Table I. Kinetic Data for the Acetolysis of Substituted *cis*-2-Phenylcyclopentyl Tosylates

Substituent	Rate constant, $10^6 k_t$, sec^{-1} 25.0°	50.0°	75.0°	Rel rate 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
(Cyclopentyl[a])	1.65	38.2	562		24.1	−4.2
p-Methoxy	3.47	79.3	1160[b]	2.51	23.3	−5.3
p-Methyl	2.19	55.4	881[b]	1.59	24.1	−3.6
m-Methyl	1.71	43.9	707[b]	1.24	24.2	−3.7
Hydrogen	1.38	34.8	552[b]	1.00	24.1	−4.6
p-Chloro	0.430[b]	12.2	214	0.312	25.0	−3.9
m-Chloro	0.263[b]	7.59	134	0.191	25.1	−4.5
p-Nitro	0.0685[b]	2.18	42.1	0.0496	25.8	−4.7

[a] H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956). [b] Extrapolated from data at other temperatures.

Since k_s involves a process that is essentially bimolecular in nature, it is not unexpected that $\Delta S^{\ddagger}$ for this process is far more negative, in the range of −20 eu.[13,14] Indeed, the value of $\Delta S^{\ddagger}$ has been utilized as a diagnostic tool for the presence or absence of aryl participation in primary systems.[5,13,14]

It is obvious that aryl participation cannot be a factor in these *cis* derivatives. The values of $\Delta S^{\ddagger}$ for the *cis*-2-aryl derivatives are remarkably constant (−3.7 to −5.3) and lie in the same range as that for the parent compound (Table I) and other secondary derivatives which have been previously classified as limiting.[10,15] Consequently, it would appear that we can exclude solvent participation, of the kind that occurs in primary derivatives, as a significant factor in these *cis* secondary derivatives.

The tertiary benzylic hydrogen and the tosyl group are in the *trans* arrangement ideal for E2 elimination.[16] However, such E2 eliminations exhibit the opposite rate influence of substituents, with *p*-nitro rate enhancing.[16] This process would also result in the exclusive formation of 1-phenyl-2-d_1-cyclopentene in the solvolysis of the tagged derivative.

The tagged olefin production corresponds precisely to that expected for formation of the 1-phenyl-2-d_1-cyclopentyl cation as the major product-determining intermediate. Thus the ratio of **2:1** corresponds almost exactly to the 2:1 ratio of protons in the α position. The ratio of **3:1** corresponds to a secondary isotope effect of 3 favoring elimination of the proton.

Consequently, we appear to be left with simple ionization to an intimate ion pair, followed by predominant (89%) migration of the tertiary benzylic hydrogen to give the tertiary cation, or with hydrogen-assisted ionization. It should be noted that the effect of *p*-methoxy on the rate is exceedingly small (×2.5). This is difficult to understand if the first intermediate is the tertiary cation, since the transition state should resemble the first intermediate, as proposed by the Hammond postulate. A *p*-methoxy substituent increases the rate of solvolysis of 1-phenylcyclopentyl chloride by a factor of 3400![17] Moreover, the effects of substituents in these *cis* derivatives are the same as those observed in the 1-aryl-*endo*-norbornyl tosylates within a factor of 2.[18] Finally, the failure to observe the usual modest rate-retarding effect of neighboring, nonparticipating phenyl in the *cis* derivative is similar to its absence in the norbornyl series[15] and may result in both series from a small compensating steric assistance.

In conclusion, the acetolysis of the *cis*-2-arylcyclopentyl tosylates appears to proceed either through a simple ionization to an ion pair, k_c, or with hydrogen participation involving only a small rate effect (a factor of approximately 2) attributable to such hydrogen participation. Consequently, these *cis* derivatives should provide satisfactory models to explore the *trans*:*cis* rate ratios[3] as a probe for aryl participation in the *trans* derivatives.

(13) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 4801 (1956).
(14) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963).
(15) For example, $\Delta S^{\ddagger}$ for the acetolysis of substituted 1-aryl-*endo*-norbornyl tosylates fall in the range of −4.4 to −7.9 eu: P. von R. Schleyer and D. C. Kleinfelter, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., 1960, p 43P.
(16) C. H. Depuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Am. Chem. Soc.*, **87**, 2421 (1965).
(17) H. C. Brown and K. Takeuchi, *ibid.*, **88**, 5336 (1966).
(18) The slightly larger effect in the *cis* derivatives could arise from the greater proximity of the substituted aryl groups in these derivatives.
(19) Purdue Research Foundation Fellow, 1966–1968. Postdoctoral Research Associate, 1968–1969, on a grant (GP 6492 X) supported by the National Science Foundation.

