Substituent Effect Studies of Aryl-Assisted Solvolyses. II.[1] The Acetolysis of 2-Phenyl-2-(substituted phenyl)ethyl *p*-Toluenesulfonates[2]

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The substituent effect on the acetolysis of 2-phenyl-2-(substituted phenyl)ethyl *p*-toluenesulfonates had a nonlinear LArSR correlation and was explicable in terms of a competitive aryl-assisted mechanism involving the X-substituted phenyl-assisted (k_M^X) pathway and the unsubstituted phenyl-assisted (k_N^X) pathway. By the application of the iterative nonlinear least-squares method based on the LArSR Eq., the substituent effect on the overall k_t was dissected into the best-fit k_M correlation of $\rho_M=-3.53$ with $r_M=0.60$, and the k_N correlation of $\rho_N=-0.88$ with σ^0. The ρ_M and r_M values for the effects of assisting aryl substituents are quite close to those of the 2-methyl-2-phenylpropyl system and the small ρ_N value with unexalted σ^0 constant for the unassisting aryls is compatible to the remote β-aryl effect. The relative rates of competing pathways dissected based on the substituent effect analysis agreed completely with the ratio of respective aryl migration products determined by the ^{13}C-tracer method. Exact rate-product correlation demonstrates that this system involves two discrete aryl-assisted pathways, k_M^X and k_N^X, which do not cross over.

In the foregoing papers,[1,3] the substituent effect on the acetolysis of 2,2-bis(substituted phenyl)ethyl tosylates (*p*-toluenesulfonates) was correlated well in terms of the LArSR Eq. 1[4]

$$\log (k/k_0) = \rho\left(\sigma^0 + r\Delta\bar{\sigma}_R^+\right) \quad (1)$$

with an r value of 0.53 and a ρ value of -4.44. The ρ and r values are very close to those for the neophyl (2-methyl-2-phenylpropyl) system,[5] suggesting the close similarity of the transition state of both systems. It was concluded that the driving force of this reaction is the anchimeric assistance by one of the two 2-aryl groups. In the symmetric diaryl system, the substituent effects on the total rates can be directly analyzed as the effect on a single pathway without taking into account competing pathways assisted by both aryls, but no direct evaluation of the assisting aryl effect can be done because the apparent substituent effect on the k_t may involve an additional effect by the unassisting-aryl substituents.

Investigation of the behavior of unsymmetrically substituted derivatives will be indispensable for clarifying respective effects of assisting and unassisting groups. First of all, we have done a study of substituent effects on the acetolysis of 2-phenyl-2-(substituted phenyl)ethyl tosylates as the simplest unsymmetric diaryl system. To analyze the substituent effect, determination of the extent of migration of an aryl group is required for the unsymmetric system and this can be done by product analysis using suitably labeled starting materials. Burr used a ^{14}C tracer to determine the migratory aptitude of tolyl group.[6] In this study, it has been extended by measurement of the ^{13}C label distribution in the acetolysis products from the tosylate labeled with ^{13}C at 2-position using ^{13}C NMR spectroscopy. The mechanism will be discussed in further detail for the acetolysis of 2-phenyl-2-(substituted phenyl)ethyl tosylates on the basis of the kinetic and ^{13}C-tracer studies.

Results and Discussion

Rate constants of acetolysis of 2-phenyl-2-(substituted phenyl)ethyl tosylates (**1**) were measured at 90.10 °C in acetic acid in the presence of 0.022 M (M=mol dm^{-3}) of sodium acetate with initial concentration 0.02 M of tosylates, under the same conditions as in the foregoing papers.[1,3] The rate data are summarized in Table 1 in comparison with the corresponding 2,2-bis(substituted phenyl)ethyl tosylates (**2**).

