Inductive Enhancement of Aryl Participation

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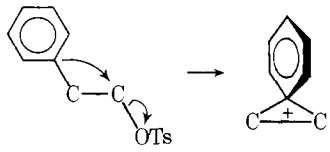
Abstract: Enhanced participation by an aryl group in solvolysis can be achieved by placing an electron-withdrawing substituent vicinal to the leaving group. We have examined the acetolysis of *meso*-1,4-diaryl-2,3-butyl ditosylates (**3**) and of 1,4-diaryl-2-butyl tosylates (**4**), in which the aryl groups are substituted with *p*-OCH_3, *p*-CH_3, H, *p*-Cl, *m*-CF_3, and *p*-NO_2. The second tosylate group provides the inductive stimulus for increased aryl participation. Comparison of the monotosylate with the ditosylate shows that the proportion of aryl participation increases from 93 to 99% for *p*-OCH_3, from 66 to 99% for *p*-CH_3, from 35 to 94% for H, and from 0 to 68% for *p*-Cl. Thus an electron-withdrawing substituent vicinal to the leaving group makes the aryl participation pathway essentially exclusive for aryl groups with substituents with $\sigma \geq 0$. Even for a substituent with a small, negative σ value, such as *p*-Cl, participation can be quite significant in the ditosylate series, while completely lacking in the monotosylate series.

The phenomenon of aryl participation has been reasonably well understood since the rapprochement of Brown and Schleyer through parallel studies of β-arylalkyl benzenesulfonates (eq 1).[2] By a number of different methods, these au-



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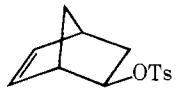
thors demonstrated the presence of two independent solvolytic pathways: solvent assistance and aryl assistance. The two pathways do not detectably cross over. Any observable rate enhancement (anchimeric assistance) must be the result of very strong aryl participation, in order to compete favorably with the strong solvent participation. The typically small rate enhancements therefore can reflect a high degree of aryl participation. By resolving the titrimetric rate constant (k_t) into solvent-assisted (k_s) and aryl-assisted (Fk_Δ, where F refers to the fraction of bridged arylonium ion that goes on to products) pathways, the authors could calculate the fraction of substrate solvolyzing by aryl participation (Fk_Δ/k_t) and the rate enhancement due to aryl participation (k_t/k_s).[2]

The current study was designed to determine whether aryl participation can be enhanced by the placement of an electron-withdrawing substituent vicinal to the leaving benzenesulfonate. Such "inductive enhancement of participation" has been observed previously for double bond assistance in the norbornenyl system.[3] Whereas *exo*-2-norborn-5-enyl tosylate (**1**) acetolyzes only 3.4 times more slowly than its saturated analogue, *cis,exo*-2,3-norborn-5-enyl ditosylate (**2**) acetolyzes



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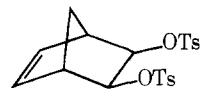

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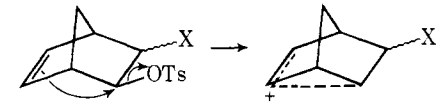
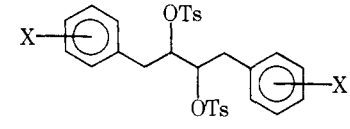
500 times more rapidly than its saturated analogue, for an overall enhancement of about 1700. A trans tosyloxy group or a cis acetoxy group has the same effect as the cis tosyloxy group in **2**. This considerable kinetic enhancement was attributed to the inductive effect of the substituent vicinal to the leaving group.[3] Departure of the tosylate group would place positive charge on the carbon atom adjacent to the remaining electron-withdrawing group. Homoallylic delocalization (eq 2) reduces this inductive destabilization. Thus the double bond in the vicinally substituted system **2** responds to the greater need for charge delocalization, with the result that homoallylic participation is much greater in **2** than in **1**.



(2)

Inductive enhancement of participation is complementary to the Gassman–Fentiman approach,[4] by which participation is reduced through increased stabilization of the localized carbonium ion. Inductive enhancement, by contrast, increases the amount of participation by making the localized carbonium ion less stable.

We wished to find out if inductive enhancement of participation is a more general phenomenon that can be applied to other forms of participation than double bond. Aryl participation, like double bond participation in **1**, is kinetically very weak. In order to study the possibility of inductively enhanced aryl participation, we needed to construct a system with the leaving group flanked by an aryl group on one side and an electron-withdrawing group on the other. For our study we selected the symmetrical system *meso*-1,4-diaryl-2,3-butyl ditosylate (**3**) as the candidate for enhanced aryl participation, and 1,4-diaryl-2-butyl tosylate (**4**) as the control for the ab-



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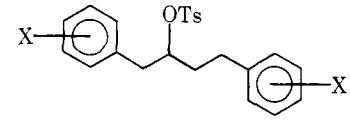
	X
a	*p*-OCH_3
b	*p*-CH_3
c	H
d	*p*-Cl
e	*m*-CF_3
f	*p*-NO_2



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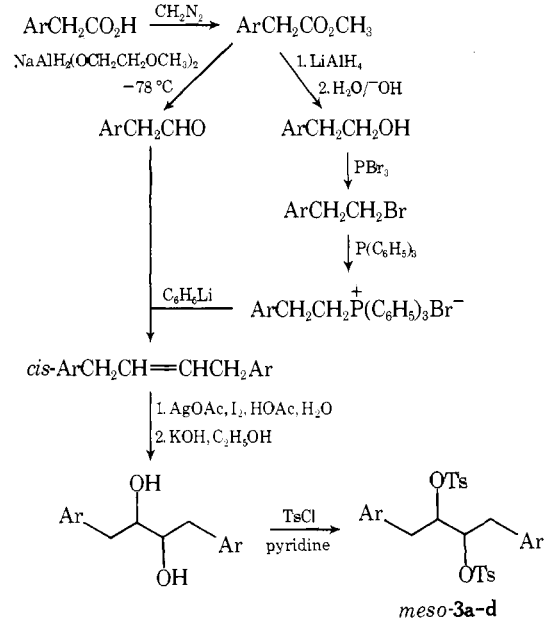
sence of enhanced participation. As in 1-aryl-2-propyl tosylates,[2] hydride shift and aryl migration are not favored pathways. Furthermore, the symmetry of **3** permits more facile syntheses. We report herein a study of inductive enhancement of aryl participation by a kinetic comparison of the ditosylates **3** with the monotosylates **4**.

Results

Most of the compounds in the ditosylate series (**3a–d**) were prepared by the method shown in Scheme I. Commercially available arylacetic acids were converted to the methyl arylacetates by diazomethane. The methyl esters were reduced on the one hand with the Vit reagent[5] to the aldehyde and on the other hand with $LiAlH_4$ to the alcohol. The 2-arylethanols were treated with PBr_3 in a manner analogous to that described

Scheme I



by Noller and Dinsmore[6] to produce the (2-bromoethyl)arenes. Conversion of the bromides to the phosphonium salts[7] and treatment with phenyllithium gave a series of Wittig reagents that were allowed to react with the previously made, analogous aldehydes. The almost exclusive product of this reaction was the *cis*-1,4-diaryl-2-butenes. The wet Prèvost hydroxylation[8] converted the cis alkenes into the meso diols, which upon treatment with tosyl chloride gave the *meso*-1,4-diaryl-2,3-butyl ditosylates (**3a-d**).

Because *m*-trifluoromethylphenylacetic acid was not available, the method of Scheme I was modified. The commercially available α'-chloro-α,α,α-trifluoro-*m*-xylene was converted to the nitrile, which was hydrolyzed to the arylacetic acid. The remainder of the sequence followed Scheme I, except that the Vit method for preparation of the aldehyde was replaced by the oxidative procedure of Collins and Hess.[9]

The nitro compound (**3f**) could not be prepared by the general procedure of Scheme I because of the sensitivity of the nitro functionality to reduction. The unsubstituted diol (Scheme I) therefore was converted to the diacetate, which was doubly nitrated according to the procedure of Ketcham et al.[10] The nitrated diacetate was then hydrolyzed to the diol, which was converted to the ditosylate (**3f**) by tosyl chloride.

The monotosylates **4a-e** were prepared by oxidative hydroboration of the alkenes to give the 1,4-diaryl-2-butanols, which were treated with tosyl chloride. For the unsubstituted nitro compound (**4f**), the alcohol was converted to the acetate, which was nitrated, hydrolyzed, and tosylated.

Acetolyses were carried out in acetic acid containing 1% acetic anhydride and a 10% equivalent excess of potassium acetate. Kinetics were measured by titrating the unreacted potassium acetate with perchloric acid. All acetolyses followed first-order kinetics. Rate constants were calculated by the infinity titer method (eq 3),

$$\ln (y - y_\infty) = -kt + \ln (y_0 - y_\infty) \quad (3)$$

in which y is the volume of perchloric acid required for titration and y_∞ is the infinity titer, at which 2 equiv of acid had been liberated. Rates were normally measured over 50-70% of the reaction. Each compound was solvolyzed at three or more temperatures. The rate constants are given in Table I for the ditosylates and in Table II for the monotosylates. The Arrhenius activation parameters (Table III) were used for calculation of the rate constants at 100 and 150 °C given in Tables I and II. The acetolysis rate of *erythro*-1,4-diphenyl-3-acetoxy-2-butyl tosylate was measured to be 1.31×10^{-3} s^{-1} at 100 °C.

