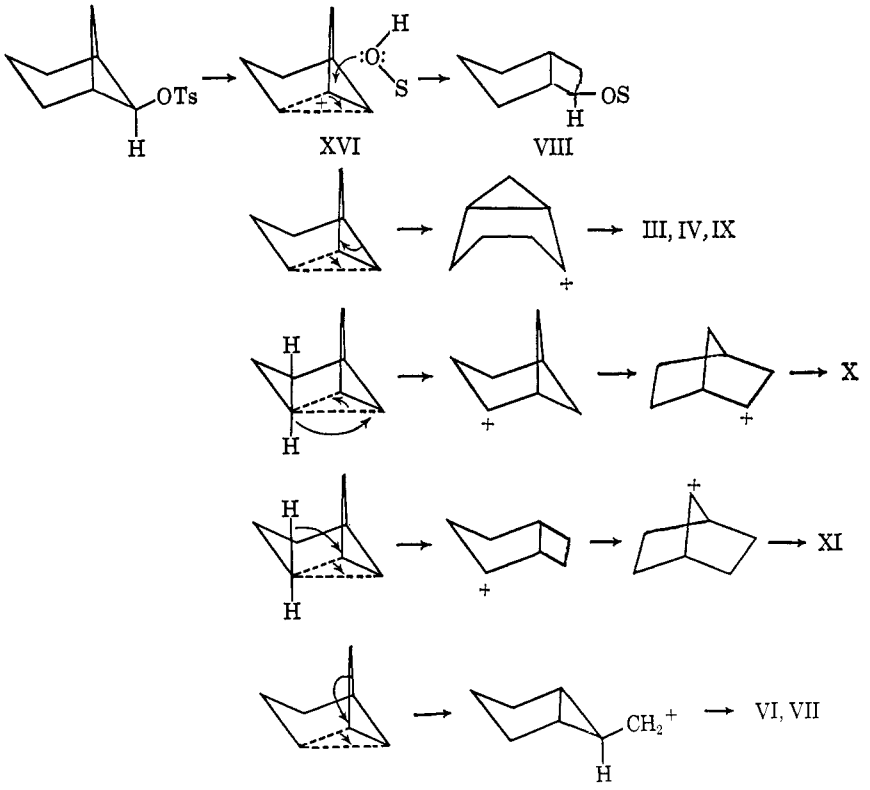
Ethanolysis of *endo*-Bicyclo[3.1.1]heptyl-6 Tosylate. Two ethanol–water mixtures were prepared having 79.95 and 95.00% ethanol by volume (the former had a density of 0.84930 at 25.0°, and the latter had 0.80321). The experiments were carried out as described above except that the base solution was prepared by dissolving sodium in the alcohol–water mixture and standardizing against hydrochloric acid solution by titration.

Acetolysis of *exo*-Bicyclo[3.1.1]heptyl-6 Tosylate. Solutions of the tosylate were prepared by weighing the tosylate into a volumetric flask and diluting to 50 ml with glacial acetic acid containing approximately 1% acetic anhydride and sufficient sodium acetate to neutralize the *p*-toluenesulfonic acid formed. Portions (3.3 ml) of the solution were placed in ampoules, and the ampoules were sealed. The ampoules were placed in a constant temperature water bath and were allowed to equilibrate. They were removed at known times, cooled rapidly to room temperature, and broken open; 3 ml of the solution was removed for titration with standard sodium acetate in glacial acetic acid. Brom phenol blue was used as the indicator.

Ethanolysis of *exo*-Bicyclo[3.1.1]heptyl-6 Tosylate. The ethanolysis was carried out in the same manner as the acetolysis runs using 79.95 and 97.75% ethanol. The latter had a density of 0.79371 at 25°.

(22) F. F. Nelson, Ph.D. Thesis, University of Wisconsin, 1960.

Scheme II



Product Studies. a. *endo*-**Bicyclo[3.1.1]heptyl-6 Tosylate.** A solution of 0.5 g of the tosylate (containing 20–30% of the *exo* isomer) in acetic acid containing a small excess of sodium acetate was allowed to stand for 15 min at room temperature. The mixture was diluted with an equal volume of water and extracted with three portions of pentane. The pentane solution was washed with water, with 2.5% sodium bicarbonate solution, and again with water. After drying, distillation gave 150 mg of a clear liquid, and a pot residue. The latter was shown by nmr to be *exo*-bicyclo-[3.1.1]heptyl-6 tosylate. The distillate was examined by vpc using a Carbowax column at 148°. The first component (19.5 min) was 4-acetoxycycloheptene, and the second component (21.5 min with a shoulder at 22.5 min) was a 4:1 mixture of *endo*- and *exo*-2-norcaranyl acetates. Both components were identified by comparison with authentic samples.

