be much smaller in the *p*-toluenesulfonate ion pairs, and this provides a consistent explanation for the relatively low sensitivity of k_{-M} to the nature of the cation.

There are several instances for aprotic solvents,[9] and one for acetic acid,[10] in which the existence of ion pairs with the formula $M^+Ac^- \cdot HAc$ has been indicated. Furthermore, dissociated acetate ion is exceptionally stable in acetic acid and should probably be formulated as $Ac^- \cdot HAc$[8] (which might be stabilized further by ultrafast proton transfer, $Ac^- \cdot HAc \rightleftarrows AcH \cdot Ac^-$). In the solid state, the existence of stable compounds such as $(n\text{-}Bu_4N^+)Ac^- \cdot HAc$ is well known. We nevertheless feel that the acetate ion pairs studied in the present work are best formulated as shown in (30), with the acetate ions in the ion pairs being solvated only by loosely attached acetic acid molecules. Otherwise we would need a far more complicated theory to account for our kinetic results.

Relationship to Ion-Pair Exchange in Solvolysis. It can be shown that K_M is related to ion-pair dissociation constants K_d according to

$$K_M = (K_d^{M^+Ac^-}/K_d^{M^+Ts^-})(K_d^{BH^+Ts^-}/K_d^{BH^+Ac^-}) \quad (31)$$

$K_d^{BH^+Ts^-}/K_d^{BH^+Ac^-}$ for the *p*-toluidinium salts has been reported to be 0.248 ± 0.003 in acetic acid at 26.7°.[8] On using that value in conjuction with K_M, we find that for tetra-*n*-butylammonium salts, $K_d^{M^+Ac^-}/K_d^{M^+Ts^-} = 11.3$, with a confidence limit estimated conservatively at ±20%.

In a recent review, Winstein, Appel, Baker, and Diaz[11] have presented a theory of ion-pair exchange in solvolysis which makes the assumptions that (a) the equilibrium constant for (32) is equal to $K_d^{M^+Y^-}/K_d^{M^+X^-}$, and (b) that the rate constant for acetolysis (33) is approximately the same for all X^- and Y^-. ($R^+||X^-$ and $R^+||Y^-$ denote solvent-separated ion-pair reaction intermediates.) The theory requires that cer-

$$R^+||X^- + M^+Y^- \rightleftarrows R^+||Y^- + M^+X^- \quad (32)$$

$$HAc + (R^+||X^- \text{ or } R^+||Y^-) \longrightarrow RAc + (HX \text{ or } HY) \quad (33)$$

tain parameters in the rate law for acetolysis be predictable from ion-pair dissociation constants. The theory seems to fit the data well for $X^- = Ts^-$ and $Y^- = ClO_4^-$.[11] However, in the case of tetra-*n*-butylammonium salts, the value of 11.3 obtained above for $K_d^{M^+Ac^-}/K_d^{M^+Ts^-}$ is in serious discrepancy with the theoretical prediction of 2.8.[11] Thus, in solvolysis as well, the reactions of acetate ion pairs display a greater specificity than do those of *p*-toluenesulfonate or (presumably) perchlorate ion pairs.

(9) M. M. Davis, "Acid-Base Behavior in Aprotic Organic Solvents," National Bureau of Standards Monograph 105, Washington, D. C., 1968, Chapter 4.

(10) A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 4484 (1964).

(11) S. Winstein, B. Appel, R. Baker, and R. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19**, 115 (1965).

Evidence Concerning the Bishomocyclobutenium Dication as a Solvolytic Intermediate

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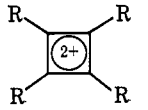
Abstract: *cis-exo*-2,3-Norborn-5-enyl ditosylate (IV) acetolyzes 500 times more rapidly than the related saturated *cis-exo*-ditosylate XI. Since a double bond is generally rate retarding in a homoallylic situation, *e.g.*, comparison of the saturated and unsaturated *exo*-monotosylates XII and XIII in the norbornyl series, a special effect must be operative. One such possibility is loss of both tosylate groups to form a bishomocyclobutenium ion. As demanded of this mechanism, acetolysis of IV for one half-life produces no acetoxy tosylate intermediate, whereas XI does produce a mixed ester. If a dication mechanism were operative, the cis relationship of the leaving groups must bring about a rate enhancement. *trans*-2,3-Norborn-5-enyl ditosylate (XIV), however, solvolyzes at a rate comparable to that of IV. Furthermore, the mixed ester *cis-exo*-2-acetoxy-3-tosyloxynorborn-5-ene (XV), for which a dication mechanism is impossible, reacts slightly more rapidly than IV. If a single explanation is to be found for the rapid reactions of IV, XIV, and XV compared to saturated models, a double ionization is excluded. Consistent with all the data for the diesters is a greatly enhanced homoallylic assistance compared to that in the monoesters. To diminish the rate-retarding effect of the electronegative substituent adjacent to the leaving group, the double bond becomes a much more effective participator than it is in monotosylates such as XII.

Experiments in highly acidic media have recently placed cyclobutenium dications (I) on firm ground.[2,3] Such molecules are isoelectronic with the



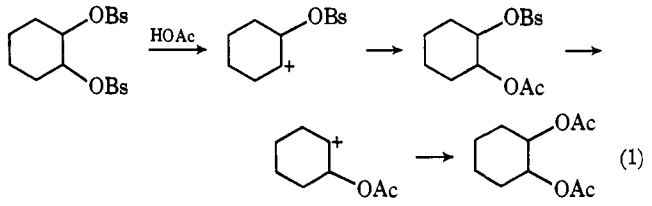
I, R = CH_3, C_6H_5

(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) G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3667 (1969); G. A. Olah and G. D. Mateescu, *ibid.*, **92**, 1430 (1970).

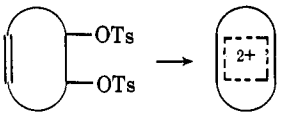
(3) Earlier work was less successful in confirming a dication; see D. G. Farnum, M. A. T. Heybey, and B. Webster, *ibid.*, **86**, 673 (1964); H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962); H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964); R. F. Bryan, *ibid.*, **86**, 733 (1964).

cyclopropenium ion, the stability of which is well documented.[4] Interest in multiply charged species led us to consider the feasibility of generating a cyclobutenium dication I by the conventional solvolysis of arenesulfonate diesters. Solvolyses of alkyl arenesulfonate diesters have previously been interpreted as proceeding in a stepwise fashion through monocationic intermediates (eq 1).[5] The presence of a strongly electron-withdrawing substituent adjacent to the leaving group



(1)

serves to reduce the rate drastically with respect to that of the monoarenesulfonate. Unsaturated diesters of the general formula II could conceivably solvolyze by loss of both tosylate groups to a planar bishomocyclobutenium ion III. It is this type of process that we chose to investigate and report on in this paper.

