Structural Effects in Solvolytic Reactions. VI. Rates and Products in the Acetolysis of Substituted *trans*-2-Phenylcyclopentyl Tosylates and Optically Active Derivatives. The Nature of the Aryl-Assisted and the Aryl-Unassisted Reaction Pathways[1]

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Abstract: The rates and the products of acetolysis of a series of substituted *trans*-2-phenylcyclopentyl tosylates were studied. An excellent Hammett plot was obtained for the compounds containing deactivating substituents, compounds which undergo solvolysis without appreciable retention. Thus, this correlation represents the aryl-unassisted rates (k_s). The unassisted rates of the parent compound and those compounds containing activating substituents were evaluated from this line to be compared with the observed rates (k_t). The magnitude of rate acceleration attributable to aryl participation (k_t/k_s) turned out to be quite small in every case, a maximum factor of 3.7 being observed for the *p*-methoxy derivative. This small factor appears not to be compatible with the previous interpretation which postulates the direct formation of a *p*-anisyl-bridged intermediate. The product–rate correlation was examined by comparing the rate-derived amount of product arising from the assisted pathway with the observed amount of retained product. The agreement between the predicted and the observed values was less satisfactory in this case than that found in the acetolysis of 3-aryl-2-butyl brosylates. This appears to indicate that the assumption that the aryl-assisted pathway leads only to the retained product may not be applicable to the present system. In order to examine this point thoroughly, we synthesized optically active *trans*-2-arylcyclopentyl tosylates and studied the polarimetric rates and the products of acetolysis. The polarimetric to titrimetric rate ratios (k_α/k_t) were determined to be 1.16, 1.82, and 2.88 for the parent, the *p*-methyl, and the *p*-methoxy derivatives, respectively. Acetolysis of active tosylate yields, in every case, almost completely racemized trans acetate (retained product) and partially racemized cis acetate (inverted product). The 3-arylcyclopentene product (Δ^3-olefin) was also found to be partially racemized but the degree of racemization was much greater than that found in the corresponding cis acetate. This suggests that the Δ^3-olefin arises from both the aryl-assisted and the aryl-unassisted pathways. In order to examine the nature of the reaction pathway leading to the 1-arylcyclopentene product (Δ^1-olefin), *trans*-2-phenylcyclopentyl-*2*-d_1 tosylate and the *p*-methoxy analog were prepared and the products of acetolysis were examined. In each case, extensively scrambled Δ^1-olefin was obtained. The formation of a major amount of 1-arylcyclopentene-*5*-d_1 indicates that 1-arylcyclopentyl cation is involved in this process as an important intermediate. The observed phenomena were consistently interpreted in terms of the previously proposed mechanism which postulates the prior formation of a tight ion-pair intermediate followed by a variety of subsequent processes such as aryl participation, solvent participation, and hydride shift.

The original theory for the acetolysis or formolysis of secondary β-phenylalkyl arenesulfonates postulated the competitive formation of phenyl-bridged and open ion intermediates *via* two distinct ionization processes, the phenyl assisted and the phenyl unassisted.[3] The latter process was described by Cram in terms of SN1 and E1 mechanisms,[3b-e] which appeared to be consistent with the interpretation by Winstein and his coworkers that the acetolysis or formolysis of secondary alkyl arenesulfonates is nearly limiting.[4,5]

As was described previously, this theory of bridged and open ions appeared to be faced with a difficulty in accounting for the apparently small magnitude of rate acceleration attributable to phenyl participation.[7,8] Unfortunately, resolution of this problem has been much delayed due to the considerable difference in opinions as to how this rate acceleration might be evaluated.[4c,9,10]

Recently, a precise and objective means of estimating the magnitude of aryl participation in the solvolysis of β-arylalkyl derivatives, which utilizes the Hammett

(1) For a preliminary report, see C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, 91, 4287 (1969).

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

(3) (a) D. J. Cram, *J. Amer. Chem. Soc.*, 71, 3863 (1949); (b) *ibid.*, 74, 2129 (1952); (c) *ibid.*, 74, 2137 (1952); (d) *ibid.*, 74, 2159 (1952); (e) D. J. Cram and F. A. Abd Elhafez, *ibid.*, 75, 3189 (1953); (f) D.J. Cram, H. L. Nyquest, and F. A. Abd Elhafez, *ibid.*, 79, 2876 (1957).

(4) (a) S. Winstein and E. Grunwald, *ibid.*, 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) Considering the classic Ingold's scheme which defines the solvolysis of secondary derivatives as borderline (between SN1 and SN2),[6] the reasons for postulating an SN1 mechanism for the phenyl-unassisted process, which were not explicitly stated by Cram,[3] would be hard to understand if one disregards the pioneer works of Winstein and his coworkers.[4]

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

(7) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, 87, 2137 (1965).

(8) Cram was aware of the result of Winstein that the acetolyses of 2-butyl and 3-phenyl-2-butyl tosylates proceed with similar rates.[3a] This was then explained in terms of similar stabilities of the bridged and open ions, *i.e.*, it was suggested that in the phenyl-bridged species the energy gained by forming a new bond (bridging bond) approximately cancels the energy needed to compensate for the loss arising from such bridging (decrease in resonance energy of the ring and the loss due to the introduction of strain).[3a] It was pointed out, however, that the proposed bridged and open ions of similar stabilities, the latter being proposed to be formed in an SN1 process, should undergo facile equilibration before being captured by solvent.[7] The problem may then be realized according to the argument presented previously.[7]

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

(10) (a) D. J. Cram, *J. Amer. Chem. Soc.*, 86, 3767 (1964); (b) D. J. Cram and J. A. Thompson, *ibid.*, 91, 1778 (1969).

plot. has been developed.[1,11-13] In the use of this method we established that the rate of acetolysis of 3-phenyl-2-butyl brosylate is accelerated by a mere factor of 3.0,[17] as compared to the predicted rate in the absence of phenyl participation.[11] This observation confirms our earlier position that the original theory involving the concurrent formation of bridged and open ions is not capable of accounting for this small rate acceleration.

Resolution of the problem now appears to be in rapid progress, largely owing to the recent recognition of the fact that the acetolysis or formolysis of secondary arenesulfonates may not be limiting, contrary to the earlier belief.[4] Schleyer and Lancelot observed that the rates and the products of solvolysis of secondary β-arylalkyl derivatives can be adequately correlated by assuming the existence of two discrete reaction pathways, the aryl assisted and the unassisted.[19] Our detailed study of the acetolysis of substituted *threo*-3-phenyl-2-butyl brosylates (I-X) indeed revealed a precise product–rate correlation.[11b,c] This requires that there should not be crossover between the two routes,[20] and, in turn, that the aryl-unassisted pathway must be assisted significantly by nucleophilic solvent participation.[22-24]

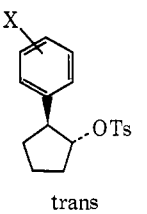
After examining the available experimental data in detail, we previously arrived at a tentative conclusion that the acetolysis of secondary β-arylalkyl arenesulfonates may be best represented by a reaction scheme which involves the initial formation of a tight ion-pair intermediate,[27-29] followed by competitive participation by solvent and by neighboring aryl.[11c] This scheme suggests the possibility that the ionization to an open ion pair may not be the sole rate-determining step but that the subsequent processes involving solvent and neighboring group may also participate in the overall rate-determining process.[11c,27,30]

In order to test whether a satisfactory product–rate correlation can be generally found in the acetolysis of other secondary β-arylalkyl systems and whether the previous interpretation based on the proposed mechanism involving tight ion-pair formation can be generally applied to the solvolytic behavior of secondary systems, we decided to study the acetolysis of the *cis*- and the *trans*-2-arylcyclopentyl systems.

