170–172°, mmp 170–171°; infrared spectrum identical with that of an authentic specimen.

Diketone 24. A solution of 300 mg of diketone **14** and 160 mg of dry potassium *t*-butoxide in 5 ml of dimethyl sulfoxide was kept at room temperature under nitrogen for 1.5 hr. Water was added and the mixture was extracted with chloroform. The extract was dried and evaporated. Alumina chromatography of the residue, 300 mg, and elution with benzene gave 70 mg of a solid whose crystallization from hexane and vacuum sublimation yielded **24**, mp and mmp 76–78°, infrared spectrum identical with that of the above sample. Elution with chloroform led to the recovery of 60 mg of starting ketone **14**.

Triketones 30. A solution of 100 mg of diketone **24**, 100 mg of dimethyl acetonedicarboxylate, and sodium methoxide (from 10 mg of sodium) in 0.5 ml of methanol was refluxed for 8 hr. The cooled mixture was acidified with 10% sulfuric acid and filtered. The precipitate was washed with water, dried, and crystallized from methanol–ether yielding 156 mg of colorless needles of triketo diester **30a**: mp 197°; infrared ($CHCl_3$), C=O and C=C 5.76 (s), 5.82 (s), 6.02 (s), 6.16 (m) μ; ultraviolet (EtOH), λ_{max} 253 mμ (log ϵ 3.96); pmr, δ 1.38 (s, 3, Me), 3.89, 3.91 (s, 3, OMe).

Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.70; H, 6.33. Found: C, 61.65; H, 6.66.

A mixture of 100 mg of **30a** and 2 ml of 10 *N* hydrochloric acid in 2 ml of methanol was heated on a water bath for 9 hr. Water was added and the mixture was extracted with chloroform. The extract was washed with saturated sodium bicarbonate solution and with water, dried, and evaporated. Sublimation (190°) of the residual solid, 60 mg, yielded white plates of triketone **30b**; mp 217–218°; infrared (Nujol), C=O 5.85 (s) μ; pmr, δ 1.57 (s, 3, Me).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.77. Found: C, 72.00; H, 8.11.

Acknowledgment. The authors are indebted to Eli Lilly and Company and the National Science Foundation for support of this investigation.

Solvolytic Studies of Bicyclooctenyl Derivatives. The Epimeric Bicyclo[3.2.1]oct-6-en-3-yl Tosylates[1]

Norman A. LeBel and Robert J. Maxwell

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received November 12, 1968*

Abstract: The synthesis and characterization of *exo*(equatorial)-bicyclo[3.2.1]oct-6-en-3-ol, *endo*(axial)-bicyclo[3.2.1]oct-6-en-3-ol, and derivatives thereof are reported. Analysis of the kinetic data from the acetolyses of these compounds and their β-tetradeuterated analogs suggests that the rates are "normal" for these constrained cyclohexyl tosylates; no anchimeric assistance seems to be provided by the double bond for the *exo* isomer, or by the axial β-hydrogen for the *endo* isomer. Preparative solvolyses show that the reaction mixtures contain products of elimination, substitution without skeletal rearrangement, as well as rearranged products. The rearranged acetates arise from the tricyclo[3.2.1.$0^{2,7}$]octan-6-yl cation, and this intermediate is generated by way of a stereospecific hydride-shift pathway. A hydrogen-bridged intermediate cation, intervening after the first-formed ion pair, nicely accommodates the data. Secondary acetolysis products are encountered as well, and mechanisms for their formation are proposed.

The unique variety of structural types available in bicyclooctene carbon skeletons provides opportunity for assessment of the relative importance of σ *vs.* β-π-(homoallylic) participation in solvolytic reactions. Often the latter type of assistance has been accompanied by the direct generation of cationic intermediates which maintain their structural integrity (show little tendency to "leak" into other systems) as evidenced by high product selectivity. The bicyclo[2.2.2]oct-2-en-5-yl tosylates are exemplary cases. The *endo* epimer **1** undergoes accelerated acetolysis directly to the bicyclo[3.2.1]oct-2-en-3-yl cation (**2**), and solvent capture gives nearly exclusively *exo*-bicyclo[3.2.1]oct-2-en-3-yl acetate (**3**).[2] On the other hand, acetolysis of *exo*-bicyclo[2.2.2]oct-2-en-5-yl tosylate (**4**) is also accelerated, and the products are *exo*-tricyclo[3.2.1.$0^{2,7}$]-octan-6-yl acetate (**6**) (90%), *exo*-bicyclo[2.2.2]oct-2-en-5-yl acetate (**7**) (~7%), and *exo*-bicyclo[3.2.1]oct-6-en-2-yl acetate (**8**) (~3%). The intermediate cation involved in the acetolysis of **4** is probably best described as an unsymmetrical cyclopropylcarbinyl cation (**5**), rather than the homoallylic designation previously used,[3] because very little of the epimer of **6** could be detected. In **5**, the *endo* lobe of the p orbital at C_6 overlaps to a significantly greater extent with the bent bond of C_2–C_7 than does the *exo* lobe with the C_1–C_7 bond, and stereoelectronic control of solvent capture would lead preferentially to **6** as the tricyclic product. No crossover between the two cationic systems **2** and **5** was noted. That **5** possesses unique stability is evidenced by its generation from the σ-route precursor **6**-OTs,[3] and by ring expansions of *anti*-2-norbornene-7-carbinyl precursors.[4,5]

The recent availability of bicyclo[3.2.1]oct-6-en-3-one (**9**)[6] prompted an extension of our studies to include the bis homoallylic *exo*- and *endo*-bicyclo[3.2.1]oct-6-en-3-yl tosylates (**10a** and **11a**), respectively). Although it was anticipated that some participation in the solvolysis of the *exo* epimer **10a** might be provided by the two-carbon-removed, but symmetrically and

(1) This work was supported by a grant (DAAROD 31-124-G749) from the U. S. Army Research Office, Durham.

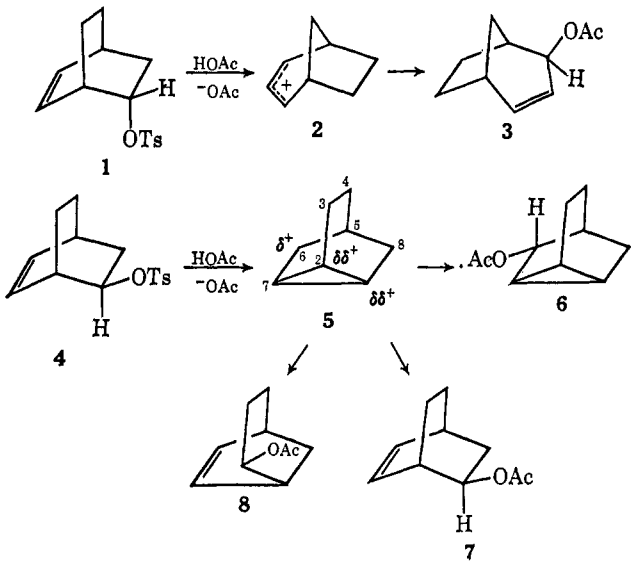
(2) (a) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1992 (1961); (b) H. L. Goering, R. W. Greiner, and M. F. Sloan, *ibid.*, **83**, 1391 (1961); (c) H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963).

(3) N. A. LeBel and J. E. Huber, *ibid.*, **85**, 3193 (1963).

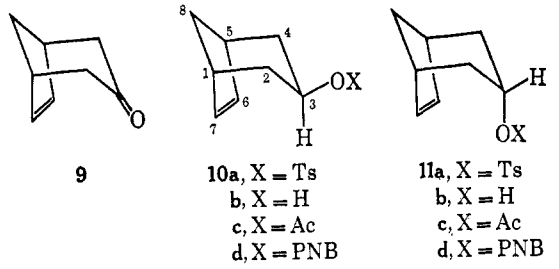
(4) J. A. Berson and J. J. Gajewski, *ibid.*, **86**, 5020 (1964).

(5) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966).

(6) N. A. LeBel and R. N. Liesemer, *J. Am. Chem. Soc.*, **87**, 4301 (1965).



favorably oriented, double bond, we were most intrigued by the possibility that a C_2–C_3 hydride shift accompanying ionization could lead to a carbonium ion related to **5**. This report presents our interpretation of the results of this study.