The acetolysis rate of **1** was effectively enhanced by electron-releasing substituents, to an extent of 100-fold for 4-OCH_2CH_2-3 relative to H, while retarded by electron-attracting ones only to an unexpectedly small extent, 8-fold for H relative to the 3,5-di-Cl substituent. The significantly unequivalent contributions of electron-releasing and attracting classes of substituents in **1** are in sharp contrast to those observed in the symmetric diaryl system **2**. The rate enhancements of electron-releasing derivatives of **2** are approximately twice as large as those of the corresponding 2-phenyl-2-(substituted phenyl)ethyl tosylate **1**; but not the square of the enhancement of the latter. On the other hand, the rates of electron-attracting derivatives are much faster in **1** than in **2**; compared with the relative rate of $k/k_0=0.015$ for $\mathbf{2}_{m\text{-Cl}}$, the rate retardation of $\mathbf{1}_{m\text{-Cl}}$ ($k/k_0=0.25$) is very small or the rate of $\mathbf{1}_{m\text{-Cl}}$ is 15 times faster than $\mathbf{2}_{m\text{-Cl}}$.

The plot of $\log (k/k_0)_1$ vs. $\log (k/k_0)_2$ in Fig. 1 clearly manifests the different characteristics between both sets of reactivities. The smooth-curved correlation appears to be evidence for the mechanistic transition in **1** with substituents, since **2** taken as the reference, the abscissa in Fig. 1, is regarded as a single process with a fixed mechanism. This nonlinear correlation can be attributed to the substituent dependence of competi-

Table 1. Acetolysis Rates[a] of 2-Phenyl-2-(X-substituted phenyl)ethyl Tosylates (**1**)

Substituents X	Temp/°C	(**1**) $10^5 k_t/s^{-1}$	$\Delta H^{\ddagger}$ [b] kcal mol^{-1}	$\Delta S^{\ddagger}$ [b] e.u.	(**2**)[c] $10^5 k_t/s^{-1}$
4-OCH_2CH_2-3[d]	80.00	64.2±0.7			
	75.00	39.4±0.2			
	55.00	4.62±0.05			
	90.10	168.6[e]	23.5	−6.8	
p-MeO	75.00	13.51±0.06			
	90.10	59.0±0.2	23.8	−8.2	174.9
3,4-di-Me	90.10	11.21±0.04			30.51
p-MeS	90.10	9.04±0.09			16.65
p-Me	90.10	6.718±0.104			14.54
p-*t*-Bu	90.10	5.770±0.016			11.99
3-Cl,4-MeO	90.10	4.567±0.033	25.2	−9.5	7.086
	115.00	45.65±0.15			
3,5-di-Me	90.10	3.747±0.15			7.600
m-Me	90.10	2.433±0.009			3.468
H	90.10	1.569±0.015	26.5	−8.0[f]	1.569
	125.00	42.95±0.17			
	135.00	98.2±0.6			
p-F	90.10	1.2685±0.0045			1.010
3-Cl,4-MeS	90.10	1.199±0.003			1.066
3-CN,4-MeO	90.10	0.8631±0.002			
p-Cl	90.10	0.6613±0.0042			0.236
p-Br	90.10	0.606±0.002	26.6	−9.5	0.1856
	135.00	39.06±0.4			
m-Cl	90.10	0.3965±0.005	26.9	−9.7	0.0239[e,g]
	100.00	1.093±0.001			
m-Br	90.10	0.383±0.002	26.8	−10.0	
	135.00	25.32±0.14			
m-CN	90.10	0.2214±0.0012			
p-CN	90.10	0.1991±0.0004			
p-SO_2Me	90.10	0.212±0.0014			
3,5-di-Cl	90.10	0.1856[e]	27.2	−9.4	
	100.00	0.5172±0.003			
	115.00	2.212±0.028			

a) In the presence of 0.022 M NaOAc. b) 1 cal mol^{-1}=4.184 J mol^{-1} and 1 e.u.=4.184 J K^{-1} mol^{-1}. c) 2,2-Bis(substituted phenyl)ethyl tosylates at 90.10 °C. d) 2-(2,3-Dihydrobenzofuran-5-yl)-2-phenylethyl tosylate. e) Extrapolated from other temperatures. f) $\Delta S^{\ddagger}=-9.5$ calculated from $k_t/2$ values. g) Corrected for aryl-assisted rate.

