(9) Collapse of solvent at C_3 of **26** and **27** might also be expected to yield 3-oxetanol products.
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(15) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 992 (1972).
(16) Supplied by Aldrich Chemical Co., Milwaukee, Wis.
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Epoxycarbinyl Solvolyses. The Solvolytic Reactions of *syn*- and/*anti*-9-Oxabicyclo[6.1.0]non-2-yl *p*-Bromobenzenesulfonates

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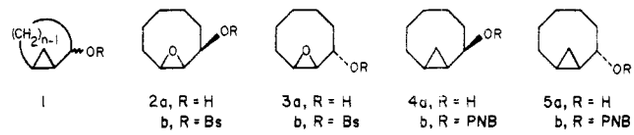
The rates of solvolysis of *syn*- and *anti*-9-oxabicyclo[6.1.0]non-2-yl *p*-bromobenzenesulfonates (**2b** and **3b**) have been determined and were found to be $\sim 10^7$ times slower than those of the corresponding cyclopropylcarbinyl analogues **4b** and **5b**. The product distributions from hydrolysis of **2b** and **3b** have been found to be quite complex and consisted of 50–60% of rearranged products, in addition to elimination and unrearranged products. *anti*-Brosylate **2b** yielded 29% of product that resulted from a transannular 6,2 hydride shift, followed by stereospecific collapse of solvent with the rearranged ion. *syn*-Brosylate **2b** yielded 2.5% of product that also resulted from a transannular 6,2 hydride shift followed by stereospecific collapse of solvent to yield the epimer of the product from **3b**. The results and product distributions were interpreted in terms of the ionization of **2b** and **3b** to conformationally different epoxycarbinyl cations with rates of interconversion that are slow relative to other product-forming reactions.

The solvolytic reactions of 2-bicyclo[*n*.1.0]alkyl systems **1** have received considerable attention,[1] along with other studies dealing with the nature of cyclopropylcarbinyl cations.[2] The structures of geometrically related epoxycarbinyl cations are also of interest. Whereas the greater electronegativity of oxygen relative to carbon would lead to the prediction that an epoxide group should not stabilize a positive charge on the adjacent carbinyl position as effectively as cyclopropyl for certain geometries, the nonbonding electrons on oxygen can potentially stabilize a positive charge on the carbinyl position by either formation of an oxabicyclobutonium ion or by a favorable lone-pair-electron interaction of the oxygen atom with the carbinyl carbon in the "bisected" geometry.[3]

The nature of the epoxycarbinyl cation clearly is a function of the system from which it is derived. It has been suggested that several acyclic epoxycarbinyl derivatives solvolyze via the intermediacy of oxabicyclobutonium ions.[4] Other acyclic epoxycarbinyl substrates in which the carbinyl carbon is secondary have been reported to solvolyze with participation of the epoxide ring in a manner similar to the participation of cyclopropyl rings in cyclopropylcarbinyl solvolyses.[5] However, several simple acyclic epoxycarbinyl *p*-bromobenzenesulfonate esters have been shown to hydrolyze *without* appreciable anchimeric assistance or participation by the epoxide ring,[6] and preliminary results indicated that the epoxide group is much less effective than a cyclopropane ring in stabilizing a positive charge on the carbinyl position in the solvolytic reactions of *syn- and anti*-9-oxabicyclo[6.1.0]non-2-yl *p*-bromobenzenesulfanates (**2b** and **3b**).[7] In this paper, we describe in more detail the hydrolysis reactions of **2b** and **3b**.

Results and Discussion

First-order rate constants for the solvolysis of **2b** and **3b** are provided in Table I, and the relative reactivities of **2b, 3b,** and the related *syn*- and *anti*-2-bicyclo[6.1.0]non-2-yl systems[1a] are provided in Table II. Of significance is the fact that the



1 **2a**, R = H; **b**, R = Bs **3a**, R = H; **b**, R = Bs **4a**, R = H; **b**, R = PNB **5a**, R = H; **b**, R = PNB

rates of solvolysis of **2b** and **3b** are estimated to be ca. 10^6–10^7 times slower than the corresponding rates for their cyclopropylcarbinyl analogues **4b** and **5b**. The slow rates of solvolyses of **2b** and **3b,** relative to **4b** and **5b,** certainly indicate that epoxide rings are not nearly as effective as cyclopropyl rings in stabilizing a positive charge on an adjacent carbon. The syn systems **2b** and **4b** are each significantly more reactive than their corresponding anti epimers **3b** and **5b,** respectively.

