mmol) of pyridine, and 68.2 mg (0.397 mmol) of *p*-toluenesulfonic acid in 10 ml of 80% aqueous acetone was heated for ten solvolytic half-lives. Analysis of the recovered alcohol showed it was unchanged.

The following experiments show that products are optically stable under the conditions of acetolysis. A 0.1 *M* solution of (+)-IV-OAc in anhydrous acetic acid containing 0.0156 *M* sodium acetate had $[\alpha]^{49}D$ +0.383°. This rotation remained constant as the solution was heated for ten half-lives for k_α. In a second experiment a solution of 0.05 *M dl*-IV-OTs was solvolyzed in acetic acid (no sodium acetate) containing (+)-IV-OAc. The rotation, $[\alpha]^{49}D$ +0.128°, remained constant for a period corresponding to more than ten half-lives for k_α. In similar experiments (−)-I-OAc and (+)-III-OAc were shown to be completely optically stable when heated at 49° in acetic acid containing 0.01 *M* sodium acetate.

Ionic Reactions in Bicyclic Systems. VI. Solvolytic Studies of Bicyclo[3.2.1]octan-2-yl and Bicyclo[2.2.2]octan-2-yl Systems[1,2]

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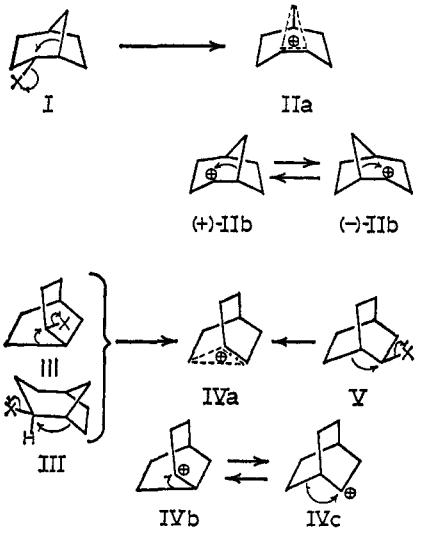
Abstract: Product compositions have been determined for acetolysis and hydrolysis (aqueous acetone) of *endo*- (I-OTs) and *exo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonates (III-OTs), bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (V-OTs), and Δ^4-cycloheptenylcarbinyl *p*-bromobenzenesulfonate (VI-OBs). Solvolyses of I-OTs and VI-OBs give similar, but not identical, mixtures of bicyclooctyl isomers I, III, and V consisting primarily of the *endo*-[3.2.1] isomer I. Solvolyses of III-OTs and V-OTs give mixtures of bicyclo[2.2.2] and *exo*-[3.2.1] isomers III and V having the same composition. These results are compatible with the view that the epimeric bicyclo[3.2.1] isomers I and III give rise to different nonclassical carbonium ions IIa and IVa, respectively, and that the bicyclo[2.2.2] isomer gives the same carbonium ion (IVa) as the *exo*-[3.2.1] isomer III. Evidently I-OTs and VI-OBs give rise to the same carbonium ion (IIa) by the σ and π routes, respectively. The small difference in product compositions is thought to result from the different locations of the anion with respect to the cation and the minor amount of *exo*-[3.2.1] and [2.2.2] isomers III and V in the product (solvent and temperature dependent) is thought to result from isomerization (leakage) of the *endo* carbonium ion system II to the [2.2.2]–*exo*-[3.2.1] system IV.

In an earlier investigation[4] it was shown that the epimeric bicyclo[3.2.1]octan-2-yl systems I and III are related to different carbonium ions, and it was suggested that the *endo* isomer I gives the symmetrical nonclassical ion IIa and the *exo* isomer III gives the asymmetric nonclassical ion IVa. It was also shown that the *exo*-[3.2.1] and bicyclo[2.2.2]octan-2-yl systems, III and V, are related to the same carbonium ion—ion-pair return results in interconversion of III-OTs and V-OTs,[4b] and solvent capture gives binary mixtures of [2.2.2] and *exo*-[3.2.1] isomers.[4,5]

Evidently the *endo* ion IIa is also obtained directly from the Δ^4-cycloheptenylcarbinyl system VI by the π route[6,7] and indirectly from the *endo*-2-norbornylcarbinyl system VII by the ring-expansion route.[8] Presumably in the latter case, the substrate does not have the required geometry for a concerted one-step transformation to the nonclassical ion.[8] Similarly, the [2.2.2]–*exo*-[3.2.1] ion IVa can be derived directly from the β-Δ^3-cyclohexenylethyl system VIII by the π route[7] and indirectly from *exo*-2-norbornylcarbinyl and



7-norbornylcarbinyl systems IX[9] and X[10] by ring-expansion routes.

