ature, the reaction mixture was washed with water and 10% aqueous $NaHCO_3$, dried, and subjected to GLC under the conditions defined above. The results reported in Tables II and IV are averages of three or more experiments, which were reproducible within ±1%.

Acknowledgments. This work has been supported in part by a grant from the Consiglio Nazionale della Ricerche.

Registry No.—**1a**, 14072-87-8; **1b**, 591-48-0; **2a**, 20887-61-0; **2b**, 7443-54-1; **3a**, 20887-60-9; **3b**, 7443-69-8; **4c**, 64199-99-1; **4d**, 64200-00-6; **4g**, 64200-01-7; **4i**, 64162-78-3; **5c**, 38512-63-9; **5c** phenylurethane, 38749-39-2; **5d**, 38512-66-2; **5g**, 64162-79-4; **5i**, 64162-80-7; **6c**, 38512-64-0; **6d**, 64199-91-3; **6g**, 64199-92-4; **6i**, 64199-93-5; **7c**, 38749-36-9; **7d**, 38512-65-1; **7e**, 38749-37-0; **7g**, 64162-81-8; **7i**, 64199-94-6; **8**, 41780-49-8; **9**, 3234-76-2; *p*-nitrobenzoyl chloride, 122-04-3.

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(19) Evidence has been presented that Me_2SO can be the actual nucleophile in the reaction of olefins with NBS in a mixture of Me_2SO and water (see ref 11).

(20) In the latter reactions, nucleophilic attack is carried out by halides on the protonated forms of the epoxides and the **4**:**5** and **6**:**7** ratios quoted in Tables II and IV must be respectively compared with the **6**:**7** and **4**:**5** ratios of Table VI.

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Epoxycarbinyl Solvolyses. Lack of Significant Participation by Epoxide Oxygen in the Hydrolysis of Acyclic Secondary Epoxycarbinyl Substrates

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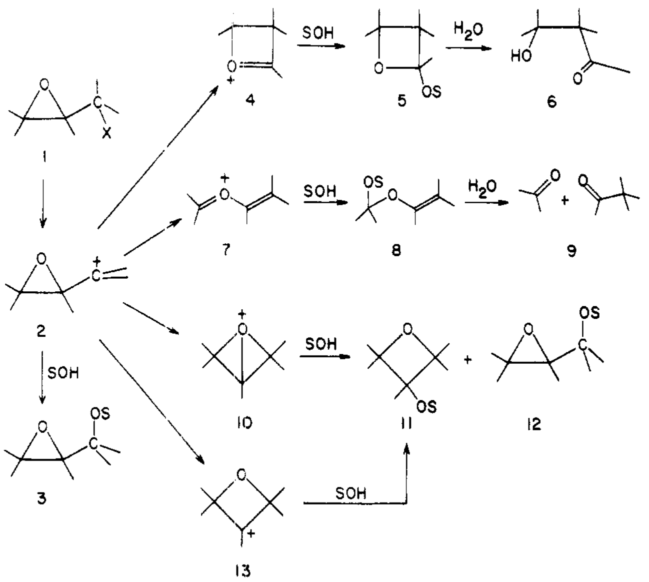
The rate constants and activation parameters for solvolysis of the diastereomeric epoxycarbinyl *p*-bromobenzenesulfonate esters **23b** and **24b** (derived from the oxides of *trans*-3-penten-2-ol) in ethanol–water mixtures have been determined. The predominant products (~88–96%) from solvolysis of **23b** and **24b** in 80% acetone–water resulted from inversion at the ionizing carbon. The product distributions suggest that neither significant amounts of oxabicyclobutonium ion intermediates nor highly stabilized epoxycarbinyl cations are formed. The rates of solvolysis of **23b** and **24b** were ~10^6 times slower than the rates of solvolysis of the corresponding cyclopropylcarbinyl analogues.