A comparison of product distributions from bicyclo[6.1.0]-non-2-yl systems is given in Table III. Whereas the product distributions from **4b** and **5b** are relatively simple,[1a] the product mixtures from **2b** and **3b** are more complex. Yet there are some striking resemblances. (1) Both **2b** and **3b** yield products with net retention of stereochemistry at C-2. Their corresponding cyclopropylcarbinyl analogues **4b** and **5b** each give greater than 99% retention of stereochemistry at C-2. (2) The syn isomers **2b** and **4b** yield significant amounts of suberaldehyde (**6**) and *cis*-3-cyclononenol (**12**), respectively. The similarities of the mechanisms leading to these products are presented in Scheme I. (3) *anti*-Epoxycarbinyl brosylate **3b** yielded a significantly greater amount (17%) of cycloheptenecarboxaldehyde (**7**) than syn isomer **2b.** A possible intermediate in the formation of **7** is the trans-fused bicyclic hemiketal **20** (Scheme II), which corresponds in structure to the trans-fused cyclobutanol **13** from *anti*-cyclopropylcarbinyl *p*-nitrobenzoate **5b.**

There are also some major differences in the solvolysis of *syn*-**2b** and *anti*-**3b,** compared with cyclopropylcarbinyl analogues **4b** and **5b.** (1) Whereas there is no detectable crossover in the product distributions from solvolyses of **4b** and **5b,** at least five products in the solvolyses of **2b** and **3b** are com-

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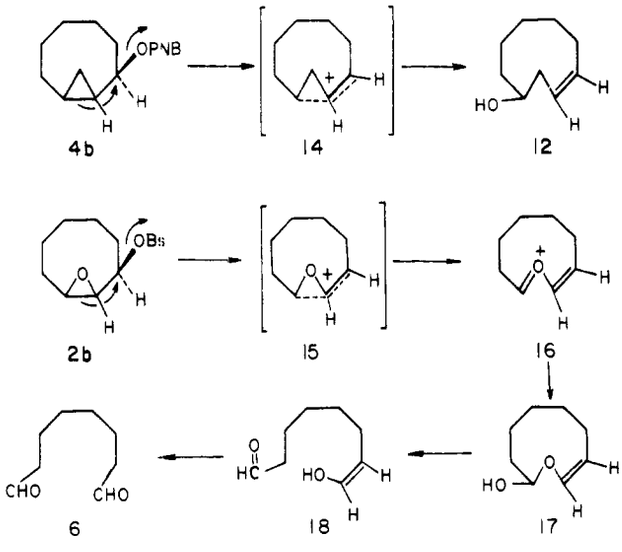
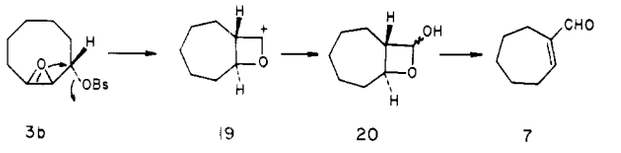
Scheme I

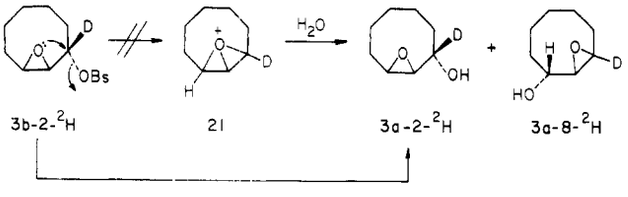


Scheme II



mon. (2) The rates of solvolyses of **2b** and **3b** are ca. 10^6–10^7 times slower than their cyclopropylcarbinyl analogues. (3) Significant amounts of hydride-shift alcohols **8** and **9** and elimination epoxides **10** and **11** are formed from **2b** and **3b.**

Simple primary and secondary acyclic unhindered substrates generally solvolyze to yield almost exclusive inverted product.[8] Those substrates that solvolyze to give products with net retention of stereochemistry at the ionizing carbon often solvolyze either with anchimeric assistance of a neighboring group or by "solvent-unassisted" ionization[9] if the backside of the ionizing carbon is hindered to solvation. Backside participation by nonbonding electrons in **2b** is severely restricted because of geometrical considerations. However, the trans geometry of **3b** is favorable for anchimeric assistance by the nonbonding electrons of the neighboring epoxide group to form an intermediate oxabicyclobutonium ion. Collapse of solvent with the oxabicyclobutonium ion might then give **3a**



and account for the net retention of stereochemistry at C-2.[10] Therefore, **3b**-*2-d* was hydrolyzed. The intermediate oxabicyclobutonium ion **21**, if formed, should lead to scrambling of deuterium between C-2 and C-8 of the major product **3a.** However, the infrared and NMR spectra of the major product were identical with the spectra of **3a**-*2-d.* Participation by the nonbonding electrons of oxygen in the solvolysis of **3b** was therefore ruled out as a major solvolytic pathway.[7]

An interesting aspect of the hydrolysis of **3b** is the formation of 29% of *anti*-9-oxabicyclo[6.1.0]nonan-3-ol (**9**) and no detectable syn isomer **8.** In contrast, hydrolysis of **2b** yielded 2.5% of the syn-alcohol **8** and no detectable anti epimer **9.** This rather stereospecific formation of **8** and **9** from **2b** and **3b,** respectively, is particularly intriguing because reduction of 9-oxabicyclo[6.1.0]nonan-3-one with sodium bis(2-methoxyethoxy)aluminum hydride yielded approximately equal amounts of **8** and **9.**

Table I. First-Order Rate Constants[a] and Activation Parameters[a] for the Solvolysis of 2b and 3b

Compd	Temp, °C	$10^5 k$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, kcal/mol
		80% Ethanol–Water		
2b	59.8	22.7 ± 0.5	25.3 ± 0.4	0.7 ± 1.3
	49.8	6.64 ± 0.26		
	40.1	1.82 ± 0.07		
	25.0	0.23[b]		
3b	100.3	12.2 ± 0.18	27.3 ± 0.1	−3.7 ± 0.4
	90.2	4.26 ± 0.004		
	80.1	1.40 ± 0.003		
	25.0	0.00089[b]		
		80% Acetone–Water		
2b	50.1	1.65 ± 0.07		
	40.0	0.43 ± 0.01		
3b	100.3	3.63 ± 0.06		
	90.1	1.24 ± 0.02		

[a] Errors are expressed in units of standard deviation. [b] Extrapolated from data at higher temperatures.

