Rates and Products of Acetolysis of *cis*-2-Arylcyclopentyl Tosylates and a Deuterium-Tagged Derivative, 1-d_1-*cis*-2-Phenylcyclopentyl Tosylate

Sir:

The available experimental data indicate that the magnitude of rate acceleration, attributable to phenyl participation, in the acetolysis of "symmetrical" β-phenylalkyl derivatives is relatively small.[1] Yet the β-phenyl group exerts major influence on the stereochemistry of the solvolysis products.[2] Originally, small rate accelerations were not considered compatible with the formation of a bridged transition state leading to a bridged intermediate.[3,4] Yet, more recently, rate accelerations of the same order of magnitude have been used to support proposals for the formation of symmetrical, relatively stable phenonium ions, as intermediates. Unfortunately, no justification for the altered theoretical position has yet appeared.

The problem is pointed up by the fact that 3-phenyl-2-butyl tosylate undergoes acetolysis not faster, but slower than 2-butyl tosylate. Various corrective terms have been utilized to support the position that a significant rate enhancement is indeed present.[5] On the other hand, other estimates have been much lower.[6] Consequently, there is a need for satisfactory procedures to achieve objective evaluations of the magnitude of rate accelerations attributable to neighboring group participation in systems such as the β-arylalkyl derivatives, as well as a need for clarification of the question as to how small a rate acceleration is compatible with the formation of bridged intermediates.

We decided to examine the rates of acetolysis of a number of substituted *cis*- and *trans*-2-phenylcyclopentyl tosylates in order to apply three different procedures, the *trans*:*cis* rate ratios, deviations from the Hammett correlation, and deviations from the Hammett–Taft correlation, to estimate the magnitude of aryl participation in the *trans* derivatives.[7] These rate enhancements were then correlated with the stereochemical results of the substitution process.[7] Similar methods were then applied to the 3-phenyl-2-butyl system.[8]

The *cis*-2-arylcyclopentanols, with the exception of the *p*-nitro derivative, were prepared either by reduction of the 2-arylcyclopentanones with disiamylborane or by inversion of the *trans* tosylates[7] with tetramethylammonium acetate. The *p*-nitro compound was obtained by nitration of the parent acetate. The

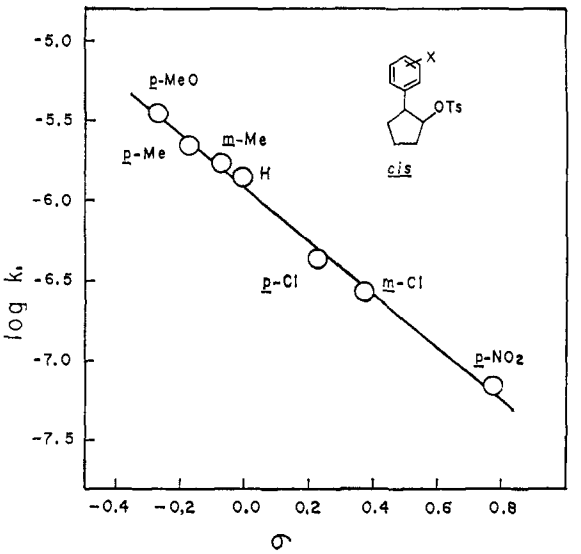


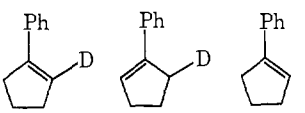
Figure 1. Rates of acetolysis at 25.0° of *cis*-2-arylcyclopentyl tosylates *vs.* the σ constants (ρ = −1.66).

1-d_1-*cis*-2-phenylcyclopentanol was obtained by reducing 2-phenylcyclopentanone with lithium aluminum deuteride and separating the *cis*–*trans* mixture by glpc.

Rate data for the acetolysis of the *cis* derivatives are summarized in Table I.

These *cis* derivatives exhibit an excellent Hammett correlation, which is linear throughout the range (Figure 1), with a ρ value of −1.66.

Solvolysis of *cis*-2-phenylcyclopentyl tosylate at 50° in the presence of a slight excess of sodium acetate yielded 4.1% of the *trans* acetate, 89% of 1-phenylcyclopentene, and 6.9% of 3-phenylcyclopentene. In order to obtain further information as to the course of the reaction, the 1-d_1 derivative was solvolyzed and 1-phenylcyclopentene isolated and examined by pmr. The results indicate formation of isomers **1**–**3**.



1, 31% **2**, 59% **3**, 10%

The acetolysis and formolysis of secondary arenesulfonates have been postulated to be essentially limiting[6,9] and such solvolyses have been discussed in terms of two distinct processes, k_c, involving ionization to a carbonium ion (or ion pair) without significant participation by a neighboring group or by a solvent molecule, and k_Δ involving anchimeric participation.[10] Both are unimolecular processes and yield values of $\Delta S^{\ddagger}$ that are very similar, generally in the range of 0 to −5 eu. On the other hand, it has been argued that solvolysis of primary derivatives proceeds with either solvent, k_s, or neighboring group participation, k_Δ.[11,12]

(1) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, 87, 2137 (1965).
(2) D. J. Cram, *ibid.*, 71, 3863 (1949); *ibid.*, 74, 2129 (1952).
(3) For example, the observation that the rates of acetolysis of *cis*- and *trans*-1,2-cyclohexanedi-*p*-bromobenzenesulfonates are very similar led the authors to suggest that solvolysis proceeds in both isomers through open, unbridged carbonium ions: S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, 70, 821 (1948). Similarly, these authors concluded that the acetolysis of *cis*-2-chlorocyclohexyl tosylate proceeds through such a k_c pathway, and Grunwald later concluded that a rate ratio of 4 for *trans*-/*cis*-2-chlorocyclohexyl tosylate was consistent with acetolysis of both isomers through open carbonium ions: E. Grunwald, *ibid.*, 73, 5458 (1951).
(4) For a recent discussion of this problem, see E. M. Kosower, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, Chapter 1, Section 5.
(5) D. J. Cram, *J. Am. Chem. Soc.*, 86, 3767 (1964).
(6) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.
(7) C. J. Kim and H. C. Brown, *J. Am. Chem. Soc.*, 91, 4287 (1969).
(8) C. J. Kim and H. C. Brown, *ibid.*, 91, 4289 (1969).
(9) E. Grunwald and S. Winstein, *ibid.*, 70, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951).
(10) S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *ibid.*, 70, 816 (1948).
(11) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, 90, 6546 (1968). These authors state that the solvolyses of secondary derivatives should also be treated in terms of k_Δ and k_s. However, they do not indicate why the position originally taken by Winstein and coworkers[9,10] with respect to secondary derivatives is no longer valid.
(12) J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *ibid.*, 91, 1154 (1969).

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).