amine, and 2,2,6,6-tetramethyl-4-piperidinol, were purchased from Aldrich Chemical Co. and used as received. All buffer solutions were 10% aqueous dioxane (v/v); an ionic strength of 0.11 was maintained with $NaClO_4$. Deuterium oxide (99.8%) was purchased from Columbia Organic Chemicals. The pK_a of 2,2,6,6-tetramethyl-4-piperidinol was estimated to be 10.0 from the pH of a 1:1 buffer solution in 10% dioxane (μ = 0.11).

Product Analysis. I. Methanolysis. To 50 ml of absolute methanol into which HCl gas had been bubbled was slowly added 5.00 g (0.038 mol) of **1** at ice-bath temperature. The solution was allowed to warm to 30°, neutralized with dilute aqueous NaOH, and extracted with four 40-ml portions of ether, and the combined ethereal extracts were dried over $MgSO_4$. Removal of ether under reduced pressure left a residue (4.51 g) which was distilled to yield 2.42 g of 2-ethyl-2-hydroxybutanal dimethylacetal: bp 64–65° (8 Torr); $n^{25}D$ 1.4214; $\delta_{TMS}^{CCl_4}$ 1.0 (t, 6 H), 1.7 (q, 4 H), 2.5 (br s, −OH), 4.1 (s, 6 H), 4.8 (s, 1 H).

Anal. Calcd for $C_8H_{18}O_3$: C, 59.2; H, 11.2. Found: C, 59.1; H, 11.1.

II. Hydrolysis. The hydrolysis product of **1** at pH 10 was determined to be 2-ethyl-2-hydroxybutanal as previously described[3] for hydrolysis at pH 4. A 60% yield of material shown by gc to be 95% pure aldehyde was obtained.

Kinetic Procedures. These have been described.[3] Rate measurements at 25, 35, and 45° (±0.1°) were used to calculate activation parameters. Kinetic runs in all buffer solutions were strictly first order to 60–75% completion.

Acknowledgments. We gratefully acknowledge support of this work by the National Science Foundation through Grants GP-7392 and GP-14693. We thank the University of Hawaii Computer Center for the donation of computer time. We are indebted to Sherwin Amimoto for assistance with computer programs. Dr. Michael A. Porzio first synthesized the epoxy ethers used in this work and carried out the methanolysis product analysis.

Structural Effects in Solvolytic Reactions. V. Rates and Products in the Acetolysis of Substituted *cis*-2-Phenylcyclopentyl Tosylates and Deuterium Tagged Derivatives. Nature of the Reaction Pathway in the Absence of Aryl Participation[1]

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

Contribution from the Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 47907. *Received September 29, 1971*

Abstract: A series of substituted *cis*-2-phenylcyclopentyl tosylates was prepared and the rates and the products of acetolysis were studied. The rate data reveal the absence of aryl participation, and the product data show no evidence for the incursion of aryl-bridged species as intermediates. Thus, the aryl-assisted pathway is effectively absent in the present system. This provides us with a representative secondary β-arylalkyl system in which the solvolysis proceeds *via* aryl-unassisted pathways only. A study of the deuterium tagged derivatives, *cis*-2-phenylcyclopentyl-*1*-d_1 tosylate and the *2*-d_1 isomer, revealed that a predominant portion of the product arises from a rearranged tertiary arylic cation. This indicates that the solvolysis pathway in the present system is characterized largely by a process involving hydride shift. However, the rates of solvolysis reveal very little effect of increasing stability of the tertiary benzylic cation center arising from the effect of activating substituents in the aromatic ring. This suggests that the first intermediate cannot be the tertiary cation. Consequently, the solvolysis is interpreted in terms of a mechanism involving the formation of a tight ion pair as the first intermediate.

The acetolysis or formolysis of secondary alkyl arenesulfonates was originally suggested by Winstein and his coworkers to be nearly limiting.[3,4] This position, which postulates the rate-determining formation of carbonium ion intermediates with little nucleophilic solvent participation, has received general acceptance.[6-12]

In line with this interpretation, the phenyl-unassisted process in the acetolysis or formolysis of secondary β-phenylalkyl arenesulfonates was first characterized by Cram with such terms as SNi and E1.[13] At the same time, however, the term "solvent participation in the ionization step," has also been used to describe the ionization process to "solvated" open ions,[14] a process

(1) For a preliminary report, see C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4286 (1969).

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

(3) Although the classic Ingold's scheme defines the solvolysis of secondary derivatives as borderline,[5] it was suggested[4] that a secondary system involving a tosyloxy group, a far better leaving group than halogen, and a solvent of low nucleophilicity, such as acetic acid or formic acid, would approach a limiting mechanism in character.

(4) (a) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 828, 846 (1948); (b) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); (c) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, 74, 1113 (1952); (d) S. Winstein and N. J. Holness, *ibid.*, 77, 5562 (1955).

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

(6) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; (b) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

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

(8) M. C. Whiting, *et al.*, *J. Chem. Soc. B*, 355, 365 (1968).

(9) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854, 1856 (1964); C. S. Foote, *ibid.*, **86**, 1853 (1966).

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

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

(12) See also: (a) J. D. Roberts, W. Bennett, R. E. McMahon, and E. W. Holroyd, Jr., *J. Amer. Chem. Soc.*, 74, 4283 (1952); (b) E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954); (c) J. O. Stoffer and J. D. Christen, *ibid.*, **92**, 3190 (1970).

(13) (a) D. J. Cram, *ibid.*, 74, 2129 (1952); (b) *ibid.*, **74**, 2137 (1952); (c) *ibid.*, 74, 2159 (1952); (d) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953).

