bridged carbocation upon loss of OTs. This process is operationally equivalent to the rearrangement of **2b** via a *trans*-bridged ion as proposed previously. Formation of the *erythro*-**2b'**, which can form *trans* deuterium-bridged carbocations, can occur only if elimination/readdition be *syn* or nonstereospecific. The results previously reported for the trifluoroacetolysis of **2a** preclude the formation of any appreciable amount of deuterium-bridged carbocation.[2]

Since the trifluoroacetolyses of simple secondary alkyl substrates seem to proceed by at least two paths, one involving a free, solvated cation and the other an intermediate that is still associated with the leaving group, the further study of optically active alkyl substrates capable of hydrogen bridging can be a useful probe of the intricate details of the intermediates involved during nucleophilic substitutions, particularly when combined with isotopic labeling studies.

Experimental Section

(*R*)-(−)-2-Butyl Tosylate (2a). (*R*)-(−)-2-Butanol (Aldrich) was reacted with purified[13] toluenesulfonyl chloride according to an established procedure.[14] The 2-butyl tosylate obtained had specific rotation $[\alpha]^{37}\,^{\circ}C_{CCl_4}$ −11.04 at 578 nm.

2-Butyl Trifluoroacetate (3). Trifluoroacetic anhydride (8 mL) was added dropwise to a solution of (*R*)-(−)-2-butanol in 60 mL dry pyridine over 15 min at 0 °C.[16] Upon completion of the reaction, the mixture was allowed to come to room temperature. It was then poured into 300 mL of ice water and extracted with ether. The ether solution was washed with 10% HCl, 10% $NaHCO_3$, and water and then dried over anhydrous $MgSO_4$. The 2-butyl trifluoroacetate was recovered upon evaporation of the ether at reduced pressure. Specific rotation $[\alpha]^{37}\,^{\circ}C_{TFA}$ −13.03 at 578 nm.

Trifluoroacetic Acid. Trifluoroacetic acid (Aldrich) for all solvolyses was freshly distilled. A small amount of trifluoroacetic anhydride (1%) was added to assure dryness.

Optical rotations were made on solutions thermostatted at 37 °C by using a Perkin-Elmer Model 141 digital polarimeter. For the kinetic studies polarimeter readings at 578 nm were taken approximately 1 min apart for at least two half-lives. Infinity readings were taken after at least 10 half-lives and again after 24 h. No significant changes in optical rotation were observed after 10 half-lives.

Acknowledgment. This work was supported in part by PSC-BHE Grant No. 13361.

Registry No. 2a, 61530-30-1; **3**, 66585-35-1.

(14) Fieser, L.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1180. 1968; Vol. 1, p 1180.

(15) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235.

(16) This procedure was adapted from Nordlander, J. E.; Deadman, W. G. *J. Am. Chem. Soc.* **1968**, *90*, 1590.

Stereochemistry of Trifluoroacetolysis of Optically Active 2-Butyl Tosylate. A Test for Hydrogen Bridging

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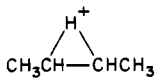
Trifluoroacetolysis of (*R*)-(−)-2-butyl tosylate at 25 °C gives 2-butyl trifluoroacetate with 7 ± 1% net inversion. The ratio of the polarimetric and spectrophotometric rate constants is 1.55, and this decreases to 1.05 in the presence of 0.125 M NaO_2CCF_3. These results are most simply and plausibly interpreted in terms of formation of an ion pair consisting of an open 2-butyl cation and a tosylate anion which gives racemized tosylate by ion-pair return and by elimination/readdition, with competitive nucleophilic solvent attack with a small overall preference for substitution on the side opposite the anion. A published proposal based on deuterium labeling studies that a hydrogen-bridged butyl cation is the predominant intermediate in this reaction does not give a simple prediction of these results.

