The Cyclopentylphenylcarbinyl Cation System[1a]

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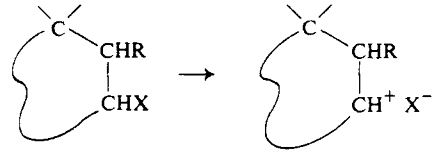
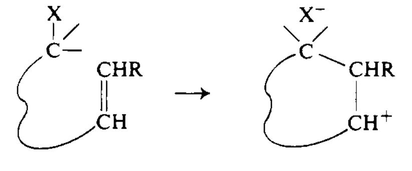
Abstract: Two π and two σ routes to the cyclopentylphenylcarbinyl cation have been examined with respect to the effect of the ionization pathway on the composition of acetolysis products formed. Unlike most other systems investigated this benzylic cation yields the most elimination product by the π routes. Deamination of cyclopentylphenylcarbinylamine in acetic acid yields products where the substitution/elimination ratio closely resembles that of products from the most direct σ route, contrary to what has usually been observed. The rates of cyclization of *trans*-6-aryl-5-hexenyl brosylates in acetic acid were observed to be correlated by σ constants somewhat better than σ^+ constants, with a ρ value of -1.73. It is concluded that the most plausible explanation for the divergence of π-route product mixtures from σ-route product mixtures is the formation of higher energy, but classical, carbonium ions in the former process. Other factors, such as carbonium ion conformation and proximity of a basic counter ion, are probably of lesser importance.

The "π route"[2] to carbonium ions, *i.e.*, the formation of cyclic structures through neighboring-group displacement reactions by double bonds during solvolytic processes, has proved to be synthetically useful[3] as well as being an interesting tool for examination of carbonium ion reactions.[4] One of the most striking features of the π route is its tendency to yield a quite different product mixture from that obtained from a σ route supposedly yielding the same carbonium ion under the same conditions of solvent, temperature, etc.[4,5] In particular, the secondary ions examined tend to yield a much higher fraction of substitution product by the π routes than by σ routes, although different π routes and different σ routes to the "same" ion also normally show divergences between themselves.[4-6] Also, a strong resemblance between π-route products and the products obtained by σ-route deamination has been noted.[4]

One interpretation of the divergence in product mixtures obtained by different routes is to attribute the large fraction of elimination product normally observed in the more direct σ routes to proton abstraction by the adjacent counter ion. The striking relationship between ion pairing and fraction of elimination in the *t*-butyl system shown by Cocivera and Winstein[7] and the work of Skell and Hall indicating that the bulk of the 2-butene formed from 2-butyl tosylate in the less basic solvents (*e.g.*, acetic acid) arises by a *cis* elimination[8] lend credence to this view. Thus, considering the general case where (1) and (2) represent a σ and π route to the same carbonium ion–anion pair, it would not seem surprising if case 2 led to considerably less elimination product than case 1 if the rate of further reaction of the carbonium ion were greater than, or of the same order as that of movement of the ions relative to each other. The rapidity with which carbonium ions react with solvent is attested to by such examples as the incompleteness of 6,2-hydride scrambling during acetolysis of the norbornyl system[9] (the 6,2-hydride shift having an estimated activation energy of less than 5.5 kcal/mol in SbF_5–SO_2–SO_2F_2 solution[10]) and the observation that the 4-octyl cation in acetic acid has a lifetime short relative to rotation about C–C single bonds.[11] (The grossly different product mixtures obtained from different conformers of the 2-bicyclo[2.2.2]octyl[12] and 2-bicyclo[2.2.2]oct-5-enyl cations[6a] is another example of the short lifetime of secondary carbonium ions.) Indeed, most of these examples imply that conformational equilibrium may not be reached, let alone an "equilibrium" disposition of cation and anion.



(1)



(2)

An alternative explanation, proposed by Bartlett,[4,5a] for this variation in product composition is that the π route always passes through a bridged species (1) which may

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[2] S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).

[3] W. S. Johnson and R. B. Kinnel, *ibid.*, **88**, 3861 (1966), and preceding papers in this series: See also W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

[4] P. D. Bartlett, E. M. Nicholson, and R. Owyang, *Tetrahedron, Suppl.*, **8**, 399 (1966). See also preceding papers in this series.

[5] (a) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *J. Am. Chem. Soc.*, **87**, 1308 (1965); (b) W. D. Closson and G. T. Kwiatkowski, *ibid.*, **86**, 1887 (1964); (c) W. D. Closson and G. T. Kwiatkowski, *Tetrahedron Letters*, 6435 (1966); (d) W. Rittersdorf and F. Cramer, *Tetrahedron*, **24**, 43 (1968); (e) see, however, H. L. Goering and G. N. Fickes, *J. Am. Chem. Soc.*, **90**, 2856, 2862 (1968).

[6] (a) J. A. Berson and J. Gajewski, *ibid.*, **86**, 5020 (1964); J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *ibid.*, **90**, 3237 (1968); (b) W. G. Dauben and G. L. Whalen, *ibid.*, **88**, 4739 (1966); W. G. Dauben and J. L. Chitwood, *ibid.*, **90**, 3835 (1968).

[7] M. Cocivera and S. Winstein, *ibid.*, **85**, 1702 (1963).

[8] P. S. Skell and W. L. Hall, *ibid.*, **85**, 2851 (1963).

[9] J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

[10] (a) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964); (b) see, however, Kosower's criticism of extending these data to acetic acid: E. M. Kosower, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 139.

[11] M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966).

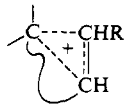
[12] J. A. Berson and M. S. Poonian, *J. Am. Chem. Soc.*, **88**, 170 (1966).

Table I. Rates of Solvolysis of 6-Aryl-5-hexenyl Brosylates and Related Compounds in Ethanol and Acetic Acid[a]

Brosylate	Temp, °C	10^5k, sec^{-1} (ethanol[b])	10^5k, sec^{-1} (acetic acid[c])
n-Hexyl	80	11.9 ± 0.2	0.416 ± 0.005
6-Phenylhexyl[d]	80	11.3 ± 0.3	0.423 ± 0.006[h]
	90	24.0 ± 0.3	1.14 ± 0.01
	100	50.8 ± 1.0	2.85 ± 0.01
6-*p*-Anisylhexyl	80	11.8 ± 0.5	0.421 ± 0.001
trans-6-*p*-Anisyl-5-hexenyl (**4a**)	80	21.9 ± 0.5	3.41 ± 0.01[h]
trans-6-*p*-Tolyl-5-hexenyl (**4b**)	80	13.6 ± 0.5	2.08 ± 0.04
trans-6-Phenyl-5-hexenyl (**4c**)[e]	80	12.0 ± 0.3	1.27 ± 0.01[h]
	90	24.1 ± 0.4	3.20 ± 0.04
	100	48.6 ± 1.7	8.49 ± 0.10
trans-6-*p*-Chlorophenyl-5-hexenyl (**4d**)	80	11.8 ± 0.4	0.805 ± 0.002
trans-6-*p*-Bromophenyl-5-hexenyl (**4e**)	80	12.1 ± 0.3	0.792 ± 0.008
trans-5-Phenyl-4-pentenyl[f]	80	9.58 ± 0.12	0.339 ± 0.003[h]
	90	20.6 ± 0.2	0.916 ± 0.010
	100	39.8 ± 1.3	2.34 ± 0.01
cis-6-Phenyl-5-hexenyl (**5**)[g]	80	11.8 ± 0.1	0.514 ± 0.011
	90	23.6 ± 0.2	1.33 ± 0.02
	100	50.6 ± 0.3	3.53 ± 0.01

[a] The rate constants are averages of two or more separate kinetic experiments. [b] Measured conductometrically. [c] Solutions were initially 0.030 M in sulfonate ester and 0.036 M in sodium acetate. [d] For ethanolysis $\Delta H^* = 19.1$ kcal/mol, $\Delta S^* = -22.8$ eu; for acetolysis $\Delta H^* = 24.5$ kcal/mol, $\Delta S^* = -14.1$ eu. [e] For ethanolysis $\Delta H^* = 17.7$ kcal/mol, $\Delta S^* = -26.6$ eu; for acetolysis $\Delta H^* = 24.3$ kcal/mol, $\Delta S^* = -12.6$ eu. [f] For ethanolysis $\Delta H^* = 18.2$ kcal/mol, $\Delta S^* = -25.6$ eu; for acetolysis $\Delta H^* = 24.8$ kcal/mol, $\Delta S^* = -13.6$ eu. [g] For ethanolysis $\Delta H^* = 18.5$ kcal/mol, $\Delta S^* = -24.4$ eu; for acetolysis $\Delta H^* = 24.8$ kcal/mol, $\Delta S^* = -13.6$ eu. [h] These values are slightly higher than reported previously in ref 13.

react with solvent at this stage in competition with decay to a classical ion (**2**). Since the stereochemistry of **1** would be expected to be relatively unfavorable to olefin formation, reaction at this stage should yield a high fraction of substitution product.



