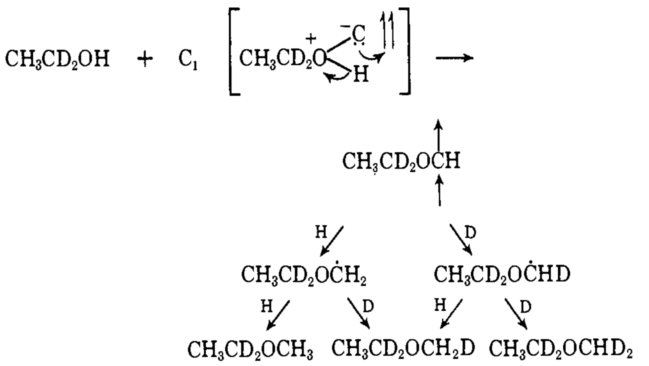
formed from ^3P carbon atoms, as illustrated for CH_3CD_2OH. However, the low degree of discrimination for abstraction from β-CH_3 or α-CD_2, shown by the ethoxymethyl radical intermediate of this mechanism, $Et\dot{O}CH_2$, is unexpected.



Dimethyl ether formed from methanol appears to be produced by at least two pathways. A d_6 component (Table IV) is not possible if a methoxycarbene intermediate is invoked in the CD_3OH experiment. If the d_6 component is removed and the other values normalized, the values listed in Table XIV are obtained. Random abstraction by this methoxycarbene intermediate is consistent with the results, again supporting the suggestion that a triplet form of the carbene is involved.

The remainder of the dimethyl ether (30–40%) is derived exclusively from methanol by dehydration: (1) 31% of the ether from CD_3OH is CD_3OCD_3, (2) 38% of the ether from $^{14}CH_3OH$ is doubly labeled, and (3) 41% of the ether from $^{13}CH_3OH$ and ^{14}C vapor is unlabeled. Dehydration to the symmetrical ether is observed only with methanol.

Table XIV. Dimethyl Ether from C_1 and CD_3OH (d_6 Component Removed)

Deuterium content	d_6 component removed	Statistical hydrogen abstraction
d_3	6.5	6.2
d_4	33.4	37.5
d_5	60.1	56.3

G. Atomic Carbon Content of the Carbon Vapor. The C_1 products from the reactions with alcohols are summarized in Table XV. Such chemical evidence indicates that the carbon arc employed in these experiments contains a minimum of 40% by weight of atomic carbon.

Table XV. Summary of Products from the Reactions of C_1 with Alcohols[a]

Products	Methanol R = Me	Ethanol R = Et	1-Propanol R = *n*-Pr	2-Propanol R = *i*-Pr
OH insertion				
$(RO)_2CH_2$	17.8	11.5	11.5	10.6
CH insertion				
α-CH	6.3	9.4	6.7	6.6
β-CH		4.4	1.8	4.5
γ-CH			2.8	
$ROCH_3$	0.8	0.3	0.1	0.2
CO	16.8	14.3	11.7	12.8
Total	41.7	39.9	34.6	34.7

[a] Weight per cent of total carbon.

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research.

Stereochemistry of Solvolysis of 2-Phenylethyl Sulfonate Esters. The Phenonium Ion–Equilibrating Classical Ions Problem

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Abstract: Solvolysis of diastereomerically pure $PhCHDCHDOSO_2Ar$ leads to product in which the extent of retention of diastereomeric configuration is in all cases twice the extent of label rearrangement in $PhCH_2C^*H_2OTs$. This relation, which is uniquely required by a symmetric phenonium ion, has been observed for 5, 15, 44, and 50% rearrangement attending solvolysis and 27% rearrangement attending deamination. Detailed kinetic inspection of the equilibrating classical ion scheme suggests that although it can account for the entropy spread associated with the k_s, k_Δ routes it cannot account adequately for other related observations.

The structure of 2-phenylethylcarbonium ions has been hotly contested.[2] Recent structural studies on the 2-phenylethyl carbonium ion in strongly ionizing, weakly nucleophilic solvents seem to support the phenonium ion formulation.[3] However, it can be argued that the structure of the cation generated in such an environment is at an extremum and is not representative of the structure of the cation generated under the more usual reaction conditions, *e.g.*, solvolysis and deamination. Of those criteria most often applied to the

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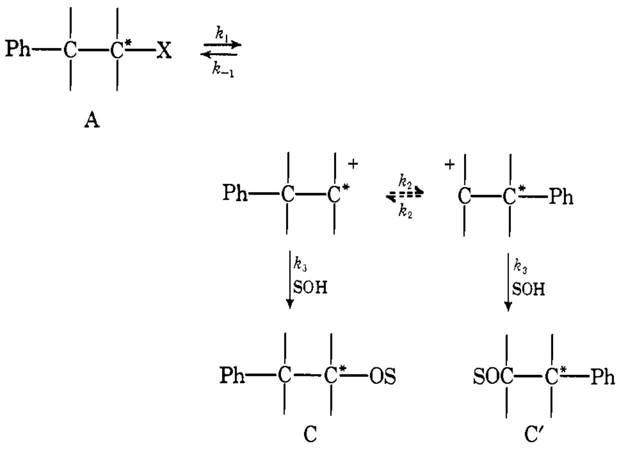
(1) Present address: Midwest Research Institute, Kansas City, Mo. 64110.

(2) (a) D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964); this is a general review defending the phenonium ion formulation. (b) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965); this is a general review defending the equilibrating classical ion formulation.