Table I. Rates of Buffered Acetolysis of *meso*-1,4-Diaryl-2,3-butyl Ditosylates (**3**)

Compd	Temp, °C	k, s^{-1}	Corr coeff
3a	100.0	$(1.35 \times 10^{-5})^a$	
(p-OCH_3)	130.0	2.11×10^{-4}	0.999
	140.0	4.61×10^{-4}	0.999
	150.0	1.12×10^{-3}	0.999
	150.0	$(1.07 \times 10^{-3})^a$	
3b	100.0	$(6.47 \times 10^{-6})^a$	
(p-CH_3)	130.0	1.19×10^{-4}	0.997
	140.0	2.76×10^{-4}	1.000
	150.0	6.53×10^{-4}	0.999
	150.0	$(6.43 \times 10^{-4})^a$	
3c	100.0	$(1.09 \times 10^{-6})^a$	
(H)	138.9	4.38×10^{-5}	1.000
	150.0	$(1.09 \times 10^{-4})^a$	
	150.8	1.17×10^{-4}	0.999
	162.4	2.97×10^{-4}	0.999
3d	100.0	$(1.84 \times 10^{-7})^a$	
(p-Cl)	149.9	3.11×10^{-5}	0.999
	150.0	$(3.20 \times 10^{-5})^a$	
	159.8	8.15×10^{-5}	1.000
	170.0	1.78×10^{-4}	0.999
3e	100.0	$(5.14 \times 10^{-8})^a$	
(m-CF_3)	150.0	$(9.21 \times 10^{-5})^a$	
	165.0	3.54×10^{-5}	1.000
	174.8	7.77×10^{-5}	0.999
	185.0	1.81×10^{-4}	0.999
3f	100.0	$(4.40 \times 10^{-8})^a$	
(p-NO_2)	150.0	$(7.31 \times 10^{-6})^a$	
	165.0	2.78×10^{-5}	0.999
	175.2	6.14×10^{-5}	0.999
	185.2	1.41×10^{-4}	0.999

[a] Calculated from the Arrhenius parameters.

Discussion

The work of Schleyer and Brown[2] demonstrated that β-arylalkyl benzenesulfonates solvolyze by two independent pathways, solvent assistance (k_s) and aryl assistance (k_Δ), whose rates sum to the overall observed rate (k_t) (eq 4).

$$k_t = k_s + Fk_\Delta \quad (4)$$

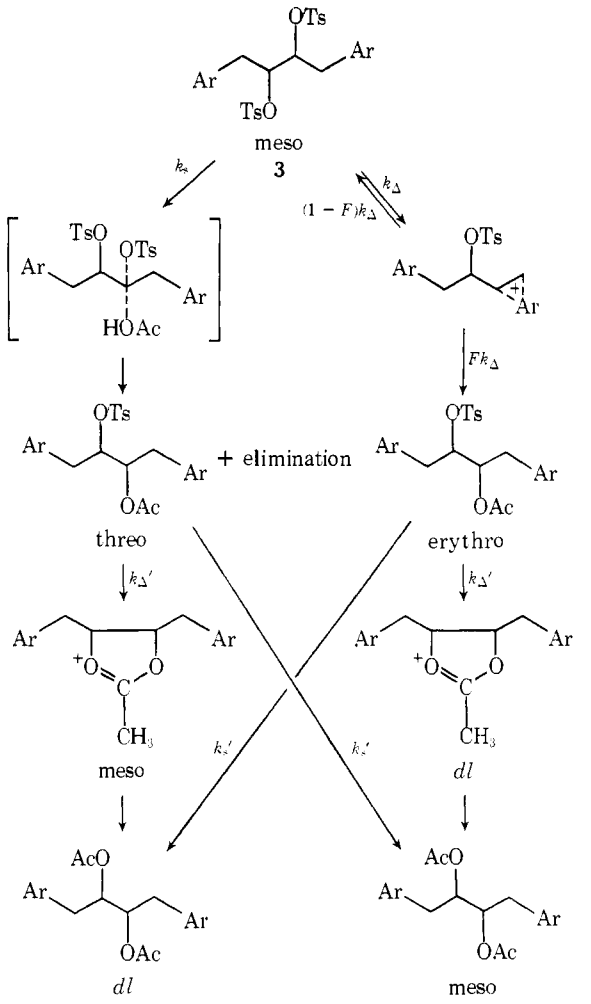
A mechanistic scheme based on these findings is illustrated in Scheme II for the acetolysis of the ditosylate series **3**. The meso substrate would give threo acetoxy tosylate by solvent assistance (k_s) and erythro acetoxy tosylate by aryl assistance (k_Δ). These threo and erythro acetoxy tosylates would collapse via acetoxyl participation (k_Δ') to give meso and *dl* acetoxonium ions, respectively, which on reaction with the second molecule of acetic acid would give the observed diacetate products (*dl* from threo, meso from erythro). The acetoxy tosylates could alternatively react directly with the second molecule of acetic acid via a second solvent participation step (k_s') to give the diacetate (meso from threo, *dl* from erythro). The acetoxy tosylates could also react via a second aryl participation step (k_Δ'', not shown in Scheme II). The fact that the erythro acetoxy tosylate acetolyzes 1000 times more rapidly than the meso ditosylate (**3c**) indicates to us that the acetoxyl participation pathway (k_Δ') is probably dominant. A similar mechanistic scheme could be written for the monotosylates, without the complications of further reaction of the acetoxy tosylate. In the ditosylate mechanism (Scheme II), our initial concern will be with the rate-determining initial step, formation of the acetoxy tosylate. We will return to a discussion of the prod-

Table II. Rates of Buffered Acetolysis of 1,4-Diaryl-2-butyl Tosylates (**4**)

Compd	Temp, °C	k, s^{-1}	Corr coeff
4a	65.0	1.87×10^{-4}	0.998
(p-OCH_3)	70.0	2.89×10^{-4}	0.999
	75.0	4.52×10^{-4}	0.999
	80.0	7.02×10^{-4}	0.999
	85.0	1.19×10^{-3}	0.998
	90.0	1.52×10^{-3}	0.999
	100.0	$(3.54 \times 10^{-3})^a$	
	150.0	$(1.03 \times 10^{-1})^a$	
4b	85.0	1.16×10^{-4}	0.999
(p-CH_3)	95.0	3.41×10^{-4}	1.000
	100.0	$(5.40 \times 10^{-4})^a$	
	105.0	8.72×10^{-4}	1.000
	150.0	$(4.10 \times 10^{-2})^a$	
4c	80.4	2.38×10^{-5}	0.998
(H)	96.0	1.18×10^{-4}	0.999
	100.0	$(1.90 \times 10^{-4})^a$	
	109.0	4.67×10^{-4}	0.999
	122.0	1.51×10^{-3}	0.997
	150.0	$(1.57 \times 10^{-2})^a$	
4d	100.0	$(7.18 \times 10^{-5})^a$	
(p-Cl)	100.0	7.37×10^{-5}	0.998
	110.0	1.85×10^{-4}	0.999
	120.0	4.74×10^{-4}	1.000
	150.0	$(5.42 \times 10^{-3})^a$	
4e	100.0	$(4.20 \times 10^{-5})^a$	
(m-CF_3)	110.0	1.06×10^{-4}	1.000
	120.0	2.34×10^{-4}	0.999
	130.0	5.53×10^{-4}	1.000
	150.0	$(2.39 \times 10^{-3})^a$	
4f	100.0	$(1.98 \times 10^{-5})^a$	
(p-NO_2)	110.4	5.34×10^{-5}	0.999
	120.0	1.25×10^{-4}	1.000
	130.0	2.95×10^{-4}	1.000
	150.0	$(1.42 \times 10^{-3})^a$	

[a] Calculated from the Arrhenius parameters.

Scheme II



uct-forming steps later. We expect that our observed first-order rate constants correspond to the first step (k_Δ, k_s) because the intermediate acetoxy tosylate could not be isolated after 1 half-life and because the prepared erythro acetoxy tosylate reacts so much more rapidly than the starting material, i.e., $k_\Delta' , k_s' \gg k_\Delta , k_s$.

Separation of the observed rate constant into the solvent-assisted and aryl-assisted components may be done[2] by examination of the Hammett plot. The plot for the monotosylate series (**4**) is quite analogous to those reported by Brown and Schleyer for their monotosylates[2] (Figure 1). When the aryl substituents are sufficiently deactivating (p-NO_2, m-CF_3, p-Cl), the substrate reacts entirely by the solvent-assisted pathway. The straight line determined by these points ($\rho = -1.04$) defines the aryl-unassisted pathway (k_s) for the remaining substituents. The deviation of the observed points from the k_s line [$\log(k_t/k_s)$] represents the rate acceleration caused by aryl participation. The fraction of substrate that solvolyzes by the aryl-assisted pathway (Fk_Δ/k_t) can then be calculated by

$$Fk_\Delta/k_t = 1 - k_s/k_t = \frac{k_t/k_s - 1}{k_t/k_s} \qquad (5)$$

(from eq 4). These observations confirm that our monotosylates **3** exactly parallel the behavior of those studied by

Table III. Activation Parameters for Buffered Acetolysis of *meso*-1,4-Diaryl-2,3-butyl Ditosylates (**3**) and 1,4-Diaryl-2-butyl Tosylates (**4**)

Compd	E_a, kcal/mol	Log A	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, gibbs	Corr coeff	No. of points
3a	27.4	11.2	26.8	−9	0.998	3
3b	28.8	11.7	28.3	−7	1.000	3
3c	29.0	11.0	28.4	−10	1.000	3
3d	32.3	12.2	31.8	−5	0.998	3
3e	32.5	11.8	32.0	−7	1.000	3
3f	32.0	11.4	31.5	−8	0.999	3
4a	21.2	9.9	20.6	−15	0.998	6
4b	27.2	12.6	26.6	−3	1.000	3
4c	27.8	12.6	27.2	−3	1.000	4
4d	27.1	11.7	26.5	−7	1.000	3
4e	25.3	10.5	24.7	−13	0.999	3
4f	26.8	11.0	26.2	−10	1.000	3

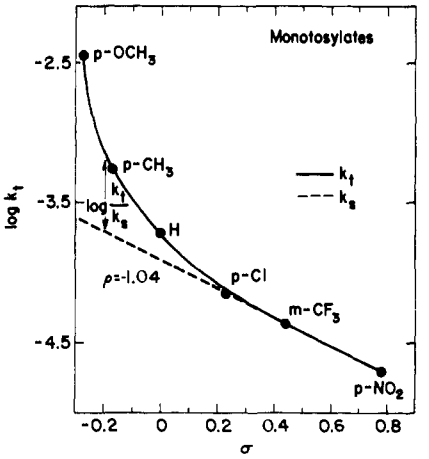


Figure 1. Log k_t vs. σ for 1,4-diaryl-2-butyl tosylates (**4**).