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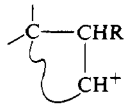

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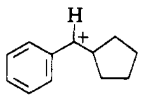
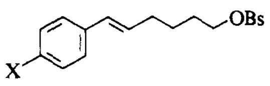
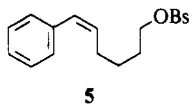


3

All of these explanations depend on a short lifetime for the carbonium ion and all of the examples examined thus far involve secondary aliphatic ions. An obvious question is whether a more stable ion, such as a secondary benzylic cation, would still show significant effects of its route of formation in its solvolysis product composition. Preliminary examination of the *trans*-6-aryl-5-hexenyl system, which yields cyclic acetolysis products characteristic of the cyclopentylphenylcarbinyl cation (**3**),[13] suggested **3** as a suitable ion for examination. It was found feasible to generate **3** by π routes from *trans*-6-phenyl-5-hexenyl (**4a**) and *cis*-6-phenyl-5-hexenyl brosylates (**5**), and by σ routes from *trans*-2-phenylcyclohexyl and cyclopentylphenylcarbinyl tosylates (**6** and **7a**, respectively). In addition, substituent effects on the π-route solvolysis of **4**, of interest with regard to the intermediacy of a bridged species, were examined, as well as the resemblance of the σ-deaminative route from cyclopentylphenylcarbinylamine (**7b**) to the solvolytic pathways. A check on the effect of basicity of the counterion in the direct σ route was made through examination of the products from cyclopentylphenylcarbinyl chloride (**7c**). The solvent system chosen for product studies was glacial acetic acid buffered with a slight excess of sodium acetate. This solvent system facilitates formation of relatively large amounts of cyclic product in the π-route solvolysis yet does not have the tendency to add to double bonds in products or reactants that more acidic solvents, *e.g.*, formic and trifluoroacetic acid, have. Also, examination of the bicyclic products from several routes to the bicyclo-[3.3.0]–[3.2.1]octyl cation system in solvents as diverse as acetic acid and 80% aqueous acetone indicates only small variation in composition on change in solvent.[14] Thus, these results are probably generally indicative of results for hydroxylic solvents.



4a, X = OCH_3
b, X = CH_3
c, X = H
d, X = Cl
e, X = Br



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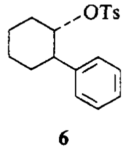

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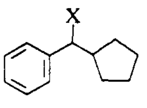

7a, X = OTs
b, X = $NH_3^+Cl^-$
c, X = Cl

The 6-Aryl-5-hexenyl System. In Table I are listed rates of solvolysis of 6-aryl-5-hexenyl brosylates and related compounds in ethanol and acetic acid. In Table II are presented acetolysis products of the 6-aryl-5-hexenyl brosylates. The other acyclic sulfonate esters yielded only unrearranged acetates on acetolysis. While all the observed substitution products were found to be stable to the reaction conditions, 1-benzylcyclopentene and benzal-

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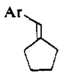
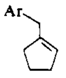
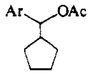
(13) W. D. Closson and S. A. Roman, *Tetrahedron Letters*, 6015 (1966).

(14) G. T. Kwiatkowski, Ph.D. Thesis, Columbia University, 1965.

Table II. Acetolysis Products from 6-Aryl-5-hexenyl Brosylates[a]

Brosylate				Unrearranged acetate
trans-p-Anisyl (**4a**)[b]	(12.5)[c]		77.9	9.6
trans-p-Tolyl (**4b**)	5.1	3.6	74.9	16.4
trans-Phenyl (**4c**)	4.8	3.3	60.4	31.5
trans-p-Chlorophenyl (**4d**)	3.6	2.0	44.5	49.9
trans-p-Bromophenyl (**4e**)	3.4	2.4	43.6	50.6
cis-Phenyl (**5**)	2.4	2.1	18.5	77.0

[a] Conditions for product studies were the same as for the kinetic studies reported in Table I except that all reactions were run at 100°. Product composition was determined by gas chromatographic analysis except where indicated; see Experimental Section for details. [b] Analyzed partly by nmr; see Experimental Section. [c] Total yield of elimination product.

Table III. Calculated Values of k_Δ and k_s for Acetolysis of 6-Aryl-5-hexenyl Brosylates at 80°[a]

Brosylate	$k_\Delta \times 10^5$, sec^{-1}	$k_s \times 10^5$, sec^{-1}	$k_\Delta \times 10^5$, sec^{-1}[b]
trans-p-Anisyl (**4a**)	3.08	0.330	3.01
trans-p-Tolyl (**4b**)	1.74	0.340	1.68
trans-Phenyl (**4c**)	0.870	0.400	0.87
trans-p-Chloro (**4d**)	0.403	0.402	0.41
trans-p-Bromo (**4e**)	0.391	0.401	0.39
cis-Phenyl (**5**)	0.118	0.396	0.12

[a] Estimated as described in text. [b] Estimated from k_{obsd}, assuming k_s is constant at 0.40×10^{-5} sec^{-1}.

cyclopentane (and presumably the related *para*-substituted compounds) were observed to slowly equilibrate on heating in acetic acid. They yielded no detectable acetate fraction, however. Thus, the relative amounts of these olefins probably are not representative of the original product mixture. In addition, a possible substitution product, 1-benzylcyclopentyl acetate, was found to undergo elimination on attempted gas chromatographic analysis. Thus, some of the observed olefinic product may have come from this rearranged substitution product. Analysis of the reaction mixtures by nmr indicated that very little of this material could be present, however.

The rates of ethanolysis of all but three of the brosylates are the same within experimental error. The modest rate accelerations observed for *trans*-6-*p*-anisyl-5-hexenyl (**4a**) and *trans*-6-*p*-tolyl-5-hexenyl (**4b**) brosylates (86 and 15%, respectively) presumably represent a modest amount of anchimeric assistance from their styryl double bonds even in ethanol since these compounds show the most extensive cyclization in acetic acid. The *trans*-5-phenyl-4-pentenyl system undergoes ethanolysis at a rate that is 0.82 that of the saturated systems. Its rate relative to these same saturated brosylates in acetic acid is 0.81. Thus, whatever the rate-retarding effects are in the 5-phenyl-4-pentenyl case, they remain constant between ethanol and acetic acid. The unsubstituted case, 4-pentenyl *p*-nitrobenzenesulfonate has an acetolysis rate relative to *n*-hexyl of 0.72 in unbuffered acetic acid, and 0.70 in buffered acetic acid.[5a] This modest difference could be due to a number of factors; the inductive effect of 4,5-double bonds on solvolysis of primary sulfonate groups is known to vary considerably with structure.[5a,15] The important points in this case are that the effect is small in the 5-phenyl-4-pentenyl system—and therefore certainly smaller still in the 6-aryl-5-hexenyl cases—and constant between ethanol and buffered acetic acid. This consideration, and the fact that **4c**, **4d**, and **4e** all undergo ethanolysis at the same rate as *n*-hexyl or 6-arylhexyl brosylates, argues that the unassisted rates of acetolysis (k_s) of the 6-aryl-5-hexenyl brosylates should be very nearly the same as that of the saturated brosylates (*ca.* 0.42×10^{-5} sec^{-1} at 80°).

