extraction was examined by nmr in each case, and no OMe-containing compounds were observed.

Methyl 1-(N-*t*-butylamino)cyclopentane-1-carboxylate (12) showed: bp 50° (0.1 mm); infrared (CCl_4): 2950 and 1735 cm^{-1}; nmr ($CDCl_3$): δ 1.03 (singlet, 9 H), 1.4–2.2 (complex, 8 H), and 3.6 (singlet, 3 H).

Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03. Found: C, 66.35; H, 10.68; N, 7.07.

Methyl 1-(N-*t*-butylamino)cyclohexane-1-carboxylate (13) showed: bp 70° (0.1 mm); infrared (liquid film): 2950 and 1740 cm^{-1}; nmr ($CDCl_3$): δ 1.05 (singlet, 9 H), 1.1–2.2 (complex, 10 H), and 3.6 (singlet, 1 H).

Anal. Calcd for $C_{12}H_{23}NO_2$: C, 67.56; H, 10.87; N, 6.57. Found: C, 67.45; H, 10.70; N, 6.41.

Methyl 1-(N-*t*-butylamino)cyclooctane-1-carboxylate (14) showed: bp 90° (0.1 mm); infrared (liquid film): 2950 and 1740 cm^{-1}; nmr ($CDCl_3$): δ 1.03 (singlet, 9 H), 1.1–2.1 (complex, 14 H), and 3.6 (singlet, 3 H).

Anal. Calcd for $C_{14}H_{27}NO_2$: C, 69.66; H, 11.28; N, 5.80. Found: C, 69.68; H, 11.10; N, 6.09.

Structural Effects in Solvolytic Reactions. II. Nature of the Intermediates Involved in the Solvolysis of Symmetrically Substituted β-Anisylethyl Derivatives

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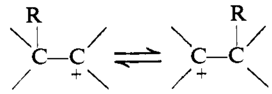
Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana 47907. Received August 29, 1966

Abstract: The rates of reaction of sodium borohydride in isopropyl alcohol with 1-*p*-anisyl-2-propanone, 3-*p*-anisyl-2-butanone, and 3-methyl-3-*p*-anisyl-2-butanone were measured. An examination of a linear free energy plot of these quantities *vs.* the rates of solvolysis of the related toluenesulfonic acid esters reveals deviations from the linear relationship previously noted for the phenyl derivatives. These deviations support the presence of moderate participation by the anisyl substituents in the solvolysis of the tosylates. The rates of formolysis of β-phenylethyl, β-*m*-tolylethyl, β-*p*-tolylethyl, and β-*p*-anisylethyl tosylates were determined. The data are not correlated by the σ^+ constants, suggesting that only a small amount of the developing positive charge in the transition state is transmitted to the aromatic ring. On the other hand, the rates of acetolysis and formolysis of substituted benzyl tosylates do give satisfactory correlations with the σ^+ constants. The observation that a *p*-methoxy group enhances the rate of solvolysis of a benzyl tosylate by a factor in the neighborhood of 100,000, as compared to a factor of only 76 for the formolysis of β-*p*-anisylethyl tosylate, is indicative of the large difference in the amount of the developing charge which is delocalized into the aromatic ring and the *p*-methoxy substituent in the two systems. It is pointed out that neighboring groups may be classified into three types: *n*-, such as RS–, R_2N–, I–, Br–, Cl–; π-, such as $CH_2{=}CH$–, *p*-$^-OC_6H_4$–, *p*-$CH_3OC_6H_4$–, C_6H_5–; and σ-, such as H_3C–. In the *n* class we have a transition between excellent groups, such as neighboring iodide (rate enhancement of 10^6), bromide (rate enhancement of 800), and chloride (negligible rate enhancement). Here current theory recognizes the possibility that there is a transition between the formation of a bridged species for a group with a large rate enhancement, such as iodine, and the absence of a bridged species in the case of a poor neighboring group, such as chlorine. In the π group we observe similar large changes in the effect of the neighboring group: β-*p*-$^-OC_6H_4$–, 10^8, β-*p*-$CH_3OC_6H_4$–, 160, β-C_6H_5–, 2.1. Yet in this π class current theory does not recognize the possibility for a similar transition in the structure of the intermediate. It is suggested that in the case of β-arylethyl derivatives current theory must be revised to consider fully bridged intermediates (arylonium ions), unsymmetrical π-bridged equilibrating cations, equilibrating essentially unbridged cations, and static classical cations. In other words, the sharp dichotomy exhibited by the present theory would appear to be better replaced by an essentially continuous spectrum of cations whose precise structure will depend upon the height of the central barrier for interconversion and the nature of its environment.

The current treatment of carbonium ions[4] appears to involve two major anomalies.[5] First, practically all carbonium ions (or ion pairs[6]) for which structures have been proposed are considered to be static classical or static bridged species. Second, the formation of stable bridged species has been frequently proposed in solvolytic reactions in cases where no significant rate enhancement is indicated.

As was pointed out,[5a] systematic lowering of the potential barrier separating two equivalent cations[6] would



be expected to result in an essentially continuous spectrum of such cations, of which three main classes may be distinguished: (A) essentially static classical ions, which can be formed and transformed into products without significant equilibration; (B) equilibrating

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[1] Research assistant, 1957–1959, on Grants G 6273 and G 2752 supported by the National Science Foundation.

[2] Research assistant, 1965–1966, on Grant G 19878 supported by the National Science Foundation.

[3] Post-doctorate research associate, 1964–1965, on Grant G 19878 supported by the National Science Foundation.

[4] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[5] (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, 87, 2137 (1965). (b) See this source and D. J. Cram, *ibid.*, 86, 3767 (1964), for leading references to the voluminous prior literature dealing with the parent β-phenylethyl derivatives.

[6] In many instances the data do not permit one to distinguish between the formation and reactions of ions or of ion pairs. Consequently, in the subsequent discussion the use of the term cation or carbonium ion shall be understood to include either the free cation or the corresponding ion pair.