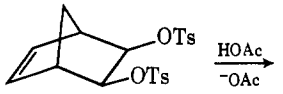


(2)

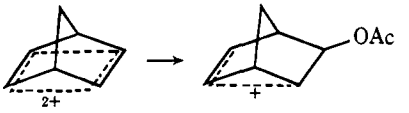
II III

The process of eq 2 requires planarity of the central four-carbon system and symmetrical placement of the double bond anti to the leaving tosylate groups. These conditions are most readily fulfilled by the conformationally rigid system *cis-exo*-2,3-bicyclo[2.2.1]hept-5-enyl ditosylate (IV). The dication that could be produced from IV has the structure V. Its bishomo π

Mechanism A

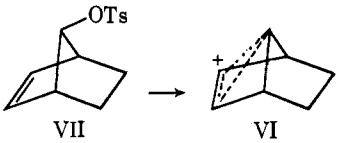


IV



V VIII

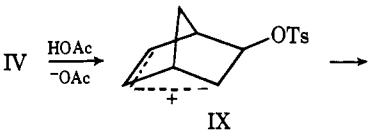
system contains $4n + 2$ electrons ($n = 0$) and is isoelectronic with the thoroughly studied bishomocyclopropenium ion VI, obtained from the arenesulfonate VII. Two general mechanisms are possible for the



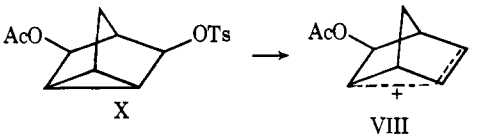
VII VI

solvolysis of IV. (A) The diester suffers loss of both groups in a concerted or nearly concerted fashion to form the dication V, which reacts with solvent in a stepwise manner to produce first the homoallylic ion VIII and finally diacetate products. (B) The diester proceeds to a homoallylic intermediate IX, which reacts

Mechanism B



IX

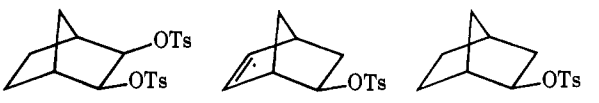


X VIII

with solvent to give an acetoxy tosylate X before loss of the second tosylate group occurs to form the homoallylic ion VIII. By the "dicationic mechanism" (A) we will mean any path that passes through the dication V. By the "stepwise mechanism" (B) we will mean any path that proceeds only by monocations or nucleophilic displacements.

Differentiation of these two mechanisms is the major subject of this paper. Since both pathways probably involve the intermediacy of the ion VIII, product studies will be of no use. One clear-cut distinction might be the observation of a mixed ester such as X. The dication mechanism could not admit of such an intermediate without ion-pair return from VIII, so solvolysis for short reaction times and search for an acetoxy tosylate could give strong evidence for a stepwise mechanism. *A product criterion for the dication mechanism is:* no acetoxy tosylate may be observed at any point during the reaction. Since ion-pair return could vitiate this criterion, it is given a lesser weighting than those based on kinetic data.

Comparison of the solvolysis rate for IV with those for related compounds has proved to be the most successful approach. We have utilized four independent kinetic tests. (1) The double bond in IV must provide particularly strong anchimeric assistance for a double ionization to occur. The extent of participation may be estimated by comparison with the saturated ditosylate XI. The "normal" effect of a double bond on sol-



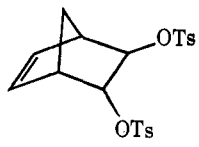
XI XII XIII

volysis of a single tosylate group may be determined by comparison of XII and XIII. For the double ionization to be preferred, the unsaturated to saturated rate ratio for the ditosylates (IV/XI) must greatly exceed that for the monotosylates (XII/XIII). *The first kinetic criterion for the dication mechanism is:* the double bond in the unsaturated ditosylate must cause a rate acceleration, which is larger than that in the monotosylate.

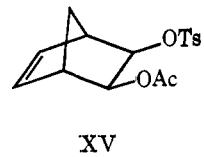
(2) *trans*-2,3-Norborn-5-enyl ditosylate (XIV) is an ideal model for the stepwise mechanism, since the *endo*-tosylate group should ionize very slowly. Kinetic studies of XIV will establish the approximate rate-retarding power of the second tosylate group. For the

(4) R. Breslow, J. T. Groves, and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 5048 (1967); D. G. Farnum, G. Mehta, and R. G. Silberman, *ibid.*, **89**, 5048 (1967).

(5) S. Winstein, C. Hanson, and E. Grunwald, *ibid.*, **70**, 812 (1948); S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *ibid.*, **70**, 816 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948); A. C. Cope and G. W. Wood, *ibid.*, **79**, 3885 (1957); A. C. Cope, S. Moon, and P. E. Peterson, *ibid.*, **81**, 1650 (1959).



XIV



XV

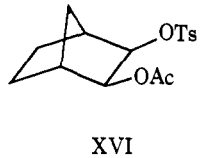
double ionization to occur, the unsaturated *cis*-ditosylate IV must react more rapidly than the trans isomer XIV. A comparable or smaller rate for IV would be consistent with a stepwise mechanism in both cases. *The second kinetic criterion is:* the cis orientation of leaving groups must convey a rate acceleration.

(3) The mixed ester XV, though not a reasonable candidate for an intermediate (*vide post*), can nonetheless serve as a good model for the stepwise mechanism. In this case, two electronegative groups are cis and exo, but only one is a good leaving group. If IV reacts by a stepwise process, XV must react more rapidly because of the somewhat smaller inductive effect of the acetate group. The double ionization of IV, however, would require a much slower rate for XV. *The third kinetic criterion is:* replacement of a tosylate group in IV by a similar substituent incapable of serving as a leaving group must convey a rate deceleration.

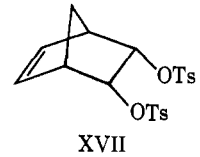
(4) Detailed examination of the kinetic behavior of IV may give some information about the mechanism. The dication pathway should produce good first-order kinetics throughout the course of the reaction, although a small rate increase may be observed from a salt effect. For the stepwise mechanism, there are two possibilities. If the intermediate acetoxy tosylate reacts more rapidly than the ditosylate, a constant first-order rate would be observed and no differentiation could be made. On the other hand, if loss of the second tosylate group occurs more slowly, as would probably be the case if the group were at the 7 position of the intermediate, the kinetics would not be cleanly first order and the rate would fall off with time. A substantial rate decrease would therefore rule out a dication mechanism. *The fourth kinetic criterion is:* the solvolysis rate must be cleanly first order throughout the course of the reaction.

