Structural Effects in Solvolytic Reactions. IV. Rates and Products in the Acetolysis of Substituted 3-Phenyl-2-butyl Brosylates. Nature of the Reaction Pathway in the Acetolysis of Secondary Alkyl Arenesulfonates[1]

Herbert C. Brown* and C. J. Kim[2]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 47907. *Received Obctober 22, 1970*

Abstract: An objective approach to the magnitude of the rate acceleration attributable to phenyl participation in acetolysis of *threo*-3-phenyl-2-butyl brosylate was developed. This approach involves determination of the rates and products of acetolysis of a series of substituted *threo*-3-phenyl-2-butyl brosylates and determination of the Hammett plot for the unassisted rate (k_s) component from the k_s values for those compounds containing deactivating substituents, followed by evaluation of the unassisted rate of the parent compound. This experimental approach yields a factor of 3 for the acceleration of the rate of acetolysis of 3-phenyl-2-butyl arenesulfonate. This small value confirms an earlier estimate which resulted in the conclusion that such a small rate acceleration did not appear to be compatible with the proposed mechanism involving the formation of a stabilized phenyl-bridged intermediate competitively with the formation of an open cation. Considerable cross-over would be expected in such a mechanism. However, the data reveal a precise correlation between rates and products. Therefore, cross-over is not significant. It follows that in the acetolysis of secondary β-arylalkyl derivatives the aryl-participated pathway must be essentially independent of the competing pathway—without significant crossover between the two paths. This apparently requires that the competing pathway must be far from limiting, implying participation by solvent sufficiently important as to render cross-over unimportant. This conclusion represents a major break with the original position that the acetolysis of secondary alkyl arenesulfonates approaches limiting in character and eliminates the apparent anomaly referred to above. Some mechanistic considerations are examined in an attempt to provide a consistent interpretation of the phenomena observed in the acetolysis of secondary alkyl arenesulfonates.

It was originally observed by Cram that acetolysis of the diastereomeric 3-phenyl-2-butyl tosylates involved substitution with predominant retention of configuration.[3] Considering that the acetolysis of simple secondary alkyl arenesulfonates proceeds with essentially complete inversion,[4] the β-phenyl group must function in some way effectively to control the stereochemistry of the solvolysis products. It was proposed that solvolysis proceeded through the concurrent formation of phenyl-bridged and open cations and that the retention was achieved through the reaction of the symmetrically bridged intermediate, the phenonium ion, with solvent.[3]

It was soon observed that in contrast to other neighboring groups the effect of the β-phenyl group on the rate was surprisingly small.[5] The early study by Winstein and his coworkers resulted in an estimated value of 6 for the rate acceleration attributable to phenyl participation in the acetolysis of 3-phenyl-2-butyl tosylate.[5] Streitwieser later arrived at an even smaller factor, 4, from his application of the Hammett–Taft correlation to the rates of acetolysis of secondary tosylates.[6]

The earlier theory for neighboring group participation proposed that participation should occur in the transition state, leading either to a static bridged ion or to a rearranged open ion.[5] At that time it was considered that the existence of participation must be reflected by a large rate acceleration attributable to participation by the neighboring group.[7] Accordingly, the direct formation of a phenyl-bridged ion in the acetolysis of 3-phenyl-2-butyl tosylate must follow phenyl participation in the transition state, and should be reflected by a large enhancement of the solvolysis rate.[8]

As was discussed previously,[9] the small rate enhancement of 4–6 did not appear to be compatible with a major phenyl involvement in the transition state apparently required by the proposed mechanism involving direct formation of the bridged ion competitively with the formation of the open ion. Recognizing this difficulty,[10a,11] Cram recently suggested that a

(1) For preliminary reports, see: (a) C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4289 (1969); (b) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. von R. Schleyer, *ibid.*, **92**, 5244 (1970).

(2) Postdoctoral Research Associate, 1968–1970, on a grant (GP 6492 X) supported by the National Science Foundation.

(3) D. J. Cram, *J. Amer. Chem. Soc.*, 71, 3863 (1949); 74, 2129, 2137 (1952).

(4) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, *ibid.*, **87**, 3686 (1965).

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

(6) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

(7) For example, a factor of 7,700,000 was estimated for the rate acceleration due to phenyl participation in the acetolysis of β,β,β-triphenylethyl tosylate.[5]

(8) A rate enhancement by a factor of 800 was considered to be consistent with the formation of a bridged ion in the acetolysis of *trans*-2-bromocyclohexyl brosylate, while an open ion formation was proposed for the cis isomer: S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 70, 821 (1948). On the other hand, a trans/cis rate ratio of 4, observed in the 2-chlorocyclohexyl brosylates, was not considered to require formation of a chloronium ion intermediate, and was indeed interpreted in terms of ionization to open ions: E. Grunwald, *ibid.*, **73**, 5458 (1951). In view of the results and conclusions of the present study, this interpretation should be subjected to reconsideration.

(9) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965).

(10) (a) D. J. Cram, *ibid.*, **86**, 3767 (1964); (b) J. A. Thompson and D. J. Cram, *ibid.*, **91**, 1778 (1969); (c) D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967).

(11) At one time the position was taken that the evidence for the bridged ion is not kinetic, but stereochemical, and it was suggested that the phenonium ion can in principle form from an initially formed open ion.[10a] However, this suggestion does not appear to be compatible with the position that a stereospecific reaction involving retention can

significant rate acceleration due to phenyl participation is indeed present in the solvolyses of the 3-phenyl-2-butyl system, and a factor of 43 was proposed for the acetolysis.[12]

Thus, various estimates for the magnitude of rate acceleration due to phenyl participation have been proposed in the past.[5,6,10b] It appears desirable to establish the precise magnitude of this rate acceleration before undertaking an objective consideration of the question as to how small a rate enhancement is actually compatible with the formation of the proposed phenonium ion in the present system, and with the formation of bridged intermediates in other systems. Why should a factor of 4 be considered to be compatible with the formation of a bridged intermediate in the 3-phenyl-2-butyl system, whereas a factor of 4 is considered to be compatible with the formation of open ions in the 2-chlorocyclohexyl system?[8]

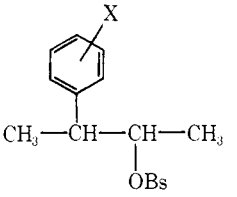
It appeared to us that it would be possible to achieve an objective evaluation of the rate enhancement in the acetolysis of 3-aryl-2-butyl arenesulfonate by determining the rates for a series of derivatives containing a wide range of substituents in the phenyl ring. Those derivatives containing deactivating substituents should solvolyze without significant participation, providing the base line for the k_s process by means of the usual Hammett correlation. This line would give the k_s values for the parent compound and for those derivatives containing activating substituents where the k_Δ process could be significant. The difference between the observed k_t values and these predicted k_s values would provide an objective evaluation of the rate enhancement accompanying aryl participation. Accordingly, we undertook to synthesize a series of substituted *threo*-3-phenyl-2-butyl brosylates and to determine their rates of acetolysis.

