

in acetic acid. Samples were withdrawn at suitable intervals by a syringe and the chromium(VI) content of the sample was determined spectrophotometrically at 350 m μ .

b. Liquid Olefins. The measurements were carried out spectrophotometrically in a cell connected to an inverted U tube. The solution of the olefin in acetic acid and an appropriate amount of sulfuric acid in acetic acid was placed in one arm, a solution of chromic acid in the other. The system was degassed by evacuation using an oil pump and liquid nitrogen bath. After thermostating the arms to $25 \pm 0.1^\circ$ the reaction was started by mixing thoroughly the contents of the two arms, turning the cell assembly upside down, inserting the cell into a thermostated cell holder of a Zeiss PMQ II spectrophotometer, and following the rate of the reaction spectrophotometrically at 350 m μ . The final mixed volume was 5 ml.

Oxidation of the solvent containing sulfuric acid was small. However, all rate constants are corrected for solvent oxidation. The corrections ranged from 2 to 7%.

The concentrations of chromic acid in all kinetic runs was about $5 \times 10^{-4} M$ except for *cis*-stilbene where it was $2.27 \times 10^{-3} M$ (kinetic runs were carried out at 440 m μ , an alternative maximum for chromium(VI)). A 20-fold excess of the liquid olefin substrates were normally used; however, runs with about 200-fold excess were also carried out in the case of slower reacting olefins. Good straight-line plots of $\log A$ vs. time were obtained generally for about two half-lives and were used for the determination of the first-order rate constants. The second-order rate constants were calculated from initial olefin concentration. The values in the Table I are averages from at least 2 to 15 kinetic runs for each olefin.

Acknowledgments. The authors wish to express their sincere thanks to Mrs. Aparna Rahman who carried out extensive preliminary measurements on a large number of the olefins, studied in this work, at The Catholic University, Washington, D. C., in 1965.

Solvolytic Displacement Reactions in Trifluoroacetic Acid. II. Trifluoroacetolysis of 1-Phenyl-2-propyl *p*-Toluenesulfonate

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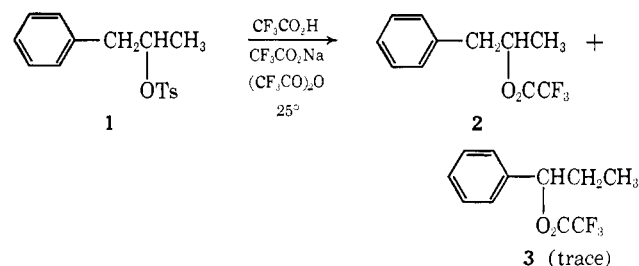
Abstract: The trifluoroacetolysis of 1-phenyl-2-propyl tosylate takes place with complete retention of configuration and in the presence of 20% excess sodium trifluoroacetate at 25.0 $^\circ$ proceeds 17.1 times as fast as that of 2-propyl tosylate. Consideration of the phenyl group inductive effect leads to a rate enhancement factor for phenyl participation of 564 in this reaction.

Trifluoroacetic acid, by virtue of its powerful ionizing ability but weak nucleophilicity, provides a medium for solvolytic displacement reactions of particularly pronounced S_N1 character.¹⁻⁵ This medium offers anions highly efficient solvation through hydrogen bonding, but possesses correspondingly poor solvating properties toward cations. As a consequence, inductive and anchimeric assistance effects play enhanced roles in carbonium ion generation in trifluoroacetic acid¹⁻⁴ relative to the more nucleophilic solvents commonly employed.