It has recently been reported[1] that the rates and products of the solvolysis in trifluoroacetic acid (TFA) of $CH_3CH_2CH(OTs)CH_3$ (**1**), $CH_3CH_2CD(OTs)CD_3$ (**2**), and $CD_3CD_2CH(OTs)CH_3$ (**3**) "are consistent with the intermediacy of a hydrogen-bridged 2-butyl cation" and led the authors "to conclude that a bridged ion . . . is the predominant intermediate." The proposed structure of the bridged ion from **1** can be represented as **4**.



4

This report has already attracted notice in the literature.[2] Further, because there is widespread interest in the possibility of hydrogen bridging in solvolysis reactions[3a,b] and alkene protonations,[3c-e] as well as a continuing interest in the details of solvolysis processes,[4] further study of the solvolysis of such simple secondary systems appeared desireable. We have now studied the reactivity of optically active 2-butyl and 2-octyl tosylates, which provide an independent insight into the behavior of such systems.

A concise statement of the stereochemical consequences expected for different mechanisms of substitution at a

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(3) (a) Nordlander, J. E.; Owour, P. O.; Cabral, D. J.; Haky, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 201–206. (b) Schneider, H.-J.; Heiske, D. *Ibid.* **1981**, *103*, 3501–3505. (c) Allen, A. D.; Tidwell, T. T. *Ibid.* **1982**, *104*, 3145–3149. (d) Nordlander, J. E.; Haky, J. E.; Landino, J. P. *Ibid.* **1980**, *102*, 7487–7493. (e) Allen, A. D.; Rosenbaum, M.; Seto, N. O. L.; Tidwell, T. T. *J. Org. Chem.* **1982**, *47*, 4234–4239.

(4) (a) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466–5475. (b) Richard, J. P.; Jencks, W. P. *Ibid.* **1982**, *104*, 4689–91, 4691–4692. (c) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1982**, *104*, 207–211. (d) Allen, A. D.; Ambidge, I. C.; Che, C.; Micheal, H.; Muir, R. J.; Tidwell, T. T. *Ibid.* **1983**, *105*, 2343–2350.

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Table I. Specific Rotations of 2-Butyl and 2-Octyl Derivatives[a]

	[α], 2-butyl system				[α], 2-octyl system			
λ, nm	ROH	ROTs	RO_2CCF_3[b]	RO_2CCF_3[c]	ROH	ROTs	RO_2CCF_3[b]	RO_2CCF_3[c]
365	−46.2	−29.6	−39.5	+3.14	−33.8	−21.9	+9.2	−2.3
436	−31.4	−20.7	−27.6	+1.99	−23.2	−15.4	+4.5	−1.2
546	−18.8	−12.4	−16.8	+1.07	−13.9	−9.4	+1.9	−0.4
578	−16.5	−10.9[d]	−14.9[d]	+0.85	−12.2	−8.4	+1.6	−0.3

[a] In CCl_4 at 25 °C, 0.1-m cells, 0.02-0.04 g/mL, ±1°. [b] Authentic material prepared from ROH, $(CF_3CO)_2O$, and pyridine. [c] Reaction product from ROTs isolated after 10 half-lives for solvolysis. [d] Dannenberg[9] et al. report values of −11.04 for 2-butyl tosylate and −13.03 for 2-butyl trifluoroacetate, both at 37 °C.

chiral center have been given by Hughes and Ingold and their co-workers:[5] "... whilst nucleophilic bimolecular substitution always leads to a complete inversion of configuration, unimolecular substitution leads either to racemization, possibly with some inversion, or, in the presence of a group which suitably binds to the cationic centre, to retention of configuration, possibly with some racemization."

This classic description was formulated more than 40 years ago, and in the intervening period the theory of solvolysis has progressed significantly, especially with the widespread appreciation of the role of ion pairs in such processes, but the basic principles laid down by Hughes and Ingold still have considerable validity today. In particular their emphasis on the stereochemistry at the site of substitution is directly applicable to the study of current mechanistic proposals, including the "S_N2 intermediate" process of Schleyer and Bentley[4a,d] and the "enforced" solvolysis process envisioned by Jencks and co-workers.[4b] Both of these processes involve nucleophilic attack by solvent on the substrate while the leaving group is still bound to the substrate and would be expected to involve essentially complete inversion of configuration. Inexplicably the use of optically active substrates has been almost totally neglected in the elucidation of these processes.