In the course of this study, we confirmed the earlier conclusion that the rate enhancement attributable to phenyl participation is indeed small. However, recent developments have suggested a new route out of this difficulty. It was originally proposed that the acetolysis of secondary alkyl arenesulfonates is essentially limiting in character.[13] A variety of experimental approaches have recently thrown doubt on this conclusion.[14,15] Indeed, Schleyer and Lancelot reported that the products and rates of solvolysis of secondary β-arylalkyl derivatives can be adequately correlated by assuming the existence of two discrete reaction pathways, the aryl assisted (Fk_Δ) and the aryl unassisted (k_s), without significant cross-over,[16] similar to the long accepted position for primary derivatives.[17]

These developments are not consistent with the long accepted position that the acetolysis of secondary alkyl arenesulfonates approaches limiting in character. They require that solvent must be involved in a significant way in the non-k_Δ pathway. Consequently, if solvent participation is comparable in magnitude to aryl participation, there would no longer be any requirement for a large rate enhancement to avoid cross-over and to direct substitution through the bridged intermediate. In order to test this possible interpretation, we undertook to examine the present system for the existence of a satisfactory product–rate correlation.[1b] The results establish the presence of an excellent correlation. Consequently, this resolves the original difficulty of the small rate acceleration in the 3-phenyl-2-butyl system.[9] Unfortunately, it introduces a new difficulty. Since the results apparently require that solvent participation is a major factor in the acetolysis of secondary alkyl arenesulfonates, we are apparently faced with a major reinterpretation of the huge amount of data involving such systems.[6]

Rate Studies

A series of substituted *threo*-3-phenyl-2-butyl brosylates (I-X) was prepared by a reaction sequence involving addition of arylmagnesium bromide to 2-butanone, dehydration of 2-aryl-2-butanol to a mixture of olefins, isolation of pure *cis*-2-phenyl-2-butene by fractional distillation with a platinum spinning band column, and hydroboration–oxidation of this olefin, followed by conversion of the pure *threo*-3-aryl-2-butanol to the brosylate.



I-X, X = *p*-MeO, *p*-Me, *m*-Me, H, *p*-Cl, *m*-Cl, *m*-CF_3, *p*-CF_3, *p*-NO_2, *m,m'*-$(CF_3)_2$

The rates of acetolysis were determined titrimetrically and the results are summarized in Table I. The data for I-*p*-MeO by Winstein and Robinson[81a] as well as those for I-*p*-NO_2 by Cram and Thompson[10b] are also included in the table.

The effects of substituents are moderately large, with the para methoxy substituent enhancing the rate of the parent compound by a factor of 59, while the meta,meta′ bistrifluoromethyl substituents retard the rate by a factor of 56. The Hammett plot of the rates at 75° reveals a satisfactory linear correlation for the deactivating groups, with $\rho_s = -1.46$.[19] On the other

never be achieved in a scheme which involves an open ion intermediate.[10a]

(12) This factor of 43 was estimated by the introduction of various corrective terms based on the polarimetric rate.[10b]

(13) (a) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, 70, 828, 846 (1948); (b) S. Winstein and N. J. Holness, *ibid.*, 77, 5562 (1955); (c) "... isopropyl *p*-bromobenzenesulfonate or bromide may approach the **Lim.** catagory in acetic acid and more closely in formic acid": S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951); (d) "To make the solvolysis of the compounds in question ... as nearly limiting (**Lim.**) with respect to the solvent role ..., we have studied acetolysis of benzenesulfonates"; ref 5.

(14) Peterson and his coworkers noted that the relative rates of solvolysis of 2-butyl and 4-chloro-2-butyl tosylates increased sharply from 19 in acetic acid, to 129 in formic acid, and to 329 in trifluoroacetic acid. They attributed the increase in relative rate to decreasing participation of solvent as the solvent was made less nucleophilic [P. E. Peterson, *et al.*, *ibid.*, **89**, 5902 (1967)]. They thus reached the conclusion that solvent participation must be quite important in the acetolysis of simple secondary alkyl tosylates.

(15) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970); J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970).

(16) P. von R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969).

(17) (a) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956); (b) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); (c) A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6546 (1968); (d) M. G. Jones and J. L. Coke, *ibid.*, **91**, 4284 (1969); (e) J. M. Harris, F. L. Schadt, P. von R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 7508 (1969).

(18) (a) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); (b) S. Winstein and R. Baker, *ibid.*, **86**, 2071 (1964).

(19) This unassisted line (k_s line) was determined by a least-squares

Table I. Kinetic Data for Acetolyses[a] of Substituted *threo*-3-Phenyl-2-butyl Brosylates

Substituent X =	10^5k, sec^{-1} 25.0°	50.0°	75.0°	100.0°	Rel rate at 75.0°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
p-MeO	1.95[b]		1060[c]		59		
p-Me	0.148	4.43	81.4[d]		4.5	25.4	0.2
m-Me		1.37	28.2		1.6	26.4	0.8
H		0.858	18.0		1.0	26.6	0.4
p-Cl		0.188	4.53		0.25	27.9	1.3
m-Cl			2.05	30.0	0.11	27.1	−2.0
m-CF_3			1.38	20.1	0.078	27.0	−3.3
p-CF_3			1.26		0.070		
p-NO_2			0.495[e]		0.028	29.0	−2.1
m,m'-$(CF_3)_2$			0.330		0.018		

[a] Each run was carried out with a 0.01 or 0.02 *M* solution of the substrate. [b] Reference 18a. [c] Estimated value. [d] Extrapolated value. [e] Estimated from the data of ref 10b.

