Solvolytic Displacement Reactions in Trifluoroacetic Acid. I. Trifluoroacetolysis of 2-Phenylethyl *p*-Toluenesulfonate. Evidence for Ethylenephenonium Ion[1a]

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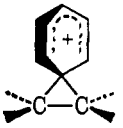
Abstract: Buffered trifluoroacetolysis of 2-phenylethyl tosylate at 72° produces pure 2-phenylethyl trifluoroacetate in virtually quantitative yield. When the reaction is carried out with 2-phenylethyl-1,1-d_2 tosylate for approximately one half-life, complete methylene-group equilibration is found in the trifluoroacetate product, whereas the recovered tosylate is only slightly rearranged. At 75.0° (unbuffered) trifluoroacetolysis of 2-phenylethyl tosylate is 3040 times as fast as that of ethyl tosylate. These results indicate the reaction to proceed entirely *via* ethylenephenonium ion. Buffered trifluoroacetolysis of 1-phenyl-2-propyl tosylate at 25.0° gives a high yield of unrearranged trifluoroacetate plus a trace of 1-phenyl-1-propyl trifluoroacetate, and proceeds 20.1 times as fast as that of 2-propyl tosylate.

In 1949 Cram[2] first proposed ethylenephenonium ion intermediates, **1**,[3] to account for the direction and high degree of stereospecificity observed in the acetolysis of the diastereomeric 3-phenyl-2-butyl tosylates. Since that time the hypothesis of such transient but discrete species has been used to correlate product, stereochemical, and kinetic data for a wide variety of reactions of β-arylalkyl systems,[4] including carbon, hydrogen, and sulfur isotopic tracer results, deuterium kinetic isotope effects, and kinetic salt effects.[4]



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Despite the apparent success of these interpretations, however, Brown and coworkers have in recent years undertaken a critical reevaluation of structures of type **1** as postulated intermediates in solvolytic displacement reactions in acetic and formic acid.[5] Their conclusions, based on new experimental results of their own as well as reexamination of the earlier literature, may be summarized as follows. (1) For substrates more highly alkyl-substituted at the β- than at the α-carbon atom and thus endowed with a driving force for carbonium ion rearrangement, and also in some cases with sterically strained ground states, the enhanced solvolysis rates commonly observed should be attributed primarily to these factors rather than to the formation of stable phenonium ions;[5b,d] the latter should be viewed as transition states.[5b,d] (2) In the solvolysis of substrates leading to symmetrical putative phenonium ions where the benzene ring bears no stabilizing substituents, *e.g.*, 2-phenylethyl and 3-phenyl-2-butyl arenesulfonates, only very slight phenyl group rate enhancements are observed, incommensurate with the formation of a fully bridged, resonance-stabilized intermediate.[5c,6] Rapidly interconverting unbridged **2** or perhaps weakly "π-bridged" carbonium ions **3** have been proposed as more consistent with these data and the related stereochemical results; a detailed mechanistic scheme in terms of equilibrating open secondary cations has been suggested to account for the solvolysis stereochemistry of the *threo*-3-phenyl-2-butyl system.[5c,7] (3) For symmetrical systems where the benzene ring bears stabilizing substituents and where distinct kinetic evidence for bridging in the ionization transition state is observed,[5d,8] *e.g.*, in the formolyses of 2-*p*-anisylethyl tosylate and 3-*p*-

(1) (a) A preliminary account of this work has been published: J. E. Nordlander and W. G. Deadman, *Tetrahedron Letters*, 4409 (1967). (b) Recipient of National Aeronautics and Space Administration Predoctoral Traineeship, 1964–1967.

(2) (a) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); (b) D. J. Cram, *ibid.*, **74**, 2129 (1952).

(3) Several alternative symmetrical formulations with more extended delocalization have also been suggested. See (a) ref 2b, (b) S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, **74**, 2165 (1952). There has been no chemical experimental basis for selection among these, although some recent nmr data for stable ethylenearonium ions have been interpreted to indicate positive charge delocalization into the three-membered ring; see below.

(4) (a) The earlier literature has been critically reviewed by A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 144–152, 159, 167–170, 181–182. (b) More recently, D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964), has provided a detailed defense of the phenonium ion concept, in rebuttal to the challenge of Brown.[5] See also (c) W. B. Smith and M. Showalter, *ibid.*, **86**, 4136 (1964); (d) C. C. Lee and A. G. Forman, *Can. J. Chem.*, **43**, 3387 (1965); (e) C. C. Lee and A. G. Forman, *ibid.*, **44**, 841 (1966); (f) C. C. Lee and L. Noszko, *ibid.*, **44**, 2481 (1966); (g) C. C. Lee and L. Noszko, *ibid.*, **44**, 2491 (1966); (h) D. Battail-Robert and D. Gagnaire, *Bull. Soc. Chim. France*, 208 (1966); (i) J. L. Coke, *J. Am. Chem. Soc.*, **89**, 135 (1967); (j) C. A. Kingsbury and D. C. Best, *Tetrahedron Letters*, 1499 (1967).

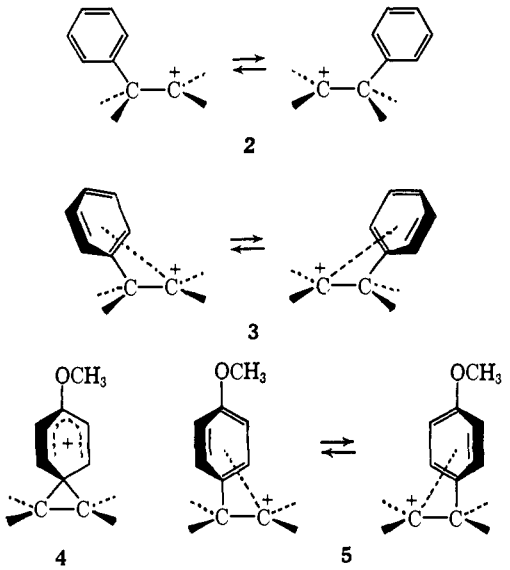
(5) (a) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 140 ff; (b) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Am. Chem. Soc.*, **87**, 1280 (1965); (c) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965); (d) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967).

(6) A single exception to this rule has been reported. F. R. Jensen and R. J. Ouellette, *ibid.*, **85**, 367 (1963), found that 2-phenylethylmercurium ion solvolyzes faster than ethylmercurium ion, by a factor of 8.3 in acetic acid at 75°, and 30.4 in formic acid at 50°. The authors ascribed the rate enhancements to phenyl participation. Brown has acknowledged that these results indicate an intermediate cation of substantially different character from that in the corresponding tosylate acetolysis.[5c]

(7) C. J. Collins, B. M. Benjamin, and M. H. Lietzke, *Ann.*, **687**, 150 (1965), have subjected this scheme to complete kinetic analysis and found it to yield reasonable values for the rate constants of the various discrete processes involved.

