Ionic Reactions in Bicyclic Systems. V. Solvolysis of *endo*-Bicyclo[3.2.1]octan-2-yl (Equatorial) *p*-Toluenesulfonate[1,2]

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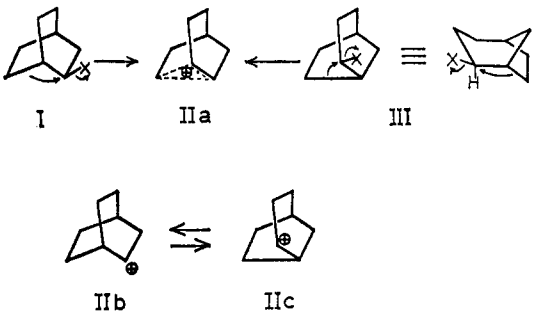
Abstract: Acetolysis and hydrolysis (80% acetone) of *endo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (IV-OTs) are accompanied by ion-pair return which results in interconversion of enantiomers of the unsolvolyzed ester; the polarimetric rate constants (k_α) are larger than the titrimetric constants (k_t) by factors of >5 for acetolysis and >3 for solvolysis in 80% acetone. The first-order rate of solvolysis is steady which shows that racemization of the unsolvolyzed ester (ion-pair return) is not accompanied by other structural changes. Acetolysis products derived from optically active IV-OTs, mainly the corresponding *endo*-acetate (IV-OAc) with small amounts of the [2.2.2] and *exo*-[3.2.1] isomers (I-OAc and III-OAc), are apparently completely racemic. These results are consistent with the view that ionization (IV; arrows) gives the symmetrical nonclassical ion Va. The small amounts of racemic I-OAc and III-OAc in the product are thought to result from isomerization (leakage) of Va to the carbonium ion system related to I and III. Addition of lithium perchlorate does not result in a special salt effect; only the normal linear pattern is observed for both the polarimetric and titrimetric rates. This indicates that ion-pair return associated with solvolysis is largely or exclusively internal return.

This is the first of a group of three papers dealing with the nature of carbonium ion intermediates involved in solvolytic reactions of the epimeric bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonates (III-OTs and IV-OTs) and bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (I-OTs). The work reported in this paper involves a kinetic and stereochemical investigation of acetolysis and hydrolysis (aqueous acetone) of the *endo*(equatorial)-[3.2.1] isomer IV-OTs.

In an earlier investigation[4,5] it was shown that the [2.2.2] and *exo*(axial)-[3.2.1]bicyclooctyl isomers (I and III) are related to the same carbonium ion system. Ion-pair return results in stereospecific interconversion of I-OTs and III-OTs and the solvolysis product is a binary mixture of [2.2.2] and *exo*-[3.2.1] isomers[4,6] containing none (aqueous acetone) or <1% (acetolysis) of the *endo*-[3.2.1] isomer,[7] *i.e.*, geometric configuration is preserved. As will be shown in the following paper, the isomeric *p*-toluenesulfonates give products having the same composition.

In the earlier papers[4,5] evidence was presented that the carbonium ion system relating the [2.2.2] and *exo*-[3.2.1] isomers (I and III) involves a bridged nonclassical ion IIa instead of a rapidly[8] equilibrating mixture of the corresponding classical ions (IIb ⇌ IIc)—the rates of both isomers appear to be accelerated[5,9] and geometric configuration is preserved.[4,6,7] Recent investigations of (a) ring expansion[10,11] and π[12] routes to this carbonium ion system and (b) solvolysis of optically active I-OBs[6b] have provided additional information supporting this view. Evidence bearing on this point is discussed in the accompanying papers[7,13] in which we present the results of our stereochemical investigations of the *exo*-[3.2.1]–[2.2.2] system.



Our earlier cursory investigation of the *endo*(equatorial)-bicyclo[3.2.1]octan-2-yl system IV[4,5] showed that acetolysis of IV-OTs gives mainly IV-OAc; the infrared spectrum of the alcohol derived from the acetate did not reveal the presence of contaminants.[4] From this it is clear that the epimeric bicyclo[3.2.1]octan-2-yl isomers (III and IV) are related to different carbonium ion systems. In the following paper it will be shown that for each of these systems the presence and location of the counterion have little effect on product distributions. This means that the difference is not due to ion-pair phenomena and thus must be in the structures of the carbonium ions. To account for the stereospecificity of solvolysis and the insulation between the carbonium ion systems it was suggested that IV may give rise to a symmetrical bridged nonclassical ion Va instead of the corresponding classical

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

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

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

(5) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961).

(6) (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).

(7) H. L. Goering and G. N. Fickes, *J. Am. Chem. Soc.*, **90**, 2856 (1968).

(8) This alternative interpretation would require that equilibration be rapid relative to solvent capture to account for the similar product distributions for the two isomers.[7]

(9) (a) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854, 1856 (1964); (b) C. S. Foote, *ibid.*, **86**, 1853 (1964).

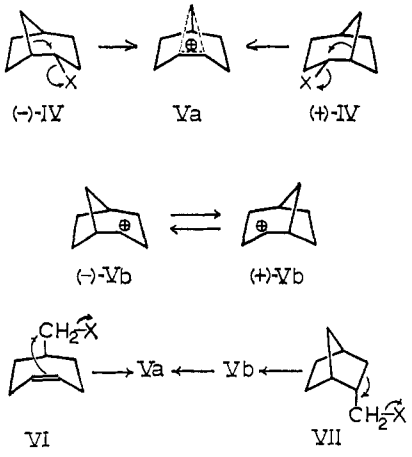
(10) (a) J. A. Berson and D. Willner, *ibid.*, **86**, 609 (1964); (b) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **86**, 595 (1964).

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

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

(13) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2862 (1968).

ion Vb. LeNy[14] has generated this carbonium ion system from Δ^4-cycloheptenylmethyl *p*-bromobenzenesulfonate (VI-OTs) by the π route and has proposed the nonclassical structure Va for reasons similar to ours. Recently Berson and Reynolds-Warnhoff[10b] have found that ring expansion of the *endo*-2-norbornylcarbinyl system VII leads to this carbonium ion and have provided convincing evidence that a symmetrical bridged intermediate is involved. In the latter case ionization (VII; arrows) cannot result in the direct formation of Va for stereoelectronic reasons and presumably gives the asymmetric classical [3.2.1] carbonium ion Vb which subsequently is converted to Va.[10]



From the symmetry properties of the *endo*-[3.2.1] system IV, it is apparent that if ionization results in direct formation of the nonclassical ion Va, active substrate will give racemic product. In this case ion-pair return results in racemization of the substrate with preservation of geometric configuration (*i.e.*, a stereospecific isomeric Wagner–Meerwein rearrangement). Solvolysis would also be expected to proceed with preservation of geometric configuration unless the initially formed symmetrical bridged ion undergoes structural change in competition with solvent capture.