Table II. Products of Acetolysis[a] of Substituted *threo*-3-Phenyl-2-butyl Brosylates

Substituent X =	Temp, °C	Product,[b] % Olefins	*tert*-Acetate	*erythro*-Acetate	*threo*-Acetate
p-MeO[c]	50.0	~0.3	0	0	99.7
p-Me	75.0	12	0	0	88
m-Me	75.0	31	0	1	68
H	75.0	38	0	3	59
p-Cl	75.0	53	1	6	39
m-Cl	75.0	76	1	11	12
m-CF_3	75.0	76	1[e]	18	6
p-CF_3	75.0	75	1	14	11
	100.0	81	1	10	8
p-NO_2[d]	100.0	68		13	1
m,m'-(CF_3)	75.0	62	3	34	1
	100.0	67	3	29	1

[a] Each run was conducted with a solution of 0.050 *M* in brosylate and 0.053 *M* in sodium acetate for 7–10 half-lives. [b] The material balance was 100 ± 5% in each case. [c] Reference 18b. [d] Reference 10b; isolated yield with the tosylate. [e] This tertiary acetate was found to undergo decomposition to a mixture of olefins under the solvolytic condition.[21]

hand, the rate constants for the derivatives containing activating substituents exhibit deviations from this line, indicating varying amounts of rate enhancement presumably due to participation by the aryl group (Figure 1).

Product Studies

The acetolysis was carried out with a solution, 0.050 *M* in I-X and 0.053 *M* in sodium acetate, for 7–10 half-lives at 75 or 100°. The present results as well as the literature data for I-*p*-MeO[18b] and I-*p*-NO_2[10b] are summarized in Table II.

On examining the data at 75°, one notices that the stereochemistry of the substitution product varies regularly from 100% retention for the para methoxy to 97% inversion for the meta,meta' bistrifluoromethyl. The amount of the tertiary acetate in the product does not appear to have any significant meaning, for it was previously shown by Cram that 2-phenyl-2-butyl acetate is unstable under the solvolytic conditions at 75° and decomposes to a mixture of olefins.[20] In the present study, we also observed that the meta trifluoromethyl substituted tertiary acetate undergoes a slow decomposition under the solvolytic condition.[21]

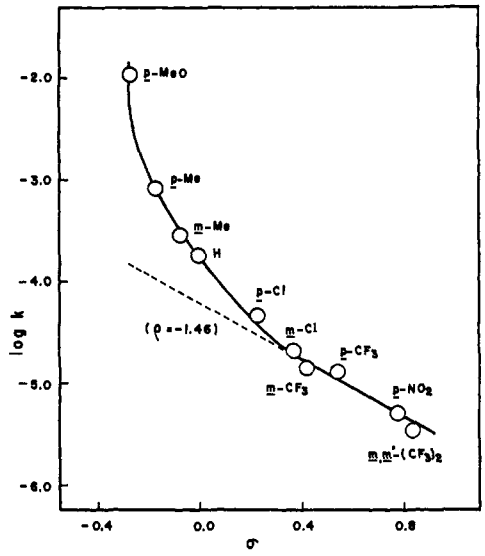


Figure 1. Rates of acetolysis of *threo*-3-aryl-2-butyl brosylates at 75.0° *vs.* the σ constants.

Magnitudes of Rate Acceleration Attributable to Aryl Participation. The k_s line in Figure 1 represents the rates of acetolysis of I-X in the absence of aryl participation. Accordingly, those compounds which deviate from this line can be regarded as undergoing solvolysis with neighboring aryl participation. The magnitude of the participation can then be estimated from the expected k_s value, the rate ratio, k_t/k_s, being the factor attributable to aryl participation. The pertinent data for this purpose are summarized in Table III.

The present results show that the factor attributed to neighboring aryl participation increases from only 1.6 for the para chlorophenyl group to a substantial 71 for the para anisyl group. The ability of the parent phenyl group in enhancing the rate is quite modest, with a factor of 3.0 indicated. This factor of 3 is in an excellent agreement with the earlier estimate by Streitwieser of 4.[6] It appears, therefore, that the considerably higher estimate of a factor of 43 by Cram is high[22]

treatment of the k_s values of the five most deactivated compounds. These k_s values were obtained by making minor corrections to the observed titrimetric rates for the small amounts of retained acetate in the products (see Table II).

(20) The decomposition product was found to consist of 43% 2-phenyl-1-butene, 3% *trans*-2-phenyl-2-butene, and 54% of the cis isomer.[3]

(21) The products are 2-aryl-1-butene (47%), *trans*-2-aryl-2-butene (3%), and the cis isomer (50%).

(22) This error seems to arise from a remarkably crude and low estimate of the rate ratio, $k_s^H/k_s^{NO_2}$, of 4.4.[10b] Cram and Thompson ap-

Table III. The Effect of Aryl Participation on the Rates of Acetolysis of Substituted *threo*-3-Phenyl-2-butyl Brosylates

X =	10^5k, sec^{-1}[a] k_t	k_s[b]	Magnitudes of rate acceleration k_t/k_s
p-MeO	1060	14.9	71
p-Me	81.4	10.7	7.6
m-Me	28.2	7.66	3.7
H	18.0	6.08	3.0
p-Cl	4.53	2.85	1.6

[a] At 75.0°. [b] Estimated from the k_s line in Figure 1.

even when one allows a correction term of $k_\alpha/k_t = 4.41$.[23]

Do the Kinetic Data Support the Theory of Bridged and Open Ions? The solvolysis of secondary alkyl derivatives in general was originally classified as borderline.[24] However, it was proposed that by shifting from the halogens to the far better tosyloxy leaving group, and by going from the aqueous solvents to the less nucleophilic solvents, such as acetic acid and formic acid, the solvolysis of secondary alkyl derivatives could be made to approach limiting in character.[13] This has been the accepted position for many years.[6,25-28]

The original interpretation for the acetolysis of secondary β-arylalkyl arenesulfonates was based on the above view and led to the theory of bridged and open ions in which it was proposed that there are two independent *ionization* steps, one leading to an open ion and the other to a bridged ion (or in some cases to a rearranged open ion).[3,5,10]

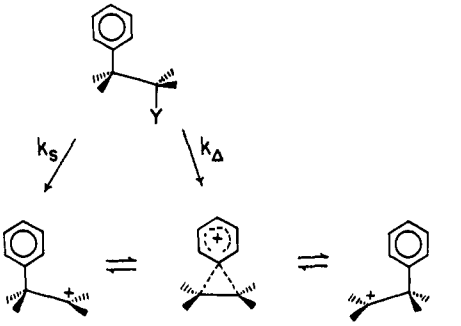
It was previously pointed out that a detailed analysis suggests some major difficulties in the proposal that acetolysis of 3-phenyl-2-butyl tosylate proceeds through the formation of open (essentially limiting) cations and phenyl-bridged cations which differ marginally in stability.[9] The observed rate ratio of 3.0 for k_t/k_s can be used in calculating k_Δ/k_s according to the following equation.[29] As the reported value for k_α/k_t is 4.41,[23]

$$\frac{k_\Delta}{k_s} = \left(\frac{k_t}{k_s}\right)\left(\frac{k_\alpha}{k_t}\right) - 1$$

the rate ratio, k_Δ/k_s, becomes 12 (= 3.0 × 4.4 − 1).[30]

It follows, then, that this rate ratio of 12 corresponds to a difference in energy of *ca.* 1.5 kcal/mol between the two transition states, one of which is supposed to lead to the phenyl-bridged ion (k_Δ) and the other to an open 3-phenyl-2-butyl cation (k_s). In solvolysis the transition state is believed to resemble the first intermediate.[32] Even if one assumes that the energy difference in the transition state doubles in the intermediate, the stabilization of the bridged species is still a small factor, only a fraction of the energy involved in the formation of such a weak bond as the hydrogen bond.