(8) (a) 2-(α-Naphthyl)ethyl tosylate undergoes formolysis 8.9 times as fast as ethyl tosylate (at 75°),[4d] and so would also belong presumably to this third classification. (b) The conjugate base of 2-*p*-hydroxyphenylethyl bromide (R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963)) constitutes a special case, reacting with enormous rate enhancement to form the neutral bridged intermediate dienone as an isolable species.

anisyl-2-butyl tosylate, the best representation of the carbonium ion intermediate formed (for the examples cited) is not **4** but rather **5**, a pair of rapidly equilibrating π-bridged cations.[5d]



Whereas Brown's criticisms of the phenonium ion concept have been in the context of solvolytic displacements, important related evidence has been the recent nmr observation by Olah and coworkers[9] of the ethylene-*p*-anisonium, -2,4,6-trimethylphenonium, and -pentamethylphenonium ions as stable species in SbF_5–SO_2 medium, from ionization of the corresponding 2-arylethyl chlorides. The C–H proton chemical shifts were appropriate for benzenonium but not phenyl rings, and methanolysis gave products of the original structure in good yields.[9a]

Additional relevant data postdating Brown's reviews[5c] have been the observations by Winstein and coworkers,[10] that 2-(9-anthryl)ethyl tosylate solvolyzes with an accelerated rate in several media, most notably formic acid, and produces in aqueous dioxane under kinetic control principally the spiro alcohol corresponding to reaction of the bridged aronium ion[10] at the *para* position.

Attention is also called to the recent report by Coke[4i] of reinvestigation of the nitrous acid deamination of 2-phenylethylamine-1-^{14}C in acetic acid. The results were concluded to indicate an ethylenephenonium ion intermediate in preference to rapidly interconverting 2-phenylethyl cations.

In the controversy over phenonium ions as solvolysis intermediates, symmetrical systems are of central concern, since their energetics are not complicated by net 1,2-aryl shift. The present paper presents some new solvent-effect data in this category. In Table I are listed comparative solvolysis rates of 2-phenylethyl tosylate and ethyl tosylate. These data were measured by Winstein and coworkers,[11] who interpreted them in terms of an increasing ratio of phenyl-assisted to solvent-assisted reaction in proceeding from solvent ethanol (highly nucleophilic,[12] poorly ionizing[13]) to formic acid (*vice versa*).

Table I. Published Titrimetric Rate Data for Solvolyses of Ethyl Tosylate and 2-Phenylethyl Tosylate at 75° [a]

Solvent	10^6k_1, sec^{-1} Ethyl tosylate	10^6k_1, sec^{-1} 2-Phenylethyl tosylate	$k_{phenylethyl}/k_{ethyl}$
C_2H_5OH	29.8	7.08	0.24
CH_3CO_2H	0.772	0.288	0.37
HCO_2H	18.9	39.4	2.1

[a] Reference 11.

The subsequent results of Lee and coworkers[14] on isotope-position rearrangements attending solvolyses of 2-phenylethyl-1-^{14}C tosylate in these media proved consistent with this interpretation, while demonstrating also that ion-pair returns contribute to the kinetics in acetic acid and, to a lesser extent, in formic acid.[14b] In Table I it is seen that 2-phenylethyl tosylate solvolyzes more slowly than ethyl tosylate in ethanol and acetic acid and only slightly faster than ethyl tosylate in formic acid. The trend, however, suggests that significant rate enhancements by β-phenyl might be found in solvents even better ionizing and/or more poorly nucleophilic than formic acid. Whereas the latter has commonly been employed as a limiting solvent in these respects, it has become apparent in recent years,[15] particularly from the work of Peterson, that trifluoroacetic acid represents extensions of these properties. Consequently we have investigated the trifluoroacetolyses of ethyl tosylate and 2-phenylethyl tosylate.

Another substrate of leading significance to the question of phenyl participation is 1-phenyl-2-propyl tosylate (**9**).[16] Here, with neighboring phenyl attached to a primary carbon and tosyloxy at a secondary center, there exists in terms of open carbonium ions an electronic bias against phenyl migration, while the phenyl group is also free from geminal crowding. As long as solvolysis gives predominantly unrearranged product, therefore, any acceleration in rate for this species over that of 2-propyl tosylate could result only from formation of a phenyl-bridged intermediate cation more stable than the alternative open secondary carbonium ion. Comparative solvolysis rates of these substrates have been studied in the more common solvents (see below), without evidence for phenyl participation. We have begun study of the products, kinetics, and stereochemistry of the trifluoroacetolysis of **7**. Our preliminary

(9) (a) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey *J. Amer. Chem. Soc.*, **89**, 711, 5259 (1967). (b) Earlier, L. Eberson and S. Winstein, *ibid.*, **87**, 3506 (1965), had similarly observed the 9-anthrylethyl bridged cation as a stable species, but from a precursor of the same structure.

(10) L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *ibid.*, **87**, 3504 (1965).

(11) (a) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952); (b) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

(12) Reference 4a, pp 63–69.

(13) (a) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961). (b) For a review on experimental criteria for solvent polarity see C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965).

(14) (a) C. C. Lee, G. P. Slater, and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1417 (1957); (b) C. C. Lee, R. Tkachuk, and G. P. Slater, *Tetrahedron*, **7**, 206 (1959); (c) see also W. H. Saunders, Jr., S. Asperger, and D. H. Edison, *J. Am. Chem. Soc.*, **80**, 2421 (1958).

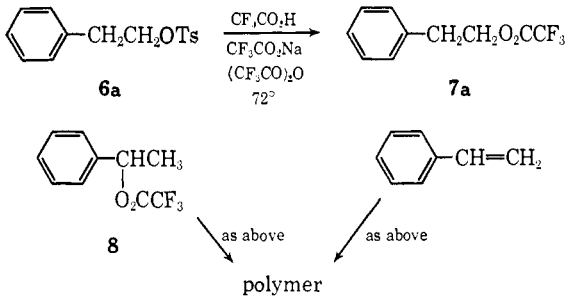
(15) (a) P. E. Peterson and R. J. Bopp, *ibid.*, **89**, 1283 (1967); (b) P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966), and previous papers in this series, particularly (c) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *ibid.*, **87**, 5169 (1965), and (d) P. E. Peterson, *ibid.*, **82**, 5834 (1960); see also (e) A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **81**, 1640 (1959); **82**, 4299 (1960).

(16) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, Jr., *ibid.*, **74**, 1140 (1952).

findings are pertinent to those for the 2-phenylethyl system and are included in this report.

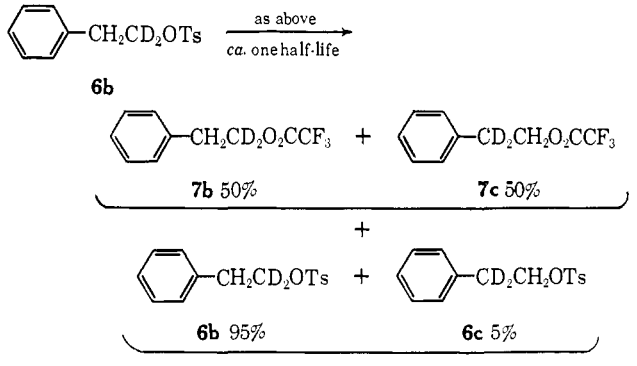
Product Studies

Trifluoroacetolysis of 2-phenylethyl tosylate (**6a**) (0.10 *M*) in the presence of sodium trifluoroacetate (0.125 *M*) and trifluoroacetic anhydride (1 wt %) for 4 hr at 72° (reflux) is a very clean reaction and produced pure 2-phenylethyl trifluoroacetate (**7a**) in 96% isolated yield (0.005-mol scale). 1-Phenylethyl trifluoroacetate (**8**), the hydride-shift product, could have been

