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Displacement stereochemistry and product-formation selectivities in the solvolysis of cyclooctyl p-bromobenzenesulfonate

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for multiple proton exchanges during an encounter. Multiple exchange during an encounter has been observed for several proton-exchange reactions,^{37a,d-f} but our data do not permit a decision as to whether the observed diminution of selectivity arises from incomplete equilibration of the isomeric bases or from multiple proton exchanges during the encounter.

We consider that the observation of positional selectivity in this exchange reaction is strong evidence for Scheme II and for the Swain–Grunwald mechanism. This mechanism is an attractive one, which must occur, and it has been widely accepted. However, the chief evidence for it is the inhibition by acid of the proton exchange of ammonium ions,^{10,38} and this inhibition is seen only in nonideal solutions. Nonideality is inherent, since $>0.1 M H^+$ is required in order that reprotonation of the intermediate be competitive with a process whose rate constant is above $10^9 s^{-1}$. Yet inhibition by acid is a thermodynamic necessity in such nonideal solutions. It is readily shown that the simplest mechanism, without k_H , leads to an observed first-order rate constant for exchange given by

$$k_{\text{obsd}} = k_2 K_a^{AH^+} [H^+] / h_0 \quad (2)$$

where k_2 is the second-order rate constant for encounter-controlled reprotonation of amine A by H^+ , and h_0 is the acidity function governing protonation of A. Since h_0 increases faster than $[H^+]$ in strong acid, k_{obsd} must decrease in acid, and since $[H^+]/h_0$ is a strong function of water activity,³⁹ a 500-fold decrease in k_{obsd} is consistent with a 7.4-fold decrease in water activity, despite a denial.^{38a} Moreover, there is an implicit assumption that k_2 is independent of acidity, whereas proton mobility does decrease at high concentrations.²² Thus nonideality taints the evidence for

the Swain–Grunwald mechanism. Our results are also obtained in nonideal solutions, but all comparisons are intramolecular, and the only uncertainty arising from nonideality is in the second-order rate constants, whose values are immaterial so long as they are accepted as being in the range of encounter control. Thus these results are an independent confirmation of the existence of the Swain–Grunwald mechanism.

Conclusions and Summary

To the best of our knowledge, here is the first demonstration of positional selectivity in an encounter-controlled proton exchange. These proton exchanges are so favorable thermodynamically that they are expected to be encounter controlled, and the second-order rate constants support this. However, positional selectivity forces us to conclude that the reaction is not completely encounter controlled. Even though hydroxide is a sufficiently strong base to remove all amidinium protons upon encounter, so that their acidity should be immaterial, it is always the most acidic proton that exchanges fastest. We therefore conclude that the Swain–Grunwald mechanism is operative and that the rate-limiting step is in part the breaking of a hydrogen bond in the amidine hydrate. Simulation, using reasonable rate constants, shows that the observed selectivity is consistent with this mechanism. We therefore conclude that these results represent independent evidence for the Swain–Grunwald mechanism.

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Registry No. 1 (R = H), 50676-76-1; 1 (R = CH_3), 52018-42-5; 1 (R = Ph), 53356-58-4; 1 (R = $CH_2N^+CC(CH_3)_2N=NC(CH_3)_2$), 79246-17-6; 2 (R = CH_3), 79734-87-5; 2 (R = Ph), 79734-88-6; 3 (n = 5), 79734-89-7; 3 (n = 7), 79734-90-0; *N,N*-dimethylacetamidinium ion, 79734-91-1.

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Displacement Stereochemistry and Product-Formation Selectivities in the Solvolysis of Cyclooctyl *p*-Bromobenzenesulfonate

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Abstract: Configurational analysis by 2H NMR of the products of solvolysis of (*E*)-cyclooctyl-2-*d* and (*E*)-cyclooctyl-4-*d* brosylate in acetic acid and 80% acetone has established that substitution without rearrangement occurs with complete retention of configuration while substitution under 1,5-hydride shift takes place with complete inversion at the migration origin. The reaction is concluded to proceed by direct initial formation of a 1,5-hydrogen-bridged cation. Solvolysis of cyclooctyl-1-*d* brosylate in several solvents has shown elimination to be favored from the C-1 over the C-5 side, whereas selectivities for competitive substitutions are similar at the two positions. Elimination is thus indicated to take place largely from first-formed tight ion pairs while displacement proceeds through more dissociated intermediates.

