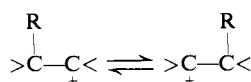


Structural Effects in Solvolytic Reactions. I. The Role of Equilibrating Cations in Carbonium Ion Chemistry. Nature of the Intermediates Involved in the Solvolysis of Symmetrically Substituted β -Phenylethyl Derivatives¹

Herbert C. Brown, K. J. Morgan,² and Frank J. Chloupek³

Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana. Received August 24, 1964

Systematic lowering of the potential barrier separating two equivalent cations



would be expected to result in three distinct classes of such cations: (A) essentially static classical cations, which can be formed and transformed into products without significant equilibration; (B) equilibrating cations which undergo rapid equilibration in the time interval between formation and conversion into products; and (C) bridged species where the potential barrier has disappeared so that resonance now occurs involving the two structures. Current interpretations assign practically all systems which have been examined to the first and third of these classes, with the intermediate class being almost unpopulated. There is a second apparent anomaly. It has been a valued and highly useful principle in organic chemistry that a decrease in the free energy of formation of the product or first intermediate in a given reaction will be accompanied by a corresponding decrease in the free energy of formation of the transition state leading to that intermediate (the Evans-Polanyi principle). Yet in the area of non-classical ions the formation of stable bridged species is frequently postulated in the absence of significant rate accelerations. It is here suggested that both anomalies may have their origin in the failure of current theory to recognize that the stereochemistry of substitution in rapidly equilibrating cations and ion pairs may proceed with retention of configuration, in a manner similar to that now postulated for bridged ions and ion pairs. It is proposed that the formation of stable bridged species should be accompanied both by large rate enhancements and retained stereochemistry of substitution. In cases involving such stereochemistry without significant rate enhancements, the possibility should be considered that the system involves rapidly equilibrating cations or ion

pairs and not a resonance-stabilized bridged cation. The symmetrically substituted β -arylethyl derivatives appear to offer full possibilities for systematic structure variations which would transform the cations produced from class A to B, and finally to C. The present paper undertakes a detailed examination of the available evidence with respect to symmetrically substituted β -phenylethyl derivatives. It is concluded that the data for these phenyl (unsubstituted aryl) derivatives fail to reveal any significant rate accelerations in their acetolyses and only slight rate accelerations in their formolyses. Yet the acetolysis results for 3-phenyl-2-butyl and related systems clearly exhibit predominant retention. Current theory interprets the reactions of these systems as proceeding through concurrently formed static classical (class A) and static bridged (class C) intermediates. It is proposed that both the absence of significant rate accelerations and the lack of any theoretical justification for the absence of the intermediate class of equilibrating cations (class B) make it desirable to reopen the question and to consider the possibility that the reactions of these systems may involve a pair of rapidly equilibrating cations or ion pairs, rather than the stable phenonium ion now postulated by current theory. A possible model for the solvolysis of 3-phenyl-2-butyl tosylate is proposed.

It was suggested 25 years ago that the isobornyl and the hydrocamphenyl cations might be a mesomeric species, rather than an equilibrating pair.⁴ This proved to be a popular proposal and the possibilities for nonclassical structures were thoroughly investigated over a wide range of carbonium ion systems.⁵ Non-classical structures have been considered for the following cations (among others): ethyl,^{6a} *n*-propyl,^{6b} 2-

(4) T. P. Neville, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939).

(5) For excellent reviews, consult (a) A. J. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, and (b) B. Capon, *Quart. Rev. (London)*, 18, 45 (1964).

(6) (a) J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, 74, 5943 (1952); (b) J. D. Roberts and M. Halmann, *ibid.*, 75, 5759 (1953); (c) J. D. Roberts, W. Bennett, R. E. McMahon, and E. W. Holroyd, Jr., *ibid.*, 74, 4283 (1952); (d) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949; (e) J. D. Roberts and J. A. Yancey *J. Am. Chem. Soc.*, 77, 5558 (1955); (f) P. D. Bartlett, *J. Chem. Educ.*, 30, 22 (1953); (g) R. Heck and V. Prelog, *Helv. Chim. Acta*, 38, 1541 (1955); (h) D. J. Cram and J. Tadanier, *J. Am. Chem. Soc.*, 81, 2737 (1959); (i) S. Winstein and N. J. Holness, *ibid.*, 77, 5562 (1955); (j) J. D. Roberts and C. M. Regan, *ibid.*, 75, 2069 (1953); (k) D. J. Cram, *ibid.*, 71, 3863 (1949); (l) S. Winstein and

(1) Presented in part at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 27, 1961, and at the Symposium on 'The Transition State,' Sheffield, England, April 4, 1962. A brief summary of these views is contained in the published lecture at the latter meeting: H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, pp. 140-158, 174-178. These views were discussed in detail at the Reaction Mechanisms Conference at Brookhaven National Laboratory, Upton, N. Y., Sept. 5, 1962.

(2) Postdoctorate research associate, 1960-1961, on Project AT(11-1)-170 supported by the Atomic Energy Commission.

(3) Postdoctorate research associate, 1961-1963, on Project AT(11-1)-170 supported by the Atomic Energy Commission.

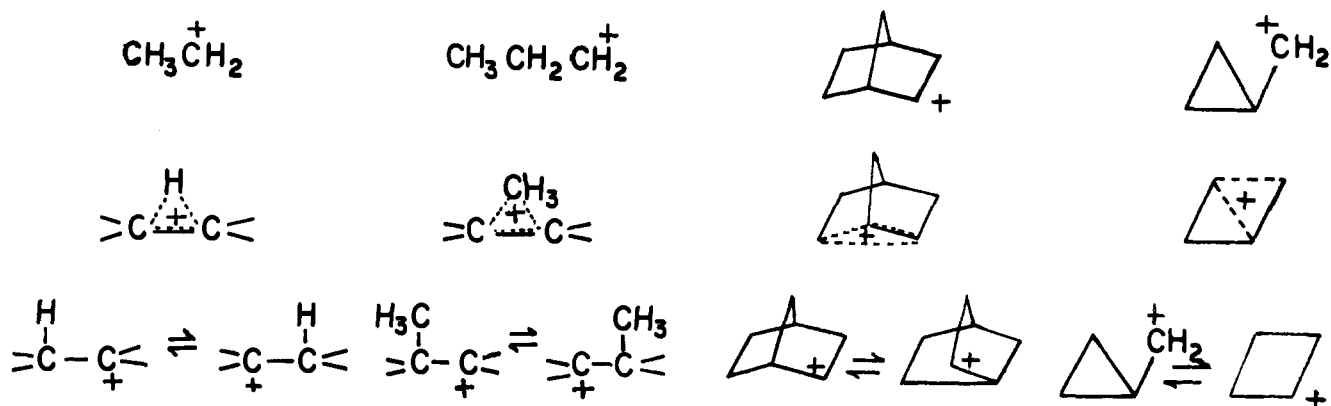


Figure 1. Carbonium ions for which electron-deficient nonclassical structures have been considered.

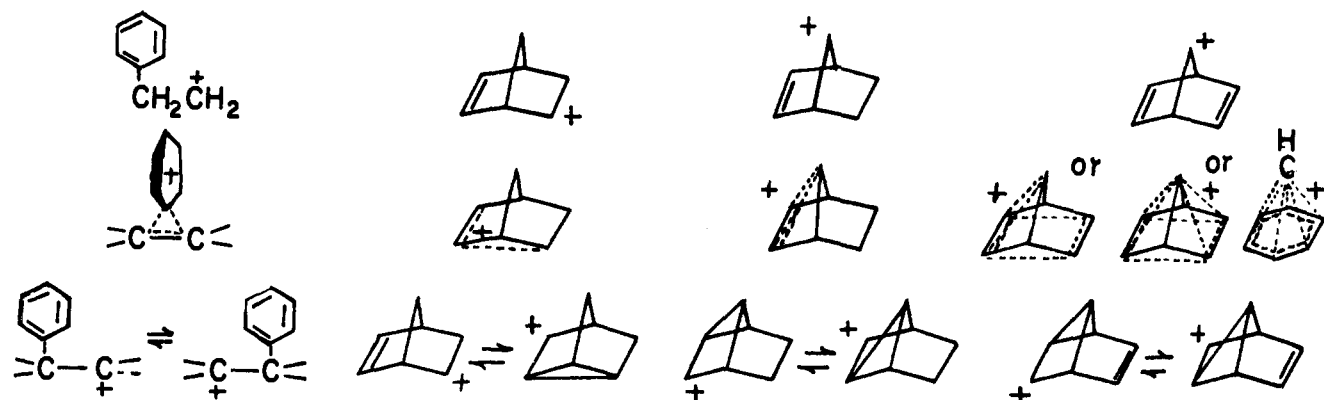


Figure 2. Carbonium ions for which normal or electron-sufficient nonclassical structures have been considered.

butyl,^{6c} *t*-butyl,^{6d} pentamethylethyl,^{6e} tri-*t*-butylcarbinyll,^{6f} cyclodecyl,^{6g} 3-cyclohexyl-2-butyl,^{6h} 4-*t*-butylcyclohexyl,⁶ⁱ β -phenylethyl,^{6j} 3-phenyl-2-butyl,^{6k} cholesteryl,^{6l} cyclopropylcarbinyll,^{6m} norbornyl,⁶ⁿ hydrocamphenyl,^{6o} dehydronorbornyl,^{6p} etc.

Some typical cations represented in their classical and proposed nonclassical structures are shown in Figures 1 and 2.

In those cases for which nonclassical structures have been considered, it is possible to represent the intermediate as an equilibrating pair of cations. On this basis the nonclassical structures would represent the transition states for the equilibrating systems (Figures 1 and 2). We are faced with the problem of deciding, in individual systems, whether the structure of the carbonium ion is best represented in its classical form, or as an equilibrating pair (or set) of cations, or as a resonance hybrid so stable that we need not consider these prior alternative structures.

By the use of isotopic tags, it has been possible to demonstrate in a large number of systems that the carbonium ion can be formed and transformed into products without the equilibration of the carbon atoms in the structure required by the bridged species. In these cases (ethyl,^{6a} 2-butyl,^{6c} cyclodecyl,⁷ *n*-propyl,^{6b} pentamethylethyl,^{6e} β -phenylethyl^{6j}), the energy pro-

files for the systems must resemble that shown in Figure 3a, where the potential barrier for interconversion of the ions is higher than the potential barrier for reaction of the ions with the solvent or other nucleophile. Consequently, in these cases the preferred path is one in which the ion is formed and transformed into product without significant equilibration of the tag.

In other cases (norbornyl,⁸ cyclopropylcarbinyll,⁹ 3-phenyl-2-butyl,¹⁰ etc.) equilibration of the tag approaches that predicted by the nonclassical structure.¹¹ Accordingly, these systems cannot be represented as a static classical structure, but must involve either bridged ions or their kinetic equivalent, a rapidly equilibrating pair (or set) of cations.

Consider what will happen to the energy profile as the potential barrier for interconversion of a pair of symmetrical cations becomes lower and lower (Figure 3a). As the barrier becomes equivalent to the barrier representing reaction of the cation with the solvent or other nucleophile, equilibration will compete with conversion of the ions into products.¹² With further

(8) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954).

(9) R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(10) W. B. Smith and M. Showalter, *ibid.*, **86**, 4136 (1964).

(11) In the norbornyl case the distribution of the radioactive carbon tag was considerably greater than anticipated purely on the basis of the bridged structure and it was necessary to consider rapid interconversion of isomeric cations through hydride shifts in order to account for the experimental results.⁸

(12) It has been concluded that unimolecular rearrangements can occur within a carbonium ion with frequencies in excess of solvent and ion-pair relaxations: P. S. Skell and R. J. Maxwell, *J. Am. Chem. Soc.*, **84**, 3963 (1962).

R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948); (m) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951); (n) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (o) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, **168**, 65 (1951); (p) S. Winstein, H. M. Walborsky, and K. C. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).

(7) V. Prelog and J. G. Traynham, "Molecular Rearrangements," P. de Mayo, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963.