The simultaneous formation of bridged and open ions of very similar stabilities should involve a rapid mobile equilibrium between the two species. Each of the two species, open and bridged, should react with



solvent at its own rate. Consequently, the products should be determined by the relative concentrations of the two species and the relative rates at which they react with solvent.[9] It follows that in such a system we should expect considerable cross-over.[33]

The presence of such cross-over in the acetolysis of a secondary system, such as 3-phenyl-2-butyl tosylate, would appear to have very important implications. A large part of the product could arise through the bridged ion only if the concentration of the open ion were quite small. But this would require that the bridged ion be much more stable than the open ion. In turn, Hammond's postulate would require that a considerable portion of this stabilization should appear in the transition state leading to this bridged ion. The kinetic data do not reveal any significant stabilization.

We are forced to the conclusion that the present results cannot be accommodated by a mechanism proposing the simultaneous formation of open (essentially limiting) and bridged ions.

Do the Stereochemical Results Require the Theory of Bridged and Open Ion? The problem facing us is that of reconciling two apparently conflicting features which characterize the acetolysis of I-H in terms of the proposed mechanism involving concurrent formation of open and bridged ions. One feature is the formation of

parently failed to observe the successful Taft–Hammett correlation of the rates of acetolysis of secondary tosylates achieved by Streitwieser.[6] This approach can be applied to arrive at an objective value for the above rate ratio by estimating the σ* constant for a para nitrobenzyl group. We have estimated this σ* constant to be +0.50, as compared to the reported value of +0.215 for a benzyl group from the ionization constants for substituted phenylacetic acids. We then examined to see if it fitted the Hammett–Taft correlation line established by Streitwieser. We observed that this point falls exactly on the line. This approach yields a value of approximately 10 for $k_s^H/k_s^{NO_2}$, in much better agreement with the present result of 12 than the value of 4.4 used by Cram and Thompson.

(23) S. Winstein and K. C. Schrieber, *J. Amer. Chem. Soc.*, 74, 2165 (1952).

(24) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(25) E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 105.

(26) N. C. G. Cambell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968); M. Pánková, J. Sicher, M. Tichý, and M. C. Whiting, *ibid.*, 365 (1968).

(27) C. S. Foote, *J. Amer. Chem. Soc.*, 86, 1853 (1964); P. von R. Schleyer, *ibid.*, 86, 1854, 1856 (1964).

(28) H. C. Brown and G. Ham, *ibid.*, 78, 2735 (1956).

(29) This is based on the proposed equations, $k_t = Fk_\Delta + k_s$ and $k_\alpha = k_\Delta + k_s$.

(30) If we consider the suggestions by Streitwieser[4] and Winstein[31] that the internal return process is important in the acetolysis of simple secondary alkyl tosylates, this factor of 12 for k_Δ/k_s might be high and should be considered as an upper limit.

(31) A. F. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, 90, 1904 (1968).

(32) G. S. Hammond, *ibid.*, 77, 334 (1955).

(33) The original mechanism did not consider the possibility for cross-over between the proposed open and bridged carbonium ion intermediates.[3] On the other hand, Winstein was aware of this possible complication. He stated:[34] "In this case [2-phenylethyl system] there is no leakage between the k_Δ route and the k_s route; that is, there is no crossing over between the two routes, which remain quite independent. With simple primary systems there is no crossing over; with secondary or tertiary systems it is more likely to have cross-over between the different routes."

(34) S. Winstein, Chemica Theorica, Conferenze VIII, Corso Estivo di Chimica, Academia Nationale dei Lincei, Rome, 1965.

predominantly (96%) retained substitution product, and the other is the absence of a significant rate acceleration attributable to phenyl participation.

It has been argued that the best evidence for the existence of bridged ions is not kinetic, but stereochemical,[10a] and that retention of configuration cannot be realized in a reaction which involves open ions.[35] On the other hand, Winstein suggested on a number of occasions the possibility that a rapidly equilibrating pair of open cations may also be capable of controlling the stereochemistry of the product, achieving predominant retention of configuration.[37]

Despite the criticisms advanced by Cram[10] against the above concept of equilibrating cations or ion pairs,[38] conclusive experimental evidence for or against this proposal does not appear to be presently available.

In this connection it is desirable to point out that solvolyses with retention have been experimentally demonstrated in systems involving open classical intermediates. Thus, Goering and Chang realized predominant retention in the solvolysis of active 2-phenyl-2-butyl *p*-nitrobenzoate in aqueous dioxane.[39] Similarly, there is no longer any reason to question the classical nature of the 2-phenylnorbornyl cation.[40] Yet solvolysis of 2-phenyl-*exo*-norbornyl chloride yields the retained product, 2-phenyl-*exo*-norbornanol, almost exclusively.[41]

Consequently, since solvolyses with retention of configuration have been demonstrated in systems involving open classical intermediates, it does not appear possible to conclude, merely on the basis of stereochemical results alone, that the appearance of retention in the reaction products requires the formation of a bridged intermediate.

What is the Source of the Dilemma in the Theory of Open and Bridged Ions? The kinetic approach of the present study confirmed the original conclusion that the rate acceleration in the acetolysis of 3-phenyl-2-butyl tosylate is small, too small to be consistent with the proposed mechanism postulating the competitive formation of bridged and open (essentially limiting) cations. Originally, we attempted to resolve this difficulty by proposing that acetolysis led to the formation of rapidly equilibrating (essentially unbridged) 3-phenyl-2-butyl cations or ion pairs.[9] The formation of such intermediates could account for the absence of a significant rate enhancement and simultaneously account for the retained stereochemistry.[37]

Recent developments which suggested that the acetolysis of secondary alkyl arenesulfonates is far from limiting[14,15] led us to explore another possible explanation for the dilemma. Perhaps the difficulty with the theory of open and bridged ions had its origin in the fact that simple open ions, essentially limiting, are not involved in the mechanism, as originally proposed.