(3) L. Eberson and S. Winstein, *ibid.*, **87**, 3506 (1965); G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *ibid.*, **89**, 711, 5259 (1967).

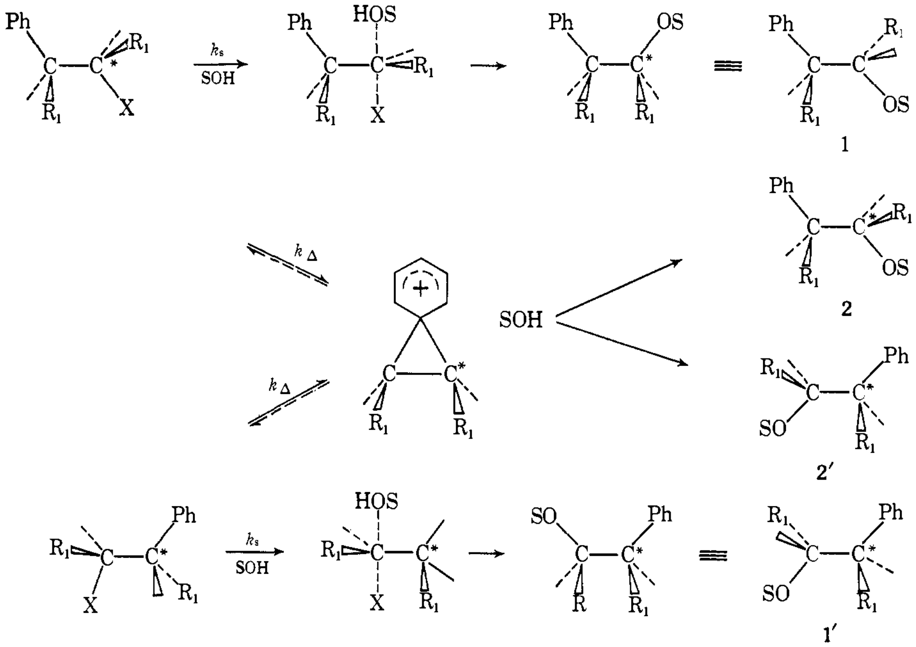


question of the nature of the 2-phenylethyl cation generated in solvolysis, the kinetic data (rate acceleration) seemed least amenable to unambiguous interpretation and the most vulnerable piece of evidence in support of a nonclassical phenonium formulation.[4] Therefore we turned to the alternate criteria of isotopic rearrangement and stereochemistry attending solvolysis, and in particular their interrelationship. To our knowledge, such tandem studies have been performed previously only on the 3-phenyl-2-butyl system.[6]

Consider first the equilibrating ion construct. As we understand it, the primary classical ions undergo rearrangement of the aliphatic carbons by migration of the phenyl (aryl) ring from one carbon to the other. Furthermore, the rapid to-and-fro motion of the aromatic effectively shields that side from solvent attack, so that the carbonium ion undergoes solvent collapse to product with only front-side attack, *i.e.*, retention of configuration relative to initial covalent reactant. This scheme has been subjected to a detailed numerical analysis[7] with the result that a reasonably large span of stereochemical results relative to rearrangement is possible. For example, the ratio, R, of concentration of product formed with retention of configuration to that formed with label rearrangement may be as low as 1.04 and as high as 2.26 in the several cases calculated. Therefore, equilibrating classical ions have the advantage of accommodating a wide variety of experimental results. However, insofar as we understand it we cannot predict *a priori* the relationship between the extent of retention and of rearrangement in the product, knowing only that $1.04 < R < 2.26$ is an acceptable range.

Consider next the phenonium ion theory,[1,8] shown in Scheme I. It is argued that solvolysis occurs by two parallel paths. The classical path, denoted by k_s, is the "normal" solvolytic route leading to product with no label rearrangement and probably occurring with complete inversion of (diastereomeric) configuration.[9] The nonclassical path, denoted by k_Δ, leads to the bridged, highly delocalized phenonium ion. Assuming that bridging is symmetrical, solvent attack occurs with equal probability at either carbon with over-all retention of (diastereomeric) configuration, but leads to label rearrangement in only half of the product molecules. Therefore a *symmetrically bridged phenonium ion demands that the amount of retention of (diastereomeric) configuration be twice that of label rearrangement,* R = 2.00.

Scheme I



One therefore has a sensitive test for the adequacy of symmetrically bridged phenonium ions. If the latter is important it uniquely requires R = 2.00, and any other result demonstrates its inadequacy. However, it must be realized that classical, equilibrating ions can also account for this ratio. Therefore such an experiment is unilaterally unique in the sense that one class of results can unequivocally demonstrate the insufficiency

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(4) However, the recent kinetic studies of Nordlander[5] furnish dramatic support of phenyl participation in 2-phenylethyl tosylate during trifluoroacetolysis.

(5) J. E. Nordlander and W. G. Deadman, *J. Am. Chem. Soc.*, **90**, 1590 (1968). This article affords an excellent analysis of the phenonium ion problem.

(6) Stereochemistry: D. J. Cram, *ibid.*, **74**, 2129 (1952), and ref 1; scrambling: W. B. Smith and M. Showalter, *ibid.*, **86**, 4136 (1964).

(7) C. J. Collins, B. M. Benjamin, and M. H. Lietzke, *Ann.*, **687**, 150 (1965).

(8) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).

(9) A. Streitwieser and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 6233 (1957).