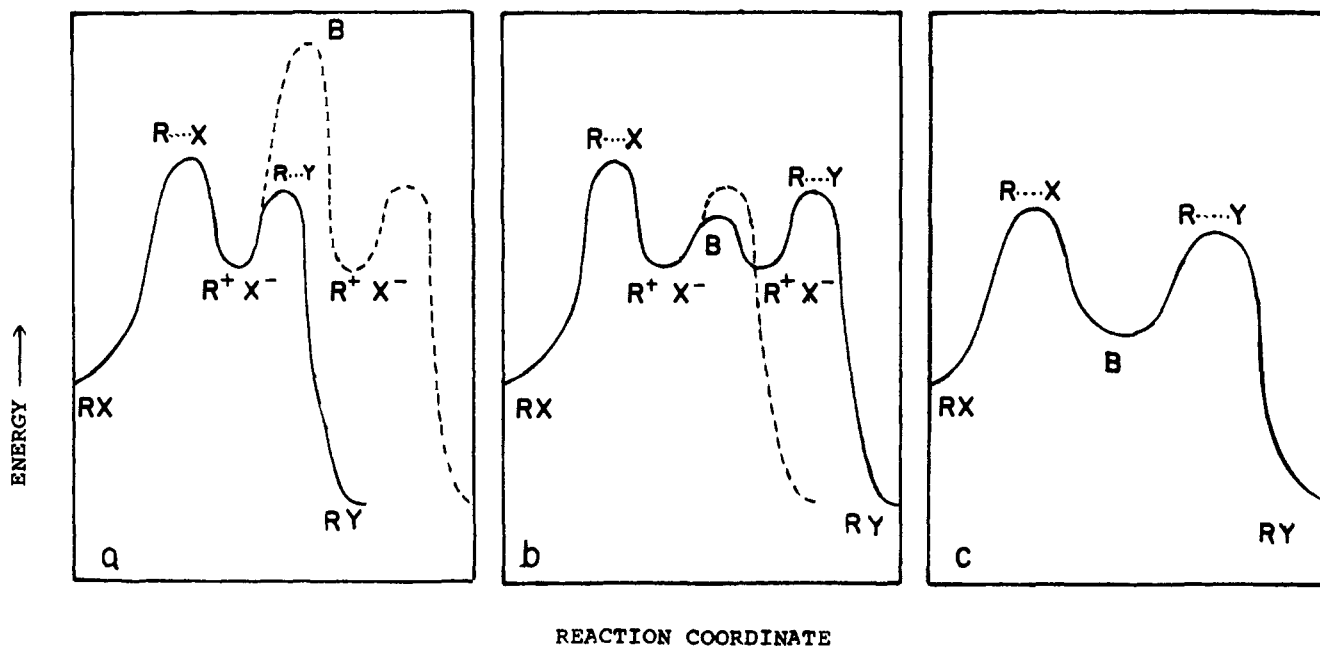


Figure 3. Representative energy profiles to illustrate carbonium ion reactions proceeding through (a) nonequilibrating cations, (b) equilibrating cations, and (c) bridged or nonclassical cations.

decrease in the barrier, equilibration of the ions will be favored over reaction with the solvent (Figure 3b). Finally, as the barrier is lowered still more, we should expect that ionization will occur directly to the stable bridged species (Figure 3c).

Consequently, we should expect carbonium ions to exhibit a regular transition from classical, essentially static systems, through classical equilibrating pairs, with varying frequencies of interconversion, to stabilized bridged nonclassical species.

Yet, in current theory, the discussion of carbonium ion structures is almost entirely in terms of either static classical structures or bridged nonclassical structures. The possibility that carbonium ions might exist as an appreciable intermediate class of rapidly equilibrating systems with unique stereochemical characteristics has been largely overlooked.

It would appear that the reason for this possible oversight has been the tacit assumption that the stereochemistry of substitution of an equilibrating pair of ions must be the same as that observed in static classical systems. The suggestion advanced by Winstein that the stereochemical results corresponding to the forma-

tion and opening of a bridged ion, $>C \equiv C<$, might, in some cases, be simulated by a dynamic pair of isomeric cations¹³ has not received adequate consideration. We believe that there is considerable merit in this proposal and suggest that the question of carbonium ion structure should be reopened to ascertain whether or not certain of the ions now assigned bridged or nonclassical structures may not be better represented as equilibrating pairs. With the rich variety of organic structures available, changes in any characteristic generally occur by small, almost indistinguishable in-

(13) S. Winstein and B. C. Morse, *J. Am. Chem. Soc.*, 74, 1133 (1952).

crements. It would be truly amazing if carbonium ions were to fall only into the static classical structure, represented by the energy profile of Figure 3a, or the static bridged structure, represented by the energy profile of Figure 3c, with almost no instances of the intermediate possibility, equilibrating cations,¹⁴ represented by Figure 3b.

Accordingly, we have for several years been pursuing a research program attempting to provide an answer to the question whether many of the carbonium ions now represented as nonclassical bridged structures may not be better represented as an equilibrating pair of ions. For this objective, the symmetrically substituted β -arylethyl derivatives appear to offer unusual possibilities for systematic variations which would transform them from static classical ions (Figure 3a), to equilibrating classical ions (Figure 3b), to static bridged ions (Figure 3c).¹⁵

The present paper is restricted to an examination of the available data for symmetrical β -phenylethyl systems.¹⁶ Derivatives containing activating groups in the aromatic nucleus will be considered in a later paper.

(14) Perhaps the only generally accepted instances of such cations at present is the 1,2,2-triphenylethyl system, to be discussed later in this paper, and the 1,2-di-*p*-anisylnorbornyl cation: P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *ibid.*, 85, 479 (1963).

(15) For example, as discussed later in this paper, the experimental data reveal little or no rate acceleration in the solvolyses of 3-phenyl-2-butyl derivatives. On the other hand, the data indicate modest rate accelerations of approximately 100 in the corresponding reactions of 3-*p*-anisyl-2-butyl, with enormous rate accelerations of the order of 1,000,000-fold in the solvolysis of the conjugate base of 2-(*p*-hydroxyphenyl)ethyl bromide. (See ref. 5b for data and pertinent references.) Yet, in spite of these enormous differences in the effects of the neighboring aryl groups, current theory interprets all of these solvolyses as proceeding through the formation of similar bridged aryl intermediates.

(16) A review of the data for such systems and a defense of the phenonium ion interpretation has recently appeared: D. J. Cram, *J. Am. Chem. Soc.*, 86, 3767 (1964). Many of the arguments presented in the present discussion were made available to Professor Cram prior to publication of his review, so that his paper may be considered in the nature of a rebuttal of the conclusions reached in the present study.

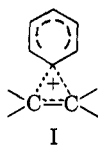
Basic Considerations

In his original study of the 3-phenyl-2-butyl system^{17,18} Cram stated that the results "unequivocally demonstrate for the first time the existence of a discrete molecular species, a carbocyclic three-membered carbonium ion as an intermediate in a Wagner-Meerwein rearrangement in an acyclic system."¹³ [(13) Such an intermediate represents not a transition state (maximum in a potential energy curve) but an actual intermediate ion containing a three-membered ring and situated at a minimum in the curve of potential energy vs. reaction coordinate.] Later he stated¹⁹: ". . . evidence was presented for the existence of a cyclic bridged ion² as a discrete intermediate in the phenyl migration that occurs during the solvolysis of the tosylates (*p*-toluenesulfonates) of the various stereoisomers of 3-phenyl-2-butanol, 2-phenyl-3-pentanol, and 3-phenyl-2-pentanol. [(2) This type of ion subsequently will be referred to as a "phenonium ion."²]"

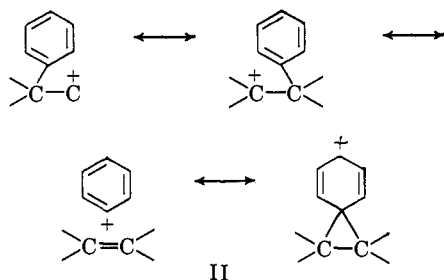
We shall adopt Professor Cram's definition and shall utilize the term "phenonium ion" to refer to a phenyl bridged species, containing a three-membered carbocyclic ring.²⁰

We shall utilize the term "participation" to refer to that stabilization of the transition state which results from bonding of the developing electron-deficient center with the neighboring group (phenyl in the cases under consideration in this paper).

In spite of the fact that phenonium ions have been with us for some 15 years, there is, as yet, little agreement as to their precise structural representation. Streitwieser utilized the structure I.



This structure is considered to be a resonance hybrid of the four structures shown in II.^{21,22}



(17) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949).

(18) The authors are indebted to Professor K. Freudenberg for calling their attention to his early proposal that such bridged aryl systems may be involved in maintaining stereochemical configuration in the reactions of the tetramethyl ether of catechin: K. Freudenberg, *Sitzungsberichte der Heidelberger Akademie der Wissenschaften*, June 19, 1927.

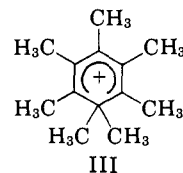
(19) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2129 (1952).

(20) The phenonium ion is usually considered to be a symmetrical species in a symmetrical system, although the possibility of an unsymmetrical structure was briefly considered for the 4-phenyl-3-hexyl system: (a) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953); (b) D. J. Cram, H. L. Nyquist, and F. A. Abd Elhafez, *ibid.*, **79**, 2876 (1957).

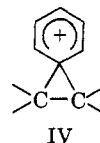
(21) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952).

(22) Professor Walter Hückel in a manuscript now in print has raised detailed objections to representation of the phenonium ion as a resonance hybrid of such high energy structures. It is true that in terms of the classical resonance approach, one would not anticipate any

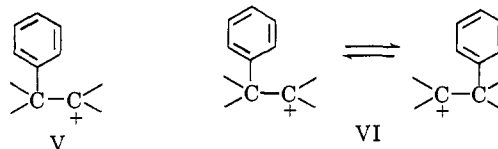
We see no advantages to such an elaborate structural representation of the phenonium ion. After all, it is merely the internal alkylation product of the β -phenylethyl cation and must correspond in structure to σ -complexes. Heptamethylbenzenonium ion²³ represents an acyclic analog (III).



Consequently, we shall use the related structural formula IV to represent the phenonium ion.



The question we shall consider in the present paper is whether the available kinetic and stereochemical data for symmetrical β -phenylethyl systems are better correlated by the usual assumption of a stable phenonium ion intermediate, or whether the data are more consistent with the formation of a classical ion (V), which in some instances may be in rapid equilibrium with its identical isomeric species (VI).

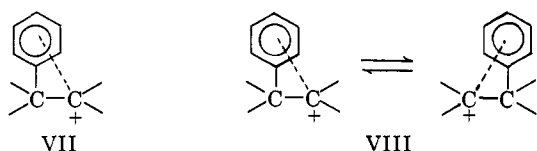


In the latter case, the transition state for the transformation of one isomer into the other would be quite similar structurally to the proposed phenonium ion. However, it would represent a maximum in the reaction coordinate, rather than occupying a minimum, representing a species of considerable greater stability than the corresponding classical ion.

There exists the possibility of a wide range of interactions between the electron-rich aromatic ring and the electron-deficient center, ranging from the purely classical structure, shown in V, at one extreme, to the symmetrical bridged species, the phenonium ion, at the other extreme. Intermediates involving such interaction between the π -cloud of the aromatic ring and the carbonium center, either in a static ion or in an equilibrating pair, may be represented as shown in VII and VIII.

large resonance stabilization for a system based upon such strained structures. However, we are still dependent upon experiment to guide theory. Should experiment establish that the phenonium ion is a stable species in certain systems, we would experience no difficulty in modifying current theory to cover this development. It is for this reason that we have preferred to examine the phenonium problem utilizing experimental, rather than theoretical considerations, such as those employed by Professor Hückel. The authors are indebted to Professor Hückel for permitting them to see his manuscript prior to publication.

(23) W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).



In view of the wide-spread tendency for transitions in organic chemistry to be gradual, it would be surprising if cases of this kind did not exist. However, since we have not been able to find any evidence for any significant phenyl participation in any of the symmetrical systems here examined, we need not consider this possibility further at this time.²⁴

It is currently recognized that ionization first proceeds to an ion pair which may undergo reaction to products without significant dissociation to a free carbonium ion. In the discussion we shall not attempt at this time to analyze the precise role of ion pairs or free carbonium ions in the reactions of the different systems under discussion. Consequently, for simplicity, we shall represent the carbonium ion either as a static classical, an equilibrating pair, or a bridged species, without attempting to show the anion which may be intimately associated with the cation in the actual intermediate formed in the reaction.

One of the problems to be considered in the present series of papers is the question whether certain representative carbonium ions currently assigned bridged or nonclassical structures may not be better represented as rapidly equilibrating cations. In order to avoid ambiguity it is desirable that we define both of the terms, "nonclassical" and "equilibrating cations."