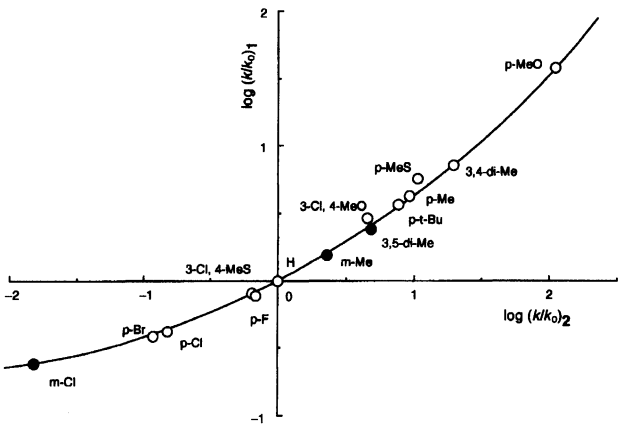


Fig. 1. Plot of log k's of acetolysis of 2-phenyl-2-(substituted phenyl)ethyl tosylate **1** vs. 2,2-bis-(substituted phenyl)ethyl tosylate **2**.

tion of two pathways with the anchimeric assistance of either an unsubstituted or substituted phenyl ring in **1**.

Figure 2 shows the substituent effect on the acetolysis of **1** in reference to σ^0, σ^+, and $\bar{\sigma}$ (denoted by $\bar{\sigma}_\Delta$) derived from the acetolysis of neophyl brosylates (*p*-bromobenzenesulfonates) which corresponds to $r=0.57$ in the LArSR Eq. 1. While no linear relationship is obtained with any conventional sets of substituent constants, the neophyl $\bar{\sigma}_\Delta$ can only provide a single smooth curve plot without any serious deviation. This can be explained by substituent dependent competition of two aryl assisted pathways assisted by substituted and unsubstituted aryls, respectively, as in Scheme 1. Sufficiently electron-releasing substituents tend to enter themselves into anchimeric assistance, more effectively stabilizing the transition state, and such compounds react predominantly by the X-substituted phenyl-assisted (k_M^X) pathway. In this case, the apparent rates indicate the substituent effect of assisting aryl group on the k_M^X

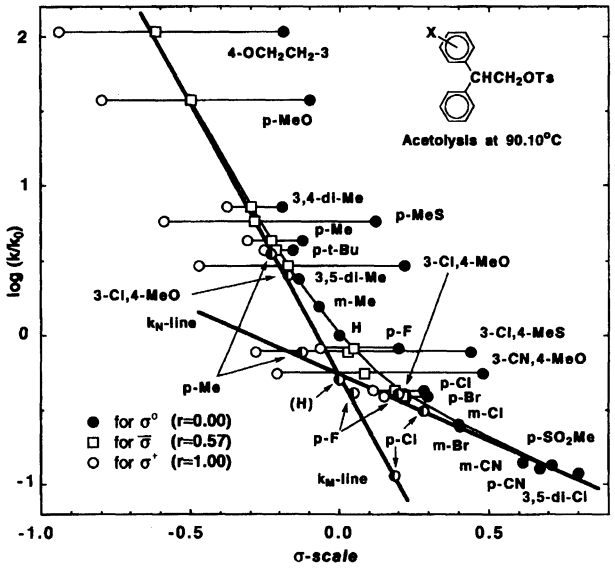


Fig. 2. LArSR plot for acetolysis of 2-phenyl-2-(substituted phenyl)ethyl tosylates: Open circles σ^+, closed σ^0, squares $\bar{\sigma}_\Delta$ (for $r=0.57$), and half-closed circles for k_M^X and k_N^X based on product analysis.

pathway. On the other hand, when the substituents are sufficiently deactivating, the unsubstituted phenyl tends to anchimerically assist predominantly and the reaction proceeds through the unsubstituted phenyl-assisted pathway (k_N^X). The apparent solvolysis rates for such compounds, therefore, expose the substituent effect of unassisting aryls on the k_N^X pathway.