Numerous publications about the solvolytic reactions of cyclopropylcarbinyl substrates have appeared during the past 20 years.[1] The stabilizing interaction of the cyclopropane ring with a developing positive charge on the carbinyl carbon is generally reflected by enhanced reactivities of cyclopropylcarbinyl derivatives, relative to model compounds without neighboring cyclopropyl groups. The geometry of the cyclopropyl group relative to the developing p orbital on the carbinyl carbon is critical, however. A "bisecting" geometry of the cyclopropyl group is most favorable, whereas a "perpendicular" geometry actually brings about a destabilizing interaction.[1,2]

More recent results have been reported on the reactions of geometrically related "epoxycarbinyl" substrates of general structure **1** under conditions that lead to the development of a positive charge on the carbinyl carbon.[3–5] Most of the reactions of epoxycarbinyl substrates are analogous to those reactions observed in cyclopropylcarbinyl solvolysis. If the intermediate from the solvolysis of **1** possesses a significant positive charge density on the carbinyl carbon (i.e., **2**), then

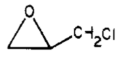
0022-3263/78/1943-0428$01.00/0

Scheme I



product 3 retaining the epoxycarbinyl structure would be anticipated. However, the epoxycarbinyl derivative 1 can also potentially rearrange in either concerted pathways or via 2 to other intermediates 4, 7, 10, or 13. Migration of the carbon–carbon bond or the carbon–oxygen bond of the epoxide group in 2 to the electron-deficient center would yield oxonium ion 4 or 3-oxetanyl cation 13, respectively, and would be analogous to the cyclopropylcarbinyl–cyclobutyl cation rearrangement. Intermediate 4, in water, would eventually yield β-ketols. In a reaction related to the cyclopropylcarbinyl–homoallyl interconversion, rupture of the carbon–carbon bond of the epoxide group in 2 yields oxonium ion 7, the precursor to carbonyl products 9. There is also the possibility that the nonbonding electrons on the oxygen in 2 would interact with the adjacent positive charge on the carbinyl carbon, thereby leading to an intermediate oxabicyclobutonium ion 10. Intermediate 10 can potentially yield products 11 and 12.

The solvolytic reactions of epichlorohydrin (14) and 3,5-dinitrobenzoate esters 15–17 have been reported to yield 3-oxetanyl products, and oxabicyclobutonium ions were suggested as possible intermediates.[3] The study of the solvolysis of epichlorohydrin (14) was hindered, however, because any solvolysis products that retained the epoxycarbinyl structure could not have survived the reaction conditions.[3a] The *erythro*- and *threo*-*p*-toluenesulfonate esters 18 and 19 hydrolyzed to yield predominantly β-ketols (>80%), presumably via a 2-oxetanyl cation 4.[5a] Anchimeric assistance by the neighboring epoxide was invoked to explain the hydrolysis product distributions.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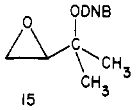
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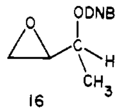
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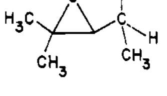
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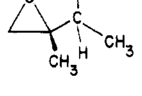
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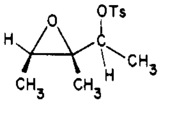
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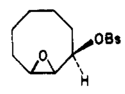
Oxabicyclobutionium ion 22 was ruled out as an intermediate in the hydrolysis of the epimeric medium-ring epoxycarbinyl brosylates 20 and 21,[4] although geometric constraints of the medium ring may have made such intermediate unlikely. Rearrangement products from intermediate oxonium ions of the structural types 4 and 7 were observed, however, in addition to products that retained the epoxycarbinyl structure. It was estimated that epimeric esters 20 and 21 were both about 6–7 powers of ten less reactive than their cyclopropylcarbinyl analogues. Likewise, it can be estimated from published rate data[5a] that 18 and 19 are considerably less reactive toward hydrolysis than related cyclopropylcarbinyl systems.[6] Therefore, the epoxide group appears much less effective than cyclopropyl for stabilizing a developing positive charge on the carbinyl carbon. These reactivities seem to be inconsistent with one set of calculations that suggest that the carbon–carbon bond of an epoxide group should stabilize the positive charge on the adjacent carbinyl carbon as effectively as carbon–carbon bonds of cyclopropanes do for certain geometries.[7]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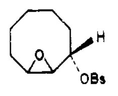
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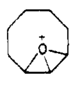
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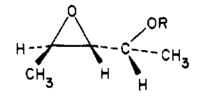
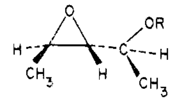
In view of the fact that medium-ring constraints in the solvolysis of 20 and 21 may have made the formation of 22 unlikely and since oxabicyclobutonium ions had already been postulated as intermediates in the solvolysis of several simple epoxycarbinyl systems,[3] we have undertaken a study of the hydrolysis of the epimeric epoxycarbinyl brosylates 23b and 24b, in which the carbinyl carbon is secondary. Esters 23b and 24b are free of any medium-ring constraints for formation of oxabicyclobutonium ion intermediates, and maximum stabilization of the developing positive charge by the epoxide ring can be attained by rotation about the C_2–C_3 bond for the preferred geometry. Compounds 23b and 24b also do not possess a β-methyl group such as *p*-toluenesulfonate esters 18 and 19. The β-methyl groups of 18 and 19 give rise to neopentyl-type structures which result in appreciable steric hindrance to solvation at the carbinyl carbon and are prone to rearrangement.[8]