Synthesis, Kinetic Results, and Product Analysis

Required for this study were compounds IV and XI–XVII. The saturated mixed ester XVI and the unsaturated *cis-endo*-ditosylate XVII were added for the sake of completeness. The alcohols leading to the unsat-

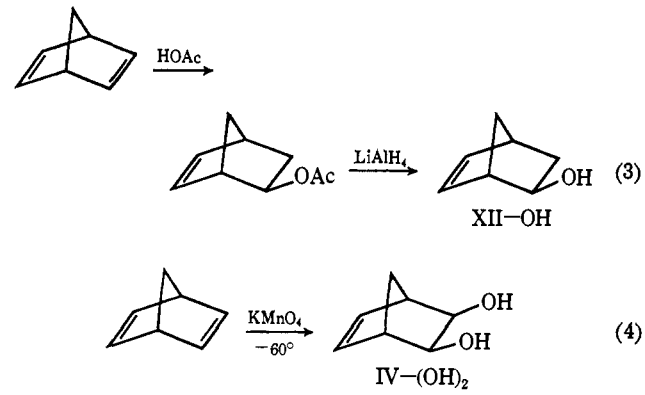


XVI



XVII

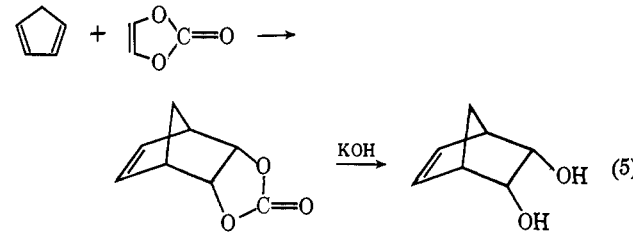
urated monotosylate[6] XII and *cis*-ditosylate[7] IV were prepared by literature procedures (eq 3 and 4). Hydrogenation of the alcohol corresponding to XII gave the saturated monoalcohol XIII–OH. The saturated diol XI–$(OH)_2$ was prepared by hydroxylation of norbornene with permanganate. The mixed diesters XV and XVI were prepared by reaction of the appropriate diol with



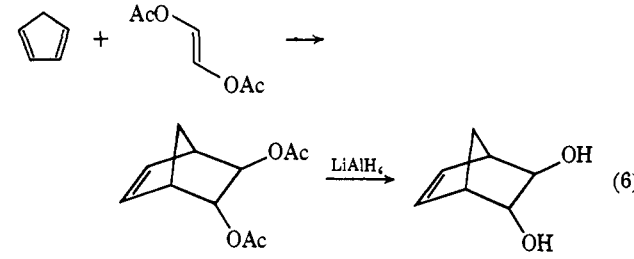
XII–OH

IV–$(OH)_2$

tosyl chloride, and treatment of the hydroxy tosylate with acetic anhydride. *cis-endo*-2,3-Norborn-5-enediol was prepared by the Diels–Alder reaction of cyclopentadiene and vinylene carbonate, and saponification of the resulting bicyclic carbonate (eq 5).[8] *trans*-2,3-Nor-



born-5-enediol was obtained from the reaction of *trans*-1,2-diacetoxyethylene[9] and cyclopentadiene, followed by reduction of the diacetate adduct (eq 6). In



all cases, crystalline tosylates were obtained by the reaction of the alcohols with tosyl chloride by the method of Tipson.[10]

Tosylate solvolyses were carried out in acetic acid containing a slightly greater than equivalent amount of potassium acetate. Rate constants were determined titrimetrically by standard techniques. A detailed description is given in the Experimental Section. For those reactions with strictly first-order behavior, rate constants were calculated from a least-squares analysis of a plot of the logarithm of substrate concentration *vs.* time. In those cases for which there were deviations from first-order behavior, initial rate constants were determined by extrapolation of concentration data to zero time and calculation of rate constants from eq 7.

$$k_t = t_i^{-1} \ln (C_0/C_t) \qquad (7)$$

Table I summarizes the rate constants and activation parameters determined for this study. The rate constants are averages of duplicate or triplicate runs with standard deviations of 5% or less. A common tem-

(6) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2733 (1966).
(7) Y. F. Shealy and J. D. Clayton, *J. Amer. Chem. Soc.*, **91**, 3075 (1969).
(8) H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954); M. S. Newman and R. W. Addor, *ibid.*, **77**, 3789 (1955).
(9) R. A. Caldwell, *J. Org. Chem.*, **34**, 1886 (1969).
(10) R. S. Tipson, *ibid.*, **9**, 235 (1944).

Table I. Rate Constants and Activation Parameters for Buffered Acetolysis of Norbornyl Derivatives

Compd	Temp, °C	k_1, sec^{-1}	Rel rate	E_a, kcal/mol	Log A	$\Delta H^{\ddagger}_{75°}$, kcal/mol	$\Delta S^{\ddagger}_{75°}$, eu
IV	75.0	8.59×10^{-6}	1.00	28.3	12.6	27.6	−3
	90.0	4.15×10^{-5}					
	100.0	1.33×10^{-4}					
	110.0	3.53×10^{-4}					
XI	75.0	1.7×10^{-8} [a]	1.98×10^{-3}	32.1	12.1	31.4	−4
	120.0	2.98×10^{-7} [b]					
	130.0	8.37×10^{-6} [b]					
	140.1	2.20×10^{-5} [b]					
	150.0	5.50×10^{-5} [b]					
XII	75.0	1.74×10^{-3}	2.03×10^{2}	21.8	11.0	21.2	−11
	50.0	1.67×10^{-4}					
	25.0	8.77×10^{-6}					
XIII	75.0	5.88×10^{-3}	6.85×10^{2}	22.8	12.1	22.2	−5
	50.0	4.82×10^{-4}					
	24.7	2.24×10^{-5}					
XIV	75.0	9.27×10^{-6} [b]	1.08	30.3	14.0	29.6	+2
	89.8	6.15×10^{-5} [b]					
	99.9	1.70×10^{-4} [b]					
XV	75.0	1.58×10^{-6} [b]	1.84	30.5	14.3	29.8	+5
	90.0	9.60×10^{-5} [b]					
	100.1	3.08×10^{-4} [b]					
XVI	75.0	3.0×10^{-7} [a]	3.49×10^{-2}	28.5	11.4	27.8	−9
	130.0	8.33×10^{-5}					
	140.1	1.98×10^{-4}					
	150.0	4.47×10^{-4}					
XVII	75.0	1.1×10^{-10} [a]	1.28×10^{-5}	34.7	11.8	34.0	−7
	184.9	1.75×10^{-5}					
	199.8	5.80×10^{-5}					

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

perature (75°) was chosen for the discussion of relative rates. In several cases, extrapolation of rates from higher temperatures was necessary. A least-squares analysis of rate data from three or four temperatures was made to determine Arrhenius parameters, from which the rate constants were calculated at 75°.