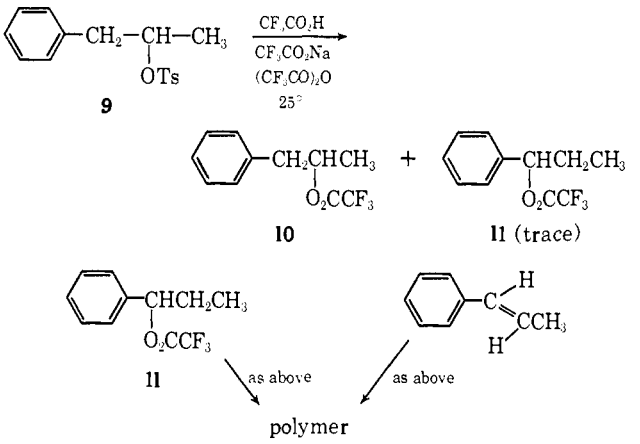


readily detected in the gas chromatographic analysis, but in fact when **8** was submitted separately to the reaction conditions, it was found to resinify rapidly; none could be recovered after 4 hr. Peterson has found[17] that *t*-alkyl trifluoroacetates exist in equilibrium with their derivative olefins in trifluoroacetic acid at 35°, and the same is doubtless true for the *sec*-benzylic trifluoroacetate **8** at 72°, since styrene was found to polymerize instantaneously in trifluoroacetic acid at room temperature.[18] In view of the very high isolated yield of unrearranged product **7a** and the absence of any visible distillation residue, however, it is evident that very little or no hydride shift occurred in solvolysis, in spite of the driving force present for formation of the *sec*-benzylic cation.

The trifluoroacetolysis was also carried out with 2-phenylethyl-1,1-d_2 tosylate (**6b**) for approximately one half-life, and the trifluoroacetate product and unreacted starting material were separated and purified. Nmr analysis showed that isotope-position equilibration was complete in the former, *i.e.*, **7b** and **7c** were present in equal amounts within experimental uncertainty (estimated ±2%). Recovered reactant was only slightly rearranged, consisting of 95% **6b** and 5% **6c** (±2%). A control experiment established that **7b** possessed complete isotope-position stability under the reaction conditions.



Trifluoroacetolysis of 1-phenyl-2-propyl tosylate (**9**) was carried out in the same medium as above, at 25° for 5.5 hr, and was found to produce in 89% isolated yield (0.005-mol scale) 1-phenyl-2-propyl trifluoroacetate (**10**) containing 0.5% of the hydride-shift product 1-phenyl-1-propyl trifluoroacetate (**11**) as judged by gas chromatographic retention time. When subjected separately to the latter reaction conditions at 0.10 *M* concentration, **11** was observed to polymerize, but much less rapidly than did 1-phenylethyl trifluoroacetate (**8**) under appropriate control conditions 47° hotter. Since polymerization is a bimolecular process, traces of **11** might reasonably be expected to survive if some were formed in trifluoroacetolysis of 1-phenyl-2-propyl tosylate (**9**), and indeed *ca.* 4% survival of **11** was found in the control experiment. Minor amounts of hydride shift have also been observed in the formolysis of this substrate.[16]



A different result was obtained when trifluoroacetolysis of 1-phenyl-2-propyl tosylate (**9**) was conducted at 25° in the absence of sodium trifluoroacetate to neutralize the toluenesulfonic acid produced. The reaction was monitored by nmr, which showed initial formation of 1-phenyl-2-propyl trifluoroacetate (**10**) at approximately the same rate as in the presence of buffer. Discoloration of the solution and subsequent separation of a polymer phase accompanied the solvolysis, however. A similar fate was suffered separately by 1-phenyl-2-propyl trifluoroacetate (**10**) in trifluoroacetic acid containing 0.5 equiv of added *p*-toluenesulfonic acid at 25°. The significance of these results will be discussed below.

Rate Studies

The solvolysis rates of ethyl tosylate and 2-phenylethyl tosylate 0.050 *M* in trifluoroacetic acid containing 1 wt % trifluoroacetic anhydride and 0.125 *M* sodium trifluoroacetate were measured spectrophotometrically, using the method developed by Peterson, *et al.*[15c] Under these conditions 2-phenylethyl tosylate exhibited good first-order behavior through at least 60% reaction at 40.0, 55.0, and 70.0°. Ethyl tosylate required considerably higher temperatures, however, and gave clean first-order plots over only 15–20% reaction. Absorption curves for longer reaction times showed increased absorbance near and beyond 273 mμ, indicating formation of an interfering side product. The nature of this process was not investigated, but may well issue from decomposition of trifluoroacetate

(17) P. E. Peterson and E. V. P. Tao, *J. Org. Chem.*, **29**, 2322 (1964).
(18) The same observation has been made by J. J. Throssell, S. P. Sood, M. Szwarc, and V. Stannett, *J. Am. Chem. Soc.*, **78**, 1122 (1956).

Table II. Spectrophotometric Rate Data for Trifluoroacetolysis[a] of Ethyl Tosylate and 2-Phenylethyl Tosylate (6a)

Reactant (0.050 *M*)	Temp, °C	10^6k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Relative k_1 75°	Relative k_1 100°
		With 0.125 *M* Sodium Trifluoroacetate				
CH_3CH_2OTs	115.0	23.8	24.6	−16.8		
	125.0	49.5				
	135.0	105				
	75.0[b]	0.531			1	
	100.0[b]	6.04				1
$C_6H_5CH_2CH_2OTs$	40.0	27.7	20.8	−13.1		
	55.0	128				
	70.0	569				
	75.0[b]	875			1650	
	100.0[b]	7004				1160
		Without Added Sodium Trifluoroacetate				
CH_3CH_2OTs	125.0	11.1	24.9	−19.4		
	135.0	25.1				
	145.0	52.4				
	75.0[b]	0.106			1	
	100.0[b]	1.26				1
$C_6H_5CH_2CH_2OTs$	60.0	83.0	20.2	−16.8		
	70.0	205				
	80.0	498				
	75.0[b]	322			3040	
	100.0[b]	2434				1938

[a] Trifluoroacetic anhydride (1 wt %) added. [b] Extrapolated or interpolated.

ion to produce difluorocarbene.[19] In spite of this complication the initial rate constants obtained are felt to be reliable. Because of it, however, kinetic measurements were also made for ethyl and 2-phenylethyl tosylates in trifluoroacetic acid without added sodium trifluoroacetate. No modification of the spectrophotometric procedure was necessary, and now in all cases good first-order plots were obtained for at least 40% reaction. The results are collected in Table II, together with rate constants extrapolated to 75 and 100° for both reactants. At 75° in unbuffered trifluoroacetic acid *the rate of 2-phenylethyl tosylate exceeds that of ethyl tosylate by a factor of 3040*, a striking departure from the results in other solvents (Table I).

The trifluoroacetolysis rate of 1-phenyl-2-propyl tosylate (**9**) at 25.0° was also measured, for comparison with that published by Peterson[15c] for 2-propyl tosylate. The result is given in Table III, together with rate constants for these substances in other solvents, from the literature. Whereas the β-phenyl analog **9** is slower than isopropyl tosylate in ethanol, acetic acid, and even formic acid, it is 20.1 times faster than the latter in trifluoroacetic acid. More complete rate measurements are in progress.

Table III. Rate Data for Solvolyses of 2-Propyl Tosylate and 1-Phenyl-2-propyl Tosylate (9)

Solvent	Temp, °C	10^6k_1, sec^{-1} 2-Propyl tosylate	10^6k_1, sec^{-1} 1-Phenyl-2-propyl tosylate	$k_{phenylpropyl}/k_{propyl}$
Ethanol	50.0	0.867[a]	0.141[b]	0.16
Acetic acid	70.0	2.55[c]	1.022[c]	0.40
Formic acid	25.0	2.38[d]	1.37[b]	0.58
Trifluoroacetic acid	25.0	2.49[d]	50.0[e]	20.1

[a] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953). [b] Reference 16. [c] W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962). [d] Reference 15c. [e] Present work.