Table I. Second-Order Constants and Related Kinetic Data for the Reaction of Sodium Borohydride with Acetone and Representative α-Aryl Derivatives

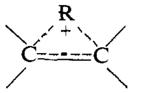
Ketone	Temp, °C	Rate constant, 10^4 l. mole^{-1} sec^{-1}	E_{act}, kcal/mole	log *A*	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
2-Propanone[a]	50.0	207	9.3	4.59	8.8	−39.1
1-Phenyl-2-propanone[a]	50.0	320	9.4	4.88	8.8	−38.4
1-*p*-Anisyl-2-propanone	0.0	13.5				
	15.0	37.4				
	25.0	73.7				
	50.0	323[b]	11.1	5.99	10.5	−33.0
3-Phenyl-2-butanone[a]	50.0	47.8	10.8	4.99	10.2	−37.8
3-*p*-Anisyl-2-butanone	0.0	0.980				
	25.0	5.67				
	45.0	20.6				
	50.0	26.9[b]	11.7	5.32	11.1	−36.0
3-Methyl-3-phenyl-2-butanone[a]	50.0	6.98	13.5	5.96	12.9	−33.4
3-Methyl-3-*p*-anisyl-2-butanone	25.0	0.698				
	40.0	2.38				
	50.0	4.86	14.9	6.78	14.3	−29.6

[a] Reference 10. [b] Calculated from rate constants at other temperatures.

cations, which undergo rapid equilibration in the time interval between formation and conversion into products, and (C) static bridged species, where the potential barrier has disappeared so that resonance now occurs involving the two structures. Consequently, the present classification of practically all known ions into the first and third of these groups must be considered to be an unexpected development requiring theoretical justification.

It has been a valued and highly useful principle in organic chemistry that a decrease in the free energy of formation of the product or first intermediate will be accompanied by a corresponding decrease in the free energy of formation of the transition state leading to that intermediate. Here also it must be considered unexpected that in so many cases the formation of relatively stable bridged species is postulated for many solvolytic reactions without any significant rate enhancements being evident in the data.

It was suggested[5a] that both anomalies might have their origin in the failure to give adequate consideration to Winstein's proposal that the stereochemical results corresponding to the formation and opening of a bridged ion



might, in some cases, be simulated by a dynamic pair of isomeric cations.[7]

In a previous publication we subjected the rate data for symmetrical β-phenylethyl derivatives to a detailed scrutiny.[5a] The results clearly establish the difficulty of demonstrating any significant rate accelerations by neighboring phenyl in such systems.[8] Indeed, in his review of that paper Professor Winstein commented: "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."

On the other hand, there can be no doubt about the ability of the β-anisyl group to participate in the solvolysis of β-*p*-anisylethyl derivatives.[9] The present investigation was undertaken in an attempt to define more precisely the magnitude of this participation in symmetrical β-*p*-anisylethyl derivatives and to inquire into the question whether the magnitude of the effect is consistent with the postulated formation of symmetrically bridged anisonium intermediates.

To this end we determined the rates of reaction of sodium borohydride with certain representative ketones containing a *p*-anisyl substituent in the α position and compared the rates of reaction with the rates of solvolysis of the related secondary tosylates.[10] We also determined the rates of formolysis of substituted β-arylethyl tosylates, $XC_6H_4CH_2CH_2OTs$, with X = H, *m*-Me, *p*-Me, and *p*-CH_3O, to ascertain whether these data can be correlated by the σ^+ constants.[11] Finally, we examined the acetolysis and formolysis of the related benzyl tosylates and examined both their correlatability by the σ^+ constants and the magnitude of the effect of a *p*-methoxy substituent in the two systems.

Results and Discussion

Rates of Reaction with Borohydride. The *p*-anisyl-substituted ketones, 1-*p*-anisyl-2-propanone, 3-*p*-anisyl-2-butanone, and 3-methyl-3-*p*-anisyl-2-butanone, were synthesized, and their rates of reaction with sodium borohydride in isopropyl alcohol were determined in the manner previously described.[10] The results are summarized in Table I.

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(7) S. Winstein and B. K. Morse, *J. Am. Chem. Soc.*, **74**, 1133 (1952).

(8) Note the summary in Table IV of ref 5a.

(9) (a) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Am. Chem. Soc.*, **74**, 1140 (1952); (b) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953); (c) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *ibid.*, **78**, 328 (1956); (d) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956); (e) A. H. Fainberg, G. C. Robinson, and S. Winstein, *ibid.*, **78**, 2777 (1956); (f) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956); (g) R. Heck and S. Winstein *ibid.*, **79**, 3432 (1957); (h) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(10) H. C. Brown, R. Bernheimer, and K. J. Morgan, *ibid.*, **87**, 1280 (1965).

(11) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

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Table II. Relative Rates of Acetolysis of Aryl-Substituted Tosylates and the Relative Rates of Reaction of the Corresponding Ketones with Borohydride

Primary tosylate	Relative rate of acetolysis at 50°	Secondary tosylate	Relative rate of acetolysis at 50°	Ketone	Relative rate of reaction with $NaBH_4$ at 50°
Ethyl	1.00[a]	2-Propyl	1.00[a]	2-Propanone	1.00[a]
2-Phenylethyl	0.35[a]	1-Phenyl-2-propyl	0.32[a]	1-Phenyl-2-propanone	1.6[a]
2-*p*-Anisylethyl	9.8[b]	1-*p*-Anisyl-2-propyl	5.2[d]	1-*p*-Anisyl-2-propanone	1.7[e]
2-*p*-Anisyl-1-propyl	180[b]	3-*p*-Anisyl-2-butyl	80.3[d]	3-*p*-Anisyl-2-butanone	0.14[e]
2-Methyl-2-*p*-anisyl-1-propyl	2560[c]	3-Methyl-3-*p*-anisyl-2-butyl	2360[e]	3-Methyl-2-*p*-anisyl-2-butanone	0.025[e]

[a] See ref 10 for data and references. [b] Reference 9b. [c] Reference 9f. [d] Reference 9a. [e] This study.

As in the case of the parent phenyl derivatives, the introduction of the aryl group into the α position of acetone results in a rate increase. Evidently the rate-enhancing inductive effect of the aryl substituent outweighs its rate-retarding steric effect. With the increasing number of methyl substituents in the α positions, the rate goes down. This is presumably a reflection of the combined rate-retarding electronic and steric effects of these substituents.