We have recently reported a case of strongly amplified phenyl-group participation in this medium. The trifluoroacetolysis of 2-phenylethyl tosylate² was found to proceed over 3000 times as fast as that of ethyl tosylate, whereas the former substrate reacts more slowly than the latter in ethanol and acetic acid and only slightly faster in formic acid. The formation of 2-

phenylethyl trifluoroacetate was shown to be accompanied by complete methylene-position interconversion,² and Jablonski and Snyder have subsequently demonstrated by stereospecific deuterium labeling that the reaction occurs with total retention of configuration.³

The powerful propensity for a β -phenyl group to assist ionization in a poorly nucleophilic medium was emphasized by preliminary results² on the buffered trifluoroacetolysis of 1-phenyl-2-propyl tosylate (**1**). This reaction took place smoothly at 25 $^\circ$ to produce 1-phenyl-2-propyl trifluoroacetate (**2**) in 89% isolated yield, containing a trace of the hydride-shift product 1-phenyl-1-propyl trifluoroacetate (**3**), which polymerized



(1) (a) P. E. Peterson and J. F. Coffey, *Tetrahedron Letters*, 3131 (1968); (b) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Am. Chem. Soc.*, **89**, 5902 (1967); (c) P. E. Peterson and R. J. Bopp, *ibid.*, **89**, 1283 (1967); (d) P. E. Peterson and R. J. Kamat, *ibid.*, **88**, 3152 (1966); (e) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *ibid.*, **87**, 5169 (1965); (f) A. C. Cope, J. M. Grisar, and P. E. Patterson, *ibid.*, **81**, 1640 (1959).

(2) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).

(3) R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1103 (1968).

(4) M. Hanack, I. Herterich, and V. Vött, *ibid.*, 3871 (1967).

(5) 2,2,2-Trifluoroethanol has recently been shown to exhibit similar properties as a solvolysis medium. See W. S. Trahanovsky and M. P. Doyle, *ibid.*, 2155 (1968).

slowly under the reaction conditions. Despite the presence of both an electronic and a steric bias against net phenyl migration in this carbonium ion system, the trifluoroacetolysis of tosylate **1** at 25 $^\circ$ was found to be 20 times as fast as that of 2-propyl tosylate. The lat-

ter substrate, in contrast, is the faster in ethanol, acetic acid, and formic acid.

In the present paper we report the results of more definitive rate measurements on these compounds, and the finding that the trifluoroacetolysis of 1-phenyl-2-propyl tosylate (**1**) proceeds with complete retention of configuration.

Kinetics Results

Our initial determination² of the first-order rate constant for trifluoroacetolysis of **1** was carried out with the substrate 0.050 *M* and sodium trifluoroacetate 0.125 *M* for comparability with the published result^{1e} for 2-propyl tosylate. In view of the notably large salt effects observed in the trifluoroacetolysis of 2-phenylethyl tosylate,² however, standard conditions for the more complete measurements reported here were taken to be 0.050 *M* tosylate in trifluoroacetic acid containing 1 wt % of trifluoroacetic anhydride and 0.060 *M* sodium trifluoroacetate.⁶ The rates were followed, as before,² using the spectrophotometric procedure of Peterson, *et al.*^{1e} Clean first-order behavior was observed through at least 75% reaction in all cases. The results are presented in Table I. Under the present conditions of 20% excess sodium trifluoroacetate the rate of 1-phenyl-2-propyl tosylate (**1**) was found to exceed that of 2-propyl tosylate by a factor of 17.1 at 25.0°, slightly less than the value of 20.1 obtained previously² when 150% excess buffer was present.

Table I. Spectrophotometric Rate Data for Trifluoroacetolysis^a of 1-Phenyl-2-propyl Tosylate (**1**) and 2-Propyl Tosylate

Reactant	Temp, °C ^b	10 ³ k ₁ , sec ⁻¹	ΔH [‡] , kcal/mol	ΔS [‡] , eu	Rel k ₁ , 25.0°
C ₆ H ₅ CH ₂ CHCH ₃ OTs	25.0	36.5	19.6	-8.7	17.1
	15.0	11.7			
CH ₃ CHCH ₃ OTs	5.0	3.20			
	50.0	50.9	19.9	-13.2	1
	40.0	10.3			
	24.9	2.11			
	25.0	2.14 ^c			

^a Reactant 0.050 *M* in trifluoroacetic acid containing 1 wt % trifluoroacetic anhydride and 0.060 *M* sodium trifluoroacetate. ^b ±0.1°. ^c Interpolated.