Discussion

The trifluoroacetolysis of 2-phenylethyl tosylate is seen from the present results to be conspicuously different in two respects from its solvolyses in the more common media.

First, isotope-position equilibration in the buffered trifluoroacetolysis of deuterium-labeled tosylate **6b** is complete, and does not result from isomerization of the reactant. Thus, the reaction is indicated to proceed by a pathway in which the two methylene groups become entirely equivalent; the mechanism has no SN2 component. Similar experiments have been carried out in other media with several 2-arylethyl-1,1-d_2 or -1-^{14}C arenesulfonates. The comparative results are presented in Table IV, expressed in terms of per cent rearrangement of C-1 to C-2 in the products, *i.e.*, half the per cent equilibration of C-1 and C-2.[20] It is seen that in no solvent other than trifluoroacetic acid is direct displacement a negligible process with 2-phenylethyl tosylate. Even if it is hypothesized, unjustifiably,[20] that methylene scrambling occurs only in the course of product formation, then simple displacement is responsible for 10, 89, and 99% of the products in formic acid, acetic acid, and ethanol, respectively. Trifluoroacetic acid, in other words, is for 2-phenylethyl tosylate the only truly limiting[21] solvolyzing medium thus far reported. With 2-aryl groups more effective in bridging than phenyl, on the other hand,

(19) I. Auerbach, F. H. Verhoek, and A. L. Henne, *J. Am. Chem. Soc.*, 72, 299 (1950).

(20) These data have not been treated, where possible (S. Winstein and D. Trifan, *ibid.*, 74, 1154 (1952); ref 3b), to account for the formation of scrambled products from reactants scrambled by way of ion-pair return, which can be appreciable in formic acid and very substantial in acetic acid; see ref 14b. Correction for this effect would lead to decreased values for per cent rearrangement during solvolysis proper and would emphasize the differences between trifluoroacetolysis and other solvolyses in isotope-position rearrangement accompanying product formation.

(21) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951).

Table IV. Isotope-Position Rearrangements (per cent C-1 to C-2) in Solvolyses of 2-Arylethyl Arenesulfonates

2-Arylethyl compd	Solvent	Temp, °C	After % react.	% rearr
$C_6H_5CH_2{}^{14}CH_2OTs$	C_2H_5OH	76	100	0.3[a]
	CH_3CO_2H	118	100	5.5[a]
			~50	4.6[b]
	90% HCO_2H	100	100	40[a]
	HCO_2H	100	100	45[a]
			~50	43.3[b]
	CF_3CO_2H	72	~50	50[c]
$2,5\text{-}Me_2C_6H_3CH_2CD_2OTs$	80% acetone	96	~100	26[d]
	CH_3CO_2H	100	~100	46[d]
α-Naphthyl-$CH_2{}^{14}CH_2OTs$	CH_3CO_2H	110.6	50	46[e]
	HCO_2H	56.5	50	50[e]
β-Naphthyl-$CH_2{}^{14}CH_2OTs$	CH_3CO_2H	110.6	50	34[f]
	HCO_2H	56.5	50	43[f]
$p\text{-}MeOC_6H_4CH_2{}^{14}CH_2OTs$	C_2H_5OH	75	100	23[g]
	CH_3CO_2H	75	100	50[g]
	HCO_2H	50	100	50[g]
$2,4\text{-}(MeO)_2C_6H_3CH_2CD_2OBs$	CH_3CO_2H	60.6	70.6	50[h]
	HCO_2H	25.0	77.6	50[h]
$3,5\text{-}(MeO)_2C_6H_3CH_2CD_2OBs$	CH_3CO_2H	100.0	74.9	14[h]
	HCO_2H	60.6	71.2	26[h]

[a] Reference 14a. [b] Reference 14b. [c] Present work. [d] D. J. Cram and L. A. Singer, *J. Am. Chem. Soc.*, **85**, 1075 (1963). [e] Reference 4d. [f] Reference 4e. [g] E. J. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958). [h] Reference 4f.

equilibration between C-1 and C-2 can be complete in formolysis and even acetolysis, as Table IV shows.

The second special feature of the trifluoroacetolysis of 2-phenylethyl tosylate is its dramatic 3040-fold rate enhancement over that of ethyl tosylate. Comparison of the trifluoroacetolysis and formolysis rate constants for the two compounds, Tables I and II, reveals that the unprecedented large phenylethyl:ethyl rate ratio in the latter solvent results from a substantial increase (8.16-fold at 75°) in the phenylethyl rate in going from formic to trifluoroacetic acid, together with an even greater decrease (179-fold at 75°) in the ethyl rate. Table V summarizes the relative rates of ethyl and 2-phenylethyl tosylates as a function of solvent. Whereas the phenylethyl rate decreases from ethanol to acetic acid, and then increases markedly through formic to trifluoroacetic acid, the solvent dependence of ethyl tosylate is irregular along this series. Formic acid offers a more effective combination of nucleophilicity plus ionizing power than either acetic or trifluoroacetic acid, the rate in the lattermost being the slowest.

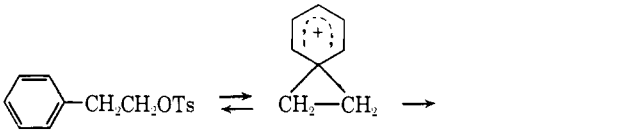
Table V. Relative Solvolysis Rates of Ethyl Tosylate and 2-Phenylethyl Tosylate as a Function of Solvent at 75° [a]

Reactant	Ethanol	Acetic acid	Formic acid	Trifluoroacetic acid
CH_3CH_2OTs	38.6	1	24.5	0.137
$C_6H_5CH_2CH_2OTs$	24.6	1	137	1118

[a] Data from Tables I and II.

The trifluoroacetolysis of 2-phenylethyl tosylate thus provides the first kinetic evidence for large anchimeric assistance in solvolysis of a symmetrical β-phenylalkyl arenesulfonate. These results (as well as those of other trifluoroacetolyses[15]) may be understood in terms of a particularly low nucleophilicity[12] and high ionizing power[13] for this medium. The poor nucleophilicity of the solvent serves in two ways to reveal the neighboring group effect: anchimeric assistance is allowed to displace nucleophilic solvent assistance in ionization of the phenylethyl substrate, and reaction of the ethyl reference substrate is, as well, less assisted by solvent nucleophilic driving force,[22] as shown in Table V. Inasmuch as the dielectric constant of trifluoroacetic acid is unexceptional (ϵ 8.32 at 25°[23]), its superior ionizing ability[15c] must derive largely from particularly effective anion solvation through hydrogen bonding.

On the basis of the rate and isotopic-tracer data, therefore, the trifluoroacetolysis mechanism for 2-phenylethyl tosylate may be represented in simplest form by eq 1, in which all product is derived from intermediate ethylenephenonium ion. Two features of this expression require qualification, however: the precise geometry of the bridged intermediate and the role of the tosylate gegenion.