Equilibrating cations may be defined as cations which undergo equilibration at a rate that is fast compared to the rate of reaction of the system with solvent or other nucleophile.

The term "nonclassical" offers some difficulty in its definition. It has been widely used for many years, and it is desirable that its definition conform to its customary usage. It is unfortunate that it does not appear to have been defined explicitly, in spite of its wide-spread use. The term appears to have been first used by Roberts^{6m} in connection with the proposed tricyclobutonium structure for the cyclopropylcarbiny cation. The *structure* proposed was clearly different from the classical *structure* for the intermediate discussed. The second appearance is due to Winstein⁶ⁿ who refers to the "non-classical structures" of norbornyl, cholesteryl, and 3-phenyl-2-butyl cations. The third such reference that we have located is the statement of Roberts^{6a}: "Recent interest in the structures of carbonium ions has led to speculation as to whether the ethyl cation is most appropriately formulated as a simple solvated electron-deficient entity, CH_3CH_2^+ , a "nonclassical" bridged ethylene-protonium ion,

(24) It should be emphasized that the methods currently available to us do not permit us to distinguish between structures involving no interaction between the π -cloud and the electron-deficient center (V and VI), and structures involving small interactions (VII and VIII). Where the interactions become sufficiently large as to influence the kinetics, we are faced with the question of deciding whether the structure of the intermediate is best represented as a symmetrical phenonium ion or as a π -bridged species. This question will be considered in detail in a paper under preparations dealing with the behavior of symmetrical β -arylethyl derivatives in which the aryl group contains activating substituents. We have reasons for proposing that the solvolysis of certain β -anisylethyl derivatives proceeds through rapidly equilibrating π -bridged intermediates.

$\text{CH}_2=\overset{\text{H}}{\text{C}}-\text{CH}_2$, or possibly as an equilibrium mixture of the two ions." It is clear from these references that the emphasis is on structures that differ markedly from the usual classical structures.

Consequently, we suggest the following definition. A nonclassical carbonium ion is a carbonium ion in which the position in the structure of one or more atoms is markedly different from that predicted on the basis of classical structural principles.

For example, the equilibrating pair of β -phenylethyl cations would be assigned structures which follow simply from classical structural principles. The transition state for the equilibration must contain the phenyl group halfway between the two carbon atoms. The phenonium ion concept proposes that this structure is not a transition state, but a stable intermediate. Clearly, this structure differs from the classical structure and is "nonclassical" according to the proposed definition.

Similarly, the norbornyl cation either exists as a rapidly equilibrating pair of classical ions with a transition state corresponding to the proposed mesomeric species, or this species is so stable that one no longer needs to consider the classical structures. In the classical structure the C-1-C-6 distance would be the usual short single-bond distance, and the C-2-C-6 distance would be a much longer nonbonded distance. In the proposed nonclassical ion these two distances are equivalent. Clearly, this ion would conform to our definition.

These two examples illustrate two different varieties of nonclassical ions. The β -phenylethyl ion possesses sufficient electrons for all the required bonds. It requires no extension of generally accepted bonding concepts to account for the structure. The sole problem is that of deciding whether its stability corresponds to that of a transition state between the equilibrating ions, or to a stable intermediate more stable than the classical ions.

On the other hand, the norbornyl cation does not possess sufficient electrons to provide for all of the bonds required by the proposed structures. One must propose a new bonding concept, not yet established in carbon structures.²⁵

It may be desirable to have separate terms to refer to these two classes of proposed nonclassical structures. It is suggested that the first group be termed "normal" or "electron-sufficient" nonclassical structures, and the second group be termed "electron-deficient" nonclassical structures.

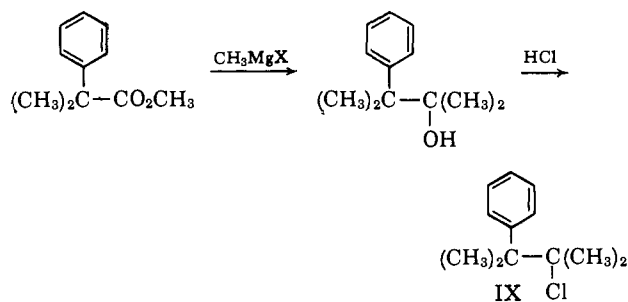
A major difference between an equilibrating pair of cations and a resonance hybrid is one of stability. Equilibration is not believed to affect the energy of the equilibrating species, whereas resonance must produce an ion of increased stability. Ever since the first applications of quantitative methods to organic chem-

(25) The existence of methyl bridges in the dimer of trimethylaluminum has been offered as justification that such half-bonds may be possible in carbon structures.^{6a} However, trimethylaluminum exists in the bridged dimeric structure only in the gas phase or in hydrocarbon media. In ethyl ether or other solvating media, it dissociates to form the "classical" addition compound of trimethylaluminum. It should be recalled that we are exploring the structure of carbonium ions in the excellent solvating media normally utilized for solvolytic reactions. The precise structure of these carbonium ions in the gas phase is an interesting, but distinct problem.

istry, it has been a cherished notion that lowering the standard free energy of the reaction product or first intermediate must lower the standard free energy of the transition state.²⁶ Consequently, it would be anticipated that solvolytic reactions leading to the formation of a resonance-stabilized bridged cation should exhibit significant rate enhancements over comparable reactions leading to the formation of either static or equilibrating classical cations. Consequently, it appears desirable to subject the available rate data on the solvolysis of symmetrical β -phenylethyl derivatives to detailed scrutiny in order to establish whether rate enhancements attributable to phenyl bridging can be demonstrated. In the absence of such rate enhancements, it would appear difficult to justify the postulated formation of a stable bridged species in these reactions.

Rate Studies

Tertiary Systems. A search of the literature revealed no kinetic data for the solvolysis of any tetra-substituted β -phenylethyl derivatives. Accordingly, 2,3-dimethyl-3-phenyl-2-butanol was synthesized and transformed into the chloride (IX) by treatment with hydrogen chloride.



We also synthesized 3,3-dimethyl-2-phenyl-2-butanol and its chloride to establish the absence of methyl group rearrangements in the course of preparing the chlorides.

2,2-Dimethylphenylacetic acid, m.p. 77–78° (Columbia Organic Chemicals), was converted to the methyl ester, b.p. 65–66° at 1 mm., in 83% yield, by treatment with diazomethane in ether. The ester was treated in the usual manner with methylmagnesium iodide to form 2,3-dimethyl-3-phenyl-2-butanol, b.p. 81–82° at 1 mm., n_D^{20} 1.5218, in 80% yield.

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 79.46; H, 10.92. Found: C, 79.6; H, 10.8.

3,3-Dimethyl-2-phenyl-2-butanol, b.p. 130–132° at 28 mm., n_D^{20} 1.5048, was obtained from phenylmagnesium bromide and pinacolone. The two alcohols were converted to the chlorides by treating with dry hydrogen chloride at 0°. The lower layer of concentrated hydrochloric acid was separated with a capillary and the upper layer was dried over calcium chloride and utilized for the rate measurements without further purification.

Both chlorides underwent solvolysis in 80% aqueous ethanol at 25° to give good, unvarying first-order constants. Both chlorides were hydrolyzed in water to which alkali was added concurrently with the hydrolysis to maintain the solutions neutral. The solutions were

extracted with pentane. Gas chromatographic examination revealed 32% of 2,3-dimethyl-3-phenyl-2-butanol from the corresponding chloride and 37% of 3,3-dimethyl-2-phenyl-2-butanol from its chloride. No other alcohols were indicated in the chromatograms. (The remaining products were olefins which were not identified.) Consequently, it was concluded that the preparation of the chlorides and their solvolysis proceeds without molecular rearrangement. The rate constants for the two chlorides, together with data for related structures, are summarized in Table I.

Table I. Rate Constants for the Solvolysis of 2,3-Dimethyl-3-phenyl-2-chlorobutane and Related Derivatives in 80% Aqueous Ethanol at 25°

Compd.	$k_1 \times 10^5 \text{ sec.}^{-1}$	Relative rate
$(\text{CH}_3)_3\text{CCl}$	0.93 ^a	1.00
	1.12 ^a	1.25
	5.19 ^b	5.6
	1.78 ^c	1.91
	0.53 ^c	0.57

^a H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **71**, 1845 (1949). ^b H. C. Brown and R. K. Kornblum, *ibid.*, **76**, 5410 (1954). ^c Present study.

The low rate of solvolysis of the tertiary benzylic chloride, 3,3-dimethyl-2-phenyl-2-chlorobutane, is worthy of note. Presumably, the low rate is the result of steric inhibition of resonance, similar to that observed in the corresponding secondary derivative, α -phenylneopentyl chloride.¹³

The replacement of one of the β -methyl groups in 2,3,3-trimethyl-2-chlorobutane ($k_1 = 1.12 \times 10^{-5} \text{ sec.}^{-1}$) by an ethyl group results in an increase in the rate by a factor of roughly four ($k_1 = 5.19 \times 10^{-5} \text{ sec.}^{-1}$). This increase is attributed primarily to the greater steric requirements of the ethyl group. The increase in strain results in an enhanced rate of ionization.²⁷

The introduction of a phenyl substituent would be expected to exert an even larger steric effect, counterbalanced by the rate-retarding inductive influence of the aromatic ring. On the other hand, significant participation by phenyl would be expected to produce a marked rate enhancement. However, this is not ob-

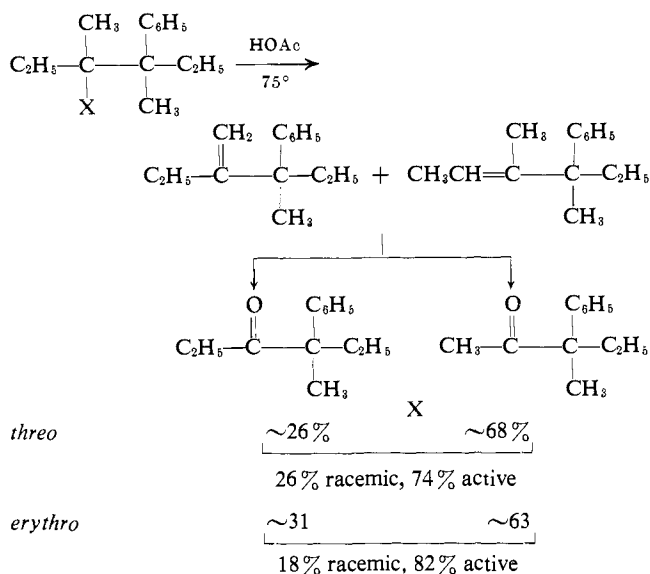
(26) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter V.

(27) H. C. Brown, *Science*, **103**, 385 (1946).

served. The rate constant for 2,3-dimethyl-3-phenyl-2-chlorobutane, $k_1 = 1.78 \times 10^{-5} \text{ sec.}^{-1}$, lies between the values for 2,3,3-trimethyl-2-chlorobutane and 2,3,3-trimethyl-2-chloropentane.

Clearly the data do not point to any significant phenyl participation in this tertiary-tertiary system.

The same conclusion is indicated by the published data on the products of acetolysis of the optically active *p*-bromobenzoates of *threo*- and *erythro*-3,4-dimethyl-4-phenyl-3-hexanol.²⁸ The products are largely the nonconjugated olefins, converted to the ketones *via* ozonolysis (X).



In the case of the acetolysis of 3-phenyl-2-butyl tosylate, the *threo* isomer gives almost completely racemic acetate, whereas the *erythro* isomer gives acetate with almost completely retained activity. This is the basis of the argument that the acetolysis proceeds through two isomeric phenonium ions.

In the present case, the *threo* and *erythro* isomers give very similar results. Although the authors originally discussed the results in terms of two phenonium ions (symmetric or *cis* from *threo* and asymmetric or *trans* from *erythro*) which readily interconvert,²⁸ the data clearly point to a failure of the phenyl group to control the stereochemistry of the reaction.¹⁶

Without either kinetic evidence or stereochemical evidence to support the formation of a phenonium ion in the tertiary-tertiary system, we must conclude that these derivatives must undergo ionization to essentially classical ions.

This is not too surprising a conclusion, since it has been pointed out that the ability of a cationic center to interact with a neighboring group decreases from primary to secondary.²⁹ Evidently a tertiary ion is so stable that it does not interact significantly with a neighboring phenyl group even when the latter is favorably located at a neighboring quaternary center.

