Tetrahedron, 1964, Vol. 20, pp. 215 to 229. Pergamon Press Ltd. Printed in Northern Ireland

PREPARATION AND SOLVOLYSIS OF THE BICYCLO[3.2.1]OCT-2-EN-8-YL *p*-TOLUENESULFONATES

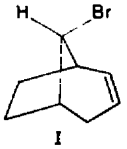
HOMOALLYLIC PARTICIPATION

N. A. LEBEL[1] and L. A. SPURLOCK[2]
Department of Chemistry, Wayne State University, Detroit 2, Michigan

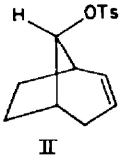
(*Received* 21 *October* 1963)

Abstract—The syntheses and proof of structure of *syn*- and *anti*-bicyclo[3.2.1]oct-2-en-8-ols are described. Kinetic analysis and product determinations for the acetolyses of the *p*-toluenesulfonates were carried out. Only the *anti*-ester (III) derives significant *anchimeric* assistance, and the *ion* generated must be different than the *classical* 8-bicyclo[3.2.1]oct-2-ene cation presumably formed from the *syn*-epimer (II). A new type of *homoallylic* cation is postulated for the solvolysis of *anti*-bicyclo[3.2.1]oct-2-en-8-yl *p*-toluenesulfonate. Comparison of these data with that from the 7-norbornenyl homologs allows several conclusions regarding the requirements for effective *homoallylic* participation.

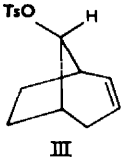
INTERACTION between a β-olefinic function and a developing carbonium ion center gives rise to *homoallylic* participation, and the resulting cationic intermediate can, in some cases, be described as a "non-classical" *homoallylic* ion.[3] Two of the many interesting problems associated with this phenomenon are the requirements for effective *homoallylic* participation imposed by the geometry of the system and by the degree of alkyl substitution of the olefin. We became interested in bicyclo[3.2.1]-oct-2-en-8-yl derivatives from the observation that *syn*-8-bromobicyclo[3.2.1]oct-2-ene (I)[4] was highly resistant toward hydrolysis. In view of the unusual solvolytic behaviour of the homologous 7-norbornenyl arenesulfonates,[5] a study of the acetolysis of the related *syn*- and *anti*-bicyclo[3.2.1]oct-2-en-8-yl *p*-toluenesulfonates (II and III, respectively) might provide useful information. The bicyclic skeleton of compounds II and III can be seen to require that the three-carbon bridge be coplanar with the bridgehead carbon atoms, and participation of the "unsymmetrical"[3] or "symmetrical"[3] homoallylic type may be of importance with the stereochemically more suitable *anti*-isomer III. The situation is also interesting by the recognition that II and III are also Δ^3-cyclohexenyl analogs of fixed conformation.



I



II



III

[1] A. P. Sloan Foundation Fellow, 1961–65.

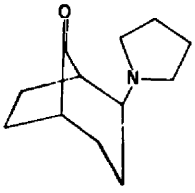
[2] U.S. Public Health Service Predoctoral Fellow, 1961–63.

[3] Pertinent discussions can be found in [a] S. Winstein and E. M. Kosower, *J. Amer. Chem. Soc.* **81**, 4399 (1959). [b] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *Ibid.* **81**, 4390 (1959), and [c] C. H. DePuy, I. A. Ogawa and J. C. McDaniel, *Ibid.* **83**, 1668 (1961).

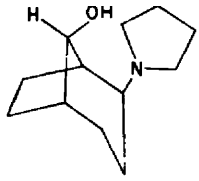
[4] N. A. LeBel, J. E. Huber and L. H. Zalkow, *J. Amer. Chem. Soc.* **84**, 2226 (1962).

[5] [a] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Amer. Chem. Soc.* **77**, 4183 (1955); [b] S. Winstein and M. Shatavsky, *Ibid.* **78**, 592 (1956); [c] S. Winstein and E. T. Stafford, *Ibid.* **79**, 505 (1957).

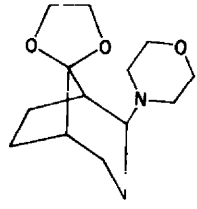
Synthetic procedure. The syntheses of the desired alcohols was based upon the N-pyrrolidyl ketone (IV) obtained by Stork and Landesman[6] from the condensation of acrolein and N-1-pyrrolidyl-cyclopentene. Reduction of IV with lithium aluminum hydride afforded the crystalline *syn*-amino alcohol V. The amine oxide degradation procedure applied to V gave *syn*-bicyclo[3.2.1]oct-2-en-8-ol (VIa), albeit in low yield. The structure and stereochemistry of VIa (and V) were confirmed by hydrogenation to the known *endo*-bicyclo[3.2.1]octan-8-ol (Xa).[7a] Infra-red studies of VIa showed intramolecular hydrogen bonding between the *syn*-hydroxyl group and the double bond ($\Delta\nu = 42\ cm^{-1}$),[8] and provides additional support for the structural assignment. Alcohol VIa was homogeneous by gas chromatography, and its epimer IXa was not detected among the pyrolysis products of the amine oxide of V.



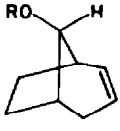
IV



V

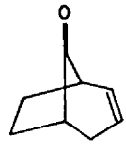


VIII

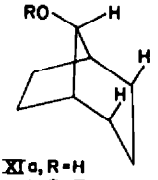


IXa, R=H
b, R=Ac

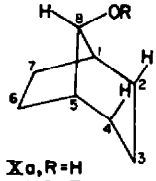
VIa, R=H
b, R=Ac



VII



XIa, R=H
b, R=Ts



Xa, R=H
b, R=Ts

Oxidation of VIa to bicyclo[3.2.1]oct-2-en-8-one (VII) proved to be very difficult. Only partial conversion was effected on prolonged treatment with chromium trioxide-pyridine or with dichromate-sulphuric acid, and in the latter case competing double bond oxidation was serious. The ketone VII could be separated by gas chromatography. A more convenient route to VII took advantage of the amine oxide pyrolysis of the N-morpholino ketal VIII.[9] The ethylene ketal of VII obtained by this procedure

[6] G. Stork and H. K. Landesman, *J. Amer. Chem. Soc.* **78**, 5129 (1956).

[7] [a] A. C. Cope, J. M. Grisar and P. E. Peterson, *J. Amer. Chem. Soc.* **82**, 4299 (1960), [b] A. C. Cope, S. Moon, C. H. Park and G. L. Woo, *Ibid.* **84**, 4865 (1962). We wish to thank Prof. Cope and Dr. Moon for an authentic sample.

[8] P. R. Schleyer, D. S. Trifan and R. Bacskai, *J. Amer. Chem. Soc.* **80**, 6691 (1958).