Table II. Relative Reactivities of Epoxycarbinyl Substrates 2b and 3b and Cyclopropylcarbinyl Substrates 4b and 5b toward Hydrolysis[a]

Compd	**2b**	**3b**	**4b**[b]	**5b**[b]
k_{rel}	259	1	1.4×10^9	1.6×10^7

[a] The solvolytic reactivity of 2-bicyclo[*n*.1.0]alkyl brosylates was estimated to be ca. 10^9 times greater than that of 2-bicyclo[*n*.1.0]alkyl *p*-nitrobenzoates. This estimate is based on rates of 0.07 s^{-1} for acetolysis of *trans*-2-bicyclo[3.1.0]hexyl tosylate at 25 °C and 8.2×10^{-7} s^{-1} for hydrolysis of *trans*-2-bicycol[3.1.0]hexyl *p*-nitrobenzoate at 100 °C in 80% acetone–water, E. C. Friedrich and S. Winstein, unpublished results. The rates of solvolysis of **2b, 3b, 4b,** and **5b** were extrapolated to 25 °C in a common solvent. [b] Reference 1a.

Two possible mechanisms can explain the formation of anti alcohol **9** from anti brosylate **3b.** One mechanism involves a 3,2 hydride shift, and the second mechanism involves a 6,2 hydride shift (Scheme III). Evidence for a 6,2 hydride shift was provided by the 100-MHz ^1H NMR spectrum[11] of the product **25** from solvolysis of *anti*-**3b**-*2-d.* A low-field methylene absorbance at δ 2.35 (1 H) was split into a doublet of triplets (J = 14.5, 4.0, 4.0 Hz). Irradiation of the α hydrogen H_3 (δ 3.9) or epoxide proton H_1 (δ 3.06, d of t, J = 10.5, 4.0, 4.0 Hz) reduced the signal for the low-field proton into a doublet of doublets (J = 14.5, 4.0 Hz). This low-field absorption must, therefore, belong to a proton located at C-2 and was assigned to the anti proton H_{2b} because models indicated that this proton is not located in the shielding cone of the epoxide ring. The syn proton H_{2a} is located in the shielding cone of the ep-

Scheme III

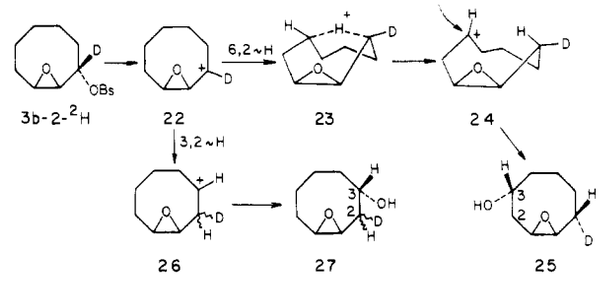


Table III. Product Distributions for Solvolyses of 2b, 3b, 4b, and 5b in 80% Aqueous Acetone

Product[a]	2a	3a	6	7	8	9	10	11
Retention time, min[b]	15.6	28.2	20.6	4.7	31.3[c]	31.3[c]	3.4	2.3
% from 2b	9.1	1.5	52.4	2.8	2.5	~ 0	28.3	2.5
% from 3b	5.1	36.0	1.9	17.4	~0	28.9	4.9	3.5

Product[d]	4a	5a	12	13
% from 4b[e]	61	<0.3	23	
% from 5b	<0.3	96		4

[a] Triethylamine was used as a buffer. Yields correspond to relative areas of product peaks on a GLC tracing. [b] Analyzed by gas chromatography on a 6 ft × ¼ in., 5% diethylene glycol succinate column. The temperature of the chromatograph oven was programmed from 60 to 160 °C at 3 °C min. [c] Epimers 8 and 9 could not be separated on GLC. However, analysis of the infrared spectra of the solvolysis compounds indicated the lack of contamination (≤ 5%) of the other epimer. [d] Reference 1a. [e] Internal-returned *p*-nitrobenzoate of 12 (16%) was also formed.

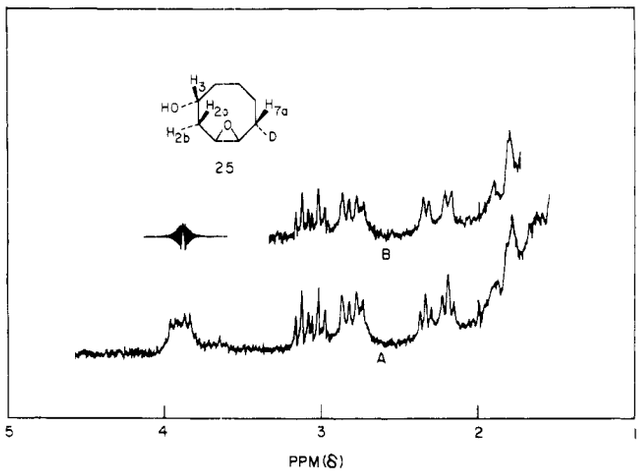


Figure 1. (A) ^1H NMR spectrum (100 MHz) of **25**. (B) ^1H NMR spectrum of **25** with H_3(δ 3.9) decoupled.

