To provide a standard for the above experiments the undeuterated ketone **1** was photolyzed and the aldehyde isolated as above: nmr (220 MHz, CCl_4) δ 4.91 (2.00 H defined), 4.54 (0.98 H), 9.67 (0.91 H).

Photolysis of Ketone 5. Ketone **5** (1.09 g) was irradiated for 3.5 hr during which time the apparatus was immersed in a circulating ice bath. The products were isolated by pouring the methanol solution into water and extracting with 1:1 ether–pentane. The extracts were dried over Na_2SO_4 and evaporated through a Vigreux column. The aldehyde corresponding to **24** was then isolated by vpc on column B: nmr (220 MHz, CD_3CN) δ 5.03 (2.00 H defined), 5.80 (0.37 H), 9.70 (0.65 H). A sample of aldehyde **24** was prepared in the same way from the undeuterated ketone (**2**): nmr (220 MHz, CD_3CN) δ 5.03 (2.00 H defined), 5.80 (0.98 H), 9.70 (0.96 H).

Acknowledgments. It is a pleasure to thank Mr. S. T. Bella for microanalyses, Miss Luz Catan for invaluable technical assistance, and Mr. Josef Nemeth for deuterium analyses. The National Science Foundation (Grant No. GB-12278), Research Corporation, and The Alfred P. Sloan Foundation generously provided funds which facilitated purchase of the 220-MHz nmr spectrometer.

Enhanced Homoallylic Participation. Bicyclo[2.2.2]octyl Systems

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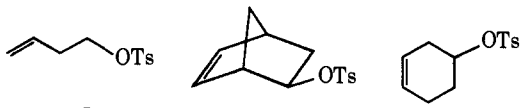
Abstract: The acetolysis of *cis-exo*-2,3-bicyclo[2.2.2]oct-5-enyl ditosylate (VI) proceeds 6850 times more rapidly than does acetolysis of its saturated analog, *cis*-2,3-bicyclo[2.2.2]octyl tosylate (VII). The corresponding monotosylate, *exo*-2-bicyclo[2.2.2]oct-5-enyl tosylate (VIII), acetolyzes only 63 times more rapidly than its saturated analog, 2-bicyclo[2.2.2]octyl tosylate (IX). The large acceleration in VI compared to VIII results from an enhanced requirement of the double bond to participate. As the first tosylate group solvolyzes, the double bond is called upon to provide greater charge dispersal because of the presence of the remaining electron-withdrawing tosylate group. This interpretation is reinforced by measurement of the solvolysis rate for *trans*-2,3-bicyclo[2.2.2]oct-5-enyl ditosylate (X). There is no evidence in any of these systems for loss of two tosylate groups to form a dicarbonium ion.

Homoallylic assistance in the solvolysis of arenesulfonate esters does not give rise to extremely large rate accelerations. Thus allylcarbinyl tosylate (I) formolyzes only 3.7 times more rapidly than *n*-butyl



I II III

tosylate,[2] *exo*-2-norborn-5-enyl tosylate (II) acetolyzes 3.37 times more slowly than *exo*-2-norbornyl tosylate,[3] and 3-cyclohexenyl tosylate (III) acetolyzes 1.26 times more slowly than cyclohexyl tosylate.[4] In the tabulation of Hanack and Schneider,[5] the largest value for k_{unsat}/k_{sat} in acetolysis is 350. The double bond in this system, (γ,γ-dimethylallyl)carbinyl tosylate, is trisubstituted. Although ions of varying symmetry have been suggested to describe double bond participation in these solvolyses,[5] we shall for simplicity utilize the term "homoallylic participation" to describe such interactions.[6] These relatively small rate accelerations, characteristic of systems with the double bond unsymmetrically disposed with respect to the leaving group, contrast with the factor of about 10^{11} in the solvolysis of *anti*-7-norbornenyl tosylate (IV),[7] in which the

IV V

symmetrical placement of the double bond permits formation of a bishomocyclopropenium ion.[7] The present studies concern only unsymmetrical (homoallylic) systems.