Results

Reduction of ketone **9**[6] with sodium borohydride in methanol gave a mixture of the two alcohols **10b** and **11b** in the ratio 25:75, respectively. The proportion obtained with lithium aluminum hydride in ether was 61:39; and with sodium and ethanol it was 95:5. We found it most convenient to separate **10b** and **11b** by preparative glpc.

The configurational assignments of **10b** (equatorial OH) and **11b** (axial OH) were suggested by the results of the sodium and alcohol reduction, and equilibration of the pure isomers with aluminum isopropoxide in isopropyl alcohol containing a little acetone gave the values 95 ± 1% of **10b** and 5 ± 1% of **11b**. Intramolecular hydrogen bonding between the *endo* OH and the C_6–C_7 π bond of **11b** was detected by infrared studies. Confirmation of these assignments was obtained by catalytic hydrogenation and comparison of the saturated alcohols and derivatives thereof with known materials.[7,8]

The nmr spectra of the alcohols **10b** and **11b** and of the corresponding tosylates **10a** and **11a** were examined. The coupling constants of the methine proton (C_8–H) were similar in magnitude to those reported for the respective saturated analogs,[9] and indicated that the compounds exist preferentially in rigid chair conformations.

Acetolyses of the tosylates were examined kinetically by the classical titrimetric procedure.[10] Good apparent first-order behavior was noted both for runs containing added sodium acetate, and for unbuffered runs. The data, together with derived activation parameters, are given in Table I.

Table I. Acetolysis Rate Constants and Activation Parameters for the Bicyclo[3.2.1]oct-6-en-3-yl Tosylates

Tosylate[a]	No. of runs	Temp, °C	Av k_1, $sec^{-1} \times 10^4$	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
exo (**10a**)	2[b]	96.05	12.4 ± 0.1		
	3[b]	76.01	1.47 ± 0.02		
	2	76.01	1.40 ± 0.02		
		25	1.4×10^{-3} [c]	27.4	+2.8
endo (**11a**)	4[b]	76.01	11.9 ± 0.2		
	2[b]	55.7	1.45 ± 0.03		
	3	76.01	13.0 ± 0.2		
		25	3.5×10^{-2} [c]	23.6	−3.6

[a] The initial concentration of tosylate in all runs was about 8.6×10^{-3} *M*. [b] Contained 1.05×10^{-2} *M* sodium acetate. [c] Extrapolated.

Bicyclo[3.2.1]oct-6-en-3-one (**9**) was subjected to exchange with sodium methoxide in deuteriomethanol to give **9**-d_4, which was then reduced to a mixture of the β-deuterated alcohols **10b**-2,2,4,4-d_4 and **11b**-2,2,4,4-d_4 (containing $\geq 95\%$ d_4 species as determined by mass spectrometry). Acetolysis of the derived tosylates at 76.01° gave the following results: for **10a**-2,2,4,4-d_4, $k = 6.75 \pm 0.2 \times 10^{-5}$ sec^{-1}; and for **11a**-2,2,4,4-d_4, $k = 5.57 \pm 0.15 \times 10^{-4}$ sec^{-1}. These may be equated to β-d_4 isotope effects of 2.16 and 2.14, respectively (any correction for undeuterated material would be negligible). If the isotope effects for the β-deuteriums are considered multiplicative (they are probably not[11]), the average $k_H/k_{\beta-D}$ for both epimers is 1.21.

Preparative acetolyses were conducted at different temperatures in acetic acid containing sodium acetate, acetic acid containing urea, and in unbuffered acetic acid. Glpc analysis of the product mixtures showed acetate and hydrocarbon fractions; however, the acetates were poorly resolved. Consequently, the products were subjected to saponification (or lithium aluminum hydride reduction), and the mixtures of alcohols and hydrocarbons were analyzed by glpc. The products were separated by glpc and were identified by comparison of infrared spectra and glpc retention times (and sometimes nmr spectra) with those of authentic materials. The structures of the products from the acetolysis of both *exo* (**10a**) and *endo* (**11a**) tosylates were similar, but the compositions of the mixtures varied significantly.

Specifically, the product mixtures can be divided into three distinct groups. In group I may be listed bicyclo[3.2.1]octa-2,6-diene (**12**), the only hydrocarbon product identified, and *exo*-bicyclo[3.2.1]oct-2-en-7-yl acetate (**13**). In the sodium acetate buffered sol-

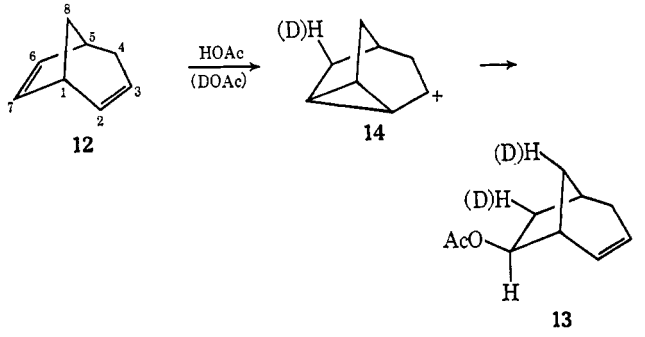
(7) B. Waegell and C. W. Jefford, *Bull. Soc. Chim. France*, 844 (1964).
(8) W. Kraus, *Chem. Ber.*, **97**, 2719 (1964).
(9) C. W. Jefford, D. T. Hill, and J. Gunsher, *J. Am. Chem. Soc.*, **89**, 6881 (1967).
(10) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **76**, 821 (1948).
(11) See (a) V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **87**, 1382 (1965); (b) *ibid.*, **87**, 1383 (1965); (c) W. H. Saunders, Jr., and K. T. Finley, *ibid.*, **87**, 1385 (1965).

Table II. Acetolysis Products from the Bicyclo[3.2.1]oct-6-en-3-yl Tosylates

Isomer	Conditions		Per cent composition[a] Group I	Group II	Group III
exo (**10a**)	NaOAc, 76°	M	45.2–38.4 **12**[b] 6.8 **13**	35.8 **11c** only	19.0–15.5 **6**[c] 2.8 **7** 0.7 **8**
	Urea, 76°		49.8 **13** only	26.5–20.6 **11c** 5.9 **15**	23.7–22.0 **7** 1.7 **8**
endo (**11a**)	NaOAc, 76°		30.7–22.6 **12**[b] 8.1 **13**	33.0–29.4 **10c** 3.6 **11c**	36.3–31.4 **6**[c] 4.4 **7** 0.5 **8**
	Urea, 56°		49.7 **13** only	27.5–24.6 **10c** 2.9 **11c**	22.8–19.6 **7** 3.2 **8**

[a] Given as area %. Precision is ±0.7% for components present in amounts of 10% and above, ±0.3% for components present in amounts below 10%. [b] Some loss of diene **12** may have occurred during work-up and analysis of the runs containing sodium acetate. [c] A small amount of (<1%) of the epimer of **6** can be detected by capillary glpc.

volyses, acetate **13** was a relatively minor component; however, in the nonbuffered and urea runs diene **12** was absent and acetate **13** was the major product. Control experiments established that **13** was not a kinetic product in these solvolyses, but rather resulted from and was the exclusive product of the addition of acetic acid to bicyclo[3.2.1]octa-2,6-diene (**12**). This addition probably involves specific proton addition to C_6 of the diene **12** giving directly the symmetrical cyclopropylcarbinyl cation **14**. This cation (**14**) is known to react to give only **13** under acetolysis conditions.[12] Support for this pathway is given by the results from addition of acetic acid O–D to **12**. The monodeuterated acetate **13** (68% d_1) was saponified,

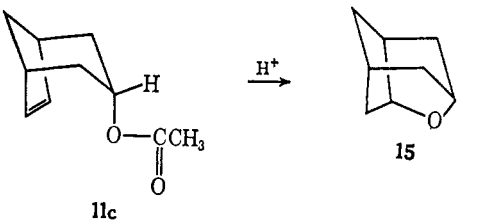


12 14 13

and the alcohol was oxidized to bicyclo[3.2.1]oct-2-en-7-one (44% d_1). This ketone was equilibrated with base in aqueous methanol; and, after recovery, it contained 35% d_1 species.

The group II series of products consists of either inverted acetate (**11c** from **10a** and **10c** from **11a**); or, in the case of the *endo* tosylate **11a** *only*, a mixture of inverted and retained acetates. It was readily demonstrated that these products were stable under the reaction conditions of acetate-buffered acetolyses. During the urea and unbuffered runs, a volatile compound was detected which showed the spectral characteristics of an ether. This product has tentatively been assigned the structure 2-oxatricyclo[3.2.1.$1^{3,7}$]-nonane (**15**), on the basis of infrared, nmr, and mass spectral determinations. It has been established that *endo*-bicyclo[3.2.1]oct-6-en-3-yl acetate (**11c**) is readily converted to **15** upon heating in acetic acid containing *p*-toluenesulfonic acid at 76°. The *exo* acetate **10c** is stable under these conditions.