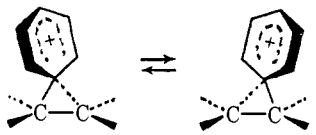
6a 12 7a (1)

Since Cram's introduction of the phenonium ion concept in 1949[2a] most experimental indications of β-aryl participation in systems with the same substituents at the α- and β-carbons have been interpreted, most economically, in terms of "fully symmetrical" bridged intermediates such as **1**, **4**, and **12**. In several

(22) This argument was first introduced by Winstein and Marshall,[11a] in explaining analogous but much less pronounced enhancements of anchimeric assistance attending a change from acetic acid solvent to formic acid.

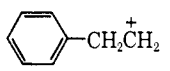
(23) (a) E. L. Mackor, P. J. Smit, and J. H. van der Waals, *Trans. Faraday Soc.*, **53**, 1309 (1957). (b) Compare with those for acetic acid, ϵ 6.15 at 20°, and formic acid, ϵ 58.5 at 16°; J. A. Riddick and E. E. Toops, Jr., in "Technique of Organic Chemistry," Vol. VII, 2nd ed, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., pp 144, 145.

discussions, however, it has been suggested[4b,14c,24] that rapidly equilibrating unsymmetrical bridged carbonium ions **13** might be important in addition to, or instead of, the symmetrical phenonium ion. Most recently Brown and coworkers[5d] have supplied impressive evidence, in the form of relatively meager *para*-substituent rate effects in the formolysis of 2-arylethyl tosylates, that only a relatively small amount of the developing positive charge in the transition states for these reactions is transmitted to the aromatic ring. To explain these results, formation of a pair of rapidly equilibrating π-bridged cations was postulated, of type **5** (above) in the case of the best bridging *p*-anisyl species.[8b] While structure **5** might appear to indicate bonding substantially different from that in **13**, scrutiny of the respective proposals for these formulations reveals that essentially the same connotations were intended, *viz.*, stabilization of the positive charge by partial delocalization into the benzene ring, with this advantage outweighing the concomitant partial loss of benzenoid aromaticity and the incursion of some bond-angle strain.[25] Thus, structures **5** and **13** differ at most in degree, not in kind. In any event, this work of Brown, *et al.*,[5d] makes clear the need to consider unsymmetrical aryl-bridged ions in formulating reaction



13

mechanisms in this area.[26] It is not possible from the present results, of course, to describe precisely the structure of the intermediate phenonium ion from 2-phenylethyl tosylate in trifluoroacetic acid, but we may note that its energy is indicated to be very significantly less than that expected for an open 2-phenylethyl cation **14**. If, as is common,[4b] a factor of 10 is used for the



14

rate-retarding inductive effect of the phenyl group,[27] then stabilization of the ionization transition state by bridging is calculated to be some 7 kcal/mol at 75°; if in addition we adopt the rough estimate that electronic effects might be approximately half-developed in the transition state, then the bridged intermediate itself is appraised to be about 14 kcal/mol more stable than 2-phenylethyl cation **14**. Actually, evidence to be discussed below leads conservatively to a factor of 30 as being more nearly correct for the phenyl-group inductive effect under the present conditions. In this case stabilizations of the transition state and intermediate are reckoned to be 8 and approximately 16 kcal/mol, respectively. On this basis the structure of the intermediate would seem to be very substantially different from that of an open 2-phenylethyl cation **14**,[28] and in the absence of more restrictive evidence we formulate it here as the symmetrical ethylenephenonium ion **12** (eq 1).

The question of the degree of association of the ionic intermediates involved in the present reactions has yet to be elucidated. As noted above, trifluoroacetolysis of 2-phenylethyl tosylate at 72° effects 10% methylene-position equilibration in unconsumed substrate after one half-life, but it is not at present clear whether this is the result of internal or external return.[29] Evidence both for ion pairs and for dissociated ions has been adduced in other solvolyses of 2-arylethyl arenesulfonates. Thus, for example, in the acetolysis and formolysis of 2-phenylethyl tosylate[14b,30] and of 2-*p*-anisylethyl tosylate[31] isotope-position rearrangements and salt effects have implicated both intimate and solvent-separated ion pairs. In the acetolysis of 2-(2,4-dimethoxyphenyl)ethyl brosylate, on the other hand, efficient common ion rate depression is observed,[31] demonstrating the intermediacy of dissociated carbonium and brosylate ions. To our knowledge there have been no reports in the literature to date dealing with ion-pair phenomena in trifluoroacetolysis reactions. This point is under investigation.

Two additional aspects of the trifluoroacetolysis kinetics of 2-phenylethyl tosylate and ethyl tosylate should also be noted briefly. One of these[32] is the sizable simple salt effects observed, added 0.125 *M* sodium trifluoroacetate causing rate increases of 2.7-fold for 2-phenylethyl tosylate and 5.0-fold for ethyl tosylate, at 75°. These values may be cited to be somewhat larger than those commonly brought about in acetic acid by added sodium or potassium acetate,[33,34]

(24) (a) J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, **75**, 2069 (1953); (b) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953).

(25) Indeed Cram and Abd Elhafez[24b] have noted that in **13** "the longer bond . . . would be more directed toward the benzene ring as a whole" than the corresponding shorter bond in the symmetrical phenonium ion **1**.

(26) For example, unsymmetrical bridging could contribute to the lesser deshielding of the methoxy protons in stable *p*-anisonium ion (by 0.20 ppm) and the *p*-methyl protons in 2,4,6-trimethylphenonium ion (by 0.32 ppm) relative to those in the corresponding benzenonium ions;[9] the authors have preferred a different explanation, however.

(27) Several different estimates of this kinetic correction factor have been made, and some comment on this point seems in order here. The value of 10 was suggested by S. Winstein, B. K. Morse, E. Grunwald K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, 74, 1113 (1952), based partly on relative carboxylic acid dissociation constants. Streitwieser[4a] next derived a value of 8 from a more direct approach, Hammett–Taft correlation of the acetolysis rates of a collection of variously substituted alkyl and cyclohexyl arenesulfonates. This number, however, is in arithmetic error; recalculation with Streitwieser's data ($\rho^* = -3.49$, $\sigma^*(C_6H_5CH_2) = +0.215$) yields 5.6. In addition, there is a notable difference between Streitwieser's ρ^* value and that determined subsequently by Pritzkow and Schöppler, −2.58 (Table III, footnote *c*), for the acetolysis of a series of acyclic secondary tosylates without heteroatom substituents. Use of the latter reaction constant generates 3.6 as the rate-retarding inductive effect expected for β-phenyl. In favor of this latter deduction is the stricter pertinence of the correlated substrates, although the reactivity range is much narrower than in Streitwieser's treatment. Finally, Brown[5c] has suggested that the most appropriate value might be 1.4, from the relative acetolysis rates of *endo*-2-norbornyl tosylate and 1-phenyl-*endo*-2-norbornyl tosylate.

(28) By way of contrast, H. C. Brown and C. J. Kim (*J. Am. Chem. Soc.*, in press) have emphasized that similar treatment of the rate data for the acetolysis of 3-phenyl-2-butyl tosylate indicates the transition state and intermediate to be stabilized by only about 1 and 2 kcal/mol, respectively, values too small, in their opinion, to justify formulation of the intermediate as a resonance-stabilized symmetrically bridged carbonium ion.

(29) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *ibid.*, **78**, 328 (1956).

(30) J. W. Clayton and C. C. Lee, *Can. J. Chem.*, **39**, 1510 (1961).

(31) Table IV, footnote *g*.

(32) Comment on this point was urged by a referee.