Several systems having these symmetry properties have been investigated including the *exo*-norbornyl,[15a] *threo*-3-phenyl-2-butyl,[15b,c] *threo*-3-*p*-anisyl-2-butyl,[15d] *trans*-2-acetoxycyclohexyl,[15e] and several allylic systems.[16] In each of these cases enantiomers give a common carbonium ion, and in all but one, the *trans*-2-acetoxycyclohexyl system,[15e] solvolysis is accompanied by ion-pair return which results in a larger first-order rate of loss of optical activity (polarimetric rate) than of solvolysis (titrimetric rate). In the present work we have used kinetic and stereochemical techniques, similar to those used earlier,[15,16] to investigate ion-pair return and the symmetry properties of the intermediate involved in solvolysis of IV-OTs. Polarimetric (k_α; eq 1) and titrimetric (k_t; eq 2) first-order rate constants for acetolysis and hydrolysis (80% acetone) have been determined and salt effects have been investigated. In addition, solvolysis products have been reexamined using an analytical method (capillary gas chromatography) superior to that used in the earlier work (infrared analysis).[4]

$$\text{(active) IV-OTs} \xrightarrow{k_\alpha} \text{(inactive) products} \quad (1)$$

$$\text{IV-OTs} \xrightarrow{k_t} \text{products} + \text{HOTs} \quad (2)$$

Results and Discussion

The *endo*-bicyclo[3.2.1]octan-2-yl system IV was prepared by the method of LeNy[14] which involves solvolysis of Δ^4-cycloheptenylmethyl *p*-bromobenzenesulfonate (VI-OBs). Acetolysis of VI-OBs at 60° in the presence of sodium acetate gave IV-OAc containing 3% of the [2.2.2] isomer (I-OAc) and 3.4% of the *exo*-[3.2.1] isomer (III-OAc); at 80° the composition is slightly different (3.5% I-OAc and 4.1% III-OAc).[17] The alcohol obtained by saponification had the same isomeric composition as the acetate. Solvolysis of VI-OBs in 80% aqueous acetone[18] (50°) gave *endo*-[3.2.1] alcohol (IV-OH) containing 1.1% I-OH, 1.4% III-OH, and 1% of the uncyclized alcohol VI-OH.

The *endo*-*p*-toluenesulfonate IV-OTs used in the titrimetric experiments was derived from IV-OH containing about 6% of the isomers. After several recrystallizations, this material still contained small amounts of I-OTs and III-OTs which resulted in a downward drift in the first-order rate of acetolysis during early stages of the reaction—good first-order behavior was observed after 10% solvolysis. From the rate constant for acetolysis of the I-OTs $\rightleftharpoons$ III-OTs equilibrium mixture[5] it can be determined that during the time required for 10% acetolysis of IV-OTs, about 85% of the contaminants are consumed. This reduces contamination to a level that does not cause a detectable disturbance. Pure IV-OTs was obtained by selective solvolysis of the more reactive isomers. Acetolysis at 49° for 24 hr results in 25% solvolysis of IV-OTs and 99% solvolysis of the I-OTs–III-OTs mixture.[5] The unsolvolyzed ester recovered after this treatment (65%) was shown to be pure IV-OTs by its kinetic behavior and infrared spectrum.

The *endo*-bicyclo[3.2.1]octan-2-yl system IV was resolved by recrystallization of the brucine salt of the acid phthalate derivative as described earlier.[6a] Resolution of *endo*-[3.2.1] acid phthalate IV-AP containing 1.3% of the isomeric acid phthalates[19] led to (−)-*endo* alcohol (−)-IV-OH, $[\alpha]^{25}D$ −19.2°,[20] which contained only trace amounts of the isomers. This alcohol gave (−)-IV-OTs, $[\alpha]^{25}D$ −27.4°, which was used in some of the polarimetric studies.

A second resolution of acid phthalate derived from IV-OH containing 6% of the isomers I-OH and III-OH provided samples of (−)-IV-OH and (+)-IV-OH (from work-up of mother liquors). The (−)-IV-OH, $[\alpha]^{25}D$ −12.6°, contained 1.5% I-OH and 0.5% III-OH and gave a *p*-toluenesulfonate derivative having $[\alpha]^{25}D$ −15.9°. The (+)-IV-OH, $[\alpha]^{25}D$ +18.9°, was contaminated with 4.4% I-OH and 9.3% III-OH and gave a *p*-toluenesulfonate derivative having $[\alpha]^{25}D$

(14) G. LeNy, *Compt. Rend.*, **251**, 1526 (1960).
(15) (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952); (b) D. J. Cram, *ibid.*, **74**, 2129 (1952); (c) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (d) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); (e) S. Winstein and D. Heck, *ibid.*, **74**, 5584 (1952).
(16) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964), and earlier papers in that series.
(17) All of the product compositions were determined by capillary gas chromatography; see following paper for experimental details.
(18) Composition based on volumes of pure components (25°) prior to mixing.
(19) Composition determined by analysis[17] of alcohol obtained by saponification.
(20) Except as noted, specific rotations are for chloroform solutions.

Table I. Titrimetric First-Order Rates of Solvolysis of *endo*-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (IV-OTs)

Run	Temp, °C	[ROTs], 10^2M	[Salt], 10^2M	10^5k_t, sec^{-1}	% inc in k_t per 0.01 M reaction
			A. Acetolysis		
1[a]	49.03	2.48	None	0.305	
2	48.86	4.67	None	0.300	2.3
3	48.86	4.51	5.01 NaOAc	0.322 ± 0.004	0
4	48.86	4.21	10.0 NaOAc	0.339 ± 0.002	0
5	48.86	4.52	10.0 NaOAc	0.339 ± 0.01	0
6	48.86	3.57	0.100 $LiClO_4$	0.319	6.3
7	48.86	3.59	0.502 $LiClO_4$	0.390	14
8	48.86	2.3	1.00 $LiClO_4$	0.487 ± 0.003[b]	16
9	48.86	2.3	3.00 $LiClO_4$	0.754 ± 0.009[c]	24
10	48.86	2.3	5.00 $LiClO_4$	1.04 ± 0.017[b]	25
11	48.86	2.3	6.00 $LiClO_4$	1.24 ± 0.014[b]	22
12	48.86	2.3	10.00 $LiClO_4$	2.01 ± 0.017[b]	18
13	48.86	2.4	10.00 $LiClO_4$ 2.4 HOTs[d]	3.21	4.1
14	79.28	4.66	None	11.6	3.7
		$\Delta H^{\ddagger}$ = 27.1 ± 0.2 kcal/mol; $\Delta S^{\ddagger}$ = 0.2 ± 0.8 eu (48.86°)[e]			
			B. 80% Acetone[18]		
15	48.86	4.70	None	0.307 ± 0.004	0
16[f]	48.86	2.9	None	0.291 ± 0.001[c]	0

[a] Data taken from ref 5. [b] Average value of three independent experiments. [c] Average value of two independent runs. [d] Acid provided by complete solvolysis of equivalent amount of IV-OTs. [e] Calculated from constants for runs 2 and 14; uncertainties calculated from estimated limiting values of the rate constants. [f] Solvent batch the same as used in the polarimetric run (run 25, Table II) but different from that used in run 15. These data provided by Mr. Richard Thies.