Primary System. Since the tertiary carbonium ion is too stable to interact with the neighboring phenyl group, it is appropriate to turn our attention to the far more active primary carbonium ion. Since we are focusing our attention on symmetrical structures, we are

(28) D. J. Cram and J. D. Knight, *J. Am. Chem. Soc.*, **74**, 5835 (1952).

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

restricted to β -phenylethyl derivatives. Fortunately, such derivatives have been subjected to intensive study.

An approximate calculation of the difference in energy between the simple classical ion and the phenonium ion for the β -phenylethyl cation suggests that the classical structure may be expected to be more stable to the extent of about 17 kcal./mole.^{61,30} However, such calculations are interesting and instructive, but cannot presently serve as a basis for theoretical conclusions. We must still depend upon experimental observations.

The rates of solvolysis of β -phenylethyl tosylate have been determined in ethanol, acetic acid, and formic acid (Table II).

Table II. Rate Constants for the Solvolysis of Ethyl Tosylate and β -Phenylethyl Tosylate at 75°

Solvent	First-order rate constant sec. ⁻¹ × 10 ⁶	
	Ethyl tosylate ^a	β -Phenylethyl tosylate ^b
Ethanol	29.8	7.08
Acetic acid	0.772	0.288
Formic acid	18.9	39.4

^a S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952). ^b Ref. 31.

The rate of ethanolysis of β -phenylethyl tosylate is smaller than that of ethyl tosylate by a factor of 4. Even in acetic acid, a less nucleophilic solvent, the rate for β -phenylethyl tosylate is smaller than that of ethyl tosylate by a factor of 2.7. Clearly, we must agree with the authors' conclusion that phenyl participation is not a significant factor in solvolysis under these conditions.³¹

In formic acid the solvolysis of β -phenylethyl tosylate proceeds at a rate that is 2.1 that of ethyl tosylate. Consequently, only in this solvent do the data indicate some degree of participation by the phenyl group.

If a phenonium ion is formed which is so stable that one does not have to consider the competitive formation of both the ions, classical and phenonium, the latter must be more stable than the former by several kilocalories per mole. Normally we would expect a significant fraction of this additional stabilization to make itself felt in the transition state. A factor of 2 corresponds to stabilization of the transition state by a relatively small factor.³² Consequently, we must conclude that the data indicate a relatively small participation, much smaller than we would expect for the formation of a stable phenonium ion, and small enough that it could be associated with the formation of an equilibrating pair of ions slightly stabilized by small

(30) Attention is called to the detailed discussion by Hückel²² of the calculations made by M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954), on the proposed phenonium structure of the β -phenylethyl cation.

(31) S. Winstein, C. R. Lindgren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

(32) It is pertinent to recall that the ethanolysis of the conjugate base of 2-(*p*-hydroxyphenyl)ethyl bromide exhibits a rate enhancement greater than 10⁶ even though the solvent is highly nucleophilic and the leaving group is bromide, rather than the much less nucleophilic brosylate: R. Baird and S. Winstein, *ibid.*, **85**, 567 (1963).

interactions of the π -cloud of the aromatic ring with the electron deficient center.³³

One case of a large rate enhancement by neighboring phenyl in a β -phenylethyl derivative has been observed. The demercuration of β -phenylethyl mercuric perchlorate exhibits a rate enhancement of 8.3 in acetic acid (75°) and one of 30 in formic acid (50°) over the rate exhibited by the corresponding ethyl derivative.³⁴ This marked difference in the results realized in the demercuration reaction from those realized in the solvolysis experiments suggests a major difference in the nature of the cationic species produced in the two reactions. Perhaps the demercuration reaction produces an essentially unsolvated isolated cation or a solvent separated species, in contrast to the solvated intimate ion pair produced in the solvolytic reaction. It would be of interest to have stereochemical and isotopic results in the mercury systems to contrast with the corresponding solvolytic data.

Study of the solvolysis of β -phenylethyl tosylate containing a radiotag in the α -position revealed that the tagged atom rearranged to the β -position to the extent of 0.3% in ethanol, 5.5% in acetic acid, and 45% in formic acid.³⁵ These results correspond to the formation of 0.6, 11, and 90% of the phenonium ion in these three solvents, provided it is assumed that the formation of a phenonium ion provides the only mechanism to achieve equilibration. It should be recalled that the phenonium ion requires full equilibration of the two atoms of the ethyl system, but full equilibration may be achieved through an equilibrating pair of ions and does not require that the reaction proceed through the phenonium ion. Consequently, it would appear that the phenonium ion is clearly not involved in any important extent in ethanolysis and acetolysis, and it can, at most, be only partially involved in formolysis.³⁶

In postulating that these exchange results involve only classical and bridged intermediates, we are again faced by the problem of accounting for the absence of the intermediate class of equilibrating cations or ion pairs.

It is desirable at this point to call attention to the commonly overlooked possibility that the use of a solvent of low nucleophilicity, such as formic acid, may have consequences other than that of diminishing the nucleophilic contribution to the ionization step. Such a solvent should exhibit decreased rates of reaction with the ions or ion pairs produced in the ionization stage. A longer lifetime for the intermediate can result in increased rearrangement or equilibration of a tag.⁶¹

The rates of acetolysis of 2-phenylethyl-1,1- d_2 and 2-phenylethyl-2,2- d_2 tosylates differ only insignificantly from the parent compound.³⁷ On the other hand, in

(33) In this discussion we are ignoring the contribution of the inductive effect of the phenyl group to the rate. We shall discuss this factor in detail when the data for the isomeric 3-phenyl-2-butyl systems are reviewed.

(34) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **85**, 367 (1963).

(35) C. C. Lee, G. P. Slater, and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1417 (1957). Since some rearrangements of the tag are observed in recovered tosylate, these figures must be reduced to obtain the actual equilibration which accompanies solvolysis: C. C. Lee, R. Tkachuk, and G. P. Slater, *Tetrahedron*, **7**, 206 (1959).

(36) It has been pointed out previously³¹ that in formic acid 2-phenylethyl is "slightly faster" than ethyl tosylate. This rate enhancement was attributed to participation by neighboring phenyl. However, it is not clear from the discussion whether the authors consider the small rate enhancement which is observed to be consistent with the formation of a symmetrical phenonium ion as the predominant intermediate in the reaction.

formolysis, 2-phenylethyl and 2-phenylethyl-2,2- d_2 tosylates react at the same rate, and with the 1,1- d_2 derivative undergoing acetolysis at a rate only 0.85 that of the other two isomers. These results led the authors to conclude that participation of the phenyl group is not important in acetolysis. Although participation is indicated in formolysis, they concluded that the relatively large difference in rate observed in the formolysis of the 1,1- d_2 and 2,2- d_2 isomers indicated that the transition state cannot resemble the proposed symmetrical phenonium intermediate at all closely. They suggest that the first intermediate following the transition state may be an unsymmetrically bridged species.

Finally, deamination of carbon-labeled β -phenylethylamine gave a product in which only 27% of the phenyl groups had migrated.⁶¹ This result cannot be rationalized with the sole intervention of a phenonium ion. In the absence of any compelling evidence to the contrary and with the knowledge of the lack of participation encountered in other deaminations,³⁸ it is clearly most satisfactory to regard this reaction as involving the partial equilibration of classical carbonium ions.

Summing up, both rate and product studies in the acetolysis of β -phenylethyl derivatives show no evidence for phenyl participation nor any evidence indicating that the phenonium ion is a significant intermediate. In formolysis there is observed a minor rate enhancement, involving a factor of 2.1, indicative of weak phenyl participation accompanied by major reshuffling of the phenyl group. However, the data fail to establish complete equivalence of the two carbon atoms, as required by the phenonium ion, so that the results can be accommodated either by requiring some path in addition to the phenonium ion, or by postulating that the reaction proceeds through an equilibrating pair of ions which reacts with solvent before complete equilibration has been achieved.

Secondary Systems. In the tertiary-tertiary systems, the failure to observe significant phenyl participation is attributed to the high stability of the tertiary carbonium ion. The tertiary cation is too stable to require assistance from the neighboring phenyl. The failure to observe significant phenyl participation in the primary-primary system is attributed to the open nature of a primary cation. The back side of the developing carbonium ion is so open to solvation by the solvent that the neighboring phenyl substituent finds it difficult to compete.

Consequently, we are left only with the secondary-secondary systems in which we can hope to observe significant rate enhancements attributable to phenyl participation in a symmetrical system.

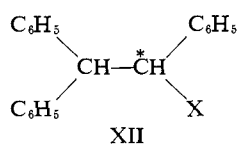
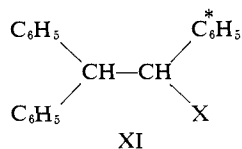
The 1,2,2-triphenylethyl provides a symmetrical system of the type we are examining. Unfortunately, no rate data are available which might bear on the question of the importance of phenyl participation in derivatives with this structure. Nevertheless, it has been subjected to exceedingly detailed examination by application of labeling techniques and the conclusion has been reached that the 1,2,2-triphenylethyl cation must be classical.³⁹

(37) W. H. Saunders, Jr., S. Asperger, and D. H. Edison, *J. Am. Chem. Soc.*, **80**, 2421 (1958).

(38) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

(39) W. A. Bonner and C. J. Collins, *ibid.*, **78**, 5587 (1956).

Solvolyses of 1-phenyl-labeled (XI) and α -carbon-labeled 1,2,2-triphenylethanol (XII), its acetate, and its tosylate were performed under identical conditions.^{40, 41}



In formic acid the products show a statistical redistribution of labeling, while in acetic acid or in aqueous acetone this is approached but not achieved. Were the reaction to proceed through the formation of a bridged ion as the sole intermediate, the preferred bridging should lead to the *trans*-phenonium ion. Any tosylate reformed by internal return on this ion would subsequently solvolyze through the same ion. This cannot lead to the migration of the labeled phenyl group and the resultant distribution of phenyl labeling would be the same as that of chain labeling. The experimental observation of a statistical distribution is not consistent with this.

By utilizing a reaction scheme involving only equilibrating classical ions, it proved possible to calculate to within the experimental precision the radiochemical distribution in the chain-labeled triphenylethyl system from the experimental data realized in the ring-labeled system.⁴¹

Further confirmation of this mechanistic scheme was provided by triple labeling experiments in which the acetate group in 1,2,2-triphenylethyl acetate was also labeled.⁴² When this compound was subjected to acetolysis, the rate of equilibration of all the labels was the same. Consequently, there is no internal return in this reaction and both bridged intermediates and completely concerted processes can be excluded as acceptable mechanisms.

The deamination of similarly double labeled 1,2,2-triphenylethylamine yields results entirely similar to those of the solvolytic reaction.⁴³ Consequently, the authors conclude that the deamination reaction likewise involves an equilibrating system of classical ions.

In spite of the conclusion that classical ions are involved in this reaction, a significant tendency is observed for retention of the original configuration of the optically active 1,2,2-triphenylethyl derivative.⁴⁴ For example, the acetolysis of active 1,2,2-triphenylethyl tosylate at 85° gives acetate with 55% gross (10% net) retention of configuration. The hydrolysis of the tosylate yields alcohol with approximately 65% (30% net) retention. Finally, deamination of the corresponding amine at -2° yields product with 75% (50% net) retention. Although these retentions are considerable below the 95% retention of configuration observed in the acetolysis of 3-phenyl-2-butyl tosylate, the results do suggest the possibility that we are observing the results of a trend, rather than totally different phenomena requiring totally different intermediates for their interpretation.

(40) W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **75**, 5372 (1953).

(41) C. J. Collins and W. A. Bonner, *ibid.*, **77**, 92 (1955).

(42) W. A. Bonner and C. J. Collins, *ibid.*, **77**, 99 (1955).

(43) W. A. Bonner and C. J. Collins, *ibid.*, **78**, 5587 (1956).

(44) C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959).