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Rates and Products of Acetolysis of *trans*-2-Arylcyclopentyl Tosylates. Evidence for Major Control of the Stereochemistry of the Substitution Process by Neighboring Aryl in the Absence of Rate Accelerations

Sir:

The acetolysis of simple secondary alkyl arenesulfonates proceeds with inversion of configuration.[1] Presumably this involves ionization to form an intimate ion pair which then undergoes substitution from the back side with displacement of the anion.[2] On the other hand, the acetolysis of 3-phenyl-2-butyl tosylate takes place with predominant (95%) retention.[3] This has been interpreted as involving the formation of a symmetrical phenonium ion intermediate, although the available evidence indicates that the rate acceleration is quite small.[4] Unfortunately, considerable difference of opinion exists as to how this rate acceleration may be estimated.[5] The 2-arylcyclopentyl system appeared to offer promise of providing an unambiguous estimate of the rate acceleration achieved by neighboring aryl

(1) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **87**, 3686 (1965).
(2) H. Weiner and R. A. Sneen, *ibid.*, **87**, 292 (1965).
(3) D. J. Cram, *ibid.*, 71, 3863 (1949); *ibid.*, **74**, 2129 (1952).
(4) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.
(5) D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964).

Table I. Kinetic Data for the Acetolysis of Substituted *trans*-2-Phenylcyclopentyl Tosylates

Substituent	Rate constant, $10^6 k_t$, sec^{-1} 25.0°	50.0°	75.0°	Rel rate 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	*trans*/*cis*
p-Methoxy	1.76[a]	43.6	681	6.02	23.9	−3.5	0.51
p-Methyl	0.470[b]	14.0	256	1.61	25.3	−2.5	0.21
m-Methyl	0.363[b]	10.7	194	1.24	25.3	−3.2	0.21
Hydrogen	0.292[b]	8.72	160	1.00	25.4	−3.3	0.21
p-Chloro	0.107[b]	3.30	62.6	0.366	25.6	−4.4	0.25
m-Chloro	0.0870[b]	2.67	50.4	0.298	25.6	−4.9	0.33
m-Trifluoromethyl	0.0770[b]	2.27	41.4	0.264	25.3	−6.2	
p-Nitro	0.0347[b]	1.03[b]	18.9[c]	0.119	25.3	−7.6	0.51

[a] A. H. Fainberg, G. C. Robinson, and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2777 (1956), report a value of 5.45 for the corresponding brosylate. [b] Extrapolated from data at other temperatures. [c] k_t at 100.0° = 234×10^{-6} sec^{-1}.

through an examination of the *cis*:*trans* rate ratios,[6] deviations from the Hammett correlation, and deviations from the Hammett–Taft correlation.

Preparation of the *trans*-2-arylcyclopentyl derivatives, with the exception of *p*-nitro, was achieved by the addition of the appropriate aryl Grignard to cyclopentanone, dehydration of the tertiary alcohol to the 1-arylcyclopentene, followed by hydroboration–oxidation to the *trans*-2-arylcyclopentanol. The *p*-nitrophenyl derivative was prepared by nitration of the parent acetate. The results for the acetolysis of the *trans* compounds are summarized in Table I.[7]

Noteworthy is the remarkably small effect of the *p*-methyl and *p*-methoxy substituents on the rates. Clearly the amount of charge delocalized in the transition state into the aromatic ring must be quite small.

Inductive influences of the aryl substituent may largely be expected to cancel out in the *cis* and *trans* isomers. Significant participation in the *trans* derivatives and its absence in the *cis* would be expected to result in a *trans*:*cis* rate ratio of >1,[6b] increasing with the introduction of activating substituents. This is not observed (Table I). Instead, the *trans*–*cis* rate ratios are less than one, possibly arising from small steric assistance in the *cis* derivative, and show no significant trend.

These rates exhibit an excellent linear plot for seven of the derivatives, with ρ having a value of −1.25.[8] Only the *p*-methoxy derivative is off the line with an indicated rate enhancement by a factor of 3. These results are to be contrasted with the behavior of the 3-aryl-2-butyl system.[10]

For a third approach we utilized the Hammett–Taft $\sigma^*\rho^*$ correlation of the rates. Streitwieser had previously treated the rates of acetolysis of a number of secondary tosylates in this manner[4] and the correlation was further explored by Harper.[11] Accordingly, the σ^* constant for the p-$O_2NC_6H_4CH_2$– group was estimated to be +0.50 in reference to the value of 0.215 for $C_6H_5CH_2$– and 0.120 for p-$CH_3OC_6H_4CH_2$–.[4] The points for these six compounds fall, with reasonably good precision, on the line defined by Harper ($\rho^* = -3.42$). Consequently, the changes in rates in both the *cis* and *trans* derivatives arise primarily from inductive influences of the neighboring aryl groups, with only a minor rate enhancement of approximately a factor of 3 in the *trans*-*p*-methoxyphenyl compound attributable to aryl participation. The products of representative solvolyses were examined and the results are summarized in Table II.

