

Substituent Effect Studies of Aryl-Assisted Solvolyses. I. The Acetolysis of 2,2-Bis(substituted phenyl)ethyl *p*-Toluenesulfonates¹⁾

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The substituent effect on the acetolysis of 2,2-bis(substituted phenyl)ethyl *p*-toluenesulfonates at 90.10 °C can be described accurately in terms of the Yukawa-Tsuno (LArSR) relationship, giving a ρ value of -4.44 and an r value of 0.53 . The substituent effect correlation of this system carrying two aryls is quite comparable to that of the 2-methyl-2-phenylpropyl system carrying a single aryl group, suggesting the close similarity in the structure of the transition states between the systems. The results can be reasonably accounted for on the basis of the accepted mechanism of this reaction, involving a rate-determining aryl-assisted transition state where only one aryl group of the two β -aryl groups participates.

The acetolysis of 2,2-diphenylethyl tosylate (*p*-toluenesulfonate) was studied earlier by Winstein et al. who found that it proceeded through the k_A process accompanying the Wagner-Meerwein rearrangement of either of two phenyl groups to form *trans*-stilbene.²⁾ However, there have been few detailed investigations on the mechanism of this reaction and all the mechanistic implications so far are virtually based on the schematic similarity to the solvolysis of neophyl brosylate (2-methyl-2-phenylpropyl *p*-bromobenzenesulfonate) as shown in Scheme 1.²⁻⁶⁾

We have undertaken extensive investigations on the mechanisms of aryl-assisted solvolyses, such as the neophyl and 2-phenylethyl systems, based mainly on the substituent effect analysis,⁷⁻⁹⁾ especially using the LArSR Eq. 1.¹⁰⁾

$$\log(k/k_0) = \rho(\sigma^0 + r\Delta\sigma_R^+) \quad (1)$$

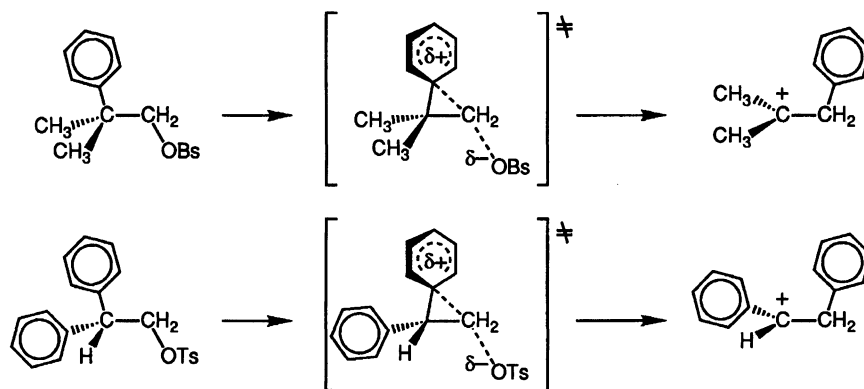
Neighboring aryl participation processes of 2-arylalkyl solvolyses all gave good linear relationships with essentially the same intermediate r values. For a typical example, the acetolysis of neophyl brosylates at 75 °C gave an excellent LArSR correlation, affording a ρ value of -3.83 and an r value of 0.57 .⁷⁾ Exalted resonance contribution indicated by an intermediate r value provides strong evidence for the significant π -delocalization by bridging between the β -aryl π -system and the carbenium center in the rate-determining transition state. The large negative ρ value of about -4 , compared with the ρ value observed in the ordinary unassisted 2-arylethyl cation reactions,³⁾ is also compatible with the geometry of the bridged transition state in the aryl-assisted solvolysis.

Through our extensive studies of substituent effects on solvolyses, we have generalized the concept of varying resonance demands in various solvolyses. This concept should apply also to the aryl-assisted mechanisms. The nature of the phenonium transition state can be widely changed by changing the two aryl groups in 2,2-diarylethyl tosylates, keeping the mechanism essentially

unchanged. In this situation, the substituent effect on the solvolysis of the 2,2-diarylethyl system promises to provide important information on the detailed mechanism of aryl-assisted solvolysis systems. As far as we are aware, there have been no data on the substituent effects of this system available in the literature except Burr's old work on the kinetic behavior of *p*-tolyl derivatives.⁵⁾ An investigation has been done of the substituent effects on the acetolysis of 2,2-diarylethyl tosylates. The kinetic analysis will be much simpler for the symmetrically substituted 2,2-diphenylethyl system where both 2-aryl groups should have the same probability of migration, contrary to unsymmetric systems suffering from competitive migrations of 2-aryl groups. In this paper, the substituent effect in the symmetric 2,2-diarylethyl system is discussed in the comparison with that on the solvolysis of neophyl brosylates.

