Structural Effects in Solvolytic Reactions. III. Nature of the Intermediate Involved in the Solvolysis of 3-Aryl-2,3-dimethyl-2-butyl Derivatives

Herbert C. Brown and C. J. Kim[1]

Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana 47907. *Received July 27, 1967*

Abstract: The rates of solvolysis of representative 3-aryl-2,3-dimethyl-2-chlorobutanes and 3-aryl-2-methyl-2-chloropropanes were measured in 80% aqueous ethanol in order to examine the importance of aryl participation in such systems. In the former series, the range of rates was only a factor of 8 (*p*-H, 1.00; *m*-Me, 1.44; *p*-Me, 2.51; *p*-OMe, 7.86). In the latter series, the effect of the substituents was even smaller (*p*-H, 1.00; *m*-Me, 1.11; *p*-Me, 1.21; *p*-OMe, 1.51). These relative rates, analyzed with the aid of the usual free energy treatments, reveal that the transition states for these solvolyses must involve only a minor amount of charge delocalization from the carbonium ion center into the aromatic ring. It has long been an accepted position in this area that the transition state must closely resemble the first intermediate, *i.e.*, the carbonium ion produced in the solvolysis. On this basis, the carbonium ion itself must involve only minor charge delocalization into the aromatic ring. The question then arises whether the intermediates in these reactions are best represented as symmetrical aryl-bridged cations (arylonium ions), or as rapidly equilibrating cations involving minor interactions between the π cloud of the aromatic ring and the carbonium center. In an attempt to answer this question, the tagged compounds, 1,1-dimethyl-d_6-2,2-dimethylpropanol, 1,1-dimethyl-d_6-2-methyl-2-phenylpropanol, and 1,1-dimethyl-d_6-2-methyl-2-*p*-anisylpropanol, were prepared and subjected to a number of representative carbonium ion reactions. It is evident that the formation of symmetrically bridged intermediates requires complete scrambling in the products, whereas rapidly equilibrating cations offer the possibility that they may be trapped and converted to products before complete scrambling has occurred. No difficulty was encountered in converting the first derivative (β-Me) into unscrambled product. In view of the small rate effects observed, the marked tendency for the second (β-Ph) and the third derivative (β-An) to yield fully scrambled products was unexpected. However, even here, reactions were found which yielded essentially unscrambled products from the β-Ph compound, while resulting in completely scrambled products from the β-An compound. Finally, dehydration of the alcohols over alumina, addition of hydrogen chloride to the olefins, and deoxideation of the alcohols with bromoform and alkali (Skell reaction) permitted the formation of largely unscrambled products from all three derivatives. These results are not compatible with the formation of symmetrically bridged arylonium intermediates. They are compatible with the formation of rapidly equilibrating unsymmetrical cations (or ion pairs), $(H_3C)_2RCC^+(CD_3)_2 \rightleftarrows (H_3C)_2C^+CR(CD_3)_2$ in which there may be more or less interaction between R and the carbonium center, with a rate of equilibration that increases in the order R = Me < Ph < An. It is proposed that the present data support the view that we must be dealing with an essentially continuous spectrum of cations, varying from static classical, to equilibrating classical, to equilibrating π bridged, to static symmetrically bridged species, rather than the sharp dichotomy of static classical and static bridged species which has been the main basis for interpreting the data in this field.

It was originally suggested that the greatly enhanced rate of formolysis of β,β,β-triphenylethyl chloride, 60,000 times greater than that of neopentyl chloride,[2,3] or of acetolysis of β,β,β-triphenylethyl tosylate, 7700 times that of neopentyl tosylate,[4] is primarily the result of phenyl bridging in the transition state.[3,5] If one assigns the usual factor of 10 for the rate-retarding inductive effect of each phenyl group,[4] then the rate enhancement becomes truly enormous, 60,000,000 for the formolysis of the chloride and 7,700,000 for the acetolysis of the tosylate.[6]

It was pointed out that a major factor in these enormous enhancements could be release of steric strain.[7,8] Indeed, a detailed examination of the rates of solvolysis of symmetrically substituted β-phenylalkyl derivatives reveals little or no rate enhancements.[7,9] For example, it would appear that *threo*- and *erythro*-3-phenyl-2-butyl tosylates provide the most favorable case for such rate enhancement due to phenyl participation in a symmetrical β-phenylalkyl system. Yet Streitwieser, basing his estimate on the use of the Taft substituent constants, concluded that the *threo* derivative undergoes acetolysis at a rate that is 4.0 times the calculated value, while the *erythro* exhibits an enhancement of 3.5.[10] Clearly, these factors of 4.0 and 3.5 are a far cry from the corresponding factor of 4,000,000 estimated for the acetolysis of β,β,β-triphenylethyl tosylate.[11]

---

(1) Purdue Research Foundation Fellow, 1966–1968.

(2) J. C. Charlton, I. Dostrovsky, and E. D. Hughes, *Nature*, **167**, 986 (1951).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 513–514.

(4) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, 74, 1113 (1952).

(5) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., p 151.

(6) Even if we adopt the somewhat smaller estimate of Streitwieser (ref 5, p 146) of 8 for the rate-retarding influence of each phenyl substituent, the estimated enhancements are still enormous, 30,000,000 and 4,000,000.

(7) H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, pp 140–158.

(8) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Am. Chem. Soc.*, 87, 1280 (1965).

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

(10) Reference 5, p 146. In this estimate Streitwieser ignored both the contribution of internal return and the counter-balancing contribution of increased steric strain accompanying the introduction of the phenyl substituent.

(11) This discussion is emphasizing acetolysis results for reasons we shall clarify later. We are not unaware of the fact that the importance of aryl participation can be modified greatly by the introduction of activating substituents or by the use of less nucleophilic solvents, but this is not pertinent to the point under discussion.

These results indicate that the ability of β-phenyl (not activated by substituents) to participate in the acetolysis of symmetrical β-phenylalkyl systems must be quite small. Consequently, it follows that the enormous rate enhancement observed in the acetolysis of β,β,β-triphenylethyl tosylate cannot be attributed to any inherent large tendency for participation by the phenyl groups, but must represent a driving force arising primarily from some other factor, such as relief of steric strain at the badly crowded quaternary center.[8,12]

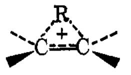
These considerations lead us to what would appear to be a major difficulty in the current interpretation of the solvolysis of *threo*- and *erythro*-3-phenyl-2-butyl tosylates.[13]

It has long been considered that in an endothermic process, such as the conversion of an appropriate derivative into the corresponding ions in a solvolysis, the transition state should resemble the first intermediate.[14] Consequently, the postulated formation of relatively stable phenonium ion intermediates in the acetolysis of *threo*- and *erythro*-3-phenyl-2-butyl tosylates[13] would be expected to be reflected in a significant stabilization of the transition state, resulting in a major enhancement in the rate. Clearly, the minor factors of 4.0 and 3.5 estimated by Streitwieser for the acetolysis of *threo*- and *erythro*-3-phenyl-2-butyl tosylate does not appear to be compatible with the postulated formation of relatively stable phenonium ion intermediates.

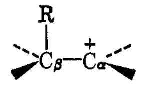
There is the possibility that Streitwieser's estimate is low. However, an exhaustive examination of all of the available data for symmetrical β-phenylalkyl systems has failed to reveal any significant rate acceleration by the neighboring phenyl group during acetolysis.[9,15,16]

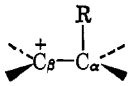
A second possibility is that, contrary to past thinking, the transition state does not resemble the first intermediate. This would be a truly revolutionary conclusion, one that would require major revision of previous interpretations of the huge mass of solvolytic data. Clearly, this is a step that we shall wish to take only as a last resort.

The third way out of the dilemma is that originally proposed by Winstein and Morse.[17] "Just as in the case of functional neighboring groups [S. Winstein, *Bull. Soc. Chim. France*, **18**, C 55 (1951) 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



may, in some cases, be simulated by a dynamic pair of isomeric cations





These one-sided structures could still involve serious delocalization of the C_β–R bonding pair. Also, without this, but with restricted rotation about the C_α–C_β 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."[18]

Experimental support for this position has been advanced by C. J. Collins and his coworkers in their classic study of the 1,2,2-triphenylethyl system.[19] Moreover, theoretical support for this position has been provided by Collins, Benjamin, and Lietzke, who demonstrated with the aid of a computer that the observed product ratios in the acetolysis of the isomeric 3-phenyl-2-butyl tosylates are consistent with reasonable values for phenyl migration, rotational isomerization, and capture of the ions by solvent.[20,21]

In his recent review article on phenonium ions,[13] Cram has taken a position which appears to be in opposition to that expressed by Winstein. Cram argues that only a bridged species can give solvolysis with retention,[22] and that stereochemistry alone suffices to identify bridged ions.

Consequently, in order to resolve this problem, we appear to be faced with the need to provide answers to two questions.

1. *Are the observed small rate effects in the acetolysis of 3-phenyl-2-butyl and related symmetrical derivatives compatible with the postulated formation of relatively stable phenonium ion intermediates?*
2. *Do the stereochemical results require a symmetri-*

---

[12] It should be pointed out that in contrast to Ingold[3] and Streitwieser,[5] Winstein and his coworkers[4] recognized that relief of steric strain could be a significant factor in the huge rate enhancement exhibited by β,β,β-triphenylethyl tosylate.

[13] For a review of the data, with literature references, see D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964).

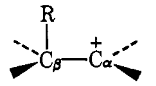
[14] G. S. Hammond, *ibid.*, **77**, 334 (1955).

[15] Although we have not found it clearly expressed in print, this situation was evidently recognized by earlier workers. In reviewing an earlier manuscript,[9] Professor Winstein wrote: "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."

[16] P. von R. Schleyer has developed a highly ingenious approach to this question. His preliminary results support the conclusion that neighboring phenyl does not make any significant contribution in systems of the type under discussion (private communication).

[17] S. Winstein and B. K. Morse, *J. Am. Chem. Soc.*, **74**, 1133 (1952), footnote 13.

[18] In line with this position, see also S. Winstein and L. L. Ingraham, *J. Am. Chem. Soc.*, **77**, 1738 (1955): "Considerable stereospecificity at C_α is also possible in rearrangement through open ion



as a result of ionization of predominantly one conformational form of the original molecule and the subsequent behavior of the intermediate or intermediates as regards rotation about the C_α–C_β bond and shift of the migrating group, R."

[19] C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959). These authors realized a maximum of approximately 75% retention in their deamination and 70% retention in their hydrolysis experiments. This is clearly lower than the 95% retention realized in acetolysis in the 3-phenyl-2-butyl system, but the difference is not incompatible with the much greater lifetime to be anticipated for a highly hindered, stabilized benzylic cation.

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

[21] A number of authors, such as J. A. Berson, *et al.*, *J. Am. Chem. Soc.*, **89**, 2590 (1967), has generously credited the senior author (H. C. B.) of the present paper for the idea that a rapidly equilibrating pair of cations might control stereochemistry, in the same manner as is postulated for a bridged cation, the so-called "windshield-wiper effect." However, it should be clear from the above discussion that Professor Winstein deserves full credit for introducing this intriguing idea—the "Winstein windshield-wiper effect."

[22] Cram's present position also appears to be in conflict with his earlier position taken to account for his observations in the deaminative acetolysis of 3-phenyl-2-butylamines: D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957). In that study he proposed that a "hot" unbridged 3-phenyl-2-butyl cation could undergo both rapid migration of the neighboring group and rapid substitution, faster than the rate of rotation about the central carbon–carbon bond, resulting in retention. On the other hand, it is his belief that the "cold" 3-phenyl-2-butyl cation, produced in the solvolysis of the tosylate, must be bridged to achieve substitution with retention.