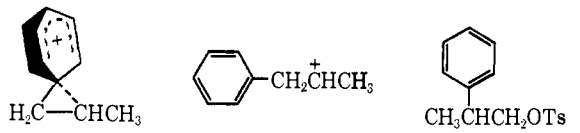
(33) Typically, 0.025 *M* potassium acetate increases the acetolysis rate of cyclohexyl brosylate by 21% at 75° (S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, 70, 821 (1948)), and 0.04 *M* potassium acetate increases the acetolysis rate of 2-phenylethyl tosylate by 70% at 75°.[11b]

(34) The concentration of sodium trifluoroacetate used in the present work was chosen to conform to that employed by Peterson and coworkers in their trifluoroacetolysis studies.[15c]

when extrapolated for concentration differences. It has been pointed out, however, that the magnitude of simple salt effects in general corresponds to the stability of the carbonium ion being formed,[35] and several values have been recorded for bridged carbonium ions in acetic acid which are substantially greater than the present effects in trifluoroacetic acid.[36] The very pronounced sodium trifluoroacetate rate enhancement with ethyl tosylate might well be due to the incursion of an SN2 process, but this cannot be the explanation in the 2-phenylethyl case, since complete methylene-group scrambling was observed with the salt present. At least with the latter substrate, therefore, the effect seems to be due simply to an increase in the ionizing power of the medium,[37] and further interpretation must await the compilation of more information.

A final point of interest in the data of Table II is the trifluoroacetolysis activation entropies. For a number of solvolyses of 2-arylethyl tosylates in common hydroxylic media it has been noted[38] that $\Delta S^{\ddagger}$ values of -9 to -12 eu were associated with those reactions judged to proceed mainly with aryl participation, while values of -17 to -21 eu appeared to characterize those reactions governed by nucleophilic solvent participation. Trifluoroacetolysis of 2-phenylethyl tosylate proceeds entirely with aryl participation, yet shows an activation entropy of -13.1 eu in the presence of sodium trifluoroacetate and -16.7 eu with no buffer added. In our view, however, no contradiction of the previous correlation is implied by the present results. The sort of mechanistic correlation as the one in question might well be anticipated for solvent systems capable of providing nucleophilic assistance to substrate ionization. The mechanism in each case would then depend on whether anchimeric assistance could supplant nucleophilic solvent assistance, and it would be unlikely for two processes of such dissimilar structural changes to have similar activation entropies.[38] In our interpretation of the present trifluoroacetolysis results, on the other hand, we have inferred a predominantly electrophilic involvement of the solvent in the rate-determining step. In such a situation activation entropies should bear little relationship to structural effects in the developing carbonium ions, and indeed we find little distinction with respect to this activation parameter between the reactions of ethyl and 2-phenylethyl tosylates, the values for the former being about 3 eu more negative, consistent with weak nucleophilic solvent assistance.

The case for the phenonium ion intermediate in trifluoroacetolysis is strongly reinforced by the 20.1 times greater rate of 1-phenyl-2-propyl tosylate (**9**) than 2-propyl tosylate. In this secondary system, moreover, a sound basis exists for correction of the rate ratio to include the phenyl-group inductive effect which would operate in a hypothetical simple ionization of **9**. Peterson and coworkers[15c] have established an excellent Hammett–Taft correlation of the trifluoroacetolysis rates of nine unbranched secondary alkyl tosylates (covering a reactivity range of nearly 50-fold at 25°), using σ_I-substituent constants[39] and finding $\rho_I = -15.7$.[40] Extrapolation to $\sigma_I = 0.097$ for the phenyl group[39] leads to a predicted 2-propyl:1-phenyl-2-propyl rate ratio of 33 in the absence of phenyl participation.[40] The full rate enhancement due to phenyl bridging is thus assessed to be a factor of 660. The primary–secondary phenonium ion represented by **15**, then, is indicated to be in the neighborhood of 7 kcal/mol[28,41] more stable than the corresponding nonbridged carbonium ion **16**. Furthermore, as a corollary from the principle of microscopic reversibility, ionization of 2-phenyl-1-propyl tosylate (**17**) must also lead to phenonium ion **15** and not to rearranged open cation **16**. Consequently, it is not to be generally presumed that phenonium ions play only a transition-state role in ionization of unsymmetrical systems such as **17** in which there is a formal structural driving force for rearrangement in terms of open carbonium ions, although evidence to this effect may be discovered, of course, in specific cases.[5b,d]



15 **16** **17**

As described above, trifluoroacetolysis of 1-phenyl-2-propyl tosylate (**9**) in the absence of sodium trifluoroacetate produced initially 1-phenyl-2-propyl trifluoroacetate (**10**) but eventually polymer. These are conditions which could facilitate repeated carbonium ion formation, by *p*-toluenesulfonic acid catalyzed dissociation of the trifluoroacetate product. Under such circumstances hydride shift in minor competition with phenyl bridging would account for the slow production of polymer, since both 1-phenyl-1-propyl trifluoroacetate (**11**) and *trans*-propenylbenzene were demonstrated also to resinify under the reaction conditions.

The results of the present work make important an explicit review of earlier generalizations on the potency of β-phenyl as a neighboring group in acetolysis and formolysis reactions.

In his initial critique[5a] of the phenonium ion hypothesis, in 1962, Brown concluded, "The results clearly indicate that the simple, unsubstituted phenyl group does not provide any significant driving force in the ionization of symmetrical derivatives," and later in the same article, "To sum up, our studies indicate that phenyl bridging is not an important factor in the ionization of phenyl-substituted alkyl *p*-toluenesulfonates except in very special (unspecified) circumstances." In 1965 Brown, *et al.*,[5b] reiterated this view, ". . .there does not appear to be any reason to consider phenyl bridging as a stabilizing effect which provides driving force to facilitate ionization," and

(35) S. Winstein and R. Adams, *J. Amer. Chem. Soc.*, 70, 838 (1948).

(36) For example 0.06 *M* potassium acetate increases the acetolysis rate of 2-*p*-anisylethyl tosylate by a factor of 3.2 at 75°,[11b] and 0.01 *M* sodium or potassium acetate increases the acetolysis rate of cholesteryl tosylate by a factor of 2.5 at 50°.[35]

(37) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, Chapter 5.

(38) (a) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, 78, 4801 (1956); (b) Table IV, footnote *d*.

(39) $\sigma_I(X) = \sigma'(X) = 0.45\sigma^*(CH_2X)$. See (a) R. W. Taft, Jr., *ibid.*, 79, 1045 (1957); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 216–227.

(40) Comparison with the ρ_I values found for acetolysis (-5.72) and formolysis (-7.79) of the same compounds shows the marked amplification of inductive effects brought about by trifluoroacetic acid.

(41) The bridged transition state is stabilized by 3.8 kcal/mol.

quoted[5c] Winstein as having expressed a similar judgment: "Actually it was clear very early that the phenyl group was one of the poorest neighboring groups and, therefore, that β-phenylalkyl systems were marginal ones."

The present data do not impugn these conclusions, but do make clear their restriction to reactions in solvents of substantial nucleophilicity, where carbonium ion charge stabilization can be effected largely through specific solvation. When this mechanism is not available, on the other hand, *i.e.*, when ionization takes place in a poorly nucleophilic medium, it is now to be recognized that phenyl bridging may be a profound stabilizing effect.

The possibility of results such as those reported here should, in fact, be acknowledged to have been anticipated recently by Brown, *et al.*:[5d] "It should be clear that the precise structure of the intermediate may well be a function of the environment. These ions are solvated, and the magnitude of the electron deficiency at the carbonium ion center will depend in part on the effectiveness of the solvation. Consequently, the environment may well shift both the transition state and the intermediate along the coordinate representing the variable nature of these electron-deficient intermediates."