Results and Discussion

Rate constants of acetolysis of 2,2-bis(substituted phenyl)ethyl tosylates were measured titrimetrically at 90.10 °C in glacial acetic acid in the presence of 0.022 M ($M = \text{mol dm}^{-3}$) of sodium acetate with an initial concentration of 0.02 M of tosylates. All kinetic runs accurately followed first-order kinetics over two half-lives and the reproducibility of rate constants from repeated runs was estimated to be within 3%. Rate constants are listed in Table 1. The values of activation entropy, $\Delta S^\ddagger$, listed in Table 1 all fell in the category of the k_A reaction.^{4b)} While Winstein et al. reported that the acetolysis of 2,2-diphenylethyl tosylate gave exclusively a phenyl-migrated product, *trans*-stilbene,²⁾ the product analysis of the acetolysis of the 2,2-bis(substituted phenyl)ethyl system in the presence of sodium acetate in this study showed that the major product was an aryl-migrated acetate, 1,2-diarylethyl acetate, accompanied with a small amount (about 25%) of the stilbene. Since no unrearranged products such as 1,1-diarylethylene or 2,2-diarylethyl acetate were detected at all in the acetolysis of 2,2-bis(*p*-chlorophenyl)ethyl tosylate, any derivative with a more electron-releasing sub-



Scheme 1. Solvolytic processes of neophyl and 2,2-diphenylethyl systems.

Table 1. Acetolysis Rates of 2,2-Bis(substituted phenyl)ethyl Tosylates (1)^{a)}

Substituent	Temp/°C	10 ⁵ <i>k_t</i> /s ⁻¹
<i>p</i> -MeO	45.00	1.431±0.004
	50.00	2.63±0.01
	75.00	40.22±0.24
	90.10	174.9 ^{b,c)}
3,4-di-Me	90.10	30.51±0.11
<i>p</i> -MeS	90.10	16.65±0.23
<i>p</i> -Me	90.10	14.54±0.30
<i>p</i> - <i>t</i> -Bu	90.10	11.99±0.04
3-Cl, 4-MeO	90.10	7.086±0.043
3,5-di-Me	90.10	7.600±0.020
<i>m</i> -Me	90.10	3.468±0.014
	90.10 ^{d)}	1.569±0.015
	125.00	42.95±0.17
<i>m</i> -MeO	135.00	98.2±0.6
	90.10	1.169±0.009
	90.10	1.066±0.004
3-Cl, 4-MeS	90.10	1.010±0.006
<i>p</i> -F	90.10	0.236±0.003
<i>p</i> -Cl	90.10 ^{e)}	0.236±0.003
	135.00	17.34±0.07
<i>p</i> -Br	90.10	0.1856±0.0007
<i>m</i> -F	90.10	0.0294 ^{f)}
	115.00	0.424±0.002
	135.00	2.836±0.006
	135.00	2.575 ^{g)}
<i>m</i> -Cl	90.10	0.0239 ^{f)}
	115.00	0.369±0.005
	135.00	2.429±0.025
	135.00	2.130 ^{g)}

a) In the presence of 0.022 M NaOAc. b) Extrapolated from other temperatures. c) $\Delta H_{90.1}^\ddagger = 23.7$ kcal mol⁻¹ and $\Delta S_{90.1}^\ddagger = -6.2$ e. u. (1 cal = 4.184 J and 1 e. u. = 4.184 J K⁻¹ mol⁻¹). d) $\Delta H_{90.1}^\ddagger = 26.5$ kcal mol⁻¹ and $\Delta S_{90.1}^\ddagger = -8.0$ e. u. e) $\Delta H_{90.1}^\ddagger = 27.5$ kcal mol⁻¹ and $\Delta S_{90.1}^\ddagger = -10.5$ e. u. f) Corrected for aryl-assisted rate: Calculated from the corrected aryl-assisted rate at 135.0 °C on the basis of a linear relationship between log *k*_{90.1°C} and log *k*_{135.0°C}. g) Corrected for aryl-assisted rate based on product analysis data. For *m*-F derivative, *k_S* product, 9.2% and aryl-migrated (*k_Δ*) product, 90.8%; for *m*-Cl, *k_S*, 12.3% and *k_Δ*, 87.7% (see Experimental).