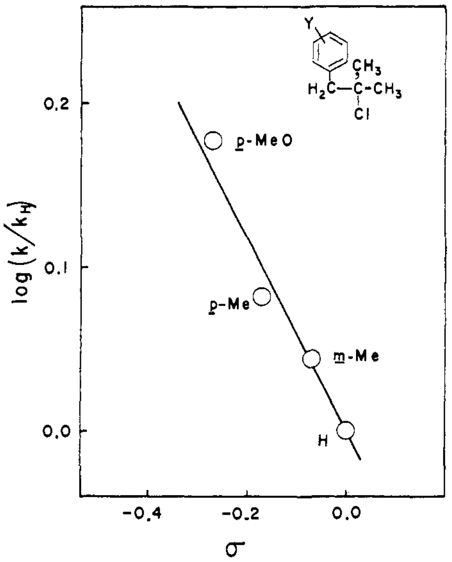


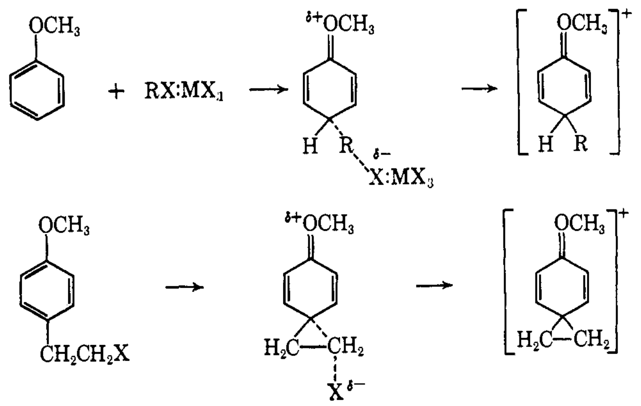
Figure 1. Correlation of the rates of solvolysis of the substituted benzyldimethylcarbinyl chlorides with the σ constants.

cal bridged intermediate, as stated by Cram, or can they be accounted for in terms of rapidly equilibrating cations or ion pairs, as suggested by Winstein?[23]

The stereochemical question is a highly interesting one. However, we feel that before we can be in position to provide an experimental answer to the stereochemical question, we must have a more reasonable basis for proceeding from the observed rate data to a decision as to whether we are dealing with static bridged ions, equilibrating π-bridged ions, or equilibrating open cations.

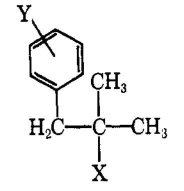
We have now accumulated a wealth of data on the effects of substituents on the rates of aromatic substitution.[24] We have achieved unexpected success in correlating such data with the σ^+ constants.[25] Consequently, it appeared to us that systematic study of the effect of representative substituents on the rates of solvolysis of symmetrical β-arylalkyl derivatives might provide us with an estimate of the amount of charge which is delocalized from the electron-deficient center to the aromatic ring in the transition state.[26]

Accordingly, we have undertaken a systematic study of the effect of substituents on the rates of solvolysis of representative symmetrical β-arylalkyl derivatives.

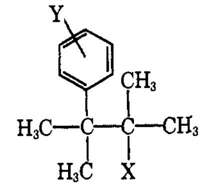


Previously, we reported our results for the primary β-arylethyl system.[27]

In the present paper we are reporting our results and conclusions for the corresponding tertiary systems, 3-aryl-2-methyl-2-chloropropane (I-Cl) and 3-aryl-2,3-dimethyl-2-chlorobutane (II-Cl).

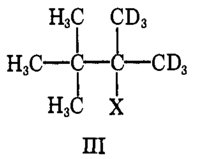


I, X = Cl; Y = H, *m*-Me, *p*-Me, *p*-MeO

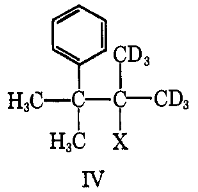


II, X = Cl, OH, ODNB; Y = H, *m*-Me, *p*-Me, *p*-MeO

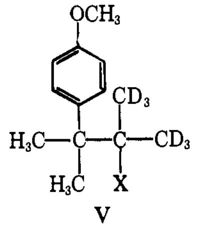
The rate data reveal that 3-*p*-anisyl-2,3-dimethyl-2-chlorobutane (II-Cl, *p*-OCH_3) undergoes solvolysis in 80% aqueous ethanol at 25° at a rate approximately eightfold that of the parent compound, 3-phenyl-2,3-dimethyl-2-chlorobutane (II-Cl, H). Consequently, the aryl participation in the anisyl derivative is indicated to represent a factor of ~8, of the same order of magnitude as that estimated by Streitwieser for the acetolysis of 3-phenyl-2-butyl tosylate (~4). Consequently, it appeared desirable to examine representative carbonium ion reactions of these tertiary derivatives (I, II) in order to establish whether the reactions involve symmetrical arylonium ions or unsymmetrical species (equilibrating open or equilibrating π bridged). Accordingly, we undertook the synthesis of the deuterium-tagged derivatives (III, IV, and V) and examined their behavior in a number of typical carbonium ion reactions.



III



IV



V

X = Cl, OH, ODNB

---

[23] A number of investigators have informed us that they are studying solvolyses in highly unusual solvents, in the hope of demonstrating large rate accelerations by neighboring phenyl, or that they are undertaking pmr studies of β-arylethyl systems with highly activating substituents, in the hope of demonstrating the existence of arylonium ions. (For example, see G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *J. Am. Chem. Soc.*, **89**, 711 (1967) and J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).) Such results are of considerable interest. However, it should be clear from the above discussion that these studies will not contribute to the questions at issue. Somehow, many investigators appeared to have gained the impression that the senior author (H.C.B.) has taken the position that arylonium ions cannot exist under any circumstances or that aryl participation can never be significant. A careful reading of our publications in this area will reveal a consistent position, summarized in the above discussion. It is our hope that the availability of this discussion will now make it possible for those interested in this area to focus their attention on the actual questions at issue.

[24] For a summary of the data with literature references, see L. M. Stock and H. C. Brown, *Advan. Phys. Chem.*, **1**, 35 (1963).

[25] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[26] After all, the proposed mechanism leading to the formation of a bridged intermediate is essentially equivalent to an electrophilic aromatic substitution.

[27] H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Am. Chem. Soc.*, **89**, 370 (1967).

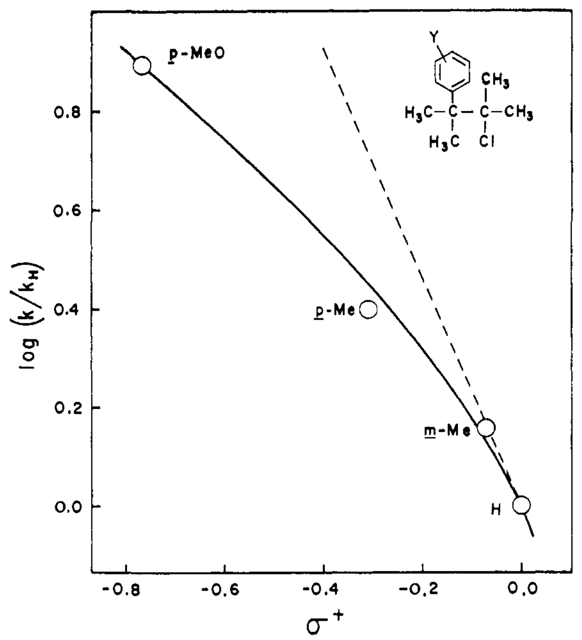


Figure 2. Correlation of the rates of solvolysis of the substituted 2,3-dimethyl-3-phenyl-2-chlorobutanes with the σ^+ constants.

Rate Studies

The rates of solvolysis of substituted benzyldimethylcarbinyl chlorides (I-Cl) were previously studied by VanderWerf and his coworkers.[28] Their results revealed very little effect of the substituent on the observed rate. We extended their study to the *p*-methoxy derivative, of major concern to the present study, and repeated their measurements for the parent compound, and the *m*-methyl and *p*-methyl derivatives in order to have data obtained with a single batch of solvent for comparison. The data are summarized in Table I.

Table I. Rate Constants and Relative Rates for the Solvolysis of Substituted Benzyldimethylcarbinyl Chlorides in 80% Aqueous Ethanol at 50.0°

Substituent Y(I-Cl)	Rate constant, 10^6k_1, sec^{-1}	Rel rate
Hydrogen	3.85[a]	1.00
m-Methyl	4.33[b]	1.11
p-Methyl	4.73[c]	1.21
p-Methoxy	5.90	1.51

[a] Previously reported,[28b] 3.95 ($\Delta H^{\pm}$ 22.9; $\Delta S^{\pm}$ −8.1). [b] Previously reported,[28b] 4.29 ($\Delta H^{\pm}$ 22.8; $\Delta S^{\pm}$ −8.0). [c] Previously reported,[28a] 1.91 at 40.8°.

It should be observed that the *p*-methoxy substituent increases the rate by a factor of only 1.5. Clearly there is no significant charge delocalization from the developing carbonium ion into the aromatic ring. The data fail to correlate with the electrophilic substituent constants, σ^+,[25] but are correlated reasonably well by the σ constants[29,30] with a reaction constant ρ of −0.65 (Figure 1).

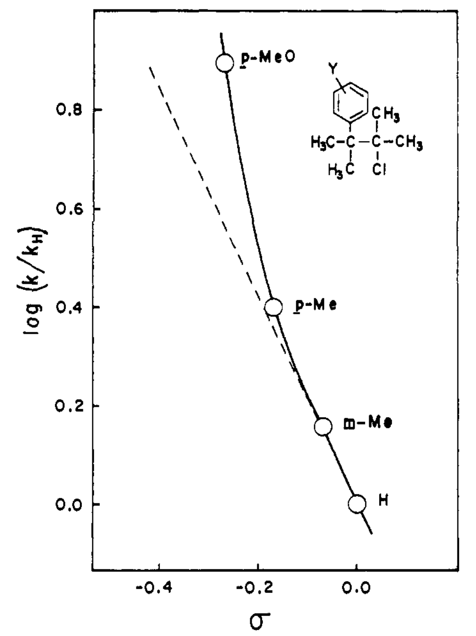


Figure 3. Correlation of the rates of solvolysis of the substituted 2,3-dimethyl-3-phenyl-2-chlorobutanes with the σ constants.

The corresponding effects of substituents in the 3-aryl-2,3-dimethyl-2-butyl chlorides (II-Cl) are larger, but still relatively small. Thus, the *m*-methyl group enhances the rate of the parent compound by a factor of 1.4, the *p*-methyl group by a factor of 2.5, and the *p*-methoxy group by a factor of 7.9 (Table II).

Table II. Rate Constants and Relative Rates for the Solvolysis of Substituted 2,3-Dimethyl-3-phenyl-2-chlorobutanes in 80% Aqueous Ethanol

Substituent Y(II-Cl)	Temp, °C	Rate constant, 10^5k_1, sec^{-1}	Rel rate
Hydrogen	25.0	1.50[a,b]	1.00
	50.0	33.1	
m-Methyl	25.0	2.16	1.44
p-Methyl	25.0	3.77	2.51
p-Methoxy	0.0	0.328	
	25.0	11.8[c]	7.86

[a] Previously reported,[9] 1.78. [b] $\Delta H^{\pm}$ 23.1; $\Delta S^{\pm}$ −3.2. [c] $\Delta H^{\pm}$ 22.7; $\Delta S^{\pm}$ −0.7.