Evidence for nonclassical intermediates IIa and IVa, instead of equilibrating classical ions[11] IIb and IVb,c, include symmetry properties and stereoselectivities of chemical capture of the intermediates.[4,5,9,12] The

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(2) This work was supported by the National Science Foundation (GP-1911) and by the National Institutes of Health (R.G. 8619).

(3) National Science Foundation Predoctoral Fellow, 1962–1964.

(4) (a) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961); (b) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961).

(5) (a) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *ibid.*, **83**, 988 (1961); (b) H. M. Walborsky, J. Webb, and C. G. Pitt, *J. Org. Chem.*, **28**, 3214 (1963).

(6) G. LeNy, *Compt. Rend.*, **251**, 1526 (1960).

(7) S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).

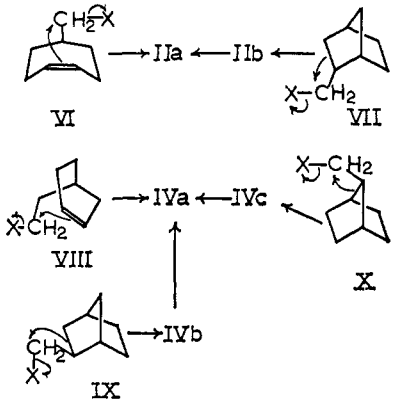
(8) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **86**, 595 (1964).

(9) J. A. Berson and D. Willner, *ibid.*, **86**, 609 (1964).

(10) (a) J. A. Berson and M. S. Poonian, *ibid.*, **88**, 170 (1966); (b) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966).

(11) See: (a) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp 140–158, 174–178; (b) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965); (c) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

(12) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).



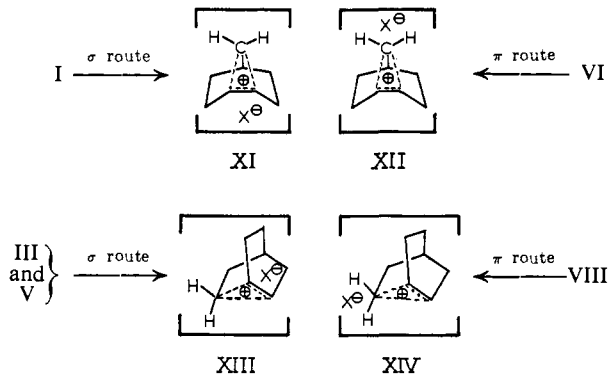
apparent anchimeric acceleration for ionization of both III-OTs and V-OTs also points in this direction for the [2.2.2]–*exo*-[3.2.1] system.[4b,13] The symmetry of the *endo* system is the same as that of the norbornyl system in that the nonclassical ion IIa is symmetrical and the classical ion IIb is asymmetric. The situation is reversed in the [2.2.2]–*exo*-[3.2.1] system; the nonclassical structure is asymmetric and one of the classical ions IVc is symmetrical.

In the preceding paper it was shown that optically active I-OTs apparently gives totally racemic solvolysis products.[14] Thus the situation is similar to that in the norbornyl system[15] in that the first capturable intermediate is symmetrical. This indicates that ionization of I leads directly to the symmetrical bridged ion IIa. In this connection it is significant that in this case,[8] as in the norbornyl system,[15b] the asymmetric classical ion IIb is captured in part when it is involved as an intermediate, *e.g.*, VII → IIb → IIa.

It has been shown that the intermediate in the [2.2.2]–*exo*-[3.2.1] system is asymmetric.[5,9,16] Formation of active III and V by solvent capture of the intermediate generated from active V-OBs,[5b] III-OTs, and V-OTs[16] (the [2.2.2] product is formed with preponderant retention of configuration) is compatible with the nonclassical interpretation but not with equilibrating classical ions—one of the partners, IVc, is symmetrical and involvement of this structure would be expected to result in loss of optical configuration. It should be noted that in this system the windshield-wiper effect[11b] cannot be called on to account for the observed stereochemical results because IVc has two equivalent blades. The stereoselectivity of chemical capture indicated by the earlier work, *endo*-[3.2.1] capture of the *endo* ion II[4a,6,8] and [2.2.2] and *exo*-[3.2.1] capture of the [2.2.2]–*exo*-[3.2.1] ion IV,[4,5,9] is the expected result for nonclassical intermediates and difficult to rationalize in terms of equilibrating classical ions. Another difficulty with the equilibrating classical ions interpretation is that the bicyclo[3.2.1]octan-2-yl ion is a partner in each system. In this case the only barrier separating the two systems would be that for conformational equilibration—as noted earler,[8,9] and indicated in the structural illustrations, the classical [3.2.1] ions IIb and IVb related to the two systems differ conformationally—and it seems doubtful that the barrier for IIb ⇌ IVb would be large enough to preclude substantial crossover in competition with solvent capture.