The measured rate of acetolysis of the 6-aryl-5-hexenyl brosylates (k_{obsd}) may also be dissected into k_s and the rate of cyclization, k_Δ, by assuming

$$k_{\text{obsd}} = k_\Delta + k_s \tag{3}$$

If we assume the rates of each process to be constant throughout the entire reaction,[16] the ratio k_Δ/k_s should be the ratio of cyclization product to normal solvolysis product. (This also assumes that cyclization is an irreversible process. No evidence to the contrary exists for these and related systems.) Although the product analyses reported in Table II are for reactions carried out at 100°, it is likely that k_Δ/k_s is relatively insensitive to temperature over the range 80–100° since the activation parameters for acetolysis of 6-phenylhexyl brosylate and *trans*-6-phenyl-5-hexenyl brosylate (**4c**) are essentially identical (see Table I). Using the rate data of Table I and product data from Table II one may calculate values of k_Δ and k_s for the 6-aryl-5-hexenyl brosylates. These are given in Table III.

The less reactive compounds all show k_s values of almost exactly 0.40×10^{-5} sec^{-1}. The lower values of k_s for **4a** and **4b** should be suspect since these compounds produce a large fraction of cyclic product and a small error in product analysis would produce a larger error in k_s. Also, it seems rather unreasonable that changing hydrogen to methyl or methoxy at the *para* position should decrease

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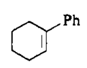
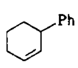
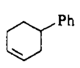
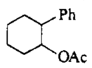
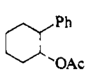
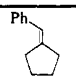
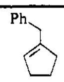
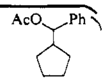
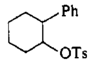
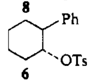
(15) W. D. Closson and G. T. Kwiatkowski, *Tetrahedron*, **21**, 2779 (1965).

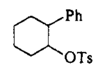
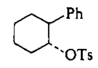
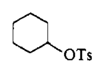
(16) A more elaborate dissection of k_{obsd} into k_Δ and k_s is presented in ref 4 and 5a that takes into account contribution of S$_N$2 reaction with sodium acetate to k_s. The simple expression used above is probably of sufficient accuracy for this data.

Table IV. Products from Acetolysis of *cis*- and *trans*-2-Phenylcyclohexyl Toluenesulfonates at 100°[a]

Reactant	% yield							
								
 **8**	93.5	1.9	1.8	< 1[b]	1.9	< 0.5[b]	< 0.5[b]	< 1[c]
 **6**	15.5	18.3	2.2	16.2	7.0	1.5	1.1	38.2

[a] See Experimental Section for details of measurement. [b] There is no evidence for the presence of these compounds in the product mixture from **8**. [c] A trace of this material could be shown to be present by nmr analysis of the acetate fraction.

Table V. Rates of Solvolysis of *cis*- and *trans*-2-Phenylcyclohexyl and Cyclohexyl Toluenesulfonates

Toluenesulfonate	Solvent	Temp, °C	10^5k, sec^{-1}
	Ethanol	67	4.11 ± 0.10
	Acetic acid[a, b]	80	14.0 ± 0.2
		90	40.8 ± 0.3
		100	117.5 ± 0.8
		67	2.89[c]
	Acetic acid[d]	80	13.8 ± 0.5[d]
	Formic acid[e]	67	436 ± 20
	Ethanol	67	0.083 ± 0.01
	Acetic acid[a, f]	80	0.81 ± 0.01
		90	2.83 ± 0.01
		100	8.94 ± 0.05
		67	0.137[c]
	Formic acid[e]	67	45.5 ± 1.8
	Ethanol	67	1.01[g]
	Acetic acid	67	1.52[g]
	Formic acid	67	808[g]

[a] Buffered with sodium acetate. [b] Activation parameters for acetolysis: $\Delta H^* = 27.4$ kcal/mol, $\Delta S^* = +1.1$ eu. [c] Estimated from data at other temperatures. [d] Unbuffered acetic acid. [e] Unbuffered "97+%" formic acid. [f] Activation parameters for acetolysis: $\Delta H^* = 31.2$ kcal/mol, $\Delta S^* = +6.0$ eu. [g] Estimated from data of S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

k_s while bromine substitution or a change in the styryl double bond to the *cis* configuration has no effect. Values of k_Δ calculated assuming a constant k_s value of 0.40×10^{-5} sec^{-1} are given in the last column of Table III. This value for k_s indicates that a 5,6-styryl double bond has the effect of reducing the unassisted rate of acetolysis by a factor of only 0.95. This is a smaller effect than was estimated for the unsubstituted double bond in 5-hexenyl *p*-nitrobenzenesulfonate (0.87)[5a] but quite in line with the ethanolysis data discussed above.

Using the k_Δ values of the last column of Table III and σ constants yields a value of ρ of -1.73 ± 0.09, with a least-squares correlation coefficient of 0.996. Use of σ^+ constants yields a value of ρ of -0.970 ± 0.172 with a correlation coefficient of 0.956. Even though a quite limited number of points is involved, a better fit is clearly obtained with σ values. This modest value of ρ and the tendency to follow σ rather than σ^+ values is similar to several other systems where an aryl-substituted cation is generated in a concerted process at some distance from the site of the leaving group. Examples would include the 6-arylcholesteryl,[17] 1-aryl-*exo*- and 1-aryl-*endo*-2-norbornyls,[18] and *trans*-2-arylcyclopropyl systems.[19] The implication is that the transition state in cyclization of **4** either has not yet developed much charge at C-6 or closely resembles the π-bridged species (**1**) postulated by Bartlett. The stability of **1** would probably not be very sensitive to substituents on an attached aryl ring.[20] The sevenfold decrease in rate of cyclization of **5** relative to **4** is similar to the fivefold difference in rates of formolysis of *trans*- and *cis*-3-penten-1-yl tosylates observed by Servis and Roberts, and their conclusion that it is due to unfavorable steric interactions in cyclization of the *cis* system[21] also seems reasonable for the phenylhexenyl case.

The 2-Phenylcyclohexyl Route. Examination of this route to **3** was of interest as a check on the possibility of 2-phenylcyclohexyl brosylate being a transient intermediate in the acetolysis of **4c**, as well as for examination of its own product pattern. Previous studies of acid-catalyzed dehydration of the 2-phenylcyclohexanols,[22] as well as nitrous acid deamination of the *trans* amine,[23] indicated

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(17) R. A. Sneen, *J. Am. Chem. Soc.*, **80**, 3977 (1958).

(18) P. von R. Schleyer and D. C. Kleinfelter, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, Abstracts, p 43P.

(19) C. H. dePuy, L. G. Schnack, and J. W. Hausser, *J. Am. Chem. Soc.*, **88**, 3343 (1966).

(20) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(21) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1331 (1965).

(22) H. J. Schaeffer and C. J. Collins, *ibid.*, **78**, 124 (1956); E. L. Eliel, J. W. McCoy, and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957).

(23) D. V. Nightingale and M. Maienthal, *J. Am. Chem. Soc.*, **72**, 4823 (1950).

that one might expect ring-contracted product from the *trans* isomer, although Cristol and Stermitz observed no ring contraction on ethanolysis of the *trans* tosylate (**6**).[24] About 40% ring contraction is observed when **6** is solvolyzed in buffered acetic acid, however. The acetolysis products of **6** and *cis*-2-phenylcyclohexyl tosylate (**8**) are shown in Table IV. Kinetic data for **6**, **8**, and cyclohexyl tosylate are presented in Table V.