These rate factors resulting from the introduction of these substituents are exceedingly small compared to those observed for typical aromatic substitution[24] or for the solvolysis of typical benzyl[27] or *t*-cumyl derivatives. These rates are not correlated by the σ^+ constants (Figure 2), and the corresponding plot using the σ constants (Figure 3) suggests a reverse curvature. Indeed the behavior is remarkably similar to that previously observed for the formolysis of the substituted β-phenylethyl tosylates.[31]

Product Studies

The deuterium-tagged alcohols, III-OH, IV-OH, and V-OH were synthesized by the action of methyl-d_3-magnesium iodide on the corresponding esters. Not only was it convenient for synthetic reasons to introduce the methyl-d_3 groups at these positions, but con-

---

(28) (a) A. Landis and C. A. VanderWerf, *J. Am. Chem. Soc.*, **80**, 5277 (1958); (b) M. M. Tassler and C. A. VanderWerf, *J. Org. Chem.*, 30, 405 (1965).

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

(30) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958).

(31) Compare Figures 2 and 3 of ref 27.

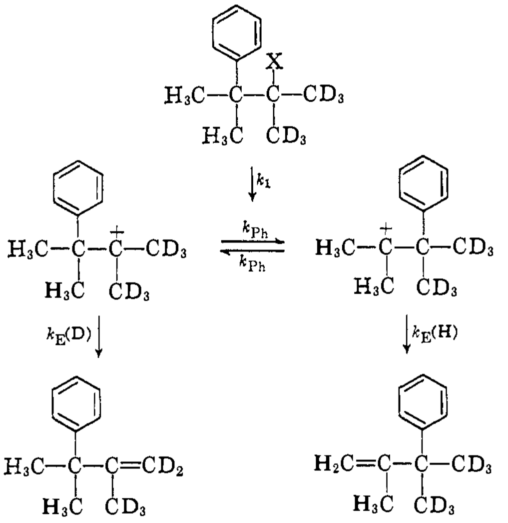


Figure 4. Process to show that the isotope effect can only serve to enhance the amount of rearranged product.

sideration of the possible contribution of isotope effects to the scrambling observed in the product makes it apparent that such isotope effects can only increase and not decrease the amount of observed scrambling.

This point may be made clearer by examination of the effect of the slower loss of a deuteron as compared to a proton from the equilibrating pair of cations (or the corresponding phenonium ion) in the process illustrated in Figure 4.

Consequently, we believe that the observed scramblings, as determined by pmr examination of the product (100% scrambling = 50% rearrangement), represents an upper limit to the amount of scrambling that would be observed in tagged systems not involving such isotope effects. Since an observation of complete scrambling had no diagnostic value in our study,[32] it was entirely satisfactory for our purposes to establish that in specific instances the observed scramblings were less than 100%, without establishing precisely the exact value that would exist in the absence of the isotope effect.

The following reactions were selected as representative of accepted carbonium ion processes, and the three tagged tertiary alcohols (III-OH, IV-OH, V-OH) and certain of their derivatives were subjected to these reactions.

$$\mathrm{ROH + HCl \longrightarrow RCl + H_2O} \tag{A}$$

$$\mathrm{ROH + CH_3OH \xrightarrow{H^+} ROCH_3 + H_2O} \tag{B}$$

$$\mathrm{RODNB + CH_3OH \longrightarrow ROCH_3 + olefin + HODNB} \tag{C}$$

$$\mathrm{ROH \xrightarrow{Al_2O_3} olefin + H_2O} \tag{D}$$

$$\mathrm{olefin + CH_3OH \xrightarrow{H^+} ROCH_3} \tag{E}$$

$$\mathrm{olefin + HCl \longrightarrow RCl} \tag{F}$$

$$\mathrm{RCl + CH_3OH \longrightarrow ROCH_3 + HCl} \tag{G}$$

$$\mathrm{RONa + CHBr_3 \longrightarrow olefin} \tag{H}$$

Roberts and Yancey have reported that treatment of ^{14}C-labeled pentamethylethanol (corresponding to III-OH) with Lucas reagent (concentrated hydrochloric acid and zinc chloride) led to a chloride with complete scrambling of the methyl groups.[33] On the other hand, treatment of the alcohol with concentrated hydrochloric acid at 0° resulted in a nearly quantitative conversion into chloride with 28% scrambling (14% rearrangement).

For our experiments we decided to use the convenient automatic hydrochlorinator recently developed in our laboratory.[34] Treatment of III-OH in carbon tetrachloride with hydrogen chloride for 45 min at 0° in this apparatus resulted in a nearly quantitative conversion into the chloride which had undergone 12% of scrambling. Under the same conditions both IV-OH and V-OH yielded chlorides which were completely scrambled. Indeed, treatment of IV-OH with hydrogen chloride at 0° for 1 min produced a product which the nmr spectrum indicated contained approximately 15% of the chloride—completely scrambled!

It is evident that even in these tertiary derivatives the aryl groups exhibit a remarkable lability.

In the next reaction each of the alcohols was dissolved in methanol, 0.5 M in sulfuric acid. The reactions were allowed to proceed at 25 or 50° until approximately 20% of the corresponding ether had formed. The ethers and olefins were isolated by glpc and subjected to pmr examination. The product from III-OH was observed to have undergone 26% scrambling, whereas the phenyl derivative yielded a product exhibiting 76% scrambling, along with the corresponding olefin which exhibited complete scrambling.[35] Both of the products from V-OH, on the other hand, contained more than 50% of the rearranged[35] product. Only trace amounts of methyl-shifted species were observed in these cases.

The 3,5-dinitrobenzoates, III-ODNB, IV-ODNB, V-ODNB, were prepared from the corresponding alcohols and were solvolyzed in absolute methanol at 75 or 100° in the presence of sodium acetate. Examination of the product by glpc indicated the presence of only the methyl ethers and the corresponding olefins. The absence of the alcohols confirms that the reaction involves alkyl oxygen fission. We are assuming that the reaction is SN1 in nature since the possibility of an SN2 process in such highly crowded tertiary derivatives has never been demonstrated.

The methyl ether from III-ODNB (20%) was essentially free of rearrangement. On the other hand, the methyl ether from the phenyl derivative IV-ODNB (10%) was 45% scrambled. Finally, the methyl ether from the anisyl derivative V-ODNB (34%) was com-

---

[32] Complete scrambling could involve either the formation of a symmetrical carbonium ion or very rapid equilibration of an unsymmetrical intermediate. However, less than complete scrambling is clearly incompatible with the formation of a symmetrically bridged cation as the sole intermediate.

[33] J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, **77**, 5558 (1955).

[34] H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

[35] The difference in the amount of scrambling observed in the substitution product and the elimination product may indicate the involvement of two different intermediates. However, the difference can also be accounted for more simply in terms of the primary isotope effect which should favor elimination in the rearranged carbonium ion, as previously discussed (Figure 4). The difference in isotope effects in the substitution and elimination processes has some interesting consequences. For example, in the equilibrated product from V-OH, the ratio of per cent rearranged to per cent unrearranged was always higher in the elimination products. For example, an iodine-catalyzed elimination reaction of V-OH gave ~60% of anisyl-shifted product, ~30% of retained product, and ~10% of methyl-shifted product, whereas an equilibrium mixture of V-Cl gave 60% of rearranged and 40% of retained structure.

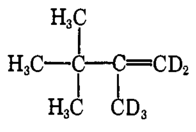
pletely scrambled. This represents an interesting case where the extent of scrambling in the captured carbonium ion varies from approximately 0% for the methyl derivative, to 50% for the phenyl, to 100% for the anisyl.[36]

Examination of the methyl ethers indicated the presence of minor amounts of methyl-shifted species (<5%) from IV-ODNB and V-ODNB. However, the amounts were so small that no analysis was undertaken.

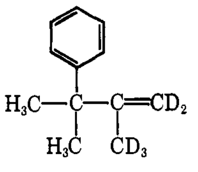
The olefin (80%) from III-ODNB was also unscrambled. That from V-ODNB (66%) was completely scrambled. However, it was unexpected that the olefin from IV-ODNB exhibited a degree of scrambling (26%) that was much less than that observed in the methyl ether product (45% scrambling). A possible explanation is that the solvolysis is accompanied by a competitive intramolecular elimination reaction, similar to that observed in the decomposition of acetates at elevated temperatures. The fact that SN1 reactions of the anisyl derivative are considerably faster could account for the observation that this competitive intramolecular elimination is less important in the anisyl derivative.

We were primarily interested in the scramblings observed in the methyl ether formed by capture of the cation. Consequently, this unexpected development offers no significant difficulty for this study. However, it suggests that one should be cautious in interpreting the course of such reactions in terms of olefin products alone.[37]

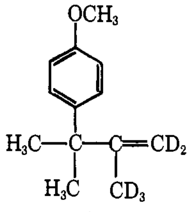
Originally we explored a number of dehydration procedures as possible routes of proceeding from the parent alcohols, III-OH, IV-OH, and V-OH, to the corresponding olefins, III-Ol, IV-Ol, and V-Ol. Many of these procedures resulted in serious scrambling of the label. Even dehydration over alumina in the initial stages of our study resulted in extensive scrambling. However, we were finally successful in developing conditions which allowed conversion of the alcohols to olefins to proceed over alumina with only minor amounts of scrambling. Consequently, we became interested in this reaction as a representative carbonium ion reaction.



III-Ol



IV-Ol



V-Ol

The dehydration of alcohols over alumina has been extensively studied by Pines and his coworkers.[38] Although the exact nature of the reaction path for the dehydration reaction is not yet clear, the reaction does exhibit many of the characteristics associated with carbonium ion reactions.[39] For example, Pillai and Pines[38c] noted that methyl group rearrangement is common in neopentyl-type alcohols, but becomes negligible in such alcohols which are tertiary and ionize easily (*e.g.*, pentamethylethanol). We have noted that the ease of dehydration of alcohols parallels the ease of formation of the carbonium ions.

In our initial experiments we passed the labeled alcohols over commercial alumina without pretreatment. The olefins obtained were extensively scrambled—10% for IV-Ol and 50% for V-Ol. It is known that the properties of alumina can be modified by controlling the amount of alkali metal ions in the material, or by pretreatment with ammonia, etc.[38a] Accordingly, we impregnated the catalyst with potassium hydroxide (1% potassium). However, over this catalyst V-OH was converted not into the olefin, but into *p*-methoxycumene.[40]

The most favorable conditions we found involved passing the alcohol dissolved in ethylenediamine concurrently over the alumina at 300°. Under these conditions the olefin IV-Ol was obtained with 0 to 5% scrambling and the olefin V-Ol with ∼20% scrambling. Pure III-Ol was obtained by treatment of the alcohol with phosphoryl chloride in pyridine.[42]

The acid-catalyzed addition of methanol[43] to IV-Ol and V-Ol was carried out at 25° in the presence of 2.0 *M* sulfuric acid. The reactions were allowed to proceed to 20% conversion of the olefin into the ether. Analysis of the ethers revealed that the product from IV-Ol had undergone 39% of net scrambling, whereas that from V-Ol was completely scrambled.

Recently, we have been successful in trapping an unsymmetrical intermediate in the hydrochlorination of 1-methyl-d_3-2-methylene norbornane.[44] Accordingly, we decided to examine the deuteriochlorination of the three olefins, III-Ol, IV-Ol, and V-Ol. We utilized the automatic hydrochlorinator[34] using sulfuric acid-d_2 in the generator flask and a concentrated solution of deuterium chloride in deuterium oxide in the buret.