+21.2°. These samples of (−)-IV-OTs and (+)-IV-OTs were used in some of the polarimetric kinetic experiments. As has already been noted, disturbances due to contamination by the more reactive I and III isomers are avoided by taking the zero point after the reactive contaminants have been consumed.

An isotope dilution method[10a,16,21] (see Experimental Section) indicated that specific rotations of optically pure IV-AP and IV-OH are $[\alpha]^{22}D$ 30.5 ± 0.9° and $[\alpha]^{25}D$ 23.8 ± 0.7°, respectively. In this determination, uncertainties, in addition to those inherent in the method, result from the presence of the contaminating isomers. A correlation of (−)-IV-OH with (+)-III-OH[13] indicates the above values are a little too high and that the highest rotation observed for IV-OH, $[\alpha]^{25}D$ −22.1°, is a better value for the specific rotation.[20] This shows that the samples of active IV-OTs used in the polarimetric experiments were of high optical purity. A sample of 94% optically pure (−)-IV-OH, $[\alpha]^{25}D$ −20.8°, containing only traces of the isomers, was converted to the acetate derivative (IV-OAc) to establish the specific rotation of the latter. The acetate obtained had $[\alpha]^{25}D$ −41.1°,[20] and −39.1° (acetic acid). Thus, optically pure IV-OAc has $[\alpha]^{25}D$ 43.7 and 41.6° (acetic acid).

Results of the titrimetric experiments are summarized in Table I. In each experiment the reaction (eq 2) was followed to about 70% completion and five or six values of the integrated first-order constant (k_t) were determined from appropriately spaced titrations. Homogeneous samples of IV-OTs (purified by selective acetolysis) were used in most of these experiments. In these cases zero points were taken immediately after temperature equilibration. The same results were obtained with samples of IV-OTs purified by recrystallization (*i.e.*, contaminated with I-OTs and III-OTs) providing that zero points were taken after 10% solvolysis—this amounts to purification by selective acetolysis of the contaminants without isolation of the "purified" homogeneous substrate. In all cases, observed infinity titers (after about ten solvolytic half-lives) agreed well with the calculated values.

Excellent first-order behavior was observed for acetolysis in the presence of sodium acetate (runs 3–5) and for solvolysis in 80% aqueous acetone[18] (runs 15 and 16). The first-order rate constants in the table for these experiments are the averages (and average deviations) of the five or six determinations of k_t for each run.

The integrated first-order constants for acetolysis in the absence of sodium acetate showed a small, but reproducible, upward trend during the reaction, *e.g.*, in run 2 the value of k_t increased from 0.304×10^{-5} at 10% solvolysis to 0.322×10^{-5} at 72% solvolysis. This upward drift in the first-order rate was increased appreciably by the presence of lithium perchlorate. For these experiments the data were treated by an empirical method used by Winstein and coworkers for similar situations.[22] This method involves least-squares extrapolation of plots of the integrated first-order constants *vs.* per cent reaction to 0% reaction. The constants in the table for these experiments are initial or extrapolated values obtained in this manner. These constants were reproducible and most of the values in the table are averages (and average deviations) of two or three independent determinations. Magnitudes of the upward drifts, expressed as per cent increase in the integrated rate constant per 0.01 M reaction, are included in the table.

The good first-order behavior for acetolysis in the presence of sodium acetate (no accumulation of *p*-toluenesulfonic acid) shows that the upward drift in the first-order rate observed in the other acetolysis

(21) Note that eq 2 in ref 10a is in error; see J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, **86**, 5710 (1964).

(22) (a) A. H. Fainberg, G. C. Robinson, and S. Winstein, *ibid.*, **78**, 2777 (1956); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2780 (1956).

experiments is not a result of isomerization of the substrate to a more reactive isomer.[23] Evidently this results from a positive salt effect of the accumulating *p*-toluenesulfonic acid.[22,24]

Addition of lithium perchlorate results in two effects. (a) The value of the initial rate constant (k_t) is increased (positive salt effect), and (b) the magnitude of the upward drift of the first-order rate during solvolysis is increased (synergistic effect of lithium perchlorate and accumulating *p*-toluenesulfonic acid). Similar behavior has been observed by Winstein and coworkers for acetolysis of several alkyl arylsulfonates.[22] This behavior, however, is not general—in some cases steady first-order rates of acetolysis are observed with and without added lithium perchlorate.[22,24,25] As shown by the final column of Table I the rate of the upward drift (not to be confused with the rate of acetolysis) increases with lithium perchlorate concentration up to about 0.03 *M* and then levels off and diminishes at higher salt concentrations, *i.e.*, the synergistic effect is largest at low salt concentrations. Similar behavior has been observed for acetolysis of cyclohexyl *p*-toluenesulfonate;[22b] however, the drifts are about twice as large in the present case.

For acetolysis in the presence of lithium perchlorate (runs 6–12) the upward drift seemed to slacken at later stages of the reaction which suggested that the synergistic effect is most pronounced at very low acid concentrations. This was confirmed by an experiment (run 13) in which 0.024 *M* *p*-toluenesulfonic acid as well as 0.1 *M* lithium perchlorate was present at the outset.[26] In this case the drift was less than one-fourth as large as when acid was not initially present; *cf.* runs 12 and 13. This shows that salt effects of lithium perchlorate and *p*-toluenesulfonic acid tend to become additive at higher acid concentrations.

A plot of the titrimetric constants (k_t) *vs.* sodium acetate concentration is linear over the range of concentrations investigated. Thus the data are correlated by the Winstein equation (3).[24] The magnitude of b_t

$$k_t = k_t^0[1 + b_t(\text{salt})] \qquad (3)$$

for this salt is 1.3, which is comparable to that observed with several other substrates.[22b,24]

The data for acetolysis in the presence of lithium perchlorate are also correlated by eq 3 for salt concentrations up to 0.06 *M*—the value of k_t for 0.1 *M* salt falls above the line. This plot is included in Figure 1 in which lithium perchlorate salt effects on the polarimetric (k_α) and titrimetric (k_t) constants are compared. This behavior, including the deviation from linearity at high salt concentrations, has also been observed with other substrates.[22b,24] The value of b_t is 53 which is somewhat higher than that generally observed (10–40)[22,24] for lithium perchlorate salt effects. However, this value is in good agreement with

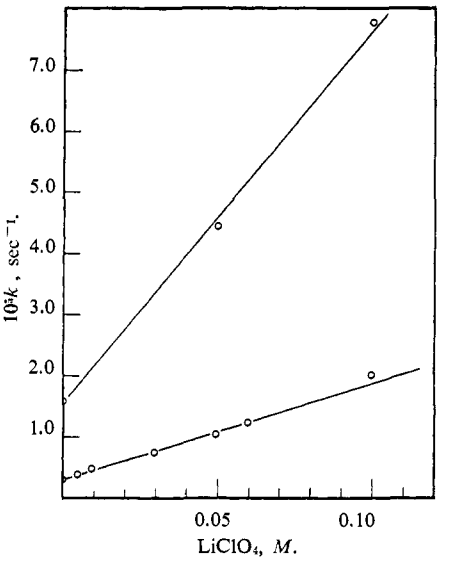


Figure 1. Effect of lithium perchlorate on k_α (upper line) and k_t (lower line) for acetolysis (48.86°) of *endo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (IV-OTs).