The substantial yield of six-ring product from both isomers rules out their possibility of being formed in significant amount during acetolysis of **4c** and **5**. For example, less than 5% of **6** could have been formed by internal return after cyclization of **4c**, and even less of **8**.

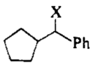
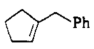
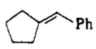
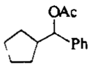
The difference in acetolysis products between **6** and **8** is striking. While about 93% of the products of **8** is 1-phenylcyclohexene, **6** yields sizeable amounts of eight different products. The preponderance of 1-phenylcyclohexene from **8** fits well with the rate enhancement of **8** relative to **6** (49-fold in ethanol, 21-fold in acetic acid, 9.5-fold in formic acid) and strongly implies anchimeric acceleration by a migrating axial benzylic hydrogen. The degree of rate enchancement is very similar to that observed in many *cis*-2-alkylcyclohexyl systems for which a similar explanation appears valid.[25] The possibility of the 1-phenylcyclohexene being derived by an E2 pathway seems doubtful in view of the identical acetolysis rates observed for **8** in the presence and absence of sodium acetate. The sharp decrease in rate enhancement of **8** relative to **6** on changing from ethanol to carboxylic acid solvents can be seen to be primarily a decrease in reactivity of **8** rather than an increase in reactivity of **6** if one compares their reactivities with that of an unsubstituted system such as cyclohexyl tosylate. This suggests the reasonable interpretation that the driving force for converting a secondary cation to a benzylic cation diminishes with increasing solvent polarity. The nonring-contracted product from **6** is also of note. The substitution/elimination ratio (0.66 ± 0.13) is unusually high for a cyclohexyl tosylate. (It is 0.15 for cyclohexyl tosylate[5a] and 0.27 for *trans*-4-*t*-butylcyclohexyl tosylate.[26]) Also, the retention/inversion ratio in unrearranged substitution product (0.44 ± 0.1) is unusually high. (For *trans*-4-*t*-butylcyclohexyl tosylate, a similar equatorial system, it is 0.02.[26]) In both these features it resembles *trans,trans*-1-decalyl tosylate (substitution/elimination = 0.92, retention/inversion = 0.49)[26] and may be caused by a similar phenomenon, *i.e.*, reaction mainly through an equatorial (chair) conformer as suggested by Whiting and coworkers for the 1-decalyl system.[26] In the case of both **6** and **8**, a significant amount of what is tentatively identified as 4-phenylcyclohexene is obtained. If our identification is correct, it must either be formed by 6,1-hydride shift at the 2-phenylcyclohexyl cation stage since none of the other acetolysis products gives rise to it under the reaction conditions, or be due to the presence of traces of 3-phenylcyclohexyl tosylates in **6** and **8**. Considering the almost universal formation of minor amounts of hydride shift product observed in solvolysis of secondary tosylates by Whiting and coworkers,[26] we prefer the former explanation.

Table VI. Rates of Solvolysis of Cyclopentylphenylcarbinyl Tosylate and Chloride

Reactant	Temp, °C	Solvent	10^5k, sec^{-1}
Tosylate	0	Ethanol	18.5 ± 0.2
	20		204 ± 4
	80		$2.7 \times 10^{5\,a}$
	80	Acetic acid	$\sim 2 \times 10^{5\,b}$
Chloride	80		8.90 ± 0.03

[a] Extrapolated from data at other temperatures. (Activation parameters for ethanolysis: $\Delta H^* = 19.2$ kcal/mol, $\Delta S^* = -5.0$ eu.) [b] Assuming roughly similar rates in ethanol and acetic acid.

Table VII. Products of Acetolysis of Cyclopentylphenylcarbinyl Derivatives[a]

	% yield		
			
OTs[b]	0.4	2.2	97.6
Cl[c]	3.0	6.6	90.4
$NH_3^+Cl^-$ [d]	2.6	0.9	96.5[e]

[a] Concentration of reactants was 0.03 *M*. [b] At 25° in presence of 0.035 *M* sodium acetate. [c] At 100° in presence of 0.035 *M* sodium acetate. [d] At 25°. [e] Total substitution product, which was composed of 16.7% alcohol and 79.8% acetate.

As noted in the Experimental Section, a rather complex scheme was necessary for analysis of the acetolysis product mixtures from **6** and **8**. While the results were reproducible, one is rather uncertain about limits of error in the case of certain of the compounds. The value for percent elimination of the benzylic ion, derived from the data in Table IV, is 6.4%. We shall assign limits of error to this number of ±2.0%, which is about three times as large as in the other systems, but admittedly it is the most poorly determined value of the set.

The Cyclopentylphenylcarbinyl Route. The most direct σ pathway to the benzylic cation was investigated through acetolysis of cyclopentylphenylcarbinyl tosylate (**7a**) and chloride (**7c**), and deamination of the amine (**7b**) in dry acetic acid. Some kinetic data for **7a** and **7c** are shown in Table VI; acetolysis products are shown in Table VII.

The great reactivity of **7a** prevented measurement of its rate of acetolysis at higher temperatures (the half-life of **7a** at 80° is probably less than 1 sec) and presented some difficulties in ensuring that conditions for product formation were as close as possible to those (dilute solution in buffered acetic acid, 100°) used for the other solvolytic routes to **3**. It was found, however, that solution of **7a** in the reaction solvent at 25° and violent injection of a concentrated dioxane solution of **7a** into buffered acetic acid at 100° yielded identical product mixtures. While the latter technique may still not have ensured reaction under the required conditions, the lack of change in product composition from 25° suggests that our observed product pattern and that characteristic of reaction at 100° are identical within experimental error.

The large amount of alcohol produced in deamination of **7b** in dry acetic acid is a phenomenon reported in several cases of deamination of cyclohexylamine deriva-

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[24] S. J. Cristol and F. R. Stermitz, *J. Am. Chem. Soc.*, **82**, 4692 (1960).

[25] M. Pankova, J. Sicher, M. Tichy, and M. C. Whiting, *J. Chem. Soc.*, *B*, 365 (1968).

[26] N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *ibid.*, 355 (1968).

tives under similar conditions.[27] The very large total fraction of substitution is similar to the results of Smith, *et al.*, who found only the corresponding alcohol on nitrous acid deamination of **7c** in water.[28]

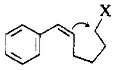
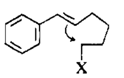
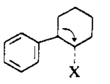
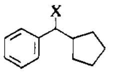
Discussion

In Table VIII are summarized the data on substitution and elimination as a function of the route to **3**. As mentioned by previous workers[22] and as we observed, 1-benzylcyclopentene and benzalcyclopentane are very easily equilibrated and are lumped together under "elimination." This may also include, as mentioned earlier, any 1-benzylcyclopentyl acetate. This unfortunately precludes identification of any hydride-shift product, and the possibility that a large fraction of elimination product has its origin in this manner must be kept in mind.

The variation in elimination/substitution ratio is relatively small compared to what is frequently found with secondary aliphatic carbonium ions. (A range from 0.39 to 50 is observed in the *cis*-*exo*-4-hydrindyl case.[4]) However, there is a clear difference in products from σ and π routes, and even the two π routes yield distinctly different portions of elimination products. Thus, even with a carbonium ion as stable as **3**, there is a clear "memory" of its route of formation.