The deuteriochlorinations were carried out under a number of representative conditions. Experiments revealed that the tertiary chlorides first formed were rapidly scrambled by further exposure to the deuterium chloride. Consequently, the reactions were carried out for short periods of time (1–5 min), and the reaction was halted before complete addition had been achieved by rapidly pumping off the free deuterium chloride. In the ab-

---

(36) We are especially interested in such gradual changes in view of the arguments presented earlier that the present sharp division of carbonium ions into essentially two distinct classes must be considered suspect.[9] We believe it is much more probable that carbonium ions exist as an essentially continuous spectrum of static classical ions, equilibrating open ions, equilibrating unsymmetrically bridged ions, and static symmetrically bridged ions.

(37) For example, the acetolysis of the related 3,4-dimethyl-4-phenyl-3-hexyl *p*-bromobenzoate produces only olefins as products. The authors based their conclusions as to the importance of phenonium ion intermediates in this reaction on the assumption that all of the olefin products arose from the corresponding carbonium ion as an intermediate: D. J. Cram and J. D. Knight, *J. Am. Chem. Soc.*, **74**, 5839 (1952).

(38) H. Pines and W. O. Haag, *ibid.*, **82**, 2471 (1960); (b) *ibid.*, **83**, 2847 (1961); (c) C. N. Pillai and H. Pines, *ibid.*, **83**, 3274 (1961); (d) K. Watanabe, C. N. Pillai, and H. Pines, *Chem. Ind.* (London), 984 (1963); (e) F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1735 (1966).

(39) For an excellent review, see M. E. Winfield, *Catalysis*, 7, 93 (1960).

(40) A similar result was realized in another experiment where the sodium alkoxide of V-OH was heated in DMSO at 75°. These reactions must be related to the cleavage reactions studied extensively by Cram and his associates.[41]

(41) D. J. Cram, A. Langemann, W. Lwowski, and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 5760 (1959).

(42) R. R. Sauers, *ibid.*, **81**, 4873 (1959). This was one of the procedures we explored early for the synthesis of the olefins. The procedure was entirely satisfactory for the production of III-Ol, but produced IV-Ol and V-Ol with 30 and 100% scrambling, respectively.

(43) *Cf.* S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962).

(44) H. C. Brown and K.-T. Liu, *ibid.*, **89**, 466 (1967). See this paper for a discussion of the hydrochlorination reaction as a representative carbonium ion reaction.

Table III. Scrambling in the Deuteriochlorination of III-Ol, IV-Ol, and V-Ol

Solvent	Temp, °C	Time, min	Scrambling, % III-Cl	IV-Cl[a]	V-Cl[a]
Methylene chloride	−75	1	~5	78	100
	0	1	0	<5	75
	25	5			63
Pentane	−75	1	0	30	100
Neat	0	5	0	(0)[b]	40

[a] The partially scrambled olefins produced by the alumina–ethylenediamine dehydration were used. [b] The addition was slow and the conversion to chloride was only 5% in 15 min.

Table IV. Summary of the Scramblings Observed in the Products Produced in Representative Carbonium Ion Reactions of the Deuterium-Labeled Derivatives

Reaction	Product	Scrambling,[a] % III-X	IV-X	V-X
(A) $ROH + HCl \longrightarrow RCl + H_2O$	Chloride	12	100	100
(B) $ROH + CH_3OH \xrightarrow{H^+} ROCH_3 + H_2O$	Ether	26	76[b]	100[c]
	Olefin		100[b]	100[c]
(C) RODNB[d] + $CH_3OH \longrightarrow ROCH_3 + HODNB$	Ether	0[e]	45[f]	100[g]
	Olefin	0[e]	26[f]	100[g]
(D) $ROH \xrightarrow{Al_2O_3}$ olefin + H_2O	Olefin		<5	20
(E) Olefin + $CH_3OH \xrightarrow{H^+} ROCH_3$	Ether		39	100[h]
(F) Olefin + $DCl \longrightarrow RCl$	Chloride	0	<5[h,i]	75[h,i]
(G) $RCl + CH_3OH \longrightarrow ROCH_3$	Ether	19	48[h]	100[h]
(NaN_3)	Ether			100[h]
	Azide			100[h]
($AgClO_4$)	Ether			100[h]
(H) $RO^-Na^+ + CHBr_3 \longrightarrow$ olefin	Olefin	0	28	74

[a] This quantity is twice the per cent of rearranged isomer. 100% scrambling means 50% *or more* of the rearranged product. (See discussion in text.) [b] 44% ether, 56% olefin, 50°. [c] 82% ether, 18% olefin, 25°. [d] 3,5-Dinitrobenzoate. [e] 20% ether, 80% olefin. [f] 10% ether, 90% olefin. [g] 34% ether, 66% olefin. [h] The starting materials were partially scrambled. These values are the corrected values of net scrambling. [i] For additional results, see Table III.

sence of the acid, the product was adequately stable for examination by pmr. The results are summarized in Table III.

The reactions at −75° were exceedingly fast and resulted in the essentially complete scrambling of the chlorides from V-Ol. Although we did not investigate this point in the present study, we have observed in other cases that huge amounts of hydrogen chloride dissolve in the solvents at −75° and these concentrated solutions are extraordinarily effective both in achieving additions and in achieving isomerizations that proceed through carbonium ions.[45]

The partially scrambled chlorides produced in these reactions, containing more or less admixed olefin, were dissolved in methanol in the presence of added sodium acetate. The methyl ether products were isolated. These revealed 19, 48, and 100% of net scramblings for the solvolysis of III-Cl, IV-Cl, and V-Cl, respectively. In the case of V-Cl, the solvolysis was also carried out in the presence of sodium azide and of silver perchlorate. However, the products were completely scrambled.

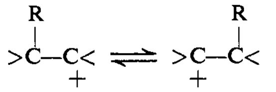
Finally, we turned our attention to the deoxideation reaction. The reaction of haloforms with alkali metal alkoxides was originally reported in 1855 by Hermann.[46] However, Skell and his coworkers have recently made an extensive study of the reaction and have concluded that it involves the conversion of the alkoxide ion to the corresponding carbonium ion.[47]

Accordingly, we treated the alcohols in tetrahydrofuran with sodium hydride to form the corresponding alkoxides and then added bromoform to induce the reaction. Yields of olefin of approximately 20% were realized. The pmr analysis indicated that no detectable scrambling had occurred in III-Ol, 28% in IV-Ol, and 74% in V-Ol.

The results of all of these product studies for the reactions of deuterium-labeled compounds are summarized in Table IV. It should be noted that little or no scrambling was realized in all reactions of the III derivatives, less than 100% scrambling was observed in seven of the eight reactions of the IV derivatives, and less than 100% scrambling in only three of the reactions of the V derivatives.

The Question of a Dichotomy *vs.* a Continuous Spectrum of Carbonium Ion Structures

We have previously pointed out the existence of two major anomalies in the current treatment of carbonium ion intermediates.[9] Systematic lowering of the potential barrier separating two equivalent cations



$$\overset{+}{>\underset{|}{\overset{R}{C}}-C<} \rightleftharpoons >C-\overset{R}{\underset{+}{C}}<$$

would be expected to result in an essentially continuous spectrum of cations in which three distinct classes may be recognized: (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) static bridged species where the potential barrier has disappeared so that resonance now occurs involving the two structures.[48] One apparent anomaly

---

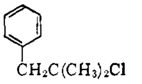
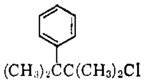
(45) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 3898, 3900 (1967).

(46) M. Hermann, *Ann.*, **95**, 211 (1855).

(47) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959); *ibid.*, **82**, 2971 (1960); P. S. Skell, I. Starer, and A. P. Krapcho, *ibid.*, **82**, 5257 (1960); P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962); P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962); R. J. Maxwell, M.S. Thesis, The Pennsylvania State University, 1963.

(48) See Figure 3 of ref 9.

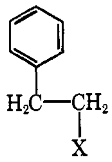
Table V. Rate Constants and Relative Rates for the Solvolysis of Tertiary Chlorides in 80% Aqueous Ethanol at 25°

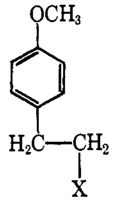
Compound	Rate constant, $10^5 k_1$, sec^{-1}	Rel rate	Compound	Rate constant, $10^5 k_1$, sec^{-1}	Rel rate
$CH_3C(CH_3)_2Cl$	0.93[a]	1.00	$(CH_3)_2\overset{H}{C}C(CH_3)_2Cl$	0.818[a]	0.88
$\overset{CH_3}{CH_2}C(CH_3)_2Cl$	1.55[a]	1.67	$(CH_3)_2\overset{H_3C}{C}C(CH_3)_2Cl$	1.12[a]	1.25
 $CH_2C(CH_3)_2Cl$	0.149[b]	0.16	 $(CH_3)_2CC(CH_3)_2Cl$	1.50[b]	1.61

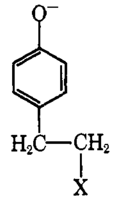
[a] H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **71**, 1845 (1949). [b] Present study.

is that 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. The second apparent anomaly has to do with the fact that it is argued that in a process such as solvolysis the transition state should resemble the intermediate closely. Yet the formation of resonance-stabilized bridged species has been postulated for many systems where the observed rate enhancements are small or negligible. Clearly these represent major anomalies which require resolution.

The problem is indicated by the fact that the formolysis of β-phenylethyl brosylate with a rate enhancement of 2.1 (relative to the ethyl derivative), the formolysis of β-*p*-anisylethyl brosylate, with a rate enhancement of 160, and the ethanolysis of the conjugate base of β-(*p*-hydroxyphenyl)ethyl bromide, with a rate enhancement of 10^8 are all presumed to lead to the formation of a symmetrical arylonium species.

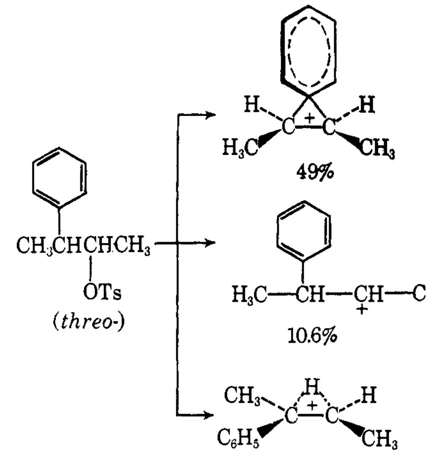

2.1


160


10^8

The problem is perhaps best exemplified by the acetolysis of 3-phenyl-2-butyl tosylate.[13,49] Here the major reaction path is postulated to involve the formation of a resonance-stabilized phenonium[50] ion. Yet, according to Streitwieser's estimate, the observed rate enhancement is only a factor of 4.[51]

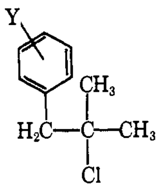
The situation is further complicated by the fact that in many systems the concurrent formation of open and bridged ions have been proposed, again without considering the possible involvement of rapidly equilibrating open ions, or of rapidly equilibrating unsymmetrically bridged ions. For example, in accounting for the products produced in the acetolysis of *threo*-3-phenyl-2-butyl tosylate, it was proposed that the reaction proceeds through three distinct intermediates, 49% through the symmetrical phenyl-bridged ion, 28.3% through the hydrogen-bridged ion, and 10.6% through the open ion (the sum, 87.9%, corresponds to the 87.9% of identified products).[49]

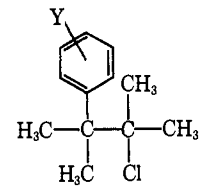


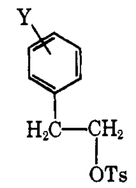
It is relatively easy to establish, as will be pointed out in the present discussion, the existence of an essentially continuous change in the degree of participation present in the transition state. The question remains as how this essentially continuous change in the transition state will reflect itself in the nature of the carbonium ion intermediate. Will this intermediate exhibit the same sort of essentially continuous change, or does ionization produce the essential dichotomy of bridged and open ions proposed by the current theory? This is a more difficult question to answer.