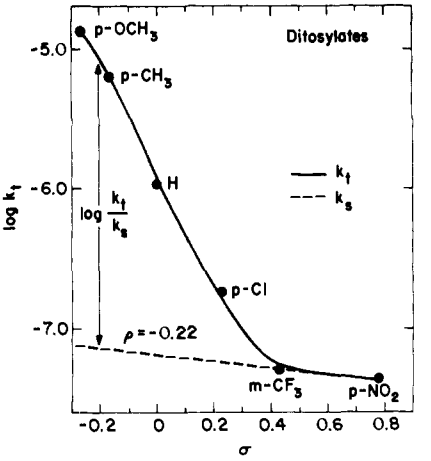


Figure 2. Log k_t vs. σ for *meso*-1,4-diaryl-2,3-butyl ditosylates (**3**).

Table IV. Partitioning of the Rates of Acetolysis at 100.0 °C of 1,4-Diaryl-2-butyl Tosylates (**4**) and *meso*-1,4-Diaryl-2,3-butyl Ditosylates (**3**)

	Monotosylates		Ditosylates	
	k_t/k_s	$100\,Fk_\Delta/k_t$	k_t/k_s	$100\,Fk_\Delta/k_t$
p-CH_3O	15.5	93	182	99
p-CH_3	2.95	66	91.2	99
H	1.55	35	16.6	94
p-Cl	1.00	0	3.16	68
m-CF_3	1.00	0	1.00	0
p-NO_2	1.00	0	1.00	0

Schleyer and by Brown.[2] Thus the second aryl group (γ to the tosylate) is entirely nonfunctional.

The behavior of the ditosylate series **4,** however, is quite different. The Hammett plot for these rate data is given in Figure 2. The line determined by *p*-NO_2 and *m*-CF_3 has a slope of only −0.22. The inductive effect of the second tosylate group reduces the sensitivity of the solvent-assisted reaction rate to the aryl substituent, so that ρ is smaller for the ditosylates than for the monotosylates. Extrapolation of this line (Figure 2) defines the rate of the solvent-assisted pathway for the remaining substituents and thereby gives the rate acceleration due to aryl participation (k_t/k_s) (Table IV).

The proportion of aryl-assisted pathway (Fk_Δ/k_t) has been calculated from eq 5 for both the monotosylate (**4**) and the ditosylate (**3**) series, and these data are also given in Table IV. In the monotosylate series, aryl assistance is observed only for *p*-OCH_3, *p*-CH_3, and H. The percentage of aryl assistance (93, 66, 35%, respectively) is quite close to the values calculated by Schleyer for the 1-aryl-2-propyl tosylates.[2] Thus introduction of the second aryl group does not alter the mechanistic situation for the monotosylate series.

In contrast, for the ditosylate series the proportion of aryl assistance has increased for all except the extremely electron-withdrawing substituents: *p*-OCH_3 and *p*-CH_3 to 99%, H to 94%, and Cl from nil to 68%. Thus the inductive effect of the second tosylate has caused the aryl group to participate much more strongly. For the three most active substituents, aryl participation has become essentially the exclusive pathway, and for *p*-Cl, aryl participation is observed for the first time. The rate acceleration (k_t/k_s) is quite large for *p*-OCH_3 and *p*-CH_3 (two orders of magnitude or more), whereas for the monotosylates no rate acceleration exceeds about 15.

An alternative, though less quantitative, approach to assessing the presence of inductive enhancement of aryl participation is by measuring a rate acceleration through comparisons of the rates of the aryl-containing compounds with suitable models lacking the aryl groups. This approach assumes that the latter systems react entirely by the k_s pathway, whereas the former react to a certain extent by aryl assistance. At 100 °C, for example, 1,4-diphenyl-2-butyl tosylate (**4c**) reacts 0.1 times as fast as 3-hexyl tosylate,[11] even though aryl participation is present to the extent of some 35% (Table IV). This overall rate deceleration results from the rate-retarding inductive effect of the phenyl group and from competition with strong solvent assistance. In contrast, 1,4-diphenyl-2,3-butyl ditosylate (**3c**) reacts 0.56 times as fast as 3,4-hexyl ditosylate.[11] Thus the increased proportion (from 35 to 94%) of aryl participation is reflected in a 5.6-fold (0.56/0.1) rate enhancement. This factor, derived from an entirely different k_s model system, compares favorably with that (16.6/1.55 = 10.7) in Table IV.

Product analysis was carried out on both the monotosylates and the ditosylates (Table V). Because the monotosylates were optically inactive, a rate/product correlation like that performed by Schleyer[2] cannot be developed, although it is to be expected that our monotosylate series should have the same behavior as Schleyer's. Unfortunately, it is impossible to relate rates and products for the ditosylates in the manner used for the monotosylates.[2] As shown in Scheme II, the intermediate acetoxy tosylate can give the product diacetate either with a single inversion via a k_s' pathway or with two inversions (retention) via an acetoxonium (k_Δ') pathway. A mixture of these mechanisms completely invalidates any effort to correlate the rates and product stereochemistry. Contributions from a second aryl participation step (k_Δ'') would complicate the situation further. In systems with predominant initial aryl participation, the meso starting material would go to a meso product if the acetoxonium pathway were the predominant reaction pathway for the acetoxy tosylate (k_Δ plus k_Δ'). Indeed, for *p*-CH_3, H, and *p*-Cl, the meso diacetate is the major product; the smaller amount of *dl* diacetate must come from the various solvent-assisted pathways (k_s plus k_Δ'; k_Δ plus k_s'). The products from *p*-OCH_3 were rearranged (aryl migration, hydride shift); all other diacetates had structures analogous to starting material. For the electron-withdrawing substituents (*m*-CF_3, *p*-NO_2), nearly equivalent amounts of meso and *dl* product diacetates were observed, as would be expected for a mixture of k_s plus k_Δ' and k_s plus k_s' mechanisms. The multiple pathways after the rate-determining step render mechanistic conclusions based entirely on product analysis very tenuous.

Because the erythro acetoxy tosylate reacts so much more rapidly than the ditosylate, we questioned whether the k_s' pathway could be competitive with the k_Δ'. In order to dem-

Table V. Products of Buffered Acetolysis of 1,4-Diaryl-2-butyl Tosylates (4) and *meso*-1,4-Diaryl-2,3-butyl Ditosylates (3)[a,b]

	Tosylate (4)		Ditosylate (3)			
				Diacetates[c]		
	Alkenes	Acetates[c]	Alkenes	Meso	*dl*	Other
p-OCH_3	4	96	8			92[d]
p-CH_3	32	68[e]	28	47	12	13
H	39	61[e]	32	49	9	10
p-Cl	50	50	32	42	18	7
m-CF_3	51	49	61	18	14	7
p-NO_2	36	64	30	35	35	0

[a] Alkene to acetate or diacetate ratios were measured by VPC analysis. [b] Meso to *dl* diacetate ratios were measured by NMR spectroscopy. [c] Except as noted, all acetates and diacetates corresponded in structure to the respective starting materials (3 or 4) and were identified by comparison with authentic materials prepared from the alcohol or diol. [d] A small amount of meso diacetate was observed in the NMR spectrum of the product mixture of the *p*-OCH_3 compound, but most of the diacetate products resulted from rearrangement (hydride or aryl shift). [e] Products of *p*-CH_3 and H tosylates contained 2 and 5% rearranged acetates, respectively.

onstrate that mixed mechanisms are indeed possible, we examined the products of acetolysis of *meso*-3,4-hexyl ditosylate.[11] The k_s plus k_s' pathway would give meso diacetate; the k_s plus k_Δ' (acetoxonium) pathway would give *dl* diacetate; of course there is no k_Δ pathway since the molecule lacks an aryl group. In fact, both products are formed, 28% meso and 16% *dl*. Clearly the k_s' and k_Δ' pathways must both be viable, although k_Δ' is dominant. As further proof, acetolysis of *erythro*-1,4-diphenyl-2-acetoxy-3-butyl tosylate (the likely first intemediate in the acetolysis of **3c**) gave 80% meso, 10% *dl*, and 10% other diacetates, again indicating that the k_s' pathway is competitive with the k_Δ' pathway. Therefore, we conclude that product analysis is not useful as a mechanistic determinant in the ditosylate series.

Summary

Inductive enhancement of aryl participation has been observed in the series of ditosylates **3**. Charge buildup on the carbon atom from which the tosylate group leaves is destabilized by the remaining tosyloxy group. Removal of charge by stronger aryl participation relieves this polar destabilization. The *p*-methoxyphenyl, *p*-tolyl, and phenyl systems react essentially entirely by the aryl participation pathway, in contrast to reduced proportions in the monotosylate series. Furthermore, the ditosylate series provides the first example of aryl participation by a *p*-chlorophenyl group. The enhanced phenyl participation is reflected in the overall rate, but correlation with product structure is not possible, because of multiple product-forming pathways following the rate-determining step.