(12) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, 32, 569 (1967).



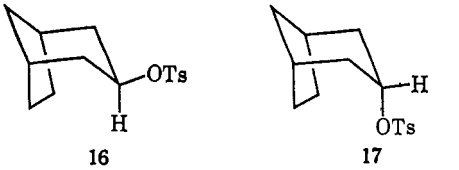
11c 15

The remaining products (group III) belong to the series of acetates (the "L series"[3–5]) that arise in buffered acetolyses that proceed by way of the cation **5**; namely, *exo*-tricyclo[3.2.1.$0^{2,7}$]octan-6-yl acetate (**6**), *exo*-bicyclo[2.2.2]oct-2-en-5-yl acetate (**7**), and *exo*-bicyclo[3.2.1]oct-6-en-2-yl acetate (**8**). Only **7** and **8** were detected in the urea and nonbuffered acetolyses of **10a** and **11a**; but this was anticipated, because it has been shown[3] that acetate **6** readily isomerizes to a mixture of **7** and **8** in acetic acid containing *p*-toluenesulfonic acid.

Typical product distributions from the preparative acetolyses of **10a** and **11a** are given in Table II. The effect of temperature on the product distributions in the acetate-buffered runs (56° *vs.* 76°) was small. Normally about 1.5 molar equiv of sodium acetate per mole of tosylate was used in the preparative and kinetic runs. When this proportion of acetate was increased threefold, the effect on the product distribution was a slight increase in the amount of inverted acetate.

Discussion

Although the tosylates **10a** and **11a** possess a rigid conformation, theoretical considerations and examination of molecular models suggest that the six-membered ring in these compounds exists as a somewhat deformed chair. Comparison of the rate constants determined for the acetolyses of related systems with the results from **10a** and **11a** (Table III) shows immediately that both of these tosylates solvolyze more slowly than their saturated analogs **16** and **17**, respectively. Originally



16 17

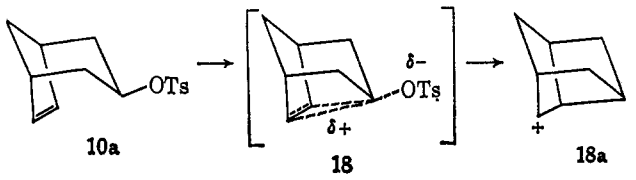
it was suspected that the double bond at C_6–C_7 in the *exo* tosylate **10a** might be able to participate in stabilization of the solvolytic transition state (indicated by

Table III. Relative Rates of Acetolysis of *p*-Toluenesulfonates at 25°

p-Toluenesulfonate	Rel rate[a]	Ref
Cyclohexyl	1.0	*b*
cis-4-*t*-Butylcyclohexyl	3.08	*c*
trans-4-*t*-Butylcyclohexyl	0.86	*c*
exo-Bicyclo[3.2.1]octan-3-yl (**16**)	10.1	9
exo-Bicyclo[3.2.1]oct-6-en-3-yl (**10a**)	3.53	This work
endo-Bicyclo[3.2.1]octan-3-yl (**17**)	110.0	9
endo-Bicyclo[3.2.1]oct-6-en-3-yl (**11a**)	73.5	This work

[a] Values obtained from data measured, extrapolated or interpolated at 25°. [b] The rate constant 4.8×10^{-8} sec^{-1} is from H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 592 (1956). [c] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

structure **18**). Such anchimeric assistance would result in a solvolysis rate for **10a** greater than that of the epimer **11a**, but the opposite was observed. In addition, no products which would be predicted to have



10a **18** **18a**

arisen from an intermediate cation such as **18a** were found in the mixtures. This lack of participation by the double bond at the "solvolytic transition state stage" of the reaction is most probably due to the fact that the C_3–C_6 (and C_3–C_7) bond distance in the 3-bicyclo[3.2.1]oct-6-enyl cation is too great to permit effective orbital overlap.

The rate ratio $k_{(endo)}/k_{(exo)}$ extrapolated to 25° for the acetolyses of the tosylates **11a** and **10a** is about 21 (Table III). This ratio for the saturated analogs, $k_{(17)}/k_{(16)}$, is 11. These values are somewhat greater than the "normal" $k_{(axial)}/k_{(equatorial)}$ rate ratio (3.6) for cyclohexyl tosylates as determined from the acetolyses of the *cis*- and *trans*-4-*t*-butylcyclohexyl tosylates.[13] It has been suggested that for the acetolysis of the bicyclo[3.2.1]octan-3-yl tosylates (**16** and **17**), the rate ratio should be higher (about 30) than that measured.[9] The reason for the discrepancy is that the axial isomer **17** actually solvolyzes slower than would be expected, possibly because the "reflex effect"[14] results in a lower seric acceleration to ionization, or because steric inhibition to ionization operates. It is possible that both effects are simultaneously operative; however, we may take note of the fact that the C_6–C_7 ethylene bridge in **11a** does not interact with the *endo*-tosylate group nearly as much as does the C_6–C_7 ethane bridge in the saturated analog **17**. Thus, steric acceleration to ionization would be even less prominent in **11a**; yet the rate ratio **11a**/**10a** is higher than that for **17**/**16**. On the other hand, steric inhibition to ionization should be less important in **11a** than in **17**, and experimentally it is observed that the rate of acetolysis of **17** and **11a** differ by only a factor of about 1.5. Operating on the assumption that the rate difference between the *exo* compounds (**16** and **10a**) is due mainly to inductive retardation by the double bond in **10a** ($k_{16}/k_{10a} \sim 2.8$); it can then be estimated that steric inhibition to ionization in **17** has a twofold rate-retarding effect over that present in **11a**.

Because of the observation that the acetolyses of **10a** and **11a** lead to significant amounts of rearranged products by way of a hydride-shift pathway (*vide infra*), it is important to know whether the rates reflect direct β-hydrogen participation. The studies with the tetradeuterated tosylates give some evidence along these lines. β-Deuterium isotope effects have been measured for the solvolysis in 50% aqueous ethanol of *cis*- and *trans*-4-*t*-butylcyclohexyl brosylates[11a,b] and for the acetolysis of cyclohexyl tosylate.[11c] The *nonmultiplicity* as opposed to the *additivity* of the β-deuterium isotope effects for each individual β-hydrogen has been cited as evidence for the importance of the hydrogen-bridging mechanism for hyperconjugative stabilization of the cyclohexyl cation. Moreover, since the geometric requirement for hydrogen bridging is quite stringent, the data were further interpreted as supporting the idea that the equatorial cyclohexyl tosylates solvolyze by way of a twist-boat transition state. The acetolyses of **10a** and **11a** gave values of $k_H/k_D = 2.16 \pm 0.1$ and 2.14 ± 0.06, respectively. These values are lower than those reported for other β-d_4 cyclohexyl tosylates (*e.g.*, for cyclohexyl tosylate, $k_H/k_D = 2.34$). Significantly, these values for the two epimers are identical within experimental error. The k_H/k_D ratio per β-deuterium for **10a** and **11a** would be 1.21 ± 0.01, assuming a multiplicity effect, that is that all β-hydrogens contribute equally to hyperconjugative stabilization regardless of their stereochemical configuration. We interpret the near identity and relatively low value of this secondary isotope effect for the epimeric tosylates **10a** and **11a** as indicating that β-hydrogen bridging is not important in stabilizing the rate-determining transition state in these solvolyses. The extent of carbonium ion development at the transition state cannot be ascertained from these data (the α-deuterium isotope effect would be a required quantity).