that for acetolysis (25°) of norbornyl *p*-bromobenzenesulfonate (b_t = 38)[22b] if a correction is made for difference in leaving groups—salt effects are usually about one-third larger for *p*-toluenesulfonates than for the corresponding *p*-bromobenzensulfonates.[22b] From the linear relationship between k_t and lithium perchlorate concentration (Figure 1) it is apparent that only a "normal" salt effect is involved, *i.e.*, there is no indication of a "special" salt effect.[22]

Kinetic data for the polarimetric experiments are presented in Table II. In these experiments solutions of optically active IV-OTs were thermostated in a specially constructed, all-glass, jacketed, 4-dm polarimeter tube and rotations were determined at appropriate intervals. The total observed change in rotation during a run was 1–2° and in all cases solvolysis resulted in complete loss of optical activity. Reactions (eq 1) were followed to 65–85% completion and excellent first-order behavior was observed for acetolysis (with and without added sodium acetate; runs 17–20) and hydrolysis in 80% acetone[18] (run 25). For these experiments the value of k_α in the table is the average (and average deviation) of 10 to 14 individual determinations for each run. The integrated constants (k_α) for acetolysis in the presence of lithium perchlorate (runs 21–23) showed upward drifts similar to, but smaller (percentagewise) than, those observed in the titrimetric experiments. In these cases the constants given in the table are initial values obtained by least-squares extrapolation of the 20 or so values of the integrated constant to 0% reaction. The magnitudes of the upward drifts in k_α are given in the last column of the table.

The sodium acetate and lithium perchlorate salt effects on the polarimetric rates are similar in many respects to those on the titrimetric rates. Lithium perchlorate results in an increase in k_α (initial values) and in an upward drift in the integrated constant during the reaction. The magnitude of this upward trend is reduced as acid concentration increases and becomes negligible at an acid concentration of about

(23) For examples where upward or downward drifts of solvolytic rates result from isomeric isomerization of the substrate (ion-pair return) see S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **73**, 1958 (1951); **74**, 2171 (1952); 77, 3054 (1955); 80, 459 (1958); S. J. Cristol and D. D. Tanner, *ibid.*, **86**, 3122 (1964); J. Meinwald and P. G. Gassman, *ibid.*, **85**, 57 (1963); K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, 30, 2278 (1965); and ref 5.

(24) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

(25) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956).

(26) The initial acid was provided by solvolysis of an equivalent amount of IV-OTs.

Table II. Polarimetric First-Order Rates of Solvolysis of *endo*-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (IV-OTs)

Run	Temp, °C	[ROTs], 10^2M	[Salt], 10^2M	10^5k_α sec^{-1}	% inc in k_α per 0.01 M reaction
			A. Acetolysis		
17	30.08	5.75	None	0.118 ± 0.005	0
18	48.86	5.70	None	1.56 ± 0.009	0
19	48.86	4.93	5.56 NaOAc	1.79 ± 0.02	0
20	48.86	8.82	11.4 NaOAc	1.80 ± 0.02	0
21	48.86	5.03	5.00 $LiClO_4$	4.44	6.9
22	48.86	5.05	10.00 $LiClO_4$	7.76	8.6
23	48.86	5.00	10.00 $LiClO_4$ 2.4 HOTs[a]	10.1	2.3
24	48.86	3.75	10.00 $LiClO_4$ 4.5 HOTs[a]	11.5 ± 0.1	0
			$\Delta H^\ddagger$ = 26.7 ± 0.1 kcal/mol; $\Delta S^\ddagger$ = −2.5 ± 0.3 eu (48.86°)[b]		
			B. 80% Acetone[18]		
25[c]	48.86	2.0	None	0.901 ± 0.008[d]	

[a] Acid provided by complete solvolysis of an equivalent amount of IV-OTs. [b] Calculated from constants for runs 17 and 18; uncertainties determined from estimated limiting values of the constants. [c] Same solvent batch as for titrimetric run 16; these determinations made by Mr. Richard Thies. [d] Average value of two independent kinetic experiments.

0.04 M (*cf.* runs 22–24). The increase in k_α (initial values) is linear with lithium perchlorate concentration and b_α (which corresponds to b_t in eq 3) is 39; for acetolysis (25°) of active *threo*-3-*p*-anisyl-2-butyl *p*-toluenesulfonate b_α = 17.[15d] A plot of k_α *vs.* lithium perchlorate concentration is included in Figure 1. Addition of sodium acetate results in only a small positive salt effect and the increase in k_α is not linear with salt concentration—rates of acetolysis in the presence of 0.05 and 0.1 M sodium acetate are indistinguishable (*cf.* runs 19 and 20).

Comparison of k_α and k_t shows that in all cases $k_\alpha > k_t$. For acetolysis (49°) k_α/k_t = 5.2 and this ratio is increased slightly by the presence of sodium acetate. The k_α/k_t ratio for 80% acetone is 3.1. It is significant that under these conditions k_α and k_t are constant throughout the reaction because this shows that the excess loss of activity is due to a first-order intramolecula; racemization of the substrate during solvolysis (eq 4).[15,16] The difference between the polarimetric and titrimetric constants corresponds to the first-order constant for racemization, *i.e.*, $k_\alpha - k_t = k_{rac}$.[15,16] The steady titrimetric rate identifies the unsolvolyzed ester as IV-OTs throughout the reaction and shows that racemization is not accompanied by other structural changes—isomerization to the more reactive [2.2.2] and *exo*-[3.2.1] isomers (I-OTs and III-OTs) would result in an upward drift in k_t. This is also shown by the fact that ester isolated after 25% acetolysis (>70% racemization) is pure IV-OTs (isomers, if present, would not be separated by fractionation).

$$\text{(active) IV-OTs} \xrightarrow{k_{rac}} \text{(racemic) IV-OTs} \qquad (4)$$

Data for the polarimetric and titrimetric experiments are compared in Table III. This table includes k_α/k_t ratios, rate constants for racemization (k_{rac}), and relative magnitudes of k_{rac}, k_α, and k_t for various conditions. These data show that salt effects are similar for all three processes. This is also shown by Figure 1. The linear increase in k_α is greater than that of k_t and thus the gap between them (k_{rac}) also increases linearly with lithium perchlorate concentration—the reason $b_\alpha < b_t$ is that k_α increases less percentagewise than k_t. As has been pointed out,[15,16] such behavior is indicative of a common rate-determining step (ionization) for the three processes.