As a simple analysis the following graphical interpretation with the aid of reasonable assumptions appears to be convenient and useful to recognize the characteristics of the substituent effects on this system. Since the apparent rate k_t is a sum of the rates for two pathways, $k_t^X = k_M^X + k_N^X$, where suffixes M and N represent the X-substituted phenyl migrating and the X-phenyl nonmigrating, respectively, the substituent effect on the k_t is described by

$$\log\left(k_t^X/k_t^H\right) = \log\left(k_M^X/k_M^H\right) + \log\left(1 + k_N^X/k_M^X\right) + C_M \quad (2)$$

or

$$\log\left(k_t^X/k_t^H\right) = \log\left(k_N^X/k_N^H\right) + \log\left(1 + k_M^X/k_N^X\right) + C_N \quad (3)$$

where C_M and C_N are constants referred to $\log(k_M^H/k_t^H)$ and $\log(k_N^H/k_t^H)$, respectively, and are -0.30 since $k_M^H = k_N^H = k_t^H/2$. For only extreme cases where the second terms on the right-hand side are neglected, a single Hammett relation for the k_M^X or k_N^X pathway may be obtained with k_t values against appropriate sets of substituent constants; for the k_M^X pathway ($k_M^X \gg k_N^X$)

$$\log\left(k_t^X/k_t^H\right) = \rho_M\bar{\sigma}_M - 0.30 \quad (4)$$

and for the k_N^X pathway ($k_N^X \gg k_M^X$)

$$\log\left(k_t^X/k_t^H\right) = \rho_N\bar{\sigma}_N - 0.30 \quad (5)$$

To the k_N correlation that refers to the substituent effects of the unassisting aryl groups, unexalted σ^0 or σ may be reasonably applied as an appropriate set $\bar{\sigma}_N$, but to the k_M correlation which refers to the substituent effects of the assisting aryl group, an enhanced resonance set of σ^+ type substituent constants should be applied. As generally observed for aryl-assisted solvolysis reactivities, the $\bar{\sigma}_\Delta$ set derived from the neophyl acetolysis would be most suitable to this system. In fact, the k_t correlation against the neophyl $\bar{\sigma}_\Delta$ gave a smooth concave plot converging to both correlation lines at either the activating or deactivating end as shown in Fig. 2, but instead the use of the conventional σ^+ for $\bar{\sigma}_M$ does not give any reasonable smooth correlation curve. As the second term on the right-hand side in Eq. 2 may be practically insignificant for substrates giving $k_N^X/k_M^X < 0.2$, i.e., $\log(1 + k_N^X/k_M^X) < 0.09$, more activating derivatives than p-Me in practice satisfy the liner k_M correlation. On the other hand, less reactive substrates than m-Cl derivative satisfy the linear k_N correlation as the second term in Eq. 3 becomes insignificant; $k_M^X/k_N^X < 0.2$. Both correlation lines intersect at the point 0.3 log-unit below the unsubstituted point in Fig. 2 (plotted as a half-closed circle), because $k_N^H = k_M^H$. Although substrates with comparable k_M^X and k_N^X values may follow either $\bar{\sigma}_M$ or $\bar{\sigma}_N$ set, one can define without difficulties the k_M and k_N correlations for this system as the lines crossing at -0.30 at $\sigma^0 = 0$ and converging to the k_t curve at either the activating or deactivating end as shown in Fig. 2. The ρ values for these correlations are estimated as a good approximation to be -3.5 for the k_M pathway and -0.8 for the k_N pathway.

We have done a precise dissection of the apparent substituent effect on overall k_t into two individual effects on the composite pathways. If the two pathways are completely non-crossover, the substituent effect on each pathway should be described in terms of the LArSR Eq. 1. For the k_M pathway,

$$\log\left(k_M^X/k_M^H\right)_1 = \rho_M\left(\sigma^0 + r_M\Delta\bar{\sigma}_R^+\right) \quad (6)$$