stituent than *p*-Cl was indicated to react exclusively through the *k_Δ* process. However, in the acetolysis of *m*-Cl and *m*-F derivatives, the *k_S* product 2,2-diarylethyl acetate arising from direct displacement by AcOH or AcO⁻ was detected to approximately one-tenth of the whole products. Acetolysis rates for these derivatives measured with the usual accuracy at 135 °C were corrected to the aryl-assisted rate (*k_Δ*) based on the product analysis data. The *k_Δ* rates for these deactivated derivatives at 90.10 °C were estimated based on the linear relation between log *k*_{90.1°C} and log *k*_{135°C} for the 2,2-diarylethyl derivatives including unsymmetrically substituted ones (in forthcoming papers).¹¹⁾

As shown in Table 1, the acetolysis rate is enhanced by electron-releasing substituents and varies with substituents over a range of 10⁴ in magnitude. The 2,2-diarylethyl acetolysis seems to be highly sensitive to substituent change in the 2-aryl moiety. This is showed by comparison with the behavior of unassisted 2-aryl-alkyl solvolyses.³⁾

The relative rates of 2,2-bis(substituted phenyl)ethyl tosylates (1) at 90.1 °C are the same in magnitude as those of the acetolysis of neophyl brosylates (2) at 75 °C,⁷⁾ which are generally taken as a reference of the substituent effect on the aryl-assisted *k_Δ* mechanism. There is, in fact, a good linear free energy relationship between both systems with excellent precision (*R*=0.998 and SD=±0.07).

$$\log (k/k_0)_1 = 1.13 \log (k/k_0)_2$$

The excellent linearity with essentially unit slope may lead to the following preliminary conclusions. The reaction mechanism remains essentially unchanged over the range of all substituents, as has already been established for the neophyl acetolysis. The rate-determining transition state of the acetolysis of 2,2-bis(substituted phenyl)ethyl tosylates most probably resembles that of neophyl brosylates. The total substituent effect for the two 2-aryl groups in the diarylethyl system corresponds in size to the effect of the single 2-aryl group in the neophyl system. That is, only one aryl group in the

diarylethyl system is effective in stabilizing the rate-determining transition state, or otherwise the ρ value for the diaryl system is half that for the neophyl one.

Figure 1 shows the Hammett plot for this system. Neither the σ^0 nor the σ^+ plot gives any reasonable single linear correlation. The ρ_m line defined by nonconjugative meta substituted and unsubstituted derivatives passes through the intermediate points between σ^0 and σ^+ for all para π -donor substituents. An application of the LArSR Eq. 1 to the rate at 90.10 °C in Table 1 results in an excellent correlation ($R=0.998$, $SD=\pm 0.077$, and $n=16$);

$$\log k/k_0 = (-4.440 \pm 0.094)(\sigma^0 + (0.526 \pm 0.027)\Delta\sigma_R^+) + 0.006$$

where the substituent parameters used are standard ones as reported previously.⁷⁾ The LArSR plot (squares) in Fig. 1 with an r value of 0.53 is excellently linear, indicating the absence of significant mechanistic change within the range of substituent changes. The intermediate r value associated with a large negative ρ value demonstrates explicitly the existence of direct π -electronic interaction of a conjugatively electron-releasing para group with the reaction center at the rate-determining step. In spite of carrying two aryl groups, both ρ and r values of the diarylethyl system are comparable with those of the neophyl one carrying single aryl. The transition state of 2,2-diarylethyl solvolysis may be most reasonably considered to be a single aryl-assisted structure like that of the neophyl one.