[9] [a] C. S. Foote, Ph.D. Thesis, Harvard University, 1961. We wish to thank Dr. Foote for a copy of this thesis. [b] C. S. Foote and R. B. Woodward, *Tetrahedron*, in press.

was identical with that described.[9] These investigators noted that the ketal was hydrolyzed with difficulty and, since their main interest lay in the saturated compounds Xa and XIa, found it convenient to reduce a mixture of ketone VII and its ketal to the saturated analogs. We were able to effect hydrolysis of the ketal in excellent yield (95%) by employing a two-phase system of ether and warm 6 N hydrochloric acid. The pure ketone VII was identical to that obtained by the oxidation of VIa, and showed an IR spectrum similar to that reported.[9a]

Several methods of reduction of VII were attempted, and in every case, the *syn*-alcohol VIa predominated over the *anti*-isomer IXa. These studies are summarized in Table 1. Equilibration of VIa could not be effected with aluminium isopropoxide in refluxing isopropanol. However, upon heating a solution of VIa in the mixture

TABLE 1. REDUCTIONS OF BICYCLO[3.2.1]OCT-2-EN-8-ONE (VII)

Method	% *syn* (VIa)[a]	% *anti* (IXa)[a]
$NaBH_4$/MeOH	91(76)[b]	9(24)[b]
$NaBH_4$/pyridine	75	25
Na/wet ether	70	30
Na/isopropanol	70[b]	30[b]

[a] Determined by gas chromatography. [b] Reported in Ref. 9. The analysis was carried out by hydrogenation of the mixture and gas chromatographic analysis of the saturated alcohols Xa and XIa.

fluorenone–aluminium t-butoxide-benzene[10] at 125°, an equilibrium mixture consisting of 20% VIa and 80% *anti*-bicyclo[3.2.1]oct-2-en-8-ol (IXa) was obtained (this same composition was obtained by approaching equilibrium from pure IXa).

Pure *anti*-bicyclo[3.2.1]oct-2-en-8-ol (IXa) was characterized in the usual way, and its assignment was confirmed by hydrogenation to *exo*-bicyclo[3.2.1]octan-8-ol (XIa).[7] Separation of IXa in pure form was best effected by gas chromatography of the equilibrium mixture. No O—H stretching vibration corresponding to intramolecular hydrogen bonding was observed in the IR spectrum of IXa.

The data described above—the resistance of VIa (and IXa) to oxidation and equilibration, and the obvious favouring of the ketal over the ketone VII and ethylene glycol at equilibrium in the presence of acid[9]—reflect the strain associated with the introduction of a trigonal carbon atom at C-8 in the bicyclo[3.2.1]oct-2-ene system. Similar results were obtained for the saturated analogs.[7,9] This strain is also evident in the high carbonyl frequency at 1758 cm^{-1} in the IR spectrum of VII. It is very interesting to note that the equilibration studies of alcohols VIa and IXa, and the product distributions from reductions of the ketone VII clearly show that the *anti*-alcohol IXa is thermodynamically more stable than its *syn*-isomer VIa, and that approach from the side of the two-carbon bridge is less hindered. *endo*-Bicyclo[3.2.1]octan-8-ol (Xa) also is less stable than its *exo*-epimer (XIa) and this is attributed to unfavourable 1,3-diaxial interactions with hydrogen atoms at C_2 and C_4.[7] However, for VIa this interaction has been removed at C_2 by introduction of the double bond and has been lessened (skewed) at C_4. An obvious conclusion is that the anti-bonding interaction provided by the double bond in the rigid Δ^3-cyclohexenyl system of VIa is at least as unfavourable as the two 1,3-diaxial hydrogen interactions of Xa.

[10] W. von E. Doering and T. Aschner, *J. Amer. Chem. Soc.* **77**, 5633 (1955).

Solvolysis studies. Alcohols VIa and IXa were converted in high yield to the *p*-toluenesulfonates II and III, respectively. Both tosylates showed good linear first order kinetics when solvolyzed in acetic acid, and, in the case of the *anti*-isomer III, in ethanol. The *syn*-isomer II was extremely unreactive, as anticipated from the qualitative observations[4] with the bromide I. Kinetic data are summarized in Table 2.

Product studies were carried out for the acetolyses of II and III in acetic acid, 0·3 M in sodium acetate. The results are given in Table 3.

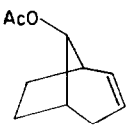
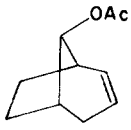
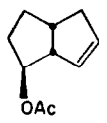
Identification of the products was conducted in the following manner. The hydrocarbon fraction was separated from the acetates by distillation. Gas chromatographic analysis showed that the hydrocarbon was essentially homogeneous, and

TABLE 2. KINETIC DATA FOR SOLVOLYSES

[ROTs]	[NaOAc]	No. of Runs	T, °C	$10^4 k$, sec^{-1} [a]
	syn-Bicyclo[3.2.1]oct-2-en-8-yl *p*-Toluenesulfonate (II)			
(10^2 M)	(10^2 N)			
3·01	3·1	3	179·5 ± 0·18	1·29 ± 0·02
2·96	3·1	2	168·3 ± 0·13	0·47 ± 0·02
			25·0	1·4 × 10^{-9} [b]
$\Delta H‡$ = 35·8 kcal/mole; $\Delta S‡$ = +2 e.u.				
	anti-Bicyclo[3.2.1]oct-2-en-8-yl *p*-Toluenesulfonate (III)			
Acetolysis				
0·796	1·0	2	84·8 ± 0·02	1·13 ± 0·05
0·720	1·0	2	76·1 ± 0·01	0·415 ± 0·002
1·006	none	1	84·8 ± 0·02	0·841
			25·0	3·6 × 10^{-4} [b]
$\Delta H‡$ = 29 kcal/mole, $\Delta S‡$ = +3 e.u.				
Ethanolysis				
1·046	none	2	84·8 ± 0·02	0·262 ± 0·004

[a] Determined by the method of least squares. [b] Extrapolated from the data at other temps.

TABLE 3. PRODUCTS OF THE ACETOLYSIS OF *syn*- AND *anti*-BICYCLO[3.2.1]OCT-2-EN-8-YL *p*-TOLUENESULFONATES

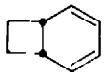
Tosylate	T	Composition, %[a]							
			Other Hydrocarbons				Other Acetates		
							A	B	
II (*syn*)	180°	32	trace[b]	21	14	30	2	1	—
	125°	23	—	30	11	33	2	1	—
III (*anti*)	100°	23	—	23	—	48	3	2	1[c]
	125°	25	—	21	—	48	3	2	—

[a] The relative % composition was obtained by gas chromatography of the total product mixture to obtain % hydrocarbon and % acetate. The acetate fraction was separated and saponified to a mixture of alcohols. Analysis of the alcohols by gas chromatography gave the relative proportions of the individual acetates.

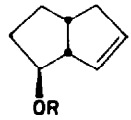
[b] Trace amounts of two components were detected.

[c] A carbonyl component not observed in sealed tube runs.

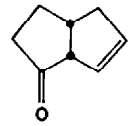
an UV spectrum suggested it to be a conjugated, homoannular diene. Identity with bicyclo[4.2.0]octa-2,4-diene (XII) was established by comparison of the IR spectrum, gas chromatographic time and the maleic anhydride adduct with those of an authentic sample prepared by the published method.[11]



XII



XIII a, R = H
b, R = Ac
c, R = Ts



XIV

The acetate fraction was poorly resolved on gas chromatography, and was subsequently saponified to the alcohols which were cleanly separated. The bicyclo-[3.2.1]oct-2-en-8-ols (VIa and IXa) from saponification of the acetates (VIb and IXb) were identified by comparison of retention times and IR spectra with those of the authentic samples. The major acetate component from the solvolysis was an unknown, rearranged acetate, which was assigned the structure *exo-cis*-bicyclo[3.3.0]oct-7-en-2-yl acetate (XIIIb) on the basis of the following evidence. The alcohol mixture from saponification was hydrogenated and the major component (formed in the same proportion) was shown to be *exo-cis*-bicyclo[3.3.0]octan-2-ol.[12] *endo-cis*-Bicyclo-[3.3.0]octan-2-ol[12] was not detected in the hydrogenation mixture, indicating that *none* of its unsaturated analogs were formed in the solvolysis. The additional information that the unidentified acetates A and B do not have the bicyclo[3.3.0]octene carbon skeleton, and are most likely double bond isomers, follows from the observations that the hydrogenated alcohols of A and B show identical retention times on gas chromatography which are different from those of either of the *cis*-bicyclo[3.3.0]octan-2-ols.