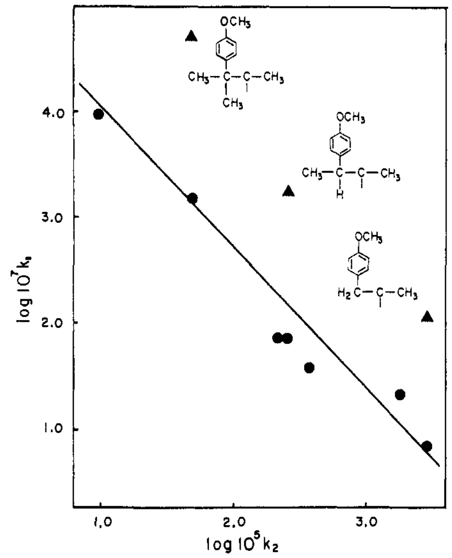

Figure 1. Linear free energy relationship between the rate constants (k_1) for the acetolysis of the tosylates and the rate constants (k_2) for the reaction of the corresponding ketones with borohydride at 50°. (The circles represent the data for the phenyl derivatives.[10])

Perhaps the most significant result is the observation that the *p*-methoxy substituent has so little effect on the rate of reaction of sodium borohydride with these ketones. In all cases the observed rate constant for the *p*-methoxy derivative agrees with that for the parent compound within a factor of two.

Rate data were available for all of the corresponding primary tosylates (Table II). However, as explained earlier, it appeared preferable to compare the rates of reaction of sodium borohydride with the ketones with the rates of acetolysis of the corresponding secondary tosylates. Unfortunately, data were not available for one of the required compounds, 3-methyl-3-*p*-anisyl-2-butyl tosylate. The preparation of this highly hindered reactive tosylate offered difficulties, and the product was not isolated in an analytically pure state. However, the crude tosylate underwent solvolysis with good first-order kinetics: 16.0°, $k_1 = 0.702 \pm 0.208 \times 10^{-5}$ sec^{-1}; 25.0°, $2.76 \pm 0.08 \times 10^{-5}$ sec^{-1}; 35.0°, $9.17 \pm 0.07 \times 10^{-4}$ sec^{-1}. These data yield a calculated rate constant of 5.50×10^{-3} at 50.0°, with $\Delta H^{\ddagger}$ of 22.6 kcal/mole and $\Delta S^{\ddagger}$ of 12.2 eu. While no great accuracy can be claimed for these data, the relative rate agrees reasonably well with that for the corresponding primary derivative and should be adequate for testing the applicability of the linear free energy relationship. The data are summarized in Table II.

In the previous study[10] it was observed that a reasonable linear free energy relationship exists between the rates of reaction of sodium borohydride with α-phenyl-substituted acetones and the rates of acetolysis of the corresponding secondary tosylates. It was concluded that the existence of this approximate linear relationship supported the conclusion that similar structural factors were influencing both reactions, pointing to the relative unimportance of participation by the neighboring phenyl group.[12]

It was of interest to test this approach for the present β-anisyl derivatives, even though the data leave no doubt of the importance of participation in these compounds. It is gratifying to note that the points for the β-anisyl derivatives all fall above the line previously established for the phenyl derivatives (Figure 1), definitely supporting the presence of participation by the anisyl groups in the solvolysis reactions. Presumably, the vertical deviation of the anisyl derivatives from the line provides an estimate of the magnitude of the participation in these three cases. Perhaps the most unexpected feature is the evidence that the deviation is so small, averaging between one and two log units. The significance of this observation will be discussed later in this paper.

Formolysis of β-Phenylethyl Tosylates. The rates of acetolysis of substituted neophyl (2-aryl-2-methylpropyl) *p*-bromobenzenesulfonates are correlated with reasonable precision by the σ^+ constants.[9g] This supports the conclusion that the solvolysis proceeds with participation by the neighboring phenyl group.

The authors represent the reaction as proceeding through the formation of a phenonium intermediate

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(12) For a discussion of the caution to be used in interpreting the existence of such limited free energy relationships, see H. C. Brown and J. Muzzio, *J. Am. Chem. Soc.*, **88**, 2811 (1966).

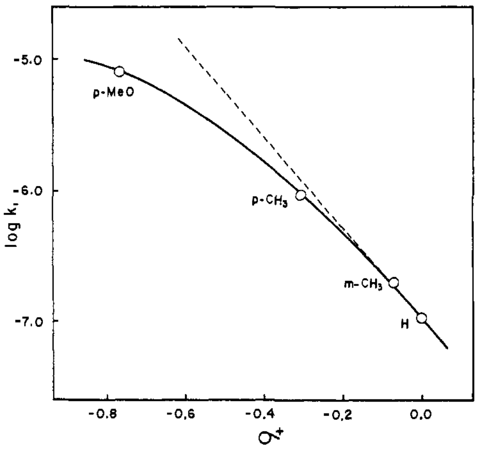
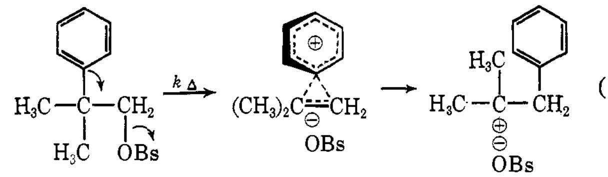


Figure 2. Free energy plot of the rates of formolysis of β-arylethyl tosylates *vs.* σ^+ constants.

(eq 1). However, this appears to be improbable.

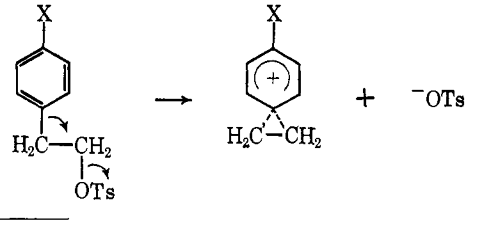


(1)

The system is presumably cascading downhill in energy from a highly unstable primary carbonium ion to a far more stable tertiary ion. There is no reason to assume that there is a significant valley in the reaction coordinate corresponding to the indicated formation of a phenonium intermediate.

As was pointed out in the earlier discussion of the related β,β,β-triphenylethyl case, both the relief of steric strain at the quaternary center and the delocalization of charge to the more receptive tertiary center could contribute to the observed driving force.[10] In order to obtain a more realistic estimate of the driving force provided by the neighboring aryl group, we should utilize symmetrical systems, where rearrangements to more stable structures are not a factor in the observed rate.[5a]

The solvolysis of β-phenylethyl tosylate containing a radio tag in the α position revealed that the tagged atom rearranged to the β position to the extent of 0.3% in ethanol, 5.5% in acetic acid, and 45% in formic acid.[13] It was concluded that these results correspond to the formation of 0.6, 11, and 90% of the phenonium intermediate in these reactions. On this basis, the formolysis of substituted β-phenylethyl tosylates should provide a useful symmetrical system in which to explore the magnitude of the participation by the aryl group and the compatibility of the data with the σ^+ constants (eq 2).