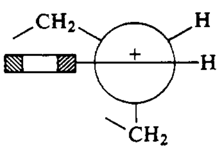
The most striking feature of the data in Table VIII is the complete reversal of the usual pattern. Here it is the π routes that lead to the most elimination. Also, the σ-deamination route exhibits the same elimination/substitution ratio, within experimental error, as does the direct σ route. This is in striking contrast with what is usually found in aliphatic systems.[4,5] A reversal of the effect of the anion in the "classical ion pair" for benzylic ions cannot simply be the answer, either, since replacement of tosylate with chloride leads to a fourfold increase in elimination in the direct σ route. This is similar to Cocivera and Winstein's results for the *t*-butyl cation, where a change in leaving group from dimethyl sulfide to chloride resulted in a sixfold increase in elimination in acetic acid.[7] The effect of a high concentration of perchlorate ion on the product composition from the *trans*-π route was also briefly examined. A concentration of 0.30 *M* lithium perchlorate *increased* the per cent elimination (in the cyclized product) from *trans*-6-*p*-chlorophenyl-5-hexenyl brosylate (**4d**) from 11 to 65%. It was shown that heating the normal product mixture with lithium perchlorate for a similar period of time converted some benzylic acetate to olefin (equivalent to increasing the fraction of elimination from 11 to 23%). The remaining elimination appears to be a true effect on the initial product-forming reactions of **3**. Clearly, the product mixture is not converging on the σ-product mix. It suggests that the increase in elimination from the cyclohexyl cation derived from 5-hexenyl *p*-nitrobenzenesulfonate caused by a high concentration of perchlorate ion[5a] may be due to some effect other than capture of free cations by the abundant anion.

Table VIII. Products of Cyclopentylphenylcarbinyl Cation in Acetic Acid as a Function of Route of Formation

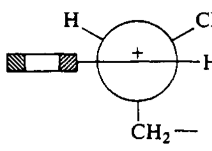
	X	Subst	Elim[a]	Elim/Subst
	OBs	80.5	19.5	0.24 ± 0.03
	OBs	88	12	0.14 ± 0.02[b]
	OTs	94	6	0.06[c]
	OTs	97.5	2.5	0.026 ± 0.004
	Cl	90.5	9.5	0.11 ± 0.01
	NH_2	96.5[d]	3.5	0.036 ± 0.004

[a] Includes both 1-benzylcyclopentene and benzalcyclopentane. [b] The *para*-substituted systems exhibit elimination/substitution ratios of 0.12–0.16. [c] Error probably large in this case. [d] Includes both alcohol and acetate.

While the small substituent effect on the cyclization of **4** can be rationalized in terms of a transition state resembling a π-bridged species such as **1**, such a species would appear to be prone neither to normal elimination[4] nor to the required 1,2-hydride shift that would also eventually give rise to elimination product. The occurrence of π-bridged cations as the immediate precursors of products in the π-route reactions thus seems unlikely. If we assume classical ions are the product precursors in all cases, then initial conformational differences in the cations derived from the *cis*- and *trans*-π routes (**9** and **10**, respectively) could conceivably account for product differences in these two cases. In **9** the phenyl ring is probably twisted relative to the plane of the carbonium ion causing the ion to be of higher energy and possibly less selective in its behavior relative to **10**. There would seem to be no gross difference in conformation between **10** and the cation derived from the direct σ route, however, yet the product mixtures from these two routes are still quite different.



9



10

A more plausible explanation arises from considering the energetics of the π and σ routes. There is probably about a 10-kcal difference in ground-state energy between **4c** and **7a**,[29] and formation of the cyclized cation **3** from **4c** is clearly a less endothermic process than from **7a**, even though the activation energy for formation from **4c** is considerably greater (> 5 kcal/mol). Thus, the transition state for the π route must lie at least 15 kcal higher above the energy of the carbonium ion intermediate than that for the σ route—if the same energy carbonium ion is produced. The π route at least has the *opportunity* of producing a "hot" carbonium ion. The extra energy could be present in the form of vibrational energy or conformational distortion, or in a relative lack of solvation. This

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(27) T. Cohen and E. Jankowski, *J. Am. Chem. Soc.*, **86**, 4217 (1964); E. H. White and F. W. Bachelor, *Tetrahedron Letters*, 77 (1965).

(28) P. A. S. Smith, D. R. Baer, and S. N. Ege, *J. Am. Chem. Soc.*, **76**, 4564 (1954).

(29) A difference close to 10 kcal/mol can be estimated from the heat of polymerization of styrene (−16 kcal/mol)[30] and the torsional strain (*ca.* 6 kcal/mol) introduced into the new five-membered ring.

(30) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, pp 87–88.

Table IX. Physical Properties of *trans*-6-Aryl-5-hexenyl Derivatives

para substituent	Alcohol	Mp, °C *p*-Nitrobenzoate	Mp, °C Brosylate	Calcd,[a] % C	Calcd,[a] % H	Found,[a] % C	Found,[a] % H
CH_3O	Mp 66–68°	—	59–60	53.65	4.98	53.62	5.02
CH_3	Bp 134–136° (0.7 mm) $n^{22}\mathrm{D}$ 1.5495	59–60	72–73.5	55.74	5.17	55.98	5.41
H	Bp 119–121° (1 mm) $n^{22}\mathrm{D}$ 1.5540	68.5–69	13–15	54.91	4.84	54.88	4.78
Cl	Bp 140° (0.6 mm) $n^{26}\mathrm{D}$ 1.5695	51–53	55–56.5	50.31	4.22	50.23	4.21
Br	Mp 40–41.5° Bp 157–160° (3.7 mm)	70.5–73	62–63.5	45.59	3.83	45.82	3.77

[a] Analysis data for brosylate.

should lead to a lowering of the selectivity of the cation in its subsequent reactions, and one might expect to see occasionally rather unusual products from the π route. The unusual transannular internal-return processes observed in solvolyses of the *cis*-4-cyclooctenyl[5c] and *trans*-5-cyclodecenyl systems[31] and the production of considerable amounts of *trans-exo*-bicyclo[4.3.0]non-2-yl acetate from acetolysis of *cis*-2-(2-vinylcyclopentyl)ethyl nitrobenzenesulfonate[5a] can be considered examples of the latter. The frequent resemblance between π-route products and σ-deamination products is then reasonable, but gross differences should also occasionally arise (as in **3**) due to the sensitivity of such high-energy species to minor conformational and solvation factors.

Experimental Section[32]

***trans*-6-Aryl-5-hexen-1-yl *p*-Bromobenzenesulfonates (4).** The general method[33] of synthesis was as follows. About 0.1 mol of the appropriate benzyltriphenylphosphonium bromide (prepared by treatment of triphenylphosphine with an equivalent amount of benzylic bromide in refluxing benzene over a 12-hr period) in 100 ml of warm dimethyl sulfoxide was added to 0.1 mol of dimsyl anion in 50 ml of dimethyl sulfoxide at 0° under nitrogen. After the solution had been stirred at 25° for 10 min, 0.1 mol of 5-hydroxypentanal[34] was added and the resulting solution stirred for 24 hr at 55°. After cooling, the reaction mixture was poured over ice and exhaustively extracted with pentane. The pentane extracts were washed with 1:1 dimethyl sulfoxide–water and saturated brine and then dried with magnesium sulfate. After evaporation of the pentane, the crude alcohol was separated from the triphenylphosphine oxide by vacuum distillation. The crude alcohols were obtained in yields of 50–60% and were converted to *p*-nitrobenzoate esters as follows. To 0.1 mol of crude 6-aryl-5-hexenol in 50 ml of pyridine at 0° was slowly added 0.11 mol of *p*-nitrobenzoyl chloride over a 15-min period. After the reaction mixture had been stirred for 4 hr at 25°, a few drops of water were added cautiously and after a few minutes of continued stirring the mixture was poured into a slurry of ice and hydrochloric acid. The resulting mixture was extracted with ether; the ether solution was washed twice with dilute HCl, and once each with water, dilute sodium bicarbonate solution, and saturated brine, then dried with magnesium sulfate. After removal of solvent the solid material was recrystallized from ether–pentane to constant melting point. In the case of *trans-p*-anisyl-5-hexenol, the crude alcohol itself was purified by recrystallization from ether–pentane. The yield of purified *p*-nitrobenzoate ester varied from 40 to 75%. The purified *trans* esters were saponified by refluxing 0.1 mol of the ester with a fourfold excess of potassium hydroxide in 750 ml of methanol for 1 hr. After removal of methanol under reduced pressure, water was added and the resulting mixture was extracted with ether. The ether extracts were washed with water and saturated brine and dried with magnesium sulfate, and the ether was removed under reduced pressure. The remaining alcohol was either distilled under vacuum or recrystallized from ether–pentane. Yields in this step varied from 75 to 90%. The purified alcohols, all shown to be free of *cis* isomer by gc, were converted to *p*-bromobenzenesulfonates (brosylates) in a manner identical with the preparation of *p*-nitrobenzoates except that the temperature was kept 10 to 25° lower during reaction in pyridine. Yields of brosylates ranged from 65 to 85% after low-temperature recrystallization from ether–pentane. Physical properties, etc., of the *trans* alcohols, *p*-nitrobenzoates, and brosylates are shown in Table IX.