The alcohol mixture obtained on saponification of the acetolysis products was partially oxidized with chromium trioxide in pyridine. This procedure gave a single ketone (XIV), which could easily be separated from the unreacted alcohols. The ketone formed a semicarbazone derivative which had a melting point identical to that reported for *cis*-bicyclo[3.3.0]oct-6-en-2-one.[13] However, the ring expansion procedure with bicyclo[3.2.0]hept-2-en-6-one[13] was repeated and pure *cis*-bicyclo[3.3.0]-oct-6-en-2-one was separated by gas chromatography. Its infrared spectrum and semicarbazone derivative were different from those of the ketone XIV obtained in this study. The pure alcohol XIIIa was also separated and its NMR spectrum confirmed the presence of two vinyl protons at $\delta = 5{\cdot}75$ p.p.m. Based upon the accepted structure of the cyclopentadiene-ketene adduct, the above data are only consistent with the assignment of the rearranged acetate as XIIIb.

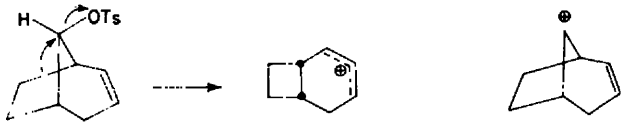
DISCUSSION

The most striking information obtainable from the data of Table 2 is the large difference in solvolytic reactivity between *syn* (II) and *anti* (III) *p*-toluenesulfonates; the factor k_{anti}/k_{syn} for acetolysis is about $2{\cdot}6 \times 10^5$ at 25°. On first principles, the

[11] A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, *J. Amer. Chem. Soc.* **74**, 4867 (1952).
[12] A. C. Cope, M. Brown and H. H. Petree, *J. Amer. Chem. Soc.* **80**, 2852 (1958).
[13] J. D. Roberts and W. F. Gorham, *J. Amer. Chem. Soc.* **74**, 2278 (1952).

same bicyclo[3.2.1]oct-2-en-8-yl cation (XVI) might be expected from both substrates. Obviously, therefore, either the acetolysis of the *anti*-isomer III is greatly accelerated by neighbouring group participation; or the *syn*-isomer is unexpectedly slow. The former explanation seems more reasonable to us, and an examination of the relative rate summary given in Table 4 makes clearer our reasons for this choice. On the one hand, *syn*-bicyclo[3.2.1]oct-2-en-8-yl *p*-toluenesulfonate (II) undergoes acetolysis about 20 times faster than 7-norbornyl tosylate. If it is accepted that the latter ionizes without *anchimeric* assistance to a "tricycloheptonium" non-classical ion[14], then the slightly higher rate for II is accommodated by a similar unassisted ionization—the rate difference is attributed to the greater strain involved with generating a *quasi*-trigonal transition state[15] at the one-carbon bridge of the norbornane skeleton. The nature of the cationic intermediate from the solvolysis of II is unknown, however the fact that ca. 40% of the solvolysis products are unrearranged acetates argues against the direct formation of an allylic carbonium ion. Moreover, a substantial and reproducible proportion is acetate of inverted configuration.

It seems quite clear, and somewhat surprising, that the ionization of II does *not* derive anchimeric assistance from methylene participation and ultimate allylic resonance stabilization (cf. XV) as does *syn*-7-norbornenyl *p*-toluenesulfonate. This may well be an indication that allylic resonance stabilization in the bicyclo[4.2.0]-oct-2-enyl system is below the energy threshold for compensation of the strain



XV XVI

associated with the ring contraction of a bicyclo[3.2.1]oct-2-ene. The production of bicyclo[4.2.0]octa-2,4-diene (XII) in the acetolysis of II is apparently subsequent to a rate-determining ionization step. In the absence of additional evidence, the cation generated from II is considered best approximated by the classical structure XVI. This same pattern of unassisted ionization also holds for *endo*-bicyclo[3.2.1]octan-8-yl *p*-toluenesulfonate (Xb),[9] which must be faster than II because of both steric (larger C_1-C_8-C_5 angle) and inductive (C_2 and C_3 are saturated) influences.

Ionization of *anti*-bicyclo[3.2.1]oct-2-en-8-yl *p*-toluenesulfonate (III) is *anchimerically* assisted. In fact, III shows an acetolysis rate of the same order of magnitude as do cyclohexyl and Δ^3-cyclohexenyl *p*-toluenesulfonates, despite the much lower angle strain associated with cation formation in these simple analogs. The origin of the acceleration must be from participation by the three-carbon bridge, and the observation from product studies that acetate IXb of retained configuration is the only *non-rearranged* product formed supports this premise.

No *syn*-bicyclo[3.2.1]oct-2-en-8-yl acetate (VIb) is produced in the acetolysis of III, and this observation coupled with the accelerated rate suggests that a cationic intermediate different from the classical ion XVI (presumed to be formed initially

[14] S. Winstein, F. Gadient, E. T. Stafford and P. E. Klinedinst, Jr., *J. Amer. Chem. Soc.* **80**, 5895 (1959).

[15] This factor appears to be the most likely cause for the difference in reactivities of bridge substituted tosylates, cf. P. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.* **83**, 182 (1961).

TABLE 4. RELATIVE RATES OF ACETOLYSIS OF *p*-TOLUENESULFONATES AT 25°

p-Toluenesulfonate	Rel. Rate[a]
Cyclohexyl[b]	1·0
Δ^3-Cyclohexenyl[c]	0·74
7-Norbornyl[d]	$1·33 \times 10^{-7}$
anti-7-norbornenyl[d]	$7·7 \times 10^{8}$
syn-7-norbornenyl[e]	$5·4 \times 10^{-6}$
exo-Bicyclo[3.2.1]octan-8-yl (XIb)	0·62
anti-Bicyclo[3.2.1]oct-2-en-8-yl (III)	0·75
endo-Bicyclo[3.2.1]octan-8-yl (Xb)[f]	$7·8 \times 10^{-5}$
syn-Bicyclo[3.2.1]oct-2-en-8-yl (II)	$2·9 \times 10^{-6}$

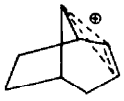
[a] Values obtained from data measured, extrapolated or interpolated at 25°.

[b] The rate constant $4·8 \times 10^{-8}$ sec^{-1} is from H. C. Brown and G. Ham, *J. Amer. Chem. Soc.* **78**, 2735 (1956).

[c] From the data given in Ref. 9a.

[d] Data of Ref. 5a. [e] Data of Ref. 5c. [f] Data of Ref. 9.

from II) is generated by ionization. This intermediate can be formulated as a *non-classical* cation of one of three types.



XVII

XVIII

XVIII a

A *homo*cyclopropenyl cation such as XVII can probably be rejected on the grounds that the constraint imposed by the bicyclic carbon skeleton precludes significant interaction between the *p*-orbital at C_3 and the vacant *p*-orbital at C_8.[16] The *unsymmetrical* homoallylic cation XVIII is of the same type as that considered to be involved in the solvolyses of cholesteryl,[17] 2-norbornenyl,[17] *exo*- and *endo*-7-isopropylidine-2-norbornenyl,[3c] *exo*-bicyclo[2.2.2]oct-2-en-5-yl[18] and possibly (although the rate data do not allow a clear-cut conclusion) the *anti*-7-camphenyl analog.[19] In most cases, the *anchimeric* assistance derived from direct ionization to these cations is substantial. However, in several of these systems, Wagner-Meerwein rearrangement of the vinyl group has been detected[3a,3c,18] and this may involve a *symmetrical homoallylic* cation such as XVIIIa as a transition state or an intermediate. It is apparent from the data described above, and from observations by other workers[9,20] that the solvolyses of *exo* (and *anti*)-8-bicyclo[3.2.1]octyl derivatives are accompanied by significant amounts of rearrangement to bicyclo[3.3.0]octyl compounds. The implication is that if III ionizes with the initial generation of XVIII, additional electron delocalization and slight change of geometry [via XVIIIa] could be expected to result in the subsequent production of *exo-cis*-bicyclo[3.3.0]oct-7-en-2-yl acetate (XIIIb) (vinyl rearrangement). This product was obtained.