oxide group and therefore should absorb at higher field than H_{2b}. The geminal coupling constant of 14.5 Hz is consistent only with structure **25**, containing two protons at C_2. A 3,2 hydride migration is ruled out, since this mechanism would produce product **27** with a deuterium atom located at C_2. The stereospecific anti structure of **25** indicates that collapse of solvent at C_3 is concurrent with a C_6–C_2 hydride shift or is rapid relative to a conformational change of the isomeric ion **24** from the geometry required for hydride shift.[12]

Stereospecific C_6–C_2 hydride migration in the solvolysis of **3b**-2-*d*, in which the hydride migrates from the backside of the ionizing center as indicated in **23**, would predict the location of the deuterium atom in **25** to be anti to the epoxide group. This stereochemical assignment was substantiated by analyzing the NMR spectra of **9** and **25**. Models indicate that the syn proton H_{7a} in **25** is in the shielding cone of the epoxide ring and should absorb at high field relative to the anti proton H_{7b}, which is in the deshielding cone of the epoxide ring. A difference in chemical shift between H_{7a} and H_{7b} should amount to ~0.8 ppm.[13] The methylene protons of **9** gave rise to complex absorptions between δ 0.5 and 2.55. Comparison

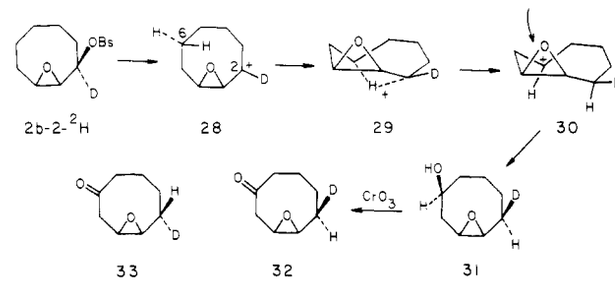
Table IV. NMR Spectral Data for Hydride Transfer Alcohols 9 and 25

Relative area of absorption	δ 9	δ 25
δ 1.85–2.55	2.5	1.6
δ 0.5–1.85	7.5	7.4

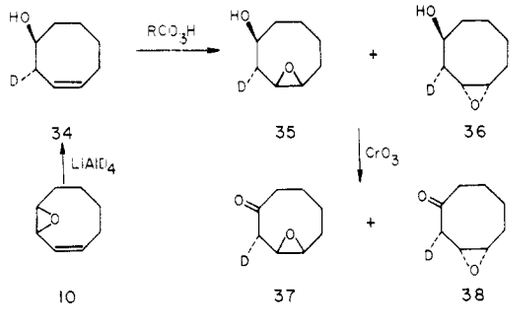
of the relative absorption area between δ 0.5 and 1.85 and δ 1.85 and 2.55 (Table IV) revealed that the position for absorption of the proton that is replaced by deuterium is between δ 1.85 and 2.55. This relatively low-field absorption for this methylene hydrogen suggests that it is located anti to the epoxide group, and therefore the deuterium atom in **25** must also be located anti to the epoxide ring.

We have also obtained evidence that **2b** undergoes a 6,2 hydride shift to yield syn product **8**. This evidence was provided by isolating the hydride-shift product **31** (Scheme IV) of the solvolysis of syn brosylate **2b**-2-*d*. Unfortunately, the NMR spectrum of **31** was too complicated to allow a structure proof in a manner analogous to the assignment of structure **25**. Indirect evidence for the structure of **31** was provided in the following manner. Oxidation of **31** with Jones reagent provided ketone **32**, which possessed an infrared spectrum clearly different from ketone **33** obtained by oxidation of the hydride-shift product **25** of the solvolysis of anti brosylate **3b**-2-*d* (Scheme III). To test if the deuterium atom in **32** was located at C_2, 9-oxabicyclo[6.1.0]nonan-3-one-2-*d* isomers **37** and **38** were synthesized by the route outlined in Scheme V.

Scheme IV



Scheme V



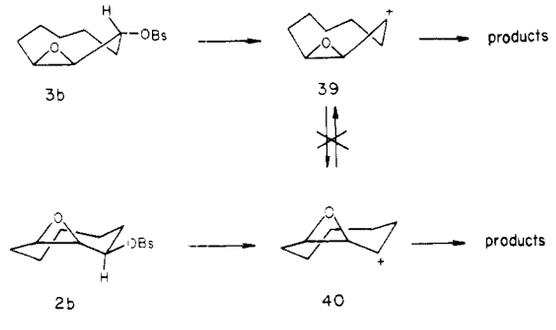
The infrared spectra of both **32** and **33** differed substantially from the infrared spectrum of pure **37** and the spectrum of a mixture of approximately equal amounts of **37** and **38.** Thus, it appears that the deuterium atom in the hydride-shift product from the solvolysis of **2b**-2-*d* is not located to any significant extent at C_2, and consequently a simple 3,2 hydride shift cannot be the major pathway for the hydride-shift product **8.** The fact that the infrared spectrum of **32** was different from that of **33** also indicated that the deuterium atom in **31** was not located in the anti-C_7 position. A mechanism that explains the observations and results in the deuterium located specifically at the syn-C_7 position is outlined in Scheme IV.[14] The stereospecific syn structure of **31** indicates that the collapse of solvent is concurrent with C_6–C_2 hydride migration or is rapid relative to a conformational change of the isomeric ion **30.**