Results

(*R*)-(−)-2-Butanol (Alfa) was converted to the tosylate by treatment with NaH and TsCl and to the trifluoroacetate of retained configuration by reaction with trifluoroacetic anhydride and pyridine. The tosylate was solvolyzed for 10 half-lives in TFA at 25 °C and isolated by extraction and VPC. Rotations of the alcohol, tosylate, trifluoroacetate, and reaction product are reported in Table I. (*R*)-(−)-2-Octanol (Aldrich) was treated similarly, and the products, 2-, 3-, and 4-octyl trifluoroacetate, were separated by gas chromatography. Optically active 2-butyl and 2-octyl trifluoroacetates were found to undergo less than 10% racemization during 10 half-lives of the solvolysis conditions.

Kinetics of the trifluoroacetolysis of the tosylates were measured polarimetrically and spectrophotometrically and gave good first-order rate plots (Table II).

Discussion

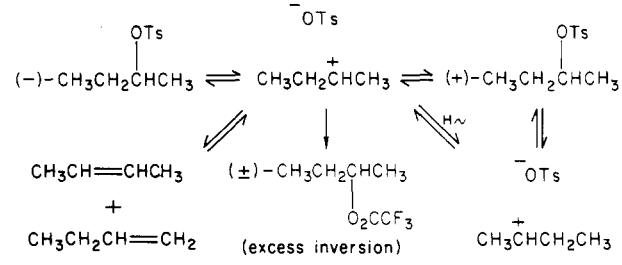
The results show that optically active 2-butyl tosylate undergoes trifluoroacetolysis with predominant racemization with some inversion to the extent of 7 ± 1%. A simple and reasonable interpretation of these data for 2-butyl tosylate is shown in Scheme I. According to this scheme initial ionization occurs to a chiral ion pair consisting of an open cation with the anion specifically located on the side from which it departed. Racemization of the chiral ion pair can occur by C–C bond rotation, hydride migration, relative motion of the cation and anion (ion tumbling), solvent displacement of the anion, or some combination of these events. Return from the ion pair gives partially racemized tosylate, and solvent bonding to the cation gives product trifluoroacetate with some net inversion. A competing racemization mechanism involves elimination to give the isomeric butenes which undergo readdition to give 2-butyl tosylate with racemization. 2-Octyl tosylate reacts similarly, except that rearrangement to the 3- and 4-octyl cations also occurs.

Table II. Polarimetric and Spectrophotometric Rates for Trifluoroacetolysis of 2-Butyl Tosylate and 2-Octyl Tosylate at 25 °C[a]

substrate	$[NaO_2CCF_3]$, M	k_α, $s^{-1} \times 10^4$[b]	k_{UV}, $s^{-1} \times 10^4$[c]	k_α/k_{UV}
2-BuOTs	0.0	1.76 (±0.02)	1.12 (±0.04)	1.55
	0.063	1.70 (±0.03)	1.55 (±0.01)	1.10
	0.125	1.73 (±0.05)	1.64 (±0.05)	1.05
2-OctOTs	0.0	2.81 (±0.06)	1.48 (±0.04)	1.90
	0.063	2.74 (±0.01)	2.28 (±0.03)	1.20
	0.125	2.75 (±0.08)	2.42 (±0.04)	1.14

[a] Average deviation of two runs in parentheses. [b] Measured at 436 nm by using a Perkin-Elmer 141 polarimeter. [c] Measured with a Cary 210 spectrophotometer at 272 nm.