Finally, the authors have demonstrated that all of the available data on the deamination of optically active 1,2,2-triphenylethylamine can be correlated quantitatively, with excellent precision, in terms of a mechanism involving open, equilibrating classical ions.⁴⁵

Consequently, there can be little room for doubt that the 1,2,2-triphenylethyl cation does not involve phenyl bridging. Presumably, this is the result of the stability of the electron-deficient center. Although the ion is secondary, it is benzylic in character and so approaches in stability the tertiary cation previously considered.⁴⁶

In 1948 Winstein and his co-workers introduced a simple, but ingenious procedure for demonstrating the importance of participation by neighboring groups.⁴⁷ In the absence of participation, similar rates would be anticipated for the acetolysis of the *cis*- and *trans*-2-substituted cyclohexyl brosylates. Indeed, the rate of solvolysis for *trans*-2-chloro is no more than a factor of four greater than that of *cis*, and it was concluded that participation is not a significant factor in this case. On the other hand, *trans*-2-bromocyclohexyl brosylate undergoes solvolysis at a rate that is 800 times greater than that of the *cis* isomer, while a rate enhancement of 1,000,000-fold is indicated for *trans*-2-iodo. Clearly rate enhancements of this order of magnitude can be used to justify the formation of relatively stable bromonium and iodonium ions as intermediates.⁴⁸ Consequently, we next turned our attention to an examination of the isomeric *cis*- and *trans*-2-phenylcyclopentyl and -cyclohexyl derivatives in order to see whether this technique might provide evidence for major phenyl participation adequate to support the conclusion that a phenonium ion intermediate is involved in their solvolytic reactions.

Rate data for the solvolysis of *cis*- and *trans*-2-phenylcyclopentyl derivatives have not yet appeared in the literature. However, rate data for the acetolysis of *trans*-2-anisylcyclopentyl brosylate are available.⁴⁹ Although the activated anisyl group might be expected to favor participation, the fact is that the observed rate constant, $13.1 \times 10^{-5} \text{ sec.}^{-1}$ at 50°, is essentially identical with the rate constant for the parent compound, cyclopentyl brosylate, $12.9 \times 10^{-5} \text{ sec.}^{-1}$.⁵⁰ It is also reported that in the acetolysis of *trans*-2-phenylcyclopentyl brosylate the possibility for phenyl participation does not influence the stereochemistry of the reaction.⁵¹ Consequently, there appears to be no

(45) C. J. Collins and B. M. Benjamin, *ibid.*, **85**, 2519 (1963).

(46) In this connection attention is called to the interesting footnote³⁹ "(4) The referee has commented that "the present system is distinctly less favorable on all counts for the non-classical ions to be of comparable stability to their open ions" and further has expressed the opinion that our present and previous work might be "quoted as evidence against non-classical ions in general." Therefore our results should not be generalized as evidence against the existence of bridged or "non-classical" ions where they are strongly supported by the experimental facts."

(47) S. Winstein, E. Grunwald, and L. I. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948); E. Grunwald, *ibid.*, **73**, 5458 (1951).

(48) In spite of the large differences in the rate enhancements exhibited by the three halogens, all three halogens appear capable of controlling stereochemistry in aliphatic derivatives: H. J. Lucas and E. S. Gould, *ibid.*, **63**, 2541 (1941). This lack of correlation between the magnitude of the participation and the ability of chlorine to control stereochemistry apparently led to the first suggestion that stereochemical control might be achieved in a dynamic pair of ions, as well as in a bridged species: S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

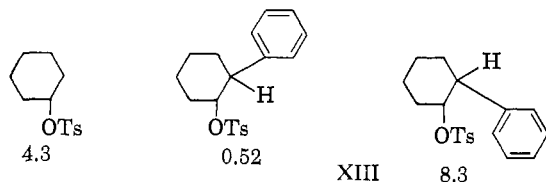
(49) A. H. Fainberg, G. C. Robinson, and S. Winstein, *ibid.*, **78**, 2777 (1956), quoting unpublished research of R. Heck.

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

(51) See footnote 7 in ref. 52, referring to unpublished results of R. Heck.

evidence favoring phenyl participation in the *trans*-2-phenylcyclopentyl system.

It has been pointed out that the angles in the cyclopentyl ring system in some instances may be less favorable for participation than those in the cyclohexyl system.⁵² Consequently, it might be anticipated that *cis*- and *trans*-2-phenylcyclohexyl tosylates might provide evidence for significant phenyl participation. Fortunately, this system has been subjected to a kinetic study.⁵³ The data are summarized below (XIII) ($k_1^{75^\circ} \times 10^5 \text{ sec.}^{-1}$).



It is evident that the *trans* isomer solvolyzes not faster, but slower, at one-eighth of the rate of the unsubstituted derivative. The *cis* isomer solvolyzes at a rate that is twice that of the parent compound and 16 times greater than that of the *trans* isomer. We can attribute the fast rate of the *cis* to steric acceleration combined with hydrogen participation (the major product isolated is 1-phenylcyclohexene). However, the slow rate of the *trans* isomer cannot be rationalized in terms of significant phenyl participation.

In the case of the cyclopentyl derivative we rationalized our failure to note phenyl participation to unfavorable bond angles. In the present case we can rationalize the failure to observe participation to the high cost in energy required to place the phenyl group in the axial position⁵⁴ where it would be in a favorable position to participate.

Finally, we turn our attention to the 3-phenyl-2-butyl system, for which the phenonium intermediate was originally proposed. Here we find that the rate of acetolysis is not greater, but smaller (0.6) than the observed rate of acetolysis of 2-butyl tosylate (1.00). The higher homologs, 4-phenyl-3-hexyl tosylate^{20a} and 2,5-dimethyl-4-phenyl-3-hexyl tosylate,^{20b} exhibit moderate increases, but no larger than would be attributed to the larger steric requirements of these systems and the relative abilities of methyl, ethyl, and isopropyl groups to stabilize a cation. The rate data are summarized in Table III.

A recent study with radiocarbon-labeled *threo*- and *erythro*-3-phenyl-2-butyl tosylate has indicated that the rate of formation of phenonium ion-tosylate ion pairs may be slightly greater in the *threo* than in the *erythro* isomer. This result implies that the energy differences between the ground state and the transition state for the ionization process must be very nearly alike. Yet, if the transition state involves an approach to a phe-

(52) S. Winstein and R. M. Roberts, *J. Am. Chem. Soc.*, **75**, 2297 (1953).

(53) I. Moritani, S. Nishida, and S. Murahasi, to be published. We are indebted to these authors for making their data available to us. Attention should also be called to ref. 21, where it is mentioned that the net effect of the phenyl group in *trans*-2-phenylcyclohexyl brosylate is more rate retarding than in 3-phenyl-2-butyl, quoting results from the Ph.D. Thesis of E. Grunwald, U.C.L.A., 1947. It is also pertinent that even with its highly activating substituent, *trans*-2-*p*-anisylcyclohexyl brosylate⁴⁹ undergoes acetolysis at a rate that is considerably slower (one-third) than the rate for cyclohexyl brosylate.

(54) D. Y. Curtin and S. Schmukler, *J. Am. Chem. Soc.*, **77**, 1105 (1955).

Table III. Rate Constants for the Solvolysis of 3-Phenyl-2-butyl Tosylate and Related Derivatives

Tosylate	Acetolysis (50°) $k_1 \times 10^5 \text{ sec.}^{-1}$	Formolysis (25°) $k_1 \times 10^5 \text{ sec.}^{-1}$
2-Butyl	0.43 ^{a,b}	5.07 ^{a,c}
3-Phenyl-2-butyl		
<i>threo</i>	0.24 ^b	22.8 ^d
<i>erythro</i>	0.27 ^b	28.0 ^d
4-Phenyl-3-hexyl		
<i>threo</i>	1.01 ^d	29.0 ^d
<i>erythro</i>	1.80 ^d	76.5 ^d
2,5-Dimethyl-4-phenyl-3-hexyl		
<i>threo</i>	1.66 ^{a,d}	10.3 ^{a,d}
<i>erythro</i>	10.6 ^{a,d}	85 ^{a,d}
3-Methyl-2-butyl		29 ^{a,d}
3-Cyclohexyl-2-butyl		
<i>threo</i>	2.60 ^e	59.5 ^e
<i>erythro</i>	6.2 ^e	159 ^e

^a Estimated from brosylate by using a conversion factor of 3. ^b Ref. 29. ^c Ref. a, Table II. ^d Ref. 20b. ^e Ref. 57.

nonium ion, the system must undergo considerably more steric crowding in the *threo* isomer, with its *cis*-methyl groups, than in the *erythro* isomer, with its *trans*-methyl groups. Consequently, this result likewise supports the conclusion that phenyl bridging cannot be significant in the transition state.

It has been suggested that the failure to observe any rate enhancement in the 3-phenyl-2-butyl system is the result of a significant rate-retarding inductive influence of the phenyl substituent.²⁹ If a factor of 10 is assigned to this factor, then the corrected rate would be sixfold greater than that of 2-butyl tosylate. It has been suggested that the proposed factor is too large, and Streitwieser has suggested that a factor of 8 be used.^{5a}

These attempts to correct for the rate-retarding inductive influence of the phenyl substituent have failed to take into account its rate-enhancing steric requirements. For example, it was pointed out earlier that 2,3-dimethyl-3-phenyl-2-chlorobutane undergoes solvolysis at a rate that is slightly faster than 2,3,3-trimethyl-2-chlorobutane (Table I). In this case the rate-enhancing influence of the phenyl group counterbalances its rate-retarding inductive effect. Similarly, *cis*-2-phenylcyclohexyl tosylate undergoes acetolysis at a rate that is twice that of the parent compound.⁵³ This case is rendered ambiguous by the possibility that hydrogen participation might be an appreciable factor in the observed rate. In the case of 1-phenyl-*endo*-norbornyl tosylate a rate that is 0.7 that of the parent compound has been observed.⁵⁵ This case would appear to be unambiguous; there is no evident means whereby the phenyl group can participate in the ionization step.

In any event, we find ourselves attempting to evaluate very small factors. In the case of *cis*- and *trans*-2-chlorocyclohexyl brosylate, the observation of a small factor of 4 favoring the *trans* isomer led Grunwald to the conclusion that participation was not a significant factor.⁴⁷ In the present system we should also expect that the formation of a stable phenonium ion should

(55) D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960.

have large kinetic consequences, far beyond the minor factors we are discussing. In the absence of any more quantitative basis for estimating the opposing steric and inductive influence of the phenyl substituent, we propose that these be considered to be approximately equal and opposite, thereby avoiding the necessity of making minor corrections of questionable validity.

It might also be argued that one should not utilize the titrimetric rate constants, but utilize instead the polarimetric constants. This introduces a possible correction term of 4–5.^{56,57} However, instead of attempting to incorporate this small factor into our considerations, let us proceed directly to the formolysis data. Internal return is a much smaller factor in formic acid ($k_{\alpha}/k_i = 1.2$),⁵⁸ rendering the proposed correction insignificant, and the low nucleophilicity of the solvent should favor phenyl participation. The available data are summarized in Table III.

It will be observed that, even with this highly favorable solvent, the observed rate enhancements are small—a factor of 5 with 3-phenyl-2-butyl. Note that the rate of formolysis of 3-methyl-2-butyl tosylate is slightly larger, while the rate for 3-cyclohexyl-2-butyl is larger still.

Again it becomes difficult to pinpoint the precise factors responsible for the small rate enhancements which are observed. What portion of the observed rate enhancements should be assigned to the steric requirements of the 3-phenyl, 3-methyl, and 3-cyclohexyl groups, what portion to phenyl participation in 3-phenyl-2-butyl, and what portion to hydrogen participation in 3-cyclohexyl-2-butyl?⁵⁸

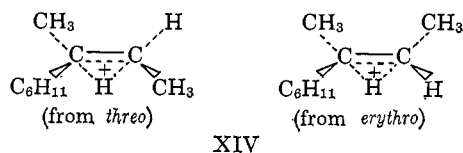
(56) S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, **74**, 2165 (1952).

(57) In his recent review,¹⁶ Cram makes the following statement with reference to the experimental observation that the rate of acetolysis of 3-phenyl-2-butyl tosylate is less than that of 2-butyl tosylate: "Brown quoted the *dissociation* rather than the *ionization* rates, which are not identical in this system due to internal return. The ionization rate of 3-phenyl-2-butyl tosylate is about 3 times as great as the rate of ionization of 2-butyl tosylate."

Unfortunately, the situation is not as simple and direct as implied in this statement. The polarimetric rate constant gives the rate of racemization of *threo*-3-phenyl-2-butyl tosylate. This may or may not be equal to the rate of ionization. The statement also implies that the titrimetric rate constant for 2-butyl tosylate is equal to its rate of ionization. This has not yet been established experimentally, and a recent study [A. Streitwieser, Jr., and T. D. Walsh, *Tetrahedron Letters*, No. 1, 27, 1963] suggests that the solvolysis of such derivatives may be more complex than has been assumed in the past. See also H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **87**, 287, 292 (1965). Many of the difficulties encountered in utilizing acetic acid as a solvent, such as internal return, special salt effects, etc., appear to become insignificant in other systems, such as water, methanol or formic acid. It is to be hoped that more data will be forthcoming for such systems.