23a, R = H
b, R = Bs


24a, R = H
b, R = Bs

Results

Epoxidation of *trans*-3-penten-2-ol with *m*-chloroperbenzoic acid yielded a mixture of diastereomeric epoxycarbinols 23a and 24a in a 65:35 ratio. The relative stereochemistry of the hydroxyl group relative to the oxirane ring for either of the products was not established. For purposes of discussion, the structure 23a was assigned to the major component of the product mixture, and, consequently, the structure 24a was assigned to the minor component. The products were separated by preparative gas chromatography and converted to their *p*-bromobenzenesulfonate esters. The rates for solvolysis of 23b and 24b were determined ethanol–water mixtures at several temperatures and are listed in Table I. The activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for solvolysis of 23b and 24b in 80% ethanol–water are also provided.

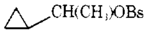
Isomer 23b hydrolyzed in 90% acetone–water to yield a mixture of epoxycarbinols containing ~96% of inverted product 24a, and ~4% of retained alcohol 23a. No products with gas chromatography retention times different from 23a and 24a could be detected. Brosylate 24b hydrolyzed under the same conditions to yield 88% of inverted product 23a and ~12% of retained product 24a. As in the hydrolysis of 23b, no other products from 24b could be detected by gas chromatographic analysis of the product mixture.

Table I. First-Order Rate Constants[a] and Activation Parameters[a] for Solvolysis of 23b and 24b in Ethanol–Water Mixtures[b]

Compd	Registry no.	Temp, °C	$10^5 k$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, kcal/mol
			80% Ethanol–Water		
23b	64312-47-6	75.00	64.8 ± 0.4		
		70.10	41.3 ± 0.6		
		64.83	26.0 ± 0.8		
		59.75	15.4 ± 0.2		
		35.2	1.34 ± 0.01		
		25.0	0.36[c]	20.8 ± 0.2	−13.6 ± 0.6
24b	64252-18-2	69.95	26.6 ± 0.7		
		64.95	16.4 ± 0.8		
		59.85	11.0 ± 0.4		
		35.2	0.99 ± 0.07[d]		
		25.0	0.29[c]	19.7 ± 0.6	−17.6 ± 1.9
			60% Ethanol–Water		
23b		35.2	2.48 ± 0.02		
24b		35.2	2.24 ± 0.01		
			50% Ethanol–Water		
23b		35.2	3.50 ± 0.01		
24b		35.2	3.76 ± 0.02[d]		

[a] Calculated by nonlinear regression analysis. Errors are given in units of standard deviation. [b] v/v. The percent listed corresponds to the percent of ethanol. Triethylamine was added as a buffering reagent. [c] Extrapolated from rates at higher temperatures. [d] Average of two kinetic runs.

Table II. Relative Rates of Solvolysis of Several Brosylate Esters in 80% Ethanol–Water at 25 °C

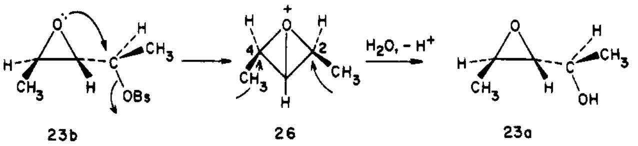
Compound	k_{rel}, s^{-1}
Isopropyl brosylate[a]	0.8
sec-Butyl brosylate[b]	1.0
23b	0.19
24b	0.15
 $\mathrm{CH(CH_3)OBs}$ (**25**)[c]	~10^6

[a] Reference 14. [b] V. J. Shiner, Jr., "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N.Y., 1970, p 129. [c] Reference 6. Rates were extrapolated to common solvent, temperature, and leaving group.