(14) Such species were usually depicted with structures which have dotted line(s) between the carbonium center and solvent molecule(s).[16,17]

proposed to be in direct competition with the phenyl-assisted ionization process leading to phenyl-bridged species.[16,17]

This apparent inconsistency is confusing, although one might compromise with a qualitative view that the aryl-unassisted ionization process in the acetolysis of secondary β-arylalkyl derivatives may have been considered by these pioneer workers to be assisted by relatively weak nucleophilic solvent participation. A more serious inconsistency seems to exist, furthermore, concerning the fate of the proposed "solvated" open ions (or ion pairs). Winstein maintained a position that in a secondary system the competition between neighboring group participation and solvent participation is primarily at the ionization step and that the open ions formed after rate-determining ionization process would lead either directly to the product or to the relatively more stable bridged species, whenever such a process becomes feasible.[18-22] Cram's mechanistic interpretation for the secondary β-arylalkyl systems, on the other hand, did not consider the possibility for the existence of such a crossover process.[13,18,24] These discrepancies in views appear to suggest that the early studies in this area failed to establish a consistent and unified mechanism for the acetolysis of formolysis of simple secondary alkyl arenesulfonates and, in turn, that the extended theory proposed for secondary β-arylalkyl systems was largely on a qualitative basis.

In recent years quantitative approaches to the relative importance of the aryl-assisted and the unassisted pathways in the solvolysis of secondary β-arylalkyl derivatives have been under active investigations.[17c,22,27-29] Schleyer and Lancelot observed that the rates and the products of solvolysis can be adequately correlated by assuming the existence of two discrete reaction pathways, the aryl assisted and the aryl unassisted.[27] This finding appears to require the absence of significant crossover between these two routes and, in turn, suggests that the aryl-unassisted process must be far from limiting. Our extensive study of the acetolysis of substituted *threo*-3-phenyl-2-butyl brosylates (I-X) indeed revealed a precise correlation between the rates and the products.[28b,c] This result led us to the conclusion that the mechanism involving the concurrent formation of bridged and open ions, with facile crossover, could no longer be accepted. This is consistent with the conclusion that the acetolysis of secondary arenesulfonates must be assisted significantly by nucleophilic solvent participation.[30,31] These developments thus suggest that a large number of the previous studies involving acetolysis of secondary alkyl arenesulfonates must be subjected to extensive reinterpretation.

In order to obtain further information about the precise nature of the aryl-unassisted pathway in secondary β-arylalkyl systems, we decided to study the rates and the products of the acetolysis of a series of substituted *cis*-2-phenylcyclopentyl tosylates, a representative secondary β-arylalkyl system in which the reaction cannot involve aryl participation. In the course of this study, we encountered phenomena pointing to the predominant importance of a process involving hydride shift. Accordingly, we synthesized deuterium tagged compounds, the *1*-d_1 and *2*-d_1 substituted *cis*-2-phenylcyclopentyl tosylates, and examined the rates and the products for these derivatives with the hope of clarifying the nature of this process.

The present system should also serve as a reference system in discussing the solvolytic behavior of the *trans*-2-arylcyclopentyl derivatives, discussed in the following paper of this series.[28d]

Rates and Products of Nondeuterated Compounds

A series of substituted *cis*-2-phenylcyclopentyl tosylates (II-X), with the exception of the *p*-nitro derivative, was synthesized by a reaction sequence which involves either the reduction of 2-arylcyclopentanone with disiamylborane[32] or the inversion of the *trans*-2-arylcyclopentyl tosylate[33] with tetraethylammonium ace-

Considering the similar structures shown for 1-phenylethyl cation,[15] which was believed to be formed without nucleophilic solvent participation, it is not clear whether such presentation was intended to indicate partial bonds between the solvent molecules and the carbonium center.

(15) S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, 74, 1147 (1952).

(16) (a) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *ibid.*, 74, 1140 (1952); (b) S. Winstein and K. C. Schreiber, *ibid.*, 74, 2165, 2171 (1952); (c) S. Winstein and R. Heck, *ibid.*, **86**, 2071 (1964).

(17) (a) D. J. Cram, H. L. Nyquest, and F. A. Abd Elhafez, *ibid.*, **79**, 2876 (1957); (b) D. J. Cram, *ibid.*, **86**, 3764 (1964); (c) D. J. Cram and J. A. Thompson, *ibid.*, **91**, 1778 (1969).

(18) Examples are as follows. (1) The acetolysis of *endo*-norbornyl tosylate was proposed to involve ionization to a solvated open ion, followed by favorable crossover to the bridged nonclassical species.[18,19] (2) In the acetolysis of 4-*tert*-butylcyclohexyl tosylate, Winstein and Holness considered the possibility of crossover from the initially formed solvated open ion to a hydrogen-bridged species.[4d] (3) A similar crossover process was postulated for the formolysis of 5-phenyl-2-pentyl tosylate, *i.e.*, the tetralin product was attributed to both the phenyl-assisted and the phenyl-unassisted processes.[20] (4) As to the β-phenylalkyl systems, Winstein stated in 1964, "In this case (2-phenylethyl system) there is no leakage between the two routes . . . . With simple primary systems there is no crossing over; with secondary and tertiary systems it is more likely to have crossover between the different routes."[19] In line with this statement, Winstein and his associates proposed that the acetolysis of 2-*endo*-benzonorbornenyl brosylate involves anchimerically unassisted ionization to a classical open ion which would largely cross over to the aryl-bridged ion.[21]

(19) S. Winstein, Chimica Theorica, Conferenze VIII, Corso Estivo di Chimica, Academia Nazionale dei Lincei, Rome, Italy, 1965, pp 251 and 262.

(20) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3105 (1957).

(21) J. P. Dirlam, A. Diaz, S. Winstein, W. P. Giddings, and G. C. Hansen, *Tetrahedron Lett.*, 3133 (1969).

(22) An altered view was recently reported: A. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 4300 (1969). The authors claim that their view has been consistent since 1951. However, this position appears to require a major revision of the previous interpretations.[4,20-21] For example, Winstein and his coworkers emphasized the similarities between the 3-phenyl-2-butyl and the benzonorbornenyl systems in terms of solvent and aryl participation.[23] For the benzonorbornenyl system, they proposed the existence of a facile crossover process[21] (1969), while such a process was denied in the 3-phenyl-2-butyl and related systems (1969).