In his review¹⁶ Cram argues in favor of introducing a number of favorable corrective terms and concludes that the rate of acetolysis does indeed exhibit an appreciable rate acceleration. He also argues that steric acceleration should not be large and should be negated by a decreased energy of solvation of the ion.

(58) In the case of 3-cyclohexyl-2-butyl tosylate it has been proposed that the solvolysis proceeds through the formation of bridged ethylene-protonium ions (XIV). Moreover, it is further proposed that this



intermediate possesses the unusual characteristic of undergoing substitution on the *same* side as the hydrogen bridge: D. J. Cram and J. Tadanier, *J. Am. Chem. Soc.*, **81**, 2737 (1959). Previously the requirement for inversion at the bridge had been considered to be a fundamental characteristic of bridged ions.

Again we find ourselves attempting to analyze minor variations in the rates of solvolysis where we should expect major increases in rate if the reaction actually proceeds through the formation of a stable phenonium ion.

In presenting this survey of the importance of β -phenyl participation in the solvolysis of β -phenylethyl derivatives, it is not intended to give the impression that other workers in the field have not recognized the situation. In his review of this paper Professor Winstein has written the authors. "Actually, it was clear very early that the phenyl group was one of the poorest neighboring groups and, therefore, that β -phenylalkyl systems were marginal ones."

Indeed, it is because such systems are marginal that they are so important in exploring the possibility that the intermediate class of equilibrating cations may be found among their members.

The phenonium ion was originally advanced to account for the unusual stereochemical results observed in the acetolysis of *erythro*- and *threo*-3-phenyl-2-butyl tosylates.¹⁷ Even though the kinetic data fails to yield evidence supporting the formation of the proposed phenonium ion as a stable intermediate, we should weigh the stereochemical results carefully in order to decide whether they require that the reaction proceeds through the proposed phenonium intermediate. However, before undertaking this analysis, it will be instructive to review the data and conclusions for the systems and results already examined. These are assembled in Table IV.

Product Studies

The classic studies of Cram on the acetolysis of the *threo*- and *erythro*-3-phenyl-2-butyl tosylates^{17,19} demonstrated that the reaction proceeds with predominant retention of configuration, in contrast to the predominant inversion observed in the acetolysis of simple secondary tosylates, and with remarkable stereochemical control at both asymmetric centers in the molecule. Thus the acetolysis of (–)-*threo*-3-phenyl-2-butyl tosylate gives, as the major product, a racemic mixture of *threo*-3-phenyl-2-butyl acetates, while (–)-*erythro*-3-phenyl-2-butyl tosylate produces, as the major product, optically pure (–)-*erythro*-3-phenyl-2-butyl acetate.

An elegant explanation of these observations was provided by the postulation of a sterically rigid phenonium intermediate; that from the *threo* diastereomer is symmetrical and can open only with inversion to give only a racemic mixture of *threo* acetates; that from the *erythro* is asymmetric and can open only with inversion to give optically pure *erythro* acetate.

However, the simplicity of this interpretation was largely lost when the products were subjected to a more detailed analysis. In acetic acid the rate of racemization of (–)-*threo*-3-phenyl-2-butyl tosylate is considerably faster than the rate of formation of toluene-sulfonic acid,^{17,56} and it has been estimated that 80% of the tosylate is racemized prior to its conversion into acetate or other products.⁵⁶ Consequently, the mechanism must be elaborated to include conversion into an intimate ion pair, which can undergo racemization through internal return,⁵⁹ prior to the formation of

(59) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952).

Table IV. Summary of the Data Bearing on the Question of Phenyl Participation in Symmetrical β -Phenylethyl Derivatives

System	Conclusion	Explanation
Tertiary-tertiary		
A. 2,3-Dimethyl-3-phenyl-2-butyl	No rate acceleration	A tertiary carbonium ion is too stable to interact with the phenyl group
B. 3,4-Dimethyl-4-phenyl-3-hexyl	No participation	Same
Primary-primary		
C. β -Phenylethyl	No rate acceleration in acetolysis; slight acceleration in formolysis	A primary ion is open to solvation and the neighboring phenyl group cannot compete with solvent
Secondary-secondary		
D. 1,2,2-Triphenylethyl	No participation	A secondary benzylic cation is too stable to interact with the phenyl groups
E. <i>trans</i> -2-Phenylcyclopentyl	No participation	Bond angles in a cyclopentyl derivative are unfavorable
F. <i>trans</i> -2-Phenylcyclohexyl	No rate acceleration	Energy to place phenyl group in axial position is high
G. 3-Phenyl-2-butyl	No rate acceleration in acetolysis; slight acceleration in formolysis	Phenyl is borderline in its ability to participate plus its unfavorable inductive effect

the postulated phenonium ion which leads to products. Furthermore, the acetolyses of the *threo* and *erythro* isomers produce from 25 to 35% olefin in addition to the acetates. When the nature of the olefin products was considered, it became apparent that simple phenonium ion intermediates alone were incapable of accounting for all of the products and it was considered necessary to add the classical 3-phenyl-2-butyl cation as well as the corresponding hydrogen-bridged species to the phenonium ion as reaction intermediates.⁶⁰

Still further elaborations of the reaction paths were invoked to account for the formation of 4% of *erythro* acetate from *threo*-3-phenyl-2-butyl tosylate (and *vice versa*)⁶¹ and for the occurrence of a small excess of *threo* acetate of retained configuration (0.6%). It was suggested that these products are derived from a small amount (*ca.* 7%) of a competing "simple" S_N1 process.

If the acetolysis is performed at lower temperatures (30°), the tertiary ester, ethylmethylphenylcarbinyl acetate, is formed. The ratio of secondary derivative, 3-phenyl-2-butyl acetate, to tertiary is 3.7. Consequently, isomerization to the tertiary ion is competitive with the proposed formation of the phenonium ion.

It is evident that if all of the acetolysis products are considered, much of the apparent simplicity of the original interpretation based upon the formation of a stable phenonium ion intermediate has been lost.

The situation becomes even more complex in the next higher symmetrical derivative, 4-phenyl-3-hexyl tosylate.^{20a} In the acetolysis of the (–)-*threo* tosylate, the *threo* acetate isolated exhibits a rotation of $[\alpha]^{20D}$

(60) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2137 (1952). For example, in the acetolysis of *threo*-2-phenyl-3-butyl tosylate at 75° it is proposed that 49% of the reaction proceeds through the phenonium tosylate ion pair to the acetate, 29.3% of the reaction proceeds through a hydrogen-bridged carbonium ion pair leading to olefins, and 10.6% proceeds through the classical 3-phenyl-2-butyl cation, also leading to olefins.

(61) In present day terminology, this represents "leakage" from the *threo* to the *erythro* system. Such "leakage" is being encountered in many solvolyses, such as those of the related pairs, *exo*-bicyclo[3.2.1]octan-2-yl and bicyclo[2.2.2]octan-2-yl, *endo*-bicyclo[3.2.1]octan-2-yl and 4-cycloheptenylmethyl, and *exo*- and *endo*-bicyclo[3.2.1]octan-6-yl systems which previously had been considered to proceed with the complete stereospecificity postulated for nonclassical intermediates: private communication from Professor H. L. Goering.

–7.42°. This corresponds to the presence of approximately 10% of optically active *threo* acetate of retained configuration, in contrast to the much smaller quantity, 0.6%, observed in the 3-phenyl-2-butyl system.

Since the *threo*-4-phenyl-3-hexyl tosylate racemizes at three times the rate that it undergoes acetolysis, it is evident that nearly 30% of the *threo* acetate product must be formed by some process that does not proceed through the postulated racemic phenonium ion. The acetates recovered also contain 5% of the *erythro* isomer.

The authors considered two possible explanations for the formation of these large quantities of acetate products which cannot arise from the proposed phenonium intermediate. It was thought that the rigidity of the phenonium ion might lead to steric crowding when bulky groups are forced into eclipsed conformations; the simple phenonium ion would then be replaced by an equilibrating mixture of unsymmetrical bridged ions. Alternatively, it was thought possible that the unexpected products might be derived from classical carbonium ions in which the substituent at the benzyl carbon atom might provide sufficient steric control of asymmetric induction.

However, analysis of the products from 2,5-dimethyl-4-phenyl-3-hexyl brosylate showed increased stereospecificity (*i.e.*, little *erythro* acetate from *threo* brosylate), in spite of the increased steric effect of the isopropyl substituents.^{20b} This is clearly not consistent with the hypothesis that increased steric interactions in the phenonium ion might favor a shift to an equilibrating pair of unsymmetrical bridged ions. The results are not inconsistent with the authors' suggestion that stereochemistry of the so-called simple substitution products might be controlled by the steric situation at the benzyl carbon, varying with the varying bulk of the phenyl and alkyl groups (methyl, ethyl, and isopropyl in the three cases reviewed).

The authors conclude: "No evidence now exists which either suggests or demands the substitution of a dynamic equilibrium between unsymmetrical bridged carbonium ions in systems where C _{α} and C _{β} carry the

same substituents. Bridged ions . . . can provide a simpler and therefore better explanation of the facts until new evidence intrudes."

Before leaving the 2,5-dimethyl-4-phenyl-3-hexyl system, attention should be called to the observation that the greater part of the reaction product involves elimination to olefin. Moreover, formation of tertiary alcohol is a major side reaction. For example, acetolysis of *threo* at 50° yields 53% olefin ($[\alpha]^{25D} -43.0^\circ$), 27% racemic *threo*, 1% *erythro*, and 12% of tertiary alcohol (partially racemic 2,5-dimethyl-4-phenyl-2-hexanol and 2,5-dimethyl-3-phenyl-2-hexanol). The *erythro* isomer yields 70% olefin ($[\alpha]^{25D} -72.1^\circ$), 19% of optically pure tertiary alcohol, 2,5-dimethyl-4-phenyl-2-hexanol, and only 3.8% of the secondary alcohol (95% *erythro*, 5% *threo*) presumed to arise via the phenonium ion.

Clearly the phenyl group is failing to compete with the tertiary hydrogen in controlling the course of the reaction. Another puzzling feature is that much more of the secondary alcohol is obtained from the *threo* isomer (which involves *cis*-isopropyl groups in the postulated phenonium ion intermediate) than in the *erythro* isomer (which can accommodate the bulky isopropyl groups in the *trans* configuration).

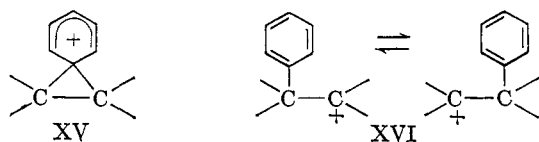
The solvolysis reactions conducted in formic acid differ appreciably from those in acetic acid, but the general pattern of the results is the same. The polarimetric and titrimetric rates are closely similar in formic acid and most of the formate is produced by a mechanism not involving preliminary equilibration through an intimate ion pair. The amount of the so-called simple substitution products (*erythro* from *threo* etc.) is less, but the products realized are similar. For example, *threo*-4-phenyl-3-hexyl tosylate yields a significant quantity of *threo* formate of retained stereochemistry. *erythro*-2,5-Dimethyl-4-phenyl-3-hexyl brosylate yields 7% of *erythro*, but 60% of optically pure tertiary formate.

It is evident from this brief review of the product studies in the solvolysis of 3-phenyl-2-butyl, 4-phenyl-3-hexyl, and 2,5-dimethyl-4-phenyl-3-hexyl sulfonate esters that the phenonium ion alone fails to provide a satisfactory interpretation of all of the results. It has proven desirable to bring in classical, hydrogen-bridged, as well as equilibrating, unsymmetrical-bridged ions to account for the experimental results.

One of the more persuasive arguments advanced for the phenonium ion hypothesis has been that it provides a simple, economical explanation of the products realized in the acetolysis of 3-phenyl-2-butyl sulfonate esters and their higher homologs. It is evident that this simplicity is not supported by a careful examination of all of the data now available.

Phenonium vs. Equilibrating Ions

The experimental results on the 3-phenyl-2-butyl^{17,18} and related derivatives^{20a,b} clearly establishes that C_α and C_β of the central β-phenylethyl system approach equivalence in the course of acetolysis and formolysis.