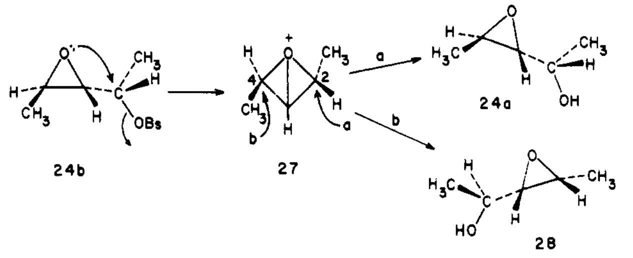
Discussion

The relative rates of solvolysis of **23b**, **24b**, and several other model compounds are listed in Table II. If an epoxide group were able to stabilize the development of a positive charge on an adjacent carbon as efficiently as a cyclopropane ring, then the relative rates of solvolysis of **23b**, **24b**, and α-methylcyclopropylcarbinyl brosylate (**25**) would be expected to be similar. As Table II indicates, however, **23b** and **24b** are about 10^6 times less reactive to solvolysis than the geometrically related cyclopropylcarbinyl analogue. Therefore, in these simple secondary acyclic epoxycarbinyl derivatives and in several medium-ring epoxycarbinyl derivatives,[4] the epoxide groups are not nearly as effective as cyclopropyl groups in stabilizing an adjacent positive charge on carbon. In fact, **23b** and **24b** are ca. five times less reactive than *sec*-butyl brosylate, an ester of similar structure to **23b** and **24b** except that the epoxide moieties of **23b** and **24b** have been replaced by ethyl groups. Because of the different structures of **23b** and **24b** compared to *sec*-butyl brosylate, the small differences of solvolytic reactivities might be attributed to either a destabilizing electronic effect of an epoxide group or to different steric requirements of an epoxide moiety relative to an ethyl group.

Scheme II

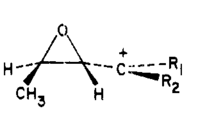


Scheme III



Because of the lack of a suitable model for estimating the rates of solvolysis of **23b** and **24b** in the absence of participation by the epoxide group, knowledge of the product compositions is essential to understanding the mechanisms of their solvolytic reactions. If **23b** were to solvolyze with participation of the *n* electrons of the adjacent epoxide group, an intermediate oxabicyclobutonium ion **26** would form (Scheme II). Because of its symmetrical structure, **26** should collapse with solvent at either C_2 or C_4 with inversion to yield a single product **23a**, an overall process that would give rise to retention of stereochemistry.[9] Ionization of the diastereomeric alcohol **24b** with participation of the *n* electrons of oxygen, however, would result in the formation of oxabicyclobutonium ion **27** (Scheme II). Intermediate **27**, however, does not possess a plane of symmetry. Whereas collapse of solvent at C_2 of **27** would yield **24a**, a process involving overall retention of stereochemistry, collapse of solvent at C_4 of **27** would yield **28**, an epoxycarbinol derived from *cis*-3-penten-2-ol.[9]

If participation by the *n* electrons of oxygen in the solvolysis of **23b** and **24b** did not occur, but rather an intermediate **29** were formed in which charge is located primarily at C_2, then solvolysis of **23b** and **24b** should yield mixtures of only **23a** and **24a**. The stabilized cyclopropylcarbinyl cation **30** yields 72% of product from collapse of water at the top side (a) and 28%



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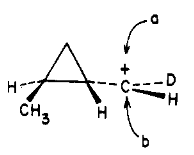

30

of product from collapse of water at the bottom side (b).[10] A stabilized cation **29** might therefore be expected to give similar results, i.e., significant collapse of solvent from both sides of the cationic center.