Nature of the Transition State

We now have data for the effect of substituents on the rates of solvolysis of three closely related systems (Table I, Table II, and, in ref 27, Table III). Before we undertake an examination of the effect of substituents and their implications, it may be appropriate to examine the behavior of the parent tertiary chlorides. Appropriate data are summarized in Table V.


I


II


VI

---

(49) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2137 (1952).

(50) We are following Cram[49] in using the term "phenonium ion" for phenyl-bridged species, containing a three-membered carbocyclic ring.

(51) We are emphasizing Streitwieser's estimate in this discussion because his approach, based on the Taft polar constants, would appear to have a more objective basis than the somewhat higher estimates that Cram has advanced[13] or the somewhat lower estimates that we have considered.[9]

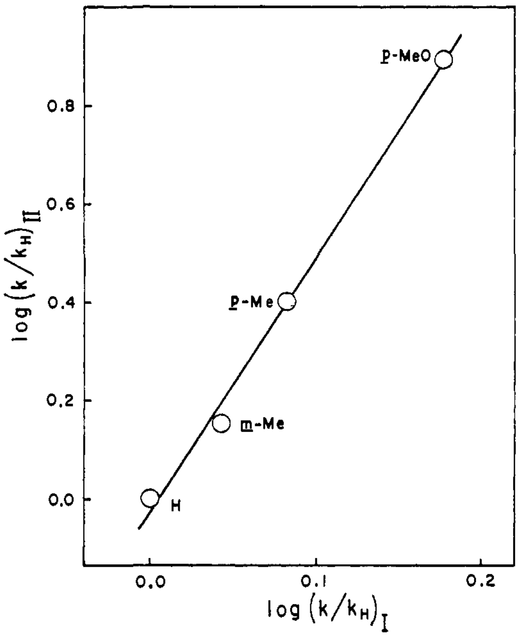


Figure 5. Linear free energy relationship between the rates of solvolysis of substituted benzyldimethylcarbinyl chlorides (I) and *t*-cumyldimethylcarbinyl chlorides (II).

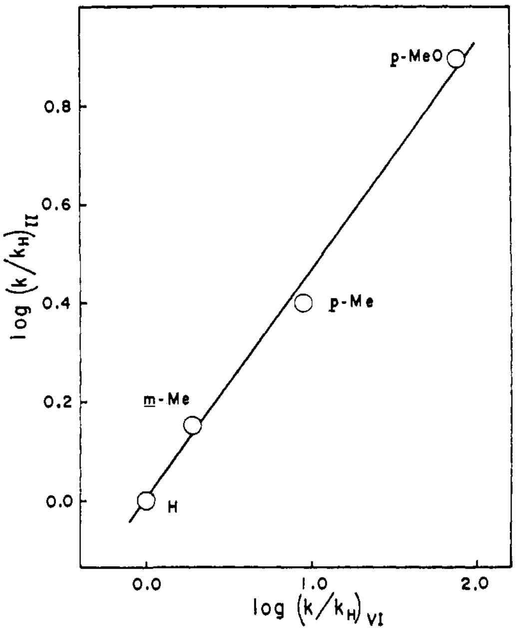


Figure 6. Linear free energy relationship between the rates o solvolysis of substituted β-phenylethyl tosylates (VI) and *t*-cumyldimethylcarbinyl chlorides (II).

The introduction of a phenyl substituent into *t*-butyl chloride to form benzyldimethylcarbinyl chloride results in a rate decrease by a factor of 6. This corresponds reasonably well to the factor of 8 estimated by Streitwieser for the inductive effect of a phenyl substituent.[6] Clearly there is no significant participation by the aromatic ring. This is in accord with the proposal by Winstein and Grunwald[52] that α substitution, in contrast to β substitution, should decrease the driving force due to participation.

On the other hand, the corresponding introduction of a phenyl group for the tertiary hydrogen of isopropyldimethylcarbinyl chloride, results not in a decrease, but in a small increase in rate ($\backsim$2). Consequently, the observed rate is approximately 16 times greater than the rate estimated on the basis of the rate-retarding inductive effect of the phenyl substituent. This could be the result of increased participation by the phenyl group brought about by a favorable effect of the β substituents,[52] or it could arise from the increased steric strain in the highly branched derivative.[53]

This difficulty emphasizes the value of the Hammett approach.[29] By introducing substituents into the *meta* and *para* positions of benzyldimethylcarbinyl chloride (I) and *t*-cumyldimethylcarbinyl chloride (II), we are in a position to modify greatly the electronic characteristic of the aromatic ring and to observe the changes of the interaction of this ring with the developing carbonium ion center without having to correct for changes in the steric contribution.

The effect of substituents in benzyldimethylcarbinyl chloride is certainly small, as indicated by a change of only 1.5 accompanying the introduction of a *p*-methoxy group. It was previously concluded that these small effects must be the result of combined inductive and resonance interactions of the substituent with the aromatic ring transmitted to the reaction center through the carbon chain.[28] This is quite reasonable and agrees with the observation that the data are correlated quite well by the σ constants (Figure 1). Certainly any interactions of the π cloud of the aromatic ring with the carbonium center must be relatively small, in the range of simple thermal energies.

The effect of substituents in the symmetrical system II are larger, but also relatively small, varying from 1.44 for *m*-Me, to 2.51 for *p*-Me, to 7.86 to *p*-MeO. There appears to be no reason why the combined inductive and resonance interactions of these substituents in the aromatic ring should be transmitted by an inductive mechanism through the chain more effectively in this structure II, than in the less substituted structure I. Consequently, we must conclude that there are weak interactions through space between the aromatic ring and the developing cationic center.

In the formolysis of β-arylethyl tosylates (VI) the reaction is presumed to proceed through symmetrical arylonium ions.[54] Here the substituent effects are considerably larger: *m*-Me, 1.88; *p*-Me, 9.01; *p*-CH_3O, 76.3. Here also the data exhibit a downward curvature, when plotted against σ^+, and an upward curvature when plotted against σ (see Figures 2 and 3 of ref 27), similar to the behavior of II (Figures 2 and 3).

Consequently, these three systems provide a gently graded series, in which the effect of the substituent increases by small, relatively regular changes: *p*-CH_3O = 1.5 in I; 7.9 in II; 76 in VI.[55] That we must be

---

[52] S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, 70, 828 (1948).

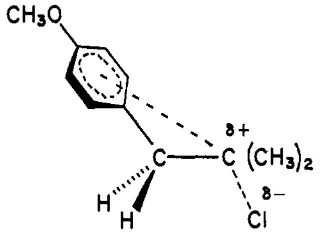
[53] H. C. Brown and R. S. Fletcher, *ibid.*, 71, 1845 (1949). For example, *t*-amyldimethylcarbinyl chloride solvolyzes at a rate 5.6 that of *t*-butyl chloride: H. C. Brown and R. K. Kornblum, *ibid.*, **76**, 4510 (1954).

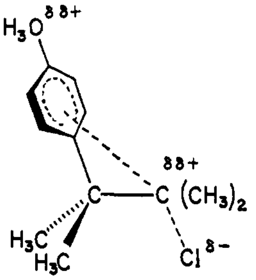
[54] In the case of the parent compound, the observation that the formolysis of a tagged derivative resulted in 45% rearrangement (90% scrambling) led to the conclusion that 90% of the reaction proceeds through the phenonium ion: C. C. Lee, G. P. Slater, and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1417 (1957).

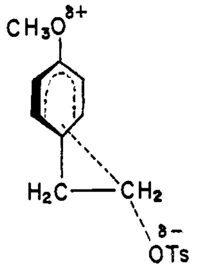
[55] It should be emphasized that the increased effect of substituents in VI may not be the result of the structural change alone, but may in part also be due to the use of the less nucleophilic solvent. The system

dealing with very similar phenomena in these three series is suggested by the linear free energy plots shown in Figures 5 and 6. Consequently, we must consider the possibility that even in the benzyldimethylcarbinyl chlorides there exist small electronic interactions transmitted through space to the developing electron-deficient center.

What changes might we anticipate in the transition state to accompany this gradual increase in the effect of the substituent? It is our belief that we should expect a gradual change from very weak contributions from the π cloud in systems such as I, to stronger and stronger interactions in systems such as II and VI, ultimately approaching closely the arylonium ion in systems involving large rate accelerations and therefore large contributions from the aromatic ring. The changes may be illustrated graphically in the following diagrams.







The gradual change in the structure of the transition state is similar to that which we have previously described for a transition from the π complex to the σ complex.[56]

Nature of the Intermediate

We are now faced with the problem of proceeding from the transition state to the intermediate. Kinetics give us direct evidence as to the stability of the transition state. We are then able to use our accumulated knowledge as to structural effects to draw conclusions as to the probable structure of the transition state. Kinetics give us no direct information as to the structure of the intermediate. However, in the past it has been customary to side step this difficulty by relying on the postulate that in solvolytic processes the transition state must resemble the first intermediate.[57]

If this postulate can be relied upon, then we would argue that I, II, and VI would ionize to cations with increasing interaction between the π cloud and the carbonium center. The first would be essentially classical, with interactions between the π cloud and the electron-deficient center that are of the order of magnitude of thermal energies. In the second case (II), the additional interaction energy in the transition state brought about by the p-methoxy group is approximately 1 kcal/mole. Consequently, even if this doubles[58] in the intermediate, it is a small factor, only a fraction of the energy in the usual hydrogen bond. In the β-anisylethyl derivative, the factor of 76 would correspond to a stabilization of 2.5 kcal in the transition state and 5 kcal in the ion, comparable in energy to a good hydrogen bond.

Of course, if the transition state resembles the first intermediate more closely, the bridging bonding energy in the intermediate would be even less, and conversely.

It should be noted that in this treatment we are proposing that systems exhibiting relatively small participations will tend to ionize to give partially bridged unsymmetrical species,[59] which may equilibrate rapidly, rather than a mixture of static classical and static symmetrically bridged ions, such as has been so often considered in previous treatments of data in this field.[49]

One tool is available which should distinguish between the formation of a symmetrical bridged species, on the one hand, and an unsymmetrical equilibrating species on the other. If a tag is introduced at an appropriate position, recovery of the product with an unsymmetrical distribution of the tag makes it definite that the reaction cannot be proceeding solely through a path involving the formation of a symmetrical bridged species.[60] The reaction must then involve the formation of an unsymmetrical species, which might be a static open ion, an equilibrating open ion, or an equilibrating partially bridged ion.

Study of the 3-aryl-2,3-dimethyl-2-butyl chlorides (II) was of particular interest because the data indicated that the accelerations observed in these derivatives were of the same order of magnitude as that observed in the acetolysis of 3-phenyl-2-butyl tosylate.

First, all of the reactions applied to the tagged pentamethylethyl system III resulted in only partial or no scrambling. The observation that there is zero scrambling in the methyl ether from the methanolysis of the 3,5-dinitrobenzoate, or in the application of Skell's deoxideation procedure[47] to the alcohol confirms the conclusion previously reached by Roberts and Yancy that the methyl-bridged nonclassical ion is not of importance in this system.[33]

In some reactions appreciable scrambling of the methyl tags occur (Table IV). Consequently, it would appear that equilibration can occur in this system, but its rate is normally slower than the rate of reaction of the cation with the usual nucleophiles. It is probable

---

II would doubtless show greater effects of the substituents in a less nucleophilic medium.