(23) D. V. Bradden, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968).

(24) If the aryl-unassisted pathway involving an open ion were to be characterized by SN1 or E1 (as was proposed by Cram[18,25]), it would most likely involve a facile equilibration between the proposed open and bridged ions.[26]

(25) See also, W. B. Smith and M. Showalter, *ibid.*, **86**, 4136 (1964).

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

(27) (a) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291 (1969); (b) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91**, 4294 (1969); (c) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4296 (1969); (d) P. v. R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297; (1969); (e) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, *ibid.*, **93**, 4829 (1971).

(28) (a) C. J. Kim and H. C. Brown, *ibid.*, **91**, 4287, 4289 (1969); (b) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970); (c) H. C. Brown, and C. J. Kim, *ibid.*, **93**, 5765 (1971); (d) C. J. Kim and H. C. Brown, **94**, 5051 (1972).

(29) (a) J. E. Norlander and W. J. Kelly, *ibid.*, **91**, 996 (1969); (b) J. E. Norlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).

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

(31) P. G. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dilland, and R. J. Kamat, *ibid.*, **89**, 5902 (1967).

(32) H. C. Brown and V. Varma, *ibid.*, **88**, 2871 (1966).

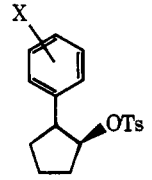
(33) For the preparation, see ref 28d.

Table I. Kinetic Data for the Acetolysis of Substituted *cis*-2-Phenylcyclopentyl Tosylates (II-X)

II-X, X =	10^6k, sec^{-1} 25.0°	50.0°	75.0°	Rel rate at 50.0°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
p-MeO	3.47	79.3		2.31	23.3	−5.3
p-Me	2.19	55.4		1.62	24.1	−3.6
m-Me	1.71	43.9		1.28	24.2	−3.7
H	1.38	34.3[a]		1.00	24.1	−4.6
p-Cl		12.2	214	0.356	25.0	−3.9
m-Cl		7.59	134	0.221	25.1	−4.5
p-NO_2		2.18	42.1	0.0635	25.8	−4.7

[a] Previous value: 34.8, ref 1.

tate. The *p*-nitro substituted compound (II-*p*-NO_2) was prepared *via* nitration of the parent acetate.



cis

II-X, X = *p*-MeO, *p*-Me, *m*-Me, H, *p*-Cl, *m*-Cl, *p*-NO_2

The rates of acetolysis were determined at two temperatures and the kinetic data are summarized in Table I.

The effects of substituents are relatively small and regular. The *p*-methoxy substituent increases the rate of the parent compound by a moderate factor of 2.3, which should be compared to the corresponding factor of 59 observed for the 3-aryl-2-butyl system.[28c] The introduction of a *p*-nitro substituent causes rate retardation by a factor of 16, which is comparable to the estimated rate ratio of 12 for $k_s^H/k_s^{NO_2}$ in the acetolysis of 3-aryl-2-butyl brosylates.[28c] Another feature of the present kinetic data is the fact that the $\Delta S^{\ddagger}$ value remains essentially constant throughout the range examined. These observations, the minor substituent effect and the constancy of the $\Delta S^{\ddagger}$ values,[34] indicate that aryl participation is not an important factor in the present system. This point can be clearly demonstrated by examining the Hammett plot (Figure 1) which shows an excellent correlation without any significant deviations of the points for the compounds containing activating substituents ($\rho = -1.56$).

The product study was carried out at 50.0° maintaining the solution, 0.050 *M* in II-X and 0.053 *M* in sodium acetate, for approximately 7 half-lives. Analyses showed that II-H gave 4% of the *trans*-acetate, 7% of 3-phenylcyclopentene, and 89% of 1-phenylcyclopentene, while II-*p*-MeO yielded only a trace amount of acetate, 2% of 3-*p*-anisylcyclopentene, and 98% of the Δ^1-olefin.

As the rate data showed no sign of aryl participation, the products must arise from the aryl-unassisted

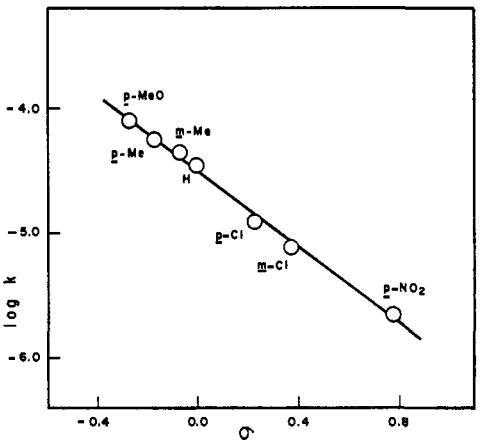


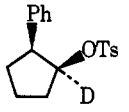
Figure 1. Rates of acetolysis of *cis*-2-acylcyclopentyl tosylates at 50.0° *vs.* the σ constants ($\rho = -1.56$).

pathway (k_s). In the acetolysis of *trans*-2-*p*-anisylcyclopentyl tosylate, there is obtained a considerable quantity (73%) of the *trans*-2-*p*-anisylcyclopentyl acetate.[28d] This presumably arises from a *p*-anisyl-bridged intermediate. The absence of any significant amount of this acetate in the acetolysis of II-*p*-MeO requires that the bridged species is not a significant intermediate in this case.

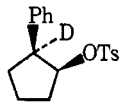
The formation of a predominant amount of 1-arylcyclopentene product is not readily explicable in terms of the interpretation that the k_s process is characterized by a transition state in which the side of the reacting center opposite to the leaving group is strongly held by solvent.[27] In order to investigate the nature of the process leading to this elimination product, we decided to examine the solvolysis products of *cis*-2-phenylcyclopentyl-*1*-d_1 tosylate (a) and the *2*-d_1 isomer (b).