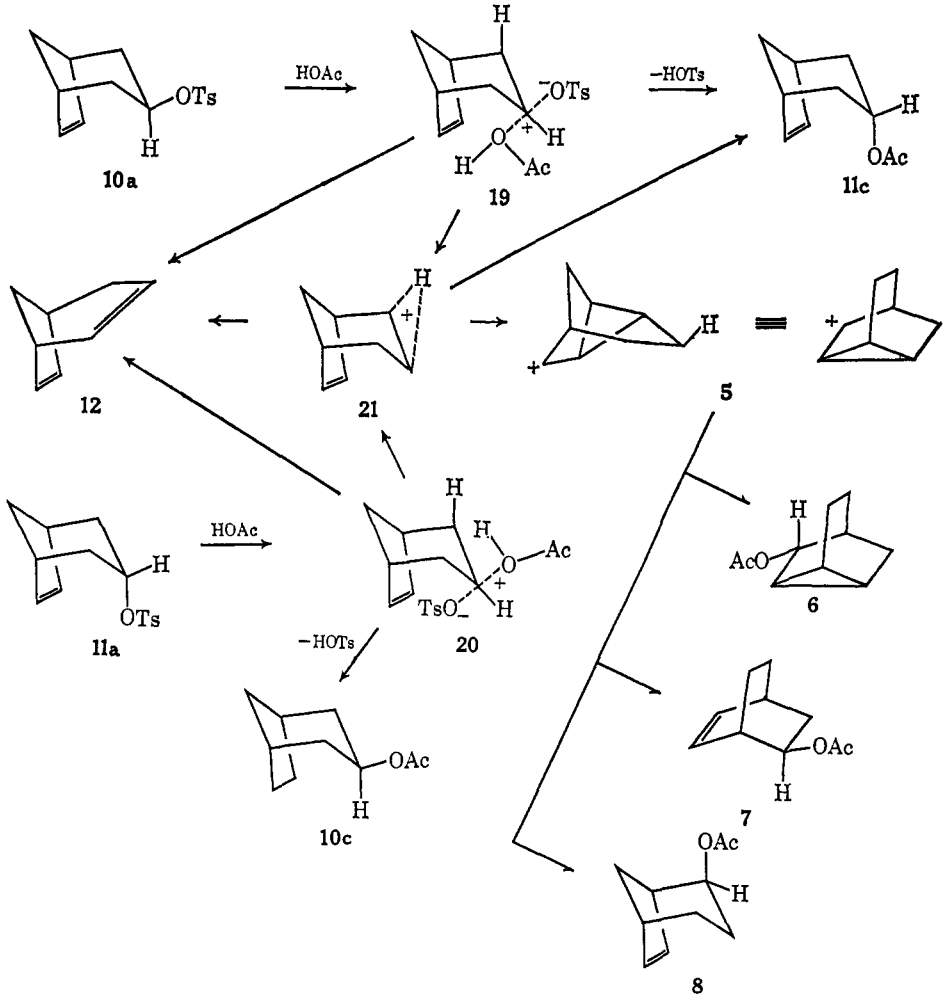
The conclusion derived from the above considerations is that the ionization rates of **10a** and **11a** are normal (not accelerated by either double bond or β-hydrogen participation after account is taken of bond angle and torsional and nonbonded strain). The question of what occurs after collapse of the solvolytic transition state can be answered by examination of the products obtained in these acetolyses reactions.

Under comparable reaction conditions the *exo*-(equatorial) tosylate **10a** gave less rearranged products than did the *endo*(axial) epimer **11a**. Other features are as follows: some acetate of retained configuration **11c** was obtained in the solvolyses of **11a**, whereas only inverted acetate **11c** was detected as the nonrearranged product from **10a**; elimination appeared to be more prevalent from **10a** than from **11a** when the acetolyses were performed in a sodium acetate buffered medium (little difference was noted in the urea and nonbuffered runs), and represented a larger proportion of the mixtures from both tosylates in the urea and nonbuffered runs; and rearrangement accounted for a higher proportion of products in the sodium acetate containing acetolyses of **11a** than in the other media, whereas the reverse was true for the acetolyses of **10a**.

Explanation of these data is made in terms of the

(13) See Table III, footnote *c*.
(14) C. Sandris and G. Ourisson, *Bull. Soc. Chim. France*, 1524 (1958).

Scheme I



sequence of steps outlined in Scheme I. Ionization assisted by backside solvation of the incipient cations at C_3 would generate the ion-pair species **19** and **20**, shown containing the nearest solvent molecule. Ion-pair return to form the tosylates of inverted configuration apparently is not important in these reactions. Control experiments in benzene and recovery of unreacted tosylate after acetolysis had established the configurational stability of **10a**. If *endo* tosylate **11a** had undergone isomerization to the *exo* isomer **10a** during the course of the acetolysis to the extent of about 10%, then **10a** should be detectable in the recovered tosylate after partial reaction. Unreacted tosylate was recovered after approximately 15, 50, and 82% reaction, and infrared and tlc examination allowed us to conclude that less than 2% of **10a** could have been present after the longer reaction time. More important, however, is the fact that capillary glpc analysis of the acetate fractions formed after about 15, 50, and 82% reaction at 56° showed that the ratio of retained acetate **11c** to inverted acetate **10c** was essentially constant. These data support our contention that isomerization of **11a** to the slower solvolyzing **10a** did not occur to any significant extent, and retained acetate is a characteristic product in the acetolysis of **11a**.

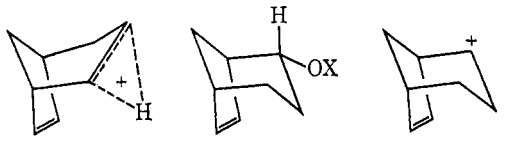
Three pathways for further reaction seems available to **19** and **20**. Collapse with the loss of *p*-toluenesulfonic acid would produce the acetate of inverted configuration. Alternatively, β-proton removal by a base would give the diene **12**. Thirdly, a β-hydrogen may compete with solvent and generate the "hydrogen-bridged" intermediate **21**. If the approximate chair structure is not greatly altered, only the hydrogens originally axial at C_2 and C_4 have their bond axes nearly parallel with the p orbital of the cation and are able to participate in bridging.

The bridged intermediate **21** also has three available pathways for reaction. These are: (1) loss of a proton to give diene **12**; (2) backside attack by solvent at C_3 ("diaxial opening") giving only *endo*-bicyclo[3.2.1]-oct-6-en-3-yl acetate (**11c**); and (3) backside displacement at C_2 by the π electrons of the C_6–C_7 double bond leading directly to the cation **5** which would, in turn, afford exclusively the series of products **6**, **7**, and **8**. Entry into the rearranged products can occur only through **21** *via* **5**, and the formation of **21** can occur at a much earlier stage in the solvolysis of **11a** (*e.g.*, ionization of the *endo*-tosyloxy group need not be too advanced before axial β-hydrogen participation comes into play) than it does in **10a** (the *exo*-tosyloxy group must depart to a high degree *before* an axial β-hydrogen can become involved in bridging). Therefore, a greater proportion of rearranged products is expected from the solvolysis of **11a**.

The observation that elimination was more important in the urea and nonbuffered run is typical for solvolysis reactions, because the media are less nucleophilic than those containing sodium acetate. The fact that both

tosylates gave similar amounts of elimination under these conditions suggests that a substantial portion of the elimination products arise from the hydrogen-bridged species **21**. The greater proportion of elimination from **10a** in acetate-buffered runs may be considered as support for the earlier premise that the carbon–tosyloxy bond is further broken in the transition state leading to **19** than in that leading to **20**.

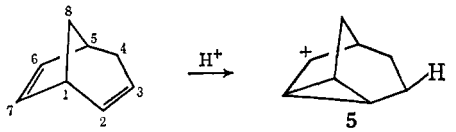
Further consideration of the structure of the hydrogen-bridged intermediate **21**, and its subsequent rearrangement to the cation **5** is appropriate at this point. The similarity of product distributions from the acetolyses of **10a** and **11a** seem to demand a common-bridged intermediate for both isomers. The isomeric intermediate **22**, in which an equatorial hydrogen at C_2 (or C_4) is involved in bridging, would seem to be



22 **23** **24**

excluded. Certainly loss of hydrogen from this intermediate would afford the diene **12**. However, attack at C_3 by solvent should give *exo*-bicyclo[3.2.1]-oct-6-en-3-yl acetate (**10c**), but none of this product of retained configuration was detected in the acetolysis of **10a**. Furthermore, rearrangement from **22** involving the one-carbon bridge should give products similar to those derived from solvolysis of *endo*-bicyclo[3.2.1]-oct-6-en-2-yl tosylate (**23**, X = Ts); and this is not the case.[15] It would also be reasonable to conclude on these bases that the rearrangement of the bridged species **21** to cation **5** is concerted and does not proceed by way of the classical 2-bicyclo[3.2.1]oct-6-enyl cation (**24**). This direct pathway, "the hydrogen migration route," is the fourth method observed for the generation of cation **5**.