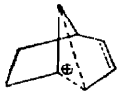
[16] See footnote 40 in Ref. 3*a*.

[17] Discussion of these systems and a summary of literature references may be found in ref. 3*a*.

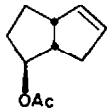
[18] N. A. LeBel and J. E. Huber, *J. Amer. Chem. Soc.* **85**, 3193 (1963).

[19] E. E. van Tamelen and C. I. Judd, *J. Amer. Chem. Soc.* **80**, 6305 (1958).

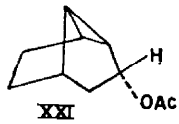
[20] S. J. Cristol, *Abstracts*, 18*th National Organic Chemistry Symposium* p. 22. Columbus, Ohio, June 16–20 (1963). S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde and K. Schwarzenbach, *J. Amer. Chem. Soc.* **85**, 2675 (1963).



XIX



XX



XXI

Another type of *non-classical* cationic intermediate must be considered. This bridged ion, XIX, would result from ionization of III with allylic methylene participation. However, if this is the case, the rearranged acetate would be expected to have the structure *exo-cis*-bicyclo[3.3.0]oct-6-en-2-yl acetate (XX) (allylic rearrangement). The available evidence seems to preclude this possibility.

We, therefore, postulate that ionization of III derives substantial anchimeric assistance (the comparative rate data for acetolysis and ethanolysis suggests that solvolysis of III is in the limiting category[21]) by formation of the *non-classical* ion XVIII. The structures and *stereochemistry* of each of the identified products can be conveniently accommodated from XVIII as shown in Scheme I.

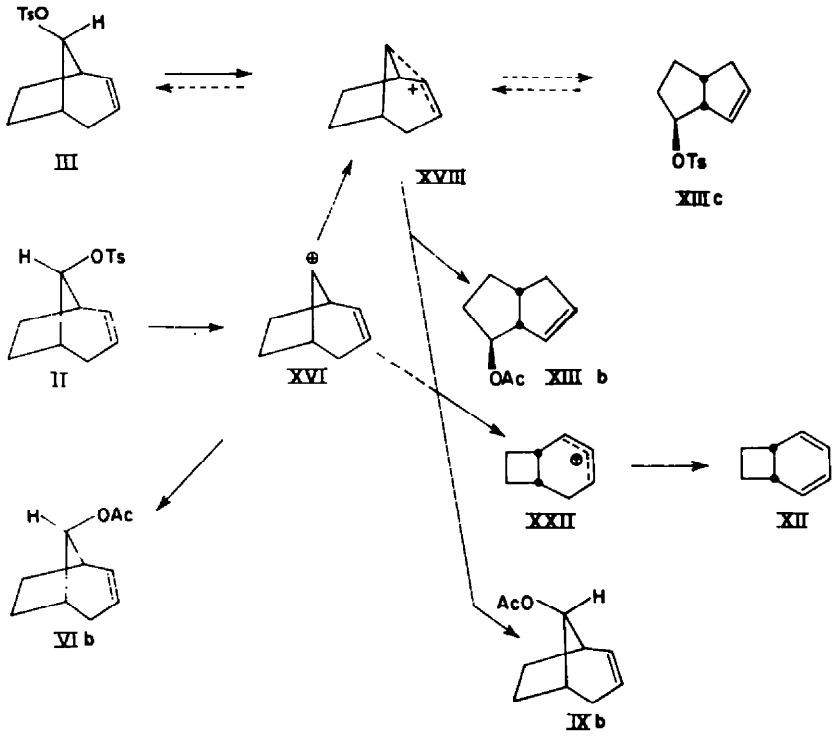
Some further comments seem in order. It might be anticipated that nucleophilic attack of XVIII would give rise to a tricyclic acetate XXI. Obviously, the product studies in this work suggest that this is not a major product of kinetic control. This result is not at all surprising with the recognition that similar products are not produced in solvolyses of *anti*-7-norbornenyl derivatives.[22] There, of course, remains the possibility that one of the very minor acetates A or B may have the structure XXI.

The saturated analogue of III, *exo*-bicyclo[3.2.1]octan-8-yl *p*-toluenesulfonate (XIb), also derives anchimeric assistance to ionization by participation of the methylene group of the three-carbon bridge.[9] Yet both of these compounds undergo acetolysis at about the same rate. It would be expected that the rate of III would be lowered relative to that of XIb by the inductive effect of the double bond and the smaller C_1-C_5-C_8 bond angle. From the comparative rate constants of the *syn* (II) and *endo* (Xb)[9] compounds, this difference should amount to at least a factor of 10 (obtained by extrapolation of the data for II to 140°. Comparison at 25°—Table 4—suggests two powers of ten, but is the result of a rather lengthy extrapolation). Thus, participation of the double bond in III is at least as effective as participation of the trimethylene bridge in XIb, and takes precedence over participation by the allylic methylene group. This may be a manifestation of the greater migratory aptitude of vinyl relative to allyl or alkyl. Geometrical factors are still obscure.

Ion-pair return occurs in the acetolysis of both *exo*-bicyclo[3.2.1]octan-8-yl *p*-toluenesulfonate (XIb)[9] and 7-norbornyl tosylate.[14] It is entirely possible that internal return obtains in the acetolysis of III. The composition of total *p*-toluenesulfonate present after 40% acetolysis was determined, and was found to be nearly exclusively III. No *exo-cis*-bicyclo[3.3.0]oct-7-en-2-yl *p*-toluenesulfonate (XIIIc) was detected. Either the rate constant for ion-pair return from XVIII to XIIIc is close to zero and/or the rate of ionization of XIIIc is extremely fast. Preliminary acetolysis data for XIIIc seem to verify the latter conclusion.

The outline of Scheme I also presents the suggestion that the *classical* cation intermediate (XVI) from II can partition itself by rearrangement to the *non-classical* ion XVIII, rearrangement to the allylic ion XXII, or direct reaction with solvent to

[21] S. Winstein, E. Grunwald and H. W. Jones, *J. Amer. Chem. Soc.* 73, 2700 (1951).
[22] S. Winstein, A. H. Lewin and K. C. Pande, *J. Amer. Chem. Soc.* 85, 2324 (1963).



give acetates VIb and IXb. This conclusion results from an examination of product compositions from the acetolyses of II and III at identical temperatures, with the assumption that all of the bicyclo[3.3.0]oct-7-en-2-yl acetate (XIIIb) arises by solvent attack on cation XVIII. There is, of course, no evidence that the allylic ion (XXII) is involved, and hydrocarbon XII may result directly by rearrangement and proton loss from XVIII.

Of the compounds whose rates of acetolysis are compared in Table 4, *anti*-7-norbornenyl *p*-toluenesulfonate retains its premier position in uniquely accelerated ionization reactions[5,22] as the "*bis-homocyclopropenyl*" connotation[5] for the cationic intermediate implies.

