

TRIFLUOROACETOLYSIS OF 2-PHENYLETHYL *p*-TOLUENESULFONATE.
EVIDENCE FOR PHENONIUM ION

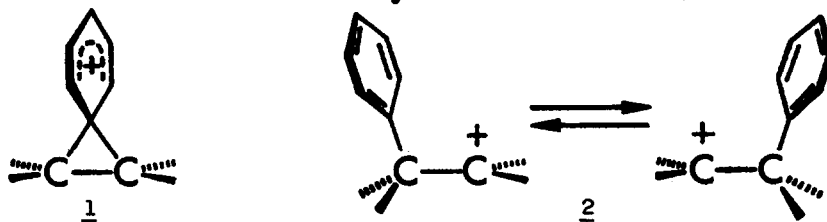
J. Eric Nordlander and William G. Deadman (1)

Department of Chemistry, Case-Western Reserve University

Cleveland, Ohio 44106

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The postulation of ethylenephonium ion intermediates 1, first made by Cram (2) on stereochemical grounds, has proved to be a highly useful concept in correlating a wide variety of product, stereochemical, and kinetic data for reactions of β -arylalkyl systems (3,4). Never-



theless, Brown and coworkers (5) have recently challenged the validity of structures of type 1. In the case of solvolysis of symmetrical systems (with respect to the possible bridged ions) unsubstituted in the phenyl ring, they have argued that persuasive kinetic evidence for phenyl participation is not found and without it phenonium ions cannot be preferred over the corresponding simple open carbonium ions (5c). Rapid Wagner-Meerwein interconversion of the latter species 2 has instead been

proposed to explain the stereochemical results (5c).

In Table I are listed solvolysis rates from the literature for ethyl tosylate and 2-phenylethyl tosylate (6). From these data the

TABLE I

Published Titrimetric Rate Data for Solvolyses of Ethyl
Tosylate and 2-Phenylethyl Tosylate at 75°. ^a

Solvent	10 ⁶ k ₁ , sec. ⁻¹		k phenylethyl k ethyl
	Ethyl tosylate	2-Phenylethyl tosylate	
C ₂ H ₅ OH	29.8	7.08	0.24
CH ₃ CO ₂ H	0.772	0.288	0.37
HCO ₂ H	18.9	39.4	2.1

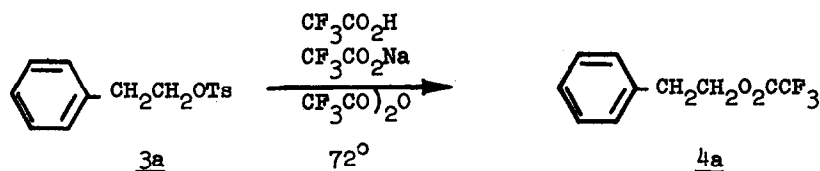
^aRef. 6.

phenylethyl: ethyl rate ratio is at most only 2.1 (uncorrected for phenyl inductive effect (3b)), but its increase in proceeding from solvent ethanol (highly nucleophilic (7), poorly ionizing (8)) to formic acid (vice versa) suggests for the phenylethyl substrate a corresponding increase in phenyl assistance relative to solvent assistance in ionization (6).

It would be logical to anticipate that substantial rate enhancements by the β -phenyl group might be found with solvents even better ionizing and/or more poorly nucleophilic than formic acid. Recent work, particularly that of Peterson and coworkers (9), has made it apparent that trifluoroacetic acid surpasses formic acid in these respects, and consequently

we have investigated the solvolyses of ethyl and 2-phenylethyl tosylate in this medium.

2-Phenylethyl tosylate 3a (0.10M) reacted cleanly in boiling trifluoroacetic acid (72°, 4 hr.) containing sodium trifluoroacetate (0.125M) and trifluoroacetic anhydride (1 wt.-%) to give exclusively 2-phenylethyl trifluoroacetate 4a in 96% isolated yield (0.005-mole scale). Rates were