Both the substituent effect and the product analy-

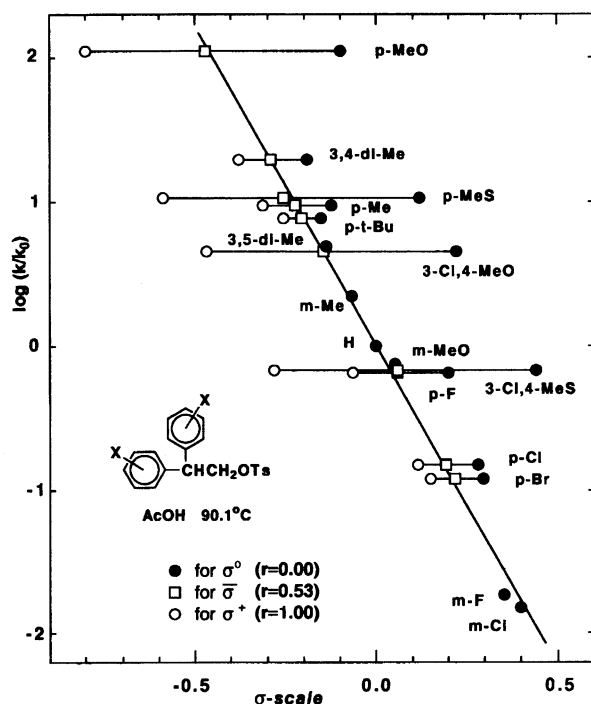


Fig. 1. LArSR plot for acetolysis of 2,2-bis(substituted phenyl)ethyl tosylates at 90.1 °C: Open circles σ^+ , closed σ^0 , and squares $\bar{\sigma}$ for $r=0.53$.

ses manifest that the acetolysis of bis-substituted 2,2-diphenylethyl tosylates proceeds through a k_A process accompanying exclusive aryl migration to give a 1,2-diarylethyl acetate with a small amount of the stilbene as described in Scheme 2. The large negative ρ value and intermediate r value are consistent with the aryl-assisted transition state but not with the two-step mechanism (Scheme 3); a rate-determining ionization step to a primary carbocation, $\text{Ar}_2\text{CHCH}_2^+$ (1_P), followed by the degenerate rearrangement of the 2-aryl group. In the latter mechanism shown in Scheme 3, both aryl groups are structurally prevented by a saturated carbon from π -delocalization interaction with the incipient carbenium center in the transition state. The substituent effect must be of σ^0 -dependence with a fairly small $|\rho|$ value, if the ionization to a primary cation (1_P) is the rate-determining step. To account for the enhanced r value, the second step should be rate-determining, $k_{-1} \gg k_2$. It is, however, highly unlikely that the simple ionization into an unstable primary cation occurs energetically so easily without aryl-assistance, in competition with the rearrangement to a far more stable secondary benzylic cation (1_C); there is no reason to assume the first simple ionization step to be rate-determining.

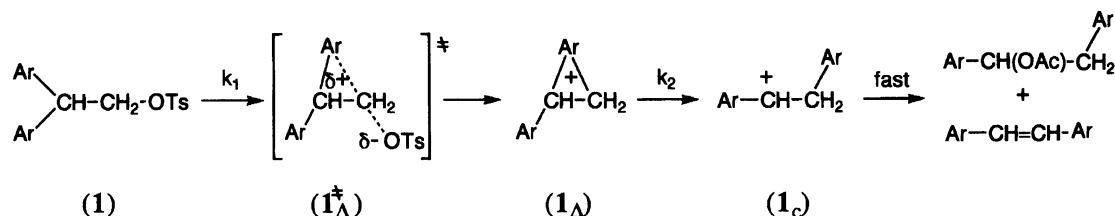
In conclusion, the intermediate r value given for this reaction must be referred to as a coefficient characteristic of the rate-determining step accompanying 2-aryl group migration. This unique r value of 0.5 can be referred to the resonance demand of the ionizing process through an aryl-assisted transition state, and ascribed in turn to the unique mode of resonance stabilization of the transition state distinctly different from that of tertiary benzylic solvolyses giving $r=1.00$. This provides strong support for our LArSR concept of the varying resonance demands.⁷⁾

In this aryl-assisted transition state, the pendant non-migrating aryl group at the 2-position also should exert most probably an additional effect to stabilize or destabilize (indirectly) the transition state. Despite the simplicity of the single reaction pathway in the symmetric diaryl system, the substituent effect cannot be treated directly in terms of the single effect of the assisting aryl group, but should be a sum of the substituent effects of both assisting and unassisting aryls.