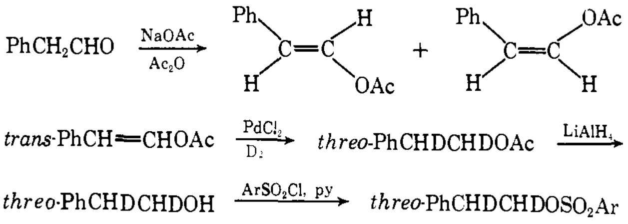
of the symmetrical phenonium ion hypothesis, but all classes of results cannot by themselves demonstrate any hierarchy of preference for either some bridged, static ion or open, equilibrating ones. On the other hand, since open, equilibrating ions do not predict uniquely the ratio of retention to rearrangement the observation of a constant value for this ratio under various conditions would require constancy in the ratios of a number of rate constants,[7] a circumstance which strains credulity.

For theoretical reasons a phenonium ion can be expected to be most important in the primary–primary 2-phenylethyl system. We therefore chose to investigate the stereochemical course attending solvolysis of 2-phenylethyl arenesulfonates, using the diastereomeric 1,2-dideuterated species, $PhCHDCHDOSO_2Ar$, as our stereochemical probes. The general utility of stereospecifically dideuterated species in determining the stereochemical course of reactions at a primary carbon atom has been commented upon previously[10] and the stereochemistry attending trifluoroacetolysis has been reported.[11]

Results

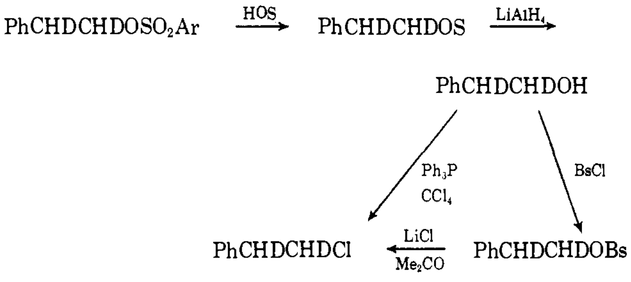
The preparation of the diastereomeric 1,2-dideuterio-2-phenylethyl compounds was accomplished by conventional procedures outlined in Chart I. Pure *trans*-2′-acetoxystyrene was obtained by low-temperature crystallization; the pure *cis* isomer was obtained by fractionation through an efficient spinning-band column of a mixture enriched in the latter. The diastereomeric purity of the final compounds is determined by the isomeric purity of the enol acetates and the stereospecificity of catalytic deuteration, since the diastereomeric center is not chemically involved in further reactions. Each of the enol acetates was shown to be at least 99% pure by vpc examination, and Smith[12] has shown that catalytic reduction of the styryl-type double bond occurs stereospecifically *cis*. Nmr analysis of the chloride (*vide infra*) derived from the alcohol demonstrated a minimum diastereomeric purity of 98%.

Chart I



Quantitative analysis of diastereomer composition was done by nmr spectroscopy, and rests on the property that the sole vicinal coupling constant of the aliphatic protons is different in the *erythro* and *threo* compounds.[10] This leads to different AB patterns for each diastereomer whose separation is determined by $|J_{erythro} - J_{threo}|$ as modified by deuterium isotope effects on the chemical shift, ν_{AB}, of the two diastereomers.[13] In practice, accurate integration was possible only when $|J_{erythro} - J_{threo}| \gtrsim 2$ Hz. Because the latter depends on the difference in rotamer population about the alkyl C–C bond, and because all oxygen derivatives, $PhCH_2CH_2OR$, have rather small conformational energy differences,[14] it was necessary to convert solvolysis products to the corresponding chloride for analysis, as shown in Chart II. We have previously shown that the conversion of alcohols to chlorides with triphenylphosphine–carbon tetrachloride occurs with inversion.[15] Known mixtures of the diastereomeric chlorides served as reference standards for integrations, performed in an atypical fashion and described in the Experimental Section.

Chart II



Solvolysis in trifluoroacetic, formic, and acetic acids with added carboxylate were conducted under conditions approximating those under which label rearrangement experiments have been described. The stereochemistry of product formation and relevant label redistribution is given in Table I. Solvolysis product was shown to be stereochemically stable under reaction conditions, and brosylate recovered after one half-life was shown to be of completely retained configuration. Consequently, the degree of retention listed in the table results from a kinetically controlled process.

Because our experiments were performed on dideuterated brosylate, whereas all of the rearrangement experiments were performed on tosylate, usually ^{14}C labeled, it was important to demonstrate (1) the absence of deuterium isotope effects on rearrangement and (2) the equivalence of tosylate and brosylate as leaving groups in the rearrangement process. Entries 3 and 4 of the table show that rearrangement in $PhCH_2CHDOBs$ and $PhCH_2CD_2OBs$ are experimentally indistinguishable. Were a significant deuterium isotope effect exerted on the rearrangement process one would expect that the mono- and dideuterated species would show different label redistributions. That this is not the case demonstrates the absence of an important isotope effect. Furthermore, that the label redistribution in deuterated product is the same as that in ^{14}C-labeled tosylate demonstrates the equivalence of the two leaving groups, at least in this set of experiments.

The results of Table I show that, to within the combined experimental error of the measurements involved, in all cases the per cent retention is twice the per cent rearrangements as demanded by a symmetrical phenonium ion.[16]

Since the solvolyses conducted above lead to rearrangement which is either close to the statistical 50% or is relatively minor ($\sim$6%), we sought an intermediate

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[10] E. I. Snyder, *J. Org. Chem.*, 32, 3531 (1967).