Stereochemical Results

1-Phenyl-2-propanol was resolved according to the procedure of Pickard and Kenyon⁷ to yield chemically pure material having [α]_D²⁴ +38.69 ± 0.01° (*c* 13.35, chloroform). The alcohol was converted to its crystalline (+)-tosylate, whose properties were essentially identical with those reported by Winstein, *et al.*⁸ The tosylate was solvolyzed at room temperature for 15 half-lives in trifluoroacetic acid (1% trifluoroacetic anhydride) buffered with sodium trifluoroacetate. Saponification of the product trifluoroacetate yielded 1-phenyl-2-propanol (uncontaminated with 1-phenyl-1-propanol) which had [α]_D²³ +38.68 ± 0.01° (*c* 4.37, chloroform).

(6) Polymerization of the reaction products from **1** takes place if the medium is unbuffered.²

(7) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 115 (1914).

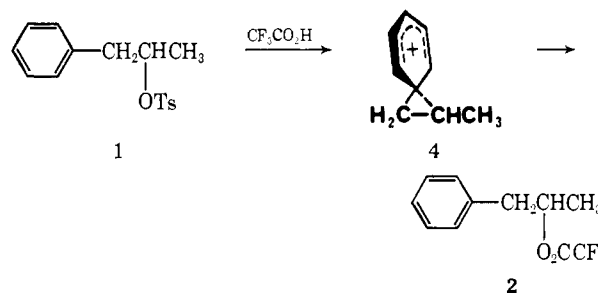
(8) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Am. Chem. Soc.*, **74**, 1140 (1952).

Thus, within experimental uncertainty the trifluoroacetolysis was found to proceed with 100% retention of configuration.

Discussion

The product, kinetic, and stereochemical results make it clear that the trifluoroacetolysis of 1-phenyl-2-propyl tosylate takes place essentially entirely by way of phenyl participation in the ionization step and formation of a bridged intermediate.

As developed previously,² the close Hammett-Taft correlation established by Peterson and coworkers^{1e} for the trifluoroacetolysis rates of a series of secondary alkyl tosylates leads to a predicted 1-phenyl-2-propyl: 2-propyl rate ratio of 1:33 in the absence of phenyl participation. Application of this inductive-effect correction to the present experimental rate ratio, therefore, augments the factor for rate enhancement by phenyl participation to 17.1(33) = 564, corresponding to a stabilization free energy of 3.8 kcal/mol in the transition state. The complete effect in the carbonium ion intermediate might reasonably be about twice as great as this, justifying the formulation of well-developed bridging in this species. If allowance is made for part of the charge to be borne by the ionization site, the intermediate may be written as **4**. The origin of the



trace quantity of hydride-shift product **3** is uncertain. Presumably it arises from hydride participation in minor competition with phenyl assistance in ionization of the tosylate **1**, although the possibility of prior ionization without rearrangement or even that of minor hydride shift within the bridged ion **4** cannot be definitely excluded.

The demonstration of complete retention of configuration in formation of the unrearranged and predominant trifluoroacetate **2** confirms the mechanism indicated by the product and rate results. Although the stereochemistry of trifluoroacetolysis of representative unassisted secondary alkyl arenesulfonates has not yet been established, there is no reason to expect it to be radically different from the norm of close to total inversion of configuration typical of acetolysis.⁹ It seems at present entirely valid, therefore, to attribute highly predominant retention by itself to bridged-ion formation in trifluoroacetic acid³ as in the more common solvents.¹⁰

In making this statement we wish to recognize and comment briefly on the controversy that presently surrounds the interpretation of stereochemical results in

(9) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *ibid.*, **87**, 3682 (1965).

