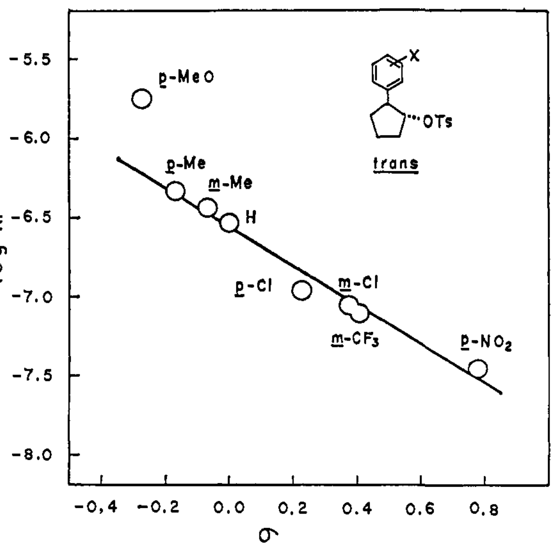

Figure 1. Rates of acetolysis at 25.0° of *trans*-2-arylcyclopentyl tosylates *vs.* the σ constants ($\rho = -1.25$).

endothermic process, such as solvolysis, the transition state must resemble the first intermediate.[13]

A second possibility is that ionization occurs to an intimate ion pair with an essentially open cation, followed by equilibration of the aromatic nucleus between the 1 and 2 positions.[14] The frequency of this equilibration would vary with the substituent in the aromatic ring and thereby control the rate of substitution with retention to substitution with inversion.[15]

A third possibility is that ionization proceeds without significant participation to an intimate ion pair with an essentially open cation, followed by a rapid, competitive attack on the back side of the ion pair by solvent and the neighboring aryl nucleus. The intermediate arising from the latter path could either be a symmetrical phenonium ion or an equilibrating π-bridged cation. In terms of this picture the deactivation of the aromatic nucleus caused by the *p*-nitro substituent would render this neighboring group incapable of competing with solvent. On the other hand, the *p*-tolyl group would compete favorably. The highly active *p*-anisyl group would produce a small amount of participation even in the transition state, adequate to account for the factor of 3.

Finally, we must consider the fourth possibility—acetolyses of secondary arenesulfonates are not essentially limiting, as originally proposed by Grunwald and Winstein,[17] so that aryl participation, k_Δ, competes with solvent displacement, k_s. If both terms are large and comparable, there would not be observed any significant rate enhancement as k_Δ replaces k_s. However, this position requires an explanation as to why the agruments based on $\Delta S^{\ddagger}$, the *m*Y treatment,[17] and α secondary isotope effects,[4] arguments which have been so long accepted, are no longer valid for supporting the conclusion that the acetolyses of secondary alkyl arenesulfonates are essentially limiting.[18] Acceptance of this position would render invalid many of the interpretations in the literature based on acetolysis (and probably formolysis) of secondary arenesulfonates.[19]

In any event, the present study makes it quite clear that major changes can occur in the stereochemistry of substitution with little or no rate enhancement in rates. The problem remains as to the most satisfactory mechanistic interpretation of this interesting result.

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[13] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955). See also the discussion by B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms 1965," Interscience Publishers, Inc., New York, N. Y., 1966, p 11.

[14] H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965).

[15] D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967), recently reported that the acetolysis of 3-(*p*-nitrophenyl)-2-butyl tosylate occurs with predominant inversion. They implied that this result disproves the earlier suggestion[16] that rapidly equilibrating cations might control the stereochemistry in the same manner as that proposed for bridged ions. However, they failed to point out that since their tag had not become equilibrated, the solvolysis had neither involved a bridged ion nor an equilibrating ion.

[16] S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952).

[17] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

[18] Recent studies have confirmed the long-held position that the acetolysis of primary arenesulfonates involves displacement by solvent, so that such solvolyses are best discussed in terms of k_Δ and k_s: J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Young, *ibid.*, **91**, 1154 (1969); A. Diaz, L. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968). The latter authors have stated that acetolysis of secondary derivatives should also be treated in terms of k_Δ and k_s. However, they have not indicated why the position originally taken by Winstein and coworkers[17] is no longer valid, nor provided any experimental evidence to support their position.

[19] For example, the Foote–Schleyer correlation was restricted to acetolysis of secondary arenesulfonates in order to avoid the problem of a significant contribution of solvent to the rate: P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964). If the acetolysis of simple secondary aliphatic and alicyclic arenesulfonates is not limiting, it will be necessary to include a term for this factor. It is not clear how one could hope to calculate a contribution from a displacement reaction with solvent, nor how it was possible to realize a linear correlation while ignoring this factor.