[11] R. J. Jablonski and E. I. Snyder, *Tetrahedron Lett.*, 1103 (1968).

[12] G. V. Smith and J. A. Roth, *J. Am. Chem. Soc.*, **88**, 3879 (1966).

[13] R. J. Jablonski and E. I. Snyder, *ibid.*, 90, 2316 (1968).

[14] R. J. Jablonski and E. I. Snyder, to be published.

[15] R. Weiss and E. I. Snyder, *Chem. Commun.*, 21, 1358 (1968).

[16] The spread in rearrangement (3–10%) reported in HOAc–KOAc is particularly vexing. Our measurements suggest 3–5% rearrangement for which the observed retention is barely within the limits prescribed by a symmetric phenonium ion and is appreciably less than that reported by others.

Table I. Stereochemistry of Solvolysis of PhCHDCHDOBs with Added Lyate Ion

Solvent	% rearrangement	% retention (±3%)
CF_3CO_2H	50 ($PhCH_2CD_2OTs$)[a]	98
HCO_2H	44.2 ($PhCH_2C^*H_2OTs$)[b] 43.0 ($PhCH_2CHDOBs$)[c] 43.7 ($PhCH_2CD_2OBs$)[c]	81
CH_3CO_2H	5.5, 7.2 ($PhCH_2C^*H_2OTs$)[d] 10 ($PhCH_2CD_2OTs$, $PhCD_2CH_2OTs$)[e] 2.8–7.0 ($PhCH_2CD_2OBs$)[c]	13

[a] Reference 5. [b] C. C. Lee, G. P. Slater, and J. W. T. Spinks, *Can. J. Chem.* **35**, 1417 (1957). [c] This work. [d] 5.5% from reference in *b*; 7.2% according to Dr. Coke, ref 17. [e] 10% from W. H. Saunders, Jr., S. Asperger, and D. H. Edison, *J. Am. Chem. Soc.*, **80**, 2421 (1958).

case as a more stringent predictive test. Recently Coke observed that acetolysis at 115° in the absence of acetate ion leads to considerably more rearrangement than that observed with added acetate.[17] Because of considerable internal return, the label redistribution in product is a function of the extent of reaction. However, one can bypass this problem by extrapolating the observed rearrangement back to zero time, a time when only originally labeled tosylate is present. A nonlinear least squares fit of Coke's data to a third-order polynomial (12 points, 4 parameters) reproduces the observations precisely and leads to 14.8% rearrangement at time zero.

The stereochemical course of such acetolyses is given in Table II. One notes that the extent of retention decreases with decreasing extent of reaction. This is consistent with Coke's observation that kinetic complications attend acetolysis, possibly arising through an acid-catalyzed component. This has been minimized in entry 4, where the product was examined at lower concentration after only 36% reaction. Another noteworthy feature is that brosylate recovered after two half-lives is of completely retained configuration, although entry 5 shows 29% rearrangement has occurred. Since one can estimate that 56% of the brosylate has been involved in the internal return process,[18] this demonstrates that such a process occurs completely with retention of configuration. Although consistent with ionization of the brosylate to a symmetrical phenonium ion pair, this observation cannot be taken as support for such a structure of the cation since other cases are known where return from the intimate ion pair occurs stereospecifically with retention of configuration.[19]

Table II. Acetolysis at 115° (No Acetate Added), 0.4 *M*

Substrate	Time, hr	Max % reaction[a]	% retention (±3%)
Brosylate	40		42
	10	74	41
	4	37	37
	4 (0.08 *M*)	36	37
	10		100 (Recovered brosylate)[c]
Tosylate	12 (0.08 *M*)		32
	3 (0.08 *M*)	20 (12)[b]	32

[a] This value is calculated from the amount of unreacted sulfonate actually isolated. [b] Calculated using Coke's titrimetric rate constant for $PhCH_2CH_2OTs$ of 1.27×10^{-5} (ref 17) and assuming an isotope effect between 1.05 and 1.12. [c] Scrambling studies ($PhCH_2CD_2OBs$) show 29% label redistribution.

Because the extent of retention attending acetolysis of the brosylate was significantly greater (37%) than that predicted from the observed rearrangement (30%), solvolytic studies were repeated with the tosylate, even though our previous observations (*vide infra*) indicated the equivalence of these leaving groups. To avoid kinetic complications, product was examined at quite low conversions and at concentrations lower than those used by Coke. Our observation of 32% retention shows that, under these conditions, the brosylate and tosylate are not stereochemically equivalent leaving groups.

Discussion

In this section we discuss the pertinence of our results to the problem at hand, then make some comments about the problem in general.

This Work. The phenonium ion hypothesis *demands* that in the product the per cent retention be twice that of rearrangement. Our work verifies this *prediction* over a reasonable span of rearrangement (6, 15, 45, and 50%) in a single system. This prediction has also been verified for deamination of 2-phenylethylamine[20] where 29% scrambling occurs. Consequently, our results lend further credence to the bridged ion hypothesis. Furthermore, insofar as the value to a theory can be judged by its predictive value, our experimental corroboration of one such prediction must be considered as a triumph of this hypothesis. However, it must be emphasized that in no way do our results prove experimentally the inadequacy of the equilibrating classical ions construct.[21] We hope that some molecular orbital calculations in progress will assist the structural formulation.