Experimental Section

Nuclear magnetic resonance spectra were obtained on Varian T-60 and Perkin-Elmer R-20B spectrometers. Infrared spectra were recorded on Beckman IR-5 and IR-10 spectrometers. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Melting points were determined in a Hershberg apparatus. All melting points and boiling points are uncorrected. Vapor phase chromatograms were obtained from a Varian Model 1520B chromatograph. A Haake NB-22 constant temperature bath and a Metrohom Hersiau Type E-415 automatic titrator were used for the kinetic measurements. The synthetic intermediates described below in the preparation of the series **3** and **4** (the aryl acetates, arylethanols, arylethyl bromides, and arylacetaldehydes) are known compounds up to the cis alkenes (Scheme I), although the characterization in the early literature (found in Beilstein) consists only of aspirator boiling points and is not useful. From the alkenes on (Scheme I), the compounds are new except for the parent alkene and diol leading to **3c** (X = H).

Kinetic Studies. Rate constants were determined by standard titrimetric procedures.[12] A known quantity of substrate was dissolved in anhydrous HOAc, and a sufficient quantity of the conjugate base was added to give a solution containing a 10% excess of base. Aliquots (2 mL) of this solution were transferred via pipet to Pyrex tubes, which were then sealed. Twelve tubes were selected for each rate determination. The tubes were placed in a constant temperature bath (±0.2 °C). After equilibration for 5–10 min, tubes were withdrawn at appropriate intervals and quenched by cooling. The contents of each tube were titrated with standard $HClO_4$ solution using 1 drop of a 0.5% solution of crystal violet as the indicator. The first tube titrated was called the zero tube, and the reaction was followed from that point. One unheated tube was also titrated to verify the initial base concentration. Infinity tubes were allowed to react for 6–10 half-lives.

Solvent. Reagent grade HOAc (99.7%) was refluxed for at least 5 h with 0.6 g of CrO_3 per liter of acid and with an amount of Ac_2O sufficient to react with any water present. The mixture was distilled through a Vigreux column, and enough Ac_2O was then added to make the distilled acid 1% by weight in anhydride.

Standard Acid. A solution approximately 5.0×10^{-3} M in $HClO_4$ was prepared by diluting 70% $HClO_4$ with reagent grade HOAc and adding enough Ac_2O to remove all the water from the solution and then leave it 1% in anhydride. The solution was allowed to stand for 2 days so the Ac_2O could react completely with any H_2O present. The $HClO_4$ solution was then titrated against potassium acid phthalate in purified HOAc with crystal violet as the indicator to determine the molarity of $HClO_4$.

Preparation of Standard KOAc. An approximately 1 M solution of KOAc in HOAc was prepared by the reaction of K_2CO_3 and HOAc. Purified HOAc was mixed with 17.325 g (0.125 mol) of K_2CO_3 and 12.797 g (0.125 mol) of Ac_2O and then diluted to 250 mL in a volumetric flask. One milliliter of this standard base solution was then diluted to 50 mL in a volumetric flask. Aliquots (2 mL) of this solution were titrated with the standard $HClO_4$ with crystal violet as the indicator to give the concentration of the original KOAc solution.

Tosylate Preparation. All tosylates and ditosylates were prepared by the method of Tipson.[13] A solution of the purified alcohol or diol in dry pyridine or pyridine/CH_2Cl_2 was treated with a 10% excess of tosyl chloride (Aldrich). This solution was kept at 0 °C until precipitation of pyridinium chloride indicated that the reaction was complete. Cold H_2O was added to the reaction mixture, and the organics were extracted into CH_2Cl_2. The organic phase was washed twice with 3 N HCl and once with saturated $NaHCO_3$ solution, and then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the impure tosylate product, which was then recrystallized twice, usually from hot acetone/hexane. Yield and characterization of individual tosylates are given below.

Product Studies. Acetolysis products of all the mono- (**4**) and ditosylates (**3**) were obtained by solvolysis in buffered solutions for 9–12 half-lives at the highest temperature for which kinetics were measured (Tables I and II). After cooling and dilution with H_2O, the solution was neutralized with 1 equiv of Na_2CO_3. The organics were extracted into ether and dried over $MgSO_4$, and the solvent was removed by distillation. The products were then analyzed by VPC on a 0.125 in. × 6 ft or a 0.125 in. × 13 ft column packed with 1% Carbowax 20M on Chromosorb G or a 0.125 in. × 6 ft column packed with 3% SE-52 on Chromosorb G. In those cases for which VPC would not separate meso- and *dl*-diacetate mixtures, the ratios of these isomers were found

by NMR analysis (acetate resonance). Comparison of VPC retention times and NMR chemical shifts with known compounds were made whenever these compounds were available. Acetates were prepared from the corresponding alcohols by treatment with an excess of Ac_2O containing 1 drop of concentrated H_2SO_4.[14] All acetates and diacetates listed in Table I that correspond in structure to the respective starting materials were identified in this fashion.

Nitrosomethylurea was prepared by the procedure of Arndt.[15,16]

Methyl 4-Methoxyphenylacetate. Diazomethane solution was generated by adding 10.3 g (0.10 mol) of nitrosomethylurea to 75 mL of 40% KOH solution and 350 mL of ether at 0 °C in an Erlenmeyer flask. The yellow ether phase was decanted into a flask that contained KOH pellets and was allowed to dry for 30 min. The CH_2N_2 solution was then added to a stirred ether solution of 8.3 g (0.05 mol) of 4-methoxyphenylacetic acid (Aldrich). After the evolution of N_2 ceased, excess CH_2N_2 was destroyed by the addition of HOAc. The ether solution was washed with saturated $NaHCO_3$ and dried with $MgSO_4$, and the solvent was removed under vacuum. The methyl ester was then distilled, bp 116–117 °C (2.5 mm). In this manner 100 g of acid was converted to 103 g (96%) of the methyl ester.

2-(4-Methoxyphenyl)ethanol. To 2.88 g (0.076 mol, 20% excess) of $LiAlH_4$ in anhydrous ether was added dropwise 22.87 g (0.128 mol) of methyl 4-methoxyphenylacetate in anhydrous ether. The reaction mixture was refluxed for 1 h, and the alcohol was then released from the alkoxide by treatment with aqueous NaOH. The white solid was filtered off, and the ether was dried over $MgSO_4$. The ether was removed by vacuum distillation, and the residue was distilled to give 17.29 g (89%) of the alcohol, bp 114–116 °C (1.6 mm).

4-(2-Bromoethyl)methoxybenzene was prepared by the treatment of 12.55 g (82.5 mmol) of the corresponding alcohol with 8.2 g (30.3 mmol, 10% excess) of PBr_3. The alcohol was placed in a 5-mL flask fitted with a Claisen adapter, an addition funnel, and a condenser with a drying tube. The flask was cooled to 0 °C, and the PBr_3 was added dropwise to the alcohol with stirring. The solution was maintained at 0 °C for 3 h and then allowed to warm to room temperature. Finally the reaction mixture was heated to 100 °C for 14 h. After the mixture had cooled, 2.7 mL of H_2O (1 mL for every 3 g of PBr_3) was added to the flask. The organic layer was separated and the aqueous layer was washed three times with CH_2Cl_2. The organic fractions were combined, washed with saturated $NaHCO_3$, and dried over $MgSO_4$, and the solvent was removed by vacuum distillation. The residue was distilled under vacuum to give 11.27 g (51%) of the desired bromide, bp 91 °C (0.5 mm).

2-(4-Methoxyphenyl)ethyltriphenylphosphonium bromide was prepared by treating 19.21 g (89 mmol) of 4-(2-bromoethyl)-methoxybenzene with 25.8 g (98 mmol) of triphenylphosphine (Aldrich), under N_2 at 90 °C for 20 h. The viscous liquid that formed was poured into anhydrous ether. The resulting hygroscopic glass was crushed, washed with anhydrous ether, and stored in a vacuum desiccator over P_2O_5. An exact yield from this nearly quantitative reaction was not determined because of the hygroscopic nature of the product.

4-Methoxyphenylacetaldehyde. A solution of methyl 4-methoxyphenylacetate (18.02 g, 0.10 mol) in 300 mL of freshly distilled ether was cooled to −78 °C in a dry ice bath. To this solution was added an ether solution of 15.88 g (0.056 mol) of 70% $NaAlH_2(OCH_2CH_2OCH_3)_2$ (Red-al, Aldrich) via syringe. The reaction mixture was kept at −78 °C for 8 h, after which time it was removed from the dry ice bath, and 100 mL of 1:5 H_2SO_4/H_2O was added. The phases were separated and the aqueous layer was extracted three times with ether. The ether extracts were combined, washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated by vacuum distillation. The residue contained the starting ester as well as alcohol by-product, but the aldehyde was separated by elution with ether/hexane on a silica gel column. The aldehyde fractions were combined and distilled to give 3.97 g (30% yield) of the desired aldehyde: bp 52 °C (0.10 mm); NMR ($CDCl_3$) δ 3.85 (d, 2 H), 4.02 (s, 3 H), 7.25 (AB q, 4 H), 9.90 (t, 1 H).