(56) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, 74, 3570 (1952).

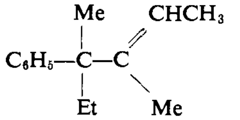
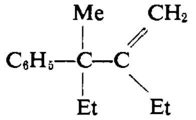
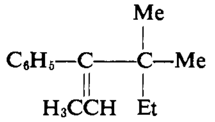
(57) Indeed, in much of the earlier literature on the subject many authors neglected to discriminate between the structure of the transition state and the structure of the intermediate. See discussion in B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms 1965," Interscience Publishers, Inc., New York, N. Y., 1966, p 11.

(58) As a rough rule of thumb it has frequently been estimated that electronic effects are only half developed in the transition state.

(59) It should be pointed out that in the past a number of authors have suggested the possibility that rapidly equilibrating unsymmetrically bridged carbonium ions might be significant in addition to, or in place of, the symmetrical phenonium ion. See, for example, S. Winstein, *et al.*, *J. Am. Chem. Soc.*, 74, 1144, 2169 (1952); J. D. Roberts and C. M. Regan, *ibid.*, 75, 2069 (1953); D. J. Cram and F. A. Abd Elhafez, *ibid.*, 75, 3189 (1953). Moreover, the latter authors suggested that in an unsymmetrically bridged ion "the longer bond. . .would be directed toward the benzene ring as a whole," as contrasted with the corresponding shorter bond in the symmetrical phenonium ion. For reasons that are not entirely clear, these early formulations as unsymmetrically bridged, rapidly equilibrating ions were displaced by the formulation as the symmetrical, resonance-stabilized phenonium ion, in spite of negligible enhancements observed in the rate studies.

(60) J. D. Roberts and his coworkers pioneering in developing this technique. See ref 33.

Table VI. Summary of Products from the Acetolysis of 3,4-Dimethyl-4-phenyl-3-hexyl *p*-Bromobenzoate

Ester	Products		
			
threo	68%	26%	6%
	26% racemic	74% active	
erythro	63%	31%	6%
	18% racemic	82% active	

that with a judicious choice of nucleophiles it would be possible to observe essentially complete scrambling in selected carbonium ion reactions of this system.

Even though the evidence is that the participation by the phenyl group in 2,3-dimethyl-3-phenyl-2-butyl derivatives (IV) must be small, we observed major scrambling. Thus, treatment of the alcohol with hydrogen chloride gave 100% scrambling. Conversion of the alcohol to the methyl ether by methanolysis in the presence of acid gave 76% scrambling. Methanolysis of the 3,5-dinitrobenzoate gave methyl ether with 45% scrambling. On the other hand, dehydration of the alcohol over alumina in the presence of ethylenediamine gave a product with negligible scrambling. Finally, addition of deuterium chloride to the tagged olefin gave the tertiary chloride with negligible scrambling.

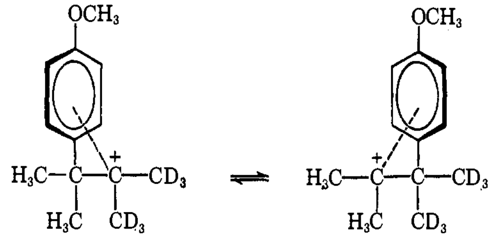
Clearly these results are most consistent with an interpretation in which the reaction proceeds through the formation of open or weakly π-bridged unsymmetrical cations which undergo exceedingly rapid equilibration, so that depending upon the rate at which the cation reacts with the nucleophile more or less scrambling results.[61]

It should be pointed out that a closely related system, 3,4-dimethyl-4-phenyl-3-hexyl *p*-bromobenzoate, was studied by Cram and Knight.[37] They examined the acetolysis of the two optical isomers. They obtained only elimination products with isomer distributions as indicated in Table VI.

These authors interpreted their results on the basis of their belief that the racemized, unconjugated olefin portion arises only from the *cis*-phenonium ion. This belief, apparently based from the earlier work on the 3-phenyl-2-butyl system,[49] led them to draw up an elaborate reaction scheme, involving two isomeric phenonium ions and other possible open ions, all interconvertable with each others, in order to account for the very similar results realized for both the *threo* and *erythro* isomers. They stated: "Although the picture could be complicated further by the intervention of other ion pairs which arise by simple ionization of the starting materials, the present data do not demand any such species." Contrary to this statement, it would appear that a mechanism based on rapidly equilibrating open ions is adequate to account for their results, and the data do not require the intervention of phenonium ions. It should be noted that the solvolysis of IV-ODNB gave us an olefinic product which had undergone 26% scrambling.[62] It may be entirely coincidental, but it is worth noting that Cram and Knight observed 26% racemization in their system.

Finally, we can turn our attention to the *p*-anisyl derivative V. Here solvolysis of the 3,5-dinitrobenzoate gave an ether product which exhibited 100% scrambling. Indeed, all of the carbonium ion reactions examined, with three exceptions, gave 100% scrambling. Dehydration of the alcohol over alumina in the presence of ethylenediamine gave an olefin with only 20% scrambling. Addition of hydrogen chloride to the olefin gave the tertiary chloride with as little as 40% scrambling (Table III). Finally, application of Skell's deoxideation technique gave an olefin with 74% scrambling.

If it is accepted that these represent reactions that proceed through carbonium ions, then it follows that the carbonium ion intermediate cannot be the symmetrical, bridged anisonium ion. On this basis the reaction must involve the formation of an unsymmetrical rapidly equilibrating π-bridged cation.



If further research should reveal that these three reactions are not satisfactory carbonium ion processes, we shall have to consider the possibility that we are dealing with a symmetrical species in this system. However, we will then be faced with the dilemma of how a stabilization of the transition state by the *p*-methoxy substituent of only 1 kcal can convert the parent ion, which is clearly not a phenonium derivative, into a symmetrical anisonium species.

---

[61] We were originally stimulated to undertake a detailed study of the 3-aryl-2,3-dimethyl-2-butyl system by the report that the pmr spectrum of the 2,3-dimethyl-3-phenyl-2-butyl cation was consistent either with its formulation as a phenonium ion, or with its formulation as a rapidly equilibrating pair of classical ions (a preference was expressed for formulation as a phenonium ion): G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 3509 (1965). More recently these authors have concluded that the spectrum is more consistent with a formulation as a rapidly equilibrating pair of ions: G. A. Olah, C. U. Pittman, Jr., E. Nammanworth, and M. B. Comisarrow, *ibid.*, **88**, 5571 (1966). Unfortunately, the authors do not make it clear as to what features about the spectrum have led them to alter their original position. However, it is quite clear from the present results that the 2,3-dimethyl-3-phenyl-2-butyl cation must exist as a rapidly equilibrating pair under solvolytic and related conditions, irrespective of its possible existence as a bridged ion under the special conditions utilized for pmr observation of carbonium ions.

[62] See footnote 37 and the accompanying discussion for our proposal that the lower scrambling in the olefin than in the methyl ether produced in the product indicates that a major portion of the reaction must involve a direct elimination. If such a reaction intervened in the study by Cram and Knights, it would introduce a major complication into the interpretation of their results since their products were entirely olefinic in character.

Conclusions

It is hoped that these results and their discussion has made clear our belief that certain anomalies exist in the carbonium ion area, anomalies which require resolution. If the transition state resembles the first intermediate, a long-accepted position in this field, how can we justify proposals for the formation of resonance-stabilized bridged ions in cases where no significant rate enhancement can be established? The evidence is that stabilization of the transition state in solvolytic processes can be varied almost continuously by small increments. Will these small increments be reflected in the formation of an essential sharp dichotomy of bridged and open ions, as is the position in currently accepted interpretations, or will these small increments be reflected in the formation of an essentially continuous spectrum of static open ions, rapidly equilibrating open ions, rapidly equilibrating partially bridged ions, and static bridged ions? If rapidly equilibrating ions constitute a significant class, why are they essentially absent from current interpretations? Can rapidly equilibrating classical ions control stereochemistry, as proposed by Winstein, or can such control be achieved only by bridged ions, as proposed by Cram?

We continue our efforts to resolve these questions.

Experimental Section

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

2,3-Dimethyl-3-phenyl-2-chlorobutane and Its Substituted Analogs. The following reaction sequence, which is represented by the parent compound, was employed for the preparation of all of the four compounds. Starting with phenylacetonitrile, dimethylation was carried out according to the procedure described by Winstein and Heck[63] to obtain α-methylhydratroponitrile in 50% yield.[64] The hydrolytic procedure was modified as follows to avoid the previously applied sealed-tube reactions. The nitrile (54 g) was quantitatively converted into α-methylhydratropic acid by refluxing for a day in a mixture of 20 ml of water, 100 ml of ethylene glycol, and 50 g of potassium hydroxide. The course of the reaction was conveniently followed by determining the amount of ammonia evolved. The acid, isolated from the salt, was converted into the ethyl ester by the usual method in nearly quantitative yield, and this product was treated with methylmagnesium iodide to obtain 2,3-dimethyl-3-phenyl-2-butanol in a yield of 85%. Hydrochlorination of the alcohol was performed in the automatic hydrochlorinator[34] and the product, 2,3-dimethyl-3-phenyl-2-chlorobutane, recrystallized from ether–pentane at −70°, was obtained as a white powder, mp 35–36°.

Benzyldimethylcarbinyl Chloride and Its Substituted Analogs. These syntheses were straightforward, involving esterification of the substituted phenylacetic acids, followed by reaction of the esters with methyl Grignard, and finally hydrochlorination of the alcohols as above. Each reaction gave an essentially quantitative yield.

Kinetic Procedure. Rate measurements were carried out according to the previously described procedure,[65] except that a mixture of 50 ml of absolute ethanol and 20 ml of pentane was used to quench each kinetic sample. For each run, 70 ml of 0.02 *M* solution was used to take nine kinetic points over two half-lives and three infinity samples. In general, two or three individual runs were conducted for each sample at a given temperature and the reaction constants averaged. These averages are reported in Tables I and II.

1,1-Dimethyl-d_6-2,2-dimethylpropanol (III-OH), 1,1-Dimethyl-d_6-2-methyl-2-phenylpropanol (IV-OH), and 1,1-Dimethyl-d_6-2-methyl-2-*p*-anisylpropanol (V-OH). Methyl-d_3 iodide[66] was used as the deuterium source. The corresponding ethyl ester was treated with 5–10% excess of methyl-d_3-magnesium iodide, which was prepared in ether, employing a Dry Ice–acetone cooled condenser to minimize the loss of methyl-d_3 iodide in the nitrogen flow. Because III-OH takes up moisture very readily to form the hydrate, the crude product in ether was first dried over calcium hydride and filtered from the solid and the solvent removed in a rotatory evaporator. Distillation at 129–130° yielded the desired alcohol. The necessity of carrying out all of the steps under moisture-free conditions should be emphasized.

3,5-Dinitrobenzoates of the Tertiary Alcohols. The method is represented by the following preparative procedure[67] for pentamethylethyl 3,5-dinitrobenzoate. Pentamethylethanol (0.58 g) in 10 ml of tetrahydrofuran was placed in a flask with a magnetic stirrer under a dry nitrogen flow. Slightly less than 1 equiv of *n*-butyllithium in pentane was added, and the mixture was stirred for 30 min. The mixture was then cooled to −70°; 5 ml of a 1 *M* solution of 3,5-dinitrobenzoyl chloride in tetrahydrofuran was added and the mixture allowed to warm up to room temperature slowly. It was stirred overnight at room temperature and then refluxed for 1 hr. After the solvent was removed, the residue was dissolved in ether; the precipitated inorganic salt was removed by filtration and pentane added to precipitate the product. Recrystallization from ether–pentane gave 0.9 g (59%) of slightly yellowish fine plates, mp 116–117°.