Kinetic Aspects of Equilibrating Primary Cations. To our knowledge, no one has demonstrated that the equilibrating ion formation is either consistent or inconsistent with certain known kinetic features of solvolysis of 2-phenylethyl derivatives. We assume the scheme previously given (*vide infra*).

1. Internal Return. Coke has unequivocally demonstrated a large amount of internal return in acetolysis.[17] Recently Winstein has shown[22] that internal return in a secondary alkyl sulfonate ester, as measured by oxygen scrambling, occurs to only a small extent (<7% in acetic acid). Extrapolation of these results to classical primary alkyl cations leads to the conclusion that one should expect insignificant internal return. Insofar as the equilibrating ions resemble classical primary

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(17) We thank Dr. James Coke for keeping us continually informed of the progress of his work and for communicating his results prior to publication (*J. Am. Chem. Soc.*, **91**, 1154 (1969)).

(18) Coke has observed that the first-order rate constant for ^{14}C rearrangement is 63% that of k_t.[17] From the extrapolated k_t of $PhCH_2CH_2OBs$ [S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 4801 (1956)] and assuming an isotope effect of 10% for $PhCH_2CD_2OBs$ (footnote *e*, Table I), one estimates for the latter a half-life of 8.3 hr for the rearrangement process.

(19) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **86**, 120 (1964).

(20) E. I. Snyder, to be published.

(21) However, see comments above regarding a constant value of *R*.

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

cations, one should reasonably expect negligible internal return, which is contrary to fact. Unless one wishes to attribute special properties to these equilibrating primary cations, which immediately detracts from their attractiveness, one must conclude that primary cations, or cation-like entities, are not involved.

2. The k_Δ, k_s Dissection. Because the rate constants k_Δ, k_s are operationally defined they are physically meaningful quantities irrespective of the kinetic scheme chosen. The physical content of these quantities in the phenonium ion scheme is obvious (*vide infra*). What we wish to do in this and the following section is to examine the physical content of k_Δ, k_s in the context of equilibrating classical ions, using the simple kinetic scheme given above.

Twice the amount of rearrangement represents all of the k_Δ process, *i.e.*, $2(\mathrm{d}C'/\mathrm{d}t) = k_\Delta A$. The remainder of the solvolytic process is associated with k_s, *i.e.*, $(\mathrm{d}/\mathrm{d}t)(C - C') = k_sA$. From the kinetic scheme for equilibrating classical ions (neglecting internal return) and the operational definitions above one can show

$$k_\Delta = \frac{2k_1k_2k_3}{(k_2 + k_3)^2 - k_2^2} = \frac{2k_1k_2}{2k_2 + k_3}$$

$$k_s = \frac{k_1k_3^2}{(k_2 + k_3)^2 - k_2^2} = \frac{k_1k_3}{2k_2 + k_3}$$

Winstein has recently shown[23] that in the solvolysis of 2-phenylethyl tosylate k_s parallels the solvolytic rate constant, k^{Et}, for ethyl tosylate, a substrate which surely solvolyzes by the classical path. He also showed that k_Δ parallels the solvolytic rate constant, k^{neo}, for neophyl tosylate, a substrate thought to ionize with phenyl participation. Although intuitively this might seem incompatible with equilibrating classical ions a more direct comparison may be made. The question to be answered is, "In the equilibrating ion framework, is it reasonable that k_s behave like k^{Et}, and that k_Δ behave like k^{neo} over a wide range of solvent types?"

A. K_Δ. In the limit of high scrambling, $k_2 > k_3$,[24] $k_\Delta \sim k_1$. Since k_1 is an ionization rate constant, it is reasonable that $k_\Delta \propto k^{\mathrm{neo}}$ in good ionizing solvents. In the limit of low scrambling, $k_3 \gg k_2$,[25] and $k_\Delta \sim 2k_1k_2/k_3$ which we rewrite as $k_\Delta = fk_1, f = 2k_2/k_3$. The equilibration process is unimolecular and should be relatively insensitive to solvent properties; consequently k_2 is approximately solvent independent. In contrast k_3 is a rate constant for nucleophilic attack by solvent on ion. Therefore f should decrease in solvents of low ionizing ability and high nucleophilicity, and in such solvents k_Δ should be decreased relative to the ionization rate constant k_1. However, the *experimental* observation[23] is that $k_\Delta \propto k^{\mathrm{neo}}$ over a range of solvents including ethanol and acetic acid—recall k^{neo} represents an ionization rate constant which should behave similarly to k_1—whereas the equilibrating classical ion scheme suggests k_Δ should fall off relative to k^{neo} in the latter solvents. Therefore the equilibrating ion scheme seems incompatible with experimental observations.

B. K_s. In the limit of low scrambling, $k_3 \gg k_2$ and $k_s \sim k_1$. Solvolysis of typical primary alkyl systems involves a rather large amount of solvent participation and is sensibly responsive to solvent nucleophilic character. For k_s (Brown scheme) to parallel k^{Et} it is necessary that the initial cation be highly solvated, which seems to be contrary to what has been stated[2] and to the assumptions used in the analysis of k_Δ above. Nonetheless, let us adopt the assumption of a highly solvated cation, for we will show that it, too, leads to inconsistencies. For in the limit of high scrambling, $k_2 > k_3$ and $k_s \sim k_1k_3/2k_2$. That is, k_s is decreased over k_1 by the ratio $k_3/2k_2 \ll 1$, and k_s should no longer parallel k_1 and whatever properties we ascribe to it. Yet Winstein has observed[23] that k_s correlates with k^{Et} even including formic acid. Since any self-contained scheme within the equilibrating classical ion formalism predicts that k_s should drop off as $k_3/2k_2$, itself variable, we conclude that the formalism cannot be reconciled satisfactorily with experiment.