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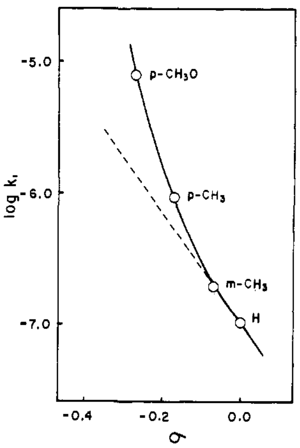

Figure 3. Free energy plot of the rates of formolysis of β-arylethyl tosylates *vs.* σ constants.

The introduction of a *m*-methyl substituent increases the rate of formolysis by a factor of 1.88 at 25°. A *p*-methyl substituent increases it by a factor of 9.01. Finally, the *p*-methoxy substituent increases the rate by a factor of 76.3. Clearly we are observing participation by the aryl ring, with significant charge delocalization into the aromatic rings containing activating substituents. The data are summarized in Table III.

Table III. First-Order Constants and Related Kinetic Data for the Formolysis of β-Arylethyl Tosylates

β-Arylethyl tosylate	Temp, °C	Rate constant, 10^5 sec^{-1}	Relative rate	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
Phenyl	25.0[a]	0.0104	1.00	24.2	−9.4
	50.1	0.271			
	75.0	4.29			
m-Tolyl	25.0[a]	0.0196	1.88	24.1	−8.4
	50.1	0.506			
	75.0	7.93			
p-Tolyl	25.0[a]	0.0937	9.01	23.0	−8.8
	50.1	2.11			
	75.0	29.4			
p-Anisyl	25.0	0.794	76.3	21.7[b]	−9.2[b]

[a] Rate constant at 25.0° calculated from data at other temperatures. [b] Reference 9b.

These data are not correlated by the σ^+ constants (Figure 2). The use of σ constants provide a better, but still not satisfactory, correlation (Figure 3). It is evident that the amount of positive charge transmitted into the ring in the transition state must be considerably smaller than in aromatic substitutions and in similar reactions which are correlated with such excellent precision by the σ^+ constants.[14]

Solvolysis of Substituted Benzyl Tosylates. There is an evident similarity in the mechanism by which a substituent, such as *p*-methoxy, can supply electron density to stabilize the benzyl carbonium ion and the phenonium ion (eq 3 and 4). This suggested the desirability of determining the effect of *p*-methoxy on the limiting rate of solvolysis of benzyl derivatives to provide a basis for comparison with the effect of *p*-methoxy

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(13) C. C. Lee, G. P. Slater, and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1417 (1957); C. C. Lee, R. Tkachuk, and G. P. Slater, *Tetrahedron*, **7**, 206 (1959).

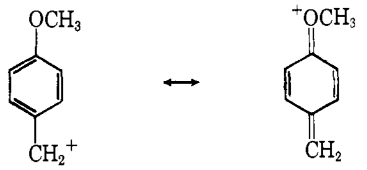
(14) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

Table IV. Summary of Rate Constants and Relative Rates for the Solvolysis of Benzyl Tosylate and Its Substitution Products

		Aqueous acetone,[a] 76.6%		Propionic acid		Acetic acid		Formic acid	
Substituted benzyl tosylate	Temp °C	10^5k_1	Rel. rate	10^5k_1	Rel. rate	10^5k_1	Rel. rate	10^5k_1	Rel. rate
Hydrogen	75.0			8.00		62.9			
	50.0			0.573		5.51			
	40.0					1.84^{c}			
	25.0	10.7	1.00	$0.0264^{c,g}$	1.00	$0.315^{c,k}$	1.00	490	1.00
m-Methyl	75.0			15.7					
	50.0			1.13					
	40.0					4.47^{b}	2.64^{b}		
	25.0	19.2	1.79	$0.0523^{c,h}$	1.98	0.872^{d}	2.77^{d}	1,430	2.92
p-Methyl	75.0			258					
	50.0			20.0					
	40.0					97^{b}	56.5^{b}		
	25.0	319	29.8	$1.01^{c,i}$	38.3	21.8^{d}	69.3^{d}	$29,900^{f}$	61
p-Methoxy	25.0	271,000	25,300	4230^{j}	160,000	$15,400^{e}$	49,000	2×10^7	40,800
	0.0			225					
m-Chloro	99.8					29.6			
	75.0					3.51			
	25.0					$0.0965^{c,l}$	0.0507	5.33	0.0109
m-Chloro-*p*-methyl	25.0							326	0.665
m-Chloro-*p*-methoxy	25.0					773	2,460		

[a] Reference 15, temperature is 25.3°. [b] Reference 17. [c] Calculated from rate data at other temperatures. [d] Calculated from the relative rates at 40° (ref 17), extrapolated to 25°, assuming constant entropy of activation, and the rate constant for benzyl tosylate at 25°. [e] Calculated from the rate constants for *m*-chloro- and *m*-chloro-*p*-methoxybenzyl tosylates. [f] Calculated from the rate constants for *m*-chloro- and *m*-chloro-*p*-methylbenzyl tosylate. [g] $\Delta H^{\ddagger}$ 22.9, $\Delta S^{\ddagger}$ −11.8. [h] $\Delta H^{\ddagger}$ 22.9, $\Delta S^{\ddagger}$ −10.6. [i] $\Delta H^{\ddagger}$ 22.2, $\Delta S^{\ddagger}$ −6.8. [j] $\Delta H^{\ddagger}$ 18.4, $\Delta S^{\ddagger}$ −3.0. [k] $\Delta H^{\ddagger}$ −21.2, $\Delta S^{\ddagger}$ −12.7. [l] $\Delta H^{\ddagger}$ 21.5, $\Delta S^{\ddagger}$ −17.4. $\Delta H^{\ddagger}$ in kcal/mole, $\Delta S^{\ddagger}$ in eu.

on the rate of formolysis of the β-phenylethyl derivative (Table III).



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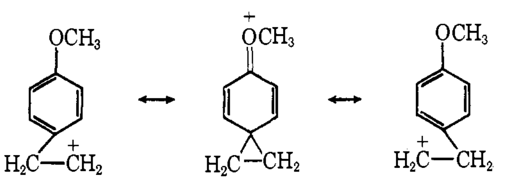

(4)

Rates of solvolysis of the benzyl tosylates in aqueous acetone have been reported.[15] The data for the four derivatives of interest (H, *m*-Me, *p*-Me, *p*-MeO) actually yield a reasonable linear relationship ($\rho = -5.8$) with the σ^+ constants.[16] However, derivatives containing deactivative substituents deviate, possibly because of increasing participation by the nucleophilic solvent. It should be noted, however, that even in this unfavorable solvent the *p*-methoxy substituent exerts a huge effect, $k_{p\text{-MeO}}/k_H = 25{,}300$, as compared to the much smaller effect of this substituent, 76.3, in the formolysis of the β-phenylethyl tosylates.