Of those cases for which strict first-order behavior was not observed, two (XIV and XV) may be explained by salt effects that cause the rates to increase slightly as the weakly dissociated potassium acetate is replaced by strongly ionized potassium tosylates. These effects were rather small. In the case of XI, however, a significant rate decrease was observed with time. This behavior is consistent with buildup of a more slowly reacting intermediate during solvolysis.

In an effort to isolate an intermediate from the reaction of the saturated ditosylate XI, a sample was solvolyzed for one half-life in buffered acetic acid and the resulting mixture fractionated by column chromatography. The products were 28% starting material, 34% acetoxy tosylate intermediate (XVIII), and 38% mono- and diacetates. Although the structure of the mixed ester has not been fully established, spectroscopic evidence proves that it has the norbornyl skeleton and that the tosylate group is probably at the 7 position. Isolation of XVIII is consistent with the stepwise mechanism expected for the saturated ditosylate. Similar efforts to detect an intermediate in the acetolysis of the unsaturated *cis*-ditosylate IV were unsuccessful. This observation is consistent with the strictly first order behavior of IV, though it does not constitute proof that IV solvolyzes by a double ionization.

Formal product determinations were made by solvolyzing samples of substrate in buffered acetic acid for a period of five–ten half-lives. After solvolysis and work-up, product mixtures were analyzed by vpc. Components of the mixtures were isolated by preparative vpc and identified by comparison of their spectral properties with those of authentic materials. The Experimental Section contains additional details.

Tables II and III list the solvolysis products and relative amounts of each obtained in the acetolyses of the norbornyl diesters included in this study. Most solvolyses also gave other products to the extent of 3–5%. These minor components could not be collected or identified, so structural conclusions could only be based on comparison of retention times with those of authentic samples. All products listed in Tables II and III were found to be stable under the conditions of solvolysis and analysis. It was also demonstrated that product distribution for IV was independent of the length of reaction up to and beyond five half-lives.

Table II. Acetolysis Products of Norbornenyl Derivatives

Compd	Products and normalized abundances, % XIX	XX	XXI
IV	39	49	12
XIV	34	62	3
XV	33	61	6
XVII	40	51	8

Table III. Acetolysis Products of Norbornyl Derivatives

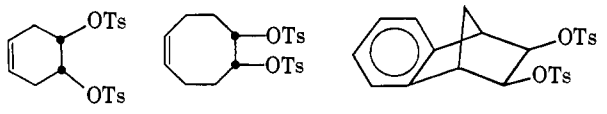
Compd	Products and normalized abundances, % XXII	XXIII	XXIV	XXV
XI	9	53	29	9
XVI	3	21	17	58

Despite vastly differing rates, the unsaturated compounds in Table II (IV, XIV, XV, and XVII) show remarkably similar product distributions. Compound XIV produces about 3% of a material with vpc retention time identical with that of *trans*-2,3-norborn-5-enyl diacetate. Neither this product nor any *cis*-2,3-diacetates were observed among the reaction products of IV, XV, or XVII. The two saturated diesters XI and XVI give large amounts of elimination products (monoacetates). Reaction product XXV has not been conclusively identified, although it has been established to be a saturated diacetate most probably of the norbornyl series (but not a 2,3 isomer or the exo-syn or exo-anti 2,7 isomers). The nmr spectrum indicates that it is quite similar in structure to the intermediate XVIII from the solvolysis of XI.

Discussion

A case for the dication mechanism in the solvolysis of IV may be based on the product criterion and the first and fourth kinetic criteria (*vide supra*). Observation of strictly first-order kinetics and absence of an acetoxy tosylate intermediate are required of such a mechanism. The kinetics proved to be quite level, and all efforts to find an intermediate failed. Isolation of a mixed ester intermediate in the solvolysis of the saturated ditosylate XI suggested that such an intermediate, if present, should have been isolable from the reaction of IV. The product and fourth kinetic criteria nonetheless do not require a dication mechanism, since reaction of an acetoxy tosylate intermediate in a stepwise process could occur much more rapidly than ionization of the first tosylate group.

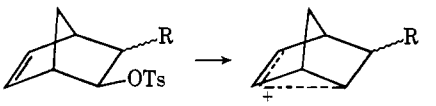
The first kinetic criterion for the dication mechanism requires that the double bond produce a considerable anchimeric assistance. In fact, IV solvolyzes 505 times (Table I) as fast as the saturated analog XI. In contrast, the unsaturated monotosylate XII reacts 3.37 times more slowly than its saturated analog XIII. For the monotosylate, homoallylic participation is therefore not sufficiently strong to give a rate acceleration. If the factor 3.37 is taken as the minimum inductive rate retardation by the double bond, then the actual acceleration in IV is at least 3.37 × 505, or 1700.[11] Model systems for the stepwise process have been examined and found to have contrasting properties. Compared to the 505-fold acceleration in IV, the unsaturated ditosylates XXVI[12] and XXVII[13] solvolyze 0.94 and 0.058 times as fast as their respective saturated analogs. In



XXVI XXVII XXVIII

these systems, a double ionization is stereoelectronically prohibited,[12,13] and in XXVII even homoallylic assistance is disfavored by the distance involved. The benzo analog of IV (XXVIII) reacts only 20 times more rapidly than XI, and furthermore produces an isolable acetoxy 7-tosylate intermediate.[14] These properties establish a stepwise mechanism for XXVIII but contrast to those for IV.

The 505-fold accelerative effect of the double bond in IV, contrasted to small or reverse effects in other unsaturated mono-(XII) or ditosylates (XXVI–XXVII), clearly demands a special interpretation for the solvolytic mechanism. That this mechanism is probably not the double-ionization process comes from application of the second and third kinetic criteria. From Table II it can be seen that the unsaturated *trans*-ditosylate reacts 1.08 times more rapidly than the *cis-exo*-ditosylate. The cis geometry therefore conveys no special properties to the system. Since both the cis-exo and the trans isomers react so much more rapidly than the saturated ditosylate XI, any "special interpretation" must be applicable to both. An alternative explanation to the dication mechanism is that homoallylic participation becomes more effective at charge dispersal when there is an electronegative substituent adjacent to the leaving group than when there is none. By this interpretation the double bond serves to remove the posi-



(8)

tive charge from the vicinity of the remaining tosylate group (eq 8, R = *exo*-OTs in IV, *endo*-OTs in XIV). Apparently σ participation cannot be enhanced in this manner (or to this extent) so the saturated compounds experience the full (or nearly full) rate retardation of the second tosylate group: monotosylate/ditosylate (saturated) = 336,000, but monotosylate/ditosylate (unsaturated) = 203. In the unsaturated monotosylate XII, solvolysis proceeds without the need of strong assistance from the double bond.