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Rates and Products of Acetolysis of *threo*-3-Aryl-2-buty Brosylates. An Experimental Approach to the Magnitude of Rate Accelerations Attributable to Aryl Participation in the Acetolysis and the Stereochemical Consequences

Sir:

The problem of small or negligible rate accelerations with stereochemical control by β-aryl groups offers a difficulty for current concepts which requires resolution.[1,2] Resolution of the problem has been complicated by the use of qualitative methods to estimate the magnitude of the rate accelerations. In the case of the *trans*-2-arylcyclopentyl tosylates we achieved excellent agreement with three different experimental approaches to the problem.[3] Accordingly, we decided to apply one of these, the Hammett correlation, to the *threo*-3-aryl-2-butyl system.[4]

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[1] H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965).

[2] This is the difficulty. It is generally assumed in interpretation of solvolytic data that the transition state resembles the first intermediate, in line with the prediction of the Hammond postulate. Control of the stereochemistry is attributed to the formation of a relatively stable symmetrically bridged arylonium ion. Yet in many such systems solvolysis proceeds with little or no rate acceleration.

[3] C. J. Kim and H. C. Brown, *J. Am. Chem. Soc.*, **91**, 4287 (1969).

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

Table I. Kinetic Data for the Acetolysis of Substituted *threo*-3-Phenyl-2-butyl Brosylates

Substituent	Rate constant, $10^6 k_t$, sec^{-1} 25.0°	50.0°	75.0°	100.0°	Rel rate 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
p-Methoxy	19.5[a]				80		
p-Methyl	1.48	44.3			6.0	25.4	0.2
m-Methyl	0.401[b]	13.7	282		1.6	26.4	0.8
Hydrogen	0.245[b,c]	8.58	180		1.0	26.6	0.4
p-Chloro	0.0460[b]	1.88	45.5		0.19	27.9	1.3
m-Chloro	0.0248[b]		20.5	300	0.11	27.1	−2.0
m-Trifluoromethyl	0.0169[b]		13.8	201	0.069	27.0	−3.3
p-Nitro	0.00365[d]				0.015	28.0[d]	−2.1[d]

[a] Reference 5. [b] Extrapolated from data at other temperatures. [c] The corresponding tosylate exhibits a rate constant of 0.0740: A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2780 (1956). [d] Calculated from the tosylate,[6] using $k_{\mathrm{ROBs}}/k_{\mathrm{ROTs}} = 3.32$.

Data for the *p*-methoxy[5] and the *p*-nitro derivatives[6] were available. The remaining compounds were prepared by a reaction sequence involving addition of arylmagnesium bromide to 2-butanone, dehydration of 2-aryl-2-butanol, separation of pure *cis*-2-aryl-2-butene by a fractional distillation with a platinum spinning-band column, hydroboration–oxidation of the olefin to obtain the *threo*-3-aryl-2-butanol, and final conversion to the brosylate.

The rate data are summarized in Table I.[7]

Solvolytic processes have been discussed in terms of three factors, k_Δ, the rate constant involving ionization with participation by a neighboring group, k_c, the rate constant involving ionization with no anchimeric assistance and no assistance from covalent solvation of C_α by a solvent molecule in the transition state, and k_s, the rate constant for reaction with such solvent participation.[8] Thus, we have

$$k_t = Fk_\Delta + k_c + k_s$$

In the acetolysis of primary arenesulfonates, k_c is usually unimportant, and $\Delta S^{\ddagger}$ for the k_s process is generally about 10 eu more negative than the k_Δ process, which is reasonable for what is essentially a bimolecular process. Indeed, the value of $\Delta S^{\ddagger}$ has been utilized as a diagnostic tool for the presence of bridging in primary derivatives.[4]

On the basis of their analysis of solvent effects, Grunwald and Winstein proposed that acetolyses of secondary alkyl arenesulfonates are essentially limiting.[9] This would mean that for such derivatives k_s would make a negligible contribution to k_t. Indeed, the small value of $\Delta S^{\ddagger}$ and its small variation for the *threo* derivatives (Table I) would appear to be in essential agreement with that proposal.