Recently, we reported that *cis-exo*-2,3-norborn-5-enyl ditosylate (V) acetolyzes 500 times more rapidly than its saturated analog,[3,8] in marked contrast with the unsaturated monotosylate II and other systems with disubstituted double bonds unsymmetrically positioned with respect to the leaving group.[3] We attributed this remarkable acceleration to an enhanced requirement of the double bond to participate.[8] More effective positive charge dispersal in the transition state can diminish the rate-retarding influence of the remaining electronegative substituent (the second tosylate group). The saturated analog of V apparently has little or no

(1) (a) Alfred P. Sloan Foundation Fellow, 1968–1970. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2970-A4,5), and by the National Science Foundation (Grant No. GP-9257); (b) National Science Foundation Predoctoral Fellow, 1966–1970.

(2) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964).

(3) J. B. Lambert and A. G. Holcomb, *ibid.*, **91**, 1572 (1969).

(4) J. B. Lambert, H. G. Smith, Jr., and A. P. Jovanovich, *J. Org. Chem.*, **35**, 3619 (1970).

(5) M. Hanack and H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967).

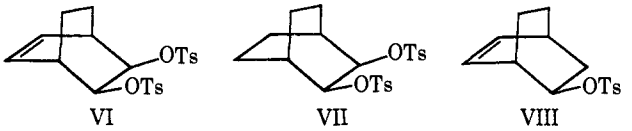
(6) S. Winstein and M. Simonetta, *J. Amer. Chem. Soc.*, **76**, 18 (1954).

(7) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, 77, 4183 (1955).

(8) J. B. Lambert and A. G. Holcomb, *ibid.*, **93**, 2994 (1971).

mechanism for charge delocalization that can be enhanced when required, by introduction of the second tosylate group.

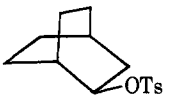
To explore the generality of this phenomenon, we chose to study the bicyclo[2.2.2]octyl system.[9] The molecular framework is somewhat less rigid than that of the norbornyl system, so improved participation might be expected because of a slightly more favorable arrangement of the double bond and the leaving group. We report herein the acetolytic behavior of *cis-exo*-2,3-bicyclo[2.2.2]oct-5-enyl ditosylate (VI) and its congeners VII–X. From the rate comparisons in this



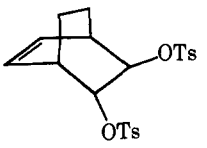
VI

VII

VIII



IX

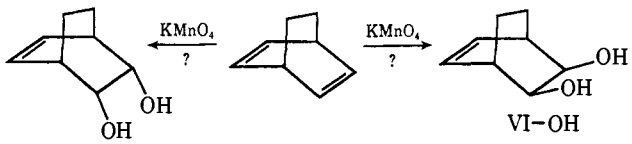


X

series, we find that the unsaturated ditosylate VI exhibits an extraordinarily enhanced homoallylic participation.

Syntheses and Kinetic Results

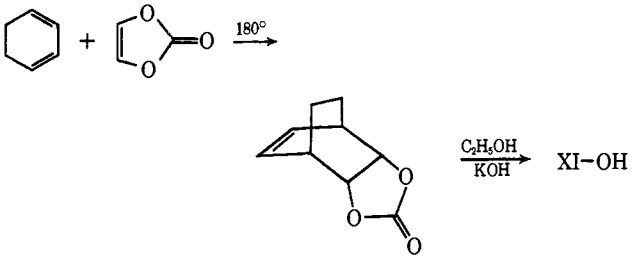
The monotosylates VIII and IX were prepared according to literature procedures.[9] The saturated *cis*-ditosylate VII was obtained by permanganate oxidation of bicyclo[2.2.2]octene to the diol[10] and conversion to the diester. Preparation of the unsaturated *cis-exo*-ditosylate VI was central to the study. Since permanganate oxidation of dienes had been used in our previous studies[3,8] to prepare unsaturated diols, we undertook the synthesis of bicyclo[2.2.2]oct-2,5-diene by the nine-step procedure of Grob, *et al.*[11] Hydroxylation of this diene produced in low yield a single diol that gave *cis*-bicyclo[2.2.2]octanol on hydrogenation. This unsaturated diol, however, could be either the cis-exo VI-OH or the cis-endo XI-OH isomer. In the bicyclo[2.2.1]heptyl series,