This requires either the proposed phenonium ion intermediate (XV) or its kinetic equivalent—a rapidly equilibrating pair of ions (XVI).

Let us consider a major difficulty with the phenonium ion hypothesis. It is usually considered that in favorable cases, such as in the formolysis of 3-phenyl-2-butyl tosylate, the phenonium ion is so stable relative to the classical species that it completely controls the substitution process. Let us attempt to estimate how great the stabilization must be to ensure that essentially all of the substitution proceeds through the bridged species.

Let us assume that the stability of the phenonium ion is so great that at equilibrium there will be present not more than 0.1% of the classical species. This would require the phenonium ion to be some 4.2 kcal. mole⁻¹ more stable than the classical structure. Yet consideration of the substitution process reveals that even stabilization of this magnitude will not ensure control of the substitution process.

The rates of substitution for each species will be given by the product of the concentration of each species and the specific rate constant for substitution at the respective carbon atoms. All of our experience argues that substitution at the carbonium center of a classical ion must be fast; there are no covalent bonds to be broken. On the other hand, substitution in the phenonium ion requires an S_N2 displacement with rupture of the bond to the phenyl ring. Our experience suggests that this should be a process which would be considerably slower than substitution at a free carbonium ion center. Consequently, even with only 0.1% of the classical ion present in an equilibrium mixture of the two ions, it is possible that a large fraction, if not all, of the substitution process might proceed through the classical ion.

We can, of course, specify that the phenonium ion is even more stable than this original estimate. However, this does not necessarily improve the situation. We are now faced with the necessity of breaking an even stronger bond in the substitution process.

Arguing against such stabilities for the postulated phenonium ion intermediates is the failure to observe any significant evidence for phenyl participation in the solvolyses (Table IV).

Since the classic paper by Evans and Polanyi, "Inertia and Driving Force of Chemical Reactions,"⁶² it has been an accepted principle that an increase in the stability of the product, or of the first intermediate following the transition state, should result in a lowering of the energy barrier and effect an enhancement in the rate.²⁶ Consequently, we should anticipate that the formation of a phenonium ion intermediate, which is several kilocalories per mole more stable than the classical ion, should exert a major influence on the solvolysis rates. The failure to observe any such kinetic effects makes it desirable to explore the possibility that the unusual stereochemical features of 3-phenyl-2-butyl and related derivatives can be accounted for in terms of the concept of rapidly equilibrating essentially classical ions (XVI).

As was mentioned earlier, this possibility has been pointed out earlier by Winstein and his co-workers.¹³ "Just as in the case of functional neighboring groups [S. Winstein, *Bull. soc. chim. France*, **18**, 55 (1951),

(62) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

and S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948)], it must be kept in mind that the stereochemical results corresponding to formation and

opening of $\begin{array}{c} \text{R} \\ \diagup \quad \diagdown \\ \text{C} \equiv \text{C} \\ \diagdown \quad \diagup \end{array}$ may, in some cases, be simulated by a dynamic pair of isomeric cations I and II. These one-sided structures could still involve quite serious delocalization of the $\text{C}_\beta\text{-R}$ bonding pair. Also, even without this, but with restricted rotation about the $\text{C}_\alpha\text{-C}_\beta$ bond and a tendency in specific cases for the entering substituent to bond finally to C_α or C_β on the side away from R, the same stereochemical results are possible."

It is evident that this proposal offers us a possible escape from the dilemma posed by the high degree of stereochemical control of substitution on the one hand, and the failure to observe significant rate enhancements on the other.

It is evident that this proposal would also provide the simultaneous resolution of a second apparent anomaly in carbonium ion chemistry—the fact that practically all current systems are presently described either as static classical cations (class A), or static bridged cations (class C), with the intermediate class of equilibrating cations (class B) being essentially unpopulated, in spite of the fact that the thermodynamics of the situation (Figure 3) appears to require the existence of such an intermediate group.

Let us consider some of the physical aspects of such an equilibrating pair. The movement of the phenyl group from C_α to C_β , if sufficiently rapid, would favor solvation of the ion on the side away from the migrating group. Consequently, collapse to product should occur preferentially on the side away from the phenyl substituent. To put this picture in slightly modified terms, the rapid movement of the phenyl group between the two carbon atoms should decrease the concentration of solvent molecules in the immediate neighborhood of the phenyl group. With the concentration on the side away from the equilibrating phenyl group not altered, substitution will occur primarily from that direction.⁶³

The entropies of activation for solvolysis of β -phenylethyl derivatives fall within the ranges of -17 to -21 and -9 to -12 e.u.^{16,64} The first range is ascribed to solvent participation, the second to phenyl participation which effectively excludes solvent. It has been considered that this provides support for the belief that solvolysis in the second group leads to the formation of the phenonium ion intermediate.¹⁶ However, it should be evident that the results can equally well be adapted to the alternative interpretation involving equilibrating ions. In a static classical ion, solvent will participate, resulting in considerable loss in the freedom of motion of the solvent molecule in forming the transition state with the sulfonate ester, corresponding to the observed entropy decrease of -17 to -21 e.u. On the other hand, if the equilibration is sufficiently rapid as to prevent the participation of the solvent in this way, a postulate already made to account for the observed stereochemistry, covalently bound

(63) At the Brookhaven conference¹ the term "windshield wiper effect" was proposed by an anonymous member of the audience. Although we are afraid that there were facetious overtones in the suggestion, the term is a simple, descriptive one, and we have no hesitation in recommending its adoption.

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

solvent will not be involved and a smaller entropy decrease would be anticipated.

The extent to which stereochemical control can be maintained in the type of equilibrating system under discussion should depend upon the frequency of the migration. Solution of the ion in a less nucleophilic solvent, such as formic acid, would be expected to increase the reactivity of the carbonium center and enhance the frequency of migration.

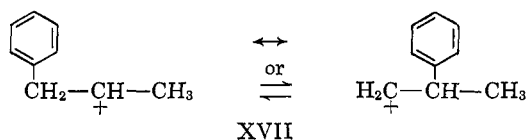
It is frequently assumed by critics of this proposal that a rapidly equilibrating pair of ions should undergo rapid rotation resulting in a loss in stereospecificity. Actually, it can be argued that the rapid migration of the phenyl group between C_α and C_β should decrease the rate of rotation of the $\text{C}_\alpha\text{-C}_\beta$ bond. Considered in terms of a simple physical picture, the initial movement of C_α and its bonded groups should be quite slow, due to inertia, in the initial stages of the rotation. If the frequency of equilibration of the phenyl group is high, the phenyl group on C_β will begin its movement back to C_α before rotation has proceeded more than a small angle. Transfer of the group from C_β to C_α will then force C_α back to its original position.

An equilibrating pair of ions permits one to account for the olefins produced without difficulty.⁶⁵ Loss of a proton to solvent in the usual manner converts the ion into the olefin. Likewise hydride ion shifts, which are difficult to account for mechanistically in a stable bridged ion, are readily accommodated within the framework of a mechanism based on equilibrating ions. Finally, the varying amounts of simple substitution products in the different systems were finally attributed by Cram to steric control of substitution at a classical carbonium ion center by the neighboring benzylic carbon and its substituents.^{20b} Consequently, even this anomaly in the phenonium mechanism is readily accommodated within the framework of a mechanism involving rapidly equilibrating classical ions.

Before concluding this discussion, it should be re-emphasized that this discussion has been restricted to simple symmetrical phenonium ions of β -phenylethyl systems.⁶⁶ It did not attempt to explore the possibility that phenonium ions may exist in other systems, nor

(65) C. J. Collins has informed us that he and his co-workers have adapted the methods, previously utilized for the 1,2,2-triphenylethyl system,⁴⁵ to the acetolysis of 3-phenyl-2-butyl tosylate. A group of 13 simultaneous equations was set up to represent the various rotations, phenyl migrations, hydrogen elimination, and substitution by solvents of equilibrating 3-phenyl-2-butyl cations. A computer was utilized to calculate the effect on the product distribution of various relative values of the rate constants. It was found possible to reproduce the observed acetolysis product distribution with quite reasonable values of the relative rate constants.

(66) Attention is called to the fascinating stereochemical results realized with the 1-phenyl-2-propyl tosylates: S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Am. Chem. Soc.*, **74**, 1140 (1952). Interpretation of the results, either in terms of the phenonium ion, or an equilibrating pair of ions, requires consideration of a new problem—to what extent can we postulate either resonance or equilibration between species which differ so markedly in energy as a primary



and secondary cation (XVII)? We are undertaking a study of the effect of substituents in the aromatic nucleus of this system in order to obtain evidence on which to base a discussion of the nature of the intermediate or intermediates involved in these solvolytic reactions.

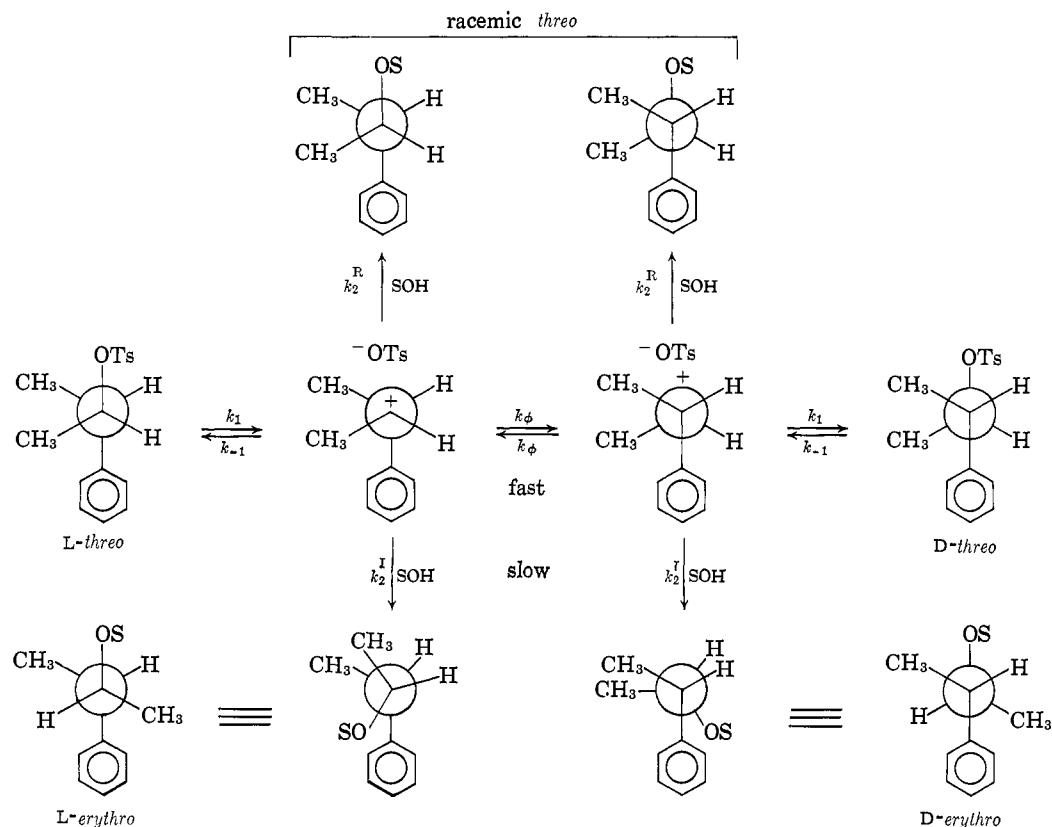


Figure 4. Possible mechanism for the solvolysis of *L-threo*-3-phenyl-2-butyl tosylate.

whether they might exist in derivatives containing highly activating groups in the aromatic nucleus. This is a subject which will be discussed in a later publication. The fact that marked rate enhancements by neighboring phenyl may be demonstrated in other systems with special geometrical requirements⁶⁷ or in derivatives containing highly activating groups is not pertinent to the present question—are the solvolytic phenomena in symmetrical β -phenylethyl derivatives better accounted for in terms of a stable phenonium intermediate, or in terms of an equilibrating pair of classical ions?

It is our position that the absence of any kinetic evidence for significant phenyl participation in symmetrical β -phenylethyl derivatives raises serious doubts that a stable phenonium ion can be involved in the solvolysis of these derivatives. Moreover, a detailed examination of the reaction products of such solvolyses reveals that they are quite complex and require postulation of species other than the phenonium ion. We recommend, therefore, that an equilibrating pair of classical ions be considered as an alternative, and, possibly, simpler explanation of the available data.