Product–Rate Correlation

It was pointed out earlier that the theory of concurrent formation of open (essentially limiting) and bridged cations, differing little in stability, leads to an expectation of equilibration between the two—with cross-over occurring between the two paths.[9] On this basis, we should not anticipate any satisfactory correlation between the observed rates and the reaction products.

On the other hand, Schleyer and Lancelot recently reported that they could achieve satisfactory product–rate correlations in the solvolysis of certain secondary β-arylalkyl derivatives.[16] The existence of such correlations implies that the bridged and nonbridged pathways are independent and distinct, without significant cross-over. Accordingly, we decided to apply their approach to the detailed data on the 3-aryl-2-butyl system available from the present study.

The proposed dissection of the titrimetric rate constant (k_t) into the aryl-assisted (Fk_Δ) and aryl-unassisted (k_s) components can be achieved by use of the previously determined k_s values in Table III. Thus, the amount of product arising from the aryl-assisted pathway is predicted from the rate data by $100(Fk_\Delta/k_t)$ ($Fk_\Delta = k_t - k_s$), which can be directly compared with the product data in Table II. It was found that the amount of retained substitution product, *threo*-acetate, agrees well with the predicted value for all of the five compounds examined (Table IV).

Table IV. Comparison of the Predicted and Observed Amount of Product Arising from the Aryl-Assisted Pathway in the Acetolysis of *threo*-3-Aryl-2-butyl Brosylates

X =	Product from the aryl-assisted pathway, % Calcd[a]	Obsd[b]
p-MeO	99	100
p-Me	87	88
m-Me	73	68
H	66	59
p-Cl	37	39

[a] Calculated by $100(Fk_\Delta/k_s)$. [b] Amount of *threo*-acetate, see Table II.

Thus, the data reveal the existence of an excellent product–rate correlation in the acetolysis of I-X, which supports the view that there are two discrete reaction pathways, the aryl assisted (Fk_Δ) and the unassisted (k_s), without any significant cross-over between these.

The Proposal for Strongly Aryl- and Solvent-Assisted Pathways. The existence of satisfactory product–rate correlation in the solvolysis of β-arylalkyl derivatives, recently described by Schleyer and Lancelot,[16] appears to require the absence of significant cross-over

(35) Cram's position on this point does not appear to be entirely consistent. For example, the acetolysis of active *threo*-4-phenyl-3-hexyl tosylate was reported to produce a substitution product containing 22% active material in the retained product along with a small amount (4.5%) of inverted product. Cram and his coworkers ascribed the formation of these products to a process involving an open classical ion.[36] This process, termed the simple substitution reaction, was thus characterized as proceeding with predominant retention (*ca.* 80%) of configuration, despite the postulated involvement of an open intermediate.

(36) (a) D. J. Cram and F. A. A. Elhafez, *J. Amer. Chem. Soc.*, **75**, 3189 (1953); (b) D. J. Cram, H. L. Nyquist, and F. A. A. Elhafez, *ibid.*, **79**, 2876 (1957).

(37) S. Winstein, *Bull. Soc. Chim. Fr.*, **18**, C55 (1951); S. Winstein and B. K. Morse, *J. Amer. Chem. Soc.*, **74**, 1133 (1952); S. Winstein and L. L. Ingraham, *ibid.*, **77**, 1738 (1955).

(38) It appears to us that these criticisms in terms of the difficulties associated with the special conformational and steric properties of equilibrating ions may also be applied to his own proposal of the simple substitution reaction, which was proposed to proceed with predominant retention in the 4-phenyl-3-hexyl system.[36] The idea that the difference in steric environment between the front and back side of the disolvated open ion controls the stereochemistry[37] appears to be also applicable to a situation where a rapidly migrating phenyl group is "solvating" one side of the carbonium intermediate.

(39) H. L. Goering and S. Chang, *Tetrahedron Lett.*, 3607 (1965).

(40) D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969).

(41) K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2693, 5270 (1968).

between the aryl-assisted (Fk_Δ) and the aryl-unassisted (k_s) pathways. The past theory of bridged and open ions which was proposed on the basis of the limiting k_s mechanism fails either to provide a satisfactory explanation for the lack of cross-over between the processes involving bridged and open ions,[3,9] or to predict the existence of satisfactory product–rate correlations in the acetolysis of secondary β-arylalkyl derivatives.[3,4]

Schleyer and Lancelot proposed that the acetolysis of secondary β-arylalkyl arenesulfonates must involve both strongly aryl- and solvent-assisted pathways, similar to the processes previously formulated for the acetolysis of primary derivatives.[16,17] This proposal indeed accounts for both the lack of cross-over and the small rate enhancement previously attributed to aryl participation. That is, as the rate of the aryl-unassisted process is also strongly accelerated by nucleophilic solvent participation, similar to the situation in primary solvolysis, the rate ratio, k_t/k_s or k_Δ/k_s, no longer gives a direct measure of aryl participation, contrary to the original expectation.[42] In this case, we are comparing two rates, both of which can be greatly accelerated by participation from the neighboring aryl group or solvent.

A problem arises as to the precise nature of the k_s process in the acetolysis of secondary derivatives. It is quite clear now that this k_s process must be very different from that involved in the solvolysis of tertiary derivatives,[15] contrary to the dominant interpretation utilized in the past. The question now arises as to whether this k_s process for secondary derivatives is similar to the k_s process for primary derivatives. This position appears to be implied by the discussion of Schleyer and Lancelot.[43]

We believe that the differences in the characteristics of the k_s process in the acetolysis of secondary derivatives and those of primary derivatives are so huge that it is necessary to consider these processes to be quite different mechanistically. This question is subjected to detailed considerations in the next section.

The Nature of the k_s[44] Pathway. The solvolysis of primary β-arylalkyl derivatives has been interpreted in terms of two independent reaction pathways, the aryl participated (Fk_Δ) and the solvent participated (k_s).[17] Discreteness of these two pathways was rationalized by considering two competing displacement processes involving the neighboring aryl and the solvent molecule.

Existence of a satisfactory product–rate correlation indicates that a dual pathway mechanism is also operating in solvolysis of secondary β-arylalkyl derivatives. The question arises as to whether the dual pathways in secondary systems are similar to those in primary. Accordingly, a detailed comparison of the characteristics of the k_s pathway in secondary solvolysis was made with the corresponding characteristics of primary solvolysis.