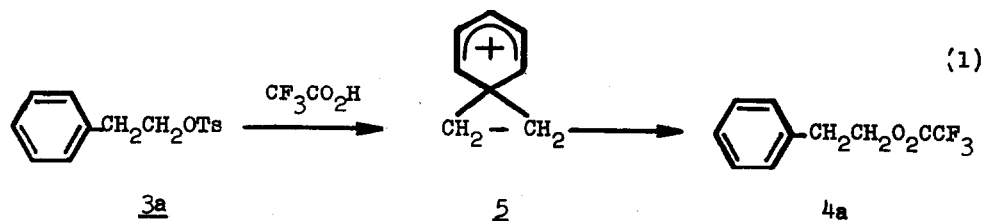
measured in unbuffered trifluoroacetic acid (1% trifluoroacetic anhydride) (10), using Peterson's spectrophotometric procedure (9c); good first-order rate constants were obtained throughout. The results are summarized in Table II.

TABLE II
Spectrophotometric Rate Data for Trifluoroacetylolysis^a of
Ethyl Tosylate and 2-Phenylethyl Tosylate

Reactant (0.050M)	Temp.	$10^6 k_1$, sec. ⁻¹	ΔH^\ddagger , kcal./mole	ΔS^\ddagger , e.u.	relative k_1	
					75°	100°
CH ₃ CH ₂ OTs	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 ₆ H ₅ CH ₂ CH ₂ OTs	60.0°	83.0	20.2	-16.8		
	70.0°	205				
	80.0°	498				
	75.0° ^b	322			3040	
	100.0° ^b	2434				1938

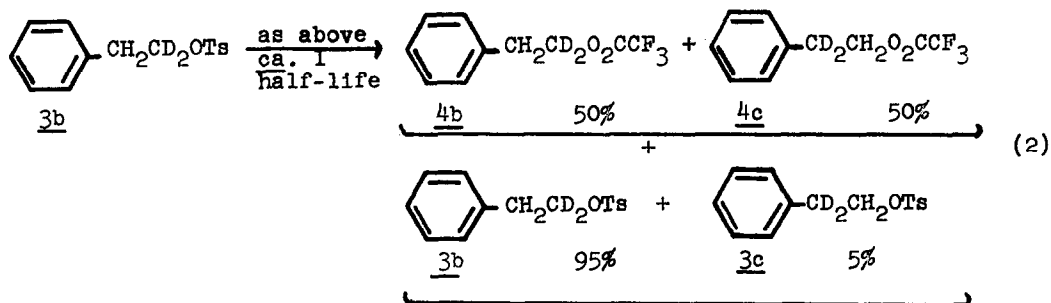
^aTrifluoroacetic anhydride (1 wt.-%) added. ^bExtrapolated or interpolated.

At 75° 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. This unprecedented rate enhancement by the phenyl group where there is no net driving force for rearrangement can reasonably be attributed only to direct formation of the ethyleneponium ion 5, as shown in eq. 1.



This simple mechanism requires that the two methylene groups become completely equivalent in the product, which was found to be the case. Trifluoroacetolysis, in buffered medium, of 2-phenylethyl-1,1-d₂ tosylate 3b was carried out for approximately one half-life at 72°, and the trifluoroacetate product and unreacted starting material were separated and purified. N.m.r. analysis showed, as expressed in eq. 2, that isotope-position equilibration was complete in the former, *i.e.* 4b and 4c were present in equal amounts within experimental uncertainty (estimated ±2%). Recovered reactant was only slightly rearranged, consisting of 95% 3b and 5% 3c (+2%). A control experiment established that 4b possessed complete isotope-position stability under the reaction conditions.

The present results may be understood qualitatively in terms of the very low nucleophilicity and high ionizing power associated with trifluoroacetic acid (9). In solvolysis reactions its poor nucleophilicity should depreciate not only the direct displacement mechanism but also specific solvation of electron-deficient centers, thereby accentuating intramolecular processes for carbonium-ion stabilization. As its dielectric



constant is unexceptional ($\rho = 8.32$ at 25°) (11) its superior ionizing ability (9c) must derive largely from particularly effective anion solvation through hydrogen bonding.

Thus, phenyl participation in ionization of 2-phenylethyl tosylate asserts itself forcefully in trifluoroacetic acid. There is every reason to expect that additional expressions of anchimeric assistance which are inconclusive in more nucleophilic media may become decisive in trifluoroacetic acid. Such research is in progress.

A detailed account of this and related work will be published shortly.

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