The actual product distributions observed in the solvolysis of **23b** and **24b**, resulting from predominant inversion at C_2, suggest that neither significant amounts of oxabicyclobutonium ions **26** and **27**, nor a highly stabilized cation **29** are formed. The results of solvolysis of **23b** and **24b** are very similar to those observed in the solvolysis of simple secondary systems such as 2-butyl or 2-octyl *p*-bromobenzenesulfonates, namely, predominant inversion at the ionizing center.[11] Such inversion is observed in acyclic systems when the intermediate is an unstabilized primary[12] or secondary cation, and results from either an S_N2-type displacement by a solvent molecule or collapse of an intermediate tight ion pair with a solvent molecule preferentially at the backside of the ionizing carbon.

The Grunwald–Winstein *m* values[13] for solvolyses of **23b** and **24b** in ethanol–water solutions (Table I) were calculated to be 0.20 and 0.34, respectively. In the absence of anchimeric assistance, low *m* values generally reflect a high degree of solvent participation at the transition state. For instance, *m* values for isopropyl brosylate and *sec*-butyl tosylate are 0.44[14] and 0.47,[15] respectively. Both low *m* values and predominant inversion at ionizing carbon are consistent with high degrees of solvent involvement of a nucleophilic nature at the transition states for solvolysis of **23b** and **24b** in ethanol–water mixtures. These results do not preclude the possibility that in more highly-ionizing, less nucleophilic solvents **23b** and **24b** may solvolyze by different mechanisms.

Experimental Section

Melting points were determined in capillary tubes and are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 257 spectrophotometer, and ^1H NMR spectra were recorded on a Hitachi Perkin-Elmer R-20A spectrometer. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of 23a and 24a. To a solution of 4.9 g (0.057 mol) of *trans*-3-penten-2-ol[16] in 100 mL of methylene chloride stirred in an ice–water bath was added 13.0 g of *m*-chloroperbenzoic acid[16] over a period of 5 min. The reaction mixture was stirred at 0 °C for an additional hour, and the solid precipitate of *m*-chlorobenzoic acid was separated by suction filtration and washed with cold methylene chloride. The filtrate was washed with saturated sodium bicarbonate solution (2 × 75 mL), and the solvent was removed at aspirator pressure. The residue was distilled in a short-path distillation apparatus under reduced pressure (15 mm) at a bath temperature of 85 °C to yield 4.1 g (70%) of a clear oil that consisted of 65% **23a** and 35% **24a**:[17] IR (CCl_4) 3600–3100 cm^{-1}.

The products were separated by preparative gas chromatography on a 12 ft × ¼ in. 20% diethylene glycol succinate (DEGS) column at 80 °C: retention time of **23a** 26.5 min; retention time of **24a** 24.0 min.

The NMR spectrum (CCl_4) of **23a** consisted of absorptions at δ 1.1–1.3 (6 H, CH_3), 2.44 (d of d, 1 H, C_3 H), 2.77 (m, 1 H, C_4 H), 3.38 (m, 1 H, CHOH), and the NMR spectrum (CCl_4) of **24a** possessed absorptions at δ 1.1–1.3 (6 H, CH_3), 2.45 (ca. t, 1 H, C_3H), 2.82 (m, 1 H, C_4H), and 3.65 (m, 1 H, CHOH).

Anal. (**24a**) Calcd for $C_5H_{10}O_2$: C, 58.80; H, 9.87. Found: C, 58.65; H, 10.05.

***p*-Bromobenzenesulfonate Ester 23b.** Powdered potassium hydroxide (4.0 g of 85% KOH, 71 mmol) was added to a solution of 142 mg (1.39 mmol) of **23a** (contaminated with 5% of **24a**) and 402 mg (1.57 mmol) of *p*-bromobenzenesulfonyl chloride in 6 mL of diethyl ether. The resulting suspension was stirred in an ice–water bath for 1 h. An additional 20 mL of diethyl ether was added, and the reaction mixture was dried with anhydrous calcium sulfate and filtered. Removal of the solvent yielded 348 mg (ca. 78%) of **23b**, which was recrystallized from a diethyl ether–pentane solution to yield 271 mg of **23b**: mp 37.5–38.5 °C; NMR (CCl_4) δ 1.1–1.4 (6 H, methyl absorptions), 2.45–2.85 (m, 2 H, protons on epoxide ring), 4.23 (pentet, 1 H, J = 6 Hz, CHOBs), 7.43 (s, 4 H, aromatic protons).

Anal. Calcd for $C_{11}H_{13}O_4SBr$: C, 41.14; H, 4.08. Found: C, 41.04; H, 4.17.