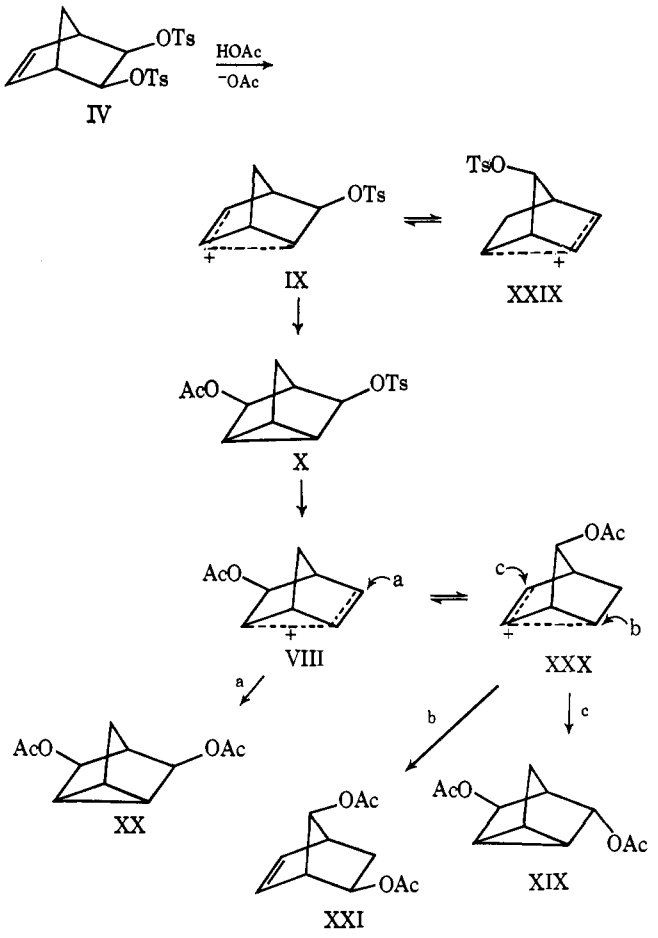
The case for turned-on homoallylic participation finds further justification from the rates of XVI and XVII. Like IV and XIV, the cis-endo isomer XVII is an unsaturated ditosylate. Unlike either of those molecules, however, XVII possesses only endo leaving groups and hence is incapable of exhibiting homoallylic assistance (eq 8). As a result, solvolysis of XVII is the slowest in the entire series (Table I), more than 100-fold down from even the saturated ditosylate XI.

Finally, the cis-exo unsaturated acetoxy tosylate XV is restricted to a stepwise process of the type given by eq 8 (R = *exo*-OAc) because only one leaving group is present. A dication mechanism is impossible, yet the compound reacts 1.84 times as fast as IV. The electronegative acetate group can serve to increase homoallylic charge dispersal in XV, just as the second tosylate group does in IV and XIV. The fact that the change from tosylate to acetate produces a smaller rate alteration in the unsaturated system (XV/IV = 1.84) than in the saturated system (XVI/XI = 17.6) further substantiates the argument that homoallylic participation has a greater capacity for increased effectiveness in the presence of an added electronegative group than does σ participation.

A stepwise mechanism that can account for the products from IV is given in Scheme I. The first-formed homoallylic ion IX may either rearrange to another homoallylic ion XXIX, in which the positive charge is

(11) J. B. Lambert and A. G. Holcomb, *J. Amer. Chem. Soc.*, 91, 1572 (1969).
(12) J. B. Lambert, H. G. Smith, Jr., and A. P. Jovanovich, *J. Org. Chem.*, 35, 3619 (1970).
(13) W. D. Closson, J. L. Jernow, and D. Gray, *Tetrahedron Lett.*, 1141 (1970).
(14) H. Tanida and T. Tsushima, *ibid.*, 3647 (1969).

Scheme I

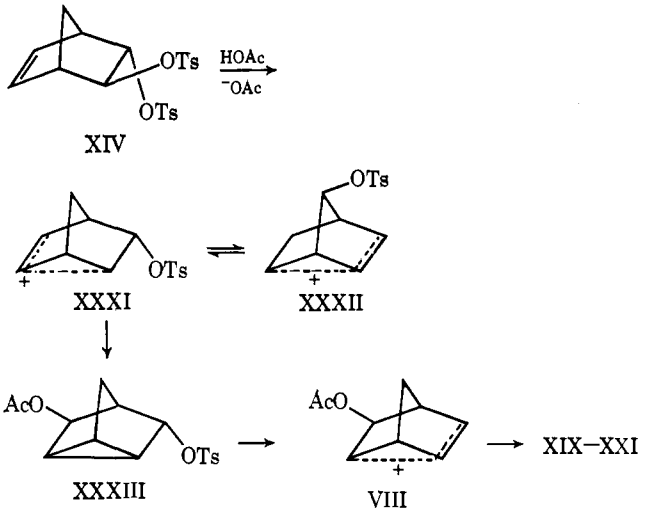


furthest removed from the remaining tosylate group, or it may react with the solvent to form the mixed ester X. This acetoxy tosylate can give the observed products by the indicated pathways, in which exo attack is presumed to dominate. It should be noted that ion XXIX can form two additional mixed esters, which can also produce XIX–XXI. Detailed consideration of this possibility, together with that of ions with higher symmetry, is presented elsewhere.[15] The mixed ester XV enters Scheme I directly at ion VIII. Similar products to IV are therefore to be expected (Table II). The products from a dication mechanism may also come from Scheme I, since ion VIII would be formed by attack of solvent on ion V.

The stepwise solvolysis of the *trans*-ditosylate XIV can be expected to proceed in a similar fashion, to produce a set of ions (XXXI, XXXII) that differs from IX, XXIX only in the stereochemistry of the residual tosylate group (Scheme II). Although the *endo*-tosylate group in XIV is not situated properly for anchimeric assistance, the same group in the nortricyclyl system XXXIII is as well situated as that in the corresponding mixed ester in Scheme I (X). The common ion VIII can then lead to the products XIX–XXI. Consideration of the paths open to ion XXXII is interesting, but leads to no new products.[15] The *cis-endo*-ditosylate XVII will also produce XXXI (Scheme II), though the process occurs without anchimeric assistance from the double bond. Product distribution for XVII is different

(15) A. G. Holcomb, Ph.D. Dissertation, Northwestern University, 1970.

Scheme II



from XIV because the solvolysis was carried out at a higher temperature (200 *vs.* 90°).