(10) See (a) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); (b) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

the acetolysis and formolysis of symmetrically substituted β -phenylalkyl substrates. Of central importance has been the acetolysis of the diastereomeric 3-phenyl-2-butyl tosylates. Cram¹¹ discovered that these reactions proceed with highly predominant retention of configuration accompanied by highly predominant interconversion of the 2 and 3 positions¹² and explained these findings in terms of fully bridged phenonium ion intermediates. Brown¹³ has challenged this view on the grounds that rate enhancements commensurate with the formulation of such intermediates are not found, estimating the experimental factor to be¹³ approximately 4 after inductive-effect correction of the observed 3-phenyl-2-butyl:2-butyl rate ratios.¹⁴ Brown has suggested^{13b} *inter alia* that the data might better be accommodated by pairs of rapidly interconverting open cations, in which phenyl migration is so rapid as to prevent back-side attack by solvent as well as rotational isomerization (the "windshield-wiper effect"). In our judgment the windshield-wiper concept is physically unsound for reasons cogently stated by Sargent^{10a} but generally unremarked by other authors. Open-ion isomerization by phenyl migration would require, of course, the acquisition of potential energy equivalent to formation of the transition state, the principal source of which must be kinetic energy absorbed in properly oriented collisions with the solvent. Many such collisions, however, will clearly be geometrically ineffective in exciting the bending vibration corresponding to phenyl shift. A substantial fraction of these, in turn, should be directionally appropriate to bonding at the carbonium ion site and subsequent product formation. Discounting the unlikely condition, then, that covalent solvent capture should require much greater activation than should vibrational excitation tantamount to rearrangement, these two processes should be in effective competition, and product formation would seem to have an entropic advantage. The windshield-wiper notion, in other words, carries the erroneous implication that energy transfer is effected from migrating phenyl to neighboring solvent, keeping the latter at bay at the backside. Quite the opposite seems altogether more realistic.

Cram has reasserted the phenonium ion interpretation¹⁵ and more recently Cram and Thompson¹⁶ have introduced new evidence from which a phenyl-assistance rate enhancement factor of 43 has been derived for the *threo* isomer. In our view this value has a more direct and thorough experimental basis than the alternative factor of 4 cited above and serves as a strong support for predominant direct formation of phenyl-bridged carbonium ions in this reaction.

Brown's challenge to phenonium ion theory, however, should be recognized as transcending his suggestion of equilibrating open ions. Indeed, this case represents simply one limiting extreme in his general pro-

posal that a continuous series of unsymmetrically bridged carbonium ions, culminating in the fully bridged phenonium ion, be considered in the interpretation of rate and stereochemical data in such systems.^{13,17} As we have pointed out previously,² the " π -bridged" carbonium ions formulated by Brown^{13,17} are essentially equivalent to the unsymmetrical phenonium ions considered earlier by Cram and coworkers¹⁸ and others.¹⁹ Evidence against such unsymmetrically bridged intermediates (in an otherwise symmetrical system) was adduced by Cram, Nyquist, and Abd Elhafez,^{13b} but Brown, *et al.*,^{13c,17} have interpreted several recent results in terms of β -aryl π -bridged cations. Whereas the " π -bridged" description seems to us unrealistic,² we see considerable value in Brown's suggestion that unsymmetrically bridged and rapidly interconverting phenonium-type intermediates be kept under consideration. Carbonium ion **4** is formulated in accordance with this view, although not uniquely so.⁸

The present trifluoroacetolysis results for 1-phenyl-2-propyl tosylate complement the thorough and instructive studies on this system in more common solvents carried out some time ago by Winstein and coworkers.⁸ In Table II are listed first-order rate constants for 1-

Table II. Relative Solvolysis Rates of 1-Phenyl-2-propyl Tosylate and 2-Propyl Tosylate

Solvent	Temp, °C	$\frac{k(\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OTs})\text{CH}_3)}{k(\text{CH}_3\text{CH}(\text{OTs})\text{CH}_3)}$
C ₂ H ₅ OH	50.0	0.16 ^{a,b}
CH ₃ CO ₂ H	70.0	0.40 ^c
HCO ₂ H	25.0	0.58 ^d
CF ₃ CO ₂ H	25.0	17.1 ^e

^a R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953). ^b Reference 8. ^c W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962). ^d Reference 1e. ^e Present work.

phenyl-2-propyl tosylate relative to 2-propyl tosylate in ethanol, acetic acid, and formic acid from the literature²⁰ as well as trifluoroacetic acid from the present work. The phenyl substituent was found to have a slight rate-retarding effect in each of the common solvents. The magnitudes and solvent dependence of the relative rates, however, were indicative of a balance between phenyl-assisted and solvent-assisted ionization, with the former being favored most in formic acid.⁸ Stereochemical results reinforced this interpretation,⁸ as summarized in Table III. The proportion of retention is seen to increase in the same sequence as $k(\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OTs})\text{CH}_3)/k(\text{CH}_3\text{CH}(\text{OTs})\text{CH}_3)$ increases.⁸ Trifluoroacetic acid now represents the first medium in which solvolysis of the 1-phenyl-2-propyl reactant proceeds entirely by anchimeric assistance.