In the preceding paper,[21] we reported the results for the cis derivatives, which show that the acetolysis of substituted *cis*-2-phenylcyclopentyl tosylate (II-X) proceeds exclusively *via* the aryl-unassisted pathway (k_s). This k_s pathway is characterized by the predominant importance of the process involving hydride shift, and the observed phenomena were consistently interpreted in terms of a reaction mechanism which formulates the initial ionization to an ion pair, followed by hydride shift or by solvent participation.[21] In this paper, we present the results of an extensive study of the acetolysis of substituted *trans*-2-phenylcyclopentyl tosylates (III-X), which includes the data obtained in the use of optically active as well as deuterium-tagged derivatives.

Rates and Products of Acetolysis of Racemic *trans*-2-Arylcyclopentyl Tosylates

The substituted *trans*-2-phenylcyclopentyl tosylates (III-X), with the exception of the *p*-nitro derivative, were prepared by treatment of cyclopentanone with arylmagnesium bromide to 1-arylcyclopentanol, dehydration of the tertiary alcohol to 1-arylcyclopentene, and hydroboration–oxidation of the olefin, followed by conversion of pure *trans*-2-arylcyclopentanol to the tosylate. The *p*-nitro-substituted compound was synthesized by nitration of the parent acetate.



trans

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

The titrimetric rate measurements were carried out at two temperatures and the observed kinetic data are summarized in Table I.

The effects of substituents are relatively small and regular, similar to those observed in the acetolysis of substituted *cis*-2-phenylcyclopentyl tosylates (II-X).[21] Thus, the *p*-methoxy substituent accelerates the rate of the parent compound by a factor of 5, while the bistri-

(11) (a) C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4289 (1969); (b) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970); (c) H. C. Brown and C. J. Kim, *ibid.*, **93**, 5765 (1971).

(12) (a) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291 (1969); (b) J. M. Harris, F. J. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 7508 (1969).

(13) For other recent quantitative methods, see ref 10b and 14–16.

(14) (a) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4294 (1969); (b) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4296 (1969); (c) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, *ibid.*, **93**, 4829 (1971).

(15) (a) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969); (b) A. F. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968).

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

(17) This factor was obtained based on the titrimetric rate. If one considers the polarimetric rate,[18] this factor becomes 4.4 × 3.0. See the previous discussions concerning this point.[11c]

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

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

(20) In a number of occasions Winstein and his coworkers suggested that in secondary systems there would be crossover between the anchimerically assisted and the unassisted routes after the ionization steps. See footnote 18 in the previous paper.[21]

(21) C. J. Kim and H. C. Brown, *ibid.*, **94**, 5043 (1971).

(22) (a) 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 communications; (b) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 4821 (1971); (c) J. M. Harris, R. E. Hall, and P. v. R. schleyer, *ibid.*, **93**, 2551 (1971).

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

(24) The aryl-unassisted process in the solvolysis of secondary β-arylalkyl derivatives was suggested by both Cram[3e,f,10] and Winstein[18,25] to involve solvent participation in the ionization step leading to "solvated" open ions. It should be pointed out, however, that this is apparently inconsistent with their own views which describe such processes in terms of an SN1 or a nearly limiting mechanism.[3,4] Considering the notion that the solvated open ion would likely cross over to the bridged species in secondary systems,[20] nucleophilic solvent participation may have been considered by Winstein to be weak enough to allow crossover between the two routes. Cram, on the other hand, did not consider such a possibility of crossover, despite the abundance of other conflicting interpretations[4,20,26] including one of his own.[5b-e] Discussions on this point have never been presented explicitly.

(25) (a) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Amer. Chem. Soc.*, 74, 1140 (1952); (b) S. Winstein and R. Heck, *ibid.*, **86**, 2071 (1964).

(26) See footnotes 6–12 of ref 21.

(27) (a) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **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).

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

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

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

Table I. Titrimetric Rate Data for the Acetolysis of Substituted *trans*-2-Phenylcyclopentyl Tosylates (III-X)

III-X X =	10^6k_t, sec^{-1} 50.0°	75.0°	Rel rate at 50.0°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Trans/cis[c] at 50.0°
p-MeO	43.6	681[a]	5.0	23.9	−3.5	0.55
p-Me	14.0[b]	256	1.6	25.3	−2.5	0.25
m-Me	10.7	194	1.2	25.3	−3.2	0.24
H	8.67[b]	160	1.0	25.4	−3.2	0.25
p-Cl	3.25[b]	62.6	0.38	25.8	−4.1	0.27
m-Cl	2.67[b]	50.4	0.31	25.6	−4.9	0.35
m-CF_3	2.27	41.4	0.26	25.3	−6.2	
p-CF_3	1.70		0.19			
p-NO_2	0.936	18.9	0.11	26.3	−4.8	0.43
m,m'-$(CF_3)_2$	0.772		0.089			

[a] Extrapolated value. $k_t = 1.76 \times 10^{-6}$ at 25.0°. [b] Average of two measurements. [c] For the rate constants of the cis isomers, see ref 21.

fluoromethyl substituents retard the rate by a factor of 11. As the aryl participation is absent in the cis system, the similar magnitude of substituent effects observed for the trans system indicates qualitatively that aryl participation is also not an important factor in the acetolysis of III-X.

The products of acetolysis of III-X were studied for all compounds, and the results are summarized in Table II. The amount of retained product, the trans acetate,

Table II. Products from Acetolysis[a] of Substituted *trans*-2-Phenylcyclopentyl Tosylates (III-X)

III-X, X =	Temp, °C	Product, %: Δ^1-Olefin[b]	Δ^3-Olefin[c]	*cis*-2-Acetate	*trans*-2-Acetate
p-MeO	50[d]	16	9	2	72
p-Me	50[d]	54	16	11	19
m-Me	50	70	13	13	4
H	50[d]	72	10	15	3
	75	73	14	11	3
p-Cl	75	73	10	16	1
m-Cl	75[d]	72	9	19	0
m-CF_3	75	70	8	22	0
p-CF_3	75	73	8	19	0
p-NO_2	75	65	6	29	0
m,m'-$(CF_3)_2$	75	57	8	35	0

[a] Each run was carried out with a solution 0.050 *M* in III-X and 0.053 *M* in sodium acetate for 7–10 half-lives. [b] 1-Arylcyclopentene. [c] 3-Arylcyclopentene. [d] Average of two runs.

decreases sharply from 72% for III-*p*-MeO to 3% for III-H, and only 1% or less of retention was detected for the six compounds containing deactivating substituents. Thus, the present result shows a complete regular change in terms of the stereochemistry of substitution, varying from 100% inversion for the compounds containing deactivating substitutions to 98% retention for the *p*-methoxy derivative.[31-33]

Magnitude of Rate Acceleration Attributable to Aryl Participation

It was proposed earlier that the large trans/cis rate ratio of 800 observed in the acetolysis of isomeric 2-bromocyclohexyl brosylates must be the result of the anchimeric assistance by the neighboring bromo group in the trans isomer, leading to a bridged intermediate, while the cis isomer ionizes to an open ion without anchimeric assistance.[34] On the other hand, the trans/cis rate ratio of 4 observed for the 2-chloro derivatives was considered to be too small to support the existence of neighboring chloro participation in the trans isomer.[35]

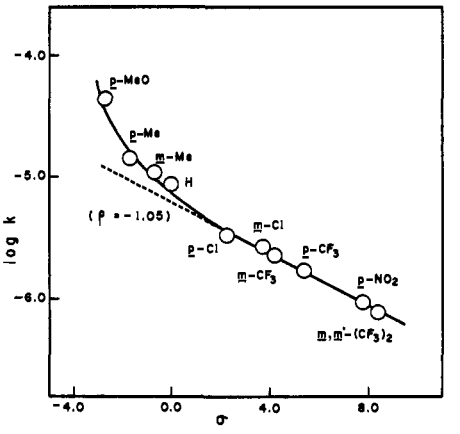


Figure 1. Rates of acetolysis of *trans*-2-arylcyclopentyl tosylates at 50.0° *vs.* the σ constants.