Rates of acetolysis at 40° for benzyl, *m*-methylbenzyl, and *p*-methylbenzyl tosylates have been determined.[17] These rates show a good linear relationship with the σ^+ values. Unfortunately, the rates are so fast in this solvent that there was no possibility for a direct measurement for the *p*-methoxy derivative at any temperature above the melting point of the solvent (16°). Another major difficulty is the highly unstable nature of this ester—it has been reported to undergo decomposition even at −70°.[18]

These difficulties suggested the use of propionic acid as a possible solvent. The rates are much slower in this solvent and the lower melting point permits operation at 0°. This provided relative rates at 25.0° of 1.98 for *m*-methyl, 38.3 for *p*-methyl, and 160,000 for *p*-methoxy. The complete data are summarized in Table IV.

The data are correlated reasonably well by σ^+ However, there is a slight curvature evident, suggesting that there may be some participation by the solvent in the parent compound. No other solvolytic work appears to have been carried out with this medium. Compared to acetic acid, the lower dielectric constant and probable higher nucleophilicity offer obvious disadvantages for the study of solvolytic reactions under essentially limiting conditions. Consequently, we turned our attention back to acetic acid to explore the possibility of extending the data of Streitwieser and Jagow to the *p*-methoxy derivative.

The following expedient was adopted. The rates of acetolysis of *m*-chlorobenzyl tosylate and *m*-chloro-*p*-methoxybenzyl tosylate were measured. By assuming that the effect of *m*-chloro was a constant in these two compounds, we were able to calculate a relative rate for the *p*-methoxy derivative. This procedure then provides relative rate values at 25° of *m*-methyl, 2.77; *p*-methyl, 69.3; and *p*-methoxy, 49,000. These data yield an excellent linear correlation with σ^+, with $\rho = -6.14$ (Figure 4). The complete data are summarized in Table IV.

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(15) J. K. Kochl and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953).

(16) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(17) A. Streitwieser, Jr., and R. H. Jagow, private communication.

(18) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3443 (1953).

Table V. Summary of Rate Data for the Acetolysis and Formolysis of Various β-Phenyl- and β-Anisylethyl Derivatives at 25°

	Acetic acid			Formic acid		
Tosylate	Phenyl, 10^5k_1 sec^{-1}	*p*-Anisyl, 10^5k_1 sec^{-1}	Rel. rate	Phenyl, 10^5k_1 sec^{-1}	*p*-Anisyl, 10^5k_1 sec^{-1}	Rel. rate
2-Arylethyl	0.04582[a]	0.00151[a]	26	0.0104[h,i]	0.794[h]	76
2-Aryl-2-methyl-1-propyl	0.00309[b]	0.537[b]	174	1.13[j]	83.1[c]	74[j]
1-Aryl-2-propyl	0.00150[d]	0.0485[d]	32	1.37[d]	51.0[d]	37
3-Aryl-2-butyl (*threo*)	0.00740[e]	0.577[f]	78	22.8[e]	500[k]	22
3-Aryl-3-methyl-2-butyl	0.596[g]	27.6[h]	46			

[a] Calculated from the data of ref 9b. [b] Reference 9d. [c] Reference 9f in the presence of sodium formate. [d] Reference 9a. Formolyses were run at 25.12°. [e] S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, **74**, 2165 (1952). [f] Reference 9h. [g] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952). [h] This study. [i] Extrapolation of the data in ref 9b gave a value of 0.00986×10^{-5}. [j] Calculated from $(k_{p\text{-MeO}}/k_{\text{H}})_{50°} = 65.6$ and $k^{50°}{}_{p\text{-MeO}} = 1.53 \times 10^{-2}$ assuming $\Delta S^{\ddagger}$(formolysis) = $\Delta S^{\ddagger}$(acetolysis).[9f] [k] Calculated from the extrapolated values[9f] of $k_\alpha = 1.49 \times 10^{-2}$ sec^{-1} and k_α(R–OBs)/k_α(R–OTs) = 2.98, assuming $k_\alpha/k_t = 1$.

Finally, we turned our attention to the possibility of obtaining such rate data in formic acid. The rate of formolysis of benzyl tosylate proved to be enormous, with a half-life at 25° of the order of approximately 2.5 min. *m*-Tolyl tosylate was even faster, with a half-life of approximately 1 min. It was obviously impossible to measure *p*-tolyl tosylate directly. Accordingly, we fell back upon the procedure previously utilized to obtain a value for the *p*-methoxy derivative in acetic acid. We ran the rate of formolysis of *m*-chlorobenzyl tosylate and *m*-chloro-*p*-methylbenzyl tosylate. This approach led to the following relative rates at 25°: *m*-methyl, 2.92; *p*-methyl, 61; *p*-methoxy (extrapolated from the σ^+ plot), 40,800. The complete data are summarized in Table IV. The correlation with the σ^+ ($\rho = -6.04$) is shown in Figure 4.

It is evident that these four approaches agree in indicating an enormous rate-enhancing effect for the *p*-methoxy substituent, varying from a low of 25,000 in aqueous acetone to a high of 160,000 in propionic acid. It is not possible to state that these solvolyses are truly limiting. However, it should be pointed out that any significant participation by the solvent would be expected to result in a lower relative rate value for *p*-methoxyl. Consequently, it appears safe to conclude that the rate-enhancing effect of *p*-methoxyl in the benzyl system must be approximately equal to or greater than 100,000.

Examination of the Effects of *p*-Methoxy in Various Systems. The difference in the effect of the *p*-methoxy substituent in the solvolysis of the benzyl tosylates and that in the formolysis of the β-phenylethyl tosylates is enormous. It points to a major difference in the amount of the developing positive charge which is delocalized into the ring in the respective transition states for the two systems. Before undertaking a detailed examination of the possible implications of this major difference, it is desirable to examine the effect of *p*-methoxy in other related systems to ascertain whether or not the small effect in the β-phenylethyl system may be anomalous and exceptional.