The demonstration that bridged ion **4** is more stable

(11) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); **74**, 2129 (1952).

(12) See also W. B. Smith and M. Showalter, *ibid.*, **86**, 4136 (1964).

(13) (a) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 140 ff; (b) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965); (c) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968).

(14) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

(15) D. J. Cram, *ibid.*, **86**, 3767 (1964).

(16) D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967).

(17) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967).

(18) (a) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953); (b) D. J. Cram, H. L. Nyquist, and F. A. Abd Elhafez, *ibid.*, **79**, 2876 (1957).

(19) (a) S. Winstein, *Bull. Soc. Chim. France*, [5] **18**, C 55 (1951); (b) S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, **74**, 2165 (1952); (c) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953); (d) W. H. Saunders, S. Ašperger, and D. H. Edison, *ibid.*, **80**, 2421 (1958).

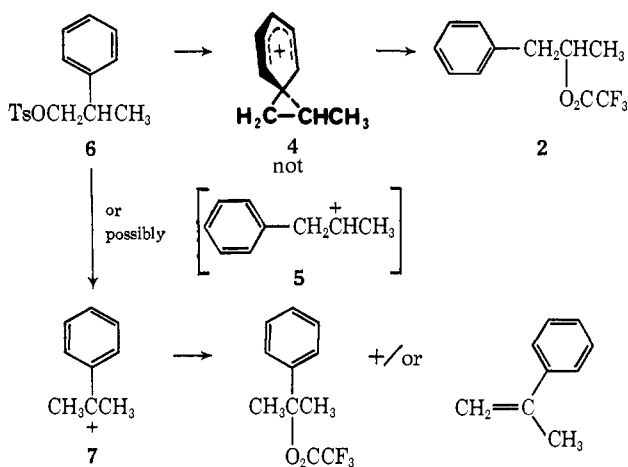
(20) In order to compare tosylates directly, data from some sources in addition to Winstein, *et al.*,⁸ have been collected in Table II; the arguments of these workers are unaffected by the selection.

Table III. Stereochemistry of Solvolysis of 1-Phenyl-2-propyl Tosylate

Solvent	% inversion	% retention
C ₂ H ₅ OH ^a	93	7
CH ₃ CO ₂ H ^a	65	35
HCO ₂ H ^a	15	85
CF ₃ CO ₂ H ^b	0	100

^a Reference 8. ^b Present work.

in trifluoroacetic acid than its open-chain secondary counterpart **5** signifies that the trifluoroacetolysis of 2-phenyl-1-propyl tosylate (**6**) must also proceed by way of **4** (unless hydrogen participation supervenes to produce the tertiary benzylic cation **7**). Thus, it is not to be generally presumed that phenonium ions play only a transition-state role in systems structurally endowed with a



driving force for rearrangement in terms of open carbonium ions, although evidence to this effect may of course be discovered in particular cases.²¹

Experimental Section

General. Melting points are corrected. Boiling points are uncorrected. Optical activities were measured on a Rudolph Model 200 photoelectric polarimeter. Specific rotations are estimated to be accurate to $\pm 0.01^\circ$.