We undertook to calculate $\Delta S^{\ddagger}$ for the two processes Fk_Δ and k_c involved in the acetolysis of *threo*-3-phenyl-2-butyl brosylate. We assumed that the *threo* acetate arose from a k_Δ process and that all other products arose from a k_c ($+k_s$) process. This gave values at 75° of $Fk_\Delta = 8.62 \times 10^{-5}$, $k_c = 9.38 \times 10^{-5}$, and at 50° of $Fk_\Delta = 4.06 \times 10^{-6}$, $k_c = 4.52 \times 10^{-6}$, giving $\Delta S_\Delta^{\ddagger} = -0.8$ eu and $\Delta S_c^{\ddagger} = -1.2$ eu. Consequently, if the entropy terms have a diagnostic value, they indicate that covalent bonding with solvent, of the kind that occurs in the acetolysis of primary derivatives, is not important in these secondary compounds.

The four least reactive derivatives are correlated linearly by the Hammett σ constants (Figure 1). However, the more reactive derivatives deviate, exhibiting enhanced rates.

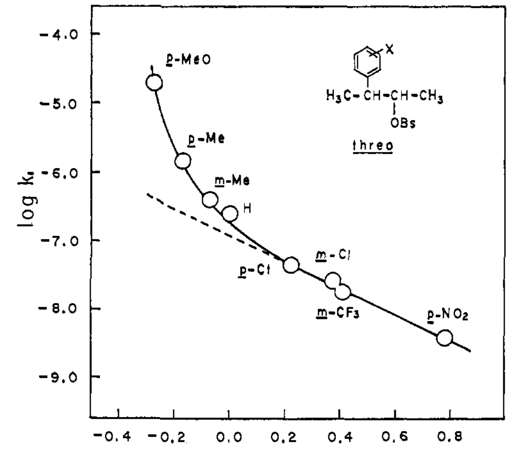

Figure 1. Rates of acetolysis at 25.0° of *threo*-3-aryl-2-butyl brosylates *vs.* the σ constants ($\rho = -2.0$).

It was estimated by Streitwieser on the basis of a Hammett–Taft $\sigma^*\rho^*$ correlation that the rate of acetolysis of the parent compound is four times greater than the predicted value, presumably the result of phenyl participation.[10] If it is assumed that the linear portion of the Hammett plot ($\rho = -2.0$) establishes the slope in the absence of significant participation,[11] then the present approach indicates the acceleration to be a factor of 3, in satisfactory agreement with Streitwieser's estimate.[12]

The rate data over the entire range are correlated with reasonably good precision by the electrophilic sub-

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(5) (a) S. Winstein and R. Baker, *J. Am Chem. Soc.*, **86**, 2071 (1964); (b) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

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

(7) See footnote 7, ref 3.

(8) S. Winstein and L. L. Ingraham, *J. Am. Chem. Soc.*, **77**, 1738 (1955). Abstracts of the Fifteenth National Organic Chemistry Symposium, Rochester, N. Y., 1957, p 29. More recently the term Fk_Δ has been used in place of k_Δ to indicate the fraction F of k_Δ which undergoes reaction to product: E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); A. Diaz, I. Lazdins, and W. Winstein, *J. Am. Chem. Soc.*, **90**, 6546 (1968).

(9) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(10) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 122–125.

(11) It should be noted that the line passes through the points for *p*-nitro and *p*-trifluoromethyl, in both of which the retained acetate constitutes only a small fraction of the total product.

(12) Corrected for k_α/k_t the estimated rate acceleration becomes approximately 15. However, since the use of k_α would presumably magnify somewhat the slope of the straight portion of the curve, the value of 15 becomes an upper limit. For a considerably larger estimate, which utilizes a qualitative quite small correction for the rate-retarding effect of a *p*-nitro substituent, see ref 6.

Table II. Products from Acetolysis of Substituted *threo*-3-Phenyl-2-butyl Brosylates

Substituent	Temp, °C	Product, % Olefin	 *t*-Acetate	 *sec*-Acetate	Acetate configuration, % *threo*	 *erythro*
p-Methoxy[a]	50	0.3	0	99.7	100	0
Hydrogen[b,c]	75	35[f]	0	53[f]	96	4
Hydrogen[d,g]	50	52.6	0.1	47.3	96	4
	75	52.1	0	47.9	97	3
p-Chloro[d]	75	48	1	51	86	14
m-Chloro[d]	100	72	2	26	57	43
m-Trifluoromethyl[d]	100	76	3	21	30	70
p-Nitro[e,c]	100	68[f]		13[f]	7	93

[a] Reference 5a. [b] D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); **74**, 2129 (1952). [c] Tosylate. [d] Present study. Each run was 0.05 *M* in the substrate and 0.053 *M* in sodium acetate. [e] Reference 6. [f] Isolated yields. Other yields by glpc. [g] S. Sivaram's data.

stituent constants, σ^+ [13] (Figure 2). This result indicates that in this system considerable charge is delocalized in the transition state into the phenyl ring and its activated derivatives. Evidently the geometrical situation is more favorable for such interaction in this system than in the corresponding *trans*-2-arylcyclopentyl derivatives.[14] Data for the products of solvolysis are summarized in Table II.