The cyclooctyl and other medium-ring systems are of distinctive importance to solvolysis theory by reason of their characteristic rearrangements under transannular hydride shift.¹ Cope and Gale² determined that net 1,5-hydride migration occurs to the

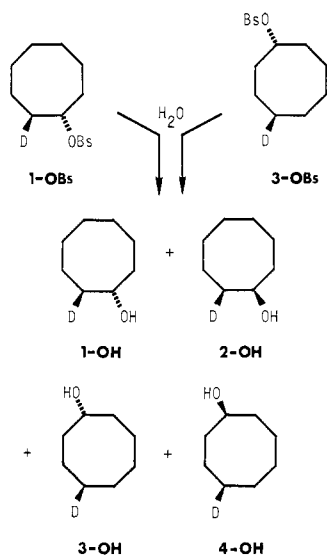
extent of 53%, 60%, and $\geq 62\%$ on solvolysis of cyclooctyl-1,2,2,8,8-*d*₅ brosylate in acetic, formic, and trifluoroacetic acid, respectively. Regioalternative rearrangements were found to be negligible.² Parker and Watt³ synthesized the *cis*- and *trans*-cyclooctyl-5-*d* brosylates and deduced a 10:1 preference for transposition of a *trans*- over a *cis*-5-hydrogen in acetolysis.

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Scheme I

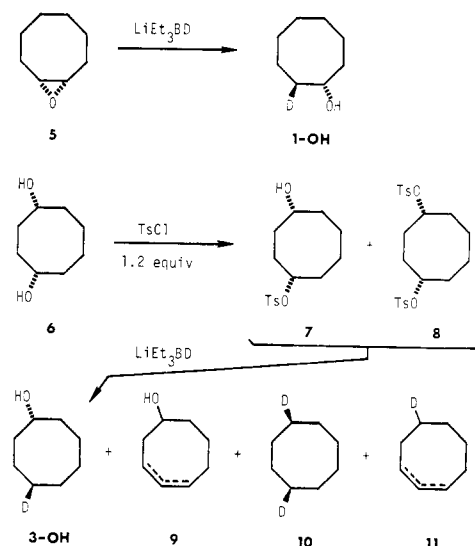


Similar stereoselectivity of hydride migration had been concluded earlier from reactions of the epimeric 5-methyl-,⁴ 5-phenyl-,^{5,6} and 5-*tert*-butylcyclooctyl⁷ tosylates.

Considerable effort has been made to ascertain whether the cross-ring hydride involvement occurs in concert with or subsequent to ionization of the leaving group. Cyclooctyl reactants solvolyze markedly faster than aliphatic and cyclohexyl models,^{3,7-16} but competing explanations have been offered for the acceleration in terms of hydride bridging (k_A reaction)^{3,7,8,10-12} or relief of steric compressions and bond oppositions on ionization (k_c).^{6,9-12,14-16} Harris, McManus, Raber, and co-workers^{14,15} have ruled out significant nucleophilic solvent assistance (k_s) by the observation that cyclooctyl tosylate solvolysis is unaffected by added azide ion and shows log k behavior linear with that of 1-adamantyl bromide in aqueous ethanol and trifluoroethanol solvents. A k_c interpretation was favored. Schneider and Thomas¹⁶ have recently found that the trifluoroethanolysis rates of the C₅-C₁₁ cycloalkyl tosylates correlate well with strain energies of activation estimated by force-field calculations, also supportive of a k_c mechanism.

Early measurements of kinetic isotope effects in multiply deuterated reactants^{12,17} were suggestive of assisted ionization but were not specifically attributable. Parker and Watt³ more recently determined $k_H/k_D = 1.04$ for *cis*- and 1.12 for *trans*-5-*d*-labeled cyclooctyl brosylate in acetolysis and judged the latter effect to be indicative of transannular participation in the ionization step. Harris, McManus, and Raber,¹⁵ on the other hand, have taken these isotope effects together with the α -*d* value of 1.18³ to be more consistent with a k_c than with a k_A process.¹⁸

Scheme II



A remarkable development since 1978 has been the direct NMR identification by Sorenson et al. of a group of low-temperature medium-ring cycloalkyl cations^{19,20} as strongly μ -hydrido-bridged structures, including the cyclooctyl, 1-methylcyclooctyl, and 1,5-dimethylcyclooctyl species.¹⁹

We report here new insights into the mechanism of cyclooctyl brosylate solvolysis gained from determination of the stereochemistry of nonrearranging and rearranging substitutions and comparative rates of competitive reactions at the corresponding positions in binary hydroxylic solvents. Schneider and Heiske have recently reported a closely related independent stereochemical investigation of the *cis*- and *trans*-3-*tert*-butylcyclooctyl tosylates.²¹

Results

Stereochemistry. The displacement stereochemistry was established by analysis of the products from (*E*)-cyclooctyl-2-*d* brosylate (1-OBs) and (*E*)-cyclooctyl-4-*d* brosylate (3-OBs). Hydrolysis of 1-OBs could yield one or both of the epimeric cyclooctanols-2-*d*, 1-OH and 2-OH, by nonrearranging reaction, and one or both of the cyclooctanols-4-*d*, 3-OH and 4-OH, by substitution through 1,5-hydride shift, as shown in Scheme I. For 3-OBs the possibilities are vice versa. Configurational identification of the proximally deuterated alcohols, 1-OH +/- 2-OH, from 1-OBs and 3-OBs was thus projected to reveal the stereochemistry of the nonrearranging and rearranging substitutions, respectively. ²H NMR was found to provide the needed resolution.