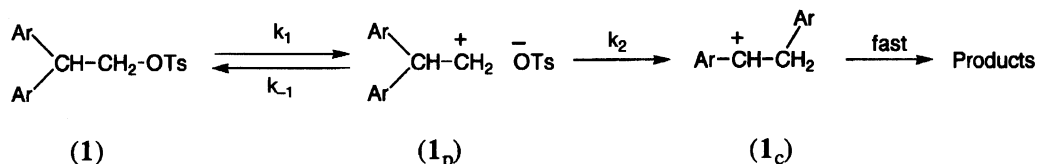
For complete understanding of the substituent effects, it appears necessary to analyze respective substituent effects of assisting and unassisting aryl groups. Unsymmetrically substituted derivatives will be helpful for clarifying this point and this will be the main subject of forthcoming papers.¹¹⁾

Experimental

Materials: Most 2,2-diarylethanol were obtained by a hydroboration-oxidation method from 1,1-diarylethyl-¹²⁾ which were prepared by dehydration of 1,1-diarylethanol, as described in detail before.¹⁾



Scheme 2. Aryl-assisted mechanism.



Scheme 3. Pre-equilibrium mechanism.

1,1-Diarylethanols were synthesized in good yield by the Grignard reaction of either appropriate substituted acetophenones with substituted phenylmagnesium bromides or the substituted benzophenones with methylmagnesium iodide. The crude 1,1-diarylethanols obtained were converted into the 1,1-diarylethylenes by heating at 100–110 °C over potassium hydrogensulfate. 1,1-Diarylethylenes were purified by silica-gel column chromatography or vacuum distillation or recrystallization from appropriate solvents. Most of the electron-releasing aryl derivatives were accompanied by dehydration during the Grignard reaction.

The 2,2-diarylethanols were prepared from 1,1-diarylethylenes by the modified Brown hydroboration-oxidation method.¹²⁾ Sodium borohydride was added to olefin in THF. Boron trifluoride-diethyl ether (1/1) dissolved in THF was added dropwise to the mixture with stirring in an ice bath. After additional stirring for a few hours at room temperature, the reaction mixture was treated with a small amount of water, with aq 10% NaOH, and then with 35% hydrogen peroxide at ice bath temperature, and was stirred for several hours at room temperature. In the case of methylthio derivatives, mild conditions were used, at 0–5 °C for 30 min with 5% hydrogen peroxide, to prevent from oxidation of sulfur. Most 2,2-diarylethanols were oils and were purified through a silica-gel column except 2,2-bis(*p*-*t*-butylphenyl)ethanol (mp 176–177 °C, recrystallized from benzene–hexane).

Several 2,2-diarylethanols were prepared from the reduction of the corresponding diarylacetic acid with LiAlH₄.

2,2-Bis(*m*-methoxyphenyl)ethanol was prepared via the corresponding acid from *m*-methoxybenzaldehyde. The benzoin derivative (mp 52–53 °C, lit,¹³⁾ mp 52.8–55.5 °C, mp 55 °C¹⁴⁾ obtained by benzoin condensation of *m*-methoxybenzaldehyde was oxidized with Fehling's solution to the benzil (mp 82–83 °C, lit,¹⁵⁾ mp 80–82 °C, mp 83 °C¹⁴⁾,^{16,17)} The benzilic acid (mp 106–107 °C, lit,¹⁸⁾ mp 105 °C) was obtained by heating the above benzil in aq KOH.^{16,17)} The bis(*m*-methoxyphenyl)acetic acid was prepared by the reduction of benzilic acid with hydroiodic acid and red phosphorus¹⁹⁾ and was purified through a silica-gel column; mp 85–86 °C.

Diphenylacetic acid was similarly obtained from benzyl-

ic acid,¹⁹⁾ mp 147–148 °C (lit,¹⁹⁾ mp 144–145 °C) and converted into 2,2-diphenylethanol; mp 60–61 °C (lit,²⁾ mp 59.1–59.5 °C).