When the acetolysis was carried out in the absence of acetate ion, the amount of acetoxycycloheptene increased at the expense of the norcaranyl acetates.

b. Ethanolysis of *endo*-Bicyclo[3.1.1]heptyl-6 Tosylate. A solution of 0.6 g of the tosylate in 50 ml of 80% ethanol containing 120 mg of sodium was allowed to stand for 8 min at room temperature. The reaction mixture was worked up as described above, and the mixture of ethers and alcohols was dissolved in pyridine and cooled to 0°. To this solution was added 2.0 g of acetyl chloride. After a few minutes, 6 ml of water was added, and the mixture was extracted with two 20-ml. portions of pentane. The pentane solution was washed with two portions of dilute hydrochloric acid, two portions of water, and two portions of 5% sodium bicarbonate solution. After drying, the pentane was removed, and distillation of the residue gave 0.2 g of a mixture of ethers and acetates. Vpc analysis indicated that the acetate products were the same as from the acetolysis. The ether:acetate ratio was 88:12.

c. *exo*-Bicyclo[3.1.1]heptyl-6 Tosylate. A solution of 2.0 g of the tosylate in 160 ml of anhydrous acetic acid containing 0.027 mole of sodium acetate was heated in a sealed flask at 120° for 15.5 hr. It was cooled, diluted with 200 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 with water. After drying, distillation of the solvent gave 1.0 g of products. Vpc analysis using a Carbowax column at 140° indicated four components. The first component (8 min, 17%) was *trans*-2-vinylcyclopentyl acetate;[23] the second (10 min, 7%) was 7-norbornyl acetate; the third (11 min, 11%) was a mixture of *exo*-bicyclo[3.2.0]heptyl-6 acetate and *exo*-norbornyl acetate; and the fourth (14 min, 65%) was a mixture of 4-acetoxycycloheptene[23] and *exo*-bicyclo[3.1.0]hexane-6-methyl acetate.[23] The last mixture could be separated using an XF-1150 column. All components were identified by comparison with authentic samples.

d. Ethanolysis of *exo*-Bicyclo[3.1.1]heptyl-6 Tosylate. The reaction was carried out essentially as described above, and the products were converted to acetates using acetyl chloride in pyridine. The ratio of ethers to acetates was 30:70. The acetates were the same as found in the acetolysis, but in a different ratio.

Bicyclo[3.1.1]heptanone-6. A solution of 5 g of *exo*-bicyclo-[3.1.1]heptanol-6, 11.2 g of aluminum *t*-butoxide, and 19.1 g of benzoquinone in 570 ml of anhydrous ether was heated to reflux for 12.5 hr. The ether was removed by distillation, and the volatile material was collected at 0.3 mm. The latter was separated by vpc using a $^3/_8$ in. DEGS column at 140°. The ketone with a retention time of 8 min was collected giving 1.3 g (26%). It had an infrared carbonyl band at 1775 cm^{-1}.

Reduction of Bicyclo[3.1.1]heptanone-6. The rate of reduction by sodium borohydride was determined at 0° in isopropyl alcohol solution as described by Brown and Muzzio.[11] The concentration of ketone was 0.00506 *M*, and of borohydride 0.00190 *M*. Assuming a 1:4 stoichiometry, good second-order kinetics were observed with $k = 1.4 \times 10^{-1}$ sec.

The product of the reduction was converted to acetates using pyridine and acetyl chloride. The acetates were isolated by vpc using a DEGS column at 140° (retention time 7.5 min). The nmr spectrum of the mixture indicated a strong triplet τ 5.31 for the $-CH$*O*Ac proton of the *endo* isomer and a weak doublet at τ 5.69 for the corresponding proton of the *exo* isomer.[5] The ratio of the areas of the two bands indicated 97.5% *endo* and 2.5% *exo* acetates.

(23) An authentic sample was kindly supplied by Dr. A. J. Ashe.