XI-OH VI-OH

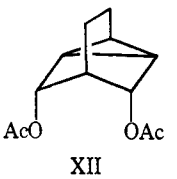
this hydroxylation proceeded entirely to the exo isomer.[3,8,12]

An authentic sample of the cis-endo isomer XI-OH may be prepared by the Diels–Alder reaction of 1,3-cyclohexadiene and vinylene carbonate[13] followed by hydrolysis of the adduct. This material proved to be identical with the unsaturated diol obtained by hydroxylation of bicyclo[2.2.2]octadiene. The latter reaction must therefore give the opposite stereochemical result (endo) from the [2.2.1] series (exo). To produce the cis-exo isomer, the endo material from either source was treated with sodium ethoxide in ethanol (see the Experimental Section).[14] Column chromatography gave a clean separation of the *exo*-diol (VI-OH, 20%), the starting *endo*-diol (XI-OH, 60%), and the *trans*-diol (X-OH, 20%). The starting material could be recycled, so sufficient amounts of the *cis-exo*- and the *trans*-diols were obtained for conversion to the sulfonate esters.

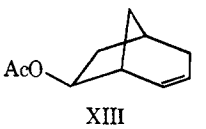


The alcohols and diols were converted to the corresponding tosylates by the method of Tipson.[15] Solvolyses were carried out in acetic acid containing potassium acetate. Rate constants were obtained in the fashion described previously[8] and are listed, together with activation parameters, in Table I. Kinetic behavior was strictly first order in all but two cases. The saturated monotosylate IX undergoes an internal-return reaction with rearrangement to a bicyclo[3.2.1]-octyl tosylate,[9] but the initial rate can be obtained quite readily. The saturated ditosylate VII exhibits a decrease in the rate with time in the same manner as its norbornyl analog.[8] This behavior is presumably due to formation of a more slowly reacting acetoxy tosylate intermediate, but no effort was made to isolate it.[8] The initial rates for VII are listed in Table I. The various rates will be compared in the Discussion.

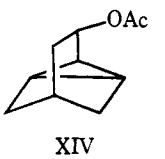
Product analysis was relatively straightforward. Products of the monotosylates have been discussed elsewhere.[9] Both unsaturated ditosylates VI and X produced better than 85% of a single crystalline material that was assigned the structure XII on the basis of the



XII



XIII



XIV

elemental analysis, the nmr spectrum (no alkenic protons; six equivalent acetate protons; only one type of C*H*OAc), and the expectation of all-exo stereochemistry (*vide infra*).[9a] The saturated ditosylate VII gave an elimination product in over 90% yield. The nmr spectrum was identical with that reported for

(9) Previous studies of monoarenesulfonate esters in this series: (a) N. A. LeBel and J. E. Huber, *J. Amer. Chem. Soc.*, **85**, 3193 (1963); (b) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961); (c) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2856, 2862 (1968); (d) R. R. Fraser and S. O'Farrell, *Tetrahedron Lett.*, 1143 (1962).

(10) S. Winstein and M. Shatavsky, *J. Amer. Chem. Soc.*, **78**, 592 (1956).

(11) C. A. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

(12) Y. F. Shealy and J. D. Clayton, *J. Amer. Chem. Soc.*, **91**, 3075 (1969).

(13) H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954); M. S. Newman and R. W. Adder, *ibid.*, 77, 3789 (1955).

(14) S. J. Angyal and R. J. Young, *ibid.*, **81**, 5467 (1959).

(15) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

Table I. Rate Constants and Activation Parameters for Buffered Acetolysis of Bicyclo[2.2.2]octyl Derivatives

Compd	Temp, °C	k, sec^{-1}	E_a, kcal/mol	Log A	$\Delta H^{\pm}$(50°), kcal/mol	$\Delta S^{\pm}$(50°), eu
VI	50.0	2.47×10^{-6}	27.0	12.6	26.3	−3
	75.0	4.96×10^{-6}				
	89.6	2.46×10^{-4}				
VII	50.0	3.6×10^{-10} [a]	30.7	11.3	30.0	−9
	124.4	2.73×10^{-6} [b]				
	143.6	1.52×10^{-6} [b]				
	159.5	6.42×10^{-6} [b]				
VIII	50.0	5.43×10^{-3}				
IX	50.0	8.6×10^{-6} [b]				
X	50.0	1.87×10^{-6}	24.2	11.6	23.5	−8
	75.0	2.77×10^{-4}				

[a] Extrapolated from the Arrhenius parameters. [b] Initial rate constant.