In summary, then, Brown has proposed[5c,d] that a continuous range of β-aryl-bridged carbonium ions require consideration, in which interaction of the benzene ring with the site of carbonium ion generation may vary from weak π-type stabilization to fully symmetrical phenonium ion formation, depending on the particular substrate structure and reaction medium. Whereas controversy is rife over the best formulation of several relevant intermediates in acetic and formic acid solvolyses, the present trifluoroacetolysis results provide forceful evidence for intermediate structures approaching the phenonium ion extreme.

Experimental Section

General. Nmr spectra were recorded on a Varian A-60 spectrometer, using dilute solutions in carbon tetrachloride containing 1 vol % tetramethylsilane. Infrared spectra were obtained with a Beckman IR-8 spectrometer, using neat liquid film samples. Melting points are corrected, boiling points uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Alcohols. 1-Phenylethanol and 1-phenyl-1-propanol were purchased from Aldrich Chemical Co. 2-Phenylethanol was purchased from Matheson Coleman and Bell. 1-Phenyl-2-propanol, bp 82–83° (5 mm), was prepared by lithium aluminum hydride reduction of phenylacetone[16] (Matheson Coleman and Bell). 2-Phenylethanol-1,1-d_2 was obtained by lithium aluminum deuteride (Ventron, Inc., Metal Hydrides Division) reduction of ethylphenyl acetate[15c] in 80% yield, bp 91–92° (7 mm). Its nmr spectrum (neat liquid sample) contained no discernable signal for protium at C-1 (<1%).

2-Phenylethyl Trifluoroacetate. In a 250-ml, round-bottomed flask, equipped with a magnetic stirrer and a pressure-equalizing dropping funnel, open to the atmosphere through a drying tube, was placed 6.1 g (0.050 mol) of 2-phenylethyl alcohol and 100 ml of pyridine, dried over potassium hydroxide. The stirred solution was cooled in an ice bath, and to it was added dropwise over 15 min 15 g (0.071 mol) of trifluoroacetic anhydride. (After about two-thirds of the anhydride had been added the solution became bright yellow-orange.) The reaction mixture was allowed to warm to room temperature and was then poured into 1500 ml of ice water in a separatory funnel. The product was extracted with three 200-ml portions of ether, which were combined, washed twice with 10% sulfuric acid and once each with saturated aqueous cadmium chloride,[5b] water, 10% sodium bicarbonate solution, and water, and dried over anhydrous magnesium sulfate. The ether was distilled off through a 40-cm Vigreux column, and the pale yellow residue was fractionally distilled through a small Claisen–Vigreux apparatus, yielding 9.0 g (83%) of a clear, colorless liquid, bp 85–86° (12 mm); ir: 1781 cm^{-1} (C=O); nmr: τ 2.82 (singlet, aromatic), 5.60 and 7.09 (triplets, J = 7.0 Hz, α- and β-CH_2 respectively).

Anal. Calcd for $C_{10}H_9F_3O_2$: C, 55.05; H, 4.16. Found: C, 55.20; H, 4.30.

2-Phenylethyl-1,1-d_2 trifluoroacetate was prepared in the same way from 2-phenylethanol-1,1-d_2. Its nmr spectrum likewise showed no protium at C-1 (<1%).

1-Phenylethyl Trifluoroacetate. Using the above procedure, from 6.1 g (0.050 mol) of 1-phenylethanol was obtained 8.1 g (0.037 mol, 74%) of ester,[42] bp 63.0–63.5° (7 mm) (lit.[42] bp 73° (15 mm)); ir: 1780 cm^{-1} (C=O); nmr: τ 2.71 (singlet, aromatic), 4.05 (quartet, J = 6.5 Hz, CHO), and 8.41 (doublet, 6.5, CH_3).

1-Phenyl-2-propyl Trifluoroacetate. Using the above procedure, from 6.8 g (0.050 mol) of 1-phenyl-2-propanol was obtained 10.0 g (0.043 ml, 86%) of ester, bp 70–71° (5 mm); ir: 1781 cm^{-1} (C=O); nmr: τ 2.77 (singlet, aromatic), 4.75 (sextet, J = 6.5 Hz, CHO), 7.09 (complex multiplet, CH_2), 8.67 (doublet, 6.5, CH_3).

Anal. Calcd for $C_{11}H_{11}F_3O_2$: C, 56.90; H, 4.78. Found: C, 56.70; H, 4.79.

1-Phenyl-1-propyl Trifluoroacetate. Using the above procedure, from 6.8 g (0.050 mol) of 1-phenyl-1-propanol was obtained 10.5 g (0.045 mol, 90%) of ester, bp 64–65° (4.5 mm); ir: 1784 cm^{-1} (C=O); nmr: τ 2.68 (singlet, aromatic), 4.21 (triplet, J = 7.0 Hz, CHO), 8.01 (irregular quintet, 7.0, CH_2), 9.10 (triplet, 7.0, CH_3).

Anal. Calcd for $C_{11}H_{11}F_3O_2$: C, 56.90; H, 4.78. Found: C, 57.05; H, 4.83.

Ethyl Tosylate. The Eastman compound was recrystallized twice from pentane–ether (8:1), mp 32.6–33.4° (lit.[11a] mp 33.5–34.2°).

2-Phenylethyl Tosylate. Reaction between 2-phenylethanol and tosyl chloride in pyridine was carried out as described by Tipson.[43] The product (70% yield, 0.10-mol scale) had mp 38.8–39.8° (lit.[5d,11b] mp 39.5–40.5°, 35.5–36.5°).

2-Phenylethyl-1,1-d_2 Tosylate. The same procedure was applied, using the labeled alcohol. Its nmr spectrum (50% solution in carbon tetrachloride) showed no protium at C-1 (<1%).

1-Phenyl-2-propyl Tosylate. This ester was prepared from 1-phenyl-2-propanol and tosyl chloride in pyridine by the procedure of Brown and Ham[44] and had mp 92.5–93.5° (lit.[16] mp 93.7–94°).

Trifluoroacetolysis Media. Trifluoroacetic acid (1800 g, Matheson Coleman and Bell) was distilled through a 1-m, vacuum-jacketed column packed with glass helices. To the middle cut (bp 71.5°, 1500 g) was added 1 wt % of freshly distilled trifluoroacetic anhydride (Matheson Coleman and Bell). Buffered medium was prepared in a 1000-ml volumetric flask by dissolving 17.0 g (0.125 mol) of sodium trifluoroacetate (Aldrich) in the previous solution and diluting up to the mark.

Trifluoroacetolysis of 2-Phenylethyl Tosylate. In a 100-ml, round-bottomed flask equipped with a reflux condenser and drying tube was placed 1.381 g (0.00500 mol) of 2-phenylethyl tosylate and 50 ml of buffered trifluoroacetic acid stock solution. The solution was boiled under reflux for 4.0 hr, cooled, and poured into 800 ml of iced water. The product was extracted into three 200-ml portions of ether, which were combined and washed with water, 10% sodium bicarbonate solution (cautiously), and water and dried over anhydrous magnesium sulfate. The ether was distilled off through a 40-cm Vigreux column, and the residue was distilled through a short-path column under vacuum, yielding 1.045 g (0.00480 mol) of colorless liquid, bp 85–86° (12 mm). This material was homogeneous by gas chromatography and had nmr and infrared spectra identical with those of synthetic 2-phenylethyl trifluoroacetate.