A Model for the Solvolysis of 3-Phenyl-2-butyl Tosylate

The acetolysis of 2-butyl tosylate proceeds with very high inversion of configuration.^{5a} On the other hand, the acetolysis of 3-phenyl-2-butyl tosylate proceeds with predominant retention of configuration.¹⁹ For example, at 75° the acetolysis of *L-threo*-3-phenyl-2-butyl tosylate produces 25.5% of *L-threo*-, 25.2% of *D-threo*-, and 2% of *erythro*-3-phenyl-2-butyl acetate, along with 35% of a mixture of olefins.¹⁸ It has been

argued that these results are not compatible with any reasonable mechanism based on equilibrating classical intermediates.¹⁶ Accordingly, it appears of interest to suggest a possible mechanism for consideration.⁶⁸

The proposed mechanism is outlined in Figure 4.

1. There is growing evidence that the acetolysis of secondary tosylates proceeds to the formation of ion pairs.^{6a} The 3-phenyl-2-butyl system fails to exhibit the special salt effect indicative of "external return".⁶⁹ Consequently, it appears reasonable to interpret the reaction as proceeding predominantly, if not entirely, through undissociated ion pairs.

2. It has been argued that the tosyl group is smaller than methyl, so that the configuration shown in Figure 4 is improbable.¹⁶ However, judged by the relative *A*-values for these substituents in cyclohexane, the difference in steric requirements is not large,⁷⁰ and may actually become inverted once the effect of solvation of the polar tosyl group is taken into account. Even without considering the effect of solvation, it was pointed out by Curtin (the Curtin-Hammett principle)

(68) In the original version of this manuscript, no detailed mechanism was suggested. It was felt that there is presently available insufficient evidence on which to base a definitive mechanism. It was feared the proposal of a definite mechanism on which criticism might be focussed might serve to distract attention from the main objective of this paper, namely, to point out that two major anomalies exist at present in the area of carbonium ion chemistry, and that these anomalies might have their common origin in the failure to recognize that substitution with retention of configuration might arise from causes other than the formation of a bridged intermediate. However, several of the reviewers of this paper urged that a specific mechanism be outlined to illustrate the point that the observed retention can be accounted reasonably, without requiring the formation of a bridged intermediate.

(69) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

(70) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(67) R. Huisgen, E. Rauenbusch, G. Seidl, and I. Winmer, *Ann.*, **671**, 41 (1964).

that, providing the barrier to rotation was not large, it was not necessary to consider the individual conformations in discussing the reactivities of a given molecule.⁷¹

3. In the ion pair, the tosyl group will surely be strongly hydrogen bonded to the solvent. Consequently, there can be little question but that the two largest groups, phenyl and the solvated anion, will prefer the *trans* arrangement shown. Since this is the most stable conformation, rotation to less stable structures (resisted by the rapid equilibration, as discussed earlier) will be unimportant during the lifetime of the ion pair.

4. The tosyl group will be partially ionized and partially solvated in the transition state. Here also the most stable arrangement should be one involving a *trans* orientation of the tosyl and phenyl groups.

5. Consequently, simple conformational considerations argue for a conversion of the 3-phenyl-2-butyl tosylate from any of the three possible conformations (the Curtin-Hammett principle), through a transition state with a preferred *trans* orientation of the phenyl and solvated tosyl groups, to the ion pair shown.

6. It is proposed that this ion pair undergoes transformation from D to L and back at a rate that is rapid compared to the rate of reaction of the ion pair with solvent.⁷²

7. In systems which are capable of undergoing facile S_N2 displacement reactions, the normal course of the reaction would involve solvent attack from the back side of the ion pair, producing acetate of inverted configuration. However, the presence of the bulky phenyl group must greatly reduce the rate of such substitution.⁷³ Superimposed on this simple steric effect of the phenyl substituent is the proposed steric influence of the rapid equilibration (windshield wiper effect).

8. With the usual inversion rendered slow by these factors, the predominant path becomes one in which a solvent molecule, presumably one which is associated with the tosylate anion in the intimate ion pair, is captured by the carbonium ion.

9. According to this interpretation the 2% of *erythro* acetate arises from the hindered S_N2 displacement on the equilibrating ion pair. The slight excess of *L-threo* acetate arises from the fact that the solvent reacts before the equilibration is 100% complete. Finally, olefin arises from a competing E₂ reaction involving solvent on the ion pair or original tosylate, as well as a competing conversion of the ion pair to a tertiary derivative by migration of the tertiary hydrogen, followed by elimination.

10. According to this suggested mechanism, the use of a less nucleophilic solvent, formic acid, should decrease the small S_N2 component, resulting in a smaller yield of *erythro* derivative. The tosyl group should be much more strongly solvated. Therefore, the ion pair should have a longer life, resulting in less excess activity in the *threo* formate, as well as less return to tosylate. Finally, the loss of protons from the ion-

pair intermediate to solvent should be reduced, causing a decrease in the yield of by-product olefin.

This mechanism would appear to offer a reasonable explanation for the available data. However, we wish to emphasize that the available experimental data do not permit one to offer a definitive interpretation at this time.⁶⁸ The above mechanism is offered primarily in the hope that it will stimulate discussion of possible mechanisms and consideration of experimental approaches that may resolve the question under review.

Conclusions

A detailed examination of all of the available kinetic data for the solvolysis of symmetrical β -phenylethyl derivatives reveals slight rate accelerations attributable to phenyl participation in the formolysis of β -phenylethyl and 3-phenyl-2-butyl sulfonate esters, but no evidence for any significant rate accelerations, attributable to the formation of a stable bridged ion, in the acetolysis of such derivatives. Yet the acetolyses of 3-phenyl-2-butyl derivatives exhibit a high degree of stereochemical control of the type normally attributed to the intervention of a bridged ion. The problem is that of reconciling these two apparently conflicting results.

As proposed for halogens, acetoxy groups, etc., the neighboring group participation theory⁵ was an excellent theory because it gave a single connected explanation for two otherwise unrelated phenomena: a pronounced acceleration in rate and a particular kind of product distribution. In the course of its extension to neighboring carbon, the observed rate accelerations became either small or absent, and it became customary to rely only on stereochemistry as a basis for postulating the formation of stable bridged species capable of controlling stereochemistry. This has led to the present situation where nearly all carbonium ion systems are described either as static classical cations (Figure 3a), or as bridged cations (Figure 3c), with the intermediate class of rapidly equilibrating cations (Figure 3b) being essentially unpopulated.

We are therefore currently faced with two anomalies in the area of carbonium ion chemistry: (1) the almost complete absence of any recognized members of the intermediate class of equilibrating cations, and (2) the failure to observe significant rate enhancements in systems where the formation of relatively stable bridged species is postulated. It is here suggested that these anomalies may have a common origin—our failure to recognize that the stereochemistry of substitution may be altered from inversion to retention by purely steric factors (including rapid equilibration).

The problem is therefore far broader than the phenonium ion question discussed in this paper. The problem appears to be that of reconciling the facts with both of two cherished notions of organic chemistry: (1) that lowering the standard free energy of a reaction product or intermediate must lower the standard free energy of the transition state, and (2) that only a bridged cation can control stereochemistry of substitution to give a high degree of retention of configuration. In recent years the predominant tendency has been the tacit assumption that the Evans-Polanyi

(71) D. Y. Curtin, *Record Chem. Progr.*, **15**, 111 (1954).

(72) A rate of interconversion that is approximately 20 times the rate of substitution would appear adequate to account for the acetolysis results.⁶⁸

(73) Many bicyclic systems also undergo S_N2 displacement reactions with great difficulty. Here also the usual inversion by solvent can be superceded by an alternative path.

principle is not applicable to this area. It is our position that the Evans-Polanyi principle has been enormously useful in organic chemistry and it should not be abandoned in this area without giving careful consideration to the alternative possibility, namely, that the absence of significant rate accelerations does indeed correspond to the nonformation of stable bridged intermediates with the stereochemical results arising from stereochemical control by steric factors including the effect of rapid equilibration.

It is common experience in organic chemistry that the enormous possibilities for structural variations make it possible to vary almost any characteristic by small, almost continuous increments. Is it not a reasonable possibility that there will be observed a gradual change in the nature of the substitution as we proceed from a static classical cation, through a rapidly equilibrating

cation, to a bridged cation? Where will the change occur? Will it occur suddenly, only after the rate of equilibration has become so rapid that we can no longer speak of equilibration, but must speak of resonance instead? Or is it a reasonable possibility that stereochemistry may be controlled by an equilibrating ion long before we reach this extreme stage?

Before concluding, we wish once again to call attention to the recently published review and defense of the phenonium ion interpretation.¹⁶ In order to avoid misunderstanding, it should be emphasized that no difference of opinion exists as to the experimental data; the difference of opinion is entirely one of interpretation. It is to be hoped that the availability of these two discussions will facilitate careful consideration of the alternative interpretations and the final resolution of this interesting problem.

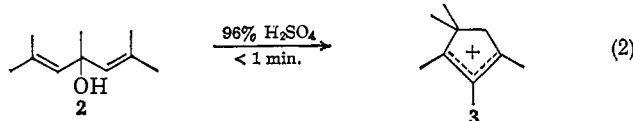
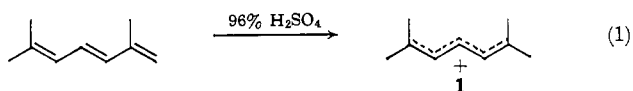
Carbonium Ions. XVIII. Cyclizations of Pentadienyl and Heptatrienyl Cations

N. C. Deno, Charles U. Pittman, Jr., and John O. Turner

Contribution from the College of Science, The Pennsylvania State University, University Park, Pennsylvania. Received January 4, 1965

The work of Sorensen and the work described herein combine to demonstrate that the cyclization of pentadienyl cations to cyclopentenyl cations is not only a general reaction but also a nearly quantitative reaction. The studies are extended to two heptatrienyl cations, one of which cyclizes while the other does not. The latter case provides the first example of the direct observation of an aliphatic trienyl cation. Two phenyl substituted allyl cations are examined: one cyclizes, one does not. Four monoaryl carbonium ions are directly observed, two indanyls, a tetrahyronaphthyl, and the 2-phenylpropyl.

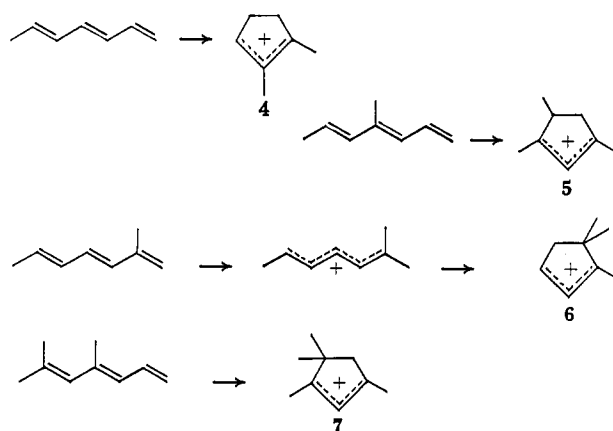
The Cyclization of Pentadienyl Cations to Cyclopentenyl Cations. In a communication,¹ the following two reactions (eq. 1 and 2) were reported. Sorensen



confirmed both reactions² and further showed that **1** slowly cyclized to the 1,2,3,4-tetramethylcyclopentenyl cation. The half-life of **1** at 25° in 96% H₂SO₄ is about 3 days, which we confirm.

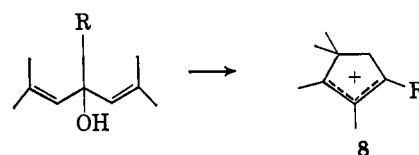
Sorensen further examined homologs of **2** in which methyl groups were successively removed. The re-

actions in 96% H₂SO₄ were



The formation of **7** has been independently confirmed by our group. The terminally alkylated allyl cations **5** and **7** were indefinitely stable whereas the trialkylated **4** and **6** were fleeting² in accord with past precedent.³

The cyclization of **2** to **3** has been extended to homologs of **2** in which the C-4 methyl has been replaced by ethyl, isopropyl, and isobutyl groups. Immediate cyclization of the dienols took place in 96% H₂SO₄ and the reaction can be represented by



(1) N. Deno and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **86**, 1871 (1964).

(2) T. S. Sorensen, *Can. J. Chem.*, in press.

(3) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).