The labeled reactant alcohols 1-OH and 3-OH were prepared as outlined in Scheme II. Ring opening of *cis*-cyclooctene oxide^{22a} (5) with lithium triethylborodeuteride afforded 1-OH. Treatment of *cis*-1,4-cyclooctanediol²² (6) with 1.2 equiv of tosyl chloride and reduction of the resulting mono- (7) and ditosylate (8) mixture with excess lithium triethylborodeuteride yielded 3-OH along with

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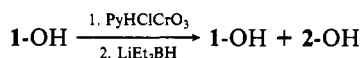
Table I. Solvolysis Products of (*E*)-Cyclooctyl-2-*d* and -4-*d* Brosylates (1-OBs and 3-OBs) at 35.5 °C

reactant	solvent	% 2- <i>d</i> alcohols		% 4- <i>d</i> alcohols	
		1-OH (<i>E</i>)	2-OH (<i>Z</i>)	3-OH + 4-OH	% olefins
1-OBs	HOAc ^a	39 ^b	0 ^b	30 ^b	31
3-OBs	HOAc ^a	31 ^b	0 ^b	37 ^b	32
1-OBs	80% Me ₂ CO ^c	41	0	37	22
3-OBs	80% Me ₂ CO ^c	34	0	44	22

^a Containing 1% (wt) of Ac₂O and 1.2 equiv of NaOAc. ^b After LiAlH₄ reduction of the acetate product. ^c Containing 1.2 equiv of 2,6-lutidine.

enols **9** and hydrocarbons **10** and **11** as byproducts. Isolation of **3-OH** from the alcohols was accomplished by simple chromatography after conversion of the enols to more adsorbent diols by hydroboration-oxidation. The *E* configuration could be assigned to **1-OH** and **3-OH** with considerable confidence from precedent direct displacement reactions with LiEt₃BH and LiEt₃BD,²³ and these identifications were confirmed by the subsequent solvolytic results.

Oxidation of **1-OH** with pyridinium chlorochromate²⁴ and LiEt₃BH reduction of the resultant ketone provided a 1:1 mixture of the original alcohol and its *Z* epimer, **2-OH**. The proton-



decoupled 15.4-MHz ²H NMR spectrum of a sample of this mixture plus an equal weight of **1-OH** with added shift reagent Ho(fod)₃ exhibited two broadened but fully resolved peaks, whose assignments followed from the relative intensities (see Experimental Section). The powerfully shifting Ho(fod)₃²⁵ was employed after Eu(fod)₃ and Pr(fod)₃ were found to produce insufficient resolution. These results together with the Eu-induced ¹H shift observations reported by Parker and Watt³ made it evident that the diastereomeric 4-labeled alcohols **3-OH** and **4-OH** would not be quantitatively distinguishable by ²H NMR under the present conditions. The signal for **3-OH** was found to be well separated, however, from those for **1-OH** and **2-OH** in the presence of Ho(fod)₃, completing development of the analytical method.

Substrates **1-OBs** and **3-OBs** were solvolyzed at 35.5 °C in acetic acid (1% acetic anhydride) buffered with sodium acetate and in 80% aqueous acetone buffered with 2,6-lutidine. Brosylate was chosen over tosylate as the leaving group to minimize substrate isomerization.^{3,12} The product mixtures were analyzed by gas chromatography for substitution vs. elimination, and the derived alcohols were separated by gas chromatography and analyzed for deuterium distribution by ²H NMR with added Ho(fod)₃. Uncertainty limits in the NMR measurements are estimated to be 3%. The results are presented in Table I. Displacement was found to proceed with 1,5-hydride shift to the extent of 43% in acetic acid (cf. 53% reported by Cope and Gale² for somewhat different conditions) and 48% in 80% acetone.

Strikingly, the nonrearranging substitutions in both solvents are revealed to take place entirely with retention of configuration, while both transannular substitutions occur exclusively with inversion at the C-5 migration origin.