***cis*-1,4-Bis(4-methoxyphenyl)-2-butene.** Dry ether (500 mL) was distilled onto 26.8 g (62.4 mmol) of 2-(4-methoxyphenyl)ethyltriphenylphosphonium bromide, which had been placed in a 1-L, three-necked flask fitted with a N_2 inlet, a condenser, and a septum. After addition of the ether was complete, an addition funnel was fitted onto the flask, and the contents were left to stir to break up the salt. After about 1 h, 26.6 mL (62.4 mmol) of 2.35 M phenyllithium was added to the salt via syringe. A brilliant red-orange solution developed as the phosphonium salt was converted to ylide. The ylide solution was stirred for 1 h. A solution of 6.43 g (48 mmol) of 4-methoxyphenylacetaldehyde in 100 mL of dry ether was added dropwise to the ylide. The reaction mixture was allowed to stir for 2 h after the addition was complete. The excess ylide was then destroyed by the addition of H_2O until discharge of the color. Following drying with $MgSO_4$ and removal of the solvent, the residue was distilled to give 9.29 g (72%) of the desired cis alkene: bp 128–131 °C (0.15 mm); NMR ($CDCl_3$) δ 3.48 (d, 4 H), 3.80 (s, 6 H), 5.65 (t, 2 H), 6.95 (AB q, 8 H).

***meso*-1,4-Bis(4-methoxyphenyl)-2,3-butanediol.** According to the hydroxylation procedure described by Gunstone,[8] 8.05 g (30 mmol) of *cis*-1,4-bis(4-methoxyphenyl)-2-butene was dissolved in 200 mL of glacial HOAc. This solution was then treated with 11.0 g (66 mmol) of AgOAc and 7.58 g (30 mmol) of I_2. This reaction mixture was allowed to stir for 4.5 h, and 30 mL of HOAc containing 0.6 ml (33 mmol) of H_2O was then added to the reaction. After heating at reflux for 1 h, the solution was allowed to cool to room temperature, and the silver salts were filtered off. The HOAc was distilled off at reduced pressure, leaving about 20 mL of a viscous brown liquid. Water was added, and the organics were extracted into ether. The ether fractions were combined and washed twice with concentrated NH_4OH and once with H_2O, and the ether was removed by vacuum distillation. The resulting viscous liquid was treated with 30 mL of 3 N ethanolic KOH solution under reflux for 1 h. After dilution with H_2O, the solution produced a yellow solid precipitate. The aqueous slurry was made acidic with concentrated HCl. The solid was filtered off and dried over P_2O_5. Two recrystallizations from acetone/hexane gave 4.01 g (44%) of the desired meso diol: mp 123–127 °C; NMR ($CDCl_3$) δ 1.86 (br s, 2 H), 2.71 (m, 4 H), 3.68 (m, 2 H), 3.70 (s, 6 H), 6.88 (AB q, 8 H). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.57; H, 7.47.

***meso*-1,4-Bis(4-methoxyphenyl)-2,3-butyl Ditosylate (3a).** The ditosylate was prepared from 1.51 g (5.0 mmol) of the diol as described above. This procedure gave 0.61 g (20%) after multiple recrystallizations: mp 174–175 °C; NMR ($CDCl_3$) δ 2.39 (s, 6 H), 2.98 (m, 4 H), 3.65 (s, 6 H), 4.90 (m, 2 H), 6.67 (AB q, 4 H), 7.20 (AB q, 4 H). Anal. Calcd for $C_{32}H_{34}O_8S_2$: C, 62.93; H, 5.61. Found: C, 62.94; H, 5.60.

1,4-Bis(4-methoxyphenyl)-2-butanol. According to a modification of the procedure of Zweifel and Brown,[17] B_2H_6 was generated by the dropwise addition of 5.5 g (38 mmol) of freshly distilled $BF_3{\cdot}Et_2O$ onto 0.88 g (23 mmol) of $LiAlH_4$ in 150 mL of ether. The B_2H_6 was swept by N_2 through a solution of 4.3 g (15 mmol) of *cis*-1,4-bis(4-methoxyphenyl)-2-butene in dry THF. After the $BF_3{\cdot}Et_2O$ had been added, the N_2 flow was left on for another 3 h. At the end of this time, 10 mL of H_2O containing 2.2 g of NaOH, followed by 6.6 mL of 30% H_2O_2, was added dropwise to the reaction mixture. This mixture was then refluxed for 2 h. The mixture was cooled, and the aqueous layer was separated, saturated with NaCl, and extracted with ether. The organic layers were combined, dried with $MgSO_4$, and filtered. Distillation of the solvent gave 3–4 mL of yellowish liquid that crystallized upon cooling. Recrystallization from benzene/heptane gave 3.05 g (71%) of white crystals: mp 74–75 °C; NMR (CCl_4) δ 1.60 (m, 2 H), 2.61 (m, 4 H), 3.57 (m, 1 H), 3.70 (s, 6 H), 6.79 (m, 8 H). Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.75. Found: C, 75.95; H, 7.89.

1,4-Bis(4-methoxyphenyl)-2-butyl Tosylate (4a). 1,4-Bis(4-methoxyphenyl)-2-butanol (1.54 g, 5.4 mmol) was treated with a 10% excess of tosyl chloride by the standard method to give 1.52 g (64%) of the desired tosylate: mp 76–79 °C; NMR ($CDCl_3$) δ 1.80 (m, 2 H), 2.36 (s, 3 H), 2.45 (m, 2 H), 2.84 (d, 2 H), 3.73 (s, 6 H), 6.65 (m, 1 H), 6.77 (m, 8 H), 7.40 (AB q, 4 H). Anal. Calcd for $C_{25}H_{28}O_5S$: C, 68.15; H, 6.41. Found: C, 67.92; H, 6.72.

Methyl 4-Tolylacetate. 4-Tolylacetic acid (Aldrich) was converted to its methyl ester by treatment with CH_2N_2 in a procedure analogous to that used to prepare methyl 4-methoxyphenylacetate. A total of 100 g of the acid was converted to its methyl ester (99 g, 90%) by this procedure, bp 58–60 °C (0.3 mm).

2-(4-Tolyl)ethanol. The reduction of 16.42 g (0.1 mol) of methyl 4-tolylacetate with 2.28 g (0.06 mol) of $LiAlH_4$ was carried out using the same method as described above for the preparation of 2-(4-methoxyphenyl)ethanol. This procedure produced 11.89 g (87%) of the desired alcohol, bp 42–43 °C (0.02 mm).

4-(2-Bromoethyl)toluene. The bromination of 9.55 g (70 mmol) of 2-(4-tolyl)ethanol with 6.75 g (25 mmol) of PBr_3 was carried out using a procedure similar to the one described for 4-(2-bromoethyl)-

methoxybenzene. This reaction gave 11.72 g (85%) of the desired bromide, bp 114–116 °C (10 mm).

2-(4-Tolyl)ethyltriphenylphosphonium Bromide. The treatment of 11.7 g (58.8 mmol) of 4-(2-bromoethyl)toluene with 16.9 g (64.7 mmol) of triphenylphosphine (Aldrich) was carried out under N_2 using the same procedure described for the preparation of 2-(4-methoxyphenyl)ethyltriphenylphosphonium bromide.

4-Tolylacetaldehyde. A solution of 8.2 g (0.05 mol) of methyl 4-tolylacetate in 150 mL of dry ether was reduced to the aldehyde by treatment with 7.2 g (0.025 mol) of Red-al (Aldrich) at −78 °C for 8 h in the manner described above for 4-methoxyphenylacetaldehyde. At the end of this time 50 mL of 1:5 H_2SO_4/H_2O was added. The layers were separated and the aqueous phase extracted with ether. The ether was then washed with saturated $NaHCO_3$ and H_2O. The ether layer was mixed with a solution of 5.5 g (0.28 mol) of $Na_2S_2O_5$ in 10 mL of H_2O. This mixture was placed in the refrigerator until the bisulfite addition product had formed. The addition product was filtered off, washed with ethanol and ether, and allowed to dry (3.52 g). The aldehyde was released from the addition product by slurrying it in 20 mL of water, adding 4.86 g (46.2 mmol) of Na_2CO_3, and extracting with ether. Removal of the ether and distillation gave 1.39 g of 4-tolylacetaldehyde (21%): bp 88–89 °C (5 mm); NMR ($CDCl_3$) δ 2.30 (s, 3 H), 3.58 (d, 2 H), 7.08 (s, 4 H), 9.70 (t, 1 H).

***cis*-1,4-Bis(4-tolyl)-2-butene** was prepared from 5.25 g (11.4 mmol) of 2-(4-tolyl)ethyltriphenylphosphonium bromide and 1.39 g (10.4 mmol) of 4-tolylacetaldehyde in the same manner as *cis*-1,4-bis(4-methoxyphenyl)-2-butene. Distillation gave 2.48 g (95%) of the desired alkene: bp 96–106 °C (0.02 mm); NMR (CCl_4) δ 2.30 (s, 6 H), 3.40 (d, 4 H), 5.60 (t, 2 H), 6.95 (s, 8 H).

***meso*-1,4-Bis(4-tolyl)-2,3-butanediol** was prepared from 2.46 g (10.4 mmol) of *cis*-1,4-bis(4-tolyl)-2-butene by treatment with 3.83 g (22.9 mmol) of AgOAc and 2.64 g (10.4 mmol) of I_2 in 6.5 mL of HOAc in the same manner used to prepare *meso*-1,4-bis(methoxyphenyl)-2,3-butanediol. Hydrolysis of the intermediate hydroxy acetate was carried out with 40% NaOH in ethanol. Recrystallization from acetone/hexane gave 0.93 g (30%) of diol: mp 132–133 °C; NMR ($CDCl_3$) δ 1.87 (s, 2 H), 2.31 (s, 6 H), 2.90 (d, 4 H), 3.92 (m, 2 H), 7.15 (s, 8 H).