The bis(*p*-methoxyphenyl)acetonitrile was obtained from anisole and mandelonitrile by the directions of Bistrzycki et al.,²⁰⁾ mp 154–155 °C (lit,²⁰⁾ mp 154.5 °C). 2,2-Bis(*p*-methoxyphenyl)acetic acid, mp 113.8–114.8 °C (lit,²⁰⁾ mp 110–111 °C), was given by hydrolysis of the above nitrile and was reduced to the corresponding alcohol, mp 90–91.5 °C (lit,²¹⁾ mp 85 °C).

According to Burr's procedure,^{5a)} di(*p*-tolyl)acetic acid (mp 142–144 °C (lit,^{5a)} mp 144 °C)) was prepared from ditolylacetonitrile via hydrolysis, and was reduced with LAH to the corresponding alcohol, mp 59–60 °C (lit,^{5a)} mp 51 °C).

Bis(*p*-chlorophenyl)acetic acid (mp 164–166 °C (lit,²²⁾ mp 164–166 °C)) obtained by hydrolysis of 2,2,2-trichloro-1,1-bis(*p*-chlorophenyl)ethane²²⁾ was converted into the alcohol; mp 99.5–102.0 °C (lit,²³⁾ mp 98.5–99.5 °C).

2,2-Bis(*m*-chlorophenyl)ethyl acetate was obtained from the treatment of the corresponding alcohol with acetic anhydride; mp 47–47.8 °C. Found: C, 62.12; H, 4.64%. Calcd for C₁₆H₁₄O₂Cl₂: C, 62.16; H 4.56%.

2,2-Diarylethyl Tosylates. The Tipson procedure²⁴⁾ was used to convert 2,2-diarylethanols into the tosylates. *p*-Toluenesulfonyl chloride was added in several portions to the 2,2-diarylethanol in pyridine at –10––20 °C for a few hours under stirring, and the reaction mixture was kept overnight in a refrigerator. The mixture was treated with ice and cold hydrochloric acid. The precipitates were recrystallized from appropriate solvents. The physical data of tosylates obtained are listed in Table 2.

Solvent: Commercial glacial acetic acid was purified by refluxing for 5 h over KMnO₄ and was distilled, bp 116–118 °C. This fraction was refluxed with an equivalent amount of acetic anhydride to the content of water in the presence of a trace of sulfuric acid and distilled through a 30 cm glass helix-packed column and was collected the constant boiling fraction (bp 118–118.5 °C). The distillate was purified by redistillation through a 90-cm glass helix-packed, vacuum-jacketed still. The purity was estimated to be >99.9% from the freezing point test.

Table 2. Physical and Analytical Data of 2,2-Bis(substituted phenyl)ethyl Tosylates

Subst. X	Mp °C	Carbon/%		Hydrogen/%	
		Found	Calcd	Found	Calcd
<i>p</i> -MeO	41.8—42.6	66.97	66.97	5.86	5.86
3,4-di-Me	69.0—69.7	73.37	73.50	6.96	6.91
<i>p</i> -MeS	68.0—68.5	62.24	62.13	5.33	5.44
<i>p</i> -Me	71.0—72.0 ^{a)}	72.50	72.60	6.47	6.36
<i>p</i> - <i>t</i> -Bu	134.0—135.0	75.20	74.96	7.91	7.81
<i>p</i> -F	104.0—104.5	65.15	64.94	4.75	4.67
3,5-di-Me	130.5—131.5	73.50	73.50	6.92	6.91
<i>m</i> -Me	106.5—107	72.75	72.60	6.36	6.36
H	115.0—116.0 ^{b)}	71.54	71.56	5.71	5.72
3-Cl,4-MeO	120.5—121.5	57.53	57.39	4.71	4.61
3-Cl,4-MeS	77.0—78.0	53.81	53.80	4.33	4.32
<i>m</i> -MeO	16—17	66.96	66.97	5.63	5.86
<i>p</i> -Br	134.5—135.5	49.63	49.43	3.55	3.56
<i>p</i> -Cl	120.5—121.3	59.99	59.87	4.35	4.31
<i>m</i> -F	95.2—96.0	64.99	64.94	4.77	4.67
<i>m</i> -Cl	71.5—72.0	59.86	59.87	4.32	4.31

a) Lit, ^{5a)} mp 72 °C. b) Lit, ²⁾ mp 116 °C, 116—117 °C. ⁶⁾

Sodium acetate (special reagent grade) was dried in vacuo over P₂O₅ on heating immediately before use. The kinetic solvent with 0.022 M sodium acetate was prepared by dissolving the corresponding amount of dried sodium acetate in purified acetic acid in a volumetric flask at 25 °C.