Stability of 1-Phenylethyl Trifluoroacetate under Trifluoroacetolysis Conditions for 2-Phenylethyl Tosylate. In a 100-ml, round-bottomed flask equipped with a reflux condenser and a drying tube was placed 1.09 g (0.050 mol) of 1-phenylethyl trifluoroacetate and 50 ml of buffered trifluoroacetic acid stock solution. The solution turned orange immediately. When heated under reflux it quickly became opaque orange, and after 4.0 hr a cloudy drop of material

(42) E. J. Bourne, M. Stacey, J. C. Tatlow, and R. Worrall, *J. Chem. Soc.*, 3268 (1958).
(43) R. S. Tipson, *J. Org. Chem.* 9, 235 (1944).
(44) H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, 78, 2735 (1956).

had separated on top of the solution. Work-up by the same procedure as for the tosylate solvolyses gave, after solvent removal, a brown-orange tar, from which no material distilled (1 mm) up to 265°.

Trifluoroacetolysis of 2-Phenylethyl-1,1-d_2 Tosylate for One Half-Life. A solution of 1.39 g (0.0050 mol) of 2-phenylethyl-1,1-d_2 tosylate in 50 ml of buffered trifluoroacetic acid, in a 100-ml, round bottomed flask equipped with a reflux condenser and a drying tube, was heated quickly to reflux (*ca.* 72°). Boiling was maintained for 20 min (calculated half-life 17.3 min), whereupon the reaction mixture was cooled in ice water and worked up in the same way as that from complete solvolysis of the unlabeled tosylate. After solvent removal, the trifluoroacetate product was distilled from the residue (0.75 mm) and a maximum temperature of 55°, into a Dry Ice cooled receiver; yield 0.32 g (0.0015 mol, 30% of reactant). The remaining oil was triturated with pentane and cooled, resulting in crystallization of the unreacted tosylate, which was collected by filtration; yield of crude material 0.62 g (0.0026 mol, 52% of reactant). Recrystallization from pentane–ether (8:1) gave 0.45 g of colorless needles, mp 38.5–39.5°. Nmr isotope-position analysis was carried out with the neat liquid trifluoroacetate and with a 50% solution of the recovered tosylate in carbon tetrachloride. The former showed 50 ± 2% of CH_2 at C-1 and at C-2. The latter showed 5 ± 2% of CH_2 at C-1, 95% at C-2.

Stability of 2-Phenylethyl-1,1-d_2 Trifluoroacetate under Trifluoroacetolysis Conditions for the Tosylate. 2-Phenylethyl-1,1-d_2 trifluoroacetate (0.060 g, 0.27 mmol) was dissolved in 0.4 ml of buffered trifluoroacetic acid in an nmr tube, which was sealed. Heating this sample at 72 ± 2° for 4 hr produced no change in its nmr spectrum, *i.e.*, no signal for protium at C-1.

Trifluoroacetolysis of 1-Phenyl-2-propyl Tosylate. A solution of 1.452 g (0.00500 mol) of 1-phenyl-2-propyl tosylate in 50 ml of buffered trifluoroacetic acid was kept at room temperature for 5.5 hr (14 half-lives), during which time it developed a pale yellow color. The reaction mixture was worked up as in the 2-phenylethyl case, final distillation giving 1.034 g (0.00450 mol, 89%) of colorless liquid, bp 70–71° (5 mm). The infrared and nmr spectra of the product were virtually identical with those of synthetic 1-phenyl-2-propyl tosylate. Gas chromatography, however, showed the presence of a second compound, in *ca.* 0.5% abundance, with the same retention time as that of 1-phenyl-1-propyl trifluoroacetate. Further efforts were not made to identify this trace product.

Stability of 1-Phenyl-1-propyl Trifluoroacetate under Trifluoroacetolysis Conditions for 1-Phenyl-2-propyl Tosylate. A solution of 1.16 g (0.0050 mol) of 1-phenyl-1-propyl trifluoroacetate in 50 ml of buffered trifluoroacetic acid at room temperature turned dark red about 1.0 hr after preparation. After an additional 30 min a polymeric phase separated. After 5.5 hr the mixture was worked up by the same procedure as for the trifluoroacetolysis of 1-phenyl-2-propyl tosylate. The residue consisted of polymer and *ca.* 0.046 g (0.2 mmol, 4% of reactant) of 1-phenyl-1-propyl trifluoroacetate.

Kinetics Procedure. The method of Peterson, *et al.*,[16c] was used. For the reactions above 25°, the tosylate (1.250 mmol) was placed in a 25-ml volumetric flask and dissolved in buffered or unbuffered trifluoroacetic acid, up to the mark. Up to 15 1.5-ml portions of this solution were sealed in 5-ml glass ampoules, which were placed together in a thermostatic bath at the desired temperature (±0.02°). The first tube was withdrawn when the bath regained the set temperature (*ca.* 45 sec), and was quenched in ice–water, as were successive samples. Each was warmed to room temperature and opened, and 1.00 ml of the solution was pipetted into *ca.* 48 ml of 95% ethanol in a 50-ml volumetric flask, followed by 95% ethanol up to the mark. The absorbance of the resulting solution was measured at the maximum near 273 mμ, using a Cary 15 spectrophotometer. All of the ethanol solutions were found not to change in absorbance for at least twice the time necessary to make the measurements. The theoretical infinity absorbance for each reaction was determined from a solution of 0.0500 *M* β-arylalkyl trifluoroacetate product in trifluoroacetic acid, diluted in 95% ethanol as above. Good first-order behavior was observed to at least 40% completion in all reactions except those of ethyl tosylate in buffered medium, at 115, 125, and 135°. In these cases after *ca.* 15% reaction the absorption curves in the region used for the kinetics showed a new component characterized by a long tail toward the visible, which increased in intensity with time. The side-reaction responsible for this complication was not investigated. It has been reported, however, that in ethylene glycol trifluoroacetate ion undergoes decomposition with formation of difluorocarbene at an appreciable rate at these temperatures.[19]

Kinetics and Isotope Effects in Solvolyses of Ethyl Trifluoromethanesulfonate[1]

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Abstract: Acetolysis of ethyl trifluoromethanesulfonate ("triflate") is 30,000 times faster than that of ethyl tosylate at 25°. Solvent effects and α- and β-deuterium isotope effects show that acetolysis and formolysis of ethyl triflate has little carbonium ion character and much nucleophilic solvent displacement or N character.

Trifluoromethanesulfonic acid is one of the strongest known monobasic acids.[2-4] The corollary that the trifluoromethanesulfonate ion should be a facile leaving group in solvolytic displacement reactions is borne out by the chemistry of alkyl esters. Several such esters are known and have been shown to be effective alkylating agents and esterification promoters. The ethyl ester alkylates benzene, pyridine, and even ethyl ether under mild conditions.[5,6] In the only reported kinetic study of such reactions, Hansen[7] found that methyl trifluoromethanesulfonate undergoes acetolysis 10^4 faster than methyl *p*-toluenesulfonate. Such high reactivity suggests that further kinetic studies could provide important new understanding of solvolytic displacement mechanisms. In particular, such studies could provide an important bridge between the displacement reactions of halides and ordinary sulfonates and compounds not amenable to kinetic study such as the alkyldiazonium ions.

In our initial study we concentrated on the acetolysis of ethyl trifluoromethanesulfonate ("triflate") and its

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