Table II. Relative Solvolysis Rates for Unsaturated Ditosylates and Related Systems

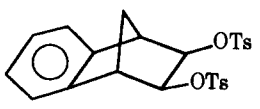
	Temp, °C				
	A[a] 50	B[b] 75	C[c] 75	D[d] 160	E[e] 90
Unsaturated *cis-exo*-ditosylate[f]	1.00[g]	1.00[g]	1.00[g]	1.00[g]	1.00[g]
Saturated *cis-exo*-ditosylate[f]	1.46×10^{-4}	1.98×10^{-3}	5.11×10^{-2} [h]	1.06	1.72×10^{1}
Unsaturated *exo*-monotosylate[f]	2.20×10^{3}	2.03×10^{2}	3.00×10^{3}	2.40×10^{3}	6.72×10^{2}
Saturated *exo*-monotosylate[f]	3.48×10^{1}	6.85×10^{2}	1.77×10^{4} [h]	3.04×10^{3}	2.93×10^{4}
Unsaturated *trans*-ditosylate	7.57	1.08		2.55	1.12×10^{1}
k_{unsat}/k_{sat}, ditosylates	6850	506	20[h]	0.94	0.058
k_{unsat}/k_{sat}, monotosylates	63	0.30	0.17[h]	0.79	0.023
Enhancement of homoallylic participation [i]	109	1700	118[h]	1.20	2.52

[a] Bicyclo[2.2.2]octyl systems; this work. [b] Norbornyl systems; ref 3 and 8. [c] Benzonorbornyl systems; ref 18. [d] Cyclohexyl systems; ref 4. [e] Cyclooctyl systems with brosylate leaving groups; ref 17. [f] In several of the compounds, the term "exo" has no significance. [g] The relative rates are calculated separately for each vertical series. [h] The saturated molecules from series B were used for comparison in this series. [i] This figure is obtained by dividing the ratio k_{unsat}/k_{sat} for the ditosylates by that for the monotosylates.

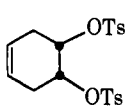
XIII,[16] but other structures may be possible. Minor products of these solvolyses were not examined.

Discussion

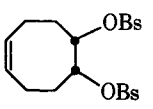
It is useful to compare the relative rates found for the bicyclo[2.2.2]octyl series A with those measured previously for the norbornyl compounds B.[3,8] Both sets of figures are listed in Table II, together with those for three other series C, D, and E to be discussed later.



C



D



E

In contrast to the norbornyl series, the double bond in the monotosylate VIII conveys a significant rate acceleration (VIII/VII = 63, *cf.* 0.30 in II). This homoallylic acceleration is one of the largest measured heretofore for a disubstituted unsaturated monotosylate.[5] It clearly indicates a strong anchimeric assistance, as LeBel and Huber[9a] pointed out some time ago.

The k_{unsat}/k_{sat} ratio for the bicyclo[2.2.2]octyl ditosylates (VI/VII) is over two orders of magnitude larger than that for the monotosylates. At 6850, this acceleration must be close to the largest measured for an allylcarbinyl system with the double bond unsymmetrically placed with respect to the leaving group. This enhanced homoallylic participation is apparently brought about by the electron-withdrawing group still present after loss of the first tosylate group. Through greater charge dispersal from the vicinity of the remaining tosylate group, the double bond can offer added stabilization not available to the saturated system VII. This additional acceleration (6850/63 = 110) is somewhat less than that in the norbornyl series (506 × 3.37 = 1700). In the latter case, the double bond offers little participation in the monotosylate II, so a greater effect is required by introduction of the second group in V. In the bicyclooctyl series, substantial assistance already present in VIII means that less additional participation is necessary when the second group is present.