To obtain additional information concerning the structure and chemistry of the two bicyclooctyl carbonium ion systems we have investigated the solvolysis products for acetolysis and hydrolysis (aqueous acetone) of *endo*- and *exo*-bicyclo[3.2.1]-octan-2-yl *p*-toluenesulfonates (I-OTs and III-OTs), bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (V-OTs), and Δ^4-cycloheptenylcarbinyl *p*-bromobenzenesulfonate (VI-OBs). We were particularly interested in the stereoselectivity of chemical capture of the two intermediates and determining if products derived from I and VI are completely different from those derived from III and V or if there is some interconversion (leakage) of the two carbonium ion systems.

It was also of interest to determine if III-OTs and V-OTs give identical product distributions (*i.e.*, first capturable intermediate common to both isomers) and to compare products derived from intermediates generated by σ and π routes. The latter comparison provides information concerning the effect of the location of the anion on the partitioning and stereoselectivity of capture of the ion. In the *endo* system the location of the counterion differs when the intermediate is generated by the two routes as illustrated by XI and XII. Similarly, in the [2.2.2]–*exo*-[3.2.1] system the location of the counterion differs for the two cases as illustrated by XIII and XIV.



Results and Discussion

The *endo*-[3.2.1] System. Results of the product studies for solvolysis of *endo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (I-OTs) and Δ^4-cycloheptenylcarbinyl *p*-bromobenzenesulfonate (VI-OTs) in acetic acid and 80% aqueous acetone[17] are summarized in Table I. The substrates were prepared from pure samples of the corresponding alcohols (I-OH and VI-OH), and reaction conditions and concentrations were similar to those used in the kinetic experiments.[14] Reactions were carried out for about ten half-periods. Products were isolated by an extraction method designed to minimize fractionation and compositions were determined by capillary gas chromatography. Values obtained for independent duplication experiments agreed to within 0.5 percentage unit for each component. For the acetolysis experiments, analysis of the acetate fraction and the alcohol mixture derived from the acetates gave the same results.

(13) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854, 1856 (1964); C. S. Foote, *ibid.*, **86**, 1853 (1964).
(14) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2848 (1968).
(15) (a) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965); (b) S. Winstein, *ibid.*, **87**, 381 (1965), and cited references.
(16) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2862 (1968).
(17) Solvent compositions based on volumes of pure components at 25° prior to mixing.

Table I. Product Composition for Acetolysis and Hydrolysis of *endo*-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (I-OTs) and Δ^4-Cycloheptenylcarbinyl *p*-Bromobenzenesulfonate (VI-OBs)

Compd[a]	Temp, °C	Composition, % I-X (*endo*-[3.2.1])	III-X (*exo*-[3.2.1])	V-X ([2.2.2])	Olefin[b]
	A. Acetolysis (X = OAc)[c]				
I-OTs	49	89.4	6.6	4.0	0
I-OTs[d]	80	82.9	8.6	5.8	2.7
I-OTs	80	83.9	8.0	5.2	2.9
I-OTs[e]	80	85.6	7.4	4.8	2.2
I-OTs	100[f]	80.4	9.6	7.5	2.5
VI-OBs	60	93.6	3.4	3.0	0
VI-OBs	60	94.0	3.3	2.7	0
VI-OBs[d]	60	93.4	3.6	3.0	0
VI-OBs	80	92.3	4.1	3.6	0
	B. 80% Acetone (X = OH)[g]				
I-OTs	49	94.9	4.1	1.0	0
I-OTs	80	92.0	5.6	2.4	0
VI-OBs[h]	49	97.5	1.4	1.1	0

[a] Substrate concentration about 0.024 *M*. [b] Olefin was predominantly bicyclo[3.2.1]oct-2-ene. [c] Except as noted, solvent contained 10% excess sodium acetate to neutralize acid formed in reaction. [d] No sodium acetate present in this experiment. [e] Sodium acetate concentration 1.0 *M*. [f] Half-life at 100° is 10–15 min. Thus much of the substrate solvolyzes at <100° during warm-up period. [g] Solvent contained 10% excess pyridine to neutralize acid formed in reaction. [h] Product contained 1% uncyclized alcohol VI-OH.

The reactions are cleanly first order under the conditions of the product studies.[14] The rate constant for acetolysis of VI-OBs at 48.86° is $1.39 \pm 0.01 \times 10^{-5}$ sec^{-1}, which is about 50% larger than k_t for the *endo*-[3.2.1] system I. The steady first-order rate shows that the substrates retain their identity throughout the reaction (*i.e.*, no rearrangement prior to solvolysis). Control experiments showed the observed products to be stable under the reaction conditions in all cases including acetolysis in the absence of added sodium acetate.