Table II. Products from Acetolysis of Substituted *trans*-2-Aryl-cyclopentyl Tosylates

Substituent	Temp, °C	Product,[a] % Olefin	% 2-Acetate	Acetate confign, % *trans*	% *cis*
p-Methoxy	50	27	73	98	2
p-Methyl	50	69	31	65	35
Hydrogen	50	82	18	18	82
m-Chloro	75	81	19	<1	>99
p-Nitro	75	71	29	0	100

[a] Each solvolysis was permitted to proceed for seven to ten half-lives. The solutions were 0.050 *M* in tosylate and 0.053 *M* in sodium acetate. Analysis by glpc.

The results present a striking series with a complete regular change in the stereochemical results, varying from 100% inversion in the *p*-nitro derivative to 98% retention in the *p*-methoxy derivative.[12] Of especial interest is the observation that the acetate product from the parent compound exhibits 18% retention and that from the *p*-methyl derivative exhibits 65% retention, even though the analyses of the rates indicate no observable rate enhancements for these derivatives.

How can we account for these results?

One possibility is to take the position that the product with retained configuration arises from symmetrically bridged arylonium ions.[3] In order to account for the absence of appreciable kinetic effects we might take the position that the transition state must involve very little participation by the aromatic ring. However, this position is not compatible with the Hammond postulate which requires that in an

(6) (a) Data for the *cis* derivatives are reported by C. J. Kim and H. C. Brown, *J. Am. Chem. Soc.*, 91, 4286 (1969); (b) see footnote 3 of this reference.

(7) We determined the titrimetric rate constants, k_t, in the absence of added salts. While it would be desirable to have the polarimetric rate constants, k_α, such measurements require the optically active derivatives. Very few rate constants of that kind have been determined.

(8) It should be noted that the value of ρ, −1.25, is slightly less negative than the value for the *cis* derivatives, −1.66,[6] and is of the same order of magnitude as ρ for the 1-aryl-*endo*-norbornyl tosylates, −1.06.[9]

(9) P. von R. Schleyer and D. C. Kleinfelter, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., 1960, p 43P.

(10) C. J. Kim and H. C. Brown, *J. Am. Chem. Soc.*, 91, 4289 (1969).

(11) J. Harper, Ph.D. Thesis, Princeton University, 1968.

(12) It has been mentioned in a footnote that the phenyl group failed to control the stereochemistry in the course of acetolysis of *trans*-2-phenylcyclopentyl brosylate: S. Winstein and R. M. Roberts, *J. Am. Chem. Soc.*, 75, 2297 (1953). On the other hand, it has been stated that the acetolysis of *trans*-2-*p*-anisylcyclopentyl brosylate involves predominantly or exclusively anchimerically assisted ionization to a bridged ion: A. H. Fainberg, G. C. Robinson, and S. Winstein, *ibid.*, 78, 2777 (1956).

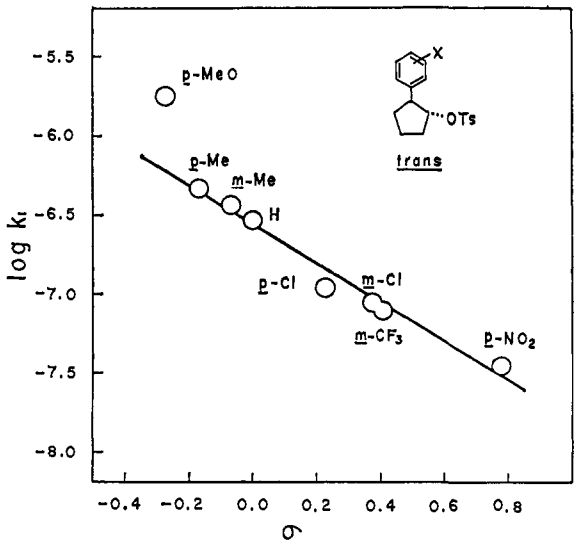

Figure 1. Rates of acetolysis at 25.0° of *trans*-2-arylcyclopentyl tosylates *vs.* the σ constants ($\rho = -1.25$).

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 $\Delta S^{\neq}$, the mY 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.

(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]

(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).