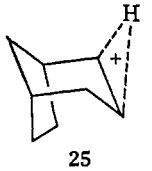
An alternate method of formation of the series of products **6**, **7**, and **8** would involve the generation of intermediate **5** by addition of a proton to C_3 of the diene **12**. Interestingly, Lansbury and Boggs were not able to distinguish between a similar scheme and the



12 **5**

direct "hydrogen migration" pathway to account for the rearrangements observed in the formolysis of *exo*-6,7-benzobicyclo[3.2.1]octen-3-yl *p*-toluenesulfonate.[16] However, the observation made earlier that **13** is the only detected product of the addition of acetic acid to diene **12** requires that the preferred protonation of **21** occurs at C_6.

As a final point, it would seem worthwhile to examine the results reported for the solvolyses of the saturated analogs **16** and **17**[9] in light of the data now available for **10a** and **11a**. The similarities in the rate data have already been discussed. The investigators found that neither **16** nor **17** gave rearranged products; however, the patterns between the products of elimination and substitution without rearrangement are in the same direction as those found for the unsaturated tosylates. Both **16** and **17** give large amounts of bicyclo[3.2.1]-oct-2-ene, but only the *endo* tosylate **17** furnishes the acetate of *retained* stereochemistry, and in appreciable amounts. It was concluded from these data that the appearance of both epimeric products from **17** points to the formation of a "solvated ion pair of long lifetime with respect to molecular relaxation processes."[9] The remarkable inference was then drawn that, since **17** can give substitution product by attack from the same side of the molecule as the leaving group, then the *endo* side of the 2-norbornyl cation should also suffer attack from this direction because it is not more hindered than the bottom side of the bicyclo[3.2.1]octyl system. Although it is well documented that the solvolysis of *exo*-2-norbornyl tosylate proceeds with anchimeric assistance and gives only products of retention, the data obtained from **16** and **17** have no bearing on the nature of the cation involved. The saturated tosylates **16** and **17** can more profitably be compared with the *cis*- and *trans*-4-*t*-butylcyclohexyl tosylates, and with **10a** and **11a** as described in this work. Participation of a β-axial hydrogen (C_2–H) in the solvolyses of **16** and **17** could produce an intermediate species (**25**) similar to **21** (Scheme I); whose constrained geometry would permit attack only from the underside of the molecule with diaxial opening. Intermediate **25** and the two "normal" ion pairs can account for all of the product and kinetic data reported for the acetolyses of **16** and **17**. It is significant to note that of two pathways available for **25**, diaxial opening to give retained acetate **17** and skeletal rearrangement, only the former product was noted. Rearrangement of **25** to the 2-bicyclo[3.2.1]octyl–2-bicyclo[2.2.2]octyl cation system cannot profit from the favorable energetics characteristic of the **21** → **5** rearrangement in the unsaturated system. More retention in the acetolysis of **17** is predicted.



25

Experimental Section[17]

Bicyclo[3.2.1]oct-6-en-3-one (9). The preparation of this compound has been discussed previously by LeBel and Liesemer.[6] Certain modifications in the final step of the reaction were made.

(15) Acetolysis of **23** (X = Ts) *does not* lead to products derived from cation **5**, but rather produces only retained acetate and acetates arising from the allylic cation **2**: N. A. LeBel and R. J. Maxwell, to be published.

(16) P. T. Lansbury and N. T. Boggs, *Chem. Commun.*, 1007 (1967).

(17) All melting points were determined in sealed capillary tubes using a Thomas-Hoover apparatus, and are uncorrected. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. The infrared spectra were determined with a Perkin–Elmer Model 237 Grating Infracord spectrophotometer. A Varian Associates A-60A spectrometer was used to examine the nuclear magnetic resonance spectra. The internal standard was tetramethylsilane. Mass spectra were obtained using an Atlas Massen spectrometer CH-4 at 70 eV ionization potential. Two separate units were used for glpc. All preparative and some analytical work was carried out with a unit employing U-shaped glass columns. The preparative column was 7 ft × 0.5 in., containing 25% Dow Polyglycol E-20,000 on 60–80 mesh Chromosorb W at 130°. Analytical columns included a 7 ft × 0.25 in. column containing 25% E-20,000 on 60–80 mesh Chromosorb W at

A solution of 1.24 g (0.179 g-atom) of lithium in 900 ml of anhydrous ammonia was prepared, then 12 g (59.7 mmol) of *anti*-8-bromotricyclo[3.2.1.0^{2,7}]octan-3-one[6] in 100 ml of anhydrous ether was added over a period of 20 min. The blue-black color of the solution persisted at the end of this addition. After 15 min of stirring, the reaction was quenched with solid ammonium chloride, followed by moist ether, and finally water. The ammonia was allowed to evaporate, and the remaining aqueous solution was extracted several times with ether. The extracts were combined, washed, and dried ($MgSO_4$). In order to remove a by-product the ether was carefully removed by distillation, and the residual slurry was taken up in a large volume of pentane. After filtration and concentration, the ketone **9** was purified either by sublimation or by preparative glpc (E-20,000, 130°). The yield was 12 g (70.5%), mp 99–101° (lit.[6] mp 99–101.5°).

An accurate yield of the by-product, mp 150–152°, was not determined, since it was never obtained in any amount larger than 100 mg: ir ($CHCl_3$) 3590 (m), 3475 (w), 3060 (m), 3005 (m), 2945 (s), 2880 (m), 1590 (w), 1465 (s), 1445 (m), 1355 (s), 1350 (w), 1280 (w), 1175 (s), 1115 (s), 1105 (s), 1100 (s), 1070 (m), 1035 (s), 1020 (s), 995 (s), 960 (w), 930 (w), 910 (w), 875 (s), 855 (s) cm^{-1}; nmr ($CDCl_3$) δ 6.09 (sep, 2), 3.57 (br s, 2), and 2.55–1.33 (m, 6).

Anal. Found: C, 78.70; H, 8.30.

Reductions of Bicyclo[3.2.1]oct-6-en-3-one (9). The product mixtures were analyzed on the E-20,000 column at 130°. The glpc retention time of the *endo* alcohol **11b** was 12.8 min and that of the *exo* isomer **10b** was 26.4 min.

A. Sodium Borohydride in Methanol. A stirred solution of 1.42 g (16.6 mmol) of bicyclo[3.2.1]oct-6-en-3-one (**9**) in 25 ml of anhydrous methanol was cooled to 0°, and 0.785 g (20.6 mmol) of sodium borohydride was added. Stirring was continued for 30 min at 0°, and for 5 hr at 25°. Work-up consisted of dilution with water followed by continuous extraction with pentane. After concentration there was obtained 1.31 g (90.5%) of a solid, consisting of 24.8% *exo* (**10b**) and 75.2% *endo* (**11b**) alcohols.

B. Sodium in Ethanol. To a solution of 400 mg (3.28 mmol) of **9** in 35 ml of absolute ethanol was added 2.04 g (0.089 g-atom) of sodium in small pieces. After the sodium had dissolved, the mixture was heated to reflux for 1 hr. After cooling, the solution was diluted to 100 ml with water and was continuously extracted with pentane. The yield of solid alcohol mixture was 300 mg (80%), of which 95.1% was *exo* alcohol **10b,** and 4.91% was *endo* alcohol **11b.**

C. Lithium Aluminum Hydride. To a suspension of 1.00 g (26.0 mmol) of lithium aluminum hydride in 50 ml of dry ether was slowly added a solution of 1.5 g (12.3 mmol) of **9** in 20 ml of dry ether. This mixture was stirred overnight under a nitrogen atmosphere. The work-up consisted of adding successively 1 ml of water, 3 ml of 15% potassium hydroxide solution, and finally 1 ml of water. The white precipitate was removed by filtration and was washed with ether. The filtrate was extracted with ether, and the combined ether layers were washed with water and dried ($MgSO_4$). This reaction afforded 99 mg (65%) of a mixture containing 61.3% **10b** and 38.7% **11b.**

endo-**Bicyclo[3.2.1]oct-6-en-3-ol (11b)** was separated from its epimer by preparative glpc (E-20,000, 130°) and had mp 188–190°.