Stereospecific hydride migrations across the top of the ring in the solvolysis of **3b** and across the bottom of the ring in **2b** suggest that the two epimeric esters undergo ionization to conformationally different ions with rates of interconversion that are slow relative to the rates of other product-forming pathways (Scheme VI). The fact that epoxycarbinyl cation **22** underwent substantial rearrangement via hydride migration suggests that the stability of the rearranged cation [9-oxabicyclo[6.1.0]non-3-yl cation (**24**)], in which the cationic center is *not* adjacent to the epoxide group, is *comparable to or greater* than that of **22** (Scheme III).

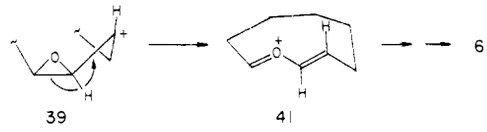
The geometries of the isomeric cations **39** and **40** also help to explain the observed product distributions from the hydrolysis of **2b** and **3b.** The geometry of epoxycarbinyl cation **39** is favorable for migration of the carbon–carbon bond of the epoxide ring to form a trans-fused 2-oxetanyl cation **19** (Scheme II). However, rupture of the carbon–carbon bond of the epoxide ring to give a ring-expanded oxonium ion **41** would require the introduction of a relatively unfavorable trans double bond.[15]

On the other hand, epoxycarbinyl cation **40** possesses a geometry that is favorable for either rupture of the carbon–carbon bond of the epoxide ring to provide a ring-expanded oxonium ion **42** that contains a cis double bond or for migration of the carbon–carbon bond to yield a cis-fused 2-oxetanyl cation **44** (Scheme VIII). The relative stabilities of ions **42** and

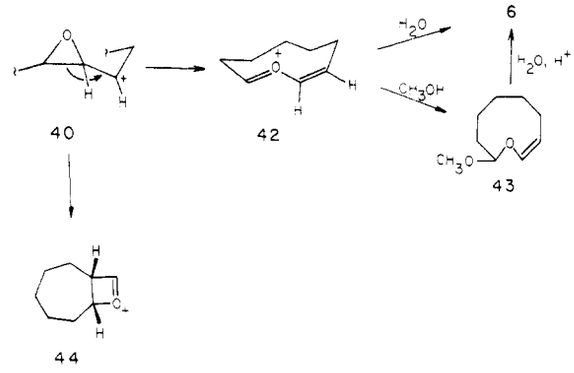
Scheme VI



Scheme VII



Scheme VIII



44 should parallel the stabilities of *cis,cis*-1,3-cyclononadiene and *cis*-bicyclo[5.2.0]non-8-ene, respectively. In the latter series, *cis,cis*-1,3-cyclononadiene is the more stable.[15] Therefore, the rearrangement pathway leading to **42** should be favored over that leading to **44** and accounts for the relatively high yield (52%) of suberaldehyde (**6**) from the hydrolysis of **2b.** The cis nature of the carbon–carbon double bond in **42** was verified by solvolyzing **2b** in methanol, where intermediate **42** is trapped by solvent to yield the stable ketal **43.**[16] The ^1H NMR spectrum of **43** revealed a value of 6 Hz for the olefinic vicincal coupling constant, which is consistent only with a cis double bond in **43.**

The observations that **2b** and **3b** undergo hydrolysis to yield epoxycarbinol products with net retention of stereochemistry at C-2 suggests that the backside of the ionizing center is not readily accessible to solvent. The entropies of activation for solvolysis of **2b** and **3b** in 80% ethanol–water were found to be 0.7 and −3.7 kcal/mol, respectively (Table I). These entropies of activation are ca. 10–18 eu higher than the entropies of activation for solvolysis of the threo and erythro isomers of 3,4-epoxy-2-pentyl brosylate in the same solvent.[6] The latter acyclic brosylates undergo predominant inversion at the ionizing center when hydrolyzed in an acetone–water solution and therefore their more negative entropies of activation may reflect the S_N2 character of the transition states. Consequently, the more positive entropies of activation for solvolysis of **2b** and **3b** may reflect the absence of strong solvation at the backsides of the ionizing centers. This lack of solvation would allow other rearrangement pathways and retention to compete successfully with inversion at the ionizing center. The puckered natures of the medium-sized rings of **2b** and **3b** clearly induce severe geometric constraints on geometries of the intermediates of solvolysis and may also be responsible for the hindrance to solvation of those intermediates.