The data in Table I show that products derived from the *endo*-[3.2.1] and Δ^4-cycloheptenylcarbinyl systems I-OTs and VI-OBs are similar but not identical. In each case, the major component is the *endo*-[3.2.1] isomer I; however, the *exo*-[3.2.1] and [2.2.2] isomers III and V are also formed. In an earlier investigation[4a] of the acetolysis of I-OTs, the two minor components were not detected by infrared analysis of the alcohol obtained by saponification of the acetate fraction.

The observed products can be accounted for in terms of initial formation of the symmetrical *endo* ion IIa by the π and σ routes. As noted later, the small difference in product distributions may be due to the different locations of the departing anion. Solvent capture of IIa would be expected to give the *endo* isomer which is the major component in the product. Isomerization (leakage) of the initially formed intermediate to the isomeric bridged [2.2.2]-*exo*-[3.2.1] ion IVa leads to the minor components III and V.

In connection with this interpretation it is important that the product derived from active I-OTs is apparently completely racemic.[14,18] Also, the ratio of leakage to capture differs for the two substrates and varies with temperature and solvent nucleophilicity in an explicable manner. From the temperature dependence of the amounts of the minor components (11% at 49° and 16% at 80° for acetolysis) it can be determined that the Arrhenius activation energy for leakage is about 4 kcal higher than for solvent capture. For both substrates less of the minor components are formed in the more nucleophilic solvent (80% acetone), as would be expected if these components result from leakage in competition with solvent capture. In this connection note also that for acetolysis at 80° leakage decreases slightly with increasing acetate ion concentration.

The similar product distributions for I-OTs and VI-OBs show that the location of the departing anion with respect to the cation (*cf.* XI and XII) has only a small effect on the fate of the intermediate.[19] The consistent difference for the two substrates is that less leakage is observed when the intermediate is generated by the π route. This small difference may result from the different locations of the anion in the two cases. In the ion-pair intermediate derived from I-OTs (XI-OTs) the anion interferes with, or precludes, *endo* solvent capture. Presumably in this case dissociation beyond the intimate ion-pair stage is required for solvent capture. For the most part, XI-OTs returns to substrate (internal return), or, in other words, substantial reversible *endo* capture by the anion is involved—the return to solvolysis ratio is 4 for acetic acid and 2 for 80% acetone.[14]

On the other hand, in the π-route ionization (XII), the departing anion does not interfere with *endo* solvent capture at any stage of the ionization–dissociation process. It should be noted that XII is not converted to XI; this would necessarily result in isomeric rearrangement of VI-OBs to I-OBs during solvolysis (ion-pair return with rearrangement) which is not observed.[20] Thus, presumably the time interval between ionization and irreversible solvent capture is somewhat shorter for the π-route intermediate and as a result less leakage occurs in this case.

The *exo*-[3.2.1]–[2.2.2] System. Results of the product studies for bicyclo[2.2.2]octan-2-yl (V-OTs) and *exo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (III-OTs) are presented in Table II. Except as noted, reaction times corresponded to about ten half-lives and concentrations were similar to those used in the kinetic experiments.[4] The before-mentioned control experiments show that the products are stable under the reaction conditions—these isomers are over ten times more reactive than I-OTs and thus conditions were milder than those for the experiments in Table I. The substrates used in these experiments were derived from pure samples of the corresponding alcohols.[4]

A complication in connection with these studies is that III-OTs and V-OTs are interconverted by ion-

(18) It should be noted that when the *exo*-[3.2.1]–[2.2.2] intermediate IV is generated from active sources, optically active *exo*-[3.2.1] and [2.2.2] products are obtained.[5,9,16]

(19) The carbonium ion generated by the ring-expansion route (solvolysis of *endo*-2-norbornylcarbinyl *p*-bromobenzenesulfonate, VII-OBs) in acetic acid at 110° also gives a very similar product distribution to that for I-OTs. However, in this case, ionization results in initial formation of the classical ion which is in part intercepted and, as a result, the product derived from active VII-OBs is partly active.[8]

(20) Rearrangement of VI to the less reactive bicyclo isomer I during solvolysis would result in a downward drift in the first-order rate. In all cases the first-order constants for solvolysis of VI-OBs were steady.

Table II. Product Composition for Acetolysis and Hydrolysis of Bicyclo[2.2.2]octan-2-yl *p*-Toluenesulfonate (V-OTs) and *exo*-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (III-OTs) at 49°

Compd	Solvent	Composition, % V-X ([2.2.2])	III-X (*exo*-[3.2.1])	I-X (*endo*-[3.2.1])	Olefin[a]
V-OTs[b]	HOAc	53.4	46.2	0.4	13
III-OTs[b]	HOAc	53.9	45.5	0.6	15
V-OTs	80% acetone	57.2	42.8	None	None
III-OTs	80% acetone	56.7	43.3	None	None
V-OTs[c]	80% acetone	56.8	43.2	None	None
III-OTs[c]	80% acetone	53.5	46.5	None	None
V-OTs	60% acetone	56.2	43.8	None	None
III-OTs	60% acetone	56.0	44.0	None	None