In conclusion, solvolysis of the unsaturated *cis-exo*-ditosylate IV is more effectively assisted by the double bond to the extent of several orders of magnitude than is the case for the geometrically identical unsaturated *exo*-monotosylate XII. From this single observation, it might be concluded either that a dication mechanism is operative, or that homoallylic assistance is exhibiting an increased capacity for charge dispersal. The observations that the unsaturated *trans*-ditosylate XIV and *cis-exo*-acetoxy tosylate XV, which have only one easily ionizable group, solvolyze at about the same rate as IV lead us to favor the mechanism of enhanced homoallylic participation. This greater participative effectiveness of the double bond is called upon to remove the positive charge from the vicinity of the remaining electronegative group.

Experimental Section

Infrared spectra were recorded on a Beckman IR-5 spectrophotometer and absorptions are reported in reciprocal centimeters. Proton magnetic resonance spectra were obtained on Varian Associates A-60 and T-60 spectrometers. Chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). Mass spectra were obtained on a CEC mass spectrometer, Model 21-104. 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 and an 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.[5] Known amounts of substrate were dissolved in accurately determined volumes of standard base so that the resulting solutions contained a twofold excess of base. These ampoules were then equilibrated with the temperature-controlling medium (±0.2°), and samples were withdrawn at appropriate intervals and quenched by cooling. Quenched ampoules were broken open and the contents were rinsed into a titration vessel with solvent, treated with indicator solution, and titrated with standard acid to determine the residual potassium acetate concentration. The first such ampoule was used as a zero point and the reaction followed from there.[15]

Solvent. Anhydrous glacial acetic acid containing 1% acetic anhydride was prepared by refluxing reagent grade acetic acid with an amount of acetic anhydride sufficient to react with any water present and with a catalytic amount of chromium trioxide.[16] After

(16) I. Gyenes, "Titration in Non-Aqueous Media," D. Van Nostrand Co., Princeton, N. J., 1967.

several hours of refluxing, dry acetic acid was distilled off. The dry acid was then made 1% in acetic anhydride.

Standard Acid. Standard perchloric acid in acetic acid containing 1% acetic anhydride was prepared by combining the calculated amounts of 70% perchloric acid, reagent grade acetic acid, and enough acetic anhydride to react with all the water present and still leave a 1% excess. Solutions were prepared to be nominally 0.02 *N* and were allowed to stand 48 hr prior to standardization with KHP in acetic acid by titration to the blue end point of crystal violet.[16]

Indicator. A 0.5% solution of crystal violet in the above solvent served as an indicator solution.[16]

Standard Base. Base solutions used in this study were prepared by dissolving anhydrous potassium acetate in the prepared solvent. Solutions were standardized by titration to the crystal violet blue end point.

Isolation of Intermediates. XI (5 mmol) was solvolyzed for one half-life in buffered acetic acid at 150°. The reaction mixture was cooled and diluted with ice water, and the aqueous mixture was extracted with ether several times. Ether extracts were combined, neutralized (sodium bicarbonate solution), washed with brine, and dried (sodium carbonate). The dried ether solution was filtered and solvent removed to leave a residue (1.5 g). The residue was swirled with hot cyclohexane and pure, insoluble starting material XI was filtered off (0.6 g). Evaporation of the cyclohexane rinse left 0.9 g of residual oil. The residue was fractionated on a silica gel column (40 g) with 2% tetrahydrofuran (THF)–hexane. The first 750 ml contained only mono- and diacetates. Eluent was then switched to 5% THF–hexane. The next 150 ml contained no material, followed by 300 ml containing 0.5 g of an oil, XVIII, which was characterized as a mixed diester by the following data: pmr (CCl_4) δ 1.50 (m, 6 H, methylene), 1.98 (s, 3 H, acetyl methyl), 2.23 (broad s, 2 H, methyne), 2.45 (s, 3 H, tosyl methyl), 4.55 (d of m, 2 H, α-C*H*O–), 7.56 (AB q, 4 H, aryl); ir ($CDCl_3$) 2959 (m), 2874 (w), 1724 (s), 1603 (w), 1449 (w), 1361 (s), 1252 (s), 1192 (s), 1179 (s), 1100 (m), 1022 (m), 1007 (s), 982 cm^{-1} (s); mass spectrum, parent ion at *m/e* 326.

Parallel work with a sample of IV gave no evidence of an intermediate mixed diester, but only starting material and completely solvolyzed product.

Product Studies. All product studies were performed in the same general manner. Samples to be solvolyzed were dissolved in buffered solution containing an excess of base. These solutions were then solvolyzed for five–ten half-lives, cooled, and diluted with ice water. The aqueous solutions were then extracted several times with ether or pentane. Combined organic extracts were rinsed with sodium bicarbonate and brine solutions prior to drying (anhydrous magnesium sulfate) and filtered, and solvent removed. Concentrated product samples were then analyzed by glc. Analytical work was performed on a $^1/_8$ in. × 6 ft column packed with SE-30 on Chromosorb G or on a $^1/_8$ in. × 11 ft column packed with Carbowax 20M on Chromosorb G. Relative percentages were obtained by the triangulation method for determining peak areas. The percentages listed in Tables II and III are averages from three to four separate determinations. Percentages are accurate to ±2%. Purified samples of product–mixture components were in general obtained by preparative glc. Diacetate materials were purified on a $^1/_2$ in. × 10 ft column packed with SE-30 on Chromosorb G and monoacetate samples were purified on a $^3/_8$ in. × 12 ft column of Carbowax 20M on Chromosorb G. In those cases for which appreciable amounts of both mono- and diesters were present in the crude product mixture, the samples were first fractionated by column chromatography. After purification, samples were used to obtain ir and nmr spectra for comparison with authentic materials. In some cases elemental analyses and mass spectra were also obtained. The descriptions follow of the preparations of authentic materials to identify the products XIX–XXIV. Only compound XXV was not identified.

Compound XXV. A sample of XXV was obtained by preparative glc [SE-30) from the solvolysis product mixture of XI or XVI: pmr ($CDCl_3$) δ 0.95–2.58 (complex absorption, 14 H, acetyl methyl at 1.97), 4.57 (broad m, 1.3 H, –C*H*O–), 4.88 (broad s, 0.7 H, –C*H*O–); ir ($CDCl_3$) 2950 (m), 2874 (w), 1721 (s), 1468 (w), 1443 (w), 1377 (m), 1366 (m), 1316 (w), 1302 (w), 1250 (s), 1203 (w), 1182 (m), 1161 (m), 1148 (w), 1135 (w), 1087 (m), 1076 (m), 1062 (s), 1022 cm^{-1} (s).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.10; H, 7.62.