***cis*-6-Phenyl-5-hexen-1-yl *p*-Bromobenzenesulfonate (5).** A solution of 10.0 g (0.046 mol) of 6-phenyl-5-hexynyl acetate[13] in 100 ml of methanol was hydrogenated over 5% palladium–barium sulfate–quinoline according to the procedure of Augustine.[35] Vacuum distillation afforded 8.86 g (88%) of *cis*-6-phenyl-5-hexenyl acetate, bp 111–113° (0.8 mm). This was converted to the alcohol with lithium aluminum hydride in the usual fashion, giving *cis*-6-phenyl-5-hexenol in 91% yield; bp 112–115 (0.9 mm); $n^{24}\mathrm{D}$ 1.5380; nmr 1.5 (multiplet, 4 H), 2.3 (multiplet, 2 H), 3.47 (triplet, 2 H), 4.02 (singlet, 1 H), 5.57 (doublet of triplets, J = 12 cps, 1 H), 6.35 (doublet of triplets, J = 12 cps, 1 H), and 7.17 ppm (singlet, 5 H). This was converted to the brosylate in the manner described previously, yielding material that after low-temperature recrystallization from ether–pentane was still an oil at room temperature (81%).

Anal. Calcd for $C_{18}H_{19}BrSO_3$: C, 54.91; H, 4.84. Found: C, 54.83; H, 4.91.

6-Phenyl-1-hexyl *p*-Bromobenzenesulfonate. Catalytic hydrogenation of *trans*-6-phenyl-5-hexenol (10% palladium on charcoal in ethyl acetate solution) yielded 6-phenylhexanol in 86% yield, bp 138–140° (3 mm) [lit.[36] bp 140–141° (3 mm)], $n^{24}\mathrm{D}$ 1.5069. This was converted to the brosylate in the usual way, yielding 72% of an oil that had an acetolysis equivalent of 397 (calcd for $C_{18}H_{21}BrSO_3$: 397).

6-*p*-Anisyl-1-hexyl *p*-Bromobenzenesulfonate. Catalytic hydrogenation of *trans*-6-anisyl-5-hexenol in a manner similar to that described above yielded 88% of 6-*p*-anisyl-1-hexanol, bp 150–152° (0.75 mm), $n^{24}\mathrm{D}$ 1.5127. This was converted to brosylate in the usual way, yielding 68% of an oil (after low-temperature recrystallization) that had an acetolysis equivalent of 425 (calcd for $C_{19}H_{22}BrSO_4$: 427).

***n*-Hexyl *p*-bromobenzenesulfonate** was prepared from 1-hexanol in the usual way, yielding, after low-temperature recrystallization, 80% of an oil that had an acetolysis equivalent of 318 (calcd for $C_{12}H_{17}BrSO_3$: 321).

***trans*-5-Phenyl-4-penten-1-yl *p*-Bromobenzenesulfonate.** A solution of 11.7 g (0.052 mol) of *trans*-5-phenyl-4-pentenyl bromide[37] and 9.27 g (0.11 mol) of sodium acetate in 10 ml of acetic anhydride

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[31] H. L. Goering and W. D. Closson, *J. Am. Chem. Soc.*, **83**, 3511 (1961).

[32] Melting and boiling points are uncorrected. Nuclear magnetic resonance spectra (nmr) were measured at 60 MHz in CCl_4, relative to tetramethylsilane internal standard. Gas chromatographic (gc) analyses were performed on a Varian A-90 instrument (thermal conductivity detection) fitted with a mechanial ("Disc") integrator.

[33] R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

[34] G. F. Woods, Jr., "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 470.

[35] R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N. Y., 1965, p 69.

[36] J. B. Conant and W. R. Kirner, *J. Am. Chem. Soc.*, **46**, 243 (1924).

[37] R. Paul, *Compt. Rend.*, **198**, 1246 (1934); *Bull. Soc. Chim. France*, [5] **2**, 311 (1935).

was refluxed for 2 days. The solution was cooled, diluted with water, and extracted with ether. The ether solution was washed with water, dilute sodium bicarbonate solution, and saturated brine, then dried with magnesium sulfate. After removal of the ether, the residue was distilled, yielding 8.22 g (77.5%) of *trans*-5-phenyl-4-pentenyl acetate, bp 143–147° (5 mm). This was converted to the alcohol by reduction with lithium aluminum hydride in the usual way, giving an 83% yield of product, bp 108–110° (1 mm). The brosylate was then prepared in the usual way in 64% yield, mp 66–67.5°.

Anal. Calcd for $C_{17}H_{17}BrSO_3$: C, 53.53; H, 4.49. Found: C, 53.64; H, 4.31.

Cyclopentylphenylcarbinyl acetate was prepared from the corresponding alcohol[22a,23] by treatment of 0.176 g (1 mmol) with 0.5 ml of acetic anhydride in 5 ml of pyridine. After stirring at 25° for 24 hr the solution was poured into a slurry of ice and hydrochloric acid and the acetate product was recovered by extraction with ether. After suitable washing and drying, the ether was evaporated yielding 0.206 g (94%) of crude acetate. This was used without further purification: ir (liquid film), 3.37, 5.81, 6.70, 6.90, 7.33, 8.10, 9.80, 10.38, 11.09, 13.17, and 14.31 μ; nmr *ca.* 1.6 (multiplet, 8 H), 1.91 (singlet, 3 H), *ca.* 2.3 (multiplet, 1 H), 5.49 (doublet, $J = 9$ cps, 1 H), and 7.20 ppm (singlet, 5 H).

Cyclopentylphenylcarbinyl *p*-toluenesulfonate (7a) was prepared from the alcohol in a manner similar to Streitwieser's synthesis of benzyl *p*-nitrobenzenesulfonate.[38] From 2.64 g (0.015 mol) of alcohol was obtained 2.58 g (50%) of the sulfonate ester, mp 52–54°. Its identity was confirmed both by nmr and sodium naphthalenide cleavage back to the starting alcohol;[39] nmr 1.7 (multiplet, 9 H), 2.30 (singlet, 3 H), 5.15 (doublet, $J = 8$ cps, 1 H), and 7.0–7.6 ppm (quartet and singlet, 9 H).

Cyclopentylphenylcarbinyl chloride (7c) was prepared by allowing a mixture of 4.76 g (0.027 mol) of the alcohol and 13.09 g (0.108 mol) of thionyl chloride to stand at 25° for 24 hr. After removal of the excess thionyl chloride under reduced pressure, the residue was distilled, yielding 4.18 g (79%) of colorless product: bp 115–119° (3 mm); nmr 1.5 (multiplet, 8 H), 2.5 (multiplet, 1 H), 4.55 doublet, $J = 9$ cps, 1 H), and 7.06 ppm (singlet, 5 H).