Products of Acetolysis of Deuterium Tagged Compounds

The preparation of *cis*-2-phenylcyclopentyl-*1*-d_1 tosylate (a) was carried out by reducing 2-phenylcyclo-



a



b

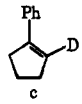
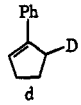
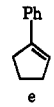
pentanone with lithium aluminum deuteride, separating the mixture of cis and trans alcohols by preparative glpc, and converting the pure cis isomer to the tosylate. The *cis*-2-phenylcyclopentyl-*2*-d_1 tosylate (b) was obtained by the treatment of *trans*-2-phenylcyclopentyl-*2*-d_1 tosylate[33] with tetraethylammonium acetate.

(34) In the acetolysis of primary β-arylethyl brosylates, the $\Delta S^{\ddagger}$ value changes characteristically from −15.2 eu for the parent compound to −8.8 eu for the *p*-methoxy substituted derivative.[35a] This observation was interpreted in terms of different reaction mechanisms, the solvent-participated pathway for the parent compound and the aryl-participated pathway for the *p*-methoxy derivative.[35]

(35) (a) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, 78, 4801 (1956); (b) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, 41, 807 (1958); (c) A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, 90, 6546 (1968).

The acetolysis was carried out in the usual manner and the 1-phenylcyclopentene product was isolated by preparative glpc to be examined by pmr. The results are summarized in Table II.

Table II. Isomer Distributions[a] in the 1-Phenylcyclopentene Products from the Acetolyses[b] of a and b

	 c	 d	 e
a →	31%	59%	10%
b →	31%	58%	11%

[a] As the deuterium content in a or b is 95.5% D, the results are corrected for 100% D. [b] Each run was carried out with a solution, 0.050 *M* in substrate and 0.053 *M* in sodium acetate, for 4 days at 50.0°.

The striking feature in the above results is the fact that the 1-phenylcyclopentene product from b has almost exactly the same deuterium distribution[36] as that from a, indicating that a common intermediate is formed in the reactions of a and b. As will be discussed later in detail, this intermediate appears to be the tertiary benzylic cation formed by hydride (in the case of a) or deuteride (in the case of b) shift. In the hope of obtaining information which would help us in understanding the nature of the process involving such hydride shift, we undertook to study the secondary isotope effects on the rates of acetolysis accompanying the introduction of deuterium into the α and β positions of the parent compound.

Secondary Isotope Effects in the *cis*-2-Phenylcyclopentyl System

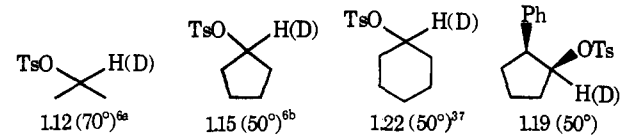
The deuterium tagged derivatives, a and b, previously utilized in the product studies were used. Three separate runs, each of which consists of simultaneous determination of the rates of acetolysis of II-H, a, and b at 50.0°, were conducted and the results are summarized in Table III.

Table III. Secondary Deuterium Isotope Effects on the Rate of Acetolysis of II-H at 50.0°

	10^5k, sec^{-1}			k_H[b]	k_H[b]
Run	II-H(k_H)	a($k_{\alpha\text{-D}}$)[a]	b($k_{\beta\text{-D}}$)[a]	$k_{\alpha\text{-D}}$	$k_{\beta\text{-D}}$
1	3.425	2.884	1.729	1.197	2.077
2	3.402	2.885	1.725	1.188	2.067
3	3.421	2.897	1.733	1.191	2.069
			Av	1.192	2.071

[a] The deuterium content in these compounds is 95.5% D. [b] Corrected for 100% D.

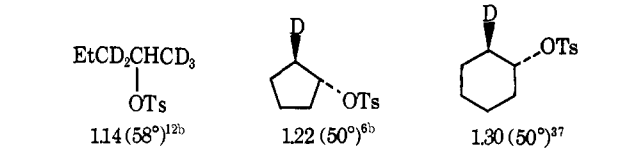
The observed α-deuterium effect, $k_H/k_{\alpha\text{-D}}$, of 1.19 is comparable to the reported values for the acetolysis of simple secondary alkyl tosylates, such as isopropyl,[6a] cyclopentyl,[6b] and cyclohexyl tosylates,[37] and all of these values for secondary derivatives are substantially



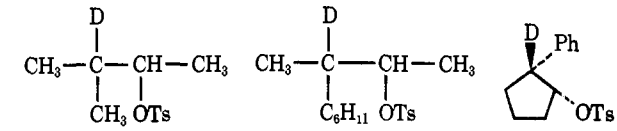
$k_H/k_{\alpha\text{-D}}$

larger than those values for acetolysis of primary tosylates, *e.g.*, $(k_H/k_{\alpha\text{-D}})_{\text{per D}}$ is 0.97 for methyl-d_3 brosylate and 1.02 for ethyl-*1,1*-d_2 brosylate.[38] Thus, the effect of substituting a cis β hydrogen in the cyclopentyl system with a phenyl group is insignificant in terms of the α-deuterium isotope effect.

On the other hand, the observed β effect, $k_H/k_{\beta\text{-D}}$, of 2.07, is considerably larger than the reported values for the acetolysis of simple secondary alkyl arenesulfonates,



$(k_H/k_D)_{per\,D}$



but is comparable to the values reported for 3-methyl-2-butyl-*3*-d_1 tosylate[39] and for diastereomeric 3-cyclohexyl-2-butyl-*3*-d_1 tosylates.[40] These higher values of the β effect indicate the existence of a special effect associated with the tertiary β hydrogen. We shall discuss this point later in some detail.

Nature of the Intermediate Leading to 1-Arylcyclopentene Product

The observation that the β-deuterated parent compound b gave a 1-phenylcyclopentene product whose isomer distribution is nearly identical with that of the product from the α-deuterated isomer a (Table II) indicates the presence of a common intermediate in these reactions. Considering that the 1-phenylcyclopentene-*5*-d_1 (d), the major isomer in the product, must be formed from a tertiary benzylic cation, f, we suggest that the common intermediate involved in acetolysis of both a and b be f (Scheme I).