Experimental Section

Melting points were determined in capillary tubes and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Model 257 spectrophotometer, and ^1H NMR spectra were obtained with either an Hitachi Perkin-Elmer R-20A or Varian HA-100 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

***anti*-9-Oxabicyclo[6.1.0]nonan-2-ol (3a).**[17] To a solution of 6.3 g (0.050 mol) of 2-cyclooctenol[18] in 125 mL of methylene chloride, stirred and cooled in an ice–water bath, was added 10.4 g of *m*-chloroperbenzoic acid[19] (85%, 0.051 mol) over a period of ~10 min. The solution was stirred for an additional hour, and the solid precipitate

of *m*-chlorobenzoic acid was removed by suction filtration. The filtrate was washed twice with saturated sodium bicarbonate solution, and the solvent was removed with a rotary evaporator to yield 7.1 g of **3a** as a clear oil: IR (CCl_4) 3600 cm^{-1}; NMR (CCl_4) δ 3.5 (m, 1 H, CHOH), 2.6–3.1 (2 H, protons on epoxide ring).

***anti*-9-Oxabicyclo[6.1.0]nonan-2-yl *p*-Bromobenzenesulfonate (3b).** A solution of 5.6 g (0.022 mol) of *p*-bromobenzenesulfonyl chloride in 16 mL of dry pyridine was cooled in an ice–water bath and 2.0 g (0.016 mol) of **3a** was added.[20] The reaction solution was allowed to stand for 12 h in the refrigerator and was then diluted with ice–water and extracted with ether. The ethereal solution was washed with cold 1 M HCl solution and with saturated sodium bicarbonate solution and was then dried with anhydrous sodium sulfate. The solvent was removed with a rotary evaporator and the residue was filtered through Alumina III with 80:20 pentane–ether. Removal of the solvent yielded 4.86 g (89%) of crude crystalline **3b,** which was recrystallized from benzene–pentane solution to yield 3.3 g of pure **3b:** mp 85.5–86.5 °C; NMR (CCl_4) δ 2.6–3.0 (2 H, epoxide protons), 4.4 (m, 1 H, CHOBs), 7.73 (m, 4 H, aromatic protons).

Anal. Calcd for $C_{14}H_{17}O_4SBr$: C, 46.54; H, 4.74. Found: C, 46.80; H, 4.69.

9-Oxabicyclo[6.1.0]nonan-2-one.[17] To a stirred solution of 3.5 g (0.025 mol) of **3a** in 60 mL of acetone at 0 °C was added 6.75 mL of Jones reagent[21a] over a period of 30 min. The reaction solution was diluted with 700 mL of water and extracted with diethyl ether (3 × 150 mL). The ethereal solution was washed with saturated sodium chloride solution and dried with anhydrous sodium sulfate. Removal of solvent left 3.1 g of oil which was distilled in vacuo to yield 2.1 g (61%) of product: bp 92 °C (0.2 mm) [lit[17] bp 115–116 °C (5 mm)]; mp 94–96 °C [lit[17] mp 92–93 °C] IR (CCl_4) 1725 cm^{-1} (C=O).

***syn*-9-Oxabicyclo[6.1.0]nonan-2-ol (2a).** A mixture of 0.61 g (4.9 mmol) of 9-oxabicyclo[6.1.0]nonan-2-one, 0.70 g (18 mmol) of sodium borohydride, and 25 mL of dry isopropyl alcohol was stirred and heated at 80 °C for 2 h. The reaction mixture was diluted with water and extracted with diethyl ether. The ethereal solution was washed with saturated sodium chloride solution and dried with anhydrous sodium sulfate. The solvent was removed and the residue sublimed at an oil bath temperature of 100 °C (3 mm): yield 0.47 g (78%). GLC analysis (5% diethylene glycol succinate (DEGS) column) revealed that the reduction was ≥98% stereospecific to yield *syn*-**2a.** The material was further recrystallized from pentane–ether solution: mp 89.5–91.0; IR (CCl_4) 3550 cm^{-1}; NMR (CCl_4) δ 2.6–3.0 (3 H, CHOH and epoxide protons), 4.35 (m, 1 H, CHOH).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.31; H, 9.77.

***syn*-9-Oxabicyclo[6.1.0]nonan-2-yl *p*-Bromobenzenesulfonate (2b)** was prepared in 81% yield by the same procedure given above for the preparation of **3b,** mp of **2b:** 117.5–118.5 °C; NMR (CCl_4) δ 2.5–3.0 (2 H, epoxide protons), 5.15 (m, 1 H, CHOBs), 7.75 (m, 4 H, aromatic protons).

Anal. Calcd for $C_{14}H_{17}O_4SBr$: C, 46.54; H, 4.74. Found: C, 46.60; H, 4.80.

Kinetics. A. Solvents. Ethanol (80%)–water and 80% acetone–water solvents were prepared by mixing 4 volumes of organic solvent and 1 volume of water at 25 °C. All solvents were distilled prior to use.

B. Procedures. Approximately 30 mg of *p*-bromobenzenesulfonate ester and 25 μL of triethylamine were dissolved in 25 mL of 80% ethanol–water. An aliquot (2.5 mL) of this solution was sealed in each of 10 ampules. The ampules were placed in a constant-temperature oil bath, thermostated to within ±0.03 °C of the stated temperatures (Table I). At a given time, an ampule was removed, and the absorbance of the solution was measured at 265 nm in a Gilford 2400 spectrophotometer.[21b]

The rates in 80% acetone–water were also determined by the sealed-ampule technique. Approximately 170 mg of *p*-bromobenzenesulfonate was dissolved in 50 mL of 80% acetone–water, and aliquots of the solution (5.5 mL) were sealed in ampules. The ampules were placed in the constant-temperature bath, and at a given time an ampule was removed and 5.0 mL of reaction solution was titrated with standard 0.01 M sodium methoxide–methanol solution to a phenolphthalein end point.