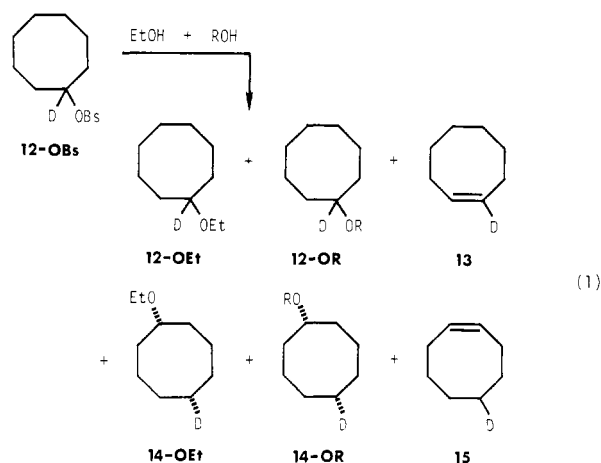
Comparative Product-Formation Selectivities. The characteristics of solvolysis with and without rearrangement were further

Table II. Solvolysis Products of Cyclooctyl-1-*d* Brosylate (12-OBs) at 35.5 °C

solvent ^a	% 12-OEt	% 12-OR	% 13	% 14-OEt	% 14-OR	% 15
HOAc ^b		39 ^c	20		29 ^c	12
80% EtOH, 20% H ₂ O ^d	12	15 ^e	42	8	10 ^e	13
60% EtOH, 40% TFE ^d	24	9 ^f	29	18	8 ^f	12
50% EtOH, 50% TFE ^d	17	17 ^f	22	16	14 ^f	14
40% EtOH, 60% TFE ^d	13	22 ^f	19	12	21 ^f	13

^a Volume %. ^b Containing 1% (wt) of Ac₂O and 1.2 equiv of NaOAc. ^c R = Ac. ^d Containing 1.2 equiv of 2,6-lutidine. ^e R = H. ^f R = CH₂CF₃.

compared by determination of the product distributions from cyclooctyl-1-*d* brosylate (**12-OBs**) in one simple and several binary buffered hydroxylic media: acetic acid, 80% aqueous ethanol, and ethanolic 2,2,2-trifluoroethanol²⁶ (TFE) of three compositions, all at 35.5 °C. The general reaction in the mixed solvents, incorporating the preceding stereochemical findings, is shown in eq 1. Quantitative analyses and small-scale isolations of the



nonisomeric products were accomplished by gas chromatography. The collected samples were then analyzed for deuterium distribution by ²H NMR, chemical shift reagents being unnecessary here. The results are presented in Tables II and III.

A control experiment was conducted to assess the extent of transannular isomerization of **12-OBs** during solvolysis in 50% ethanolic trifluoroethanol. ¹H NMR analysis of the reactant recovered after 1.0 half-life showed it to contain 11% of **14-OR** (R = Bs).

Discussion

The finding of substitution in two representative solvents both with and without rearrangement solely on the face of the ring originally bearing the leaving group is strong evidence for product formation at both electrophilic sites from a hydrogen-bridged cyclooctyl cation. The stereochemistry is characteristic of *k_A* solvolysis, as exemplified by select β-arylalkyl sulfonates,²⁷ *anti*-7-norbornenyl tosylate,²⁸ 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl *p*-nitrobenzoate,²⁹ and the coupled 1-methyl-2-adamantyl tosylate

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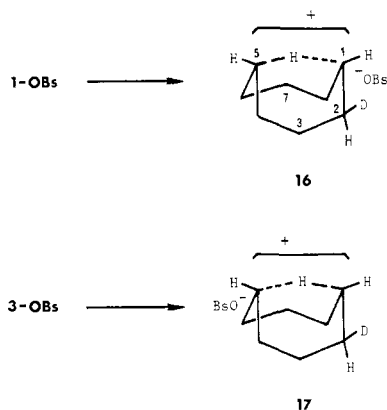
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and 4-methyl-4-protoadamantyl 3,5-dinitrobenzoates.³⁰ Reaction at a secondary center by the k_c mechanism, in contrast, is ordinarily marked by variable measurable competition between inversion and retention pathways.^{31,32} k_s -Type solvolysis occurs with predominant to complete inversion of configuration.^{27a,33} The present stereochemical results for nonrearranging displacement thus support the evidence of Harris et al.^{14,15} against an appreciable k_s component in cyclooctyl solvolysis.

The stereochemical findings are additionally significant in demonstrating that the substitutions under transannular rearrangement do not proceed by way of a discrete carbenium ion at C-5. The conformational flexibility of such an intermediate would be expected to lead to an observable fraction of rearranged alcohol with retained as well as inverted configuration.