EXPERIMENTAL[23]

2-N-*Pyrrolidylbicyclo*[3.2.1]*octan*-8-*one* (IV). The amino ketone (IV) was prepared from 1-N-pyrrolidylcyclopentene and acrolein[6] in 92% yield, b.p. 89–91° (0·08 mm) (lit.[6] b.p. 110–115° at 0·5 mm).

The *picrate* was crystallized from ethanol m.p. 186–187° (lit.[6] m.p. 180–181°).

syn-2-N-*Pyrrolidylbicyclo*[3.2.1.]*octan*-8-*ol* (V). To 13 g $LiAlH_4$ in 1300 ml anhydrous ether was

[23] M.ps are corrected and b.ps are uncorrected. IR spectra were determined with a Beckman IR-4 Recording Spectrophotometer or a Perkin-Elmer Infracord using sodium chloride optics. The UV spectrum was measured on a Cary 14 Recording Spectrophotometer. NMR determinations were carried out on a Varian Associates DP-60 Spectrometer; approximately 20% solutions in CCl_4 were employed with tetramethylsilane as the internal standard. Chemical shifts were obtained by the audio side-band technique. The gas chromatography analyses and separations were obtained by employing 8 mm O.D. glass U-columns, six ft. in length. Packing materials were 25% γ-methyl-γ-nitropimelonitrile on 35–80 mesh base-washed firebrick for hydrocarbons, 25% Silicone gum rubber on base-washed firebrick for hydrocarbons and acetates, and 25% Polyglycol E-4000, or E-9000 on base-washed firebrick for alcohols. Analyses are by Midwest Microlabs, Inc., Indianapolis, Indiana.

added with stirring a solution of 128·6 g (0·67 mole) aminoketone IV in 200 ml ether over a period of 1 hr. The mixture was then heated at reflux for 24 hr: after which 13 ml water, 39 ml 15% KOHaq. and 13 ml water were added dropwise in succession. The solution was filtered and the precipitate was washed several times with ether. The filtrate and washings were combined and dried ($MgSO_4$) and the ether was distilled to give a semi-solid (98 g). Recrystallization from acetone afforded 77·0 g (60%) of aminoalcohol[24], m.p. 120–120·8°; IR ($CHCl_3$), 3720, 3510, 1247, 1094, 1053 and 870 cm^{-1}. (Found: C, 74·02; H, 10·97; N, 6·90; Calc. for $C_{12}H_{21}NO$: C, 73·80; H, 10·84; N, 7·17%).

The *methiodide* was prepared and was recrystallized from absolute ethanol, m.p. 218·1–218·7°. (Found: C, 46·39; H, 7·26; N, 4·07; I, 37·37; Calc. for $C_{13}H_{24}NOI$: C, 46·30; H, 7·17; N, 4·15; I, 37·63%).

2-N-*Pyrrolidylbicyclo*[3.2.1]*octan*-8-*ol*-N-*oxide*. To 40·0 g (0·20 mole) aminoalcohol V in 25 ml glacial acetic acid was added dropwise with stirring, 48 ml (0·25 mole) 40% peracetic acid. The temp was maintained at 0° during the addition which required 2 hr. The reaction mixture was transferred to the refrigerator overnight. Potassium hydroxide (20% aqueous solution) was added with cooling until the mixture was alkaline. The solution was then saturated (K_2CO_3) and extracted with three-100 ml portions $CHCl_3$. The extracts were dried and concentrated *in vacuo* (40° at 50–70 mm) to give 57·4 g solid, m.p. 104–109° dec. No attempt was made at further purification.

syn-*Bicyclo*[3.2.1]*oct*-2-*en*-8-*ol* (VIa). The crude amine oxide was pyrolized in approximately nine 6 g portions. The pyrolysis apparatus consisted of a round-bottomed boiling flask fitted with a magnetic stirring bar, N_2 inlet capillary and a distillation head leading to traps cooled in Dry Ice-acetone. Decomposition set in at 185–195° at 2·5 mm and large amounts of resinous material remained in the pyrolysis flask. The contents of the traps were dissolved in ether, and the ether solution was washed with two-40 ml portions of 10% HCl. The acidic extract was back-washed with 50 ml pentane and the combined organic layer washed (sat. $NaHCO_3$aq.), and dried. Concentration gave 7·08 g of a yellow liquid. The crude material was chromatographed on Merck acid-washed alumina, and elution with 10% ether in pentane afforded 4·6 g (18%) VIa, m.p. 117–118°. IR (CCl_4) 3617, 3578, 3472,[25] 1399, 1153, and 1081 cm $^{-1}$. NMR (20% CCl_4), 1·90 δ (multiplet); 2·64 δ (singlet); 3·90δ (triplet); 5·62δ (quartet). (Found: C, 77·22; H, 9·74; Calc. for $C_8H_{12}O$: C, 77·37; H, 9·74%).

The p-*nitrobenzoate* was prepared and was recrystallized from pentane, m.p. 121·5–122·5°. (Found: C, 65·68; H, 5·46; N, 5·06; Calc. for $C_{15}H_{15}NO_4$: C, 65·92; H, 5·53; N, 5·13%).

endo-*Bicyclo*[3.2.1]*octan*-8-*ol* (Xa). The unsaturated alcohol VIa (150 mg, 1·2 mmoles) was hydrogenated with 5% Pd-C catalyst in 5 ml methanol. Hydrogen (1 mole) was taken up in 15 min. The mixture was filtered and the solvent evaporated to give 0·145 g (95%) of saturated alcohol Xa, m.p. 198–199°(lit.[7a] m.p. 199–200·5°). A mixture m.p. with an authentic sample[7] showed no depression.

The p-*toluenesulfonate* was crystallized from an ether–pentane mixture, m.p. 73–75° (lit.[9a] m.p. 75·7–76·1°).

syn-*Bicyclo*[3.2.1]*oct*-2-*en*-8-*yl* p-*toluenesulfonate* (II). To a solution of 1·8 g (0·015 mole) of *syn*-bicyclo[3.2.1]oct-2-en-8-ol in 8 ml. of pyridine was added dropwise at 0° with stirring, 4·0 g (0·021 mole) of *p*-toluenesulfonyl chloride in 8 ml pyridine. After 2 hr at 0°, the mixture was stirred for an additional 12 hr at room temp, and then was poured into ice-water. The precipitate was collected and was washed with water. Recrystallization from an ether–hexane mixture gave 3·8 g (94%) *p*-toluenesulfonate II, m.p. 90·5–91·5°. IR (CCl_4): 1370, 1188, 1178, 1025, 980, 860 and 846 cm^{-1}. (Found: C, 64·59; H, 6·29; S, 11·35; Calc. for $C_{15}H_{18}SO_3$: C, 64·72; H, 6·52; S, 11·52%).

2-N-*Morpholinobicyclo*[3.2.1]*octan*-8-*one* was prepared in 51% yield from 1-N-morpholinocyclopentene and acrolein as described by Woodward and Foote,[9] b.p. 123·5–124·5 (0·2 mm) (lit.[9] b.p. 127–140° at 0·2 mm), n_D^{25} 1·5173 (lit.[9] n_D^{25} 1·5176).

2-N-*Morpholinobicyclo*[3.2.1]*octan*-8-*one ethylene ketal* (VIII). From 126 g (0·61 mole) N-morpholinoketone, 126 g (0·66 mole) *p*-toluenesulfonic acid monohydrate and 378 g (6·1 moles) ethylene glycol,[9] there was obtained 111 g (72%) of ketal, b.p. 125–127° (0·4 mm) (lit.[9] b.p. 114–122° at 0·25 mm), n_D^{25} 1·5128 (lit.[9] n_D^{25} 1·5130).