The available data for the acetolysis and formolysis of various β-phenylethyl derivatives are summarized in Table V.

Rate data for the acetolysis of *trans*-2-anisylcyclopentyl and -cyclohexyl tosylates have been published.[9e] Unfortunately, although the rate constants for the corresponding phenyl derivatives have apparently been measured,[19] they have not yet appeared in the literature. However, it is quite clear from the values that in these two systems the *p*-anisyl–phenyl relative rates must be quite small, less than a factor of 10.

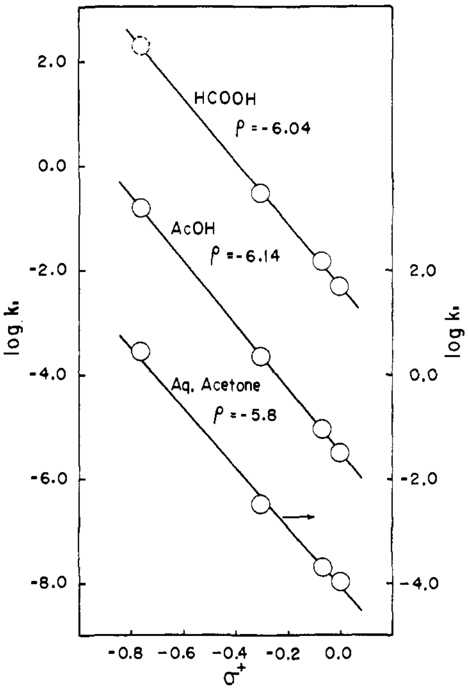

Figure 4. Correlation of the rates of solvolysis of the benzyl tosylates with the σ^+ constants.

The results reveal that the small rate-enhancing effect of the *p*-methoxy substituent in the formolysis of β-arylethyl derivatives is not anomalous, but is actually larger than most of the values. Only in the case of the acetolysis of the neophyl derivatives, a system involving driving force associated with rearrangement from a primary structure to a tertiary cation, is there observed a larger effect.

The relatively small effect of the *p*-methoxy substituent in the formolysis of β-arylethyl derivatives, as compared to its much larger effects in the solvolysis of the benzylic derivatives and in the great majority of

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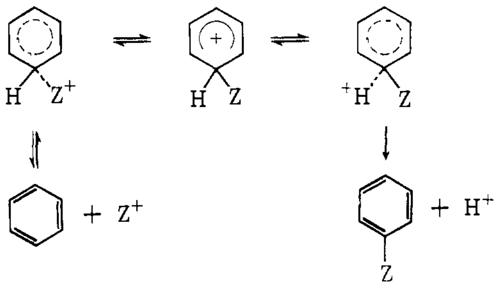
(19) See ref 9a and footnote 7 in S. Winstein and R. M. Roberts, *J. Am. Chem. Soc.*, 75, 2297 (1953).

aromatic substitutions,[14] must be diagnostic of the nature of the transition state. Accordingly, it is appropriate that we now turn our attention to a consideration of the nature of this transition state.

The Transition State. The failure of the formolysis data for the β-arylethyl tosylates to correlate with the σ constants (Figure 3), with a strong upward curvature for the *p*-methyl and *p*-methoxy derivatives, suggests that the solvolysis proceeds with increasing participation by the aryl groups containing activating substituents. On the other hand, the failure to correlate with the σ^+ constants (Figure 2) indicates that the participation and accompanying charge delocalizing is far less than is usually observed in the great majority of aromatic substitutions, in spite of the fact that the proposed mechanism is formally an electrophilic substitution of the developing electron-deficient center onto the ring.

Electrophilic aromatic substitutions are believed to proceed through one of two significant transition states—either that involving the formation of a bond between the electrophile and the aromatic, leading to the σ complex, or that involving breaking of a bond in the σ complex, leading to product (eq 5).[14,20]

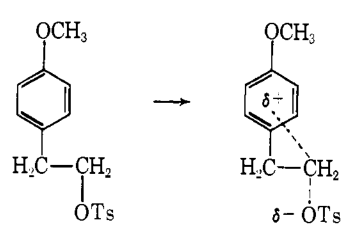


(5)

The unexpected success of the σ^+ constants in correlating so many electrophilic substitutions[14] must mean that the electronic demands upon substituents must be very similar in the σ complex to those in the *t*-cumyl solvolyses used to obtain these constants. Moreover, it follows that in the great majority of electrophilic substitutions the transition state involved in the substitution must resemble the σ complex rather closely.

In a few cases, such as protodestannylation,[21] the data are not correlated satisfactorily by the σ^+ constants. Indeed, the behavior resembles that in Figure 2 (relative rate for *p*-methoxy is 63). In such cases it has been suggested that the transition state for the reaction must more nearly resemble the π complex than the σ complex.

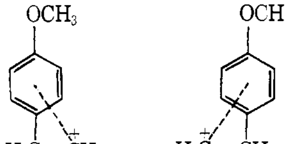
Consequently, both the small rate enhancement observed for the *p*-methoxy substituent and the marked deviation from the σ^+ treatment suggest that the transition state for the formolysis of β-anisylethyl tosylate resembles the π complex more closely than it does the σ complex (the anisonium ion). Accordingly, the transition state for the formolysis can be represented as in eq 6.



(6)

The Intermediate. Having decided that the transition state for the formolysis of β-anisylethyl tosylate must resemble the π complex more than the σ complex, we are faced with the usual problem of how to proceed from the transition state to the first intermediate following the transition state.

In recent years it has been customary to rely upon the Hammond postulate[22] to conclude that in an endothermic process, such as solvolysis, the transition state must resemble the first intermediate.[4] On this basis we should conclude that the solvolysis in the case under consideration proceeds to the formation of a rapidly equilibrating pair of π-bridged cations (or ion pairs) with the anisonium ion representing a transition state rather than an intermediate (eq 7).



(7)

This is, of course, in line with our suggestions that we should expect an essentially continuous spectrum of cations (static classical, equilibrating classical, equilibrating partially bridged, static fully bridged), rather than the essential dichotomy of ions of the currently accepted theory.

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.

It should also be evident that stereochemistry does not assist us in fixing the precise structure of the intermediate. Winstein has proposed that rapidly equilibrating classical ions may well give the same stereochemical results as a bridged ion.[7] It should be evident that the rapidly equilibrating π-bridged ions should also exhibit these same stereochemical characteristics. Finally, we are exploring the possibility that even static classical ions, where the structure inhibits approach from the back side, may well undergo substitution with retention.[10,23]

We believe that a more extensive knowledge of the effect of substituents in representative β-arylethyl derivatives will provide us with a better understanding of the importance of bridging in the transition state as a function of structure, and, hopefully, a better understanding of the structure of the intermediate formed in the solvolysis.