Anal. Calcd for $C_8H_{12}O$: C, 77.41; H, 9.69. Found: C, 77.38; H, 9.84.

endo-**Bicyclo[3.2.1]octan-3-ol.** *endo*-Bicyclo[3.2.1]oct-6-en-3-ol (**11b**) (30 mg, 0.2 mmol) was hydrogenated with 5 mg of platinum oxide in 10 ml of 80% acetic acid. One mole of hydrogen was taken up in 48 min. The mixture was filtered, and the catalyst was washed with ether. After drying the ether was removed by distillation, and the solid residue was purified by sublimation. The yield of saturated alcohol was 16.8 mg (55%), mp 199–202° (lit.[7,8] for *endo*-bicyclo[3.2.1]octan-3-ol, mp 206–206.5°). Analysis by glpc (20% XE-60, 147°) showed one component with a retention time of 20.4 min. The retention time of the unsaturated alcohol **11b** was 16.6 min. The ir ($CHCl_3$) of the hydrogenated alcohol contained the same bands reported for the authentic compound.[8]

exo-**Bicyclo[3.2.1]oct-6-en-3-ol (10b)** showed mp 90.5–92.0°.

Anal. Calcd for $C_8H_{12}O$: C, 77.41; H, 9.69. Found: C, 77.14; H, 9.52.

The nmr spectrum ($CDCl_3$) showed the C_3–H at δ 3.72 (1 H, tr of tr, J_{aa} = 9.5 Hz, J_{ae} = 6.5 Hz); the olefinic protons were at 5.80 (2 H, broadened s).

exo-**Bicyclo[3.2.1]octan-3-ol.** A solution of 25 mg (0.2 mmol) of *exo* alcohol **10b** in 8 ml of 80% acetic acid was hydrogenated with 5 mg of platinum oxide. The work-up was the same as that described for the *endo* epimer. After removal of the solvent by distillation, the crude residue was purified by sublimation. A crop weighing 11 mg (43%) was obtained, mp 112–114° (lit.[7,8] for *exo*-bicyclo[3.2.1]octan-3-ol, mp 114–115°). The ir agreed with that reported.[8] Analysis by glpc (XE-60, 147°) showed one peak with a retention time of 27.4 min; the retention time of the unsaturated alcohol **10b** on this column was 23.2 min.

Equilibration of the Bicyclo[3.2.1]oct-6-en-3-ols. A mixture of 200 mg (1.6 mmol) of *exo* alcohol **10b,** 303 mg (1.6 mmol) of freshly distilled aluminum isopropoxide, 20 ml of isopropyl alcohol, and two drops of acetone was heated to reflux. Aliquots of 2 ml were removed at intervals and diluted with 20 ml of water and 4 ml of 2 *N* hydrochloric acid. This aqueous solution was extracted several times with pentane. The pentane fractions were dried, concentrated to a volume of 1 ml, and analyzed by glpc (E-20,000, 130°). The final composition after 172 hr was 94.7% *exo* alcohol **10b,** and 5.3% *endo* alcohol **11b.** The same composition was reached by starting with the pure *endo* alcohol **11b.**

endo-**Bicyclo[3.2.1]oct-6-en-3-yl Acetate (11c).** A solution containing 87 mg (0.7 mmol) of *endo* alcohol **11b** and ten drops of dry pyridine in 3 ml of acetic anhydride was heated to 85° for 11 hr. After cooling, the mixture was poured into 50 ml of ice–water and was extracted with pentane. After drying and removal of the solvent, the product was distilled at 72° (5 mm). The pure acetate **11c** (92 mg, 78%) showed only one peak by glpc (E-20,000, 130°).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.40; H, 8.44. Found: C, 72.19; H, 8.39.

exo-**Bicyclo[3.2.1]oct-6-en-3-yl Acetate (10c).** The same procedure as outlined above was employed to prepare the *exo* acetate **10c.** From 100 mg (0.81 mmol) of *exo* alcohol there was obtained 100 mg (60.5%) of product **10c,** distilled at 31° (0.1 mm). Analysis by glpc (E-20,000, 130°) also showed one peak having the same retention time as that of the *endo* acetate **11c.**

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.40; H, 8.44. Found: C, 72.18; H, 8.31.

endo-**Bicyclo[3.2.1]oct-6-en-3-yl *p*-Toluenesulfonate (11a).** To a solution of 444 mg (3.6 mmol) of *endo* alcohol **11b** in 4 ml of dry pyridine at 0° was added slowly a solution of 1.04 g (0.55 mmol) of *p*-toluenesulfonyl chloride in 5 ml of pyridine. The mixture was stirred for an additional hour at 0°, and was then stored in the refrigerator. After the usual work-up, drying, and removal of the solvent, the residue was recrystallized from a mixture of ether and pentane to give 850 mg (86%) of tosylate **11a,** mp 87–89°.

Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.73; H, 6.51; S, 11.52. Found: C, 64.73; H, 6.41; S, 11.44.

The nmr spectrum (CCl_4) showed the equatorial methine proton (C_3–H) as a septuplet at δ 5.74, $J_{AX} \sim J_{BX}$ = 3.25 Hz. The spectrum was invarient over the temperature range of 0–68°.

exo-**Bicyclo[3.2.1]oct-6-en-3-yl *p*-Toluenesulfonate (10a).** Following a procedure similar to that employed above, 900 mg (7.3 mmol) of *exo* alcohol **10b** was treated with 2.1 g (11.0 mmol) of *p*-toluenesulfonyl chloride. After work-up and recrystallization from a mixture of ether and pentane, 1.92 g (95%) of the tosylate **10a** was obtained, mp 61–63°.

Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.73; H, 6.51; S, 11.52. Found: C, 64.87; H, 6.47; S, 11.26.

The nmr absorption (CCl_4) for the axial C_3-proton occurred at δ 4.46 (triplet of triplets, J_{AX} = 9.5 Hz, J_{BX} = 6.5 Hz).

Thermal Stability of *endo*-Bicyclo[3.2.1]oct-6-en-3-yl *p*-Toluenesulfonate (11a). A. A nmr tube containing 35 mg of *endo* tosylate **11a,** one drop of pyridine, and 0.25 ml of benzene was purged with nitrogen and sealed, and the spectrum was determined over a 500-cps scan. The tube was then immersed in a constant-temperature bath at 76° for 1 hr, and was again analyzed by nmr. The spectrum was identical with that of the unheated sample. Finally the sample was heated for 28 hr. The nmr showed absorption at δ 4.92 with an integrated area corresponding to 40% *endo* tosylate **11a** and at δ 5.17 indicating the presence of 60% *exo* tosylate **10a.**

130°, and a 6 ft × 0.25 in. GE XE-60 silicone nitrile polymer 60–80 mesh Chromosorb P maintained at 167°. The carrier gas was helium operated at 10–11 psig. Most of the analytical gas chromatography was performed using a F & M Model 810 gas chromatograph instrument. The columns and conditions were: (a) 15 ft × 0.125 in. containing 15% E-20,000 on 60–80 mesh Chromosorb W, column temperature, 130°; (b) 8 ft × 0.25 in. containing 20% γ-methyl-γ-nitropimelonitrile on 60–80 mesh Chromosorb P at 130°; and (c) 6 ft × 0.25 in. containing 20% glycerol on 60–80 mesh Chromosorb W at 95°. The injection port was maintained at 170°, the detector at 210°. The helium gas flow was 5.0 on the rotometer, and 60 psig at the tank for all the columns described above.

Acetolyses of *endo*-Bicyclo[3.2.1]oct-6-en-3-yl *p*-Toluenesulfonate (11a). **A.** Two combustion tubes, each containing 100 mg (0.36 mmol) of *endo* tosylate in 5 ml of anhydrous acetic acid, were purged with nitrogen and sealed. One tube was placed in a constant-temperature bath operated at 55.7°, and the other in a bath set at 76.01°. After approximately 20 hr, the tubes were removed and opened, and the contents were diluted with 100 ml of water. The aqueous solution was extracted several times with pentane. The pentane extracts were washed until neutral to litmus and dried ($MgSO_4$), and the solvent was removed by careful distillation. Analysis by glpc using several columns showed that the acetate–hydrocarbon mixtures could not be well resolved. The mixture was, in each case, saponified with potassium hydroxide in methanol, and the corresponding alcohols were well separated by glpc.

B. Two samples, each containing 100 mg (0.36 mmol) of the *endo* tosylate **11a,** 44 mg (0.54 mmol) of sodium acetate, and 5 ml of anhydrous acetic acid, were heated at 56 and 76.01°, respectively, for approximately 20 hr. The work-up and saponification conditions were as previously described.