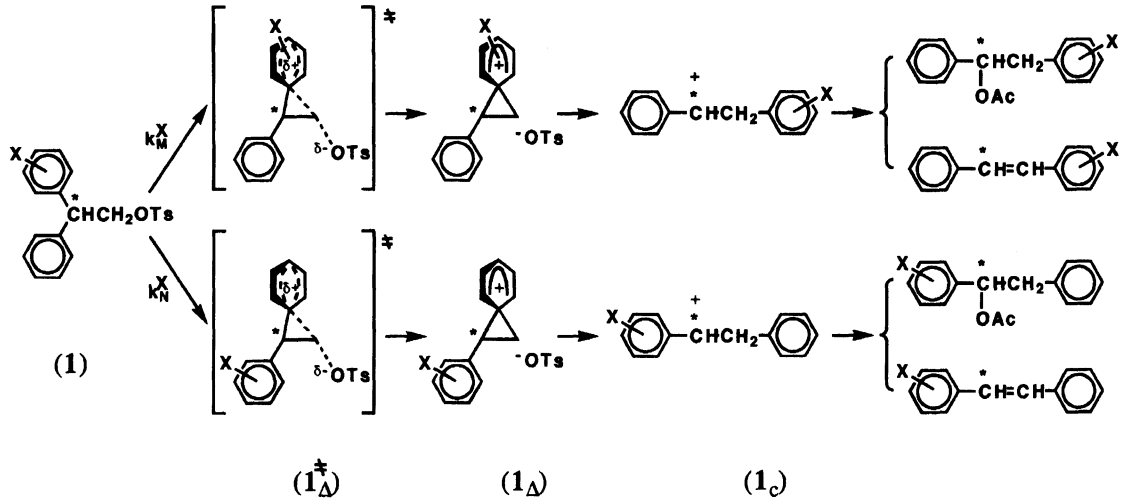
and for the k_N pathway,

$$\log\left(k_N^X/k_N^H\right)_1 = \rho_N\left(\sigma^0 + r_N\Delta\bar{\sigma}_R^+\right) \quad (7)$$

Since $k_t^X = k_M^X + k_N^X$, the apparent rates are given by

$$k_t^X = k_M^H 10^{\rho_M(\sigma^0 + r_M\Delta\bar{\sigma}_R^+)} + k_N^H 10^{\rho_N(\sigma^0 + r_N\Delta\bar{\sigma}_R^+)} \quad (8)$$

The ρ and r values for each process may be determined statistically by an iterative calculation using the nonlinear least-squares Gauss–Newton method,[7—9] which is based on minimizing the residual sum (SS) of the



Scheme 1. Acetolysis scheme of 2-phenyl-2-(substituted phenyl)ethyl tosylate.

squares of the differences between observed and calculated k_t values.[9]

$$SS = \sum W\,(k_t(\text{obsd}) - k_t(\text{calcd}))^2$$

where W $(=1/(k_t(\text{obsd}))^2)$ is the weight of rate data. Since extensive data of the acetolysis rates have been measured in this study, substituents involved in this correlation satisfy the minimal basis set requirement for the LArSR correlation analysis, i.e., the minimal requirement of entire nonlinearity (or a high degree of randomness) between σ^0 and $\Delta\bar{\sigma}_R^+$.[5b,10] The application of the iterative nonlinear least-squares method to the set of apparent k_t of **1** in Table 1 results in the following correlations for the k_M and k_N pathways:

$$\log\left(k_M^X/k_M^H\right) = (-3.53 \pm 0.06)\left(\sigma^0 + (0.60 \pm 0.01)\,\Delta\bar{\sigma}_R^+\right)$$

and

$$\log\left(k_N^X/k_N^H\right) = (-0.88 \pm 0.03)\,\sigma^0$$

The substituent parameters used are taken from the previous paper.[5] The combined correlation reproduces the $\log(k_t^X/k_t^H)_1$ values with excellent precision (SD= ±0.03). The substituent effect on the k_N process was treated simply with σ^0, to reduce the number of variables in Eq. 8, based on an assumption that the process should involve no significant π-interaction between the aryl group and the reaction center ($r_N=0$). Furthermore, the result of this analysis is virtually identical with the result ($\rho_\Delta=-3.66$ and $r_\Delta=0.58$ for k_M correlation and $\rho=-0.86$ for k_N^X one) with $\bar{\sigma}_N$ fixed as σ scale ($r=0.26$). The r_M value for the aryl-assisted k_M process is found to be quite close to that of the neophyl system.[5] These results lend support to the assumption used for the graphical analysis that the $\bar{\sigma}_\Delta$ value of $r=0.57$ can be used as a reference resonance demand scale for the aryl-assisted pathway. A small $|\rho_N|$ value is reasonable for a fairly remote distance from the carbocationic reaction center. These best-fit correlation lines for both k_M and k_N processes are drawn in Fig. 2.