A question may arise as to whether the tertiary cation, f, is the first intermediate or whether there exists another intermediate prior to the formation of f. This problem will be the subject of the following discussions.

Nature of the Pathway to the Tertiary Cation

It was suggested in the previous section that the Δ^1-olefin may be formed almost exclusively from a tertiary arylic cation, g, which must arise *via* hydride shift in the course of the acetolysis of II-X. There appear three possible routes to this cation (Scheme II): A, direct

(36) Equilibration between the isomeric products is not likely to take place, for the isomer distribution remained unchanged after an extended period under the solvolysis conditions.

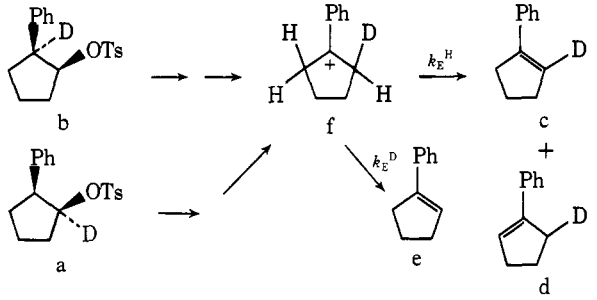
(37) W. H. Saunders, Jr., and K. T. Finley, *J. Amer. Chem. Soc.*, 87, 1384 (1965).

(38) E. S. Lewis, C. J. Brown, and W. C. Herdon, *Can. J. Chem.*, 39, 954 (1961).

(39) S. Winstein and J. Takahashi, *Tetrahedron*, 2, 316 (1958).

(40) D. J. Cram and J. Tadanier, *J. Amer. Chem. Soc.*, 81, 2737 (1959).

Scheme I

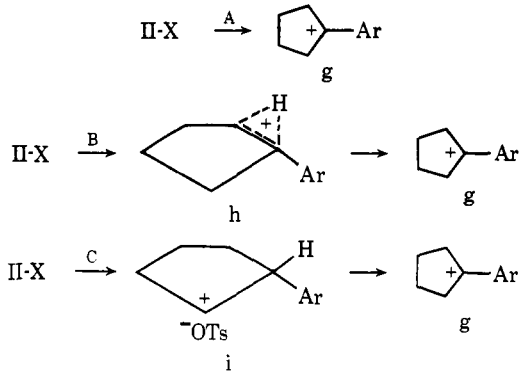


c:d ≃ 1:2 (statistical)

c:e = k_E^H:k_E^D ≃ 3:1

ionization to g; B, ionization to a hydrogen-bridged species, h, which leads to g; and C, ionization to a tight ion pair, i, followed by subsequent hydride shift to g.

Scheme II

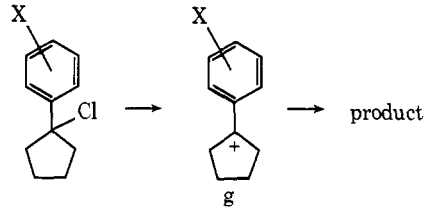


The first two possibilities (A and B) are expected to accompany "hydrogen participation" according to the original theory for neighboring group participation.[4a,b,41] Indeed a large number of experimental data obtained for various systems has been interpreted to be consistent with these kinds of mechanisms.[13,17,39,40,42–44]

It should be noted, however, that some of the recent studies of the solvolysis of simple secondary derivatives propose that the reaction involves a tight ion-pair intermediate,[45–47] the formation of which may not, in some cases, be rate determining.[45,48] Namely, this proposal suggests the possibility that the nonlimiting nature of a given secondary system may be due not to the nucleophilic solvent participation in the rate-determining ionization process but to the rate-determining subsequent process which involves nucleophilic solvent attack on the initially formed ion-pair intermediate. Should this suggestion be reasonable, it then becomes also possible to propose that in a secondary system containing a neighboring group, the neighboring group rearrangement may take place after the ionization to an ion pair. Thus, this possibility proposes that the competition between the solvent and the neighboring group may occur only after the ionization to a tight ion pair, and if these subsequent steps contribute significantly to the overall rate-determining process, we would observe phenomena indicating the existence of solvent and neighboring group participation, the mechanism being different from the original view.[4,41] Indeed, we have previously proposed[28c] that this kind of mechanism may best represent the acetolysis of secondary β-arylalkyl arenesulfonates. The mechanism C in Scheme II is in accordance with this general possibility.[28c,45,49]

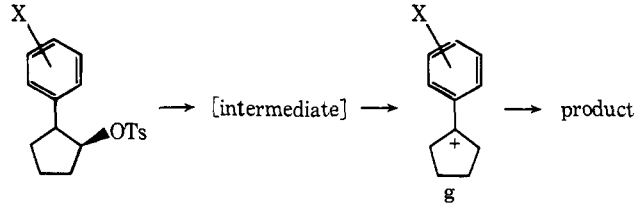
Examination of the results obtained in this study in terms of these three mechanisms is carried out stepwise as follows.

Firstly, in the mechanism A the driving force must be the formation of a resonance-stabilized tertiary cation. The transition state is then expected to reflect this stability to a great extent. For example, in the solvolysis of substituted 1-phenylcyclopentyl chloride, the introduction of a *p*-methoxy substituent increases the rate of the parent compound by a large factor of 3400.[50] This observation was consistently explained in terms of a mechanism involving the direct formation of a resonance-stabilized tertiary cation, g ($k_{p\text{-MeO}}/k_H$ = 3400).



As mentioned previously, a predominant portion of the product from the acetolysis of II-X appears to arise from the same tertiary cation, g. However, we observed a very small substituent effect, the relative rate, $k_{p\text{-MeO}}/k_H$, being only a factor of 2.3 (Table I). We must then conclude that the tertiary arylic cation, g, cannot be the first intermediate in the acetolysis of II-X, but must be formed indirectly from another intermediate ($k_{p\text{-MeO}}/k_H$ = 2.3).