Scheme I



The observation that k_α is 1.55 times as great as k_{UV} for 2-butyl tosylate and 1.90 times greater for 2-octyl tosylate shows that some racemization of the tosylates is occurring. The formation of rearranged tosylates at rates comparable to the rates of product formation was observed directly in the experiments with the deuterated tosylates **2** and **3**.[1]

The importance of an elimination/readdition pathway was shown by experiments by Dannenberg et al.[1] in which solvolysis of 2-butyl tosylate in CF_3CO_2D (99% d_1) at 37 °C was observed to give 2-butyl trifluoroacetate containing 40% deuterium and solvolysis of $CD_3CD_2CH(OTs)CH_3$ (**3**) in CF_3CO_2H was found to give 30% loss of deuterium in formation of trifluoroacetate product. These reactions involve readdition of toluenesulfonic acid to butene to regenerate 2-butyl tosylate, as was shown directly by the

(5) Bateman, L. C.; Church, M. C.; Hughes, E. D.; Ingold, C. K.; Taher, N. A. *J. Chem. Soc.* **1940**, 979–1011.

formation of this compound on reaction of *E*-2-butene (0.5 M) in CF_3CO_2H with 0.15 M TsOH.[1] It was further observed with the deuterated tosylates **2** and **3** that during the early stages of the reaction, the peaks due to rearranged tosylate appeared at roughly the same rate as those due to products.[1]

The further observation[1] that the trifluoroacetate from $CH_3CH_2CD(OTs)CD_3$ (**2**) in CF_3CO_2H had lost less than 1% deuterium is not inconsistent with the importance of the elimination/readdition pathway, as loss of deuterium in this system would involve two such steps with an unfavorable primary isotope effect on the second (eq 1 and 2). Assuming that elimination/readdition occurs to the

$$CH_3CH_2\underset{\displaystyle OTs}{\underset{|}{C}}DCD_3 \rightleftharpoons CH_3CH{=}CDCD_3 \rightleftharpoons$$

2

$$CH_3\underset{\displaystyle OTs}{\underset{|}{C}}HCHDCD_3 \longrightarrow CH_3CH{=}CHCD_3 \quad (1)$$

$$CH_3CH{=}CHCD_3 \longrightarrow CH_3\underset{\displaystyle OTs}{\underset{|}{C}}HCH_2CD_3 + CH_3CH_2\underset{\displaystyle OTs}{\underset{|}{C}}HCD_3 \quad (2)$$

extent of 40% (the result for **1** in CF_3CO_2D) on each step and that there is a primary isotope effect, $k(H)/k(D)$, of 2 for proton loss from the rearranged tosylate in eq 1 leads to a crude prediction of less than 3% deuterium loss, which is identical with that observed within the experimental error.

It does not appear that the degree of involvement of 1-butene in these processes can be evaluated from the known facts. The formation of "olefin" as observed by NMR was reported during solvolysis in the presence of NaO_2CCF_3,[1] but no evidence was presented on the regiochemical composition of this material.

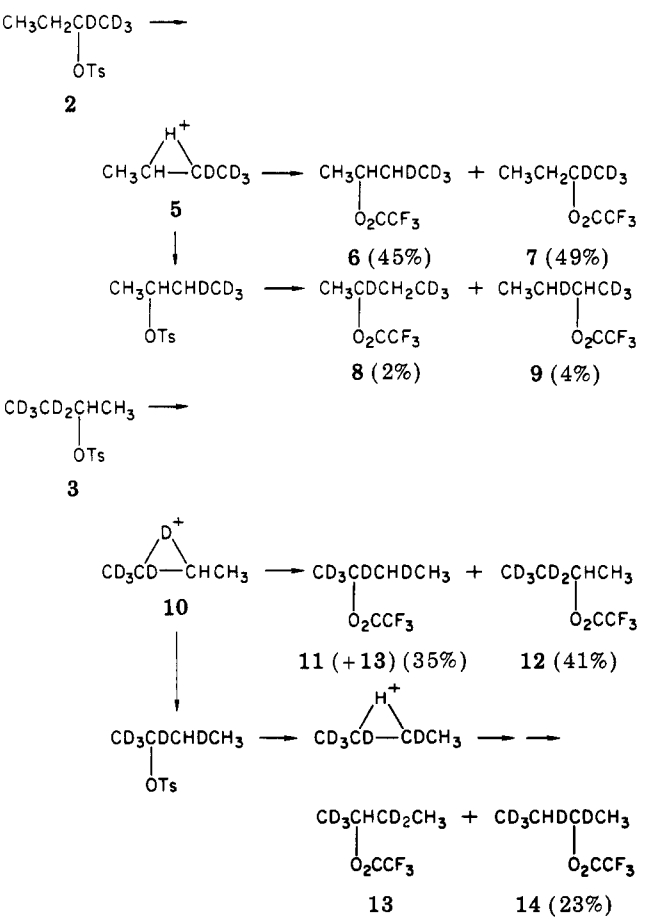
The occurrence of the elimination/readdition pathway has also been demonstrated in a closely related system, namely the trifluoroacetolysis of 2-propyl brosylate.[6]