3. Activation Entropies. It has been observed that the activation entropy for the assisted solvolysis, $\Delta S_\Delta^{\ddagger}$, is generally less negative than that for the unassisted route, $\Delta S_s^{\ddagger}$. Winstein has interpreted this[26] as support for his hypothesis, and Brown has qualitatively rationalized this observation as being consistent with his proposal.[2]

According to transition-state theory

$$\frac{\ln k}{T} = \frac{\ln \nu}{T} + \frac{\Delta S^{\ddagger}}{RT} - \frac{\Delta H^{\ddagger}}{RT^2}$$

$$\frac{\partial \ln k}{\partial T} = \frac{1}{\nu}\frac{\partial \nu}{\partial T} + \frac{\Delta H^{\ddagger}}{RT^2}$$

Assuming the frequency factor and its temperature dependence is the same for the k_2 and k_3 processes—$\nu = kT/h$ according to theory—then

$$\frac{\Delta S^{\ddagger}}{R} = \ln k + T\frac{\partial \ln k}{\partial T}$$

or

$$\frac{\Delta S_{\mathrm{X}}^{\ddagger} - \Delta S_{\mathrm{Y}}^{\ddagger}}{R} = \ln \frac{k_{\mathrm{X}}}{k_{\mathrm{Y}}} + T\frac{\partial}{\partial T}\left(\ln \frac{k_{\mathrm{X}}}{k_{\mathrm{Y}}}\right)$$

for two processes X and Y. Since $k_\Delta/k_s = 2k_2/k_3$, in the Brown formalism, and since

$$\frac{\partial \ln (2k_2/k_3)}{\partial (1/T)} = -T^2\frac{\partial \ln (2k_2/k_3)}{\partial T} = \frac{-(E_2 - E_3)}{R}$$

where E_2, E_3 are *experimentally observed* activation energies, then

$$\frac{\Delta S_\Delta^{\ddagger} - \Delta S_s^{\ddagger}}{R} = \ln \frac{2k_2}{k_3} + \frac{(E_2 - E_3)}{RT}$$

The experimental observation is that $\Delta S_\Delta^{\ddagger}$ is less negative than $\Delta S_s^{\ddagger}$. For $k_2 \gg k_3$ this requires only that the first term on the right be of greater absolute magnitude than the second term when the latter is negative. For $k_3 \gg k_2$ this requires that the second term be positive and of greater absolute magnitude than the first. Some estimate of the required values of E_3 is possible.

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[23] A. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, 90, 6546 (1968). We thank Dr. Winstein for sending us a preprint of this work.

[24] The ratio of rearranged to unrearranged product, C'/C, is $k_2/(k_2 + k_3)$. For 45% rearrangement $k_2 \sim 4.5k_3$, so that the inequality $k_2 \gg k_3$ holds only in the cases where rearrangement is very close to statistical. However, the denominator of k_Δ and k_s varies as $2k_2 + k_3$, permitting k_3 to be disregarded.

[25] For 5% rearrangement $k_3 = 18k_2$.

[26] See Winstein and Heck, ref 18.

It is known for one system[27] that vicinal hydride transfer has an activation energy under 11 kcal/mol. Assuming a like activation energy in the 2-phenylethyl system and knowing that in this system phenyl migration competes with hydride transfer to the exclusion of the latter means that $E_2 \sim 8$ kcal/mol. If $k_3 = 18k_2$ (5% rearrangement) and $\Delta S_{\Delta}^{+} - \Delta S_{s}^{+} = 8$ eu, this requires $E_3 \sim 5$ kcal/mol. If $k_2 = 4.5k_3$ (45% rearrangement), $E_3 \sim 7$ kcal/mol. Values of activation energies for solvent attack on primary cations do not seem to be known yet, but the stated limits seem reasonable. Therefore it appears that *at this time* equilibrating classical ions can account for the observed entropy differences.[28]

Experimental Section

Nmr spectra were obtained with an A-60 spectrometer utilizing an NMR Specialties HD-60A spin decoupler. All melting and boiling points are uncorrected.

2′-Acetoxystyrene.[29] The *p*-toluenesulfonic acid catalyzed reaction of phenylacetaldehyde with isopropenyl acetate afforded only 31% of the vinyl acetate with a *cis:trans* ratio of 1.5. A solution of the aldehyde (100 g, 0.83 mol) in acetic anhydride (168 g, 1.64 mol) containing freshly fused potassium acetate (20 g, 0.2 mol) was heated at 165° for 4 hr. The cooled mixture was diluted with 750 ml of a 2:1 pentane–ether mixture and 500 ml of a 25% NaOH solution was slowly added with continual cooling. The organic layer was washed, dried (K_2CO_3), concentrated, then distilled to afford 92 g of product (68%), bp 96–98° (5 mm), with a *cis:trans* ratio of 0.33. Two recrystallizations from pentane (2–3 ml/g of acetate) afforded 39 g of pure *trans*-acetate, mp 32.5–33.0°, with no evidence of the *cis* isomer from vpc examination (SF-96, 127°). The mother liquors from the crystallization were concentrated, then fractionated through a Nester-Faust annular spinning-band column to afford 20 g of pure *cis* enol acetate, bp 101 (12 mm), n^{20}D 1.5491, with no *trans* isomer present according to vpc data.