[a] Olefin fraction predominantly bicyclo[3.2.1]oct-2-ene; composition similar for V-OTs and III-OTs. [b] Product compositions determined from composition of alcohols obtained by saponification of acetate fraction. [c] Solvolysis interrupted at 10% completion.

pair return during solvolysis[4b] which reduces any spread in product compositions that might exist for the two isomers. For acetolysis the return (equilibration of III-OTs and V-OTs) to solvolysis ratio is about 4.[4b,21] This means that starting with either isomer, about 80% of the substrate is equilibrated prior to solvolysis, or to put it another way, at complete reaction only 20% of the product is derived from unrearranged substrate. Less return, relative to solvolysis, is involved in aqueous acetone. For I-OTs the ratio of return (racemization) to solvolysis drops from 4 in acetic acid to 2 in 80% acetone.[14] A similar reduction would be expected for III-OTs and V-OTs in which case at complete reaction at least one-third of the product is derived from unrearranged substrate. Even less equilibration prior to solvolysis would be expected in 60% acetone.[22]

As shown in Table II, isomeric compositions of the products differ slightly for acetolysis and hydrolysis in aqueous acetone. However, with one possible exception the product compositions are the same (within limits of reproducibility) for the two isomers. The possible exception is for 10% solvolysis in 80% aqueous acetone—this is an important pair of experiments because during the first 10% reaction over 90%[23] of the products are derived from unrearranged substrates. The composition for V-OTs agrees well with that for complete reaction; however, the composition for III-OTs is slightly different. The observed spread corresponds to about 94% of the III-OTs giving the same intermediate as V-OTs and the other 6% giving III-OH. However, it is not clear if this discrepancy results from slightly different product distributions or from experimental difficulties such as isolating products from dilute solutions without isomeric fractionation. It should also be noted that contamination of the sample of III-OTs with 0.2% by weight of the corresponding alcohol would result in the observed spread, and we cannot be certain that the substrate purity was >99.8%. In any event, III-OTs and V-OTs give very similar, if not identical, product distributions for both acetolysis and hydrolysis in aqueous acetone which shows that the two isomers give rise to the same product-forming intermediate.

Solvent capture of the intermediate derived from III-OTs or V-OTs is essentially completely stereoselective. In aqueous acetone the product is a pure binary mixture of [2.2.2] and *exo*-[3.2.1] isomers V and III. These results are in good agreement with those obtained earlier by infrared analysis for solvolysis of V-OTs in 80% acetone.[4a] The results are similar for acetolysis; in this case the product contains about 0.5% of the *endo*-[3.2.1] isomer I, trace amounts of two other acetates discussed below, and an olefinic fraction. It is significant that the acetolysis product is essentially the same as that reported by Winstein and Carter[7] (54% V-OAc; 46% III-OAc) for acetolysis of β-Δ^3-cyclohexenylethyl *p*-bromobenzenesulfonate (VIII-OBs) at 100°. This is important because it shows that (a) III, V, and VIII give the same product-forming intermediate (the first two by σ routes and the latter by the π route) and (b) the location of the departing anion (*cf.* XIII and XIV) has little, if any, effect on product distribution. This means that the observed stereoselectivity for solvolysis of III or V cannot be attributed to a directive influence of the leaving group as has been recently suggested.[24] Thus the different product distributions for the epimeric [3.2.1] *p*-toluenesulfonates I-OTs and III-OTs must be a result of carbonium ion intermediates which differ structurally rather than only in the locations of the departing anions.

From the stereoselectivity of chemical capture of the intermediate generated from III-OTs or V-OTs, it appears that for each isomer, ionization results largely or exclusively in direct formation of the bridged ion IVa. In the following paper evidence is presented that ionization of V-OTs may involve a small amount of parallel unassisted ionization to give IVc.

Acetolysis of III-OTs and V-OTs gives trace amounts of two acetates in addition to the isomers included in Table II. One of these (~0.4%) was identified as *exo*-bicyclo[3.2.1]octan-6-yl acetate (XVI-OAc) by (a) comparison of the gc retention time with that of an authentic sample[25a] and (b) oxidation of the alcohol derived from the acetate to the corresponding ketone, bicyclo[3.2.1]octan-6-one, which in turn was identified by comparison with an authentic sample.[25a,26] This product results from a 6,2-hydride shift which converts IVa to XV. Capture of the latter gives XVI. In other work[25b] it has been shown that XV (generated from *exo*-bicyclo[3.2.1]octan-6-yl *p*-toluenesulfonate (XVI-OTs)) undergoes substantial 2,6-hydride shift to give IVa. The XV → IVa transformation in competition with solvent capture is much more important than the reverse process observed in this work. The other acetate (~0.5%) in the product was not identified but was shown not to be the epimer of XVI-OAc.