The excellent correlation provides strong support for the mechanism (in Scheme 1) of the acetolysis of the 2,2-diarylethyl system proceeding through competitive two non-crossover k_Δ pathways. The reaction consists of the major contribution from assisting-aryl with a minor contribution from unassisting-aryl. It is concluded that the energetic contribution from the secondary carbocation intermediate ($\mathbf{1_c}$) next to the phenonium intermediate is not important in the rate-determining step.

The symmetric diaryl system **2** will provide a good test for the elucidation as the sum of two different substituent effects on a single pathway with single transition state. The rate of the single k_Δ process may be given as a good approximation by a product $f_M f_N$ of partial rate contribution factors of assisting and unassisting aryls, f_M and f_N, respectively. The substituent effect of symmetric **2** can be described as follows.

$$\log\left(k_t^X/k_t^H\right)_2 = \log f_M^X f_N^X / f_M^H f_N^H$$

Then, provided no interaction between f_M and f_N,

$$\log\left(k_t^X/k_t^H\right)_2 = \log f_M^X f_N^H / f_M^H f_N^H + \log f_M^H f_N^X / f_M^H f_N^H \quad (9)$$

The first term on the right-hand side of Eq. 9 corresponds to the substituent effect for the aryl-assisted pathway, and the second term to the substituent effect for the aryl-unassisted pathway of 2-aryl-2-phenylethyl tosylates **1**. Therefore,

$$\log\left(k_t^X/k_t^H\right)_2 = \log\left(k_M^X/k_M^H\right)_1 + \log\left(k_N^X/k_N^H\right)_1 \quad (10)$$

Substituting the k_M and k_N correlations for **1** into Eq. 10, can an approximate LArSR correlation be derived for symmetric 2,2-diarylethyl system **2**.

$$\log\left(k_t^X/k_t^H\right)_2 = -3.53\left(\sigma^0 + 0.60\Delta\bar{\sigma}_R^+\right) - 0.88\sigma^0$$
$$= -4.41\left(\sigma^0 + 0.48\Delta\bar{\sigma}_R^+\right)$$

or

$$= -3.66\left(\sigma^0 + 0.58\Delta\bar{\sigma}_R^+\right) - 0.86\left(\sigma^0 + 0.26\Delta\bar{\sigma}_R^+\right)$$
$$= -4.52\left(\sigma^0 + 0.52\Delta\bar{\sigma}_R^+\right)$$

A fairly good agreement of the ρ and r values with apparent values, $\rho=-4.44$ and $r=0.53$, for **2** reported in the foregoing paper[1,3] lends strong support for the adequacy of our assumption of the additivity of individual effects of assisting and unassisting aryls on the apparent rate of single aryl-assisted process of symmetric 2, 2-diarylethyl system **2**. The minor discrepancy of both ρ and r values can be attributable to the minor but not negligible deviation from the exact additivity of substituent effects, or more probably to the inadequacy of the use of either fixed σ^0 or σ reactivity for the unassisting aryl effect.