The availability to cyclooctyl brosylate of conformations favorable to k_s solvolysis^{14,15} is evidenced by the substantial S_N2 reactivity of cyclooctyl bromide¹⁰ and *trans*-2-acetoxycyclooctyl bromide.³⁴ The solvolytic ionization mechanism actually operative must be compensated kinetically over this possibility. We conclude on this basis that the stereochemical data point to *trans*-5-H-assisted ionization with direct formation of a bridged cation, tightly paired with brosylate anion. Thus, we consider **16** to be the first intermediate from 1-OBs and **17** from 3-OBs. The conformations depicted for **16** and **17** have C-3 and C-7 nonequivalent in accordance with Sorensen's finding for the stable bridged cyclooctyl cation.¹⁹ The hydride bridges here are drawn as unsymmetrical in allowance for the cation-stabilizing effect of the brosylate counterions.



The hydride-participation and steric-relief theories for the cyclooctyl rate enhancement can be seen in the light of the stereochemistry as complementary rather than alternative. Thus, on ionization of 1-OBs in a conformation generative of **16** 1,5-H-H compression is replaced by attractive interaction between the bonding electrons of the *trans*-5-hydrogen and the back lobe of

the incipient vacant p orbital at C-1. Possible ionization proceeding from other conformations would be assisted by strain relief⁹ but not charge delocalization and would therefore be disfavored relative to the direct formation of **16**.

Additional mechanistic information is contained in the product distributions from the 1-*d* reactant, 12-OBs, Tables II and III. These data show the selectivities for product formation with and without rearrangement to be substantially different in one respect while notably similar in another. Specifically, the proportion of elimination is consistently and in certain cases markedly higher from the C-1 than from the C-5 side. This observation is consistent with evidence from several laboratories^{32,33g,h,35,36} that tightly paired gegenion functions as the principal base in E1 eliminations in weakly basic media. Further support for this hypothesis is furnished by the finding that in the solvolyses of 12-OBs in ethanolic trifluoroethanol an increase in trifluoroethanol content leads to a decreased yield of unrearranged olefin, **13**, but no change in the proportion of rearranged olefin, **15** (Table II). As electrophilic solvation of brosylate in the initial tight ion pair is increased by enrichment of the medium in trifluoroethanol, the effectiveness of the counterion as a base in the E1 reaction should decrease. These combined results along with the measurement of only minor substrate isomerizations in the acetolysis³ and 50% ethanolic trifluoroethanolysis of 12-OBs show that C-1 and C-5 maintain predominant structural nonequivalence at the tight ion-pair stage of reaction.

In contrast to the discrepant elimination/substitution ratios, the selectivities for competitive nucleophilic attachments, EtOH vs. H₂O or TFE, are nearly the same for the nonrearranging and rearranging pathways. The principal intermediates for displacement product formation are thus comparatively similar in structure and environment at C-1 and C-5. These must be solvent-separated ion pairs or possibly more dissociated cyclooctyl cations in view of the complete retention of configuration attending nonrearranging substitution. Here the bridging would be more nearly symmetrical than in **16** and **17**. These species must be formed wholly or for the most part irreversibly from the initial contact ion pairs in view of the elimination results for 12-OBs discussed above. Total substitution is in general greater at C-1 than at C-5, although in ethanolic trifluoroethanol these data converge as the fraction of trifluoroethanol is increased to 60%. In this last solvent, then, the highly solvated brosylate ion ceases to exercise a regiochemical influence on completion of the displacement process. It continues nevertheless to effect preferred elimination on the C-1 side, presumably at the earlier tight ion-pair stage, as discussed.

Schneider and Heiske²¹ have established the same stereospecificity in solvolysis of the diastereomeric 3-*tert*-butylcyclooctyl tosylates as that found here for the *d*-labeled reactants. Their stereochemical characterization of the cyclooctyl system thus constitutes a general precedent, uncomplicated by the spatial requirements of the large alkyl substituents.

We differ from these authors somewhat in mechanistic interpretation, however. Schneider and Heiske propose that the stereospecificity in displacement could be attributed to steric pro-

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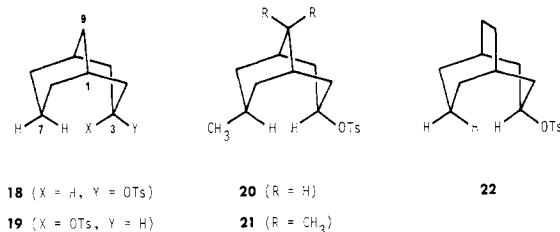
Table III. Comparative Selectivities in the Formation of Unrearranged and Rearranged Products in Solvolysis of Cyclooctyl-*l*-*d* Brosylate (12-OBs) at 35.5 °C

solvent ^a	unrearranged products			rearranged products		
	% elimin	% ethyl ether in subst prod	$k_{\text{EtOH}}/k_{\text{ROH}}$	% elimin	% ethyl ether in subst prod	$k_{\text{EtOH}}/k_{\text{ROH}}$
HOAc	34			29		
80% EtOH, 20% H ₂ O	61	44	0.62	42	44	0.65
60% EtOH, 40% TFE	47	73	1.28	32	69	1.14
50% EtOH, 50% TFE	39	50	0.76	32	53	0.82
40% EtOH, 60% TFE	35	37	0.67	28	36	0.64