As to mechanism B, the following arguments may be presented. (1) Acetolysis of *cis*-2-phenylcyclopentyl-



(41) This theory suggests that participation should occur when a system undergoes direct ionization either to a bridged species or to a rearranged classical ion. In the acetolysis or formolysis of secondary systems the so-called driving force for neighboring group participation has been estimated on the ground that ionization to an unrearranged open ion corresponds to the rate-determining step accompanied by little assistance from solvent or neighboring group.[4,7,19] In this connection the acetolysis of *endo*-norbornyl or *endo*-benzonorbornenyl sulfonate, proposed to involve ionization to an open ion followed by rearrangement to the bridged species, was considered to proceed without participation.[15,21]

(42) (a) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, 74, 1127 (1952); (b) S. Winstein and J. Schwartz, Abstracts of the 15th National Organic Chemistry Symposium, Rochester, N. Y., 1957, p 39.

(43) E. D. Hughes, C. K. Ingold, and J. B. Rose, *J. Chem. Soc.*, 3839 (1953).

(44) V. J. Shiner, Jr., and J. G. Jewett, *J. Amer. Chem. Soc.*, 87, 1382, 1383 (1965).

(45) (a) R. A. Sneen and J. W. Larsen, *ibid.*, 91, 6031 (1969); (b) *ibid.*, 91, 362 (1969); (c) *ibid.*, 88, 2593 (1966); (d) H. Weiner and R. A. Sneen, *ibid.*, 87, 292 (1965); (e) *ibid.*, 87, 287 (1965).

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

(47) A. F. Diaz, I. Lazdins, and S. Winstein, *ibid.*, 90, 1904 (1968).

(48) See also, C. G. Swain and A. MacLachlan, *ibid.*, 82, 6095 (1960).

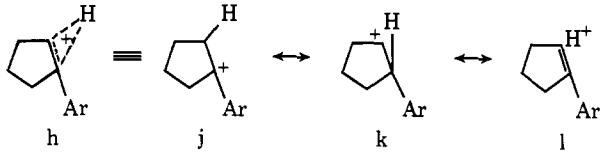
(49) Sneen and Collins conducted a detailed study of the solvolysis of neomenthyl and menthyl brosylates in aqueous acetone, examining the effects of added sodium azide. The authors concluded that the tight ion-pair hypothesis[45] is consistent with the observed phenomena: M. A. Collins, Ph.D. Thesis, Purdue University, 1968.

(50) H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, 88, 533 (1966).

2-d_1 tosylate (b) gives the 1-phenylcyclopentene product which has exactly the same deuterium distribution as that from the 1-d_1 isomer a (Table II). This result suggests that the hydrogen-bridged ion h is not an important intermediate in the above reaction, for if a significant amount of the product were to be formed from h, a considerably larger amount of the deuterium free isomer, e, should have been observed for b than for a.

(2) It was previously proposed by Streitwieser[6] that the α-deuterium isotope effect should become smaller as the reaction center becomes more crowded in the transition state. Namely, an SN2 transition state or a transition state involving neighboring group participation is expected to be characterized by a small magnitude of the α-deuterium isotope effect.[6] Accordingly, if the first intermediate is the hydrogen-bridged ion, the transition state, which should resemble this intermediate, would be expected to yield a small α effect. Contrary to this expectation, we find a large α effect for II-H, $k_H/k_{\alpha\text{-}D}$ = 1.19 (Table III), which is considerably greater than that for a typical SN2 solvolysis, such as the acetolysis of primary arenesulfonates ($k_H/k_{\alpha\text{-}D}$ = *ca.* 1.00).[51] Although the present consideration is qualitative, the observed α-deuterium effect does not appear to support the mechanism A or B, in which the transition state must have an extensively developed bridging bond.

(3) Finally, if the hydrogen-bridged ion h is the first intermediate which rearranges further to the stable tertiary arylic cation g, it would be difficult to understand why the rearranging hydrogen stops at a half-migrated stage instead of cascading down to the energy minimum corresponding to the resonance-stabilized tertiary arylic cation. Considering the following resonance for the bridged ion, it appears to be unreasonable to put a large energy barrier between the structures j and the tertiary benzylic cation g.

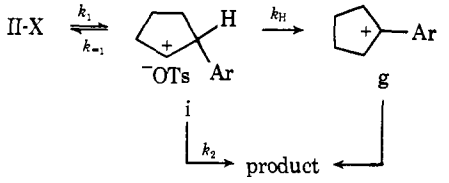


The above considerations suggest that the mechanisms A and B are not entirely consistent with the results. Yet, the observed large β-deuterium effect ($k_H/k_{\beta\text{-}D}$ = 2.07) indicates the existence of hydrogen participation. We believe that the phenomena observed in this study can be better explained in terms of the ion-pair mechanism (Scheme II, path C), which is examined in the next section.

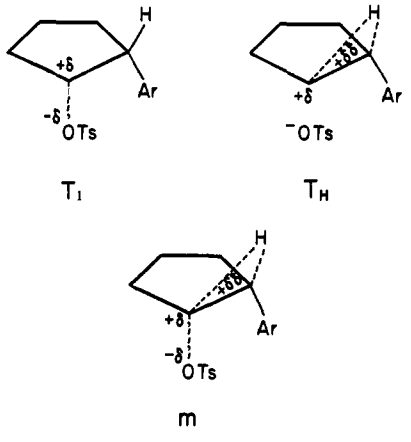
The Possibility of a Mechanism Involving an Open Ion Pair as the First Intermediate

This possibility is illustrated fully in Scheme III. As we find no evidence for aryl participation in the present system, the k_p[28c] process from i is excluded from the scheme.[54] Thus, the initially formed ion-pair intermediate, i, leads either to the tertiary ion, g, by hydride shift (k_H) or to the products, the olefins and the inverted substitution products, by solvent participation (k_2).