It appears highly desirable to resolve the question whether we are dealing with an essential dichotomy of ions, as current theory suggests,[4] or with an essentially continuous spectrum of such ions.

The Nature of Bridged Cations as a Function of the Neighboring Group. It is important to point out that

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[20] E. Berliner, *Progr. Phys. Org. Chem.*, 2, 253 (1964).

[21] C. Eaborn and J. A. Waters, *J. Chem. Soc.*, 542 (1961).

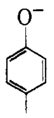
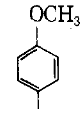
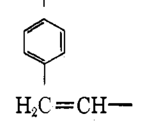
[22] G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

[23] C. W. Shoppee and G. A. R. Johnstoh *J. Chem. Soc.*, 3261 (1961); H. L. Goering and S. Chang, *Tetrahedron Letters*, 3607 (1965).

the present problem is not restricted to neighboring aryl groups, but is far more general. It is especially interesting to note that present theory treats neighboring halogen quite differently from neighboring aryl, even though the phenomena involved appear identical.

Neighboring groups[24] may be divided into three major classes: *n*-, π-, and σ- (Table VI).

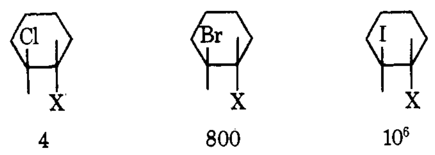
Table VI. Classification of Neighboring Groups

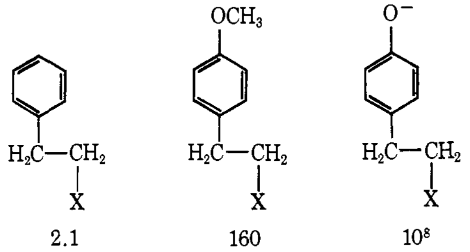
n-	π-	σ-
RS		CH_3
R_2N		
I		
Br		
Cl		

The available data suggest that with few exceptions the most effective neighboring groups are to be found in the *n* classification. Similarly, if we compare the donor effectiveness of these groups toward strong Lewis acids, such as boron trifluoride or aluminum tribromide, the strongest donors are in the *n* family. Indeed, a π donor such as benzene exhibits only very weak donor–acceptor interaction with one of the most favorable Lewis acids, aluminum bromide dimer.[25] There appears to be no experimental evidence for such donor–acceptor interaction involving a member of the σ class in symmetrical systems, even though participation by σ electrons has frequently been postulated in many solvolytic reactions.[26,27]

Even within each class there are wide variations in the relative effectiveness of the groups. Consider the following results for neighboring halogen[28] (eq 8) and neighboring aryl groups[9b,29] (eq 9).

(In the cyclohexyl derivatives, the magnitude of the participation is estimated from the *trans/cis* rate ratios in the acetolysis of the brosylates. In the β-arylethyl derivatives, the first two values are obtained from the rates of formolysis, relative to ethyl arenesulfonate. The last value is an estimate from ethanolysis of the bromide.[29])

 (8)

 (9)

The range in reactivities exhibited by the two series is remarkably similar. Yet it was concluded that the factor of 4 exhibited by neighboring chloride was too small to indicate participation adequate to justify formation of a bridged intermediate in the solvolysis.[28] On the other hand, the factor of 2.1 is no longer considered to be too small to justify bridging to form a phenonium ion.[30]

This would appear to represent a serious inconsistency in the theory which should be resolved.

In the case of neighboring halogen the vast difference in the magnitude of the participation in the transition state was considered to point to the formation of different types of intermediates following the transition state. Yet in the case of neighboring aryl, differences of the same order of magnitude are no longer considered indicative of significant changes in the nature of the first intermediate.

Clearly we need to give the data and concepts in this field careful reconsideration to eliminate such ambiguities and discrepancies.

Experimental Section

Rates of Reaction with Sodium Borohydride. The procedure followed was similar to that utilized earlier.[31] As in the previous case ethanol was added to each flask receiving an aliquot to prevent precipitation of unreacted ketone and its interference with the analytical procedure for borohydride. Because of the fast rate exhibited by 1-*p*-anisyl-2-propanone, the tips were cut off of the pipets to achieve rapid transfer of the aliquots.

Rates of Acetolysis. The general procedure utilized was that of Winstein and Grunwald.[32] However, where the rate of solvolysis was relatively fast, we utilized reaction flasks with a long narrow neck instead of ampoules. That this modification introduces no difficulty is indicated by the observation that the rate constant for the solvolysis of isopropyl brosylate at 70.0° was measured as $7.03 \pm 0.07 \times 10^{-5}$ sec^{-1} (lit.[32] 6.94×10^{-5} sec^{-1}).

Rates of Formolysis. The procedure utilized was that of Winstein and Heck.[9f] The procedure was tested with cyclopentyl tosylate. Three successive determinations at 25.0° gave values of 72.4, 72.8, and 75.5×10^{-5} sec^{-1} (lit.[33] 74.7×10^{-5} sec^{-1}).

The exceptionally fast rates exhibited in the formolysis of the benzyl tosylates necessitated a modified procedure. Sufficient compound to prepare a solution of approximately 0.04 *M* was introduced in the reaction flask (containing a long narrow neck) which had been equilibrated with the bath. While the flask was vigorously swirled in the bath, the appropriate quantity of equilibrated solvent was added. Aliquots were withdrawn with a 5-ml automatic fast-draining pipet and run into a 125-ml erlenmeyer flask containing 20 ml of dioxane and 20 drops of the indicator, bromocresol green. The inverse mixing procedure was also used, with no evident change in results. Three people generally col-

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[24] For an excellent recent review, see B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

[25] S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 903 (1966).

[26] P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

[27] All of our efforts to obtain independent experimental supporting evidence for such σ participation in the transition states of symmetrical norbornyl systems, with accompanying charge delocalization from the 2 to the 1 and 6 positions, have thus far been unsuccessful: H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

[28] (a) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948); (b) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948); (c) E. Grunwald, *ibid.*, **73**, 5458 (1951).

[29] R. Baird and S. Winstein, *ibid.*, **85**, 567 (1963).

[30] D. J. Cram, *ibid.*, **86**, 3767 (1964).