Table III. Summary of Solvent and Salt Effects on Polarimetric (k_α), Titrimetric (k_t), and Racemization (k_{rac}) Rate Constants for Solvolysis of *endo*-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (IV-OTs) at 48.86°

Runs[a]	[Salt], 10^2M	k_α/k_t	10^5k_{rac},[b] sec^{-1}	Rel rates[c] k_α	k_t	k_{rac}
			A. Acetolysis			
2 and 18[d]	None	5.2	1.26	1	1	1
3 and 19[e]	5 NaOAc	5.6	1.47	1.15	1.07	1.17
5 and 20[e]	10 NaOAc	5.3	1.46	1.15	1.13	1.16
10 and 21[f]	5 $LiClO_4$	4.3	3.40	2.8	3.5	2.7
12 and 22[f]	10 $LiClO_4$	3.9	5.75	5.0	6.7	4.5
13 and 23[f]	10 $LiClO_4$ 2.4 HOTs	3.1	6.9	6.5	10.7	5.5
			B. 80% Acetone[18]			
16 and 25[e]	None	3.1	0.610	0.58	0.97	0.48

[a] Data for each row computed from values of k_α and k_t obtained from indicated experiments. [b] $k_{rac} = k_\alpha - k_t$. [c] Values of k_α, k_t, and k_{rac} relative to those for acetolysis in the absence of salt. [d] Initial value of k_t obtained by extrapolation used in the calculations. [e] Both polarimetric and titrimetric first-order rates steady throughout the reaction. [f] Initial values of k_α and k_t used in the calculations.

The present results parallel those of related investigations[15,16,27] and are accommodated by the Winstein solvolysis scheme[27] which involves ion-pair intermediates. According to this interpretation racemization associated with solvolysis of IV-OTs results from internal return as illustrated in Chart I and summarized by eq 5. Providing that ionization results in

$$\text{R—OTs} \underset{k_1}{\overset{k_\alpha}{\rightleftharpoons}} [\text{R}^+\text{OTs}^-] \xrightarrow{k_2} \text{products} \qquad (5)$$

direct formation of a symmetrical intimate ion pair—this is indicated by the failure to detect capturable asymmetric intermediates—k_α corresponds to the rate of ionization and k_{rac} is the rate constant for ion-pair return. The relationships between k_t and k_{rac} and the constants in the scheme (and eq 5) are

$$k_t = k_\alpha k_2/(k_1 + k_2) \qquad (6)$$

$$k_{rac} = k_\alpha k_1/(k_1 + k_2) \qquad (7)$$

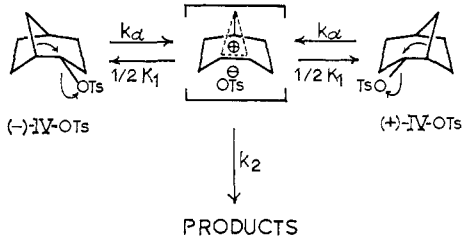
(27) S. Winstein, P. E. Klinedist, Jr., and G. C. Robinson, *J. Am. Chem. Soc.*, **83**, 885 (1961), and earlier papers in that series.

Rearrangement of eq 6 gives

$$k_\alpha/k_t = (k_1/k_2) + 1 \qquad (8)$$

which shows the relationship between the observed k_α/k_t ratios and k_1/k_2 (partitioning of the intermediate). From the data in Table III it is apparent that $k_1 > k_2$ for all conditions investigated.

Chart I



Presumably a so-called solvent-separated ion pair[27] (not included in Chart I or eq 5) is involved in the product-forming step—for reasons given elsewhere,[15d] in systems of this type there is probably little, if any, direct conversion of the intimate ion pair to solvolysis product. It has been shown[27] that in some cases ion-pair return involves return from the solvent-separated ion pair (external ion-pair return) in addition to that from the intimate ion pair (internal return). In such cases the addition of lithium perchlorate results in a "special" salt effect[22]—presumably the salt intercepts that fraction of the solvent-separated ion pair which otherwise would return to substrate.[15d,27] However, if only internal return is involved only a "normal" linear positive salt effect is observed, *i.e.*, lithium perchlorate has a positive salt effect on the rate of ionization and only a small effect on partitioning of the intimate ion-pair intermediates.[15d,22]

From Figure 1 it is apparent that addition of lithium perchlorate results in only a "normal" salt effect on the rate of acetolysis. Thus, according to this criterion, the observed ion-pair return is largely, if not exclusively, internal return as indicated in Chart I. It is interesting to note that this behavior parallels that of the *exo*-norbornyl system.[22b,28]

Comparison of the lithium perchlorate normal salt effects on the titrimetric (k_t) and polarimetric (k_α) rates of acetolysis (Table III and Figure 1) shows that lithium perchlorate increases the rate of ionization (k_α) and decreases internal return relative to solvolysis (k_1/k_2). From the k_α/k_t ratios it can be seen that k_1/k_2 (eq 8) decreases from 4.2 to 2.9 as lithium perchlorate concentration increases to 0.1 *M*. It is this reduction in internal return, relative to solvolysis, that causes k_t to be a little more sensitive than k_α to changes in salt concentration ($b_t = 53$; $b_\alpha = 39$). These results are qualitatively in accord with those reported for the *threo*-3-*p*-anisyl-2-butyl system[15d] and with earlier observations that internal return tends to decrease with increasing polarity of the medium.[15,16] It should also be noted that the upward drifts in k_α and k_t, which occur throughout the acetolysis when lithium perchlorate is present, show similar dependencies on salt concentrations and again k_t is more sensitive than k_α. This suggests that the synergistic salt effect of lithium perchlorate and accumulating *p*-toluenesulfonic acid responsible for these drifts also involves an increase in the rate of ionization and a decrease in the k_1/k_2 ratio as the reaction progresses.

Under the conditions of the kinetic experiments acetolysis of IV-OTs in the presence of 0.05 *M* sodium acetate gives 89.4% IV-OAc, 6.6% of the *exo*(axial)-[3.2.1] isomer III-OAc, and 4% of the [2.2.2] isomer I-OAc[7]—the latter two isomers were not detected by the analytical method (infrared analysis) used in the earlier work.[4] Solvolysis in 80% acetone in the presence of a slight excess of pyridine gives 94.9% IV-OH, 4.1% III-OH, and 1.0% I-OH; detectable amounts of olefin are not formed in either case.[7] Control experiments confirmed the earlier observation[4] that under these conditions products are not isomerized.

As has already been mentioned, solvolysis of active IV-OTs results in first-order loss of optical activity and solutions after ten half-periods do not have detectable rotations (±0.003°). The acetolysis was examined more carefully than hydrolysis (80% acetone) and control experiments showed that under conditions of the polarimetric experiments (with and without added sodium acetate) the resulting acetates are optically stable. To determine the maximum rotation that would obtain if acetolysis proceeded with preservation of optical configuration, account must be taken of that fraction of the substrate that racemizes (internal return) prior to solvolysis. It can be shown[15a] that the fraction of the product derived from active substrate corresponds to k_t/k_α which for acetolysis is 0.19, or to put it another way, the average optical purity of the unsolvolyzed ester is 19% of the original value. From this it can be seen that the maximum optical purity of the product (complete preservation of optical configuration) is 19% of that of the substrate. From the relative rotations it can be determined that if the product were 19% as optically pure as the substrate the final rotations would have been as high as 0.4°. In fact, the observed rotation was 0 ± 0.003° in every experiment which means that the intermediate derived from active substrate gives solvolysis products which are at least 99% racemic. As has been mentioned, this suggests that the internal return product is likewise completely racemic.