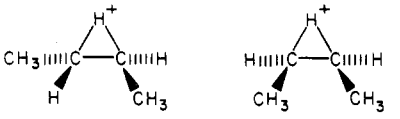
The observed effect of NaO_2CCF_3 on the rate of the reaction (Table II) also supports these interpretations. Within the experimental error the only effect of the added buffer is to increase k_{UV}, the rate of product formation. This would be the result if the buffer consumes the strong acid formed and thereby prevents reformation of 2-butyl tosylate from the intermediate butenes formed in the reaction. The report[1] of an observable buildup of olefin as a transient intermediate during 2-butyl tosylate solvolysis in the presence of NaO_2CCF_3 fits in with this view. Reaction of NaO_2CCF_3 with the 2-butyl cation after racemization to give product trifluoroacetate instead of return to tosylate could also increase k_{UV}.

Ion pair return is also consistent with the results of Paradisi and Bunnett[7a] and Winstein and co-workers[7b] of ^{18}O scrambling in the solvolysis of 2-propyl benzenesulfonate in TFA (containing 0.1 M NaO_2CCF_3) to the extent of 30%[7a] and 2-octyl brosylate[7b] (containing 0.025 M NaO_2CCF_3) to the extent of 33%.

The present results may be contrasted with studies of the ethanolysis of optically active benzyl-α-*d* tosylate[8a] and the acetolysis of 2-octyl tosylate,[8b] both of which proceed with complete inversion by a solvent participation (k_S) route. The small inversion component for 2-butyl tosylate in TFA indicates a k_c route for this system involving an ion pair and also is evidence that simple bridged intermediates **4*E*** and **4*Z*** are not significant in trifluoroacetolysis of 2-butyl tosylate, at least not as species that can control the stereochemistry of substitution. The *E* ion should be favored and according to the criterion set out by Hughes and Ingold should give mainly retention of configuration. The *Z* ion would give racemized product, but even if formation of the *E* and *Z* ions is competitive net retention should occur.[9]