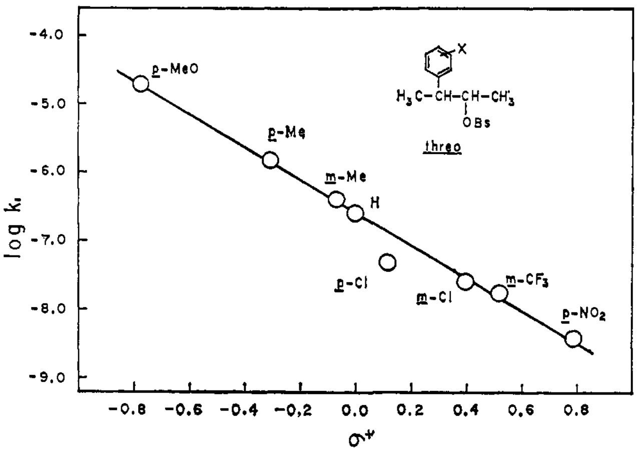

Figure 2. Rates of acetolysis at 25.0° of *threo*-3-aryl-2-butyl brosylates *vs.* the σ^+ constants ($\rho = -2.4$).

A striking feature is the regular increase in the yield of secondary acetate from *p*-nitro to *p*-methoxy. At the same time the percentage of acetate product which arises from stereochemical retention increases from 7% for *p*-nitro to 100% for *p*-methoxy. The results on the yield of acetate product were much less regular in the case of the *trans* series,[3] increasing markedly only for the *p*-methoxy derivative, the only derivative which exhibited a rate enhancement over that predicted by the correlation.

The percentage of retention in the acetate products in the *trans* series rises regularly from 0% for *p*-nitro to 98% for *p*-methoxy,[3] and in the *threo* series from 7% for *p*-nitro to 100% for *p*-methoxy. Consequently, both series exhibit a variation in the stereochemistry of substitution over almost the entire possible range from 100% inversion to 100% retention. At the same time application of the same quantitative approach, the Hammett correlation, to the data reveals only minor rate enhancement in the *trans* series, whereas major rate enhancement attributable to aryl participation is indicated in the *threo* series.

This suggests that the rate data may not reveal rate enhancements in systems which undergo substitution with retention. Such cases would be consistent with a mechanism in which stereochemistry was controlled by rapidly equilibrating cations,[1,15] or with a mechanism in which ionization occurred to an essentially unbridged ion pair, followed by bridging prior to attack of solvent,[16] or with a mechanism involving competing k_s and k_Δ processes that are comparable in magnitude.[17]

These results point up the urgent need to clarify the precise processes involved in the acetolysis of secondary alkyl arenesulfonates.

(13) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(14) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *ibid.*, **88**, 5350 (1966).

(15) S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952).

(16) See ref 3 for a fuller consideration of the possibilities.

(17) This problem of an objective approach to rate enhancements in the acetolysis of secondary β-arylakyl arenesulfonates and the precise processes involved in such solvolyses is considered in an accompanying group of publications by C. J. Lancelot, J. J. Harper, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4291, 4294, 4296, 4297 (1969).

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Participation by Neighboring Aryl Groups. I. Determination of Assisted and Nonassisted Solvolysis Rates by Hammett Correlation[1]

Sir:

Phenonium ions were first postulated as intermediates in the solvolysis of β-arylalkyl systems in order to explain the remarkable stereochemical product control by the aryl groups.[2] For example, acetolysis of *erythro*-3-phenyl-2-butyl tosylate gave acetate (68% yield) with 96% retention of configuration.[2] In contrast, the observed rate enhancements, if any, produced by β-aryl groups are typically quite small. In fact, if titrimetric rates are compared, both diastereomeric 3-phenyl-2-butyl tosylates acetolyze almost two times *slower* than the parent 2-butyl tosylate.[3]

(1) This set of four communications was presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract ORGN 4, and at the Conference on Carbonium Ions, Cleveland, Ohio, Oct 1968.

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

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