Cyclopentylphenylcarbinylamine (7b) was prepared from phenyl cyclopentyl ketone in the manner of Smith, *et al.*,[28] bp 135–137° (10 mm); n^{22}D 1.5453 (lit. bp 146° (21 mm),[28] 156° (35 mm),[40] n^{25}D 1.5455[28]). This was converted to the hydrochloride by passing dry hydrogen chloride through an ether solution of the amine and collecting the resulting white precipitate, mp 298° (lit.[28] mp 280°).

Benzalcyclopentane and 1-Benzylcyclopentene. To a stirred mixture of cyclopentylphenylcarbinol (1.76 g, 0.01 mol) in 50 ml of pyridine at 0° was added dropwise 0.765 g (0.005 mol) of phosphorus oxychloride in 25 ml of pyridine. After the solution had been stirred at 0° for 30 min, it was refluxed for 2 hr. After cooling, the mixture was poured into a slurry of ice and hydrochloric acid and extracted with ether. After the ether extract was suitably washed and dried the solvent was removed, leaving 0.84 g (52%) of crude olefin. This was shown, by gas chromatography on a 5-ft SF-96 column at 170°, to consist of two components in 36:64 ratio. Collection of the first component yielded 1-benzylcyclopentene: ir (liquid film), 3.29, 3.40, 6.23, 6.71, 6.91, 9.33, 9.66, 9.73, 10.38 μ (lit.[22b] ir: 9.32, 9.70, and 10.4 μ); nmr *ca.* 1.6 (multiplet, 2 H), *ca.* 2.2 (multiplet, 4 H), 3.14 (doublet, $J = 3$ cps, 2 H), 5.19 (multiplet, 1 H), and 7.04 ppm (singlet, 5 H). Collection of the second component yielded benzalcyclopentane: n^{21}D 1.5742 (lit.[22b] n^{20}D 1.5742); ir (CS_2), 3.41, 6.22, 6.74, 9.82, 11.00, and 11.65 μ (lit.[22b] ir: 9.84, 10.99, and 11.61 μ); nmr *ca.* 1.6 (multiplet, 4 H), 2.4 (multiplet, 4 H), 6.17 (multiplet, 1 H), and 7.02 ppm (singlet, 5 H).

***trans*-2-Phenylcyclohexyl *p*-toluenesulfonate (6)** was prepared from a commercial mixture (Aldrich Chemical Co.) of *cis*- and *trans*-2-phenylcyclohexanol according to the method of Cristol and Stermitz.[24] From 200 g (0.57 mol) of the alcohol mixture was obtained 40 g of *trans*-tosylate which after recrystallization from ethanol had mp 131–132° (lit.[24] mp 130–131°).

***cis*-2-Phenylcyclohexanol** was obtained from the commercial mixture of alcohols by selective acetylation of the equatorial *trans* alcohol.[41] A solution of 11.5 g (0.113 mol) of acetic anhydride and 9.0 g of pyridine in 100 ml of benzene was added to 35.3 g (0.20 mol) of the alcohol mixture (known by gas chromatographic analysis to be 43% *cis*, 57% trans). The mixture was stirred at 25° for 48 hr, washed with water, and dried with magnesium sulfate. Evaporation of the benzene under reduced pressure yielded 33 g of material which was chromatographed on 1 kg of alumina. Elution with pentane gave 22.6 g of crude *trans*-2-phenylcyclohexyl acetate; elution with ether yielded 7.6 g of *cis*-2-phenylcyclohexanol, which, after recrystallization from pentane had mp 44–46° (lit.[42] mp 42–43°).

***cis*-2-Phenylcyclohexyl *p*-Toluenesulfonate (8).** A pyridine (25 ml) solution of 5.67 g (0.032 mol) of *cis*-2-phenylcyclohexanol and 6.70 g (0.035 mol) of *p*-toluenesulfonyl chloride was stirred at 25° for 48 hr. Isolation in the usual manner and recrystallization from ethanol yielded 7.10 g (67%) of the *cis* tosylate, mp 103.5–104° (lit.[24] mp 102–103°).

2-Phenylcyclohexyl acetates were obtained by acetylating the commercial mixture of *cis* and *trans* alcohols with acetic anhydride in pyridine solution in the usual way, and collecting pure samples by preparative gas chromatography on a 5-ft SE-30 column at 150°. The earlier peak was identified as *cis*-2-phenylcyclohexyl acetate on the basis of its nmr spectrum and lithium aluminum hydride reduction to *cis*-2-phenylcyclohexanol: nmr 1.7 (multiplet, 8 H), 1.79 (singlet, 3 H), 2.7 (multiplet, 1 H), 5.10 (narrow multiplet, 1 H), and 7.10 ppm (singlet, 5 H). The later peak was identified similarly as *trans*-2-phenylcyclohexyl acetate: nmr 1.6 (multiplet, 8 H), 1.62 (singlet, 3 H), 2.6 (multiplet, 1 H), 4.91 (broad AB_2 sextet, 1 H), and 7.11 ppm (singlet, 5 H). The alcohol, obtained from the acetate by lithium aluminum hydride reduction was identified as *trans*-2-phenylcyclohexanol on the basis of its mp 58–58.5° (lit. mp 56–57°,[22b] 56–57.5°[42]) and comparison with a sample obtained by sodium naphthalenide cleavage[39] of the pure *trans*-tosylate.

1- and 3-Phenylcyclohexenes. To a stirred solution of 1.76 g (0.01 mol) of the commercial mixture of 2-phenylcyclohexanols in 50 ml of pyridine at 0° was added dropwise 0.765 g (5 mmol) of phosphorus oxychloride in 25 ml of pyridine over a period of 30 min. The mixture was stirred at 0° for 30 min and refluxed for 2 hr. After cooling, the mixture was poured into a mixture of ice and hydrochloric acid and extracted with ether. After suitable washing and drying with magnesium sulfate, the ether was removed under vacuum and the residue distilled, affording 0.71 g (45%) of product, bp 65–75° (1 mm). Gas chromatographic analysis (6-ft SF-96 column at 175°) revealed only two major peaks. The first peak (*ca.* 24%) was collected and identified as 3-phenylcyclohexene on the basis of ir and nmr spectra: ir (CS_2), 11.35, 12.67, 13.80, and 14.87 μ (lit.[22b] ir: 11.37, 12.70, 13.86, and 14.88 μ); nmr 1.7 (multiplet, 4 H), 2.0 (multiplet, 2 H), 3.25 (multiplet, 1 H), 5.61 (multiplet, 2 H), and 6.98 ppm (singlet, 5 H). The second peak (*ca.* 76%) was collected and identified as 1-phenylcyclohexene: ir (CS_2), 9.47, 10.85, 12.44, and 13.47 μ (lit.[22b] ir: 9.44, 10.86, 12.44, and 13.48 μ); nmr 1.7 (multiplet, 4 H), 2.2 (multiplet, 4 H), 5.89 (multiplet, 1 H), 7.05 ppm (multiplet, 5 H).

Benzylcyclopentane was prepared by catalytic hydrogenation (platinum in ethyl acetate) of a small sample of a mixture of 1-benzylcyclopentene and benzalcyclopentane, bp 62–67° (1 mm) [lit. bp 70–72° (5 mm),[23] 103–104° (12.5 mm)[22b]], n^{25}D 1.5130 (lit.[23] n^{20}D 1.5255).

1-Benzylcyclopentanol was prepared from benzylmagnesium chloride and cyclopentanone in the usual way in *ca.* 50% yield, mp 58–60° (lit. mp 59.5–61°,[22b] 58–60°[22a]).

Acetates of other alcohols were prepared on a small scale by treatment of the corresponding pure alcohol with acetic anhydride in pyridine and isolation in the usual way. These were usually used for identification purposes without further purification. In all cases ir and nmr spectra agreed with the assumed structure.