^a See Table II, footnotes *a*, *b*, *d*.

tection of the backside of the reaction center by a closely proximate transannular hydrogen atom.²¹ Along the nonrearranging pathway this condition would have to hold through conversion of an initial tight ion pair to a solvent-separated ion pair from which substitution with retention could result. Retention should be substantially favored at this stage by the enhanced nucleophilicity of a hyperpolarized solvent molecule within the field of an ion pair.³⁷ Examination of models in the light of the general conformational flexibility established for cyclooctane derivatives,²¹ however, reveals several conformers available to a localized *tight* ion pair that lack backside protection and ought to give rise to competitive substitution with inversion. Similarly, a carbenium ion generated by 1,5-hydride shift would have to undergo complete product formation prior to pseudorotation of the ring²¹ in order to produce the wholly inverted substitution observed at C-5. An additional argument against simple cyclooctyl cation intermediates, as pointed out by Schneider and Heiske,²¹ is the absence in both studies of displacement products formed with vicinal hydride shift, typically detected at significant minor levels in secondary alkyl solvolyses.³³

The present results afford an instructive comparison with those for the solvolysis of some bicyclic analogues. *exo*-3-Bicyclo[3.3.1]nonyl tosylate (**18**) is configurationally suited to ionization with transannular hydrogen participation, but does not exhibit strong bridging. Moodie, Parker, and Watt³⁸ found acetolysis to occur with 6% overall 7,3-hydride shift, producing mainly but not entirely the *exo* acetate at both centers. *Exo* substitution was also favored in reaction of the *endo* tosylate, **19**, but the extent of rearrangement was not determined.



Cross-ring hydrogen shift increases in solvolyses of the *exo*-7-methyl-*exo*-3 tosylate, **20**, where a driving force for conversion of a secondary to a tertiary carbenium ion is present. Rearrangement has been found to occur to the extent of 9–34% in carboxamide solvents³⁶ and 55% in both acetic acid³⁹ and 80% EtOH.⁴⁰ In aqueous ethanolysis of the *exo*-7,9,9-trimethyl derivative, **21**, rearrangement reaches 100%.⁴¹ It can be concluded

that the *gem*-dimethyl grouping in **21** blocks formation of the chair-boat or boat-boat conformation from which **18** and **20** undergo *k_s* solvolysis.

Ourisson et al.⁴⁰ have inferred from a nonlinear Hammett-Taft correlation for solvolysis of a set of *exo*-7-substituted *exo*-3-bicyclo[3.3.1]nonyl tosylates that **20** solvolyzes distinctively with transannular hydride assistance. (Analogous results had been obtained earlier for longifolene derivatives.⁴²) Parker and Graham³⁹ and Saito and Okamoto³⁶ and their co-workers, on the other hand, have measured null isotope effects for solvolyses of *endo*-7-deuterated **20** and on this basis have considered that a *k_c* rather than *k_d* mechanism must be operative.

The more flexible *exo*-3-bicyclo[3.3.2]decyl tosylate (**22**) shows behavior indicative of predominant reaction through a 7,3-hydride-bridged ion. Doyle and Parker⁴³ have reported the acetolysis of **22** to proceed with 48% transannular hydride shift and a 5:1 preference for *exo* over *endo* substitution.

A unified interpretation of the collective data is that all the cyclooctyl reactants under discussion, except **19**, ionize with some degree of transannular C–H bond participation, with the extent of bridging in the intermediate cations and competitive *k_s* reaction being broadly and independently variable. It is reasonable that the medium-ring proximity effect¹ that gives rise to μ -hydride migrations in these systems and controls solvolysis at each stage as well as stable-ion structure in the parent cyclooctyl case should play a general if sometimes marginal role in ionization along this series.

Experimental Section

Capillary melting points were obtained with a Thomas-Hoover apparatus and are uncorrected. Boiling points are uncorrected.

¹H NMR spectra were recorded at 60 MHz on a Varian A-60-A or EM-360-A spectrometer using CCl₄ as solvent and Me₄Si as internal standard. ²H NMR spectra were obtained at 15.4 MHz on a Varian XL-100-15 Fourier-transform spectrometer with modulated proton decoupling, using fluorobenzene for external lock. The solvent was CCl₄ containing 1% of CDCl₃ as internal standard. The chemical shifts are reported in ppm from (CD₃)₄Si.⁴⁴ Ho(fod)₃ was purchased from Norell, Inc., and stored in a desiccator over P₂O₅.