(1) $\Delta S^{\neq}$. The markedly different $\Delta S^{\neq}$ values for the k_Δ and k_s processes in the solvolysis of primary β-arylethyl systems have been used as diagnostic evidence for the discreteness of the two pathways.[10,17] The considerably lower value for the k_s process (*ca.* -20 eu) as compared to that for the k_Δ process (*ca.* -10 eu) was presented as evidence for the major solvent involvement in the transition state of the k_s process and its absence in the transition state for the k_Δ process. For the secondary derivatives, *e.g.*, *threo*-3-phenyl-2-butyl tosylate, the $\Delta S^{\neq}$ values for the k_Δ and k_s pathways are about the same (*ca.* -1.0 eu).[45] Pritzkow and Schöppler,[46] who conducted a detailed study of the acetolyses of a number of primary and secondary alkyl tosylates, concluded that the characteristically different $\Delta S^{\neq}$ values between the primary and secondary systems reflect the degree of nucleophilic solvent involvement in the transition state.

(2) Secondary Isotope Effects. The α- and β-deuterium isotope effects on the rates of acetolysis were found to be insignificantly small (with $k_H/k_D \simeq 1.01$) for primary derivatives, but are substantial (with $k_H/k_D \simeq 1.15$) for secondary.[47] These results were accounted for by an SN2 type of primary solvolysis and by an SN1 type of secondary solvolysis.[6]

(3) ρ Values. The Hammett plots of the acetolysis rates of primary β-arylethyl tosylates yield a quite small ρ value of -0.1,[17e] whereas those of secondary β-arylalkyl derivatives gave substantially larger ρ values ($-0.8 \sim -1.6$).[16,48] Similarly, the Hammett–Taft plot of the rates of acetolysis of secondary alkyl tosylates gave a satisfactory correlation with $\rho^* = -3.4$,[6,49] while such a correlation failed to exist for the rates of acetolysis of primary alkyl tosylates.[46]

(4) Lyate Ion Effects. The effects of added sodium acetate ion on the rates of acetolysis of simple primary and secondary alkyl tosylates were studied by Pritzkow and Schöppler,[46] who found that the rates for the primary derivatives were more strongly enhanced by added sodium acetate than the secondary derivatives.

In fact, it was even concluded by these authors that the acetolysis of secondary tosylates proceeds *via* an SN1 mechanism, whereas the acetolysis of primary derivatives involves an SN2 mechanism.[46,50]

(5) Hydride Shift. The k_s process in the solvolysis of primary derivatives is generally realized to yield mostly the inverted substitution product,[51] fitting nicely to the SN2 mechanism. Significant hydride

(42) On the basis of $k_s \simeq k_c$ for the acetolysis of substituted cyclohexyl arenesulfonates, Winstein estimated the so-called driving force for neighboring group participation, $L = RT \ln (k_\Delta/k_c)$.[13a,25,34]

(43) These authors stated,[16] "Either the current theory of nucleophilically unassisted secondary solvolysis is incorrect, or we lack a satisfactory explanation for the experimentally observed correspondence of rate and product data . . .. We therefore propose that k_s for simple secondary as well as for primary β-arylalkyl systems should be strongly accelerated by solvent assistance." These authors also recognize significant differences in k_s processes for primary and secondary derivatives, as will be discussed in a publication by them.

(44) The term k_Δ, k_s, and k_c were defined as the anchimerically assisted, the solvent-assisted, and the totally unassisted processes, respectively: S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, 3, 1 (1958). In most cases, however, the term k_s was generally used to refer to the anchimerically unassisted route, and this process for the acetolysis of secondary arenesulfonates was considered to be close to k_c.[13,42]

(45) Calculated from the unpublished data of S. Sivaram.

(46) W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, 95, 834 (1962).

(47) See the summary in ref 6.

(48) C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, 91, 4286, 4287 (1969).

(49) J. Harper obtained $\rho^* = -2.8$ for compounds containing electron-releasing substituents; Ph.D. Thesis, Princeton University, 1968.

(50) Peterson and his coworkers[14] noted that since the ratio of nucleophilicities of acetate ion to that of acetic acid may well be lower than the comparable ratio (*e.g.*, that of CH_3O^- and CH_3OH) characteristic of a more nucleophilic solvent, the rate of solvolysis that is not limiting but has some SN1 character, such as the acetolysis of secondary arenesulfonates, must be considerably less sensitive to added sodium acetate than that of a pure SN2 reaction.

(51) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, 79, 6233 (1959).

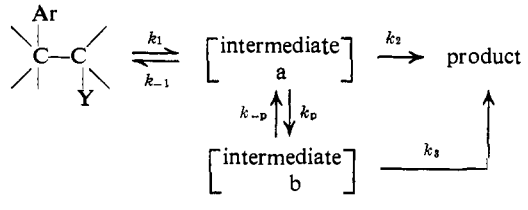
shift to the benzylic species is not observed. On the other hand, the k_s products from the acetolysis of secondary β-arylalkyl derivatives, such as 3-phenyl-2-butyl tosylate, consist of a variety of elimination as well as substitution products, a substantial portion of which arises *via* processes involving hydride shift.[52]

The above features indicate that the nature of the k_s process in the acetolysis of secondary alkyl derivatives must be intrinsically different from that of primary. The experimental data for the primary k_s process show all of the characteristics of a true SN2 displacement reaction involving solvent. On the other hand, no evidence for strong nucleophilic solvent participation in the secondary k_s process could be detected in the present considerations. Indeed, these characteristics were previously considered to lend support for an SN1 (essentially limiting) mechanism. Now that we have concluded that the effective absence of cross-over requires two independent pathways, it would appear that the limiting mechanism for the secondary solvolysis can no longer be accepted. However, neither do the data appear to be compatible with the clean SN2 mechanism which is formulated for the primary solvolysis.

We believe that the results can be accommodated in terms of an alternative scheme which postulates the prior formation of a tight open ion pair, followed by competitive participation by solvent and by the neighboring aryl group. This mechanism is developed and examined in the next section.

The Possibility of a Mechanism Involving an Open Ion Pair as a Common Intermediate to Both the Aryl-Assisted and the Unassisted Pathways. The view that the k_s pathway in the acetolysis of secondary β-arylalkyl derivatives is strongly assisted by solvent is faced with a major difficulty in accounting for the huge amount of data which has been interpreted in the past in terms of an essentially limiting mechanism for secondary acetolysis. A possible means of avoiding this difficulty is indicated by the reaction scheme (Scheme I) outlined below.