Scheme II

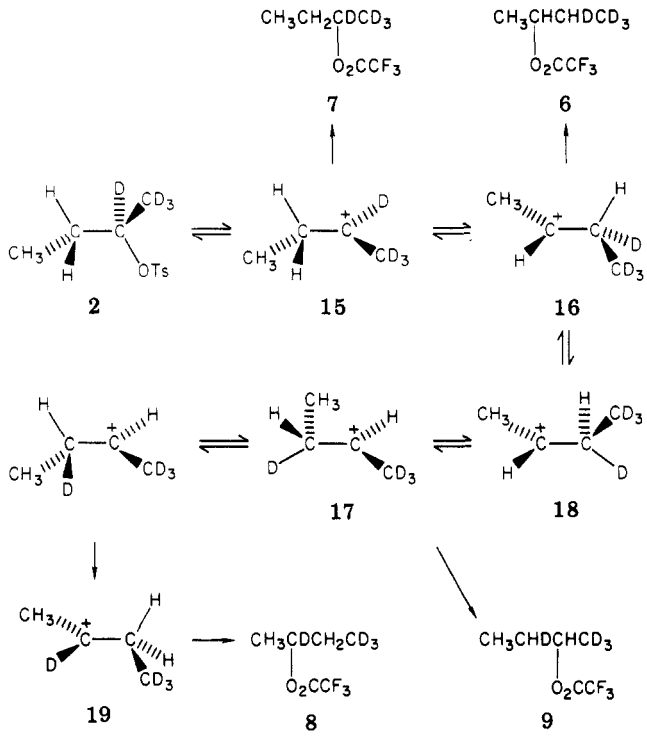




The intermediacy of open ions as in Scheme I was suggested[1] to be incompatible with the isotope distribution in the products from **2** and **3** (Scheme II). The crucial assumption[1] was made that in the open ion path for **2** (Scheme III) the transformation of **16** to **17**, involving deuterium migration, should be less efficient than the reversion of **16** to **15** by a factor of 2.4. This value is an estimate[10] for the ratio of rate limiting hydrogen participation in FSO_3H solvolysis of CH_3CH_2OTs relative to CD_3CH_2OTs. Thus this model involves a different reaction type (hydrogen participation in tosylate solvolysis as compared to hydrogen migration in a cation) for a different carbon structure in a different solvent. Furthermore the

(6) Shiner, V. J., Jr.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 6528–6529.
(7) (a) Paradisi, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 946–948. (b) Diaz, A. F.; Lazdins, I.; Winstein, S. *Ibid.* **1968**, *90*, 1904–1905.
(8) (a) Streitwieser, A. Jr.; Wolfe, J. R., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 4912–4914. (b) Streitwieser, A., Jr.; Walsh, T. D.; Wolfe, J. R., Jr. *Ibid.* **1965**, *87*, 3682–3685. (c) See also: McManus, S. P.; Roberts, F. E.; Lam, D. H.; Hovanes, B. *J. Org. Chem.* **1982**, *47*, 4386–4388.
(9) Similar experimental results to those reported here have been obtained independently by Dannenberg and co-workers. See *J. Org. Chem.*, preceding paper in this issue.
(10) Myhre, P. C.; Evans, E. *J. Am. Chem. Soc.* **1969**, *91*, 5641–5644.

Scheme III



conversion of **16** to **17** involves a conformational change from **16** to **18** that was not considered in the previous discussion.[1] A difference in ΔG^* of 1 kcal/mol between the paths of **16** to **15** and **17** corresponds to a rate difference of a factor of 9 and would be sufficient to quantitatively explain the product distribution in terms of Scheme I, and such a value does not appear unreasonable. In view of the inadequacy of the comparative models available for either the bridged or open schemes it appears prudent to interpret the observed isotopic distribution with due consideration of the other available results.

The isotope effect argument against open ions[1] was that the observed rate ratio, $k(2)/k(3)$, of 1.1–1.2 differed from a model calculation of 0.79–0.85. However, the experimental rate ratio was based on rates reported as ±10% and the models chosen must have considerable uncertainty as well, as there are increasing indications[4c,11] that such isotope effects are structure, solvent, temperature, and mechanism sensitive in ways that are difficult to predict quantitatively.

Independent experimental results that favor the intermediacy of the open as opposed to bridged structures for the 2-butyl cation in trifluoroacetic acid include a linear free energy correlation of trifluoroacetolysis rates of secondary alkyl tosylates with σ^* constants.[12a] This behavior has been found to hold for other solvents as well, and other cases proposed to react with hydrogen participation have been found to deviate from such correlations.[12b] The kinetics of trifluoroacetic addition to 2-butene have also been interpreted in terms of open 2-butyl cation intermediates.[3c]

In summary, the observations of predominant racemization with some inversion during trifluoroacetolysis of (*R*)-(−)-2-butyl tosylate, as well as some internal return with racemization, are as predicted for the involvement of unbridged 2-butyl cations (Scheme I). Species with hydrogen bridging sufficiently strong to control stereochemistry do not predict this behavior. The arguments presented[1] that the deuterium labeling results rule out open ions appear to rest on questionable models, and there is other independent evidence for the intermediacy of open 2-butyl cations in trifluoroacetic acid.