***threo*(*erythro*)-2-Phenylethanol-1,2-d_2.** Deuteration of pure *trans* (or *cis*) enol acetate was performed in ethyl acetate using 1–2 mol % $PdCl_2$ or 0.1 mol % Pd on charcoal (10%) at 30–40 psig. In one experiment the acetate was isolated and purified, and showed 1.92 deuterium atoms per molecule.[30, 31] Usually solvent was removed and the crude acetate was reduced with lithium aluminum hydride in the usual manner. The alcohol was isolated by distillation, bp 84–87° (4 mm). An analytically pure sample, n^{20}D 1.5310 (lit.[32] n^{20}D 1.5179), had 1.88 deuteriums per molecule, with the distribution determined mass spectrometrically as 0% d_0, 8.3% d_1, 89.5% d_2, 2.2% d_3, 0% d_4 and higher. Consequently little, if any, exchange was occurring upon catalytic reduction.

***threo*(*erythro*)-2-Phenylethyl-1,2-d_2 Sulfonate Esters.** The brosylate was prepared by adding brosyl chloride (*ca.* 20% excess) to a cooled solution of alcohol in pyridine (*ca.* 2 mol of base per mole of alcohol). After 2 hr at −20°, the mixture was acidified, and the solid was collected by filtration, dried, and recrystallized from either 10:1 hexane–ether, cyclohexane, or 5:1 pentane–ether, mp 60.0–60.5° (lit.[26] mp 59–60°). The brosylate contained 1.89 deuteriums per molecule. Tosylate, prepared in a similar manner, was recrystallized from hexane, mp 39.2–39.8°.

***erythro*-2-Phenylethyl-1,2-d_2 Chloride.** A solution of 2.56 g (7.4 mmol) of *threo*-brosylate in 50 ml of anhydrous acetone was stirred with 0.350 g (8.2 mmol) of anhydrous lithium chloride at ambient temperature for 24 hr. Acetone was evaporated *in vacuo* and 75 ml of hexane was added with vigorous stirring. Solids were removed by filtration, and product was isolated by distillation, bp 70–71° (6 mm) (lit.[33] bp 69° (5 mm)). Examination by vpc indicated a purity of at least 98%. The deuterium decoupled nmr spectrum showed a single AB quartet, $J = 8.0$ Hz, with a maximum of 2% of the *threo* isomer present as indicated by integration (*vide infra*). The diastereomeric purity of the sulfonate esters was always at least 98%, as determined by this method.

Formolysis. Formolysis of 12.4 g of *threo*-brosylate was conducted as described by Lee, and Spinks[34] for 20 hr at reflux using the same concentrations as the authors. Examination of the solution showed the presence of only 2-phenylethyl formate. No styrene or 1-phenylethyl formate could be detected, although control experiments demonstrated that the former could survive solvolysis conditions. The cooled mixture was poured onto ice–water, made basic with carbonate, and extracted with ether (eight 50-ml portions). Solvent was evaporated at reduced pressure and the residue was distilled to afford 4.85 g of product whose composition, according to vpc analysis (SF-96, 145°), was 85% 2-phenylethyl formate and 15% of the corresponding alcohol. The amount of product isolated accounts for 92% of reactant. The formate–alcohol mixture was converted to alcohol with lithium aluminum hydride, thence to brosylate, and finally to chloride. Integration of the nmr spectrum of the latter (*vide infra*) showed the sample was 81% *erythro*-chloride. On a separate experiment pure *threo*-formate (from *threo*-alcohol in anhydrous formic acid at reflux for 5 hr) was shown to be diastereomerically stable under the solvolysis conditions (less than 2% *threo*-chloride obtained after work-up as above). Brosylate was also shown to be stable by reisolating unreacted brosylate after solvolysis for *ca.* one half-life at reflux (12 min; 51% isolated) and converting it to the chloride which contained less than 2% *threo* isomer.

Deuterium scrambling was determined in 2-phenylethyl-1-d_1 brosylate (*via* $PhCH_2CHO + LiAlD_4$) and 2-phenylethyl-2,2-d_2 brosylate (*via* $PhCH_2CO_2CH_3 + LiAlD_4$; 1.89 deuteriums per molecule)[31] under formolysis conditions. In the former case analyses were performed on alcohol, obtained by hydrogenolysis of the reaction product. In the latter case analyses were performed on the brosylate made from the alcohol; the ester showed 1.84 deuteriums per molecule,[31] demonstrating the absence of external hydrogen exchange.[35] In both cases integration was performed by the method described below, and samples of undeuterated alcohol (brosylate), monodeuterated unscrambled alcohol, and dideuterated unscrambled brosylate served as reference standards for relative intensities of the various proton signals. The observed scrambling amounted to 43.0 and 42.7%, respectively.