Bicyclo[3.2.1]*oct*-2-*en*-8-*one* (VII). The N-morpholino ketal VIII (111·0 g, 0·44 mole) was oxidized

[24] This product was initially prepared by Donald O. Rickter in the course of a National Science Foundation High School Teachers' Program in the summer of 1959.

[25] O—H stretching frequencies were determined on a Perkin-Elmer 237 Grating Infracord Spectrophotometer using 0·07 M solutions in CCl_4 in 3 mm cells.

in methanol with 30% H_2O_2aq. Platinum black was added to decompose the excess peroxide. After filtration, the solvents were evaporated at 65° (15 mm).

The crude N-oxide was pyrolized without purification in roughly 4 equal portions at 85–135° and 1 mm, in the apparatus described above. The contents of both traps were dissolved in 100 ml ether, and this solution was shaken vigorously with two-100 ml portions of *warm* 6 N HCl. The acidic solution was back extracted with 75 ml ether and 75 ml pentane. The combined organic layer was then washed (30 ml 10% HCl aq. and $NaHCO_3$ aq.) and dried. Evaporation of the solvent, followed by distillation of the product, b.p. 69–70° (5 mm) (lit.[9] b.p. 130° (pot) at 25 mm) afforded 10·8 g (20%) of bicyclo[3.2.1]oct-2-en-8-one (VII), n_D^{25} 1·4951. IR (CCl_4) 1758, 1634, 1189, 1115, and 1032 cm^{-1}, λ_{max}^{EtOH} 293 (ϵ 42). (Found: C, 78·16; H, 8·35; Calc. for $C_8H_{10}O$: C, 78·65; H, 8·25%).

The 2,4-*dinitrophenylhydrazone* crystallized from ethanol as orange needles, m.p. 175–176° (lit.[9] m.p. 176·4–177·2°).

Reductions of bicyclo[3.2.1]*oct-2-en-8-one* (VII)

Analyses of the product mixtures were performed by g.c. on a polyglycol E-9000 column at 146°. The *syn*-isomer had a retention time of 14 min and the *anti*, 21·2 min.

A. *Sodium borohydride in methanol.* A solution of 3·00 g (0·024 mole) of ketone VII in 75 ml methanol was cooled to 10°, and 0·95 g (0·025 mole) $NaBH_4$ was added. The mixture was stirred at 15–20° for 3 hr. Hydrolysis was effected by the addition of water and 15% KOH aq. After dilution with 200 ml water and continuous extraction with pentane for 18 hr, there was obtained 3·01 g (98%) of solid alcohol mixture, consisting of 91% VI and 9% IXa.

B. *Sodium borohydride in pyridine.* A mixture of 0·100 g (0·0008 mole) of ketone VII and 0·050 g (0·0013 mole) $NaBH_4$ was heated at 100° in 7 ml dry pyridine for 20 hr. Workup in the usual manner gave 0·080 g (79%) alcohol mixture, consisting of 75% VIa and 25% IXa.

C. *Sodium in moist ether.* To a solution of 0·050 g (0·0004 mole) of ketone VII in 2 ml ether over 2 ml saturated K_2CO_3 aq. was added over 3 hr 0·150 g (0·0065 g atom) of Na metal in small pieces. When all the Na had reacted, 10 ml water was added. The ether layer was separated and was washed with water. After drying and distillation of the solvent, 0·042 g (83%) alcohol mixture was obtained which analyzed for 70% VIa and 30% IXa.

Equilibration of the bicyclo[3.2.1]*oct-2-en-8-ols.* A mixture of 0·62 g (0·005 mole) of *syn*-alcohol (VIa), 1·23 g (0·005 mole) aluminum t-butoxide, and 0·009 g fluorenone (0·00005 mole) in 10 ml benzene was sealed in a tube and heated at 120–125° for 36 hr. After cooling, the contents of the tube were washed with 10% HCl aq. until neutral, and then with saturated $NaHCO_3$ aq. The benzene solution was dried and chromatographed on 18 g alumina (Merck acid-washed). The alcohol fraction was eluted with 20% ether in pentane. Careful distillation of the solvent gave 0·502 g (84%) white needles, m.p. 92–95°. The alcohol mixture consisted of 20% VIa and 80% IXa. The same composition was reached by equilibration of a mixture rich in *anti*-isomer IXa.

anti-*Bicyclo*[3.2.1]*oct-2-en-8-ol* (IXa). The equilibrium mixture of alcohols (2·6 g) was chromatographed on 260 g alumina (Merck-acid washed), with 5% ether in pentane as eluant. The alcohols began to elute after thirty-two 200 ml fractions. Six initial fractions yielded 0·350 g of predominantly *syn*-isomer; eighteen middle fractions yielded 1·470 g of 15% *syn*-, 85% *anti*-isomer; and nine final fractions afforded 0·347 g of 2% *syn*- 98% *anti*-isomer. Pure IXa was obtained by gas chromatography, m.p. 110–111°. IR (CCl_4): 3628, 3489,[25] 1179, 1072, 1059, 1013 and 962 cm^{-1}. NMR (20% CCl_4): 2·16δ (multiplet); 3·24δ (multiplet); 4·13δ (singlet); 5·56δ (multiplet). (Found: C, 77·65; H, 9·90; Calc. for $C_8H_{12}O$: C, 77·37; H, 9·74%).

The p-*nitrobenzoate* was recrystallized from pentane, m.p. 86·5–87·5°. (Found: C, 65·75; H, 5·63; N, 5·03; Calc. for $C_{15}H_{15}NO_4$: C, 65·92; H, 5·53; N, 5·13%).

anti-*Bicyclo*[3.2.1]*oct-2-en-8-yl* p-*toluenesulfonate* (III). By a procedure similar to that employed with the *syn*-isomer, 0·347 g (0·003 mole) IXa was reacted with *p*-toluenesulfonyl chloride to give a product, which after three recrystallizations from pentane afforded 0·550 (71%) of tosylate III, m.p. 58·8–59·7°. IR (CCl_4): 1370, 1188, 1178, 983, 946, 877, and 848 cm^{-1}. (Found: C, 64·76; H, 6·50; S, 11·29; Calc. for $C_{15}H_{18}SO_3$: C, 64·72; H, 6·52; S, 11·52%).

Acetolysis of syn-*bicyclo*[3.2.1]*oct-2-en-8-yl* p-*toluenesulfonate* (II). A sample (3·30 g, 0·012 mole) of *p*-toluenesulfonate II was dissolved in 30 ml glacial acetic acid which was 0·5 M in sodium acetate, and 20 ml of additional acetic acid was added. The solution was sealed in a tube and heated at 180° for 15 hr (calc to be roughly ten half-lives). After cooling, the contents of the tube were poured into

250 ml water and 100 ml pentane. The aqueous solution was extracted with two 100-ml portions pentane; and the pentane extracts were combined and washed (sat. $NaHCO_3$ aq.) until the washings were basic. After drying, the solvent was distilled to give an oil which was analyzed by g.c. (Silicone oil column, 135°). The composition was determined as hydrocarbon (32%) and acetates (68%). Distillation of the oil afforded 0·090 g of a hydrocarbon fraction b.p. 61–63° (145 mm) and 1·20 g of acetate mixture, b.p. 90–100° (20 mm).

Gas chromatography on γ-nitro-γ-methylpimelonitrile column at 80° showed the hydrocarbon fraction to consist of three components: one (ret. time = 10·5 min) comprised 94% of the mixture; the other two (ret. times = 11·7 and 19 min) amounted to only 2·2% and 3·8% and were not further investigated. The major component was inseparable on g.c. from an authentic sample of bicyclo[4.2.0]-octa-2,4-diene,[11] and the IR spectra were identical.