Gas chromatographic analyses and separations were performed on a Varian Model 920 instrument using Carbowax 20M 25% on 60–80 mesh Chromosorb W, AW/DMCS, as the stationary phase.

(*E*)-Cyclooctanol-2-*d* (**1-OH**). *cis*-Cyclooctene oxide^{22a} (12.6 g, 0.10 mol), prepared in 88% yield from *cis*-cyclooctene and *m*-chloroperoxybenzoic acid by the procedure described by Fieser and Fieser,⁴⁵ was reacted with 110 mL of 1.00 N LiEt₃BD (0.11 mol) in tetrahydrofuran (Aldrich) using the method of Brown, Kim, and Krishnamurthy²³ modified to include boiling under reflux for 3 h. Alcohol **1-OH** was obtained in 89% yield following distillation: bp 101–103 °C (20 mmHg) [lit.⁴⁶ bp 111.3–111.7 °C (25 mmHg), unlabeled]; ¹H NMR similar to that

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recorded by Pouchert and Campbell⁴⁷ for cyclooctanol; ²H NMR (52 mg of product plus 53 mg of Ho(fod)₃ in 350 μ L of CCl₄) δ -35.64 (s).

(E)- and (Z)-Cyclooctanol-2-d (1-OH + 2-OH). A sample of 1.50 g (11.6 mmol) of the (E)-alcohol, 1-OH, was oxidized in 86% yield to cyclooctanone-2-d by means of 3.85 g (17.8 mmol) of pyridinium chlorochromate (Aldrich) in CH₂Cl₂ buffered with 2.93 g (35.7 mmol) of sodium acetate in accordance with the procedure of Corey and Suggs.²⁴ The ketone (1.20 g, 9.40 mmol) was then reduced with 15.0 mL of 1.00 N LiEt₃BH (15.0 mmol) in THF (Aldrich) by the method of Brown, Kim, and Krishnamurthy,²³ generating 1.10 g (8.74 mmol, 93%) of the mixed diastomeric alcohols 1-OH + 2-OH: ²H NMR (40 mg of the product plus 40 mg of 1-OH plus 80 mg of Ho(fod)₃ in 400 μ L of CCl₄) δ -35.68 (s, intensity, 3, 1-OH), -36.79 (s, intensity 1, 2-OH), the signals being virtually base line resolved.

(E)-Cyclooctanol-4-d (3-OH). (Z)-1,4-Cyclooctanediol (**6**) (14.4 g, 0.10 mol), obtained from the epoxidation-formolysis of cyclooctene as reported by Cope, Fenton, and Spencer,^{22a} was esterified with 22.8 g (0.12 mol) of freshly recrystallized (hexane) *p*-toluenesulfonyl chloride in 200 mL of dry pyridine at -5 $^{\circ}$ C for 24 h, and workup was conducted as described by Fieser and Fieser.⁴⁸ The oily crude product was reacted with 190 mL of 1.00 N LiEt₃BD (0.19 mol) in THF following the procedure of Parker and Watt.³ The distilled product (20 mmHg) was shown by gas chromatography and ¹H NMR to be a mixture of cyclooctene and cyclooctane (3%), 3- and 4-cyclooctenols (18%), and cyclooctanol (79%). On silica gel chromatography the cyclooctene and cyclooctane were eluted with hexane and then the alcohols with ether. The mixed alcohols (10.0 g) were treated with 7.6 mL (80 mmol) of borane-dimethyl sulfide complex (Aldrich), and the resultant boranes oxidized to the diols with alkaline hydrogen peroxide by the method developed by Lane.⁴⁹ The desired 3-OH was separated from the more strongly adsorbent diols by silica gel chromatography with 50% hexane in ether as eluant. The yield was 6.7 g (52 mmol, 52% from **6**): bp 101-103 $^{\circ}$ C (20 mmHg) [lit.⁴⁶ bp 111.3-111.7 $^{\circ}$ C (25 mmHg), unlabeled]; ¹H NMR closely similar to that recorded by Pouchert and Campbell⁴⁷ for cyclooctanol; ²H NMR (48 mg of 3-OH plus 47 mg of Ho(fod)₃ in 350 μ L of CCl₄) δ -23.77 (s).

Cyclooctanol-1-d (5-OH). Reduction of 12.6 g (0.10 mol) of cyclooctanone with 110 mL of 1.00 N LiEt₃BD (0.11 mol) in THF by the method of Brown, Kim, and Krishnamurthy²³ produced by 11.7 g (91 mmol, 91%) of 5-OH: bp 101-103 $^{\circ}$ C (20 mmHg) [lit.⁴⁶ bp 111.3-111.7 $^{\circ}$ C (25 mmHg), unlabeled]; ²H NMR δ 3.76 (s); the ¹H NMR spectrum showed no absorption at this position, indicating \geq 98% deuteration.