Accordingly, if we apply this interpretation to the present system, both the small magnitudes and the constancy of the observed trans/cis rate ratios of 0.24–0.55 (Table I) support the conclusion that aryl participation is not important in the acetolysis of *trans*-2-arylcyclopentyl tosylates (III-X). However, as was pointed out in the previous study, a precise and quantitative consideration on the magnitude of rate acceleration due to aryl participation can be made by analyzing the Hammett plot.[11,12]

The Hammett plot of the rates at 50.0° is shown in Figure 1. The k_s line which represents the aryl-unassisted rates was determined by a least-squares treatment of the points for the six compounds containing deactivating substituents ($\rho = -1.05$). The aryl-unassisted rates (k_s) of the parent compound and the compounds containing activating substituents were estimated from this k_s line, and then the rate ratio, k_t/k_s, which is a measure of aryl participation, was calculated for each compound (Table III).

(31) It has been noted that the phenyl group failed to control the stereochemistry in the course of acetolysis of *trans*-2-phenylcyclopentyl brosylate.[32] On the other hand, the acetolysis of *trans*-2-*p*-anisylcyclopentyl brosylate was proposed to involve predominantly or exclusively anchimerically assisted ionization to a bridged ion.[33]

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

(33) A. H. Fainberg, G. C. Robinson, and S. Winstein, *ibid.*, 78, 2777 (1956).

(34) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, 70, 821 (1948).

(35) E. Grunwald, *ibid.*, 73, 5458 (1951).

Table III. The Effect of Aryl Participation on the Rates of Acetolysis of III-X

III-X X =	10^6k, sec^{-1} [a] k_t	k_s [b]	Magnitude of rate acceleration k_t/k_s
p-MeO	43.6	11.8	3.7
p-Me	14.0	9.3	1.5
m-Me	10.7	7.3	1.5
H	8.67	6.15	1.4

[a] At 50.0°. [b] Estimated from the correlation in Figure 1.

The result shows that the magnitudes of rate acceleration are relatively small in the acetolysis of III-X, as compared to those observed in the acetolysis of substituted *threo*-3-phenyl-2-butyl brosylates (I-X).[11c] Thus, the rate of the parent compound is accelerated by a mere factor of 1.4, indicating that the effect of phenyl participation is indeed insignificant in the reaction of III-H. As to the rate of the *p*-methoxy compound, the observed rate ratio of 3.7 is still a small factor, a factor which does not appear to support the previous interpretation that III-*p*-MeO undergoes ionization to a bridged ion with extensive *p*-anisyl participation.[33]

The Theory of Bridged and Open Ions

It was previously established that the magnitude of rate acceleration attributable to phenyl participation is a factor of 3.0 (k_t/k_s = 3.0) in the acetolysis of *threo*-3-phenyl-2-butyl brosylate.[11] It was then concluded that this small rate acceleration does not support the original theory which proposes the direct formation of a phenyl-bridged species competitively with the formation of an open ion. The present results appear to lead us to the same conclusion according to the following arguments.

The kinetic data for the acetolysis of III-*p*-MeO can be characterized by k_t/k_s = 3.7 (Table III) and k_α/k_t = 2.88 (*vide infra*). Then, according to the theory of bridged and open ions, the ratio of the rate of the bridged anisonium ion formation (k_Δ) to the rate of the open cation formation (k_s) becomes a factor of approximately 10.[35] This rate ratio of 10 corresponds to a difference in energy of approximately 1.4 kcal/mol between the two transition states, one of which is supposed to be extensively assisted by neighboring *p*-anisyl participation leading to a bridged ion, and the other without participation to an open cation. Considering the accepted theory that the transition state resembles the first intermediate,[37] it must then be concluded that the stabilities of the bridged and the open ions should be very similar.

This situation is remarkably similar to that which we encountered in the acetolysis of 3-phenyl-2-butyl brosylate, and the same discussion[11c] would lead one to the same conclusion that the kinetic data do not support the theory of bridged and open ions. The predominant formation of retained product (72%) with high stereospecificity (98% retention over 2% inversion) should then be interpreted by a reaction mechanism other than the original theory which postulates the direct and concurrent formation of bridged and open ions.

(36) Calculated by the previously described equation, $k_\Delta/k_s = (k_t/k_s)(k_\alpha/k_.) - 1$.

(37) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

Product–Rate Correlation

According to the previously described procedure,[11,12] the rate-derived measure of aryl participation was compared with the product-derived measure of aryl participation. The predicted amounts of product arising from the aryl-participated pathway are given by $100(k_t - k_s)/k_t$ and these values are compared with the amounts of retained product, the trans acetate (Table IV).

Table IV. The Predicted and Observed Amounts of Product Arising from the Aryl-Assisted Pathway in the Acetolysis of III-X

III-X X =	Product from the aryl-assisted pathway, % Calcd[a]	Obsd[b]
p-MeO	73	72
p-Me	34	19
m-Me	32	4
H	29	3

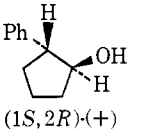
[a] Calculated by $100(k_t - k_s)/k_t$; see Table III. [b] Amount of trans acetate, see Table II.

The agreement between the predicted and observed values is excellent for the *p*-methoxy compound, but the data for other compounds show less satisfactory agreement.

This result indicates that either a really satisfactory product–rate correlation does not exist in the acetolysis of III-X, or the assumption that the assisted pathway leads only to the retained substitution product is incorrect in the present system. Accordingly, in order to test whether some of the elimination product may be attributed to the assisted pathway, we decided to study the acetolysis of optically active *trans*-2-arylcyclopentyl tosylates.

Preparation of Optically Active Compounds

Resolution of racemic *trans*-2-arylcyclopentanols was carried out *via* the L(−)-α-methylbenzylamine salts of the acid phthalates. The absolute configuration of (+)-*trans*-2-phenylcyclopentanol was reported to have a 1*S*,2*R* arrangement as shown below.[38] The observed



(1*S*,2*R*)-(+)

values of $[\alpha]_D$ of the pure (+) alcohols are +62.1, +61.4, and +59.9 for the parent, the *p*-methyl, and the *p*-methoxy derivatives, respectively.