Scheme I



This scheme rests on the basic frame of Sneen's interpretation of the solvolysis of secondary alkyl derivatives through a tight ion pair intermediate.[53] The first intermediate, a, can thus be characterized as an open, unsymmetrical, tight ion pair, formed without significant solvent participation. This tight ion pair leads either to the product by solvent attack (k_2), or to the second intermediate, b, by the neighboring aryl participation (k_p), or to the starting material by the internal return process (k_{-1}).[54] An arbitrary energy diagram corresponding to the present scheme is illustrated in Figure 2. As the k_p process is absent in a simple alkyl system, it seems to be convenient to regard the k_p process as a "leakage" pathway (shown with broken line in the figure).

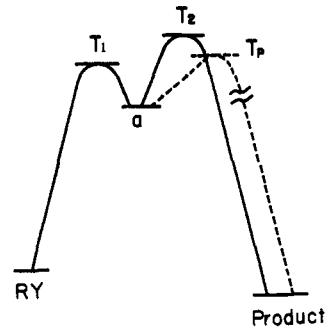


Figure 2. Energy diagram representing reaction Scheme I. The solid line shows the unassisted pathway and the broken line, the aryl-participated pathway.

The kinetic expressions corresponding to Scheme I are as follows.

The rate constant for product formation, k_t, is given by

$$k_t = \frac{k_1(k_2 + Fk_p)}{k_{-1} + k_2 + Fk_p} \quad (1)$$

where F stands for $k_3/(k_3 + k_{-p})$. Designating k_Δ as the overall rate constant for product formation *via* the aryl-assisted pathway, and k_s as that *via* the unassisted pathway, one obtains

$$k_\Delta = \frac{k_1 Fk_p}{k_{-1} + k_2 + Fk_p} \quad (2)$$

$$k_s = \frac{k_1 k_2}{k_{-1} + k_2 + Fk_p} \quad (3)$$

and

$$k_t = k_\Delta + k_s \quad (4)$$

Accordingly, the following product–rate correlation can be derived

$$\% \text{ product } \textit{via} \text{ assisted pathway} = \frac{100Fk_p}{k_2 + Fk_p} = \frac{100k_\Delta}{k_t} \quad (5)$$

$$\% \text{ product } \textit{via} \text{ unassisted pathway} = \frac{100k_2}{k_2 + Fk_p} = \frac{100k_s}{k_t} \quad (6)$$

These equations of product–rate correlation are quite similar to those for the simple dual pathway mechanism involving direct displacement reactions by neighboring aryl and solvent. There is, however, a complication in the present case in estimating the k_s values, for the term k_s is formulated as a function of Fk_p (eq 3). This difficulty can be eased to some extent by the following argument.

Designating k_t^0 as the rate constant in the absence of participation, one obtains

$$k_t^0 = \frac{k_1 k_2}{k_{-1} + k_2} \quad (7)$$

As the k_t^0 values would likely give a linear Hammett plot (the unassisted or normal line), the deviation of a

(52) Cram estimated that *ca.* 20% of the product from the acetolysis of I-H arises from the tertiary benzylic cation.[3]

(53) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362, 6031 (1969); H. Weiner and R. A. Sneen, *ibid.*, **87**, 292 (1965).

(54) For simplicity, the hydride shifting process, which can possibly take place from a, is included in the k_2 process in the present scheme. Discussions on this point will be presented in detail in the next paper in this series.

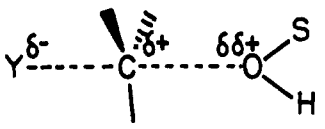


Figure 3. The imaginary transition state for the unassisted overall process (k_s).

k_t point from this line can be expressed as

$$k_t - k_t^0 = \frac{k_{-1}}{k_{-1} + k_2} k_\Delta \qquad (8)$$

Then, if one introduces an assumption of $k_{-1} \gg k_2$, eq 8 reduces itself to $k_t - k_t^0 \simeq k_\Delta$, and one finds that this situation corresponds to $k_t^0 = k_s$.

Accordingly, for systems where a condition of $k_{-1}/k_2 \geq 20$ (<5% error is allowed) is satisfied, good product–rate correlations can possibly be obtained by use of the Hammett plots.

An important point in this argument is that even if one assumes the rate ratio, k_{-1}/k_2, to be 20–1000, the corresponding energy difference between the two energy maxima, T_1 and T_2 in Figure 2, becomes only 2–4 kcal/mol. The consequence is that the transition state for the overall aryl-unassisted pathway is represented not by the structure of a typical SN2 transition state but by that which can be imagined by combining T_1 and T_2. This imaginary transition state, depicted in Figure 3, should closely resemble the tight ion pair intermediate, involving both a considerable degree of charge separation in the C–Y bond[55] and weak partial bonding with a solvent molecule.

The present scheme thus provides us with a k_s transition state which can adequately account for the observed $\Delta S^{\pm}$ values, secondary isotope effects, ρ values, etc., while a satisfactory product–rate correlation can still be expected according to the existing conditions. It should also be noted that although the k_s process in this mechanism may indeed be approaching the limiting solvolysis, the energy diagram in Figure 2 (solid line) is far from that of a typical SN1 reaction. We, therefore, conclude that the present possibility also leads to a conclusion that the acetolysis of simple secondary arenesulfonates is not limiting, the existence of significant nucleophilic solvent participation being evident.

Solvent and aryl participation, although relatively modest, must be sufficiently strong to prevent crossover. The overall aryl-assisted pathway (k_Δ) may also be characterized by modest aryl participation, even if one assumes full bridging in the second intermediate, b. That is, if the levels of T_1 and T_p in Figure 2 are comparable, the overall transition state (Figure 4) should be the result of merging T_1 and T_2 together. Accordingly, the observation of the small magnitude of rate acceleration is not inconsistent with the present interpretation.

Conclusion

The so-called phenonium *vs.* equilibrating ion controversy[9,10] had its origin in the difficulty we encountered

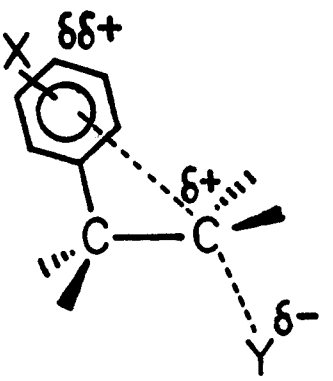


Figure 4. The imaginary transition state for the assisted overall process (k_Δ).

in trying to account for the evident minor rate enhancement in the acetolysis of 3-phenyl-2-butyl tosylate with the proposed mechanism involving concurrent formation of bridged and open (essentially limiting) ions. Originally we attempted to resolve the difficulty by introducing rapidly equilibrating cations as a means of accounting for the stereochemistry[37] without requiring a large rate enhancement. The conclusion that the acetolysis of secondary alkyl arenesulfonates can no longer be considered essentially limiting[14,15] provides an alternative means of revising the original mechanism and resolving the difficulty. As was pointed out earlier,[16] if this position is accepted, it will mean that the huge mass of solvolytic data involving acetolysis (and probably, formolysis) of secondary alkyl arenesulfonates must be subjected to reconsideration and reinterpretation.