(21) This is similar to the return to solvolysis ratio ($k_{rac}/k_t \sim 4$) for acetolysis of I-OTs.[14]

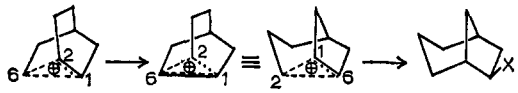
(22) In aqueous acetone the ratio of return to solvolysis decreases as water content increases, *e.g.*, see H. L. Goering and R. W. Greiner, *J. Am. Chem. Soc.*, 79, 3464 (1957).

(23) This estimate is based on the assumption that the return to solvolysis ratio is 2. For the method used to make this estimate see S. Winstein and D. Trifan, *ibid.*, 74, 1154 (1952).

(24) N. C. Deno, *Progr. Phys. Org. Chem.*, 2, 146 (1964).

(25) (a) We are indebted to Dr. T. Padmanathan of these laboratories for providing an authentic sample; (b) T. Padmanathan, unpublished results.

(26) V. N. Ipatieff, J. E. Germain, W. W. Thompson, and H. Pines, *J. Org. Chem.*, 17, 272 (1952).

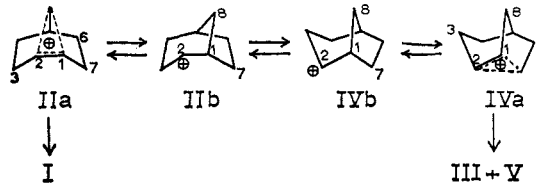


IVa XV XVI

The olefin fraction derived from III-OTs and V-OTs consisted of four components and again the composition was the same for the two isomers: 67% bicyclo[3.2.1]octene-2,[27] 20% bicyclo[2.2.2]octene,[4a] 13% of an unidentified component thought to be tricyclo[2.2.2.0^{2,6}]octane,[28] and a trace of bicyclo[3.2.1]octene-6.[25] The bicyclooctenes were identified by comparison of gc retention times with those of authentic samples.[25a]

Very little leakage to the *endo* system (IV → II) is associated with solvolysis of III-OTs and V-OTs: <1% for acetolysis and none in aqueous acetone. Leakage in the reverse direction is substantially more important. Similar behavior has been observed[9] when the two carbonium ion systems are generated by ring-expansion routes.

Recently, Berson and coworkers[8,9] have presented evidence that the mechanistic pathway connecting the two carbonium ion systems involves the chair and boat conformers of the classical [3.2.1] ion IIb and IVb[29]—crossover is accompanied by partial capture of the classical [3.2.1] intermediate which leads to a higher proportion of the *exo*-[3.2.1] isomer than is formed from IVa. This is also observed in the present work. The [2.2.2]/*exo*-[3.2.1] isomer ratio for III-OTs and V-OTs (capture of IVa) is 1.2 for acetolysis and 1.3 for 80% acetone at 49° (Table II). Under these conditions, leakage from the *endo* system gives a V/III ratio of 0.6 for acetolysis and 0.25 for 80% acetone (Table I). Evidently, the difference cannot be attributed to different locations of the counterion, and thus, the greater proportion of III in the crossover product presumably results from capture of the classical [3.2.1] carbonium ion. According to this interpretation about half of the III-OAc in the acetolysis product of I-OTs is derived from the classical intermediate; the rest of this isomer and all of the [2.2.2] isomer are derived from IVa. In the more nucleophilic 80% acetone, a larger fraction of the classical intermediate is intercepted enroute. In this case about 80% of the III-OH derived from I-OTs results from capture of the classical intermediate.



IIa IIb IVb IVa

I III + V

There is evidence that the excess *exo*-[3.2.1] isomer associated with IIa → IVa leakage is derived from the chair (IIb) instead of the boat (IVb) conformer. Deamination of *exo*-2-norbornylcarbinylamine (IX-NH_2) presumably results in the initial formation of the boat classical ion IVb. In acetic acid this reaction gives a V-OAc/III-OAc ratio that is similar to that for acetolysis of III-OTs and V-OTs.[9] Evidently solvent capture of IVb in competition with IVb → IVa is not important enough to alter the V/III isomer ratio very much.

If IIb is the source of the excess *exo* isomer in the product from I-OTs, part of the *endo* isomer I must also be derived from this intermediate. There is evidence[8] that the *endo*/*exo* capture ratio for IIb may be as high as four in which case as much as 13% of the *endo* isomer I is derived from this intermediate. Involvement of classical species in reactions of the *endo* (II) and [2.2.2]–*exo*-[3.2.1] carbonium ion systems has been noted earlier.[8] This, and the absence of a large driving force for ionization of I, III, and V, indicate that the energy difference between the classical and nonclassical ions is not as large in these systems as in [2.2.1]bicyclic systems.