Table II also contains the relative rates for other unsaturated ditosylates and dibrosylates.[17,18] Participation by a benzo group (series C) is somewhat less

(16) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 5594 (1969). This product could arise from XIV by thermal means; XIV in turn requires a hydride shift for formation. The products of the saturated ditosylate were not further investigated.

(17) W. D. Closson, J. L. Jernow, and D. Gray, *Tetrahedron Lett.*, 1141 (1970).

(18) H. Tanida and T. Tsushima, *ibid.*, 3647 (1969).

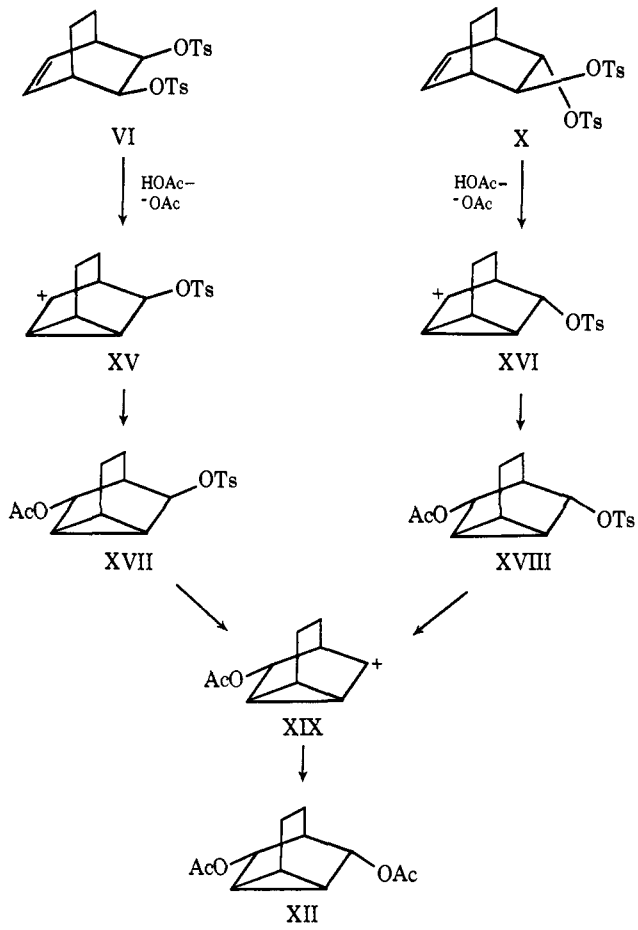
than that by a double bond (series B) in the norbornyl systems. Thus, in the benzo series, k_{unsat}/k_{sat} is only 0.17 for the monotosylates and 20 for the ditosylates, compared to 0.30 and 506, respectively, in the norbornyl compounds B. The enhancement of homoallylic participation (20/0.17 = 118) is also smaller, so the benzo group must be less effective than the double bond in providing the increased anchimeric assistance needed when a second tosylate group is present. Interestingly, the two monocyclic systems D and E appear to offer little or no enhancement of homoallylic participation in the presence of a second tosylate group. In these cyclohexyl and cyclooctyl systems, k_{unsat}/k_{sat} is almost the same in the monotosylate and ditosylate compounds (D, 0.79 and 0.94; E, 0.023 and 0.058). Anchimeric assistance by the double bond must be so unfavorable or even entirely absent that introduction of the second tosylate group cannot be compensated for by enhanced homoallylic participation. This low activity in series D and E arises from a poor stereoelectronic arrangement of the double bond and the leaving group. Enhanced homoallylic participation is only to be expected when the double bond is satisfactorily positioned for participation, as it is in the bicyclic systems A–C.