The *maleic anhydride adduct* was crystallized from pentane, m.p. 139·5–141·5° (lit.[11] m.p. 140–143·5°).

The acetates (1·20 g, 0·006 mole) were dissolved in 40 ml methanol containing 4·5 g (0·080 mole) KOH and the solution was stirred at room temp for 12 hr. Water was added and the suspension was continuously extracted with pentane. After drying and distillation of the solvent, there was recovered 0·842 (99%) of the alcohol mixture which was analyzed by g.c. (Polyglycol E-4000 at 146°). The percentages are based on the total acetolysis product.

(1) exo-*Bicyclo*[3.3.0]*oct*-7-*en*-2-*ol* (XIIIa). The major component (30%) of the product (ret. time = 18·5 min) was identified by its IR spectrum and retention time which were identical with those of *exo*-bicyclo-[3,3.0]oct-7-en-2-ol procuced in the acetolysis of *anti*-bicyclo[3.2.1]oct-2-en-8-yl *p*-toluenesulfonate (III) (described later).

(2) anti-*Bicyclo*[3.2.1]*oct*-2-*en*-8-*ol* (IXa) was the component of next largest amount (21%), and was identified by its IR spectrum and retention time (20·2 min) on g.c.

(3) syn-*Bicyclo*[3.2.1]*oct*-2-*en*-8-*ol* (VIa) was also present (14%) and was identified by its IR spectrum and retention time (10·3 min).

Also present were two minor components A and B (2% and 1%, respectively) with retention times of 14·4 and 16·5 min, respectively. Since they were poorly resolved from VIa and XIIIa, no further investigation was attempted.

Acetolysis of anti-*bicyclo*[3.2.1]*oct*-2-*en*-8-*yl* p-*toluenesulfonate* (III). A 2·20 g (0·008 mole) sample of the *anti p*-toluenesulfonate III was dissolved in 30 ml glacial acetic acid which was 0·5 M in sodium acetate, and 20 ml of acetic acid was added. The solution was heated at 100° for 3 hr (about ten half-lives). The mixture was worked up in the same manner described for the *syn*-isomer and g.c. analysis indicated 23% hydrocarbon and 77% acetates. Distillation of the crude products yielded 0·169 g of hydrocarbon fraction, b.p. 103–105° (pot) (30 mm) and 0·780 g of acetate mixture, b.p. 135–145° (pot) (10 mm).

Analysis by g.c. (γ-nitro-γ-methylpimelonitrile column, 80°) showed the volatile fraction to consist of a single hydrocarbon. The diene was identified by its IR spectrum and retention time (9·9 min) which were identical with the bicyclo[4.2.0]octa-2,4-diene produced in the acetolysis of the *syn-p*-toluenesulfonate.

The acetates (0·780 g, 0·004 mole) were saponified, and the alcohol mixture was isolated by continuous extraction with pentane to give 0·530 g (99%). Analysis (Polyglycol E-9000, 150°) gave the following percentages (based on total acetolysis product).

(1) anti-*Bicyclo*[3.2.1]*oct*-2-*en*-8-*ol* (IXa) was found to comprise 23% of the mixture and was identified by its IR spectrum and retention time.

(2) exo-*Bicyclo*[3.3.0]*oct*-7-*en*-2-*ol* was detected in 48% yield (ret. time = 20·1 min) and was isolated only by collection from the g.c. column. A sample obtained in this manner was homogeneous on four g.c. columns (Polyglycols E-4000 and E-9000, γ-nitro-γ-methylpimelonitrile, and TCEP) and boiled at 71–72° (3 mm), n_D^{25} 1·5019. IR (cap): 3311, 1335, 1085, 1062, 1007, 968 and 708 cm^{-1}. NMR (20% CCl_4): 2·11δ (multiplet): 3·95δ (singlet); 5·75δ (singlet).

The p-*nitrobenzoate* was recrystallized from pentane, m.p. 67·5–68·5°. (Found: C, 65·63; H, 5·39; N, 5·20. Calc. for $C_{16}H_{15}NO_4$: C, 65·92; H, 5·53; N, 5·13%).

There were also detected three minor components, A, B and C (3%, 2% and 1%) of retention times 12·6, 15·6 and 17·9 min, respectively. The products A and B were inseparable on g.c. from the minor components produced by acetolysis of the *syn-p*-toluenesulfonate (II). Since the production of C may be inhibited by displacement of air over the acetolysis by nitrogen, it is assumed that this product is a ketone resulting from air oxidation of a carbonium ion.

A synthetic mixture of *syn*-bicyclo[3.2.1]oct-2-en-8-ol (VIa) and the acetolysis alcohol mixture showed a sixth peak (ret. time = 14·1 min) indicating that only a trace, at best, of this isomer was formed.

Structure proof of exo-*bicyclo*[3.3.0]*oct-7-en-2-ol* (XIIIa).

A *Hydrogenation of the alcohols.* Two hundred milligrams (0·0017 mole) of the alcohol mixture was hydrogenated with 5% Pd-C catalyst in 5 ml methanol One mole of hydrogen was taken up in 45 min. The mixture was filtered, and the methanol was evaporated to give 0·190 g (94%) of saturated alcohol mixture which was analyzed by g.c. (polyglycol E-4000, 146°). The major component (ret. time = 17 min) was inseparable from, and had an identical IR spectrum with that of an authentic sample[18] of *exo-cis*-bicyclo[3.3.0]octan-2-ol.

B. *Manganese dioxide treatment of the alcohol mixture.* A 0·100 g (0·0008 mole) sample of the alcohol mixture and 0·420 g (0·0048 mole) "active" manganese dioxide[26] were stirred in 8 ml pentane for 12 hr. IR analysis of the product indicated a very small amount of a non-conjugated ketone (carbonyl band 1742 cm^{-1}) had been formed. Gas chromatography analysis indicated 7% of the major component XIIIa had been oxidized.

C. *Chromium trioxide oxidation of the alcohol mixture.* To a solution of 0·340 (0·0034 mole) chromium trioxide in 5 ml pyridine at 0° was added dropwise with stirring 0·32 g (0·0026 mole) of alcohol mixture. The reaction mixture was stirred at 0° for 7 hr, poured into 20 ml ice-water, and the products were extracted with two-10 ml portions of ether and with 10 ml pentane. The combined extracts were washed (10% HCl aq. and then sat. $NaHCO_3$ aq.). The product (0·284 g) showed a strong carbonyl band at 1742 cm^{-1}, in addition to the hydroxyl band at 3311 cm^{-1} in the IR spectrum. Chromatography on 3 g alumina (Merck acid-washed) column gave 0·50 g ketone eluted by a 1% ether–pentane mixture and 0·217 g alcohol fraction eluted by a 10% ether–pentane mixture. The ketone fraction, was analyzed by g.c. (polyglycol E-9000, 150°) and showed 90% of a major component (ret. time = 10 min) and two minor components of retention times 11 min (4%) and 12 min (6%). An authentic sample of bicyclo[3.2.1]-oct-2-en-8-one (VII) was inseparable from the component present in 4% quantity. The alcohol fraction on g.c. analysis indicated that 21% of the major component XIIIa (ret. time = 20·1 min) had been oxidized.

A *semicarbazone* of the ketone fraction was recrystallized from ethanol–water, m.p. 166·5–167·2°.

Bicyclo[3.2.0]*hept-2-en-6-one.* The adduct of cyclopentadiene and ketene was prepared[18] in 5·8% yield, b.p. 64–65° (15 mm) (lit.[18] b.p. 83–84° at 51 mm).