As the rotational values of the corresponding cis alcohols and the Δ^3-olefins are needed in evaluating the optical purities of the solvolysis products, we undertook to prepare optically active *cis*-2-arylcyclopentanols and 3-arylcyclopentenes. The pure (+)-*trans*-2-arylcyclopentanol was converted to the tosylate (+)-III-X and this was treated with tetraethylammonium acetate in dry acetone to obtain roughly equal amounts of the cis acetate and the Δ^3-olefin with a trace amount of Δ^1-olefins. After lithium aluminum hydride treatment, each component was isolated and subjected to specific

(38) H. B. Hopps, Ph.D. Thesis, Purdue University, 1962.

rotation measurement. The cis alcohols, thus obtained, gave $[\alpha]_D$ values of −90.4 (X = H), −80.5 (X = *p*-Me), and −74.6 (X = *p*-MeO). The values for the Δ^3-olefins were −216.7 (X = H), −214.5 (X = *p*-Me), and −201.5 (X = *p*-MeO). These values should represent the optically pure isomers, provided the reaction of (+)-III-X with tetraethylammonium acetate does not involve any significant racemization. In order to examine this point, we carried out the following experiment.

The (−)-*cis*-2-phenylcyclopentanol, obtained in the above reaction sequence, was converted to the tosylate, treated with tetraethylammonium acetate in dry acetone, and then with lithium aluminum hydride, followed by the isolation of the trans alcohol. This double inversion product was found to have $[\alpha]_D$ +61.7, which is almost the same as that of the original alcohol, $[\alpha]_D$ +62.1. Consequently, it appears to be safe to conclude that the reaction of (+)-III-X with tetraethylammonium acetate proceeds with net inversion. On the other hand, it was previously established that the reaction of *trans*-2-phenylcyclopentyl-*2*-d_1 tosylate gives Δ^3-olefin product without any detectable amount of scrambling of the deuterium tag.[21] Accordingly, the $[\alpha]_D$ values observed in this study for (+)-*trans*-2-arylcyclopentanols, (−)-*cis*-2-arylcyclopentanols, and (−)-3-arylcyclopentenes may be used as the absolute standards in determining the optical purities of the solvolysis products (Tables XIII and XV).

Polarimetric Rates

The polarimetric rates of acetolysis of III-X were determined in the use of the (−) isomers. Each run was carried out with a solution 0.050 *M* in (−)-III-X and 0.055 *M* in sodium acetate while the titrimetric rate measurement was performed simultaneously. Both the polarimetric and the titrimetric rates exhibit good first-order plots up to 75% reaction. The results are summarized in Table V.

Table V. Polarimetric and Titrimetric Rates of Acetolysis[a] of Substituted (−)-*trans*-2-Phenylcyclopentyl Tosylates at 50.0°

(−)-III-X X =	$10^5 k$, sec^{-1} k_α	k_t	k_α/k_t
p-MeO	15.5	5.38	2.88
p-Me	2.58	1.42	1.82
H	1.04	0.893	1.16

[a] Each run was carried out with a solution 0.050 *M* in substrate and 0.055 *M* in sodium acetate.

In each case, it was observed that the polarimetric rate is considerably greater than the titrimetric rate, indicating the existence of the internal return process. The k_α/k_t values are determined to be 2.88 (III-*p*-MeO), 1.82 (III-*p*-Me), and 1.16 (III-H).

It may also be worth commenting briefly on the effect of added sodium acetate on the titrimetric rate. Comparing the titrimetric rates in Table I (the results in the absence of salt) with those in Table V (the results in the presence of 0.055 *M* NaOAc), one notices that the effect of added sodium acetate is significantly large for the *p*-methoxy derivative (with a rate increase of 23%), while such effect is small for the parent and the *p*-methyl compounds (with a rate increase of 2–3%). The small increase in rate observed for III-H and III-*p*-Me can well be attributed to the normal salt effect. The unusually large salt effect observed for III-*p*-MeO may be best accounted for in terms of the concept of special salt effect which has been extensively explored by Winstein and coworkers.[39] Discussions on this point will not be presented in this paper.

Products of Acetolysis of Active Tosylates

Each run was conducted with a solution, 0.150 *M* in (+)-III-X and 0.165 *M* in sodium acetate, at 50° for approximately 10 half-lives. After treatment with lithium aluminum hydride, each component of the reaction products was isolated by preparative glpc to be subjected to optical rotation measurement. The observed values of specific rotation were compared with those of optically pure compounds to determine the optical purities of the products. The results are summarized in Table VI.

It was revealed that the retained substitution product (trans alcohol) was almost completely racemized in every case while partial racemization occurred in other products. The cis alcohol was racemized to the extent of 42 and 13% in the acetolyses of (+)-III-*p*-Me and (+)-III-H, respectively. The activity of the cis alcohol from (+)-III-*p*-MeO was not examined due to the limited amount of this product formation (2%). The Δ^3-olefins were found to contain more racemized isomers, compared to the corresponding cis alcohols; *i.e.*, 92, 75, and 46% racemizations were observed for the 3-arylcyclopentenes from (+)-III-*p*-MeO, (+)-III-*p*-Me, and (+)-III-H, respectively. This observation indicates that the reaction pathway leading to the cis alcohol is not solely responsible for the formation of the Δ^3-olefin.

The present study does not give any information on the nature of the reaction pathway leading to 1-arylcyclopentene (Δ^1-olefin) due to its optically inactive structure. As this olefin consists of a major portion of the acetolysis product of III-X (Table II), the characteristic of the pathway to this product must contribute significantly to the overall solvolytic behavior of III-X. In order to investigate this point, we decided to study the acetolysis of deuterium-tagged compounds, *trans*-2-phenylcyclopentyl-*2*-d_1 tosylate (III-*d*-H) and the *p*-methoxy-substituted derivative III-*d*-*p*-MeO).

Products of Acetolysis of *trans*-2-Arylcyclopentyl-*2*-d_1 Tosylates

The *trans*-2-arylcyclopentyl-*2*-d_1 tosylates (III-*d*-X; X = H and *p*-MeO) were prepared *via* hydroboration–oxidation of 1-arylcyclopentene using diborane-d_6. Acetolysis was carried out according to the usual procedure and the 1-arylcyclopentene product was isolated to be examined by pmr. The results are summarized in Table VII.

As is shown in Table VII, the deuterium tag was extensively scrambled in each case. The formation of a major amount of 1-arylcyclopentene-*5*-d_1 isomer, b-X, is somewhat unexpected, for 1-arylcyclopentyl cation, d-X, appears to be the only reasonable precursor for this product.[11] If this is true, then the formation of this tertiary arylic cation must be explained in terms of

(39) See ref 33 and references cited therein.

Table VI. Products of Acetolysis of Substituted (+)-*trans*-2-Phenylcyclopentyl Tosylates[a] and the Amount of Racemization

Substituent	Δ^1-Olefin % yield	Δ^3-Olefin % yield	Δ^3-Olefin [α]D	Δ^3-Olefin % racem[b]	Cis alcohol % yield	Cis alcohol [α]D	Cis alcohol % racem[b]	Trans alcohol % yield	Trans alcohol [α]D	Trans alcohol % racem[b]
p-MeO	13	8	−15.4	92	2			77	0	100
p-Me	58	16	−53.1	75	9	−46.4	42	17	<+0.1	100
H	70	12	−117.4	46	15	−78.8	13	3	~+2	~97

[a] Each run was carried out with a solution 0.150 *M* in substrate and 0.165 *M* in sodium acetate for *ca.* 10 half-lives at 50.0°, followed by treatment with lithium aluminum hydride. [b] Calculated based on the values in Tables XIII and XV.