Preparations of Olefins by Sauers' Method.[42] The olefins, 2,3,3-trimethyl-1-butene, 2,3-dimethyl-3-phenyl-1-butene, and 2,3-dimethyl-3-(*p*-methoxyphenyl)-1-butene were obtained from the corresponding tertiary alcohols by the action of phosphoryl chloride in pyridine. Dehydration of 1,1-dimethyl-d_6-2,2-dimethylpropanol (III-OH) gave pure olefin, III-Ol, without any methyl group rearrangement. IV-OH and V-OH were also subjected to this reaction, but the olefins obtained showed 30 and 100% scrambling, respectively.

Hydrochlorination of III-OH, IV-OH, and V-OH in the Automatic Hydrochlorinator.[34] Into the reaction flask, previously flushed thoroughly with hydrogen chloride, was injected 1.5 ml of a 50% solution of III-OH in carbon tetrachloride at 0° and the reaction mixture was stirred vigorously for 45 min. As soon as the reaction had stopped absorbing hydrogen chloride, the flask was submitted to a rotatory evaporator to remove the excess acid and the solvent at reduced pressure. The crude product was sublimed at approximately 20 mm, and the white crystals were examined by pmr.

Since the chlorides from IV-OH and V-OH, by this procedure were completely scrambled, we undertook to examine products formed under conditions of partial conversion. IV-OH and V-OH were treated as described above for 1 min at 0°, and the resulting reaction mixtures in carbon tetrachloride were submitted directly to pmr examination after removal of the excess hydrogen chloride. Each of the reaction mixtures was found to contain approximately 10–15% of the corresponding chloride product which had undergone full equilibration of the aryl group. The results are summarized in Table IV.

Acid-Catalyzed Methylation of the III-OH, IV-OH, and V-OH. IV-OH (0.92 g) was dissolved in 20 ml of a 0.5 *M* solution of sulfuric acid in absolute methanol and the solution maintained at 50° for 14 hr. The reaction mixture contained 28.2% of olefin, 22.4% of methyl ether, and 49.4% of the starting material, together with trace amounts of the methyl group shifted products which were excluded from the present analysis. V-OH was treated similarly at 25° for 4.5 hr to obtain 3.4% of olefin, 15.5% of ether, and 81.1% of the starting material. A reaction of III-OH at 50° for 9 hr resulted in about 50% of methyl ether formation, isolated by preparative glpc by the use of a tricresylphosphate column at 100°. The results are summarized in Table IV.

Methanolysis of III-ODNB, IV-ODNB, and V-ODNB. Baker analytical reagent grade methanol was used as the solvent. III-ODNB (1.58 g, 5 mmol) and 0.43 g (5.25 mmol) of sodium acetate were dissolved in 50 ml of solvent, and the mixture was sealed in a tube. The sealed tube was kept at 100° for 24 hr. A small portion

---

[63] S. Winstein and R. Heck, *J. Am. Chem. Soc.*, 78, 4801 (1956).

[64] An improved yield of 80% was obtained for the *p*-methoxy-substituted compound by the use of a reduced amount of solvent.

[65] H. C. Brown and R. K. Kornblum, *J. Am. Chem. Soc.*, 76, 4510 (1954).

[66] Stohler Isotope Chemicals, Montreal 26, Canada, Lot No. 2710, 99.5 atom % D.

[67] J. H. Brewster's method (*J. Am. Chem. Soc.*, 77, 6214 (1955)) provides both a simple procedure and a high yield for ordinary tertiary alcohols. However, although we realized a 90% yield for *t*-butyl alcohol by his method, practically no product was obtained for pentamethylethanol.

Table VII. Summary of Physical Constants

Compound		Hydrogen		*m*-Methyl		*p*-Methyl		*p*-Methoxy	
		Obsd	Lit.	Obsd	Lit.	Obsd	Lit.	Obsd	Lit.
$YC_6H_4CH_2CO_2Et$	Bp, °C (mm)			120–121(13)	115(15)^{a}	123–124(15)	72–74(0.9)^{b}	142–144(10)	157–158(19)^{c}
	$n^{20}\mathrm{D}$			1.4973		1.4965		1.5064	
$YC_6H_4CH_2C(CH_3)_2OH$	Bp, °C (mm)	94–95(10)	94–95(10)^{d}	109–110(11)	84–87(0.5)^{e}	115–116(13)	86–88(1)^{d}	133–134(9.5)	
	$n^{20}\mathrm{D}$	1.5150		1.5129		1.5121		1.5226	
$YC_6H_4CH_2C(CH_3)_2Cl$	Bp, °C (mm)	82–84(9)	88–90(10)^{d}	98–99(9)	59–59.5(0.9)^{e}	106–107(10)	104–104.5(10)^{d}		
	$n^{20}\mathrm{D}$	1.5152		1.5137		1.5135			
	Mp, °C							33–34	
$YC_6H_4C(CH_3)_2CN$	Bp, °C (mm)	119–121(21)	114–116(20)^{f}	123–124(13)	119–120(15)^{g}	116–117(11)	122–123(12)^{h}	140–142(10)	110(3)^{i}
	$n^{20}\mathrm{D}$	1.5062		1.5089		1.5050		1.5153	
$YC_6H_4C(CH_3)_2CO_2H$	Mp, °C	79–80	80–81^{j}	71.5–73	73–74^{g}	80.5–81.5	82^{h}	88–90	89–90^{f}
$YC_6H_4C(CH_3)_2CO_2Et$	Bp, °C (mm)	110–111(11)	68–71(0.5)^{k}	82–83(2)		118–120(8)		142–143(10)	68–71(0.5)^{k}
	$n^{20}\mathrm{D}$	1.4930		1.4945		1.4929		1.5017	
$YC_6H_4C(CH_3)_2C(CH_3)_2OH$	Bp, °C (mm)	108–109(8)	81–82(1)^{l}	68–70(1)		68–70(1)		145–146(8)	
	$n^{20}\mathrm{D}$	1.5221	1.5218^{l}	1.5199		1.5200		1.5272	
$YC_6H_4C(CH_3)_2C(CH_3)_2Cl$	Mp, °C	35–36		28.5–29.0				85.5–86.5	
	$n^{20}\mathrm{D}$					1.5259			
$YC_6H_4C(CH_3)_2C(CH_3)_2ODNB^{m}$	Mp, °C	128.5–129.5						140–141	
$YC_6H_4C(CH_3)_2C(CH_3){:}CH_2$	$n^{20}\mathrm{D}$	1.5115^{n}						1.5198^{n}	
$(CH_3)_3C(CH_3)_2COH$	Bp, °C (mm)	128–129	129–131^{o}						
$(CH_3)_3C(CH_3)_2CCl$	Mp, °C	135–136.5^{p}	130.2–132.6^{o}						
$(CH_3)_3C(CH_3)_2CODNB$	Mp, °C	116–117							

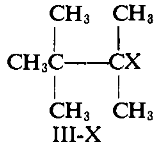
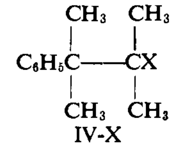
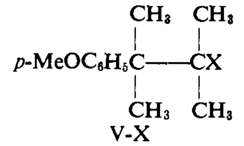
[a] B. van Zanten and W. Th. Nauta, *Rec. Trav. Chim.*, **79**, 1211 (1960). [b] A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958). [c] K. Kindler, W. Metzendorf, and D.-Y. Kwok, *Ber.*, **76B**, 308 (1943). [d] Reference 28a. [e] Reference 28b. [f] A. Jönsson, *Acta Chem. Scand.*, **8**, 1203 (1954). [g] R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3432 (1957). [h] A. Lambert, J. D. Rose, and B. C. L. Weedon, *J. Chem. Soc.*, 42 (1949). [i] Reference 62. [j] A. Bistrzycki and L. Mauron, *Ber.*, **40**, 4371 (1907). [k] E. V. Heningen, *J. Am. Chem. Soc.*, **74**, 4861 (1952). [l] Reference 9. [m] 3,5-Dinitrobenzoate. [n] Purified by preparative glpc. [o] Reference 33. [p] Measured in a sealed tube.

Table VIII. Summary of Analytical Data

Substituent	Calcd, %				Found, %			
	C	H	Cl	N	C	H	Cl	N
	2,3-Dimethyl-3-phenyl-2-chlorobutane and Its Substitution Products							
H	73.28	8.65	18.07	...	73.31	8.90	17.79	...
m-Me	74.11	9.03	16.86	...	74.26	9.04	16.92	...
p-Me	74.11	9.03	16.86	...	74.51	9.17	16.62	...
p-MeO	68.87	8.39	15.67	...	68.85	8.29	15.45	...
	2-Methyl-3-phenyl-2-chloropropane and Its Substitution Products							
H	71.21	7.77	21.02	...	71.43	8.02	21.11	...
m-Me	72.71	8.32	18.97	...	73.05	8.14	19.02	...
p-Me	72.71	8.32	18.97	...	72.96	8.16	19.09	...
p-MeO	66.49	7.61	17.85	...	66.21	7.50	17.95	...
	3,5-Dinitrobenzoates							
A^{a}	54.19	5.85	...	9.03	54.26	5.85	...	8.72
B^{b}	61.28	5.41	...	7.52	61.48	5.56	...	7.66
C^{c}	59.69	5.51	...	6.96	59.95	5.53	...	6.99

[a] Pentamethyl ethyl. [b] 2,3-Dimethyl-3-phenyl-2-butyl. [c] 2,3-Dimethyl-3-(*p*-methoxy phenyl)-2-butyl.

Table IX. Pmr Peak Positions[a] of the Protons Used in the Analyses

X	 $CH_3C(CH_3)_2C(CH_3)_2X$ III-X		 $C_6H_5C(CH_3)_2C(CH_3)_2X$ IV-X		 $p\text{-}MeOC_6H_5C(CH_3)_2C(CH_3)_2X$ V-X	
	β-CH_3	α-CH_3	β-CH_3	α-CH_3	β-CH_3	α-CH_3
OH	0.92	1.16	1.37	1.05	1.36	1.07
Cl	1.07	1.56	1.56	1.50	1.53	1.47
ODNB	1.14	1.66	1.59	1.70	1.57	1.69
OCH_3	0.89	1.04	1.35	0.98	1.32	0.97
N_3	...	...	...	...	1.35	1.17

Olefins[b]	Vinyl[c]	Allylic methyl[d]	*gem*-Dimethyl
III-Ol	4.58, 4.65	1.72	1.05
IV-Ol	4.85, 4.95	1.50	1.41
V-Ol	4.84, 4.94	1.52	1.38

[a] Shown in δ units (ppm) relative to TMS. [b] Nondeuterated analogs. [c] Two peaks with fine structures. [d] Quartet with coupling constants of about 1 cps.

of the reaction mixture was subjected to glpc analysis using precautions not to lose the extremely volatile olefinic component. A 4 ft × 0.25 in. column packed with tricresylphosphate on Chromosorb at 40° was used. The analysis revealed the formation of 19.9% of the methyl ether and 80.1% of olefin. The remaining major portion of the reaction mixture was mixed with 10 ml of pentane and poured into 50 ml of ice-cold water. The pentane layer was separated and the aqueous layer was extracted four more times with 10-ml portions of pentane. The combined pentane extracts were washed several times with ice-cold water and then condensed to approximately 5 ml by distilling off the solvent carefully at a bath temperature of 40°. The condensed solution was then chromatographed on about 30 g of activated alumina with pentane. The fraction containing the olefinic component was condensed to about 2 ml in the same way and was subjected to preparative glpc separation. The ethereal component was isolated by evaporating off the solvent from the second fraction and was then purified by glpc.