Rate constants for 80% ethanol–water solutions were obtained by nonlinear regression analysis of the data, for each kinetic run, by a Wang 700 calculator computer. The rate constants for 80% acetone–water were obtained by least-squares plots of ln ($V_\infty - V_t$) vs. time, where V refers to titrant volume.

Products from the Hydrolysis of 2b. A solution of 47 mg of **2b,** 100 μL of triethylamine, and 5.0 mL of 80% acetone–water was sealed in an ampule and heated at 60.0 °C for 22.5 h. The reaction solution was diluted with water and extracted several times with diethyl ether. The ethereal solution was washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. Removal of solvent yielded 16 mg (ca. 85–90%) of oil that was analyzed by gas chromatography on a 5% diethylene glycol succinate column (6 ft × ¼ in). The product distribution and relative GLC retention times are given in Table III.

The products were separated by preparative GLC and identified by comparison of their GLC retention times and infrared and NMR spectra with those of authentic samples where appropriate. Products **10** and **11** were compared with authentic samples prepared by monoepoxidation of 1,3-[22] and 1,4-cyclooctadiene,[23] respectively. Suberaldehyde (**6**) was reduced with lithium aluminum hydride, and the reduction product was compared with authentic 1,8-octanediol.[24] The infrared spectrum of the unsaturated aldehyde **7** was identical with that published for cycloheptenecarboxaldehyde.[25] Products **8** and **9** could not be separated on GLC, but their structures were assigned based on the comparison of their infrared and NMR spectra with the spectra of a mixture of *syn*- and *anti*-9-oxabicyclo[6.1.0]nonan-3-ol prepared by epoxidation of 3-cyclooctenol and by their lithium aluminum hydride reduction to known *cis*- and *trans*-1,3- and 1,4-cyclooctanediols.[12,26]

Products from Hydrolysis of 3b. A solution of 87 mg of **3b,** 100 μL of triethylamine, and 5.0 mL of 80% acetone–water was sealed in an ampule and heated at 100 °C for 43.5 h. The products were isolated and characterized by the same procedure outlined above for the hydrolysis of **2b.** Relative yields are given in Table III.

Preparation of 2a-*2-d*. 9-Oxabicyclo[6.1.0]nonan-2-one (0.8 g) in 10 mL of absolute ethanol was reduced with sodium tetradeuterioborate ($NaBD_4$, 0.25 g)[27] to yield 0.46 g (57%) of product, which was purified by sublimation at 100 °C (3 mm). The NMR spectrum of the product was similar to that for **2a** except that the absorption due to H-2 at δ 4.35 was absent. **2b-*2-d*** was prepared from **2a-*2-d*** by the same procedure for preparation of **2b** above.

2-Cyclooctenone, bp 62 °C (1.5 mm) [lit[28] bp 89 °C (14 mm)], was prepared in 75% yield by Jones oxidation of 2-cyclooctenol.

2-Cyclooctenol-*1-d*. A mixture of 1.04 g of 2-cyclooctenone (8.4 mmol), 353 mg of sodium tetradeuterioborate,[27] and 15 mL of absolute ethanol was stirred at room temperature for 1 h. The reaction was diluted with water and the product extracted into diethyl ether. The ethereal solution was washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. The solvent was removed to yield 1.4 g of clear oil. GLC analysis of the product on a 7% carbonwax–5% KOH column (6 ft × ¼ in.) showed the presence of ~80% of 2-cyclooctenol-*1-d* and 20% of cyclooctanol.[29]

***anti*-9-Oxabicyclo[6.1.0]nonan-2-ol-*2-d* (3a-*2-d*).** The crude 2-cyclooctenol-*2-d* from above, 1.3 g (containing 20% of cyclooctanol) in 20 mL of methylene chloride, was epoxidized with 2.33 g of 85% *m*-chloroperbenzoic acid by the procedure utilized for the preparation of **3a,** yield 1.8 g of a clear oil. The product was purified by chromatography on 15 g of Alumina III. The cyclooctanol component was eluted from the chromatography column with 20% ether–pentane, and **3a**-*2-d* was eluted from the column with ether. A center fraction contained 0.6 g of **3a**-*2-d* which produced only one peak on gas chromatography (5% diethylene glycol column). The NMR spectrum of the product was similar to that of **3a,** except that the absorption due to H-2 at δ 3.5 was absent. **3b**-*2-d* was prepared from **3a**-*2-d* by the same procedure for the preparation of **3b** above.

3-Cyclooctenol-anti-*2-d* (34). 1,3-Cyclooctadiene monoepoxide **10** was reduced with lithium tetradeuterioaluminate ($LiAlD_4$)[27] to **34.**[22] It was assumed that the deuterium was introduced trans to the resulting hydroxyl group.