Table VII. Isomer Distribution[a] in the 1-Arylcyclopentene Product from the Acetolysis[b] of III-*d*-X

	a-X	b-X	c-X
III-*d*-*p*-MeO →	22%	38%	40%
III-*d*-H →	27%	47%	26%

[a] As the deuterium content in III-*d*-X is 95.5% D, the results are corrected for 100% D. [b] Each run was conducted with a solution, 0.050 *M* in III-*d*-X and 0.053 *M* in sodium acetate, at 50° for ~7 half-lives.

a process involving some sorts of hydride shift. This problem shall be discussed later in detail.

Nature of the Reaction Pathways

We have previously suggested that the solvolysis of secondary β-arylalkyl derivatives may be adequately represented by a reaction scheme which formulates initial ionization to a tight ion-pair intermediate,[27] followed by a variety of competing subsequent processes involving aryl participation, solvent participation, leaving group participation, and hydride shift.[11c,21] The experimental data obtained for the acetolysis of 3-aryl-2-butyl brosylates[11] and *cis*-2-arylcyclopentyl tosylates[21] were consistently explained in terms of this mechanism. Accordingly, the observed phenomena in this study shall be examined on the basis of the above reaction scheme.

As the bulk and the apparent complexity of the experimental data we collected in this study do not appear to permit us to present a simple summarizing discussion at this point, we shall examine each solvolysis product separately in terms of the nature of the reaction pathway, and later discuss the overall picture.

(1) Inverted Product. This product appears to arise from the aryl-unassisted pathway (k_s) which involves solvent attack on the tight ion-pair intermediate from the other side of the leaving group. The fact that the cis alcohols from the acetolysis of (+)-III-H and (+)-III-*p*-Me are partially racemized (to the extent of 13 and 42%, respectively) can be attributed to the existence of so-called return processes associated with the aryl-participated pathway. The observation that the polarimetric rate is significantly greater than the titrimetric rate (k_α/k_t = 1.16 for III-H and 1.82 for III-*p*-Me, Table V) indeed indicates the existence of such return processes. A simple calculation predicts that the product from the aryl-unassisted pathway should be racemized to the extent of approximately $100[1 - (k_t/k_\alpha)]$.[40] Then, the predicted amount of racemized isomer in the inverted product becomes 14% for the parent compound and 45% for the *p*-methyl compound. These values agree well with the observed values of 13 and 42% racemization for the cis alcohols from the acetolysis of III-H and III-*p*-Me, respectively (Table VI). We then conclude that the inverted products arise solely from the aryl-unassisted pathway (k_s).

(2) Retained Product. The trans alcohol, obtained from the acetolysis of (+)-III-X, is practically 100% racemized in every case (Table VI). This observation shows that this product arises from an intermediate which is quite different in nature from that leading to the inverted product. According to the previous scheme, this intermediate, possibly an aryl-bridged species, may arise from the initially formed tight ion pair by the aryl-participated process. In any event, the fact that this process is characterized by complete racemization should lead us to the conclusion that the retained product arises solely from the aryl-assisted pathway (k_Δ).[41]

(3) Δ^3-Olefin. The observed amounts of racemization in the Δ^3-olefins from the acetolysis of (+)-III-X are 46, 75, and 92% for the parent, the *p*-methyl, and the *p*-methoxy compounds, respectively (Table VI). The values for the parent and the *p*-methyl compounds (46 and 75%) are considerably higher, compared to the amounts of racemization observed in the inverted products, 13 and 42%, respectively. This suggests that the k_s process is not entirely responsible for the Δ^3-olefin formation. A simple explanation may be given that the Δ^3-olefin arises from both the aryl-unassisted and the aryl-assisted pathways.

According to the above assumption that both the k_Δ and the k_s[41] pathways lead to Δ^3-olefin, we can divide the Δ^3-olefin product into two parts, one of which would have undergone 100% racemization *via* the k_Δ pathway, and the other, to the extent of *ca.* $100[1 - (k_t/k_\alpha)]$% racemization *via* the k_s pathway. The re-

(40) Referring to Scheme I in ref 11c, if a condition of $k_{-1} + k_2 \gg k_p$ is satisfied, the optical purity of the k_s product should become equal to 100 (k_t/k_α).

(41) It appears desirable at this point to comment on the definitions of the terms k_Δ, k_s, and k_c. Winstein and his coworkers defined these terms as the anchimerically assisted, the solvent-assisted, and the totally unassisted *ionization rates*, respectively.[42] In most cases, however, the term k_s was generally referred to the anchimerically unassisted ionization rate (k_s was used even for tertiary derivatives[43]), and this process for the acetolysis of secondary arenesulfonates was considered to be close to k_c.[4,20,26] Considering the recent proposals[27,30] that the ionization process may not correspond to the rate-determining step in some secondary systems, it should be more suitable to define k_s simply as the rate of product formation *via* the anchimerically unassisted pathway irrespective of its identity with the ionization rate. In this respect, we defined k_Δ and k_s as *the overall rates of product formation via* the aryl-assisted and the aryl-unassisted pathways.[11c] The proposal to use Fk_Δ and k_s as the ionization rates to bridged and "solvated" open ions ($k_t = Fk_\Delta + k_s$) in secondary systems should be evaluated by further experimental evidence.

(42) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, 3, 1 (1958).

(43) J. P. Dirlam and S. Winstein, *J. Amer. Chem. Soc.*, 91, 5905 (1969); see footnote 8a therein.

sults of such considerations are summarized in Table VIII.

Table VIII. Dissection of the 3-Arylcyclopentene Product into Two Parts, Assuming both k_Δ and k_s Routes Lead to This Product

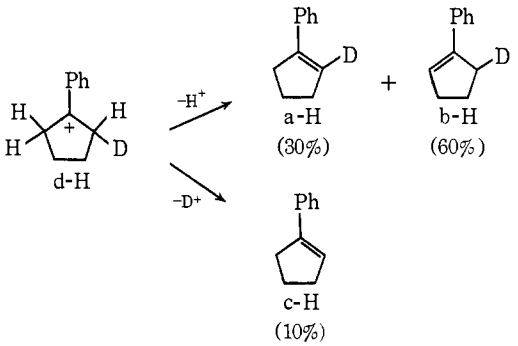
Substituent	Total yield of Δ^3-olefin,[a] %	% Δ^3-olefin produced By k_s[b]	By k_Δ[c]
p-MeO	8	22	78
p-Me	16	45	55
H	12	63	37

[a] See Table VI. [b] Assumed to be 65, 45, and 14% racemized for the *p*-methoxy, the *p*-methyl, and the parent compound, respectively. [c] Assumed to be 100% racemized.

Thus, the present analysis shows that approximately 6% out of 8% of 3-*p*-anisylcyclopentene product may be attributed to the aryl-assisted pathway, while the remaining 2% can be ascribed to the unassisted process. Similarly, 16% of 3-*p*-tolylcyclopentene product can be divided into 9 (k_Δ) and 7% (k_s), and 12% of 3-phenylcyclopentene product obtained in the acetolysis of (+)-III-H may arise partially from the k_Δ process (4%) and partially from the k_s process (8%).