The results show that (a) ionization gives a symmetrical carbonium ion system (capturable intervening asymmetric species are not detected) and (b) products are derived from this intermediate (by internal return and solvolysis) with nearly complete preservation of geometric configuration. With regard to the latter point, note that for acetolysis 80% of the initially formed product results from internal return (complete preservation of geometric configuration) and 20% from solvolysis, *i.e.*, $k_1/k_2 \approx 4$. Thus the 10% of the solvolysis products in which configuration is lost represents only 2% of the total initial product derived from the intermediate. The situation is similar for solvolysis in 80% acetone. In this case solvolysis products represent 33% of the initial product ($k_1/k_2 = 2$) and the 5% of the solvolysis products in which configuration is lost is <2% of the total. Thus in both cases about 98% of the initial product derived from the intermediate has the *endo*(equatorial) configuration.

(28) S. Winstein and E. Clippinger, *J. Am. Chem. Soc.*, 78, 2784 (1956).

The proposal[4,5] that ionization of IV-OTs results largely or exclusively in direct formation of the symmetrical nonclassical ion Va, as illustrated in Chart I, provides a simple and straightforward interpretation of these results. The partial loss of geometric configuration in the product-forming step(s) can be accounted for in terms of isomerization (leakage) of the initially formed symmetrical ion to the bridged ion IIa related to the [2.2.2]-*exo*-[3.2.1] system. As will be discussed in more detail in the following paper, it seems likely that the pathway for leakage is Va → Vb → IIc → IIa. In this connection it is significant that anchimeric acceleration is small at best.[5,9a,29] This suggests[9a] that the energy difference for the nonclassical Va and classical Vb ions is small relative to cases where large driving forces are observed and thus isomerization *via* the classical intermediate, in competition with solvent capture, seems reasonable.[10a]

A rapidly equilibrating pair of classical carbonium ions has been proposed[31] as an alternate to the corresponding nonclassical structure for similar cases. This alternative interpretation, *i.e.*, (+)-Vb ⇌ (−)-Vb instead of Va, leads to several apparent difficulties including accounting for the observed symmetry properties and stereoselectivity of chemical capture of the intermediate. In this connection, it is pertinent that evidence has been presented that the classical [3.2.1] ion Vb (generated from *endo*-2-aminomethylnorbornane by the ring-expansion route) is intercepted in part in aqueous acetic acid and gives an *endo*/*exo* product ratio of 4 or less.[10b] In the present case there is no indication of capturable initially formed asymmetric species and the *endo*/*exo* product ratio is 23 for hydrolysis (80% acetone) and 13 for acetolysis. For the carbonium ion derived from the epimer, II-OTs, this ratio is ~0.01 for acetolysis and zero for hydrolysis.[7] Evidence that the location of the counterion, with respect to the *endo*-[3.2.1]carbonium ion V, has only a small effect on product distributions is presented in the following paper. Thus, the stereoselectivity cannot be attributed to ion-pair phenomena (as has been suggested for the [2.2.2]-*exo*-[3.2.1] system[32]) and must be a consequence of structural features of the carbonium ion itself. The bridged structure Va accounts for the stereoselectivity in an obvious way.

A corollary of the equilibrating classical ion hypothesis is that the partners are separated by an activation barrier. Evidently this barrier is assumed[31] to reflect the energy difference between the classical and nonclassical structures. As has been pointed out for a similar case,[33] failure to intercept initially formed asymmetric classical ions requires interconversion of the enantiomeric classical ions Vb at a frequency corresponding to little, if any, activation energy. It would be expected that the required reorganization of the solvation shell for such a process would result in a barrier large enough for solvent capture to compete with interconversion.[34]

In our view, the nonclassical interpretation (Chart I) represents a consistent and reasonable correlation of the present results. It should be noted that the apparently small anchimeric acceleration suggests the possibility of simultaneous assisted (to give Va) and unassisted (to give Vb) ionization reactions. The results seem to indicate that assisted ionization is the major reaction; however, partial entry to the carbonium ion system *via* Vb cannot be ruled out. This raises the possibility that more careful scrutiny of the products than was attempted in the present work may reveal the presence of an intervening asymmetric intermediate.

Experimental Section

Δ^4-Cycloheptenylmethyl *p*-Bromobenzenesulfonate (VI-OBs). Δ^4-Cycloheptenylmethanol, bp 80–81° (1 mm), was obtained by reduction ($LiAlH_4$) of Δ^4-cycloheptenecarboxylic acid, mp 70.9–73.9° (lit.[35] mp 65–67°), which in turn was prepared by the Stork–Landesman method.[35] The alcohol (shown to be homogeneous by gc[17]) was converted to the *p*-bromobenzenesulfonate derivative by a previously described procedure[36] for preparation of *p*-toluenesulfonate derivatives. One recrystallization from ether–pentane gave VI-OBs, mp 55.0–55.6° (lit.[14] mp 53.5–55°), in 93% yield. The sample used for product studies[7] and determination of the rate of acetolysis (48.86°) was recrystallized three additional times.

***endo*-Bicyclo[3.2.1]octan-2-ol (IV-OH). A. By Acetolysis of VI-OBs.** Acetolysis of VI-OBs at 60° for 48 hr followed by isolation and saponification of the resulting acetates by a previously described procedure[36a] gave an 80% yield of *endo*-bicyclo[3.2.1]-octan-2-ol (IV-OH), mp 174.5–177.7° (lit.[36a] mp 175.7–176.7°). The infrared spectrum of this material was indistinguishable from that of a sample prepared by a different route.[36a] However, gc[17] showed that the alcohol contained 3.0% of the [2.2.2] isomer I-OH and 3.6% of the *exo*-[3.2.1] isomer III-OH. The acetate from which the alcohol was derived had the same composition.

B. By Hydrolysis of Δ^4-Cycloheptenylmethyl *p*-Bromobenzenesulfonate (VI-OBs) in 80% Acetone. A solution of 36.6 g (0.106 mol) of VI-OBs and 9.3 g (0.13 mol) of pyridine in 400 ml of 80% acetone[18] was sealed in a heavy-walled ampoule and heated at 48.86° for 8 days. Most of the acetone was removed by distillation (steam bath), and the resulting solution, from which alcohol had precipitated, was diluted with 350 ml of water and continuously extracted with pentane for 24 hr. The cold extract, to which ether was added for complete solution of the alcohol, was washed with one 25-ml and two 15-ml portions of cold 2% hydrochloric acid and then with three 10-ml portions of saturated potassium carbonate solution and dried over magnesium sulfate. Removal of solvent by distillation left 12.1 g (91% yield) of *endo*-bicyclo[3.2.1]octan-2-ol (IV-OH), mp 170.3–173.6°. Analysis by gc[17] showed that this material contained 1.4% I-OH, 1.1% III-OH, and 0.9% Δ^4-cycloheptenylmethanol (VI-OH).