In connection with the preferred IIa → IVa direction for crossover it is of interest that preliminary equilibration studies show that under the conditions of the acetolysis experiments I-OAc has a lower ground-state free energy than III-OAc and V-OAc (the last two are very similar). Thus leakage is favored in the direction leading to the carbonium ion related to the less stable bicyclooctyl isomers. For acetolysis (49°) $\Delta F^{\ddagger}$ for capture and leakage is about 1.5 kcal for II and 3.5 kcal for IV. Unless the free-energy barrier for solvent capture is >2 kcal higher for II than for IV, which seems unlikely, IV has a lower free energy than II.

In conclusion, the present results suggest that ionization of I-OTs results largely or exclusively in direct formation of the symmetrical nonclassical carbonium ion II. The most important evidence is that the product from active I-OTs is completely racemic even though the asymmetric classical [3.2.1] ion IIb is capturable when present. It should also be noted that the *endo*/*exo* capture ratio is much higher than would be expected for the classical [3.2.1] ion in either conformation. Moreover, it is clear that the counterion location has no effect on the stereoselectivity of chemical capture. In fact, if the counterion had any effect, inversion (to give *exo* product), instead of retention, would be the expected result.[30]

Evidently III-OTs and V-OTs for the most part are converted directly to IVa. The important evidence here is that the first product-forming intermediate is common to both substrates. The stereoselectivity of chemical capture of the intermediate (essentially complete preservation of geometric configuration) also indicates that a bridged intermediate is involved.

Experimental Section

Materials. The Δ^4-cycloheptenylcarbinyl *p*-bromobenzenesulfonate (VI-OBs) and *endo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (I-OTs) used in the present work are described in the preceding paper. Bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (V-OTs), mp 54.3–55.8° (lit.[4a] 54.2–55.0°), and *exo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (III-OTs), mp 51.8–52.8° (lit.[4b] 51.0–52.6°), were prepared from isomerically homogeneous samples of the corre-

(27) H. L. Goering and U. Mayer, *J. Am. Chem. Soc.*, 86, 3753 (1964).

(28) This same hydrocarbon is present in the acetolysis product of XVI-OTs.[25b]

(29) Factors relating the chair (IIb) and boat (IVb) intermediates to IIa and IVa, respectively, include orbital geometries[8] and relative locations of nuclei bonded to the electron-deficient carbon atoms. In IIa, C_1–C_7 and C_2–C_3 are coplanar, which corresponds to the geometry of the chair conformer; the C_1–C_8 and C_2–C_3 bonds are coplanar in IVa, which corresponds to the geometry of the boat conformer.

(30) For examples in which solvolysis of secondary arylsulfonates results in partial or extensive inversion of configuration see: R. A. Sneen, *et al.*, *J. Am. Chem. Soc.*, 87, 292 (1965); 88, 2593 (1966); A. Streitwieser, *et al.*, *ibid.*, 87, 3682, 3686 (1965); and S. Winstein and N. J. Holness, *ibid.*, 77, 5562 (1955).

sponding alcohols by a previously described method.[4] The three bicyclooctyl acetates I-OAc, III-OAc, and V-OAc were prepared by heating the corresponding alcohols in freshly distilled acetic anhydride in the presence of anhydrous sodium acetate. The solvents were prepared as described in the preceding paper.

Product Studies. A. Acetolysis. In a typical experiment, a 10-ml portion of the reaction mixture was sealed in an ampoule and heated at the desired temperature for ten half lives—acetolysis rate constants for I-OTs,[14] III-OTs,[4b] and V-OTs[4b] were reported earlier and that for VI-OBs is reported in this paper. The substrate concentration was about 0.025 *M*. After cooling, the reaction mixture was diluted with 80 ml of water and extracted with freshly distilled pentane in a continuous extractor for 24 hr. The organic extract was washed with 5% aqueous potassium carbonate, dried ($MgSO_4$), and concentrated to about 1 ml by careful fractionation. The concentrated acetate mixture was analyzed by capillary gas chromatography (gc) as described below. In a control experiment it was shown that when a C-8 hydrocarbon (*m*-xylene) is added at the outset, it is recovered without loss. This suggests that little, if any, olefin is lost during extraction and concentration of the pentane extract.

The gc peaks for the [2.2.2] and *exo*-[3.2.1] acetates V-OAc and III-OAc overlapped when appreciable amounts of these isomers were present. For this reason the relative amounts of these isomers in the products derived from III-OTs and V-OTs could not be determined by analysis of the acetates. In these cases, after analysis of the concentrated pentane extract to determine the olefin composition and relative amounts of acetate and olefin, the pentane was removed and replaced with 5 ml of 1.5 *M* methanolic potassium hydroxide. After refluxing for about 2 hr, the solution was diluted with about 40 ml of water and continuously extracted with pentane for 24 hr. The extract was dried ($MgSO_4$) and concentrated to about 1 ml by distillation, and the alcohol composition was determined by gc.