The low reactivity and the product stereochemistry in series D has been interpreted[4] in terms of the predominance of solvent participation (k_S) over any form of anchimeric assistance (k_Δ). Series D and probably E as well therefore have the least amount of charge development at carbon in the transition state. For this reason, addition of a second tosylate group has a relatively small effect of about the same magnitude for both the unsaturated and the saturated systems. Thus, the ratio k_{mono}/k_{di} is 2400 for the unsaturated cyclohexyl compounds and 2900 for the saturated compounds.[4] In the saturated norbornyl and bicyclooctyl systems, this ratio is 3.4×10^5 and 2.4×10^5, respectively. This vastly increased ratio must be due to a considerably greater charge build-up in the transition state, which is, therefore, more senstive to the presence of the second tosylate group. In the unsaturated norbornyl and bicyclooctyl systems, the k_Δ term is undoubtedly dominant because of the large k_{unsat}/k_{sat} ratios and the extensive rearrangement. The reduced values of the ratio k_{mono}/k_{di} (B, 203; A, 2190), with respect to the saturated systems, therefore quantitatively reflect the homoallylic removal of the charge from the vicinity of the remaining tosylate group, as described above.

It should be noted that the unsaturated *trans*-ditosylate X in the bicyclooctyl series solvolyzes 7.6 times more rapidly than the cis isomer VI. Although the data are not available for the saturated trans compound, it is safe to conclude that there is an extremely large degree of homoallylic participation in X. In X only one group is properly positioned (exo) for assistance from the double bond, so a double ionization of both tosylate groups to a dicarbonium ion is impossible.[8] The more rapid rate for the trans compound than for the cis-exo isomer VI precludes a dicarbonium ion pathway for the latter molecule as well.

The mechanism for the production of XII from the acetolyses of both VI and X is given in Scheme I. The first step in both cases is loss of a single *exo*-tosylate group to form the ions XV and XVI, in which the charge, though delocalized, is probably concentrated on the indicated carbon atom. Exo attack, *i.e.*, from the side of the 1-bridge rather than the 2-bridge, is preferred in ions of this sort,[9,16] so the indicated tricyclic acetoxy tosylate intermediates XVII and XVIII are formed. Although the *endo*-tosylate group is not properly situated for assistance from the double bond in X, the same group in XVIII is approximately as well situated for cyclopropyl participation as that in XVII. The intermediates probably converge to the ion XIX, and thence to the diacetate XII by exo attack.

Scheme I



Experimental Section

All melting points and boiling points are uncorrected. Melting points were determined in a Thiele-tube apparatus. Infrared spectra were recorded on a Beckman IR-5 spectrophotometer. Proton magnetic resonance spectra were obtained on Varian Associates A-60 and T-60 spectrometers. Elemental analyses were performed by Miss Hildegard Beck of Northwestern University and by Micro-Tech Laboratories, Inc., of Skokie, Ill. Analytical vapor phase chromatograms were obtained from an F & M Scientific Model 700 chromatograph or a Varian Aerograph Series 1520B chromatograph. Preparative work was done with the F & M instrument. Titrations were performed with a Metrohm Dosimat E415 piston buret (Brinkmann Instruments).

Kinetic Studies. Rate constants were determined by standard titrimetric procedures. The methods used have been presented in detail elsewhere.[8]

Tosylates were prepared by the method of Tipson,[15] from the alcohols and diols described below. A more detailed description of the procedures has been given elsewhere.[8]

cis-**2,3-Bicyclo[2.2.2]octanediol (VII-OH)**[19] was prepared by the reaction of bicyclo[2.2.2]oct-5-ene and potassium permanganate according to the method of Winstein and Shatavsky.[10]

cis-**2,3-Bicyclo[2.2.2]octyl ditosylate (VII)** was prepared from the saturated diol in 30% yield:[15] mp 148.5–149.9°; pmr ($CDCl_3$) δ 163 (complex absorption, 10 H, methyne and methylene), 2.43 (s, 6 H, tosyl methyl), 4.67 (broad s, 2 H, -C*H*O-), 7.56 (ABq, 8 H, aryl); ir ($CDCl_3$, cm^{-1}) 2941 (m), 2874 (w), 1603 (m), 1456 (m), 1368 (s), 1337 (s), 1190 (s), 1176 (s), 1100 (s), 1041 (s), 1011 (s), 989 (s). *Anal.* Calcd for $C_{22}H_{26}S_2O_6$: C, 58.64; H, 5.82. Found: C, 58.63; H, 5.89.

cis-endo-**2,3-Bicyclo[2.2.2]oct-5-enediol (XI-OH).** A solution of 5 g of vinylene carbonate and 5 g of 1,3-cyclohexadiene in 20 ml of benzene was sealed in a Pyrex tube and heated at 180° for 12 hr. The tube was cooled and opened, and the volatile contents were removed under reduced pressure to give 8 g of pastelike residue. Recrystallization (benzene) gave 3.7 g of white crystals (46%): mp 143–144°; pmr ($CDCl_3$) δ 1.70 (m, 4 H, methylene), 3.02 (broad s, 2 H, methyne), 4.72 (s, 2 H, -C*H*O-), 6.22 (t, 2 H, vinyl). *Anal.* Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.23; H, 5.95.