Resolution of the *endo*-Bicyclo[3.2.1]octan-2-yl System IV. In a typical experiment, IV-OH was converted to *endo*-bicyclo[3.2.1]-octan-2-yl acid phthalate (IV-AP), mp 117.3–119.2° (lit.[6a] mp 114–117°), in 90% yield by a previously described procedure.[6a] This material was purified by two recrystallizations from a methylene chloride–pentane mixture and contained 1.3% of the isomeric acid phthalates I-AP and III-AP.[19]

The acid phthalate IV-AP was resolved as follows.[6a] A solution of 22.7 g (0.0830 mol) of IV-AP in 20 ml of dry acetone was added to a refluxing solution of 32.8 g (0.0830 mol) of brucine in 450 ml of dry acetone. After standing overnight in a refrigerator 46.6 g of brucine salt was collected, mp *ca.* 123–125° dec, $[\alpha]^{25}D$ −25.0° (*c* 1.5, *l* 4).[20] Six recrystallizations from 120 ml of a 5:1

(29) For acetolysis (49°) k_t for IV-OTs is 2.2 times that (obtained by extrapolation of rate data at 75°[30]) for *trans*(equatorial)-4-*t*-butylcyclohexyl *p*-toluenesulfonate. The rate of ionization of IV-OTs is 11 times that of solvolysis of *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate.

(30) S. Winstein and J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955).

(31) (a) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp 140–158, 174–178; P. S. Skell and R. J. Maxwell, *J. Am. Chem. Soc.*, **84**, 3963 (1962); H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965); (b) H. C. Brown, *et al.*, *ibid.*, **86**, 5003, 5004, 5006, 5007, 5008 (1964).

(32) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 147 (1964).

(33) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).

(34) Berson and Reynolds-Warnhoff[10b] have provided convincing evidence that in this system the classical [3.2.1] ion Vb and the corresponding symmetrical bridged ion Va are separated by an activation barrier. It seems reasonable that reorganization of the solvation shell is responsible for this barrier.

(35) G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5129 (1956).

(36) (a) H. L. Goering, R. W. Greiner, and M. F. Sloan, *ibid.*, **83**, 1391 (1961). (b) In the present work the reaction period was 20 hr at room temperature instead of 48 hr at 0°.

acetone–methanol mixture gave 19.0 g of brucine salt, mp 129–137° dec, $[\alpha]^{25}D$ −32.8° (*c* 1.5, *l* 4). Decomposition of the salt with 10% hydrochloric acid gave 6.70 g (87% yield) of (−)-*endo*-bicyclo[3.2.1]-octan-2-yl acid phthalate ((−)-IV-AP).[37] After two recrystallizations from benzene–hexane the remaining 6.12 g had mp 117.0–118.9°, $[\alpha]^{28}D$ −24.3° (*c* 1.5, *l* 4).[20]

Saponification of this acid phthalate derivative with 1.5 *M* methanolic potassium hydroxide (2.5-hr reflux) gave 2.71 g (96%) of (−)-*endo*-bicyclo[3.2.1]octan-2-ol ((−)-IV-OH),[37] mp 173.6–176.1°, $[\alpha]^{25}D$ −19.2° (*c* 1.5, *l* 4), −24.7° (*c* 1.4, *l* 4, 95% ethanol), $[\alpha]^{25}_{365}$ −67.3° (*c* 1.5, *l* 4); lit.[6a] mp 178–180°, $[\alpha]^{24}D$ −8.2°. The gas chromatogram showed that this product contained only traces of the isomeric bicyclic alcohols. As will be shown below, optically pure IV-OH has a rotation of about $[\alpha]^{25}D$ 22.1°.[20] Thus the sample described above was about 87% optically pure.

To establish the rotational relationship between IV-OH and the corresponding acetate (IV-OAc), (−)-IV-OH, $[\alpha]^{25}D$ −20.8° (94% optically pure), was acylated as follows. A solution of the alcohol in acetic anhydride containing sodium acetate was heated on a steam bath for 2.3 hr. A large excess of water was added and the resulting solution stirred for 24 hr to hydrolyze the excess anhydride. The product was isolated by continuous extraction with pentane. The extract was washed with 5% potassium carbonate and dried (Na_2SO_4). After removal of pentane by distillation under reduced pressure the residual acetate was shown to contain only a trace of the isomeric bicyclic acetates by gc. The (−)-IV-OAc obtained in this manner had $[\alpha]^{25}D$ −41.1° (*c* 0.59, *l* 4),[20] −39.1° (*c* 0.36, *l* 4; acetic acid).[37] This shows that optically pure IV-OAc has $[\alpha]^{25}D$ 43.7[20] and 41.6° (acetic acid).

Determination of the Optical Rotation of *endo*-Bicyclo[3.2.1]-octan-2-yl Acid Phthalate (IV-AP) by Isotope Dilution Analysis. The procedure used is based on that reported earlier.[10a] *endo*-Bicyclo[3.2.1]octan-2-yl acid phthalate-^{14}C (IV-AP-^{14}C) was prepared[6a] from 1.16 g (9.20 mmol) of racemic IV-OH and 1.36 g (9.20 mmol) of phthalic anhydride-7-^{14}C (Tracerlab Inc., 0.238 μCi/g). After two recrystallizations (methylene chloride–pentane) a 79% yield of IV-AP-^{14}C, mp 113.8–117°, activity[38] 89,820 ± 900 cpm/mmol, was obtained. This labeled acid phthalate was later found to contain 7.4% of the bicyclic isomers.[19] A mixture of 0.9998 g of the above-described *dl*-IV-AP-^{14}C (this contains 0.926 g of the *endo* isomer) and 2.002 g of (−)-IV-AP (only traces of isomers), $[\alpha]^{28}D$ −15.1°, was converted to the brucine salt which was reresolved to constant rotation, $[\alpha]^{29}D$ 33.7°, by six recrystallizations from a 7:1 acetone–methanol mixture. Decomposition of the salt gave 0.676 g of (−)-IV-AP, mp 117.5–118.9°, $[\alpha]^{25}D$ −26.6°, activity 22,616 ± 115 cpm/mmol. From these data it can be calculated[10a,21] that the partially resolved (−)-IV-AP that was diluted with the racemic labeled acid phthalate was 50% optically pure and thus the calculated specific rotation for optically pure IV-AP is 30.5 ± 0.9°[20] (uncertainty calculated from estimated limiting values of the data).

Saponification of (−)-IV-AP, $[\alpha]^{25}D$ −26.6° (methanolic KOH), gave (−)-*endo*-bicyclo[3.2.1]octan-2-ol ((−)-IV-OH),[37] mp 178–179.9°, $[\alpha]^{25}D$ −20.8° (*c* 0.67, *l* 4). This material contained only traces (<0.1%) of the bicyclic isomers. From this it can be calculated that optically pure IV-OH has $[\alpha]^{25}D$ 23.8 ± 0.7°.[20] As will be shown in a following paper,[13] a correlation of active IV-OH and III-OH suggests that the above values may be a little high and that $[\alpha]^{25}D$ 28.3° for IV-AP and $[\alpha]^{25}D$ 22.1° for IV-OH (highest observed rotations) are more reliable values for rotations of the optically pure compounds.