Bicyclo[3.3.0]*oct-6-en-2-one* (XX) *and bicyclo*[3.3.0]*oct-6-en-3-one.* The ring expansion of bicyclo-[3.2.0]hept-2-en-6-one was carried out by a procedure similar to that reported.[18] The resulting ketone mixture was analyzed by g.c. (polyglycol E-9000 at 150°). The major component (ret. time = 9 min) comprised 67% of the mixture and the minor component (ret. time = 10·6 min), 33% of the mixture. The minor component was separated by g.c. and identified as bicyclo[3.3.0]oct-6-en-3-one by hydrogenation to the saturated ketone. The IR spectrum was identical to that reported for bicyclo[3.3.0]-octan-3-one.[18] The major component was separated by g.c. The IR spectrum, refractive index and g.c. ret. time were different from those of ketone XIV.

The semicarbazone of bicyclo[3.3.0]oct-6-en-2-one was prepared, and melted at 175–175·5° after recrystallization from 95% ethanol A mixutre m.p. of the *semicarbazone* and the semicarbazone of ketone XIV (m.p. 166·5–167·2°) showed a slight depression, m.p. 164–168·5°.

Kinetic studies. J. T. Baker Co. reagent-grade glacial acetic acid, containing 1% by weight of added acetic anhydride, was used for the acetolysis runs, and in the preparation of the standard solutions. Standard perchloric acid (0·05 N) in glacial acetic acid was prepared and standardized against potassium acid phthalate.[27] An 0·03 N sodium acetate solution in glacial acetic acid was prepared[27] and was standardized against standard perchloric acid in glacial acetic acid.

Three drops of a 0·2% solution of crystal violet in glacial acetic acid was used as the indicator. In titrations of solutions containing sodium acetate, the end point was taken as the color change from violet to blue. In the non-buffered titrations, the end-point was compared to a red-violet blank of crystal violet in glacial acetic acid.

The constant-temp bath, controlled by an H-B Differential Temperature Controller, was filled

[26] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.* 1094 (1952).

[27] J. Fritz and G. Hammond, *Quantitative Organic Analysis* p. 265. John Wiley, New York (1957).

Table 5. Acetolysis of *syn*-bicyclo[3.2.1]oct-2-ene-8-*p*-toluenesulfonate at 179·5 ± 0·18°
Run No. 1: 0·41944 g *p*-Toluenesulfonate in 50·00 ml 0·031 N Sodium Acetate solution

t, sec	ml $HClO_4$ (0·046 N)	$[ROTs]_t \times 10^5$	$-\ln [ROTs]_t$
0	—	3·002	1·521
600	3·01	2·772	1·567
1800	2·48	2·278	1·643
3600	2·02	1·856	1·731
5400	1·57	1·446	1·840
7200	1·14	1·054	1·977
9000	1·02	0·934	2·030
10800	0·82	0·752	2·124
14400	0·52	0·480	2·318
21600	0·46	0·420	2·376
86400	0·06	0·058	3·231

t 1/2 = 5,500 sec
$k_1 = 1·26 \times 10^{-4}$ sec^{-1}

Acetolysis of *anti*-bicyclo[3.2.1]oct-2-ene-8-*p*-toluenesulfonate at 84·8 ± 0·02°
Run No. 6: 0·1108 g *p*-Toluenesulfonate in 50·00 ml 0·010 N Sodium Acetate solution

t, sec	ml $HClO_4$ (0·015 N)	$[ROTs]_t \times 10^5$	$-\ln [ROTs]_t$
0	—	7·96	2·099
360	3·20	7·64	2·117
1260	2·88	6·68	2·175
2160	2·68	6·06	2·218
2760	2·48	5·46	2·263
3360	2·42	5·28	2·277
4560	2·16	4·48	2·349
8160	1·64	2·90	2·538
15360	1·11	1·30	2·886
72660	0·70	0·04	4·398

t 1/2 = 5,875 sec
$k_1 = 1·18 \times 10^{-4}$ sec^{-1}

Run No. 9: 0·1399 g *p*-Toluenesulfonate in 50·00 ml of Glacial Acetic Acid

t, sec	ml NaOAc (0·0110N)	$[ROTs]_t \times 10^5$	$-\ln [ROTs]_t$
0	0·00	1·01	1·997
300	0·08	0·99	2·004
900	0·40	0·93	2·033
2400	0·91	0·82	2·084
3600	1·28	0·75	2·125
4800	1·58	0·69	2·161
7800	2·42	0·52	2·282
1500	3·59	0·29	2·541
100200	4·98	0·02	4·000

t 1/2 = 8,450 sec^{-1}
$k_1 = 8·41 \times 10^{-6}$ sec^{-1}
k_1(0·010 N acetate)/k_1 (no salt) = 1·34

with mineral oil. Temperatures were determined with thermometers calibrated by the National Bureau of Standards.

The acetolysis procedure was essentially that reported.[28] In runs with sodium acetate, the *p*-toluenesulfonate was weighed into a 50 ml volumetric flask and was diluted to volume with standard sodium acetate in glacial acetic acid. Aliquots (5 ml) of this solution were sealed into Pyrex 8640 tubes, which were placed in the constant temp bath. Tubes were withdrawn at intervals, and were rapidly cooled to room temp and titrated with standard perchloric acid. In runs without sodium acetate, the *p*-toluenesulfonic acid generated was titrated directly with standard sodium acetate solution. A similar procedure was followed for the ethanolyses, and liberation of *p*-toluenesulfonic acid was followed by titration with standard sodium methoxide in methanol to the brom thymol blue endpoint.

Most runs were followed to 80–90% completion. Rate constants were determined graphically by measuring the slope of plots of ln [ROTS] versus time. Thermodynamic quantities were calculated by the following equations:

$$\Delta H^{\ddagger} = [(T_1T_2)/T_2 - T_1] \log (k_2/k_1)\, 2{\cdot}303\ R$$

and

$$\Delta S^{\ddagger} = (\Delta H^{\ddagger}/T) + 2{\cdot}303\ R\ [(k/T) - \log (k/h)]$$

Final reaction rates were extrapolated to 25° by the equation:

$$\log k = \log (k_2T_1/T_2) - [\Delta H^{\ddagger}(T_2 - T_1)/2{\cdot}303\ R\ T_2T_1]$$

Typical kinetic data are given in Table 5.

Partial acetolysis of anti-*bicyclo*[3.2.1]*oct*-2-*ene*-8-*yl* p-*toluenesulfonate*. A 0·200 g (0·7 mmole) sample of the *anti p*-toluenesulfonate was dissolved in 2·5 ml glacial acetic which was 0·5 M in sodium acetate. The solution was heated at 84° for 1 hr (about 40% reaction). The mixture was worked up in the same manner described for the complete acetolyses affording 0·147 g crude mixture. The hydrocarbons and acetates were evaporated (35–40° at 0·02 mm) yielding 0·091 g of semi-solid the IR spectrum of which showed only a trace of acetate contamination and was essentially identical with the IR spectrum of the starting *p*-toluenesulfonate. The crude material moved as a single spot on a thin-layer chromatoplate (silica-gel, benzene as solvent). Recrystallization gave a solid, m.p. 53–55°. A mixture m.p. with an authentic sample of the *anti p*-toluenesulfonate was undepressed.

Acknowledgment—The generous support of the Alfred P. Sloan Foundation is gratefully recognized.

[28] S. Winstein, C. Hanson and E. Grunwald, *J. Amer. Chem. Soc.* **70**, 812 (1948).