Acetolysis Product Analyses. Acetolyses were conducted by heating a 0.03 *M* solution of sulfonate ester in 0.036 *M* sodium acetate in acetic acid in a sealed flask for at least ten solvolytic half-lines at 100°. The reaction mixture was cooled, diluted with an equal volume of water, and exhaustively extracted with pentane. The pentane solution was washed with water, dilute sodium carbonate solution, and saturated brine, then dried with magnesium sulfate. The pentane was then carefully removed under slightly reduced pressure. Recovery of solvolysis product was usually better than 90% and the loss was assumed to be nonselective since

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(39) W. D. Closson, P. Wriede, and S. Bank, *ibid.*, **88**, 1581 (1966).

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(42) F. R. Alexander and A. Mudrak, *J. Am. Chem. Soc.*, **72**, 1810 (1950).

trial runs with known mixtures resulted in about the same fraction of recovery, but no fractionation. The product mixtures were analyzed by gc using one or more of the following 5 ft × 0.25 in. columns: 20% SF-96, 20% SE-30, 20% Carbowax 20M. Each reaction mixture was analyzed at a single attenuator setting. In the cases of the unsubstituted systems (**4c**, **5**, **7a**), known mixtures of the solvolysis products were used to calibrate the gc data. In these cases the olefins were the most minor components, but due to their short retention times, they appeared as relatively narrow, well-separated peaks. For these small peaks, the reproducibility in measurement of their areas was at least ±10%. For peaks that constituted more than 10% of the total reaction mixture, reproducibility in measurement of their areas (either by mechanical integration, or cutting and weighing) was about ±2%. Since one can simply look at the ratio of the same olefins to the same tertiary acetate or alcohol in all three cases, differences in the substitution/elimination ratio in these systems are quite real. It was found that a typical 12-carbon olefin (1-benzylcyclopentene) had a molar response factor of 1.1 as compared to either cyclopentylphenylcarbinyl acetate or *trans*-6-phenyl-5-hexenyl acetate. This same ratio was used without further testing for the *para*-substituted systems. Product percentages are the average of two or more analyses. Whenever possible, samples of each product were collected and their spectral properties compared with those of authentic or analogous samples. In the case of some of the *para*-substituted systems, some of the products produced in low yield (such as the olefins), of which a reasonably sized sample could not be collected, were identified on the basis of gas chromatographic retention time and analogy with other systems. The analysis of the acetolysis mixture from *trans*-6-phenyl-5-hexenyl brosylate (**4c**) is presented as a typical case. From 1.97 g (0.0050 mol) of **4c** in 167 ml of 0.036 *M* sodium acetate in acetic acid was obtained 0.963 g of product that was found to consist of 3.3% benzylcyclopentene, 4.8% benzalcyclopentane, 60.4% cyclopentylphenylcarbinyl acetate, and 31.5% *trans*-6-phenyl-5-hexenyl acetate. No product having a phenylcyclohexyl skeletal structure was detected. Reduction of the reaction mixture with lithium aluminum hydride and analysis of the resulting olefin–alcohol mixture reconfirmed the identification of the acetate products.

Acetolysis Products from *trans-p*-Anisyl-5-hexenyl *p*-Bromobenzenesulfonate (4a). From 0.640 g (1.5 mmol) of **4a** in 50 ml of 0.036 *M* sodium acetate in acetic acid was obtained 0.341 g (94%) of product which by gc analysis was found to consist of two olefins amounting to *ca.* 90% of the mixture and one acetate (*ca.* 10%), identified as *trans*-6-*p*-anisyl-5-hexenyl acetate. The nmr spectrum of the product mixture, however, showed both an inordinately intense acetate methyl peak, and a doublet at 5.4 ppm ($J = 9$ cps), characteristic of the benzylic proton in cyclopentylarylcarbinyl acetates, indicating that the benzylic acetate was eliminating to olefin on gc analysis. By comparing the integrated value of the 5.4-ppm doublet with the value for the methoxyl methyl, the percentage of benzylic acetate was estimated. Knowing this and the fraction of unrearranged acetate (whose structure was confirmed by lithium aluminum hydride reduction to alcohol and comparison with an authentic sample) the total percentage of olefin could be calculated. The average of two separate experiments gave 12.5% of a mixture of 1-*p*-methoxybenzylcyclopentene and *p*-methoxybenzalcyclopentane, 77.9% cyclopentyl-*p*-anisylcarbinyl acetate, and 9.6% *trans*-6-*p*-anisyl-5-hexenyl acetate as the composition of the product mixture.

Acetolysis Products from *trans*-2-Phenylcyclohexyl *p*-Toluenesulfonate (6). From 9.90 g (0.030 mol) of **6** in 1 l. of 0.036 *M* sodium acetate in acetic acid was obtained 5.87 g (85%) of product. Gas chromatographic analysis on an SE-30 column at 170° showed four hydrocarbon peaks accounting for the rest. The first hydrocarbon peak (1.1%) was identified as 1-benzylcyclopentene; the second hydrocarbon peak (18.3%) was collected and identified as 3-phenylcyclohexene. The third peak (2.2%) had a retention time different from that of any expected product and was tentatively identified as 4-phenylcyclohexene. The fourth peak (17.0%) was a mixture of benzalcyclopentane and 1-phenylcyclohexene. A sample of this peak was hydrogenated over platinum in ethyl acetate and analyzed on a Carbowax 20M column at 175° and found to be 6.6% benzylcyclopentane and 93.4% phenylcyclohexane, identified by comparison with authentic samples. The first acetate peak (54.4%) was a mixture of cyclopentylphenylcarbinyl acetate and *cis*-2-phenylcyclohexyl acetate. Analysis of a sample of this mixture by nmr, utilizing the different positions of the benzylic protons, indicated that it was 70.5% benzylic acetate and 29.5% *cis*-2-phenylcyclohexyl acetate. The last peak (7.0%) was identified as *trans*-2-phenylcyclohexyl acetate. A similar procedure was used for the analysis of the acetolysis products from *cis*-2-phenylcyclohexyl tosylate (**8**).

Stabilities of acetolysis products to acetolysis conditions were tested by heating solutions of the compounds in question in buffered acetic acid at 100° for a period corresponding to ten half-lines for acetolysis of the slowest reacting precursor (*cis*-6-phenyl-5-hexenyl brosylate), and then isolation and analysis as described above. Though small samples were used, recovery of material was in the range of 89 to 96%. The following compounds were recovered unchanged with no detectable amount (no more than 0.5%) of other products present: cyclopentylphenylcarbinyl acetate, *cis*- and *trans*-6-phenyl-5-hexenyl acetates, *cis*- and *trans*-2-phenylcyclohexyl acetates, and 1- and 3-phenylcyclohexenes. A mixture of 41% 1-benzylcyclopentene and 59% benzalcyclopentane had changed to a 30–70% mixture, however. 1-Benzylcyclopentanol and the corresponding acetate were both found to undergo elimination on attempted gc analysis.

Kinetic Experiments. Acetolyses were performed using the ampoule technique. Titrations were performed by adding a measured amount of 0.050 *M* perchloric acid in acetic acid to the sample and back-titrating with standard sodium acetate in acetic acid, using bromophenol blue indicator. The reported rate constants are the average of two or more duplicate kinetic experiments. Ethanolyses and formolyses were performed conductometrically. About 20 mg of sulfonate ester in 10 ml of absolute ethanol was placed in a conductance cell in a thermostated bath. After allowing 10 to 15 min for thermal equilibration, readings of conductance on an Industrial Instruments, Inc., conductivity bridge (Model RC 1632) were taken during at least the first three half-lines of reaction. Infinity readings were made after a period of ten half-lines. A linear relationship between conductivity and concentration of sulfonic acid was assumed, and instantaneous rate constants were calculated from the expression

$$k = \frac{2.303}{t} \log \frac{\Omega_\infty - \Omega_0}{(\Omega_\infty - \Omega_0) - \Omega_t}$$