Product compositions for acetolysis of I-OTs, III-OTs, V-OTs, and VI-OBs are given in Tables I and II. Control experiments with mixtures of acetates of known composition showed that the isolation procedure (*i.e.*, extraction and concentration of the pentane extract) and hydrolysis of the acetate fraction do not result in fractionation of the isomers. Duplicate experiments showed that compositions are reproducible to within about 0.5 percentage unit for each component. Control experiments showing that the products are stable under the conditions of the product studies are presented in the preceding paper.

B. Hydrolysis in Aqueous Acetone. In these experiments, 10-ml portions of reaction mixtures were sealed in ampoules and heated for ten half-periods. The substrate concentrations were about 0.025 *M*, and a slight excess of pyridine was added to neutralize the acid produced by solvolysis. The contents of the ampoules were transferred to a 100-ml flask and allowed to evaporate under an air jet until crystallization began. The resulting mixture was diluted with 90 ml of water and continuously extracted with pentane for 24 hr. The extract was cooled, washed with cold 2% hydrochloric acid to remove the pyridine and then with saturated potassium carbonate, and dried ($MgSO_4$). The extract was concentrated to about 1 ml and analyzed by gc.

A control experiment that shows (a) the components in the product are stable under the conditions of the solvolysis and isolation, and (b) the isolation procedure does not result in isomeric fractionation, is described in the preceding paper.

The products resulting from 10% solvolysis of III-OTs and V-OTs in 80% acetone at 48.86° (Table II) were determined as follows. The time required for 10% solvolysis of V-OTs (20 min) was determined from the rate constant.[4b] That for 10% solvolysis of III-OTs was estimated to be 33 min—this estimate is based on the assumption that the relative rates of solvolysis of III-OTs and V-OTs in 80% acetone is the same as in acetic acid.[4b]

Reaction mixtures were prepared by dissolving about 0.73 mmol of substrate and 0.414 mmol of pyridine in 10 ml of preheated (48.86°) 80% acetone. The solutions were maintained at 48.86° for the indicated periods after which the reactions were quenched by chilling in an ice bath. The chilled solutions were concentrated under an air jet until crystallization began and then rapidly extracted thoroughly with ether—solutions were kept cold to avoid reaction of the unsolvolyzed *p*-toluenesulfonate. After drying ($MgSO_4$) the ether extract was evaporated to near dryness under reduced pressure, and the volatile components were vacuum transferred at room temperature (0.1 mm). The vacuum-transferred fraction was taken up in ether and washed with cold 2% hydrochloric acid and saturated potassium carbonate. The dried ($MgSO_4$) ethereal solution was concentrated to about 1 ml and analyzed by gc.

The following control experiment was carried out to determine if the unsolvolyzed ester is converted to product after the reaction is quenched. A solution of 97.8 mg (0.348 mmol) of V-OTs, 13.1 mg (0.104 mmol) of V-OH, and 25.8 mg (0.328 mmol) of pyridine in 10 ml of cold 80% aqueous acetone was prepared and treated in the manner described above for the quenched reaction mixtures. The recovered V-OH was found to contain 0.7% III-OH which shows that any product formed from the unsolvolyzed ester after quenching is negligible.

Product Analysis by Gas Chromatography. Capillary columns and flame ionization detection were used and components were identified by comparison of their retention times with those of authentic samples. In these comparisons peaks were superimposed. Compositions were determined from integrations of peak areas. Acetates were analyzed using 150- and 300-ft stainless steel columns coated with Ucon Polar (LB-550-X). The operating temperature was about 150° for the 300-ft column and about 90° for the 150-ft column. The retention times (minutes) with the 150-ft column at 91° were: XVI-OAc, 29.8; V-OAc, 31.0; III-OAc, 31.6; I-OAc, 32.0. These columns are satisfactory for analysis of the acetolysis product of I-OTs but not for the products derived from III-OTs and V-OTs because of overlap of the V-OAc and III-OAc peaks when these isomers are present in large amounts.

Olefin compositions were determined with a 300-ft Ucon Polar column and an operating temperature of 91°. The following retention times (minutes) were observed: bicyclo[3.2.1]oct-6-ene,[25] 22.6; bicyclo[2.2.2]octene,[4a] 23.8; bicyclo[3.2.1]oct-2-ene,[27] 24.6; unidentified hydrocarbon thought to be tricyclo[2.2.2.$0^{2,6}$]octane, 28.6.

Alcohols were analyzed with a 150-ft column coated with TCEP at an operating temperature of 90–100°. The bicyclic alcohols I-OH, III-OH, and V-OH were nearly completely resolved. Retention times (minutes) at 90° were: III-OH, 22; V-OH, 24; I-OH, 25.