Kinetic Measurements: Acetolysis rates were titrimetrically measured by the usual ampoule technique. Substrate was weighed out and made up to a concentration of 0.02 M in acetic acid buffered with 0.022 M sodium acetate at room temperature. About 11 cm³ portions of the solution were sealed in ampoules. Thirteen sealed ampoules were allowed to react in a thermostatted bath (±0.02 °C). The reaction was stopped at appropriate intervals by immersing an ampoule in an ice bath. At room temperature, a 10 cm³ sample was pipetted out into 25 cm³ of glacial acetic acid and titrated with approximately 0.028 M standard perchloric acid in glacial acetic acid. α -Naphtholbenzein and crystal violet in glacial acetic acid were used for the indicator.

All kinetic runs were followed to about 2.5 half-lives completion and indicated excellent first-order kinetics. All the rate constants were calculated by a least-squares method and uncertainties of duplicated run were estimated to be within 3%.

Product Analysis. The product analysis for the acetolysis of *m*-Cl, *m*-F, and *p*-Cl bis-substituted 2,2-diphenylethyl tosylates was done using a Hitachi Perkin-Elmer R-22 FT ¹³C NMR spectrometer operating at 22.63 MHz and an Iatroscan TH-10 TLC/FID Analyzer (Iatron Lab., Inc.). The 0.02 M solution of the substrate dissolved in acetic acid (50 cm³) buffered with 0.022 M NaOAc was allowed to react over 10 half-lives at 90.10 °C or 135.00 °C in a sealed ampoule. After evaporation of acetic acid under reduced pressure, the residue was extracted with CCl₄, treated in the usual way, dried over MgSO₄ and evaporated. The residue in about 1 cm³ of CCl₄ solution was measured by ¹³C NMR in the pulsed FT mode. For the acetolysis product of 2,2-bis(*m*-chlorophenyl)ethyl tosylate at 135.00

°C, the ratio of 1,2-bis(*m*-chlorophenyl)ethyl acetate to 2,2-bis(*m*-chlorophenyl)ethyl acetate was easily calculated to be 81.7:18.3, from the peak intensities of methylene carbons of both acetates. On the other hand, measurement of stilbene or diphenylethylene suffered from difficulties due to overlapping of the olefin carbon signals to the benzene ring of the final products. The components of acetates and olefin were measured with Iatroscan by the quantitative ionization analysis of separated products on the chromatrod using FID. 2,2-Bis(*m*-chlorophenyl)ethyl and 1,2-bis(*m*-chlorophenyl)ethyl acetates assigned to a low spot were clearly differentiated from a high spot of 3,3'-dichlorostilbene, giving acetates:stilbene=67.3:32.7. There was no spot to be identified with the authentic sample of 1,1-bis(*m*-chlorophenyl)ethylene, of which the *R_f* value was higher than that of stilbene. Combining the products analysis data by the ¹³C NMR and the Iatroscan (TLC), compositions of all the products were calculated to be 1,2-bis(*m*-chlorophenyl)ethyl acetate (54.9%), 3,3'-dichlorostilbene (32.7%), and 2,2-bis(*m*-chlorophenyl)ethyl acetate (12.3%). The products from the competing *k_Δ* pathway were estimated to be 87.7%.

The final acetolysis products of the 2,2-bis(*m*-fluorophenyl)ethyl tosylate at 135 °C was also the rearranged secondary acetate (66.9%), 3,3'-difluorostilbene (23.9%), and 2,2-bis(*m*-fluorophenyl)ethyl acetate (9.2%), giving 90.8% of the *k_Δ* component in overall *k_t*.

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