(4) Δ^1-Olefin. It was previously suggested that the Δ^1-olefin product from the acetolysis of *cis*-2-phenylcyclopentyl-*2*-d_1 tosylate, or the *1*-d_1 isomer, appears to arise exclusively from a tertiary benzylic cation, d-H.[21] Presumably this cation arises from the initially formed tight ion-pair intermediate *via* a process involving hydride shift. It followed that the observed amounts of a-H, b-H, and c-H in a ratio of approximately 3:6:1 may be a general feature associated with the formation of d-H (Scheme I).[21]

Scheme I



As to the acetolysis of III-*d*-X, the formation of a major amount of b-X (Table VII) indicates that d-X is also an important intermediate in the process of Δ^1-olefin formation. If we assume that all of b-H (47%) arises from the tertiary benzylic cation, d-H, this ion should also be responsible for the formation of *ca.* 24% of a-H and *ca.* 8% of c-H according to the ratio shown in Scheme I. Thus, approximately 79% (47 + 24 + 8) of the 1-phenylcyclopentene product from the acetolysis of III-*d*-H may be ascribed to a process involving the formation of d-H.

As to the remaining 21% (3% of a-H and 18% of c-H), a direct elimination process involving a tight ion-pair intermediate, an apparent cis elimination process, appears to provide an economic explanation. In this case, the formation of the small amount of a-H can be adequately accounted for by the partial scrambling of the isotope tag in the starting material *via* the return process associated with the phenyl-assisted pathway.

A problem arises at this point as to what is the nature of the process which could account for the formation of the tertiary benzylic cation, d-H, in the acetolysis of III-*d*-H. It seems that d-H is not the first intermediate, for a concerted *cis*-hydride shift appears to be quite unreasonable. Accordingly, it would appear that d-H arises directly or indirectly from the initially formed tight ion-pair intermediate.

Considering the role of the leaving group at the stage of tight ion-pair formation, this leaving group anion can in principle attack either the carbonium center to return to the starting material or the β hydrogen, directly or indirectly through the surrounding solvent molecules, to give elimination products. These processes may be characterized by a term, "leaving group participation," in the sense that the leaving group is competing with solvent or with the neighboring aryl group in the reaction processes involving the tight ion pair. According to this possibility, the 1-arylcyclopentene product obtained in the acetolysis of III-X may be attributed exclusively to the process involving leaving group participation. In this case, it is not entirely unreasonable to speculate that the tertiary arylic cation formation may be the result of either a hydride shift (apparent cis hydride shift from the tight ion-pair intermediate) assisted by the leaving group or a facile elimination–readdition type of process.

Reexamination of the Product–Rate Correlation

In the previous section we found that the rate-derived amount of product attributable to the k_Δ pathway agrees well with the amount of retained product in the case of the *p*-methoxy compound, but the agreement is poor in other cases (Table IV). As the later discussion suggested, a portion of the Δ^3-olefin may also arise from the aryl-assisted pathway (Table VIII). Accordingly, we shall reexamine the product–rate correlation, incorporating the data in Table VIII. The pertinent data are summarized in Table IX.

Table IX. Comparison of the Predicted and Observed Amounts of Product Arising from the Aryl-Assisted Pathway in the Acetolysis of III-X

III-X X =	Predicted amount of k_Δ product,[a] %	Retained product,[a] %	Δ^3-Olefin from k_Δ,[b] %	Total obsd amt of k_Δ product, %
p-MeO	78[c]	72	6	78
p-Me	34	19	9	28
H	29	3	4	7

[a] See Table IV. [b] See Table VIII. [c] The k_t value in Table V was used in this calculation.

The agreement between the predicted and the observed amounts of k_Δ product is satisfactorily good in the cases for III-*p*-MeO and III-*p*-Me, but the data for the parent compound still exhibit a considerable discrepancy. The origin of this discrepancy is not clear at the present time. Nevertheless, the present

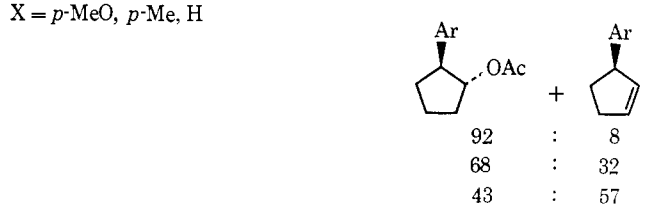
data appear to point to the existence of a satisfactory product–rate correlation in the acetolysis of III-X.

The Nature of the k_Δ Intermediate

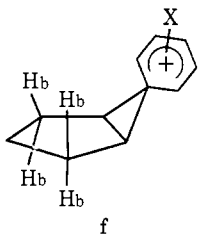
The acetolysis of secondary β-arylalkyl arenesulfonates was previously suggested to proceed *via* the initially formed tight ion-pair intermediate.[11c] The aryl-unassisted pathway (k_s) may then be characterized by such subsequent processes as the solvent participation leading to the inverted as well as some of the elimination products, the hydrogen participation leading to a rearranged cation,[21] and the leaving group participation which leads either to the starting material, some of the elimination products, or possibly to a rearranged cation.

The aryl-assisted pathway (k_Δ) may also be characterized by a process involving aryl participation leading from the tight ion-pair intermediate to either a rearranged cation, a symmetrical aryl-bridged ion, or an equilibrating pair of π-bridged unsymmetrical species. In the acetolysis of 3-aryl-2-butyl brosylates, this intermediate (designated as b in Scheme I in ref 11c) was attributed to account for the formation of only the retained substitution product.[11c]

The detailed experimental data obtained for the acetolysis of *trans*-2-arylcyclopentyl tosylates reveal that this k_Δ intermediate in the present system is responsible not only for the retained product formation but also for some of the Δ^3-olefins (see Table IX). In some quantitative words, we can roughly estimate the following substitution *vs.* elimination ratios.



Considering the possibility that this k_Δ intermediate may be represented by a fully σ-bridged arylonium ion, depicted as f, it would appear that hyperconjugative charge delocalization into the β hydrogens (H_b) will be unimportant in the structure of f. Accordingly, should f represent the k_Δ intermediate, the formation



f

of a significant amount of elimination product cannot be accounted for by the usual E1 type of process, but a special mechanism would be required.[44]

(44) Cram suggested that the phenonium ion proposed in the acetolysis of 3-phenyl-2-butyl and related sulfonates does not lead to the Δ^3-olefin product.[3] On the other hand, in the acetolysis of *threo*-3-*p*-anisyl-2-butyl brosylate, Winstein and Baker observed the formation of *ca.* 0.2% of 3-*p*-anisyl-1-butene, the only other product being the retained substitution product (99.8%). These authors proposed that the postulated *p*-anisonium ion could account for the small amount of terminal olefin formation, although a detailed mechanism was not presented: S. Winstein and R. Baker, *J. Amer. Chem. Soc.*, 86, 2071 (1964).

The possibility of the equilibrating π-bridged unsymmetrical cations, on the other hand, could, in principle, account for the elimination product formation as well as the large substituent effect on the ratio of substitution *vs.* elimination. Such a possibility may have a better chance in the present system where the fully σ-bridged structure of f could involve considerable internal strain due to the bicyclo[3.1.0]hexane structure.

The above arguments are strictly qualitative and, in this connection, the question of the nature of the k_Δ intermediate may depend upon the future developments in elucidating the nature of the process leading to the optically active retained product.[45]

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 X and the analytical data in Table XI.