Acetolysis with Acetate. A solution of 2.98 g (8.90 mmol) of *erythro*-brosylate and 1.4 g (17 mmol) of anhydrous potassium acetate in 24 ml of glacial acetic acid was heated at reflux for 20 hr. Processing like that described for formolysis followed by hydrogenolysis afforded alcohol (0.764 g). A solution of the latter (0.615 mol) in 5 ml of dried (P_2O_5) carbon tetrachloride was treated with 1.5 g (0.57 mol) of triphenylphosphine at 55° for 6 hr. The cooled solution was diluted with pentane and chilled; phosphine oxide was removed by filtration and the filtrate was concentrated. Unreacted alcohol and unprecipitated oxide were readily removed by eluting the filtrate through *ca.* 5 g of Florisil with pentane. Concentration followed by distillation afforded 0.49 g of chloride, whose composition was 13.4% *threo*, 86.6% *erythro*. Scrambling was measured using dideuterated brosylate as described for formolysis. Because of the low degree of scrambling the data can be processed in various ways. Assuming all the signal at the 1 position of

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[27] M. Saunders, P. R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964). The applicability of these results to the 2-phenylethyl cation may well be questioned but more appropriate data are lacking. However, Saunders has stated [*ibid.*, **90**, 2436 (1968)] that "hydride shifts are generally more rapid than analogous methide shifts." He has estimated the methide shift occurring in the degenerate rearrangement of the 3-methyl-2-butyl cation "is probably less than 4 kcal/mol."

[28] Note that the difference in entropy for the k_{Δ}, k_s processes is a function only of the k_2, k_3 processes, *i.e.*, the *difference* in entropy is determined solely by processes occuring *after* the rate-determining ionization (k_1). This arises because the k_{Δ} and k_s processes are differentiated (in the Brown scheme) after the rate-determining transition state. That this point may be overlooked is exemplified by a referee's remarks. "In my opinion this [entropy] discussion by Brown . . . is patently erroneous to begin with; he argues for governance of the activation entropy by rapid phenyl equilibration, a phenomenon which clearly must *follow* the rate-determining transition state if it occurs at all."

[29] P. Z. Bedoukain, *J. Am. Chem. Soc.*, **66**, 1325 (1944).

[30] Although the deuterium supplied was quoted as 99.5% deuterium, mass spectral examination of some samples showed about 5% total hydrogen. With these later samples only about 1.8 deuteriums per molecule were incorporated into the ester.

[31] Deuterium analyses were performed by Mr. Josef Nemeth, Urbana, Ill.

[32] "Dictionary of Organic Compounds," Vol. 4, 4th ed, Oxford University Press, New York, N. Y., 1965, p 2687.

[33] P. Ruggli, *Helv. Chim. Acta*, **28**, 674 (1945).

[34] C. C. Lee, R. Tkachuk, and G. P. Slater, *Can. J. Chem.*, **35**, 1417 (1967).

[35] Analysis by nmr showed both reactant and product contained the same deuterium content (2.02 D per molecule), a value some 5% higher than that obtained from the falling-drop method.

scrambled product is real leads to 7% scrambling; correcting the signal at the 1 position for background noise leads to 3% scrambling.

Acetolysis without Acetate. Brosylate or tosylate, usually 2–6 g, depending on reaction time, was dissolved in sufficient glacial acetic acid to afford solutions either 0.4 or 0.08 *M*, and heated at 115 ± 1° for the times indicated. The mixture was concentrated at 15 mm and poured into iced excess aqueous sodium carbonate, which was extracted with several portions of ether. Evaporation of the dried ($MgSO_4$) ether extract affords an oil from which unreacted sulfonate ester could be readily precipitated by addition of pentane followed by refrigeration. The filtrate was again concentrated and acetate was generally distilled at 5–10 mm. Hydrogenolysis followed by the usual work-up gave alcohol, isolated by distillation, which was converted to chloride with triphenylphosphene in carbon tetrachloride as described. Chloride was isolated by distillation and was homogeneous by vpc examination. The configuration of unreacted sulfonate ester was determined by direct conversion to the chloride, as previously described.

In a separate experiment *threo*-acetate was held at 115 ± 1° in acetic acid containing 1 equiv of *p*-toluenesulfonic acid at 0.4 *M* concentration for 42 hr. The chloride ultimately obtained was pure *erythro* product, demonstrating the configurational stability of the acetate under solvolysis conditions. Scrambling in unreacted brosylate was determined using $PhCH_2CD_2OBs$.

Quantitative Analysis. A mixture of *erythro*- and *threo*-2-phenylethyl chloride showed two superimposed AB quartets, $J = 8.5$ and 6.5 Hz, respectively, $\nu = 190$ Hz, from TMS, $\nu_{AB} = 46$ Hz. The high-field, benzylic signals were considerably broadened because of long-range couplings to aromatic protons and the *erythro–threo* signals overlapped badly. Of the low-field signals, the higher field members overlapped badly because of a differential deuterium isotope effect on the chemical shift which resulted in $\nu^{erythro} \neq \nu^{threo}$. The lower field members showed base-line resolution under optimum operating conditions and were used for quantitative analysis. Integration was performed in the normal sweep mode by taking the A-60 amplifier output into a voltage-frequency converter (Dymec Model 2210, 0.25% linearity) and monitoring the output of the latter on a frequency counter (Hewlett-Packard Model 521C). Mixtures of chlorides of known *erythro–threo* content were prepared from pure materials and served as reference standards. Analyses were performed by integrating 8–12 sweeps of the spectrum of the unknown, either preceded or/and followed by integration of the relevant signals of the reference standard(s). Composition of the unknown was determined by comparison of the ratio of integrals in unknown with that of the reference standards adjusted by a (usually small) linear correction. The average deviation in integration was usually less than ±1.3%, but sometimes was twice that high, depending primarily on spectrometer and decoupler frequency stability. Composition of a given sample determined at widely different times was reproducible to within 1%. It is estimated that the absolute error in measurements is no more than ±3%.

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