Scheme III



One of the virtues of proposing i, presumably an intermediate of relatively high energy, would be to enable one to visualize the transition state with a structure similar to i. Thus, as to the process leading to the tertiary ion, the two apparent energy maxima, T_1 and T_H (corresponding to the steps k_1 and k_H, respectively), may closely resemble the tight ion-pair intermediate. Yet, if T_H, in which the C_2–H bond is partially broken, contributes significantly to the overall rate-determining step, the process can be characterized by "hydrogen participation" in a different sense from the original definition.[4,41,55]



A predominant portion (*ca.* 90%) of the product of acetolysis of II-H appears to arise from this process involving hydride shift. Accordingly, the overall transition state for this process is expected to determine the characteristics of the acetolysis. If we assume that the overall transition state can be represented by a combination of T_1 and T_H, the present scheme appears to provide us with adequate explanation for the kinetic data. Namely, the consideration that charge delocalization into the aromatic ring would be expected to be negligible in these structures explains the linear Hammett plot which shows no significant deviations of the points for the compounds containing activating substituents (Figure 1). As to the "normal" α-deuterium isotope effect observed in the acetolysis of II-H ($k_H/k_{\alpha\text{-}D}$ = 1.19),[51] an explanation that the migrating hydrogen is

(51) A value of 1.22 was suggested for a limiting case.[52,53] The slightly smaller value observed in the present study (1.19) may be claimed to be due either to the existence of relatively "weak" hydrogen participation, or to the existence of the solvent-assisted pathway (*vide infra*), or possibly to the relatively smaller steric requirements of the migrating hydrogen which might be ineffective in restricting the out-of-plane C_α–H bending motion. However, it is doubtful whether the present criterion can be meaningfully applied in discussing such a small quantitative difference.

(52) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 2551 (1971).

(53) V. J. Shiner, Jr., and R. D. Fisher, *ibid.*, **93**, 2551 (1971), and references cited therein.

(54) One of the referees of this paper argued that no one would expect aryl bridging in this system because of the unfavorable geometry. However, an aryl-bridged species was proposed to form in the *endo*-2-benzonorbornenyl system,[21] where the geometry would be equally unfavorable. Such a question should be examined not by speculations but by experimental results.

(55) If T_1 and T_H are comparable energetically, the overall transition state would become equivalent to m. However, the present possibility does not involve any nonclassical concepts.

Table IV. Summary of Physical Data

Substituent	Mp, °C		Bp, °C (mm)		nD	
	Obsd	Lit.[a]	Obsd	Lit.[a]	Obsd (20°)	Lit. (25°)[a]
			Substituted *cis*-2-Phenylcyclopentanol			
p-MeO			138–140 (3)		1.5483	
p-Me			118–120 (5)	74–75 (0.1)	1.5410	
m-Me			117–118 (4)		1.5423	
H			111–113 (5)	65 (0.15)	1.5460	1.5444
p-Cl			136–137 (4.5)	85 (0.2)	1.5609	
m-Cl			132–133 (3.5)	90–91 (0.1)	1.5614	
p-NO_2	66.5–67.5					
			Substituted *cis*-2-Phenylcyclopentyl Tosylate			
p-MeO	81–82					
p-Me	89–90	89–90				
m-Me	90.5–91.5					
H	97–98	97–98				
p-Cl	107–108	108				
m-Cl	81–82	81–82				
p-NO_2	98–99					

[a] Reference 57.

Table V. Summary of Analytical Data of Substituted *cis*-2-Phenylcyclopentyl Tosylates

Substituent	Calcd, %				Found, %			
	C	H	S	N	C	H	S	N
p-MeO	65.88	6.40	9.24		65.94	6.59	9.23	
p-Me	69.07	6.71	9.69		69.15	6.49	9.53	
m-Me	69.07	6.71	9.69		68.85	6.78	9.71	
H	68.34	6.37	10.12		68.44	6.43	10.11	
p-Cl	61.62	5.46	9.14		61.67	5.35	9.03	
m-Cl	61.62	5.46	9.14		61.52	5.67	9.07	
p-NO_2	59.83	5.30	8.86	3.88	59.76	5.52	8.91	3.96

sufficiently remote from the carbonium center in T_H should be consistent with the theory proposed by Streitwieser.[6] Finally, the relatively high β-deuterium isotope effect in the acetolysis of II-H ($k_H/k_{\beta\text{-}D} = 2.07$) may be the result of the combined effects of hyperconjugative destabilization of T_I by substituting the tertiary β hydrogen with deuterium and destabilization of T_H caused by the difficulty of loosening a C–D bond compared to a C–H bond.

As was mentioned previously, the product data for the acetolysis of a and b (Table II) indicate that almost all of the 1-arylcyclopentene product arises from the process involving hydride shift. This leaves the other products, 3-arylcyclopentene and the trans acetate, to be attributed to the k_2 process in Scheme III. Although this is a minor pathway which accounts for *ca.* 10% of the product from the acetolysis of II-H and only *ca.* 2% in the case of II-*p*-MeO, an interesting problem arises as to what could be the nature of this process which leads only to the Δ^3-olefin and the inverted substitution product, in the absence of a significant amount of Δ^1-olefin formation.

An economic explanation would be to propose that the Δ^3-olefin arises from the tight ion-pair intermediate by a mechanism involving cis elimination. This process may involve the solvent (or the leaving group) attack from the same side of the leaving group, while the solvent attack from the opposite side of the leaving group yields the trans acetate.