Nortricyclyl Acetate (XXIII). Norbornadiene (5.0 ml) and 20 ml of 0.02 *N* perchloric acid in acetic acid were shaken together[17] for 30 min at 45–50°. The dark reaction mixture was then diluted with 100 ml of pentane. The resulting mixture was extracted with water to remove acid. The organic layer was washed with base and brine solutions, dried (sodium carbonate), filtered, and concentrated. The residual oil was vacuum distilled (74–76° (14 mm)) to give 4.5 g of clear liquid. Glc revealed a mixture of 84% tricyclic ester and 16% olefinic ester. A sample was purified by preparative glc (SE-30 at 155°).

exo-**2**-*syn*-**7-Norborn-5-enyl Diacetate (XXI).** A solution of norbornadiene (4.6 g or 50 mmol) in dry benzene was treated over a 2-hr period with 24 g of lead tetraacetate.[18] The resulting mixture was stirred for 3 days at ambient temperatures, then filtered to remove the lead diacetate formed. The filter cake was washed with benzene and discarded, and the filtrates were concentrated under reduced pressure. The residual oil was vacuum distilled and the distillate was allowed to crystallize. The resultant crystals were purified by filtration and by cold pentane wash to give 3.2 g of material, mp 30–42°. Two more recrystallizations from pentane gave 2.4 g of XXI, mp 48–49°, lit.[18] 48°.

exo-**2**-*syn*-**7-Norbornyl Diacetate.** A sample of XXI was hydrogenated in ethyl acetate (PtO_2), worked up, and purified *via* preparative glc. This sample was used for spectral comparisons.

exo-**3**-*endo*-**5-Nortricyclyl Diacetate (XIX).** The diol corresponding to XIX was prepared by the method of Ferretti and Tesi[19] in two steps from norbornadiene and converted to the diacetate by treatment with acetic anhydride.[20]

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.83; H, 6.73. Found: C, 63.08; H, 6.91.

exo,exo-**3,5-Nortricyclyl Diacetate (XX).** The diol corresponding to XX was prepared from norbornadiene in two steps by the method of Schaefer[21] and converted to the diacetate by treatment with acetic anhydride.[20]

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.83; H, 6.73. Found: C, 62.56; H, 6.81.

Tosylate Preparation. All tosylates and ditosylates were prepared by the standard method described by Tipson.[10] A solution of purified alcohol or diol was dissolved in dry pyridine, cooled, and then treated with a 10% equivalent excess of recrystallized tosyl chloride. The mixture was then allowed to stand at about 0° until precipitation of pyridinium hydrochloride was complete. The time required varied from 8 hr to 3 weeks as one went from simple alcohols to *cis*-diols and on to *trans*-diols. When tosylate formation was deemed complete, the pyridine solution was quenched with ice water and the resulting mixture stirred for 15 min. The aqueous mixture was extracted several times with either pentane or ether to dissolve the tosylate product. Organic extracts were combined and washed with 3 *N* HCl to remove all the pyridine, then rinsed with a saturated sodium bicarbonate solution, and finally rinsed with brine solution. The dried (magnesium sulfate) solutions of tosylate were filtered and evaporated to dryness under reduced pressure, leaving the tosylate as a residual solid or oil. These residues were then purified by recrystallization from suitable solvents that varied depending upon the particular tosylate. Yields of purified materials ranged from 25 to 60%. The individual tosylates are characterized in the later paragraphs.

exo-**2-Norborn-5-enyl Tosylate (XII).** The corresponding acetate XXII was prepared by the method of Cristol, *et al.*,[6] and reduced to the alcohol by lithium aluminum hydride. The tosylate was purified by recrystallization from pentane, mp 49–51°.

exo-**2-Norbornyl tosylate (XIII)** was prepared from the saturated alcohol[22] and recrystallized from ether–pentane, mp 58–60°.

Mixture of *cis*- and *trans*-Diacetoxyethylene. The method of Caldwell[9] was used to prepare an approximately equimolar mixture of the two isomers in two steps from cyclooctatetraene.

trans- **and** *cis*-**2,3-Norborn-5-enyl Diacetate.** The above diacetate mixture (93 mmol; 13.5 g) and 9.2 g of dicyclopentadiene (140 mmol) were sealed in Pyrex tubing and heated at 185–190° for 22 hr. The tubes were cooled and opened and the contents was distilled under reduced pressure to give some starting materials, then the desired products plus some dimer. The total yield was about 11.4 g of material.

(17) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2726 (1966).
(18) K. Alder, F. H. Flock, and H. Wirtz, *Chem. Ber.*, **91**, 609 (1958).
(19) A. Ferretti and G. Tesi, *J. Chem. Soc.*, 5203 (1965).
(20) S. Winstein, H. V. Hess, and R. E. Buckles, *J. Amer. Chem. Soc.*, **64**, 2796 (1942).
(21) J. P. Schaefer, *ibid.*, **82**, 4091 (1960).
(22) K. Alder and H. F. Rickert, *Justus Liebigs Ann. Chem.*, **543**, 1 (1940).

trans-**2,3-Norborn-5-enyl Ditosylate (XIV).** A mixture of *cis*- and *trans*-norborn-5-enyl diacetates was reduced by lithium aluminum hydride in refluxing ether. After refluxing overnight, the mixture was hydrolyzed with a minimum of water and dilute base and then filtered, and the filter cake washed well (boiling THF). Combined filtrates were dried (sodium sulfate) and filtered, and the solvent was evaporated to give the theoretical amount of residue. This residue was fractionated by column chromatography (silica gel) using a 25% THF–hexane solution as eluent. Initial eluent contained starting material plus *endo*-diol followed by the desired pure *trans*-diol. The above procedure on a preparative scale gave the diol in about 10–15% yield after purification by recrystallization (ether–cyclohexane). The ditosylate was prepared from the parent diol by the standard method and purified by recrystallization (ethyl ether) with a yield of 30%: mp 84.5–86.0°; pmr ($CDCl_3$) δ 1.91 (broad s, 2 H, methylene), 2.62 (s, 6 H, tosyl methyl), 3.12 (m, 2 H, methyne), 4.06 (broad s, 1 H, *exo*-C*H*O–), 4.95 (broad d, 1 H, *endo*-C*H*O–), 6.22 (d, 2 H, vinyl), 7.54 (AB q, 8 H, aryl).

Anal. Calcd for $C_{21}H_{22}S_2I_6$: C, 58.04; H, 5.11. Found: C, 58.15; H, 5.25.

trans-**2,3-Norborn-5-enyl Diacetate.** A small sample of XIV-$(OH)_2$ was treated with an excess of acetic anhydride–sulfuric acid[20] to give a sample of the diester which was purified by glc (SE-30) and used for comparative purposes.

trans-**2,3-Norbornyl Diacetate.** A sample of the above unsaturated diester was treated in a Parr hydrogenation apparatus (PtO_2), and the resultant product was purified by preparative glc (SE-30).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.47; H, 7.59.

cis-endo-**2,3-Norborn-5-enyl Ditosylate (XVII).** The diol corresponding to XVII was prepared by the procedure of Kwart and Newman[8] and converted to the ditosylate in the normal fashion: mp 168.0–169.5°; pmr ($CDCl_3$) δ 1.33 (AB q, 2 H, methylene), 2.43 (s, 6 H, methyl), 3.05 (broad s, 2 H, methyne), 4.94 (t, 2 H, *exo*-C*H*O–), 6.14 (t, 2 H, vinyl), 7.56 (AB q, 8 H, aryl).