***meso*-1,4-Bis(4-tolyl)-2,3-butyl ditosylate (3b)** was prepared by the method described above by treating 0.93 g (3.44 mmol) of *meso*-1,4-bis(4-tolyl)-2,3-butanediol with 1.44 g (7.57 mmol) of tosyl chloride in pyridine. This reaction gave 1.74 g (87%) of the desired ditosylate: mp 163–164 °C; NMR ($CDCl_3$) δ 2.31 (s, 6 H), 2.36 (s, 6 H), 2.87 (d of d, 4 H), 4.70 (t, 2 H), 7.05 (m, 16 H). Anal. Calcd for $C_{32}H_{34}O_6S_2$: C, 66.41; H, 5.92. Found: C, 65.82; H, 6.01.

1,4-Bis(4-tolyl)-2-butanol was prepared from 2.10 g (9.2 mmol) of *cis*-1,4-bis(4-tolyl)-2-butene in an oxidative hydroboration procedure analogous to that used to prepare 1,4-bis(4-methoxyphenyl)-2-butanol. Recrystallization from hexane gave 1.36 g (58%) of alcohol: mp 51.5–53.5 °C; NMR (CCl_4) δ 1.60 (m, 2 H), 2.25 (s, 6 H), 2.65 (m, 4 H), 3.60 (m, 1 H), 6.95 (s, 8 H).

1,4-Bis(4-tolyl)-2-butyl Tosylate (4b). Treatment of 1.0 g (3.94 mmol) of 1,4-bis(4-tolyl)-2-butanol with 0.83 g (4.35 mmol) of tosyl chloride was carried out in the standard manner. Recrystallization from acetone/hexane ave 1.13 g (70%) of the tosylate: mp 84–87 °C; NMR (CCl_4) δ 1.75 (m, 2 H), 2.17 (s, 6 H), 2.29 (s, 3 H), 2.40 (m, 2 H), 2.72 (d, 2 H), 4.50 (m, 1 H), 6.71 (s, 8 H), 7.19 (aromatic AB, 4 H). Anal. Calcd for $C_{25}H_{28}O_3S$: C, 73.49; H, 6.91. Found: C, 73.48; H, 7.08.

2-Phenylethyltriphenylphosphonium bromide was prepared in a manner analogous to that used to prepare 2-(4-methoxyphenyl)ethyltriphenylphosphonium bromide from 9.35 g (50 mmol) of phenethyl bromide (Aldrich) and 18.5 g (55 mmol) of triphenylphosphine (Aldrich).

***cis*-1,4-Diphenyl-2-butene** was prepared from 44.7 g (0.10 mol) of 2-phenylethyltriphenylphosphonium bromide and 9.6 g (0.80 mol) of phenylacetaldehyde (Aldrich) in a manner analogous to that used to prepare *cis*-1,4-bis(4-methoxyphenyl)-2-butene. Distillation gave 12.88 g (77%) of the desired cis alkene: bp 89–90 °C (0.02 mm) [lit.[18] 176–178 °C (17 mm)]; NMR (neat) δ 3.40 (d, 4 H), 5.70 (t, 2 H), 7.15 (s, 10 H).

***meso*-1,4-Diphenyl-2,3-butanediol.** A solution of 2.08 g (10 mmol) of *cis*-1,4-diphenyl-2-butene in 65 mL of HOAc was treated with 3.68 g (22 mmol) of AgOAc and 2.54 g (10 mmol) of I_2 in the same manner used to prepare 1,4-bis(4-methoxyphenyl)-2,3-butanediol. After two recrystallizations from acetone/hexane, 1.16 g (48%) of white platelets was collected: mp 137–139 °C (lit.[18] 137–138 °C); NMR ($CDCl_3$) δ 1.97 (s, 2 H), 2.94 (m, 4 H), 3.80 (m, 2 H), 7.18 (s, 10 H).

***meso*-1,4-Diphenyl-2,3-butyl Ditosylate (3c).** The treatment of 1.11 g (4.59 mmol) of *meso*-1,4-diphenyl-2,3-butanediol with 1.92 g (10.1 mmol) of tosyl chloride in pyridine was carried out by the standard procedure to give 1.08 g (43%) of the desired ditosylate: mp 121–122 °C; NMR ($CDCl_3$) δ 2.20 (s, 6 H), 2.95 (d of d, 4 H), 4.73 (t, 2 H), 7.13 (m, 18 H). Anal. Calcd for $C_{30}H_{30}S_2O_6$: C, 65.41; H, 5.40. Found: C, 65.56; H, 5.45.

1,4-Diphenyl-2-butanol was prepared from 3.3 g (0.016 mol) of *cis*-1,4-diphenyl-2-butene by the oxidative hydroboration procedure described above for bis(4-methoxyphenyl)-2-butanol. Recrystallization from ether/pentane gave 2.0 g (55%) of white crystals: mp 27–29 °C; NMR ($CDCl_3$) δ 1.85 (m, 2 H), 2.25 (br s, 1 H), 2.71 (m, 4 H), 3.77 (m, 1 H), 7.20 (s, 10 H).

1,4-Diphenyl-2-butyl tosylate (4c) was prepared by the standard procedure from 1,4-diphenyl-2-butanol: mp 51–52 °C; NMR ($CDCl_3$) δ 1.94 (m, 2 H), 2.41 (s, 2 H), 2.47 (m, 2 H), 2.97 (d, 2 H), 4.65 (t, 1 H), 7.12 (d, 10 H), 7.40 (AB q, 4 H). Anal. Calcd for $C_{23}H_{24}SO_3$: C, 72.59; H, 6.38. Found: C, 72.69; H, 6.41.

Methyl 4-Chlorophenylacetate. The conversion of 99.5 g (0.585 mol) of 4-chlorophenylacetic acid (Aldrich) to its methyl ester was carried out in 12 batches by treatment of an ether solution of the acid with CH_2N_2 in the manner described previously for methyl 4-methoxyphenylacetate. The batches were combined and distilled from P_2O_5 to yield 102.6 g (95%) of the ester: bp 68–70 °C (0.05 mm); NMR (CCl_4) δ 3.47 (s, 2 H), 3.59 (s, 3 H), 7.18 (s, 4 H).

2-(4-Chlorophenyl)ethanol. The reduction of 18.46 g (0.10 mol) of methyl 4-chlorophenylacetate with 2.28 g (0.06 mol) of $LiAlH_4$ was carried out using the same procedure described for the preparation of 2-(4-methoxyphenyl)ethanol. Distillation of the residue gave 14.97 g (96%) of the desired alcohol: bp 70–71 °C (0.3 mm); NMR (CCl_4) δ 2.75 (t, 2 H), 3.70 (m, 2 H), 7.10 (AB q, 4 H).

4-(2-Bromoethyl)chlorobenzene. The treatment of 14.97 g (0.096 mol) of 2-(4-chlorophenyl)ethanol with 10.3 g (0.036 mol) of PBr_3 was carried out in the manner previously described for the preparation of 4-(2-bromoethyl)methoxybenzene. Distillation of the resulting liquid gave 20.43 g (97.5%) of the desired bromide: bp 60–61 °C (0.3 mm); NMR (CCl_4) δ 3.00 (m, 2 H), 3.40 (m, 2 H), 7.10 (AB q, 4 H).

2-(4-Chlorophenyl)ethyltriphenylphosphonium Bromide. Preparation of this phosphonium bromide by the treatment of 20.43 g (0.093 mol) of 4-(2-bromoethyl)chlorobenzene with 26.8 g (0.102 mol) of triphenylphosphine was carried out in the manner described for the preparation of 2-(4-methoxyphenyl)ethyltriphenylphosphonium bromide.

4-Chlorophenylacetaldehyde. The reduction of an ether solution of 18.5 g (0.10 mol) of methyl 4-chlorophenylacetate with 14.4 g (0.05 mol) of Red-al (Aldrich) was carried out in a manner analogous to that described in the preparation of 4-tolylacetaldehyde. Distillation of the residue recovered from the bisulfite addition product gave 2.39 g (15%) of the aldehyde: bp 62–63 °C (0.02 mm); NMR ($CDCl_3$) δ 3.60 (d, 2 H), 7.18 (AB q, 4 H), 9.65 (t, 1 H).

***cis*-1,4-Bis(4-chlorophenyl)-2-butene** was prepared from 8.25 g (17.1 mmol) of 2-(4-chlorophenyl)ethyltriphenylphosphonium bromide and 2.39 g (15.5 mmol) of 4-chlorophenylacetaldehyde in the manner described above for *cis*-1,4-bis(4-methoxyphenyl)-2-butene. Distillation gave 2.73 g (63.5%) of the cis alkene: bp 127–129 °C (0.05 mm); NMR ($CDCl_3$) δ 3.45 (d, 4 H), 5.70 (t, 2 H), 7.20 (AB q, 8 H).

***meso*-1,4-Bis(4-chlorophenyl)-2,3-butanediol** was prepared by the treatment of 2.76 g (10.0 mmol) of *cis*-1,4-bis(4-chlorophenyl)-2-butene in 65 mL of HOAc with 3.68 g (22.0 mmol) of AgOAc and 2.54 g (10.0 mmol) of I_2 in the manner described previously for *meso*-1,4-bis(4-methoxyphenyl)-2,3-butanediol. Recrystallization from heptane gave 1.33 g (52.5%) of the diol: mp 138–140 °C; NMR ($CDCl_3$) δ 1.80 (s, 2 H), 2.65 (d, 4 H), 3.60 (m, 2 H), 7.14 (AB q, 8 H). Anal. Calcd for $C_{16}H_{16}Cl_2O_2$: C, 61.75; H, 5.18. Found: C, 61.77; H, 5.27.