C. Two samples were prepared containing 100 mg (0.36 mmol) of the *endo* tosylate **11a,** 41 mg (0.54 mmol) of urea, and 5 ml of anhydrous acetic acid, and these were subjected to the same conditions described under A and B. The saponification procedure is described below.

Each sample of the acetate–hydrocarbon mixture was dissolved in 5 ml of methanol containing 187 mg (4.8 mmol) of potassium hydroxide. The solution was stirred for about 14 hr at room temperature. Water was added to a volume of 50 ml, and the solution was then extracted several times with pentane. After drying ($MgSO_4$), the pentane was removed by distillation until approximately 2 ml of solution remained. Several acetate–hydrocarbon mixtures were treated with lithium aluminum hydride in ether. The product compositions from these reactions were found to be identical with those obtained using potassium hydroxide and methanol.

The products, after saponification, from the acetolysis of *endo*-bicyclo[3.2.1]oct-6-en-3-yl *p*-toluenesulfonate (**11a**) were separated by preparative glpc [E-20,000, 130°], and were characterized using an analytical E-20,000 column. Typical weight percentages of each product obtained from the buffered runs are given in Table II. The order in which the components are described below is that of increasing retention time on glpc.

1. Bicyclo[3.2.1]octa-2,6-diene (12) was one of the major products (22–32%) of the buffered runs containing sodium acetate, but was absent in all nonbuffered runs. The diene **12** was identified by a comparison of its retention time and ir spectrum with those of an authentic sample.

2. This component has been tentatively identified as 2-oxatricyclo[3.2.1.$1^{3,7}$]nonane (**15**). It is a volatile solid, mp 174–176°; nmr ($CHCl_3$); δ 4.46 (s, 1), 4.12 (s, 1), and 2.75–0.92 (m, 10); molecular weight 124 (mass spectroscopy).

Anal. Calcd for $C_8H_{12}O$: C, 77.43; H, 9.67. Found: C, 77.26; H, 9.56.

3. ***endo*-Bicyclo[3.2.1]oct-6-en-3-ol (11b)** was a minor component (0.9–3.6%) of these reactions. It was identified by its ir spectrum and glpc retention time.

4. ***exo*(axial)-Bicyclo[3.2.1]oct-6-en-2-ol (8)**[3,18] was also a minor component (0.9–3.4%), and it was produced in too small an amount to be isolated. It was identified by its retention time on glpc, and by consideration of the known rearrangement[3] of *exo*-tricyclo[3.2.1.$0^{2,7}$]octan-6-yl acetate (**6**) to a mixture of this acetate and *exo*-bicyclo[2.2.2]oct-2-en-5-yl acetate (**7**) in nonbuffered media.

5. ***exo*-Bicyclo[3.2.1]oct-6-en-3-ol (10b)** was one of the major products (19–33%).

6. ***exo*-Bicyclo[2.2.2]oct-2-en-5-ol (7-OH)** was a major constituent (2.7–26%) in the nonbuffered and urea containing solvolyses. It was identified by its ir spectrum and glpc retention time.

7. ***exo*-Bicyclo[3.2.1]oct-2-en-7-ol (13)** was a major component (2.7–24%) in all nonbuffered and urea containing runs. Identification was secured through the melting point (47–48°), ir spectrum, and glpc retention time compared with those of a sample generously provided by Professor J. A. Berson.

8. ***exo*-Tricyclo[3.2.1.$0^{2,7}$]octan-6-ol (6)** was a major constituent (28–31%) of the sodium acetate buffered solvolyses. It was identified by its melting point (125–126°) (lit.[3] mp 125–127°), ir spectrum, and retention time.

Stability of *endo*-Bicyclo[3.2.1]oct-6-en-3-yl Acetate (11c) under Acetolysis Conditions. **A.** In a combustion tube were combined 76 mg (0.45 mmol) of *endo* acetate **11c,** 55 mg (0.68 mmol) of sodium acetate, and 5 ml of anhydrous acetic acid. The tube was sealed and the solution was heated at 96° for 25 hr, whereupon it was subjected to the same work-up and saponification procedures previously described. Analysis by glpc (E-20,000, 130°) showed only one component with a retention time identical with that of the *endo* alcohol **11b.**

B. A tube containing 50 mg (0.30 mmol) of the *endo* acetate **11c,** 38 mg (0.20 mmol) of *p*-toluenesulfonic acid and 5 ml of anhydrous acetic acid was sealed and heated at 76° for 26 hr. After work-up and saponification, the mixture was analyzed by glpc which showed that the major component (>95%) had a retention time the same as the component tentatively identified as 2-oxatricyclo[3.2.1.$1^{3,7}$]nonane (**15**) found in the acetolyses of both *endo* and *exo* tosylates. The identity of the two minor components was not determined.

Stability of Bicyclo[3.2.1]octa-2,6-diene (12) under Acetolysis Conditions. **A.** A combustion tube containing 100 mg (0.94 mmol) of bicyclo[3.2.1]octa-2,6-diene (**12**), 90 mg (1.1 mmol) of sodium acetate, and 5 ml of anhydrous acetic acid was sealed and heated at 76° for 25 hr. Work-up was carried out according to the usual procedure. Analysis by glpc (E-20,000, 130°) showed only two components: unreacted diene **12** (75%) and *exo*-bicyclo-[3.2.1]oct-2-en-7-yl acetate (**13**) (25%).

B. Using a procedure identical with that above, 100 mg (9.4 mmol) of the diene **12** and 90 mg (0.80 mmol) of *p*-toluenesulfonic acid in 5 ml of anhydrous acetic acid was heated at 76° for 25 hr. The glpc (E-20,000 at 130°) trace revealed only one component which was shown to be *exo*-bicyclo[3.2.1]oct-2-en-7-yl acetate (**13**).

***Partial Acetolysis of endo*-Bicyclo[3.2.1]oct-6-en-3-yl *p*-Toluenesulfonate (11a).** A tube containing 100 mg (0.36 mmol) of *endo* tosylate **11a** and 39 mg (0.48 mmol) of sodium acetate in 5 ml of anhydrous acetic acid was heated at 76° for 9 min (~45% reaction). The solution was diluted with water and extracted with pentane. After drying and removal of the solvent, the acetate–tosylate mixture was warmed *in vacuo* (40°, 0.1 mm) until all of the acetates were removed, and only a white solid remained mp 85–87° (mmp 85–87.5°). The ir spectrum (CS_2) of this recovered tosylate was identical with that of the authentic *endo* tosylate **11a.** Thin layer chromatography on silica gel indicated that $\leq$2% of *exo* tosylate **10a** could have been detected.

A sample of 320 mg (11.5 mmol) of tosylate **11a** was dissolved in 16 ml of anhydrous acetic acid containing 141 mg (17.3 mmol) of sodium acetate, and the mixture was heated at 56 ± 1.5° under nitrogen. Aliquots were removed at 10-, 81-, and 200-min intervals corresponding to 15, 50, and 82% reaction, respectively. Each aliquot was worked up to separate the acetate fraction from unreacted tosylate. The unreacted tosylates were examined by ir and by tlc (silica gel, 1:3 ether–hexane eluent), and *exo* tosylate **10a** could not be detected. Control experiments established that $\leq$2% of **10a** could have been detected in the recovered **11a.** Analysis of the acetate fractions by capillary glpc (Perkin-Elmer Model F-11) on a SCOT column of Dow Polyglycol E-20,000 at 55° showed the following area ratios of inverted acetate **10c** to retained acetate **11c**: 37/1 after 15% reaction, 33/1 after 50% reaction, 32/1 after 82% reaction.

Thermal Stability of *exo*-Bicyclo[3.2.1]oct-6-en-3-yl *p*-Toluenesulfonate (10a). A nmr tube containing 30 mg (0.108 mmol) of *exo* tosylate **10a** in 0.25 ml of "Spectrograde" benzene was sealed and examined by the nmr technique. The vinyl protons of **10a** are distinctly separated from those of the *endo* tosylate **11a,** occurring at about δ 4.9. The sample was then heated to 76° for 18 hr, and the nmr spectrum was again recorded and showed no bands at δ 5.3 (*endo* tosylate **11a** vinyl proton region).

Acetolyses of *exo*-Bicyclo[3.2.1]oct-6-en-3-yl *p*-Toluenesulfonate (10a). The procedures used were essentially those described previously for the solvolyses of the *endo* isomer. The *exo* tosylate **10a** was solvolyzed in anhydrous acetic acid containing urea at 76 and 96°, in nonbuffered anhydrous acetic acid at 76 and 96°, and in anhydrous acetic acid containing sodium acetate at 56, 76, and 96°. The work-up of the acetates and subsequent saponification to the alcohols was also unchanged. Except in the cases which are specifically noted, all analytical and preparative glpc analyses were accomplished using a E-20,000 column at 130°.