9-Oxabicyclo[6.1.0]nonan-3-ol (8 and 9). 3-Cyclooctenol (3.90 g, 31 mmol) was epoxidized with 6.2 g of *m*-chloroperbenzoic acid (85%, 31 mmol) by the procedure outlined for the preparation of **3a.** The product was distilled in vacuo: yield 2.56 g (58%); bp (0.4 mm) 100 °C; IR (CCl_4) 3610 cm^{-1}; NMR (CCl_4) δ 3.8–4.3 (2 H, CHOH), 2.75–3.55 (2 H, epoxide protons). The product became semicrystalline upon standing and contained approximately equal amounts of **8** and **9.**

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.48. H, 9.80.

Relatively pure (ca. >90%) **8** was prepared by heating 55 mg of a mixture of **8** and **9,** 50 mg of lithium aluminum hydride, and 1 mL of tetrahydrofuran at 65 °C for 1.5 h. GLC analysis of the isolated products (5% diethylene glycol succinate column) indicated that approximately two-thirds of the reactant mixture had been reduced to diols. The remaining epoxy alcohol was isolated by preparative GLC. The infrared spectrum of the material indicated that it consisted of ca. >90% of **8** and ca. <10% of **9.**

9-Oxabicyclo[6.1.0]nonan-3-one. A sample of 59 mg (0.41 mmol) of a mixture of **8** and **9** in 3 mL of acetone was oxidized with 0.10 mL of Jones Reagent.[21a] The reaction solution was diluted with water and extracted with diethyl ether. The ethereal solution was washed with saturated sodium chloride solution and dried with anhydrous sodium sulfate. Removal of solvent left 24.4 mg of crude product (42%). Pure product was isolated by preparative GLC on a 5% diethylene glycol succinate column (6 ft × ¼ in., 100 °C): mp 68–70 °C; IR (CCl_4) 1705 cm^{-1} (C=O). The product was unstable to gas chromatography temperatures above 120 °C.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.27; H, 8.81.

9-Oxabicyclo[6.1.0]nonan-3-ol-*2-d* (35 and 36) was prepared by the epoxidation of **34** with *m*-chloroperbenzoic acid by the procedure outlined above. Relatively pure **35** was prepared by the procedure above for the preparation of **8**.

37 was prepared by Jones oxidation[21] of **35**, and a mixture of **37** and **38** was prepared by the oxidation of a mixture (ca. 50:50) of **35** and **36**.

Methanolysis of 2b. A solution of 2.0 g of **2b**, 2.8 mL of triethylamine, and 40 mL of methanol was sealed in a large ampule and heated at 80 °C for 3 h. The reaction solution was diluted with 500 mL of saturated sodium chloride solution and extracted twice with diethyl ether (total 500 mL). The ethereal solution was dried with anhydrous calcium sulfate and concentrated to a volume of ca. 5 mL by distillation of solvent through a 10-cm fractionating column. The residual solution was analyzed by gas chromatography on a 6 ft × ⅛ in., 10% silicone DC-550 column. The product mixture consisted of 38% of elimination products **10** and **11**,[30] 47% of ketal **43**, and 15% of three unidentified products, presumably the methyl ethers of **2a**, **3a**, and **8**. The major product **43** was separated from the rest by preparative chromatography on a 6 ft × ⅜ in., 10% SE-30 column: isolated yield 0.20 g (ca. 25%); UV (cyclohexane) 215 nm (ϵ 294); IR (CCl_4) 1650 (C=C) cm^{-1}; IR (CS_2) 760, 767 (CH=CH) cm^{-1}; NMR (CCl_4) δ 1.6 (m, 8 H), 2.1 (m, 2 H, allylic), 3.34 (s, 3 H, OCH_3), 4.48 (t, J = 5 Hz, 1 H, $CHOCH_3$), 4.85 (q, J = 6 Hz, 1 H, $CH{=}CHCH_2$), 6.04 (d, J = 6 Hz, 1 H, $OCH{=}CH$); molecular weight (mass spectrum) 156.

Hydrolysis of 43. A solution of 9 mg of **43**, 0.10 mL of 5% HCl, and 1 mL of 75% acetone–water was allowed to stand at 0 °C for 30 min. The reaction solution was diluted with water and the product was extracted into diethyl ether. The ethereal solution was dried with anhydrous sodium sulfate, and the solution was concentrated to ca. 0.3 mL by removal of solvent. Only one product was detected by gas chromatographic analysis of the residual solution on a 6 ft × ¼ in., 10% apiezon L column. The product was isolated by preparative GLC: yield 3.0 mg (ca. 37% isolated yield) of a clear oil with an infrared spectrum identical with that of suberaldehyde.

Registry No.—**2a**, 31821-36-0; **2a**-*2-d*, 64312-50-1; **2b**, 31186-86-4; **3a**, 31821-35-9; **3a**-*2-d*, 64252-80-8; **3b**, 31186-87-5; **8**, 64312-49-8; **9**, 29077-87-0; **10**, 6690-12-6; **25**, 64252-79-5; **34**, 64252-78-4; **43**, 64252-77-3; 2-cyclooctenal, 3212-75-7; *p*-bromobenzenesulfonyl chloride, 98-58-8; 9-oxabicyclo[6.1.0]nonan-2-one, 57260-84-1; 2-cyclooctenone, 1728-25-2; 2-cyclooctenol-*d*, 64252-76-2; 3-cyclooctenol, 4114-99-2; 9-oxabicyclo[6.1.0]nonan-3-one, 64252-75-1; sodium tetradeuterioborate, 15681-89-7.

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