***endo*-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (IV-OTs).** *endo*-Bicyclo[3.2.1]octan-2-ol (IV-OH), containing 6% of the isomeric alcohols (I-OH and III-OH), was converted[36] to the *p*-toluenesulfonate derivative (IV-OTs) in 95% yield. After four recrystallizations from ether–pentane (64% recovery) the melting point was 79.3–80.1° (lit.[4] 80.1–80.8°). The infrared spectrum was indistinguishable from that of a sample[4] derived from IV-OH prepared by a different synthetic route.[36a] However, an initial downward drift in the first-order rate of acetolysis showed that this material was still contaminated with the more reactive [2.2.2] (I-OTs) and *exo*-[3.2.1] (III-OTs) isomers.

Purification of the contaminated ester was effected by selective acetolysis of the reactive contaminants as follows. A solution of 22.9 g of crude IV-OTs (prepared from IV-OH containing 6% of the isomers) in 350 ml of anhydrous acetic acid was heated at 48.86° for 24 hr (25% solvolysis for IV-OTs and *ca.* 99% solvolysis for I-OTs and III-OTs[5]). After cooling, the solution was poured into 1 l. of cold water and the precipitated unsolvolyzed ester (IV-OTs) was collected and dried *in vacuo* at room temperature. Four recrystallizations from ether–pentane gave IV-OTs, mp 80.6–81.6°, in 64% over-all recovery. The infrared spectrum of this material was indistinguishable from that of a sample purified only by recrystallization; however, this material did not show an initial downward drift in the first-order rate of acetolysis.

Optically active IV-OTs was prepared[36] from active IV-OH and purified by recrystallization (ether–pentane). In a typical experiment a sample of (−)-IV-OH, $[\alpha]^{25}D$ −19.2°,[20] gave (−)-IV-OTs.[37] After two recrystallizations the yield was 72%, mp 64–67.5°, $[\alpha]^{25}D$ −27.5° (*c* 1.5, *l* 4).[20]

Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.25; H, 7.19. Found: C, 64.35; H, 7.20.

Using a value of $[\alpha]^{25}D$ 22.1° for optically pure IV-OH and assuming no optical fractionation during isolation and recrystallization—rotations of the crude, once recrystallized, and twice recrystallized samples were −28.0, −27.5, and −27.5°, respectively—gives $[\alpha]^{25}D$ 31.6°[20] for optically pure IV-OTs.

Kinetic Experiments. A. Materials. The solvent for the acetolysis experiments was prepared as follows. Reagent grade acetic acid was refluxed with the calculated amount of acetic anhydride for 13 hr and distilled. Additional acetic anhydride was added so that the concentration was 0.01 *M*.

The lithium perchlorate used in the kinetic experiments was dried for 48 hr at 111° (0.1 mm) just prior to use. The sodium acetate was anhydrous reagent grade material.

Aqueous acetone (80%) was prepared by mixing one volume of conductivity water and four volumes of purified acetone[39] at 25°.

B. Titrimetric Experiments. Rates of acetolysis were determined as described earlier.[5] Rates of solvolysis in 80% acetone[18] were determined in a similar manner except that aliquots were titrated to the phenolphthalein end point with 0.05 *M* aqueous sodium hydroxide. In all cases solvolysis equivalents determined from the infinity titers were within 2% of the theoretical values.

C. Polarimetric Rates. Solutions were prepared using thermostated solvents containing sodium acetate or lithium perchlorate when present. After thorough mixing the solution was quickly delivered into an all-glass, jacketed, 4-dm polarimeter tube (central filling) and rotations were taken at appropriate intervals. Constant temperature was maintained by circulating water from the thermostat used for the titrimetric experiments through the tube jacket and the jacket of the polarimeter tube compartment. To avoid temperature drops and fluctuations the circulating water was delivered by a vacuum-jacketed glass tube. The polarimeter was an O. C. Rudolph and Sons Model 80 high-precision polarimeter equipped with a photoelectric attachment and oscillating polarizer.

Total changes in observed rotations of from 1 to 2° were followed with a precision of ±0.003°. Infinity rotations after ten half-lives were 0 ± 0.003° in all cases.

Product Studies. Experimental details for isolation of products and analysis by capillary gas chromatography are presented in the following paper.

The following control experiments showed that the bicyclic [3.2.1] (IV-OAc and III-OAc) and [2.2.2] (I-OAc) acetates are stable under the conditions of the kinetic experiments. (a) A 0.1 *M* solution of an acetate mixture (2.1% I-OAc, 3.7% III-OAc, and 94.2% IV-OAc) in anhydrous acetic acid containing 0.016 *M* sodium acetate was heated at 49, 80, 100° for ten titrimetric half-lives. (b) A 0.03 *M* acetic acid solution of the above acetate mixture containing 0.0229 *M* *p*-toluenesulfonic acid was heated for ten half-lives at 80°. (c) An acetic acid solution containing 0.04 *M* III-OAc and 0.005 *M* sodium acetate was heated at 49° for ten half-lives. In all cases gc analysis[17] of the recovered acetates showed that no rearrangement had occurred.

The following experiment shows that solvolysis products for hydrolysis of IV-OTs in 80% acetone in the presence of excess pyridine are stable under the reaction conditions. A solution of 47.2 mg of I-OH (the most reactive bicyclic system), 38.3 mg (0.421

(37) In all cases infrared spectra of solutions of optically active compounds were indistinguishable from those of authentic racemic samples.

(38) Activities were determined with a Packard Tri-Carb liquid scintillation spectrometer, Model 314-DC (toluene–2,5-diphenyloxazole solution). We are indebted to Professor C. Heidelberger for making these facilities available. The reported activities are the average of single counts of duplicate samples.

(39) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, 75, 3445 (1953).

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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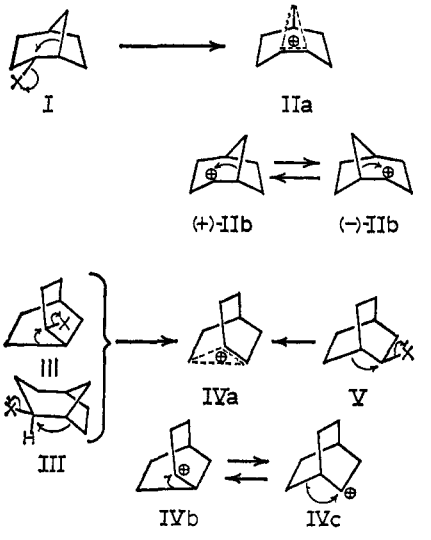
Abstract: Product compositions have been determined for acetolysis and hydrolysis (aqueous acetone) of *endo*-(I-OTs) and *exo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonates (III-OTs), bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (V-OTs), and Δ^4-cycloheptenylcarbinyl *p*-bromobenzenesulfonate (VI-OBs). 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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(3) National Science Foundation Predoctoral Fellow, 1962–1964.

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