[31] H. C. Brown, O. H. Wheeler, and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957).

[32] S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 846 (1948).

[33] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, **74**, 1127 (1952).

laborated in these fast reactions: one recorded the time, a second pulled the samples, and a third prepared the kinetic solution.

Preparation of the Ketones. 1-*p*-Anisyl-2-propanone was obtained in 29% yield following the procedure of Winstein and his co-workers.[9a] 3-*p*-Anisyl-2-butanone was obtained in 78% yield by the procedure of Jönsson,[34] bp 90.0–91.0° (3 mm), n^{20}D 1.5215. 3-Methyl-3-*p*-anisyl-2-butanone was prepared in 78% yield following the general procedure of Suter and Weston,[35] bp 92–95° (2.5 mm), n^{20}D 1.5183.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.93; H, 8.39. Found: C, 74.78; H, 8.38.

The semicarbazide was prepared and melted at 207–209° (from methanol).

3-*p*-Anisyl-3-methyl-2-butyl Tosylate. Reduction of the ketone with lithium aluminum hydride yielded 3-methyl-3-*p*-anisyl-2-butanol, bp 117–121° (3.5 mm), n^{20}D 1.5269.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.24. Found: C, 74.24; H, 9.24.

The *p*-nitrobenzoate (from methanol) exhibited mp 133.5–134.7°.

Anal. Calcd for $C_{19}H_{21}O_6N$: C, 66.46; H, 6.17. Found: C, 66.68; H, 6.17.

In a test tube was placed 1.01 g (5.2 mmoles) of 3-*p*-anisyl-3-methyl-2-butanol in 300 mg of dry pyridine. A solution of 1.09 g (5.7 mmoles) of *p*-toluenesulfonyl chloride in 550 mg of dry pyridine was added, and the reaction mixture was maintained at 20° for 60 hr. Water was added and the product extracted with chloroform. Evaporation of the dried chloroform leaves a colorless liquid which soon becomes tan, then pink, in color. No crystals could be obtained, even as low as −78°. Good first-order kinetics were obtained for the crude product. The acetolysis results indicated the presence of 72% of the tosyl ester.

Preparation of the β-Arylethyl Tosylates. 2-*p*-Anisylethanol, mp 28–29°, 2-*p*-tolylethanol, bp 90–94° (3 mm), and 2-*m*-tolylethanol, bp 87–88° (2.5 mm), were prepared by reduction of authentic samples of the corresponding acids. They were converted into the corresponding tosyl esters by the usual pyridine procedure. The physical constants are summarized in Table VII.

Preparation of the Benzyl Tosylates. For the most part the corresponding benzoic acids were available commercially. The acids were recrystallized to constant melting point and then reduced to the corresponding benzyl alcohols with lithium aluminum hydride.

m-Chloro-*p*-methoxybenzyl alcohol was prepared by the following procedure. The ethyl ester of anisic acid (60 g, 0.33 mole) was mixed with 0.35 mole of sulfuryl chloride. The reaction mixture was heated on a hot water bath until the weight corresponded to the formation of the ethyl ester of *m*-chloro-*p*-methoxybenzoic acid. The product was taken up in ether and recrystallized from pentane to give 45 g (63%) of fine white needles, mp 75–76° (lit.[36] 76°).

Table VII. Physical Properties of the Substituted Benzyl and 2-Phenyl Tosylates[a]

Tosylate	Obsd mp, °C	Lit. mp, °C
2-*p*-Anisylethyl	59.5–61	57–58[b]
2-*p*-Tolylethyl	69–70	
2-*m*-Tolylethyl	39–40	
2-Phenylethyl	39.5–40.5	35.5–36.6[b]
p-Methoxybenzyl[d]		
m-Chloro-*p*-methoxybenzyl[e]		
p-Methylbenzyl[f]	49.5–50.5	57.9–58.5[c]
m-Methylbenzyl	60.5–61.5	65.1–65.5[c]
Benzyl	58–59	58.5–58.9[c]
m-Chlorobenzyl[g]	80.5–81.5	81.5–82[c]
m-Chloro-*p*-methylbenzyl	59.5–60.5	

[a] All tosylates except the *p*-methoxybenzyl derivatives, which were too unstable to isolate, were subjected to microanalysis and yielded analytical data within the accepted limits. [b] Reference 9b. [c] Reference 18. [d] This compound decomposes relatively rapidly, even at −70° (ref 18). [e] Although reasonably stable at room temperature, attempts to measure the melting point were unsuccessful because of a rapid decomposition to a red mass above room temperature. The material was conveniently handled as an ether solution at −70°. [f] The melting point is only approximate because of the rapid decomposition. [g] The stability of these benzyl tosylates parallels their solvolytic rates. This intermediate, which exhibited the slowest rate of those examined, was also the stablest and could be stored for months in the refrigerator without evident change.

The ester was reduced with lithium aluminum hydride to give *m*-chloro-*p*-methoxybenzyl alcohol,[37] bp 158–160° (7 mm), n^{20}D 1.5681.

The benzyl tosylates were generally prepared following a procedure developed by W. J. Hammar of this laboratory. The procedure may be illustrated by the following preparation.

Benzyl alcohol (5.0 g, 0.046 mole), dissolved in 25 ml of anhydrous ether, was injected into a 100-ml, three-necked flask fitted with a thermometer well, serum cap, nitrogen inlet, and a stirring bar. (The flask had been flushed with nitrogen and a nitrogen atmosphere was maintained.) This solution, cooled to 0°, was treated with 26.6 ml (0.046 mole) of 1.74 *M* methyllithium in ether. Then *p*-toluenesulfonyl chloride (8.81 g, 0.046 mole) was added with stirring at such a rate as permitted maintaining the temperature within the flask below 20°. After 2.5 hr at room temperature, the reaction mixture was passed through a sintered glass funnel to remove lithium chloride. The filtered solution was then cooled in a −80° bath to precipitate the product, which was collected on a filter. The crude product was recrystallized from pentane at −10°. The product, mp 58–59°, was obtained in a yield of 7.0 g (58%).

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(34) A. Jönsson, *Acta Chem. Scand.*, **8**, 1203 (1952).

(35) C. M. Suter and A. W. Weston, *J. Am. Chem. Soc.*, **64**, 533 (1942).

(36) B. Jones and J. Robinson, *J. Chem. Soc.*, 3845 (1955).

(37) R. G. Naik and T. S. Wheeler, *ibid.*, 1780 (1938).