***meso*-1,4-Bis(4-chlorophenyl)-2,3-butyl Ditosylate (3d).** A solution of 1.0 g (3.22 mmol) of *meso*-1,4-bis(4-chlorophenyl)-2,3-butanediol in dry pyridine was treated with 1.67 g (8.8 mmol) of tosyl chloride. Recrystallization from acetone/hexane gave 0.9305 g (52%) of the ditosylate: mp 177–182 °C; NMR ($CDCl_3$) δ 2.33 (s, 6 H), 2.83 (d of d, 4 H), 4.60 (t, 2 H), 6.91 (AB q, 8 H), 7.19 (AB q, 8 H). Anal. Calcd for $C_{30}H_{28}Cl_2O_6S_2$: C, 58.15; H, 4.55. Found: C, 58.21; H,

4.57.

1,4-Bis(4-chlorophenyl)-2-butanol. Diborane, generated by the dropwise addition of 4.32 g (29.5 mmol) of BF_3·Et_2O into 0.69 g (18.0 mmol) of $LiAlH_4$ in 150 mL of ether, was used in the oxidative hydroboration of 3.26 g (11.8 mmol) of *cis*-1,4-bis(4-chlorophenyl)-2-butene. Treatment of the alkylborane with 1.6 g of NaOH in 7.5 mL of H_2O followed by 4.95 mL of 30% H_2O_2 gave 2.04 g (58.5%) of alcohol after recrystallization from heptane: mp 70–74 °C; NMR (CCl_4) δ 1.65 (m, 3 H), 2.50 (m, 4 H), 3.60 (quintet, 1 H), 7.05 (m, 8 H).

1,4-Bis(4-chlorophenyl)-2-butyl Tosylate (4d). According to the procedure described above, 1.0 g (3.4 mmol) of 1,4-bis(4-chlorophenyl)-2-butanol was treated with 0.78 g (4.08 mmol) of tosyl chloride. Upon workup and recrystallization from acetone/hexane, 0.9448 g (62%) of tosylate was obtained: mp 117–120 °C; NMR ($CDCl_3$) δ 2.00 (m, 2 H), 2.45 (s, 3 H), 2.50 (m, 2 H), 2.85 (d, 2 H), 4.62 (quintet, 1 H), 7.02 (m, 8 H), 7.34 (aromatic AB, 4 H). Anal. Calcd for $C_{23}H_{22}Cl_2O_3S$: C, 65.32; H, 5.48. Found: C, 64.58; H, 5.47.

3-Trifluoromethylphenylacetic Acid. After the procedure of Adams and Thal,[19] 25.0 g (0.129 mol) of α'-chloro-α,α,α-trifluoro-*m*-xylene (Aldrich) in 20 mL of ethanol was added to a solution of 7.6 g (0.155 mol) of NaCN in 7.0 mL of H_2O. This mixture was refluxed for 5 h, and the inorganic salts were filtered off. Ethanol was distilled from the filtrate until the phases separated. A saturated NaCl solution was added, and the organic phase was extracted with ether and dried. Removal of the solvent and distillation of the remaining liquid gave 19.45 g (81.5%) of nitrile: bp 51–54 °C (0.1 mm); NMR (CCl_4) δ 3.65 (s, 2 H), 7.45 (s, 4 H).

Hydrolysis of 19.45 g (0.105 mol) of nitrile was carried out with a refluxing mixture of 30 mL of H_2O and 22 mL of concentrated H_2SO_4. After 3 h, the hot, heterogeneous mixture was poured into ice, and a white solid formed. After drying and recrystallization from hexane, 23.20 g (quantitative) of acid was obtained: NMR (CCl_4) δ 3.65 (s, 2 H), 7.40 (m, 4 H).

Methyl 3-trifluoromethylphenylacetate was prepared by treating a total of 43 g (0.206 mol) of 3-trifluoromethylphenylacetic acid with CH_2N_2 in the same manner as used to produce methyl 4-methoxyphenylacetate. Distillation from P_2O_5 gave 39.84 g (87%) of ester; bp 57–58 °C (0.2 mm).

2-(3-Trifluoromethylphenyl)ethanol. A solution of 20.0 g (0.092 mol) of methyl 3-trifluoromethylphenylacetate in ether was reduced to the alcohol with 2.3 g (0.06 mol) of $LiAlH_4$, by a procedure similar to that described for the preparation of 2-(4-methoxyphenyl)ethanol. Distillation gave 14.22 g (81%) of the desired alcohol: bp 56–62 °C (0.075 mm); NMR (CCl_4) δ 1.30 (s, 1 H), 2.65 (t, 2 H), 3.65 (t, 2 H), 7.28 (m, 4 H).

3-(2-Bromoethyl)trifluoromethylbenzene. The treatment of 7.0 g (36.8 mmol) of 2-(3-trifluoromethylphenyl)ethanol with 4.1 g (14.6 mmol) of PBr_3 in a manner similar to that described for the preparation of 4-(2-bromoethyl)methoxybenzene gave 8.66 g (93%) of the desired bromide: bp 88–90 °C (5 mm); NMR (CCl_4) δ 3.32 (m, 4 H), 7.32 (m, 4 H).

2-(3-Trifluoromethylphenyl)ethyltriphenylphosphonium Bromide. The treatment of 8.66 g (34.2 mmol) of 3-(2-bromoethyl)trifluoromethylbenzene with 9.9 g (37.7 mmol) of triphenylphosphine was carried out in the same way as described above for 2-(4-methoxyphenyl)ethyltriphenylphosphonium bromide.

3-Trifluoromethylphenylacetaldehyde was prepared using a modification of the procedure reported by Collins and Hess.[9] A solution of 56.8 g (0.222 mol, sixfold excess) of CrO_3·Py_2, prepared from CrO_3 (Baker) and pyridine (Mallinckrodt), was made by dissolving the complex in 500 mL of anhydrous CH_2Cl_2 in a three-necked flask fitted with a mechanical stirrer and an addition funnel. A solution of 7.15 g (37.6 mmol) of 2-(3-trifluoromethylphenyl)ethanol in 50 mL of anhydrous CH_2Cl_2 was added in one portion to the red chromium solution. A black tar precipitated instantly. The solution was filtered through a Celite pad, washed with 200 mL of 5% NaOH, 2 × 100 mL of 5% HCl, saturated $NaHCO_3$, and brine, and dried over $MgSO_4$. After filtration and removal of the solvent, the remaining viscous liquid was distilled to give 4.77 g (70%) of the aldehyde: bp 35 °C (0.03 mm); NMR (benzene-d_6) δ 2.85 (d, 2 H), 7.05 (br s, 4 H), 9.06 (t, 1 H).

***cis*-1,4-Bis(3-trifluoromethylphenyl)-2-butene** was prepared from 10.4 g (20.2 mmol) of 2-(3-trifluoromethylphenyl)ethyltriphenylphosphonium bromide and 3.73 g (19.3 mmol) of the aldehyde to give, after distillation, 4.56 g (69%) of the desired alkene: bp 97–99 °C (0.05 mm); NMR (CCl_4) δ 3.52 (d, 4 H), 5.72 (t, 2 H), 7.35 (br s, 8 H).

***meso*-1,4-Bis(3-trifluoromethylphenyl)-2,3-butanediol** was prepared by the treatment of 3.53 g (10.3 mmol) of the cis alkene in 65 mL of glacial HOAc with 3.62 g (22.6 mmol) of AgOAc and 2.61 g (10.3 mmol) of I_2 in the same manner used to prepare the *p*-methoxy diol. Recrystallization from acetone/hexane gave 1.83 g (47%) of diol: mp 125–128 °C; NMR δ 1.93 (br s, 2 H), 2.75 (m, 4 H), 3.60 (br m, 2 H), 7.35 (br s, 8 H). Anal. Calcd for $C_{18}H_{16}F_6O_2$: C, 57.14; H, 4.26. Found: C, 57.06; H, 4.22.

***meso*-1,4-Bis(3-trifluoromethylphenyl)-2,3-butyl Ditosylate (3e).** The treatment of 1.0 g (2.64 mmol) of *meso*-1,4-bis(3-trifluoromethylphenyl)-2,3-butanediol with 1.1 g (5.81 mmol) of tosyl chloride in pyridine was carried out as described above. Recrystallization from acetone/hexane gave 1.10 g (61%) of the desired ditosylate: mp 147–148 °C; NMR ($CDCl_3$) δ 2.33 (s, 6 H), 3.00 (d of d, 4 H), 4.72 (t, 2 H), 7.20 (br m, 16 H). Anal. Calcd for $C_{32}H_{28}F_6O_6S_2$: C, 55.97; H, 4.11. Found: C, 55.70; H, 3.94.

1,4-Bis(3-trifluoromethylphenyl)-2-butanol. Diborane prepared from the dropwise addition of 3.2 g (22.8 mol) of BF_3·Et_2O to 0.51 g of $LiAlH_4$ in 150 mL of ether was bubbled through a THF solution of 3.0 g (8.72 mmol) of *cis*-1,4-bis(3-trifluoromethylphenyl)-2-butene. The alkylborane solution was then treated with 1.2 g of NaOH in 5.5 mL of H_2O followed by 3.7 mL of 30% H_2O_2, in the same manner used to prepare the *p*-methoxy alcohol. Repeated attempts failed to bring about crystallization, so the crude alcohol was used without purification: NMR (CCl_4) δ 3.8 (br m, 2 H), 2.4 (m, 4 H), 3.4 (m, 1 H), 7.2 (br s, 4 H), 7.3 (br s, 4 H).