The carbonate was converted to the *endo*-diol by hydrolysis in basic aqueous ethanol. After recrystallization the yield was 85%: mp 205–206°; pmr ($CDCl_3$) δ 1.39 (m, 4 H, methylene), 2.78 (broad s, 2 H, methyne), 3.09 (s, 2 H, hydroxyl), 3.55 (broad s, 2 H, -C*H*O-), 6.29 (m, 2 H, vinyl); ir ($CDCl_3$, cm^{-1}) 3367 (s), 2933 (m), 1403 (w), 1174 (m), 1062 (s). *Anal.* Calcd for $C_8H_{10}O_2$: C, 68.53; H, 8.85. Found: C, 68.54; H, 8.63.

Equilibration of the Diol XI-OH. A solution of XI-OH (1.6 g) in 30 ml of absolute ethanol was treated with 1.5 g of metallic sodium. After evolution of gas had ceased, the solution was washed into a large Pyrex tube with 10 ml of alcohol. The tube was sealed and heated at 180° for 3 or 4 days. The tube was then cooled, opened, and diluted with water. The ethanol was removed under reduced pressure, the aqueous residue was salted and extracted several times with ether, and the extract was dried ($MgSO_4$). After drying, filtration, and solvent removal, 1.5 g of residue was recovered.

Fractionation of the Equilibration Mixture. A column of silica gel (150 g) was packed as a slurry with 10% THF–hexane. A solution of equilibrated diols (3.6 g) obtained from XI-OH was added to the top of the column and eluted. The first 1.25 l. of eluent contained only traces of oil. The next 1.25 l. contained 0.75 g of a pure component A. The next 500 ml gave a mixture of A and XI-OH. At this point, the elution solvent was changed to 30% THF–hexane. The next 2.5 l. contained 2.1 g of crude XI-OH plus traces of a third component C. At this point, elution with pure ether began, and the next 2 l. contained pure C (0.8 g).

Characterization of Component A (VI-OH). Crude A was recrystallized (hexane) to give 0.6 g of reasonably pure material. Sublimation (90° (1 mm)) gave 0.55 g (20%) of a material that was characterized as the diol VI-OH: mp 213–215°; pmr ($CDCl_3$) δ 1.00 (half of AA'BB'q, 2 H, methylene), 1.87 (other half of AA'-BB'q, 2 H, methylene), 2.58 (s, 2 H, hydroxyl), 2.98 (s 2 H, methyne), 3.56 (s, 2 H, *endo*-C*H*O-), 6.16 (q, 2 H, vinyl); ir ($CDCl_3$, cm^{-1}) 3636 (w), 3424 (m), 3058 (w), 2950 (s), 1471 (w), 1395 (m), 1374 (w), 1264 (w), 1152 (m), 1094 (m), 1063 (s), 1004 (s), 992 (m). *Anal.* Calcd for $C_8H_{12}O_2$: C, 86.54; H, 8.63. Found: C, 68.87; H, 8.81. Hydrogenation of either pure A or XI-OH gave *cis*-2,3-bicyclo[2.2.2]octanediol.