***p*-Bromobenzenesulfonate ester 24b** was prepared from 30 mg of **24a** (containing ~4% of **23a**) by the same procedure outlined above for the preparation of **23b**. The product was further dried under vacuum (2 mm): yield 74 mg (~78%) of clear oil; NMR (CCl_4) δ 1.1–1.4 (6 H, methyl absorptions), 2.40–2.75 (m, 2 H, protons on epoxide ring), 4.14 (pentet, 1 H, J = 6 Hz, CHOBs), 7.43 (s, 4 H, aromatic protons).

Anal. Calcd for $C_{11}H_{13}O_4SBr$: C, 41.14; H, 4.08. Found: C, 41.07; H, 4.21.

Kinetic Procedures. A. Approximately 15 mg of **23b** or **24b** and 15 μL of triethylamine were dissolved in 25 mL of an ethanol–water solution. Approximately 2.5 mL of this solution was sealed in each of ten ampules. The ampules were then 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.[18]

B. The rates of solvolyses of **23b** and **24b** at 35.2 °C were determined by monitoring the absorbance of the reaction solution at 265 nm in the thermostated cell compartment of a Gilford 2400 spectrophotometer.

Rate constants were obtained by nonlinear regression analysis of the data, for each kinetic run, by a Wang 700 calculator computer.

Product Analyses. A solution of ca. 30 mg of **23b** or **24b**, 1.2 mL of 90% acetone–water (v/v), and 30 μL of triethylamine was sealed in an ampule and placed in an oil bath for 20 h (ca. 10 half-lines). The reaction solution was diluted with ca. 10 mL of water and continuously extracted with diethyl ether for 6 h. Most of the organic solvent was distilled through a 10-cm column packed with glass helices, and the residual solution was analyzed by gas chromatography on a 10% diethylene glycol succinate column (15 ft × ⅛ in.) at 90 °C. Cyclopentanol (7.0 mg) was added to the product mixture to serve as an internal standard for chromatographic analysis. The yields from the hydrolysis of **23b** and **24b** were generally 85–95%.

The products from the hydrolysis of **23b** were **24a** (~96%) and **23a** (~4%). The major product was separated by preparative GLC and identified as **24a** by its infrared spectrum. The minor product possessed the same GLC retention time as **24a**.

The products from the hydrolysis of **24b** (estimated to contain ~4% of **23b**) were ~84% of **23a** and ~16% of **24a**. Both products were separated by preparative GLC and identified by infrared spectroscopy. Since it was estimated that **24b** was contaminated with ~4% of **23b**, the product composition was corrected for the fact that **23b** undergoes predominant inversion when hydrolyzed. Therefore, we estimate that pure **24b** yields ~88% of **23a** and ~12% of **24a**.

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Registry No.—**23a**, 26091-69-0; **24a**, 22520-29-2; *trans*-3-penten-2-ol, 3899-34-1; *p*-bromobenzenesulfonyl chloride, 98,58,8.

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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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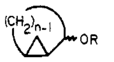
The rates of solvolysis of *syn*- and *anti*-9-oxabicyclo[6.1.0]non-2-yl *p*-bromobenzenesulfonates (**2b** and **3b**) have been determined and were found to be ~10^7 times slower than those of the corresponding cyclopropylcarbinyl analogues **4b** and **5b**. The product distributions from hydrolysis 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]

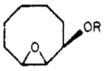
The nature of the epoxycarbinyl cation clearly is a function of the system from which it is derived. It has been suggested that several acyclic epoxycarbinyl derivatives solvolyze via the intermediacy of oxabicyclobutonium ions.[4] Other acyclic epoxycarbinyl substrates in which the carbinyl carbon is 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

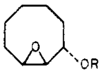
First-order rate constants for the solvolysis of **2b** and **3b** are provided in Table I, and the relative reactivities of **2b**, **3b**, and the related *syn*- and *anti*-2-bicyclo[6.1.0]non-2-yl systems[1a] are provided in Table II. Of significance is the fact that the rates of solvolysis of **2b**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



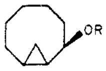
1



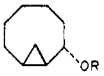
2a, R = H
b, R = Bs



3a, R = H
b, R = Bs



4a, R = H
b, R = PNB



5a, R = H
b, R = PNB

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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