Experimental Section

(*R*)-(−)-2-Butanol (from Alpha Products) and (*R*)-(−)-2-octanol (from Aldrich) were converted to the tosylates[12a] by reaction with NaH and TsCl by using procedures we have reported elsewhere.[4c,d] 2-Butyl tosylate was an oil that showed no extraneous NMR signals. The 2-octyl tosylate contained 2-octanol and 2-octyl chloride and so was purified by HPLC. Rate constants obtained from the purified and unpurified material were the same.

2-Butyl and 2-octyl trifluoroacetates were obtained by reaction of the optically active alcohols with trifluoroacetic anhydride and pyridine[3c,e] and were purified by gas chromatography with a 3 m × 10 mm Carbowax column.

Product analyses were carried out by allowing the reaction to proceed for 10 half-lives, pouring into water, extracting with ether, and isolating the trifluoroacetates by VPC with a 3 m × 10 mm Carbowax column. 2-Octyl tosylate gave a product containing 50% 2-octyl trifluoroacetate, 35% 3-octyl trifluoroacetate, and 15% of the 4-isomer.

Kinetics were measured as shown in Table II with 10^{-2} M tosylate solutions for the polarimetric runs and 10^{-3} M solutions, measured at 272 nm, for the UV runs. The k_{UV} values for 2-butyl and 2-octyl tosylates at 25 °C with 0.125 M NaO_2CCF_3 of 1.64×10^{-4} s^{-1} and 2.42×10^{-4} s^{-1}, respectively, compare well to published[12a] rate constants of 1.46×10^{-4} s^{-1} for 2-butyl tosylate and 2.49×10^{-4} s^{-1} for 2-heptyl tosylate under the same conditions.

To test for the optical stability of the products 0.214 mmol each of (*R*)-(−)-2-butyl trifluoroacetate, toluenesulfonic acid hydrate, and trifluoroacetic anhydride were dissolved in 1.2 mL trifluoroacetic acid. This solution was found to lose 4% of its optical activity in 5.5 h at 25 °C and 14% in 22.5 h. The half-life for k_α was 1 h at 25 °C. Similarly a solution of 0.104 mmol of (*R*)-(−)-2-octyl trifluoroacetate was 2% racemized in 5 h and 8% racemized in 22 h under the same conditions. The half-life for k_α was 0.7 h.

Acknowledgment. Financial support of this research by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We are especially grateful to Professor J. J. Dannenberg for communicating his own results on this system[9] and for stimulating and helpful discussions.

Registry No. (*R*)-(−)-1, 61530-30-1; (*R*)-(−)-2-octyl tosylate, 27770-99-6; (*R*)-(−)-2-butyl trifluoroacetate, 66585-35-1; (*S*)-(+)-2-butyl trifluoroacetate, 66585-22-6; (*R*)-(−)-2-octyl trifluoroacetate, 87337-94-8; (*S*)-(+)-2-octyl trifluoroacetate, 87337-93-7.

(11) (a) Shiner, V. J., Jr.; Neuman, T. E.; Fisher, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 354–355. (b) McLennan, D. *J. Chem. Soc., Perkin Trans. 2*, **1981**, 1316–1324.

(12) (a) Peterson, P. E.; Kelley, R. E., Jr.; Belloli, R.; Sipp, K. A. *J. Am. Chem. Soc.* **1965**, *87*, 5169–5171. (b) Bentley, T. W.; Bowen, C. T. *J. Chem. Soc., Perkin Trans. 2*, **1978**, 557–562.