***trans*-2-Phenylcyclopentanol and Its Substituted Analogs.** The synthesis, except the *p*-NO_2 compound, was carried out according to the following reaction sequence represented by the parent compound. Cyclopentanone (17 g) was treated with 0.25 mol of phenylmagnesium bromide in ether, and the crude 1-phenylcyclopentanol thus obtained was subjected to dehydration according to the procedure described by Garbisch.[46] Hydroboration–oxidation[47] of 1-phenylcyclopentene was performed according to the previously described procedure. The product contained a small amount of the tertiary alcohol, which was eliminated by the similar method described previously.[11c] Pure *trans*-2-phenylcyclopentanol (22 g) was isolated at the final stage: bp 128–130° (6.5 mm); n^{20}D 1.5489.

***trans*-2-(*p*-Nitrophenyl)cyclopentanol.** *trans*-2-Phenylcyclopentanol (13 g) was converted to the acetate, which was nitrated according to the procedure described for the cis isomer.[21] The *p*-nitro isomer was isolated from the crude reaction mixture by recrystallization from ether–pentane and then from methanol: faintly yellow powder; mp 76.2–77.2°. The overall yield was 60%. This acetate (11 g) was hydrolyzed by the given procedure.[21] Pure *trans*-2-(*p*-nitrophenyl)cyclopentanol was obtained as faintly yellow powder from ether–pentane in 86% yield, mp 62.7–63.7°.

***trans*-2-Phenylcyclopentanol-2-d_1 and Its *p*-Methoxy Substituted Analog.** 1-Phenylcyclopentene (14.4 g) was hydroborated with diborane-d_6 which was generated from lithium aluminum deuteride[48] according to the procedure described by Depuy and his coworkers.[49]

Rate and Product Studies in the Use of the Racemic *trans*-2-Arylcyclopentyl Tosylates. The procedures are the same as were described previously.[11c]

(±)-*trans*-2-Phenylcyclopentyl Acid Phthalate and Its Substituted Analogs. *trans*-2-Phenylcyclopentanol (87 g), phthalic anhydride (100 g), and pyridine (100 g) were placed in a flask, heated at 100° for 3 hr with stirring, cooled to *ca.* 50°, and then poured into 500 ml of ice–water. To this mixture was added 200 ml of concentrated hydrochloric acid solution, and the precipitation of a big chunk of pastelike substance was observed. The aqueous layer was decanted and extracted with chloroform, which was used to dissolve the paste. This chloroform solution was washed with water and filtered through a layer of anhydrous sodium sulfate. The clear solution thus obtained was distilled at a reduced pressure in order to remove the solvent, yielding brown heavy syrup. Attempts to recrystallize this syrup were unsuccessful. Accordingly, this syrup was dis-

(45) For example, the acetolysis of optically active *threo*-3-phenyl-2-butyl tosylate gives a small but significant amount of active *threo*-3-phenyl-2-butyl acetate (*ca.* 2% after correcting for the amount of the starting material racemized due to the internal return process). This product cannot arise from the symmetrically bridged phenonium ion, but must be ascribed either to the k_s process or to the k_Δ process involving unsymmetrically bridged ion. Research in this area is in progress with S. Sivaram.

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

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

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

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

Table X. Summary of Physical Data

Substituent	Mp, °C		Bp, °C (mm)		n^{20}D	
	Obsd	Lit.	Obsd	Lit.	Obsd	Lit.
			Substituted 1-Phenylcyclopentene			
p-MeO	91.5–92.5	87–90[b]				
p-Me	52.5–53.5	52[b]				
m-Me			118–120 (9)		1.5695	
H			100–102 (8)	72–74 (1.5)[c]	1.5735[a]	1.5732[a,e]
p-Cl	73–74	71.5–72[c]				
m-Cl			124–126 (6)		1.5875	
m-CF_3			120–121 (19)		1.5052	
p-CF_3	86–87					
m,m'-$(CF_3)_2$	41–41.5		146–148 (8.5)			
			Substituted *trans*-2-Phenylcyclopentanol			
p-MeO			120–122 (1)		1.5512	
p-Me			139–141 (7)	90 (0.2)[d]	1.5434	
m-Me			131–132 (5)		1.5445	
H			128–130 (6.5)	110–113 (2)[e]	1.5489	1.5478[a,e]
p-Cl			124–126 (3)	110 (0.2)[d]	1.5607	
m-Cl			130–131 (4)	106 (0.2)[d]	1.5609	
m-CF_3			119–120 (4.5)		1.4880	
p-CF_3	44.7–45.5					
p-NO_2	62.7–63.7					
m,m'-$(CF_3)_2$			122–123 (7)		1.4501	
			Substituted *trans*-2-Phenylcyclopentyl Acetate			
H			135–137 (8)		1.5175	
p-NO_2	76.2–77.2					
			Substituted *trans*-2-Phenylcyclopentyl Tosylate			
p-MeO	89.5–90.5					
p-Me	88–89	88–89[d]				
m-Me	32.5–33					
H	69–70	68–69[d]				
p-Cl	93–94.5	92–93[d]				
m-Cl	49–50	55–56[d]				
m-CF_3	50–51					
p-CF_3	113–114					
p-NO_2	121–122					
m,m'-$(CF_3)_2$	69–70.5					

[a] 25°. [b] J. Pascual and R. Crespo, *An. Real. Soc. Espan. Fis. Quim., Ser. B*, **48**, 273 (1952). [c] E. W. Garbisch, *J. Org. Chem.*, **26**, 4165 (1961). [d] C. H. Depuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Amer. Chem. Soc.*, **87**, 2421 (1965). [e] W. H. Tallent, *J. Org. Chem.*, **21**, 862 (1956).

Table XI. Summary of Analytical Data of Substituted *trans*-2-Phenylcyclopentyl Tosylates

Substituent	Calcd, %				Found, %			
	C	H	S	N	C	H	S	N
p-MeO	65.88	6.40	9.24		65.70	6.57	9.48	
p-Me	69.07	6.71	9.69		69.11	6.66	9.70	
m-Me	69.07	6.71	9.69		69.24	6.82	9.79	
H	68.34	6.37	10.12		68.31	6.28	10.16	
p-Cl	61.62	5.46	9.14		61.67	5.23	8.94	
m-Cl	61.62	5.46	9.14		61.77	5.51	9.23	
m-CF_3	59.36	4.98	8.34		59.32	5.03	8.51	
p-CF_3	59.36	4.98			59.36	5.02		
p-NO_2	59.83	5.30	8.86	3.88	59.54	5.24	8.94	3.94
m,m'-$(CF_3)_2$	53.08	4.01			53.36	4.22		

solved in sodium carbonate solution at *ca.* 50° and cooled to 0°, when formation of white precipitates was observed. The solid was filtered, washed with ether, and converted back to the acid phthalate by HCl treatment. The acid phthalate thus purified was colorless syrup, yield 145 g (87%). A similar procedure was used in preparing the *p*-methoxy- and the *p*-methyl-substituted analogs.

L(−)-α-Methylbenzylamine Salts of Acid Phthalates. *trans*-2-Phenylcyclopentyl acid phthalate (125 g) was dissolved in 1 l. of anhydrous acetone, to which 49 g of L(−)-α-methylbenzylamine[50] was added slowly with a good stirring. The solution became warm and white solid precipitated out within 1 hr after the addition was complete. The mixture was kept stirring for an additional 4 hr at room temperature and cooled to 0°, and the solid was filtered. The solid was recrystallized from acetone: fine white needles; mp 146–147°; $[\alpha]_D$ +42.7; yield 70 g. From the filtrate *ca.* 100 g of brown heavy oil was recovered which had an approximated rotation of $[\alpha]_D$ −39.8.