1,4-Bis(3-trifluoromethylphenyl)-2-butyl Tosylate (4e). It was assumed that the hydroboration reaction used to produce 1,4-bis(3-trifluoromethylphenyl)-2-butanol gave a 100% yield or 3.2 g (8.7 mmol) of alcohol. The crude alcohol was therefore treated with 1.83 g (9.6 mmol) of tosyl chloride. Recrystallization from acetone/hexane gave 1.74 g (39% from the alkene) of the desired tosylate: mp 91–93 °C; NMR ($CDCl_3$) δ 2.00 (m, 2 H), 2.35 (s, 3 H), 2.67 (m, 2 H), 2.95 (d, 2 H), 4.72 (m, 1 H), 7.33 (m, 12 H). Anal. Calcd for $C_{25}H_{22}F_6O_3S$: C, 58.13; H, 4.29. Found: C, 58.04; H, 4.33.

***meso*-1,4-Diphenyl-2,3-butyl Diacetate.** According to the procedure of Winstein,[14] 1.35 g (5.57 mmol) of *meso*-1,4-diphenyl-2,3-butanediol was treated with 5 mL of Ac_2O and 1 drop of concentrated H_2SO_4. The mixture was allowed to stir overnight and was then poured into H_2O. The diacetate was extracted from the aqueous phase with $CHCl_3$. The organic layers were combined, washed with saturated $NaHCO_3$, and dried with $MgSO_4$. Recrystallization gave 1.67 g (92%) of the desired diacetate: mp 100–101 °C; NMR ($CDCl_3$) δ 1.87 (s, 6 H), 2.87 (d, 4 H), 5.24 (t, 2 H), 7.15 (s, 10 H).

***meso*-1,4-Bis(4-nitrophenyl)-2,3-butanediol.** After a modification of the procedure of Ketcham,[10] 1.67 g (5.1 mmol) of 1,4-diphenyl-2,3-butyl diacetate was treated at −45 °C (dry ice/chlorobenzene slush) with 5 mL of a 13:4 mixture of Ac_2O and 90% HNO_3. The mixture was stirred for 3 h and poured into 200 mL of H_2O. The yellow solid was collected, dried, dissolved in a minimum volume of hot CH_3OH, and treated with 3 g (11 mmol) of 15% NaOH. Concentrated HCl was added to neutralize the solution. The solution was concentrated and poured into H_2O. The yellow solid that precipitated was collected, dried, and recrystallized from acetone/hexane to give 0.26 g (15.5%) of the diol: mp 213–214 °C; IR 3540 (OH), 1940, 1810, 1760 (para-substituted aromatic), 1510, 1340 cm^{-1} (aromatic NO_2). Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.85; H, 4.84; N, 8.34.

***meso*-1,4-Bis(4-nitrophenyl)-2,3-butyl Ditosylate (3f).** The treatment of 0.7880 g (2.37 mmol) of *meso*-1,4-bis(4-nitrophenyl)-2,3-butanediol with 1.0 g (5.22 mmol) of tosyl chloride was carried out as described above. Recrystallization from CH_2Cl_2/hexane gave 0.60 g (25%) of the desired ditosylate: mp 198–201 °C dec; IR 1940, 1810, 1760 (para-substituted aromatic), 1510, 1340 (aromatic NO_2), 1370, 1160 cm^{-1} (sulfonate ester). Anal. Calcd for $C_{30}H_{28}N_2O_{10}S_2$: C, 56.23; H, 4.40; N, 4.37. Found: C, 55.97; H, 4.35; N, 4.36.

1,4-Diphenyl-2-butyl Acetate. A solution of 5.73 g (27.5 mmol) of *cis*-1,4-diphenyl-2-butene was treated with B_2H_6 in the manner described above for the preparation of 1,4-bis(4-methoxyphenyl)-2-butanol. The crude alcohol was then treated overnight with 6.5 mL of a mixture of 10 mL of Ac_2O and 1 drop of concentrated H_2SO_4. The Ac_2O was hydrolyzed with H_2O, and the solution was then neutralized with Na_2CO_3. The organic phase was extracted with ether and dried over $MgSO_4$. Removal of the ether and distillation of the remaining residue gave 4.79 g of acetate (65% from the alkene): bp

104–110 °C (0.02 mm); NMR (CCl_4) δ 1.79 (m, 2 H), 1.85 (s, 3 H), 2.50 (m, 2 H), 2.76 (d of d, 2 H), 5.01 (m, 1 H), 7.05 (s, 5 H), 7.10 (s, 5 H).

1,4-Bis(4-nitrophenyl)-2-butanol. 1,4-Diphenyl-2-butyl acetate (15.39 g, 0.057 mmol) was treated with a nitrating mixture of 17.5 mL of fuming HNO_3 and 56.5 mL of Ac_2O.[10] After 4 h at −45 °C, the mixture was poured into H_2O and the organics were extracted into ether. The organic phase was neutralized with Na_2CO_3 and dried over $MgSO_4$. Removal of the solvent left about 15 mL of yellow oil, which was dissolved in the minimum amount of hot CH_3OH and treated with 15% NaOH solution. After acidification with concentrated HCl and concentration of the solution, crystals of the desired alcohol were obtained. Recrystallization from CH_2Cl_2 gave 0.90 g (6.5%) of the desired alcohol: mp 151–154 °C; NMR ($CDCl_3$) δ 1.80 (m, 3 H), 2.86 (m, 4 H), 3.80 (m, 1 H), 7.75 (AB q, 8 H). Anal. Calcd for $C_{16}H_{16}N_2O_5$: C, 60.75; H, 5.10; N, 8.86. Found: C, 60.60; H, 4.97; N, 8.79.

1,4-Bis(4-nitrophenyl)-2-butyl Tosylate (4f). A solution of 0.8975 g (2.84 mmol) of 1,4-bis(4-nitrophenyl)-2-butanol was treated with 0.78 g (4.1 mmol) of tosyl chloride in the manner described above. Recrystallization of the resulting crude tosylate gave 0.913 g (68%) of pure tosylate: mp 149–152 °C; NMR ($CDCl_3$) δ 2.05 (m, 2 H), 2.42 (s, 3 H), 2.80 (m, 2 H), 3.06 (d, 2 H), 4.82 (t, 1 H), 7.62 (m, 12 H). Anal. Calcd for $C_{23}H_{22}N_2O_7S$: C, 58.71; H, 4.71; N, 5.96. Found: C, 58.81; H, 4.69; N, 5.96.

***erythro*-1,4-Diphenyl-3-acetoxy-2-butyl Tosylate.** A solution of 0.75 g (3.1 mmol) of *meso*-1,4-diphenyl-2,3-butanediol in pyridine was treated with 0.65 g (3.4 mmol) of tosyl chloride according to the usual procedure. After workup the residue was treated with an excess of Ac_2O, to which 1 drop of concentrated H_2SO_4 had been added.[14] This solution was stirred overnight, and the excess anhydride was hydrolyzed with water. The organics were extracted into ether, washed with saturated $NaHCO_3$, and dried over $MgSO_4$. Removal of the solvent left a viscous oil, which crystallized upon cooling. Three recrystallizations from ether/hexane gave 0.646 g (46%) of the desired erythro acetoxy tosylate: mp 86.5–88 °C; NMR ($CDCl_3$) δ 1.86 (s, 3 H), 2.36 (s, 3 H), 2.90 (m, 4 H), 5.00 (m, 2 H), 7.12 (m, 14 H). Anal. Calcd for $C_{26}H_{26}O_5S$: C, 68.46; H, 5.98. Found: C, 68.84; H, 6.07.

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Remarkable Activation of Anionic Nucleophiles toward *p*-Nitrophenyl Acetate by Aqueous Trioctylmethylammonium Chloride: A New Class of the Hydrophobic Aggregate[1]

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Abstract: Trioctylmethylammonium chloride (TMAC), a typical phase transfer catalyst, forms aggregates in aqueous solutions at very low concentrations (10^{-4}–10^{-5} M). The aggregate was inferred to be much smaller than the conventional globular micelles from the data of surface tension and specific conductance. The dissociation of 2,6-dichlorophenolindophenol, which is commonly used for detection of the critical micelle concentration of the cationic micelle, was enhanced in proportion to the TMAC concentration at 10^{-4}–10^{-5} M. This lack of the critical phenomenon suggests the progressive formation of the tight ion pair between the phenolate anion and the cationic TMAC aggregate. The reactivity of lauryl-substituted hydroxamate and imidazole nucleophiles toward *p*-nitrophenyl acetate was remarkably enhanced in the presence of 7×10^{-5} M TMAC in water at 30 °C, pH 9. The rate enhancements amounted to 500 to 10^4 times, and were much larger than those produced by the conventional hexadecyltrimethylammonium bromide (CTAB) micelle. Less hydrophobic hydroxamate and imidazole nucleophiles were not activated by addition of TMAC. The dissociation of the hydrophobic nucleophiles was promoted in the presence of the TMAC aggregate and, for example, $pK_{a,2}$ of the lauryl-substituted imidazole was lowered by 2.5 p*K* units relative to that of the hydrophilic counterpart. Therefore, the large rate enhancement observed is produced by adsorption of hydrophobic nucleophile onto TMAC aggregates by which highly nucleophilic ion pairs are formed. Finally, the acetylimidazole intermediate is hydrolyzed very rapidly, and the imadazole–TMAC system is an extremely efficient catalyst for the hydrolysis of phenyl esters.

In recent years, a wide variety of reactions have been studied in aqueous micellar systems, in connection with the enzyme reaction mechanism.[2] Particularly interesting is the large rate enhancement observed for the reaction of anionic nucleophiles with phenyl esters in the presence of cationic micelles. These nucleophiles include hydroxamate,[3,4] oximate,[5] thiolate,[6] and