There appears to be another possibility that the solvent approach is exclusively from the opposite side of the leaving group. In this case, the solvent molecule has three choices for a place to attack, the carbonium center, the tertiary β hydrogen, and the secondary β hydrogen, which may lead to the trans acetate, the Δ^3-olefin, and the rearranged tertiary cation, respectively. This possibility suggests an interesting problem that the hydride shift may not be a process of a bare hydrogen migration, but the solvent may be assisting to some extent by helping to loosen the C–H bond.[56]

Considering these two possibilities, although we are not in a position to present a detailed discussion at this time, the importance of nucleophilic solvent participation in the overall transition state is still a matter of question as to whether the process involving hydride shift involves strong solvent participation or not. Nevertheless, we believe that the experimental results of the present study are consistently explained by proposing the mechanism shown in Scheme III.

Experimental Section

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

***cis*-2-Phenylcyclopentanol and Its Substituted Analogs.** The following two preparative procedures were employed for the parent compound. (1) *m*-Chloroperbenzoic acid (30 g, 70% pure) was dissolved in 400 ml of chloroform and the solution was cooled to 0° before adding 18 g of 1-phenylcyclopentene.[33] The mixture was stirred for 2 hr at 0° and 1 hr at room temperature. The reaction mixture was then cooled to 0°, filtered to remove the solid, and condensed to *ca.* 50 ml, and then 100 ml of pentane was added. This solution was washed three times with sodium carbonate solution and the solvent was removed. The residue was dissolved in 50 ml of ether to be shaken vigorously with 50% sulfuric acid solution. After work-up, the crude ketone was distilled at 128–130° (8 mm)

(56) Cram and Tadanier suggested at one time that the migrating hydrogen is hydrogen bonded to a solvent molecule.[40]

and then recrystallized from pentane: yield nearly quantitative; mp 35–36°; lit.[57] bp 130° (10 mm), mp 35–36°. This procedure appears to be much cleaner than that involving oxidation of *trans*-2-phenylcyclopentanol. 2-Phenylcyclopentanone (10 g), thus obtained, was then reduced with disiamylborane at 0° according to the previous procedure.[32] A glpc analysis of the product showed 91% of *cis*-2-phenylcyclopentanol and 9% of the trans isomer. Pure cis isomer (5 g) was obtained by a careful chromatographic separation on activated alumina,[57] bp 111–113° (5 mm), n^{20}D 1.5460.

(2) Tetraethylammonium acetate was prepared by the procedure described by Steigman and Hammett.[58] *trans*-2-Phenylcyclopentyl tosylate[33] (10 g) and tetraethylammonium acetate (33 g) were dissolved in 300 ml of dry acetone and refluxed overnight before removing the solvent at a reduced pressure. The residue was taken up in pentane and washed with water. A glpc analysis of this mixture showed the presence of 54% of 3-phenylcyclopentene, 46% of *cis*-2-phenylcyclopentyl acetate, and a trace amount of 1-phenylcyclopentene. No trace of trans acetate was detected. This mixture was then treated with lithium aluminum hydride and 2 g of pure *cis*-2-phenylcyclopentanol was isolated at the final stage.

Other substituted analogs, except the nitro compound, were synthesized similarly.

***cis*-2-(*p*-Nitrophenyl)cyclopentanol.** *cis*-2-Phenylcyclopentyl acetate (3.7 g) was mixed with 10 ml of acetic anhydride and 7 ml of glacial acetic acid and cooled to 0°. To this solution 2 ml of 90% nitric acid in 5 ml of acetic acid was added dropwise at 0° with a good stirring. The reaction mixture was stirred for an additional 2 hr at 0° and overnight at room temperature before being poured on 100 ml of ice–water. The solid was filtered and recrystallized from ether–pentane. Yellow crystals (1.9 g) were obtained which were found to be practically pure *cis*-2-(*p*-nitrophenyl)cyclopentyl acetate, mp 98–100°. The acetate (1.8 g) was dissolved in 25 ml of 0.5 *M* hydrochloric acid in dry methanol and refluxed for 5 hr and the acid, solvent, and methyl acetate were removed at a reduced pressure. The residue was recrystallized from ether–pentane at −10° to yield 1.4 g of yellow powder, mp 66.5–67.5°.

***cis*-2-Phenylcyclopentanol-*1*-d_1.** 2-Phenylcyclopentanone (9 g) was treated with 1 g of lithium aluminum deuteride[59] in ether. The reduction resulted in 43% of *cis*-2-phenylcyclopentanol-*1*-d_1 and 57% of the trans isomer. This mixture was subjected to a chromatographic separation to obtain 2 g of pure cis isomer. A preparative glpc separation was also carried out in another run.

***cis*-2-Phenylcyclopentanol-*2*-d_1.** *trans*-2-Phenylcyclopentyl-*2*-d_1 tosylate[33] (11 g) was treated with 40 g of tetraethylammonium acetate according to the previously described procedure. After lithium aluminum hydride treatment, 2.5 g of pure *cis*-2-phenylcyclopentanol-*2*-d_1 was obtained. The pmr spectrum was consistent with the structure and the later study in the use of optically active compound[28d] confirmed that the above reaction proceeds with net inversion. Examination of the pmr spectrum of the 3-phenylcyclopentene product also revealed that the deuterium is exclusively at the 3 position, showing no sign of isotope scrambling.

***p*-Toluenesulfonates.** The procedure was previously described.[10]

Rate and Product Studies. The procedure was described in the previous paper.[28c] In determining the kinetic isotope effects, simultaneous rate measurements of all three compounds, the parent (II-H), the α-deuterated (a), and the β-deuterated (b) compounds, were carried out in order to minimize the error. Three individual sets of such measurements were conducted.

The 1-phenylcyclopentene component of the acetolysis product of α- or β-deuterated compound was isolated by preparative glpc and examined by pmr. The peaks were repeatedly integrated with a slower sweep time and the average values of more than 15 of such integrations were used in calculating the deuterium distribution. A controlled experiment showed that the above deuterium distribution does not change after a prolonged standing under the solvolytic condition.

(57) C. H. Depuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Amer. Chem. Soc.*, 87, 2421 (1965).

(58) J. Steigman and L. P. Hammett, *ibid.*, 59, 2536 (1937).

(59) Metal Hydride, Inc., Beverly, Mass., 95.5% D.