IV-ODNB (0.945 g) and 1.02 g of V-ODNB were solvolyzed in methanol in the presence of 5% excess sodium acetate at 75° for 8 days (for IV-ODNB) and 45 hr (for V-ODNB), respectively.

Glpc analyses of the reaction mixtures showed the presence of small amounts of methyl-migrated species (both olefinic and ethereal). These were completely neglected in the present study. Thus, excluding the methyl group rearranged products, formed in an amount of less than 5% of the total product in both cases, 9.8% of methyl ether and 90.2% of olefin were obtained from IV-ODNB. Similarly, the reaction mixture from V-ODNB was found to contain 34.4% of the substitution product and 65.6% of the elimination product. Isolation of the individual components from the reaction mixtures was carried out by means of either column chromatography on activated alumina or preparative glpc with Carbowax 20M or silicone oil columns.

Controlled experiments were conducted by treating the nondeutrated analogs of IV-OH, IV-OCH_3, and IV-Ol separately under the solvolytic conditions. In each case the starting material was recovered unchanged. The experimental results are summarized in Table IV.

Dehydration of IV-OH and V-OH over Alumina. Alcoa F-20 (mesh size 80–200) or Merck aluminum oxide (Lot No. 71707) was used as the catalyst. The catalyst (1 g) was packed in a 1 ft × 0.25 in. stainless steel column to be installed in an Aerograph G.C. Model A-90-C. The temperature was set at 280–310°, and the column was maintained overnight at this temperature under a slow helium flow, before use. The reaction was performed by injecting a 20% solution of the alcohol in ethylenediamine with a rate of about 50 μl/min, while the carrier gas flow was kept at about 500 cc/min. A maximum of 5 ml of such solution was injected for each run, and the catalyst was changed at every run to standardize the condition. The conversion realized was usually in the range between 30 and 50%. The scramblings observed are summarized in Table IV.

Acid-Catalyzed Addition of Methanol to IV-Ol and V-Ol. To 5 ml of 2 *M* sulfuric acid in methanol was added 0.17 g of 5% scrambled IV-Ol which was obtained from the dehydration over alumina described above. The solution was kept at 25° for 60 hr, forming 19% of the addition product. V-Ol, which contained 10% of the aryl group migrated isomer, was treated similarly at 25° for 23 hr. A glpc analysis showed a presence of 22.2% of the corresponding methyl ether. The scrambling indicated by the pmr study was corrected for the scrambling in the original compound. The experimental results are summarized in Table IV.

Deuteriochlorination of III-Ol, IV-Ol, and V-Ol. Deuterium chloride was generated in the automatic hydrochlorinator, employing concentrated deuteriochloric acid in deutrium oxide and deuteriosulfuric acid. Deuteriosulfuric acid was prepared by the method of Herber.[68] In general, 0.2 ml of the olefin in 1 ml of solvent, if the reaction was carried out in solution, was treated with deuterium chloride under the given reaction condition with efficient stirring. The excess acid was pumped out immediately after the reaction was stopped; the solvent was removed, and the resulting reaction mixture was submitted to pmr analysis. As the olefins, IV-Ol and V-Ol, were already partially scrambled, the net amount of scrambling was calculated in each case. The results are presented in Table III. The partially scrambled V-Cl was found to be stable in carbon tetrachloride, exhibiting no additional scrambling after standing for 1 week.

Product Studies for the Methanolysis of III-Cl, IV-Cl, and V-Cl. III-Ol (0.2 g) in 3 ml of methylene chloride was treated with deuterium chloride in the automatic hydrochlorinator at 0° for 5 min. After removing the solvent as well as the excess acid, the crude III-Cl was solvolyzed at 25° for 8 days in 20 ml of methanol containing 0.1 *M* sodium acetate. Only the methyl ether was isolated for analysis. In the same manner, IV-Cl, containing 5% of rearranged isomer, was obtained in 38% yield from 0.3 g of IV-Ol. The methanolysis of this crude IV-Cl was carried out at 25° for 8 days in the presence of sodium acetate. Neat V-Ol (1.0 g), which contained 15% of aryl group rearranged isomer, was treated with deutrium chloride at 0° for 5 min, resulting in 40% of chloride formation, bearing 28% of rearranged (~40% net scrambling) product. This mixture of V-Cl and V-Ol was divided into three portions in a ratio of 1:1:2. The first portion was subjected to methanolysis with added sodium acetate at 25° for 3 days. The second one was shaken with 20 ml of 0.1 *M* silver perchlorate solution in methanol for 3 min at room temperature. The remaining last portion was dissolved in 20 ml of methanol saturated with sodium azide to solvolyze at 25° for 3 days. Each of the ethereal components, as well as the azide derivative from the last batch, was isolated and the amount of scrambling was determined. The results are summarized in Table IV.

Deoxideation Reactions.[47] In 2 ml of tetrahydrofuran, 0.36 g of IV-OH was dissolved and added to a 50-ml flask containing 0.48 g of sodium hydride. The mixture was gently refluxed for 1 hr to form the sodium alkoxide. Then 1.5 g of bromoform was injected slowly at the reflux temperature. A violent reaction was observed at the earlier stage of the addition, but the excess bromoform did not react with the excess sodium hydride. A 10% solution of methanol in tetrahydrofuran was cautiously added to the reaction mixture until no further vigorous reaction occurred. A glpc analysis of the reaction mixture showed the presence of 20% of olefinic

---

(68) R. H. Herber, *Inorg. Syn.*, 7, 155 (1963).

product on the basis of recovered starting material, together with some unidentified by-products. III-OH and V-OH were treated similarly, except that the product from III-OH was collected directly from the reaction flask in a cold trap. The results of the pmr analyses of the products are summarized in Table IV.

Pmr Studies. Both Varian Models A-60 and A-60A were used in the present study. The spectra of IV-ODNB, V-ODNB, and their nondeutrated analogs, were taken in chloroform-d_1 and all of the other spectra in carbon tetrachloride. The peak positions of the protons which were used in the analyses are collected in Table IX. The amount of scrambling in each of the reaction products was, in most cases, determined by integrations which were made several times in order to minimize the error. But, in those cases where the peak separations are not great enough, the spectra were taken with slower sweep time and the peak heights were used for analyses. An internal standard technique was also employed for the determination of the per cent scrambling in each of the olefinic products IV-Ol and V-Ol. For this purpose, desoxybenzoin was chosen and the methylene group absorption peak (δ 4.05) of the standard was compared with the vinyl proton peaks of the sample.

Oxidation of Thioethers to Sulfoxides by Iodine. II.[1] Catalytic Role of Some Carboxylic Acid Anions[2]

K.-H. Gensch, I. H. Pitman, and T. Higuchi

Contribution from the School of Pharmacy, University of Wisconsin,
Madison, Wisconsin, and Department of Pharmaceutical Chemistry,
University of Kansas, Lawrence, Kansas. Received October 14, 1967

Abstract: Mono- and dicarboxylate ions are shown to catalyze the oxidation by aqueous iodine of aliphatic and alicyclic thioethers to sulfoxides. For example, the rate of oxidation of tetrahydrothiophene to tetrahydrothiophene 1-oxide at pH 8 and 25° is 20 times faster in a 1×10^{-3} *M cis*-1,2-cyclohexanedicarboxylate buffer than in water (both solutions being 6×10^{-2} *M* in potassium iodide). Kinetic results suggest that acyloxysulfonium ions are intermediates in the oxidations and that these ions are converted to sulfoxides by nucleophilic displacements at the carbonyl carbon atom rather than by nucleophilic displacement at the positively charged sulfur atom.

The oxidation of thioethers to sulfoxides by aqueous iodine has been shown[1] to be strongly catalyzed by several inorganic nucleophiles, especially doubly charged anions such as HPO_4^{2-}, $HAsO_4^{2-}$, and CO_3^{2-}. To account for this catalysis, an oxidation mechanism was proposed[1] which involved (a) addition of iodine to the thioether followed by ionization of the complex to yield an iodosulfonium ion, (b) displacement of iodide from the iodosulfonium ion by the catalyst (*e.g.*, HPO_4^{2-}) to yield an acid sulfonium ion, and (c) hydrolysis of the acid sulfonium ion to yield the sulfoxide plus an acid derivative (*e.g.*, $H_2PO_4^-$).

The present report is concerned with details of the mechanism of catalysis of the same reaction by several polycarboxylate and monocarboxylate ions. Therefore, comparative kinetic data are presented for the iodine oxidation of tetrahydrothiophene to tetrahydrothiophene 1-oxide in aqueous phthalate, succinate, 2-phenylsuccinate, citrate, *cis*- and *trans*-1,2-cyclohexanedicarboxylate, acetate, propionate, and *n*-hexanoate buffers. Data for the oxidation of diethyl sulfide and benzyl methyl sulfide to diethyl sulfoxide and benzyl methyl sulfoxide, respectively, by iodine in *cis*-1,2-cyclohexanedicarboxylate buffers are also discussed.

We have shown in a preliminary communication[3] that phthalate ion catalyzed the iodine oxidation of tetrahydrothiophene to tetrahydrothiophene 1-oxide and that during the process phthalic anhydride was formed. We have also described[4] an asymmetric oxidation of benzyl methyl sulfide to optically active benzyl methyl sulfoxide by iodine in a *d*-2-methyl-2-phenylsuccinate buffer.

A likely intermediate in these oxidations is a positively charged acyloxysulfonium ion (*e.g.*, **3**). Conversion of this species to the sulfoxide could be initiated either by back-side attack of water or hydroxide ions on the sulfur atom or by nucleophilic attack (intramolecular or intermolecular) on the carbonyl carbon atom. The identification of phthalic anhydride during the iodine oxidation of tetrahydrothiophene in phthalate buffer[3] suggests that in this case, and possibly in other dicarboxylate systems, intramolecular reaction at the carbonyl carbon atom is the preferred route. However, the likely intermediate in monocarboxylate-catalyzed systems could not be converted to the sulfoxide by intramolecular nucleophilic attack. Reaction of monocarboxylate ions at the sulfur atom would only regenerate the same acyloxysulfonium ion and thus not affect the kinetics of the conversion to the sulfoxide. On the other hand, the monocarboxylate ion could participate in nucleophilic reactions at the carbonyl group either by acting as a nucleophile or as a general base (*cf.* the role of carboxylate ions in the hydrolysis of carboxylic acid anhydrides[5]). Thus, a kinetic dependence on the concentration of monocarboxylate ions of this step of the reaction would strongly suggest that the acyloxysulfonium ion was converted to the sulfoxide by reactions at the carbonyl carbon atom.

---

(1) T. Higuchi and K.-H. Gensch, *J. Am. Chem. Soc.*, **88**, 5486 (1966).

(2) This research was supported in part by grants from the National Institutes of Health under GM-05830. Please address all correspondence to Professor T. Higuchi at Pharmaceutical Chemistry Laboratory, School of Pharmacy, University of Kansas, Lawrence, Kan. 66044.

(3) T. Higuchi and K.-H. Gensch, *J. Am. Chem. Soc.*, **88**, 3874 (1966).

(4) T. Higuchi, I. H. Pitman, and K.-H. Gensch, *ibid.*, **88**, 5676 (1966).

(5) A. R. Butler and V. Gold, *J. Chem. Soc.*, 2305 (1961); D. G. Oakenfull, T. Riley, and V. Gold, *Chem. Commun.*, 385 (1966).