Racemic 1-Phenyl-2-propanol and 1-Phenyl-2-propyl Tosylate. These compounds were prepared as described previously.²

(+)-1-Phenyl-2-propanol. Following the procedure of Pickard and Kenyon⁷ the racemic alcohol was converted to its acid phthalate, and the diastereomeric brucine salts of the half-ester were

(21) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Am. Chem. Soc.*, **87**, 1280 (1965).

separated by fractional crystallization from acetone. Six successive crystallizations yielded material having mp 151.0–152.5° (lit.⁷ mp 153°) and $[\alpha]^{25D} -4.95^\circ$ (*c* 13.15, chloroform) (lit.⁷ $[\alpha]D -4.98$). The acid phthalate regenerated⁷ from this salt was saponified⁷ to produce the optically active alcohol, which was fractionally distilled under vacuum. The center cut (bp 70–74° (1.5 mm), lit.⁷ bp 125° (25 mm)) had $[\alpha]^{25D} +38.69^\circ$ (*c* 13.35, chloroform) (lit. $[\alpha]^{20D} +26.55^\circ$ (neat),⁷ $[\alpha]^{30D} +28.3^\circ$ (neat),²² $[\alpha]^{23D} +27.05^\circ$ (neat),⁸ $[\alpha]^{27D} +27.0^\circ$ (neat)⁸).

(+)-1-Phenyl-2-propyl Tosylate. The (+)-1-phenyl-2-propanol was converted to its tosylate by reaction with toluenesulfonyl chloride in pyridine in the usual manner.²³ After two recrystallizations from hexane the ester had mp 70.5–71.5° (lit.⁸ mp 71–72°) and $[\alpha]^{24D} +24.60^\circ$ (*c* 9.08, chloroform) (lit. $[\alpha]D +24.97^\circ$,²⁴ $[\alpha]^{25D} +23.33^\circ$ (*c* 15.86, chloroform),⁸ $[\alpha]^{26D} +26.1^\circ$ (*c* 17.1, benzene)⁸).

Trifluoroacetolysis of (+)-1-Phenyl-2-propyl Tosylate. A solution of 3.4 g (0.012 mol) of the (+)-1-phenyl-2-propyl tosylate in 200 ml of distilled trifluoroacetic acid containing 1 wt % trifluoroacetic anhydride and 3.4 g (0.025 mol) of sodium trifluoroacetate was allowed to stand at room temperature for 6.0 hr with exclusion of atmospheric moisture and was then poured into 600 ml of ice water. The mixture was extracted three times with pentane, and the combined pentane solution was washed with water (until the aqueous phase was no longer acidic to indicator paper) and dried over anhydrous magnesium sulfate. After distillation of the pentane the residual crude trifluoroacetate was boiled under reflux with 100 ml of 6 *N* potassium hydroxide solution for 4 hr. The alkaline mixture was extracted with three 75-ml portions of ether, and the combined ether solution was washed with water and dried over anhydrous magnesium sulfate. The ether was removed by atmospheric distillation, and the residue was fractionally distilled under vacuum, yielding a center cut of 0.93 g (0.0068 mol) of 1-phenyl-2-propanol, bp 75° (1.33 mm). The vapor phase chromatogram of this material showed no evidence for 1-phenyl-1-propanol, under conditions where 0.2% of this isomer could readily have been detected. The corresponding trifluoroacetate must have polymerized² nearly completely under the reaction conditions, and some additional separation may have occurred in distillation. The alcohol had $[\alpha]^{25D} +36.68^\circ$ (*c* 4.37, chloroform), corresponding to 99.97% retention of configuration relative to the alcohol from which the starting tosylate was prepared.

Rate Measurements. To purified trifluoroacetic acid was added 1 wt % of trifluoroacetic anhydride,² and the resultant solution was made 0.060 *M* in sodium trifluoroacetate as described earlier.² The rates of trifluoroacetolyses run above room temperature were measured spectrophotometrically by the previously reported adaptation² of the procedure of Peterson, *et al.*¹⁶ Reactions below room temperature were run in thermostated volumetric flasks, from which aliquots were periodically withdrawn with rapid-flow pipets and quenched in 95% ethanol as usual.²

Acknowledgment. Support of this work by National Science Foundation Grant GP-8421 is gratefully acknowledged.

(22) P. A. Levene and P. G. Stevens, *J. Biol. Chem.*, **89**, 471 (1930).

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

(24) H. Phillips, *J. Chem. Soc.*, **123**, 44 (1923).