Experimental Section

Materials. The purity and identity of all of the compounds which were utilized in the present study were established by elementary analyses, determination of the physical properties, and examination of spectra. The observed physical properties are summarized in Table V and analytical data in Table VI.

***cis*-2-Phenyl-2-butene and Its Substituted Analogs.** Treatment of 2-butanone with phenylmagnesium bromide gave 2-phenyl-2-butanol, which was dehydrated to a mixture of olefins according to the procedure of Garbisch.[57] This mixture, consisting of 67% *cis*-2-phenyl-2-butene, 26% *trans*-2-phenyl-2-butene, and 6% 2-phenyl-1-butene, was subjected to fractional distillation in a platinum spinning band column and fractions containing glpc pure *cis*-2-phenyl-2-butene component were collected, bp 97–98° (31 mm), n^{20}D 1.5424. Other substituted analogs were prepared similarly.

***threo*-3-Phenyl-2-butanol and Its Substituted Analogs.** Hydroboration and oxidation[58] of *cis*-2-phenyl-2-butene yielded the desired *threo*-3-phenyl-2-butanol with a small amount of the tertiary alcohol. This mixture was treated with iodine in refluxing benzene to achieve selective dehydration of the tertiary alcohol. The resulting olefin was eliminated by means of chromatographic separation on alumina and the glpc pure fractions of *threo*-3-phenyl-2-butanol were collected and distilled, bp 95–96° (8 mm), n^{20}D 1.5193. Other substituted analogs were synthesized similarly except that in some cases the spinning platinum band column was employed in order to obtain pure threo alcohol from the hydroboration–oxidation product mixture.

***threo*-3-Phenyl-2-butyl Brosylate and Its Substituted Analogs.** The pyridine method described by Brown and Ham[28] was used in the present preparations.

Kinetic Procedures. Acetic anhydride was added to Baker reagent glacial acetic acid to make a solution 0.2% in acetic anhy-

(55) There is a possibility that the charge separation in this case is larger than that in the transition state for the solvolysis of tertiary derivatives. This might explain why some of the ρ values for tertiary systems ($\rho = -0.64$ for solvolysis of substituted benzyldimethylcarbinyl chlorides in aqueous ethanol[56]) is smaller than those observed for secondary systems, $\rho = -0.8$ to -1.6.

(56) H. C. Brown and C. J. Kim, *J. Amer. Chem. Soc.*, 90, 2082 (1968).

(57) E. W. Garbisch, *J. Org. Chem.*, 26, 4165 (1961).

(58) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 83, 2544 (1961).

Table V. Summary of Physical Data

Substituent	*p*-Me	*m*-Me	H	*p*-Cl	*m*-Cl	*m*-CF_3	*p*-CF_3	*m*,*m*'-$(CF_3)_2$
			Substituted *cis*-2-Phenyl-2-butene					
Bp, °C (mm)	80–81 (7)	75–76 (5)	97–98 (31)[a]	89–90 (6)	89–90 (4)	61–62 (4)	89–91 (11)	89 (22)
$n^{20}D$	1.5390	1.5384	1.5424[b]	1.5570	1.5595	1.4760	1.4807	1.4388
			Substituted *threo*-3-Phenyl-2-butanol					
Bp, °C (mm)	106–107 (5)	97–98 (7)	95–96 (8)[c]	109–110 (5)	68–69 (2)	95–97 (7)	102–103 (8)	109–110 (17)
$n^{20}D$	1.5150	1.5173	1.5193[d]	1.5357	1.5350	1.4643	1.4642	1.4292
			Substituted *threo*-3-Phenyl-2-butyl Brosylate					
Mp, °C	97–98	47.5–48.5	94–95[e]	68.5–69.5	91.5–92.5	50–51	75–76	119.5–120.5

Literature values: [a] 193 (760). [b] 1.5402 at 25°. [c] 105 (10). [d] 1.5167 at 25°. [e] 93–94, D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3863 (1949); **74**, 2137, 2129 (1952).

Table VI. Summary of Analytical Data of Substituted *threo*-3-Phenyl-2-butyl Brosylates

	Anal.									
	Calcd, %					Found, %				
Substituent	C	H	Cl(F)	S	Br	C	H	Cl(F)	S	Br
p-Me	53.27	5.00		8.36	20.85	52.98	5.04		8.58	
m-Me	53.27	5.00		8.36	20.85	53.07	5.18		8.58	
H	52.04	4.64		8.68	21.64	52.11	4.72		8.40	
p-Cl	47.60	4.00	8.78	7.94	19.79	47.40	3.91	8.78		19.70
m-Cl	47.60	4.00	8.78	7.94	19.79	47.39	3.83	8.51		19.40
m-CF_3	46.69	3.69	(13.03)	7.33	18.27	46.41	3.97	(13.13)	7.42	

dride and this batch was used as the solvent for all rate measurements. In general, each run was carried out with a 0.02 *M* brosylate solution, using 14 ampoules which were sealed under nitrogen atmosphere. Four of these were used for the infinity samples and the rest for the kinetic points. Each kinetic point was determined by titrating a 5-ml aliquot of the sample solution with 0.02 *M* sodium acetate solution, using bromocresol green as the indicator.

Product Studies. A batch of solution containing 0.053 *M* sodium acetate and 0.1 *M* acetic anhydride was prepared for this purpose. In general, 5 mmol of the substrate was dissolved in 100 ml of the above solution to be sealed in an ampoule under nitrogen atmosphere. This ampoule was kept at an appropriate temperature for 7–10 half-lives. The reaction mixture was then poured on 300 ml of ice–water, which was extracted four times with 50-ml portions of ether–pentane (1:1). The combined organic layer was washed with water, sodium carbonate solution, and then water, and then condensed to *ca.* 50 ml before subjecting to a glpc analysis.

Acknowledgments. We wish to thank Professor Schleyer and Dr. Lancelot for exchange of views and discussions. Helpful suggestions and comments by Professor Sneen are also greatly appreciated.