The same reaction was carried out with 180 g of *trans*-2-*p*-tolylcyclopentyl acid phthalate in 600 ml of ether–acetone (1:1) solvent, using 68 g of L(−)-α-methylbenzylamine. A small amount of pentane was added to the reaction mixture to induce the precipitation after the reaction was carried out for 3 hr. The solid was filtered, recrystallized from ether–acetone–pentane: mp 149–150°; yield 70 g. The filtrate yielded *ca.* 160 g of brown oil. Similarly, the reaction of the *p*-methoxy derivative (0.65 mol scale) was carried out in pure ether. The solid melted at 142–143°, yield 90 g, and the oil weighed *ca.* 200 g.

(+)-*trans*-2-Phenylcyclopentyl Acid Phthalate, Partially Active (−)-Isomer, and Their Substituted Analogs. Each portion of the previously obtained salts was dissolved in acetone–water and a sufficient amount of hydrochloric acid was added at 0° with

(50) Aldrich Chemicals, Milwaukee, Wis.

a good stirring. The acid phthalate was taken up in benzene and washed with water, and the solvent was removed. The yields and observed rotations of these acid phthalates are summarized in Table XII.

Table XII. Yields and Rotation of the Resolved Acid Phthalates

Starting material, amine salt Substituent X =	Batch	Acid phthalate Yield, %	Acid phthalate [α]D[a]
H	Solid, (+)	~100	+106.8
	Oil, (−) rich	87	−76.5
p-Me	Solid, (+)	~100	+117.3
	Oil, (−) rich	94	−58.2
p-MeO	Solid, (+)	92	+116.7
	Oil, (−) rich	88	−47.1

[a] Due to the difficulties associated with the purification procedures, these values may not be claimed to be accurate.

The recovery of L(−)-α-methylbenzylamine was also performed for further use by sodium hydroxide treatment and extraction with ether, followed by steam distillation.

(+)-*trans*-2-Phenylcyclopentanol, (−) Rich Isomer, and the Substituted Analogs. (+)-*trans*-2-Phenylcyclopentyl acid phthalate (50 g) and 32 g of sodium hydroxide were dissolved in 260 ml of water to be refluxed for 10 hr while stirring. After cooling to room temperature, the upper product layer was separated in pentane and washed with water, and the solvent was removed. Distillation gave 25 g (95% yield) of (+)-*trans*-2-phenylcyclopentanol: bp 117–118° (5 mm); n^{20}D 1.5489; [α]D +62.1. Other compounds were obtained similarly, except that the hydrolysis product obtained from the (−) rich acid phthalate of the *p*-methoxy derivative could be optically fractionated by recrystallization (Table XIII).

Table XIII. Specific Rotations and Melting Points of Optically Active *trans*-2-Arylcyclopentanols and Tosylates

Products, substituent =	Mp, °C	[α]D
Substituted *trans*-2-Phenylcyclopentanol		
H (+)		+62.1[b]
(−) rich		−46.1
p-Me (+)		+61.4
(−) rich		−32.0
p-MeO (+)	47.5–48.5	+59.9
(−) 1st crop	47.5–48.5[a]	−58.5
2nd crop	47–48	−58.1
3rd crop	Oil	~0
Substituted *trans*-2-Phenylcyclopentyl Tosylate		
H (+)	85.5–86[c]	+44.8[c]
(−)	85.5–86[a]	−44.6
p-Me (+)	109.5–110.5	+39.8
(−)	109.5–110.5[a]	−39.9
p-MeO (+)	109–110	+36.3
(−)	109–110	−36.5

[a] The results after two–four recrystallizations. [b] Hopps reported +45.8.[38] [c] Hopps reported mp 78–83°, [α]D +47.7.[38]

(+)-*trans*-2-Phenylcyclopentyl Tosylate and Other Optically Active Tosylates. In these preparations optical fractionation was observed in every case during the recrystallization steps. Thus starting with 16.2 g of (−) rich *trans*-2-phenylcyclopentanol, fractional recrystallization gave the products in Table XIV. The other data are summarized in Table XIII.

Table XIV

Crop, g	Mp, °C	[α]D
1st, 11.7	85.5–86	−44.6
2nd, 8.2	85–86	−44.3
3rd, 3.0	67.5–74	−21.3
4th, 3.5	66–68	−1.0

(−)-*cis*-2-Phenylcyclopentanol and Its Substituted Analogs. (+)-*trans*-2-Phenylcyclopentyl tosylate (5 g) and tetraethylammonium acetate (16.5 g) were dissolved in 150 ml of anhydrous acetone to be refluxed for 18 hr. The solvent was then distilled off at a reduced pressure and the residue was taken up in pentane to be washed with water. A glpc analysis showed the presence of 53% of 3-phenylcyclopentene, 46% of the cis acetate, less than 1% of 1-phenylcyclopentene, and no trace of the trans acetate. The Δ^3-olefin was isolated by glpc and the rotation was measured, [α]D −216.7. The *cis*-2-acetate portion ([α]D −47.1) was treated with lithium aluminum hydride and pure *cis*-2-phenylcyclopentanol was isolated by glpc, [α]D −90.4. Similar reactions were carried out with the *p*-methyl- and *p*-methoxy-substituted derivatives with the results summarized in Table XV.

Table XV. The Reaction Products of (+)-*trans*-2-Arylcyclopentyl Tosylates with Tetraethylammonium Acetate, Followed by Lithium Aluminum Hydride Reduction

Starting material substituent	[α]D	Products: Δ^3-Olefin % yield	Δ^3-Olefin [α]D	Cis alcohol % yield	Cis alcohol [α]D
H	+44.8	53	−216.7	46	−90.4
p-Me	+39.9	55	−214.5	42	−80.5
p-MeO	+36.4	51	−201.5	47	−74.6

The Doubly Inverted (+)-*trans*-2-Phenylcyclopentanol. Approximately 1 g of the (−) cis alcohol was converted to the tosylate, and the crude tosylate was directly submitted to the tetraethylammonium acetate treatment in order to avoid any optical fractionation during the purification step. The reaction mixture was then treated with lithium aluminum hydride and pure trans alcohol was isolated by glpc. Examination by a polarimeter revealed that this doubly inverted *trans*-2-phenylcyclopentanol retains most of the original activity ([α]D +62.1), *i.e.*, [α]D +61.7.

Product Studies with (+)-Tosylates. The usual procedure was employed in use of a solution of 0.150 *M* in the tosylate and 0.165 *M* in sodium acetate. Each component of the reaction products was isolated and its specific rotation was determined to be compared with the values in Table XV. The results are summarized in Table VI.

Rate Studies with (−)-Tosylates. A solution containing 0.050 *M* of tosylate and 0.055 *M* of sodium acetate was prepared for this purpose. For each run 18 ampoules, each containing 5.5 ml of the kinetic solution, were used to determine both the polarimetric and titrimetric rates simultaneously. The polarimetric rate measurements were performed by means of the usual quenching technique and the reading of each kinetic sample was taken at room temperature after 10 min from quenching. The titrimetric rates were measured by taking two 2.0-ml aliquots from each kinetic sample which were titrated with 0.02 *M* $HClO_4$ solution, recording the average of these double titrations to be used as one kinetic point.

Specific Rotation Measurements. All measurements were carried out in chloroform using a 2-dm tube at 25–27°. The concentration was chosen to be in the range of 2–6 g/100 ml of $CHCl_3$.