Characterization of Component C (X-OH). Crude C was recrystallized from ether to give 0.7 g of diol. Sublimation gave 0.6 (20%) of pure material, which was characterized as the *trans*-diol X-OH: mp 237–240°; pmr ($CDCl_3$) δ 1.41 (broad m, 4 H, methylene), 2.58 (broad s, 4 H, methyne and hydroxyl), 3.48 (broad s, 2 H, -C*H*O-), 6.25 (m, 2 H, vinyl); ir ($CDCl_3$, cm^{-1}) 3636 (w), 3448 (m), 2950 (m), 1605 (w), 1462 (w), 1376 (w), 1220 (m), 1053 (s). *Anal.* Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.67; H, 8.83. Hydrogenation gave *trans*-2,3-bicyclo[2.2.2]octanediol.

exo-cis-**2,3-Bicyclo[2.2.2]oct-5-enyl ditosylate (VI)** was prepared from VI-OH by the usual means.[8,15] After several recrystallizations (ether–pentane), the yield was 45%: mp 110.0–112.5°; pmr ($CDCl_3$) δ 1.07 (m, 2 H, methylene), 1.97 (m, 2 H, methylene), 2.47 (s, 6 H, tosyl methyl), 2.80 (broad s, 2 H, methyne), 4.44 (broad s, 2 H, *endo*-C*H*O-), 6.50 (m, 2 H, vinyl), 7.56 (ABq, 8 H, aryl); ir ($CDCl_3$, cm^{-1}) 3058 (w), 2950 (m), 2882 (w), 1603 (m), 1368 (s), 1350 (m), 1192 (s), 1179 (s), 1100 (m), 1040 (m), 1008 (m), 984 (s). *Anal.* Calcd for $C_{22}H_{24}S_2O_6$: C, 58.91; H, 5.39. Found: C, 59.30; H, 5.50.

trans-**2,3-Bicyclo[2.2.2]oct-5-enyl ditosylate (X)** was prepared from X-OH: mp 107–108.5°; pmr ($CDCl_3$) δ 1.50 (d of m, 4 H, methylene), 2.54 (s, 6 H, tosyl methyl), 2.86 (broad s, 2 H, methyne), 4.33 (m, 1 H, *endo*-C*H*O-), 4.52 (t, 1 H, *exo*-C*H*O-), 6.18 (m, 2 H, vinyl), 7.56 (unsymmetrical ABq, 8 H, aryl); ir ($CDCl_3$, cm^{-1}) 3067 (w), 2950 (m), 2882 (w), 1603 (m), 1366 (s), 1190 (s), 1176 (s), 1099 (m), 1057 (m), 1053 (m), 978 (s). *Anal.* Calcd for $C_{22}H_{24}S_2O_6$: C, 58.91; H, 5.39. Found: C, 59.11; H, 5.36.

exo-**2-Bicyclo[2.2.2]oct-5-enol (VIII-OH)** was prepared by literature procedures.[9]

exo-**2-Bicyclo[2.2.2]oct-5-enyl tosylate (VIII)**[9a] was prepared from a sublimed sample of VIII-OH. Several recrystallizations (pentane) gave a low-melting material (below 10°): pmr ($CDCl_3$) δ 1.40 (m, 4 H, methylene), 2.40 (s 3 H, methyl), 2.63 (m, 2 H, methyne), 4.44 (m, 1 H, -C*H*O-), 6.50 (m, 2 H, vinyl), 7.56 (ABq, 4 H, aryl).

2-Bicyclo[2.2.2]octanol (IX-OH) was prepared by hydrogenation of *endo*-bicyclo[2.2.2]oct-5-enol.[9b]

2-Bicyclo[2.2.2]octyl tosylate (IX) was prepared from IX-OH and recrystallized from pentane (57%).[9b]

Solvolysis Products of VII. From the solvolysis of 0.5 g of VII, only one product (>95%) was observed by glc analysis. The material was collected and found to have an nmr spectrum identical with that reported for XIII, although other structures are possible.

cis-**6,8-Tricyclo[3.2.1.0^{2,7}]octyl Diacetate (XII).** The solvolysis of 0.4 g of VI yielded a reaction mixture with only one significant component (85–90%) by analytical glc. The product was recrystallized from ether to give a crystalline material, mp 114–115.5°, after sublimation at 85° (10 mm). The nmr spectrum (see text) requires a fully saturated, and hence tricyclic, *cis*-diacetate. The stereochemistry may be either di-endo or di-exo. The latter was selected on a purely mechanistic basis.[9a] *Anal.* Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.51; H, 7.21.

(19) H. M. Walborsky and D. F. Loncrini, *J. Amer. Chem. Soc.*, **76**, 5396 (1954).