Anal. Calcd for $C_{21}H_{22}S_2O_6$: C, 58.04; H, 5.11; S, 14.76. Found: C, 57.68; H, 5.20; S, 14.71.

cis-exo-**2,3-Norborn-5-enyl Ditosylate (IV).** The method of Shealy and Clayton[7] was utilized to prepare the diol, which was converted to the ditosylate in the standard fashion. The ditosylate was recrystallized from ethyl ether: mp 87.5–89.0°; pmr ($CDCl_3$) δ 1.93 (AB q, 2 H, methylene), 2.47 (s, 6 H, tosyl methyl), 2.90 (broad t, 2 H, methyne), 4.47 (d, 2 H, *endo*-C*H*O–), 6.09 (t, 2 H, vinyl), 7.56 (AB q, 8 H, aryl); ir ($CDCl_3$) 2985 (w), 1605 (m), 1458 (w), 1368 (s), 1348 (m), 1192 (s), 1179 (s), 1100 (m), 1049 (m), 1009 (m), 999 (m), 871 cm^{-1} (s).

Anal. Calcd for $C_{21}H_{22}S_2O_6$: C, 58.04; H, 5.11; S, 14.76. Found: C, 57.83; H, 5.31; S, 14.47.

cis-exo-**2-Hydroxy-3-tosyloxynorborn-5-ene.** The unsaturated diol obtained in the preparation of IV (6.35 g or 50.4 mmol) in 80–90 ml of dry pyridine was treated with 10% excess tosyl chloride (55.5 mmol) and allowed to stand in the refrigerator for 1 day. It was then worked up in the usual manner to give 10.8 g of a solid, which was recrystallized from ether and filtered, and the filter cake washed with hot pentane to give 5.2 g of IV. The mother liquor was "recrystallized" twice from ether–pentane to give 3.0 g of oily hydroxy tosylate (22%). It is important that all diol be removed from the monoester before proceeding.

cis-exo-**2-Acetoxy-3-tosyloxynorborn-5-ene (XV).** The above hydroxy ester was treated with acetic anhydride–sulfuric acid to give 3.0 g of an oil that was recrystallized three times (hexane) to give 2.3 g of XV (67%): mp 60–61°; pmr ($CDCl_3$) δ 1.88 (s with shoulder, 4 H, acetyl methyl and 1 methylene), 1.98 (half of AB q, 1 H, methylene), 2.47 (s, 3 H, tosyl methyl), 2.73 (broad s, 1 H, methyne), 3.00 (broad s, 1 H, methyne), 4.46 (AB q with fine structure, 2 H, -C*H*O–), 6.41 (s, 2 H, vinyl), 7.51 (AB q, 4 H, aryl); ir (CCl_4) 3003 (w), 1748 (s), 1603 (w), 1374 (s), 1248 (s), 1236 (s), 1192 (s), 1182 (s), 1105 (s), 1072 cm^{-1} (s).

Anal. Calcd for $C_{16}H_{18}SO_5$: C, 59.60; H, 5.04; S, 9.94. Found: C, 60.28; H, 5.64; S, 9.45.

cis-exo-**2,3-Norbornanediol** was prepared by the reaction of norbornadiene and potassium permanganate according to the method of Winstein and Shatavsky.[23]

cis-exo-**2-Hydroxy-3-tosyloxynorbornane.** In a representative synthesis, 4.7 g (36.5 mmol) of the above saturated diol in 75 ml of dry pyridine was treated with 10% excess (40 mmol) tosyl chloride and the mixture allowed to stand in the refrigerator for 30 hr. Work-up of the mixture gave 9.4 g of a paste-like solid. This solid was recrystallized from ether to give 5.1 g of crude XI. The filtrate was evaporated to give 4.3 g of an oily residue. The residue was next treated with 400 ml of hot hexane and the resulting solution separated from an insoluble residue. The volume of the solution was reduced on a steam bath until a cloudiness developed. At this time, the solution was cooled in the freezer. The oil that had solidified was broken up and filtered to give 2.1 g of the hydroxy ester (21%).

cis-exo-**2-Acetoxy-3-tosyloxynorbornane (XVI).** Ether (10 ml) containing 2.8 g of the hydroxy ester was treated with 3.5 ml of acetic anhydride–sulfuric acid and the mixture allowed to stand for several hours. The mixture was then taken up in 50 ml of ether and this solution washed with water, bicarbonate of soda, and brine solutions to remove all acid and acetic anhydride. The ether solution was then treated with Norit, filtered, dried (magnesium sulfate), and refiltered; solvent was removed to give 3.0 g of oil, which solidified on standing. This material was recrystallized (hexane) three times to give 2.6 g of XVI (81%): mp 85.0–86.5°; pmr (CCl_4) δ 1.23 (broad t, 6 H, methylene), 1.83 (s, 3 H, acetyl methyl), 2.17 (broad s, 2 H, methyne), 2.40 (s, 3 H, tosyl methyl), 4.46 (AB q, -C*H*O–), 7.48 (AB q, 4 H, aryl); ir (CCl_4) 2976 (w), 1748 (s), 1377 (s), 1245 (s), 1195 (s), 1186 cm^{-1} (s).

Anal. Calcd for $C_{16}H_{20}SO_5$: C, 59.23; H, 6.23; S, 9.88. Found: C, 59.49; H, 6.25; S, 9.53.

cis-exo-**2,3-Norbornyl ditosylate (XI)** was prepared in the normal fashion from the above saturated diol[23] and purified by recrystallization from methanol: mp 131–133°; pmr ($CDCl_3$) δ 1.20 (m, 4 H, C-5, 6 methylene), 1.77 (AB q, 2 H, C-6 methylene), 2.40 (broad s, 2 H, methyne), 2.47 (s, 6 H, tosyl methyl), 4.47 (d, 2 H, *endo*-C*H*O–), 7.56 (AB q, 8 H, aryl); ir ($CDCl_3$) 2967 (w), 1603 (w), 1460 (w), 1368 (m), 1348 (m), 1193 (s), 1181 (s), 1101 (w), 1032 (m), 1002 (m), 927 (m), 870 cm^{-1} (s).

Anal. Calcd for $C_{21}H_{24}S_2O_6$: C, 57.77; H, 5.55; S, 14.69. Found: C, 57.39; H, 5.60; S, 15.02.

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