Cyclooctyl Brosylates 1-OBs, 3-OBs, and 5-OBs. The labeled brosylates were synthesized from the corresponding alcohols by reaction with recrystallized (hexane) *p*-bromobenzenesulfonyl chloride in pyridine by the method of Tipson.⁵⁰ The labile esters were purified by three successive recrystallizations from hexane at -10 to -20 $^{\circ}$ C and solvolyzed promptly. Yields were 75-79%. The products had ¹H NMR spectra as expected.⁴⁷

Cyclooctyl 2,2,2-Trifluoroethyl Ether. Preparation of this ether was carried out for identification of the labeled trifluoroethanolysis products. Cyclooctanol (2.0 g, 16 mmol) was converted to its potassium salt by reaction with 0.72 g (18 mmol) of KH (Ventron, protective mineral oil removed by three washings with dry pentane) in 20 mL of dry THF. 18-Crown-6 (0.20 g) (Aldrich) was added, followed by 4.8 g (19 mmol)

of trifluoroethyl tosylate (Aldrich). The mixture was boiled under reflux for 48 h, cooled to room temperature, and poured into 100 mL of cold water. The product was extracted into three 30-mL portions of ether, and the combined ether solution was washed with saturated aqueous sodium chloride and dried over MgSO₄. After solvent evaporation and short-path distillation, a pure sample of the cyclooctyl trifluoroethyl ether was isolated by preparative gas chromatography: bp 172-173 $^{\circ}$ C; ¹H NMR δ 1.29-1.93 (m, 14 H, ring CH₂), 3.51-3.75 (m, 1 H, >CHO-), overlapping with 3.82 (q, *J* = 10.3 Hz, 2 H, CH₂CF₃).

Anal. (Galbraith Laboratories, Inc., Knoxville, Tenn.) Calcd for C₁₀H₁₈F₃O: C, 57.35; H, 8.14. Found: C 57.28; H, 8.19.

Solvolyzes. The solvolyses in acetic acid were carried out in the presence of 1% (wt) of acetic anhydride and 1.20 equiv of sodium acetate. For the other solvolyses 1.20 equiv of 2,6-lutidine was employed as buffer. In each case the initial substrate concentration was 0.10 M and the reaction was carried out in a tightly closed pressure bottle immersed in a thermostatic water bath at 35.5 $^{\circ}$ C. The product mixtures were poured into 500 mL of ice water and extracted with two 300-mL portions of pentane. In the case of acetolysis the pentane solution was washed twice with water and once with 5% sodium bicarbonate solution. From the other solvolyses the pentane solution was washed successively with cold 5% hydrochloric acid, water, and sodium bicarbonate solution. The product solutions were dried over anhydrous K₂CO₃ and concentrated by distillation of the pentane through a 40-cm Vigreux column. The crude acetolysis products were further treated with LiAlH₄ in anhydrous ether in the usual manner⁵¹ to reduce the acetates to alcohols.

The ratios of alcohol to olefin products were determined by calibrated gas chromatography. Preparative gas chromatography was used to separate the products for label-position analysis.

Determination of Substrate Isomerization in the Ethanolic Trifluoroethanolysis of 5-OBs. Cyclooctyl-1-d brosylate (**5-OBs**) (3.5 g, 10.0 mmol) was solvolyzed at 35.5 $^{\circ}$ C in 100 mL of 50% ethanolic trifluoroethanol containing 0.54 g (5.0 mmol, 0.50 equiv) of 2,6-lutidine and a trace of Congo Red indicator. On attainment of the end point (change from red to light blue) the reaction was quenched and worked up as described above. The ¹H NMR spectrum of the resultant solvent-free mixture showed a weak broad signal for the >CHO- proton in rearranged brosylate centered at δ 4.18 and free from overlap with other absorptions. Integration of this band against the aromatic absorption for the residual reactant showed the starting material to have been 11% isomerized during 1.0 half-life for solvolysis.

Note Added in Proof. Hydride participation in cyclooctyl tosylate solvolysis has also been implicated in a recent comprehensive rate/solvent correlation.⁵²

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Registry No. 1-OH, 79734-92-2; 1-OBs, 79734-93-3; 2-OH, 55693-43-1; 3-OH, 79734-94-4; 3-OBs, 79734-95-5; **5**, 4925-71-7; **6**, 73982-04-4; 12-OH, 79734-96-6; 12-OBs, 58378-55-5; cyclooctyl 2,2,2-trifluoroethyl ether, 79734-97-7.

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