1. Bicyclo[3.2.1]octa-2,6-diene (**12**) comprised 25–49% of the sodium acetate buffered solvolyses.

2. This component has been tentatively identified as 2-oxatricyclo[3.2.1.$1^{3,7}$]nonane (**15**). It amounted to 6–20% of the product mixtures in the urea and nonbuffered acetolyses.

(18) Prepared by Mr. J. R. Menke.

3. *endo*-**Bicyclo[3.2.1]oct-6-en-3-ol (11b)** represented 10–36% of the product mixtures.

4. *exo*(**axial**)-**Bicyclo[3.2.1]oct-6-en-2-ol (8-OH)** was a minor (0.7–2.6%) component.

5. *exo*-**Bicyclo[2.2.2]oct-2-en-5-ol (7-OH)** varied from 1.6 to 28% in these mixtures.

6. *exo*-**Bicyclo[3.2.1]oct-2-en-7-ol (13-OH)** was the major product (2.4–68%) in the nonbuffered acetolyses.

7. *exo*-**Tricyclo[3.2.1.0^{2,7}]octan-6-ol (6-OH)** appeared only in the sodium acetate buffered solvolyses (6–14%).

8. *endo*-**Tricyclo[3.2.1.0^{2,7}]octan-6-ol** was identified in the 96° sodium acetate buffered acetolysis. It was identified in the following manner. The epimeric tricyclic alcohols were separated by 1 min on the E-20,000 column, and their order of elution was reversed on the glycerol column. Addition of authentic *endo*-tricyclo[3.2.1.0^{2,7}]octan-6-ol[3] to the saponified acetolysis mixture enhanced only the peak at 26.9 min (glycerol column at 105°).

Acetolysis of *exo*-Bicyclo[3.2.1]oct-6-en-3-yl *p*-Toluenesulfonate (10a) with Excess of Sodium Acetate. Two tubes were prepared containing: (a) 100 mg (0.36 mmol) of *exo* tosylate **10a** and 44 mg (0.54 mmol) of sodium acetate in 5 ml of anhydrous acetic acid; and (b) 100 mg (0.36 mmol) of *exo* tosylate and 132 mg (1.6 mmol) of sodium acetate in 5 ml of anhydrous acetic acid. Each was heated to 76° for 22 hr and worked up with pentane, and the acetates were saponified with potassium hydroxide in methanol. Analysis of the two samples was accomplished using glpc (E-20,000 at 130°) with the results given in Table IV.

Table IV

%					
12	**11b**	**8-OH**	**7-OH**	**13-OH**	**6-OH**
		(a) Normal Buffer			
38.3	37.4	0.3	2.7	6.3	15.0
		(b) Excess Buffer			
38.2	41.5	0.4	2.0	4.4	13.5

Reaction of Bicyclo[3.2.1]octa-2,6-diene (12) with Acetic Acid-OD. A solution containing 7.4 g (69.4 mmol) of the diene **12** and a few milligrams of *p*-toluenesulfonic acid in acetic acid-OD (97% OD by nmr) was heated at 70° for 2 days. Analysis of the mixture by glpc (E-20,000 at 130°) after work-up indicated **13**: 69% d_1, 13% d_0, ~8% d_2. Reduction with lithium aluminum hydride and crystallization afforded 5.42 g (92%) of *exo*-bicyclo[3.2.1]oct-2-en-7-ol (**13-OH-*d***). The alcohol was oxidized (85% yield) to bicyclo[3.2.1]oct-2-en-7-one using chromium trioxide in pyridine. The ketone was recovered in pure form by column chromatography with silica gel. Mass spectrographic analysis showed the compound to contain 54% d_0, 44% d_1, and ~2% d_2 species. This sample was then placed in a flask containing 5 ml of water, 1 ml of methanol, and 50 mg of potassium hydroxide and heated at 50° for 2 hr. The usual work-up was employed. Mass spectrographic analysis now showed that the sample contained 65% d_0, 35% d_1, and <0.2% d_2 species.

2,2,4,4-Tetradeuteriobicyclo[3.2.1]oct-6-en-3-one (9-d_4). To a solution of 484 mg (0.021 g-atom) of sodium in 12 ml of methanol OD was added 500 mg (4.1 mmol) of bicyclo[3.2.1]oct-6-en-3-one (**9**). The solution was heated to 50° for 2 hr, and was then diluted with 6 ml of deuterium oxide. The deuterated ketone **9-d_4** was recovered by continuous extraction with pentane. After sublimation there was obtained 350 mg (70%) of deuterated ketone, mp 99–101°. The above sequence was repeated using 700 mg (5.73 mmol) of **9**, and there was recovered 700 mg (97%) of the pure ketone-d_4. The extent of deuterium incorporation in these two samples was not determined.

endo-**Bicyclo[3.2.1]oct-6-en-3-yl-2,2,4,4-d_4 *p*-Toluenesulfonate (11a-d_4).** The tetradeuterated ketone **9-d_4** was reduced with sodium borohydride in methanol. After work-up, the *endo*-d_4 alcohol (**11b-d_4**) was collected by glpc (58% recovery), mp 188–191°. Mass spectrometry indicated 98% d_4, 2% d_3. The tosylate **11a-d_4** was prepared in the usual manner, mp 86.5–87.5°.

exo-**Bicyclo[3.2.1]oct-6-en-3-yl-2,2,4,4-d_4 *p*-Toluenesulfonate (10a-d_4).** In this case the ketone **9-d_4** was reduced with lithium aluminum hydride. Separation of the *exo*-d_4 alcohol (**10b-d_4**) by glpc gave a product having mp 89–90°, 95% d_4 and 5% d_3. The tosylate **10b-d_4** melted at 60–61.5° after recrystallization.

Kinetic Studies. The standard solutions were prepared using J. T. Baker Co., reagent grade glacial acetic acid containing 1% by weight of added acetic anhydride. The perchloric acid solution (0.0154 *N*) in glacial acetic acid was prepared and standardized against potassium acid phthalate. The perchloric acid solution was in turn used to determine the normality of the solution of sodium acetate in glacial acetic acid, which was found to be 0.0101 *N*.

The indicator for the titrations was a 0.2% solution of crystal violet in glacial acetic acid. Two drops of the indicator were used in each determination. The buffered sodium acetate solutions were titrated to an end-point color change of violet to blue. In the nonbuffered titrations, the end-point was taken to be the color change of blue to violet. In all cases, it was discovered that the end point could be more easily discerned if an incandescent light bulb were placed behind the sample being titrated.

The constant-temperature bath, controlled by a Sargent H-B differential temperature controller, was filled with Ucon Fluid 50-HB-280-X. Temperatures were determined with thermometers calibrated by the National Bureau of Standards.

The acetolysis procedure used was essentially that first described by Winstein.[10] The sulfonate ester was weighed into a 50-ml volumetric flask, and was diluted to volume with the standard sodium acetate in glacial acetic acid solution. Five-milliliter aliquots were sealed into Pyrex combustion tubes (Corning No. 8640) which were then placed in the constant-temperature bath. Tubes were removed at recorded intervals, rapidly cooled to room temperature, and opened, and the contents were titrated with standard perchloric acid solution. In the nonbuffered runs, the *p*-toluenesulfonic acid generated was titrated directly with the standard sodium acetate solution. Duplicate runs were made in all cases. The data on the deuterated tosylates were obtained sometime after those from the nondeuterated samples. To insure the validity of the rate constants obtained with the deuterated tosylates, the unlabeled counterpart was again run, and the rate constant so obtained was nearly identical with that value found earlier.

The runs were followed to 80–90% completion. Rate constants were determined by a least-square plot of log [ROTs] *vs.* time and were obtained with the aid of a computer. The values were also plotted graphically. Thermodynamic quantities were calculated using

$$\Delta H^{\pm} = [T_1T_2/(T_2 - T_1)] \log (k_2/k_1)2.303R$$

and

$$\Delta S^{\pm} = (\Delta H^{\pm}/T) + 2.303R[\log (k_r/T) - \log(k/h)]$$

Final reaction rates were extrapolated to 25° by

$$\log k = \log (k_2) - [\Delta H^{\pm}(T_2 - T_1)/2.303RT_2T_1]$$