This additivity analysis is to a first approximation applied to the dissection of apparent rates of the unsymmetric system **1** into respective pathways. Only given the sets of apparent k_t values, $(k_t^X)_2$, $(k_t^H)_2$, and $(k_t^X)_1$, the simple additivity method can be used to estimate the rates, k_M^X and k_N^X, of composite aryl-assisted pathways in the unsymmetric system **1** without aid of substituent $\bar{\sigma}$ parameters. In the aid of partial rate contribution of $f_M f_N$,

$$\left(k_t^X\right)_1 = k_M^X + k_M^H = f_M^X f_N^H + f_M^H f_N^X$$
$$= f_M^X f_N^X / \left(f_N^X/f_N^H\right) + f_M^H f_N^H \left(f_N^X/f_N^H\right) \quad (11)$$

Since $f_M^X f_N^X = (k_t^X)_2/2$ and $f_M^H f_N^H = (k_t^H)_2/2$, Eq. 11 is rewritten by a quadratic equation with $P = f_N^X/f_N^H$ as the variable.

$$\left(k_t^H\right)_2 P^2 - 2\left(k_t^X\right)_1 P + \left(k_t^X\right)_2 = 0 \quad (12)$$

The equation can be solved for P to give the estimated rates of k_M^X and k_N^X for **1**:

$$k_M^X = f_M^X f_N^H = \left(k_t^X\right)_2/2P \text{ and } k_N^X = f_M^H f_N^X = \left(k_t^H\right)_2 \times P/2 \quad (13)$$

The dissected rates for composite pathways agree well with those according to the iterative least-squares method as compared in Table 2.

In this approximation, it should be mathematically impossible to differentiate between the migrating and non-migrating substituents. Nevertheless, it can virtually be assigned based on the fact that the non-migrating group exerts main contribution to the k_M rate. For typical derivatives in the substituted phenyl system, the validity of the dissection method must be tested by comparing with other experimental values.

Table 2. Summary of Dissection of Rates into X-Substituted Phenyl-Assisted (k_M^X) and X-Substituted Phenyl-Unassisted (k_N^X) Pathways of 2-Phenyl-2-(X-substituted phenyl)ethyl Tosylates[a]

X	k_M^X		k_N^X	
	$10^{-5}/s^{-1}$			
	Additivity[a]	LArSR[b]	Additivity[a]	LArSR[b]
p-MeO	57.8	57.1	1.19	1.01
3,4-di-Me	10.0	9.89	1.20	1.22
p-MeS	8.25	10.0	0.792	0.648
p-Me	5.72	5.64	0.997	1.06
p-*t*-Bu	4.79	4.74	0.982	1.13
3-Cl,4-MeO	3.84	4.04	0.723	0.529
3,5-di-Me	2.60	2.53	1.146	1.09
m-Me	1.56	1.45	0.871	0.949
p-F	0.554	0.591	0.715	0.551
3-Cl,4-MeS	—[c]	0.783	—[c]	1.12
p-Cl	0.201	0.190	0.460	0.468
p-Br	0.165	0.152	0.441	0.454
m-Cl	0.025	0.032	0.371	0.368

a) Based on simple additivity rule of rate constants; calculated by Eq. 13. b) Based on LArSR substituent effect analysis; calculated by the iterative least-squares method based on Eq. 8 with fixed $r_N=0.0$. c) Mathematically unsolved (see Text).

For verifying the dissection of the overall substituent effect into the two components for the k_N and k_M pathways, these results have been compared with those obtained by a method completely independent of kinetic analysis. The mechanism proposed for this reaction will be further established by the fact that the migratory aptitude of each aryl group is parallel with its enhancement of acetolysis rate. If the products are kinetically controlled ones, the apparent k_t can be dissected on the basis of migratory aptitude from the product analysis into the composite rates.

$$k_M^X = \left(k_t^X\right)_1 \times (\%\text{X-phenyl migration}/100)$$
$$k_N^X = \left(k_t^X\right)_1 \times (\%\text{phenyl migration}/100) \quad (14)$$

In this study the product analysis has been done by using the ^{13}C-tracer analysis method for representative substituted phenyl derivatives. The 2-phenyl-2-(substituted phenyl)ethyl-2-^{13}C labeled tosylates in the presence of 0.022 M NaOAc in acetic acid were allowed to react at 90.1 °C for more than ten half-lives, and the ^{13}C-label distributions in the resultant products have been measured by ^{13}C NMR spectroscopy. The products were exclusively aryl-migrated ones, 1,2-diarylethyl acetates and stilbenes (see Table 5 in Experimental). The migratory aptitudes calculated based on the peak intensities of enriched ^{13}C signals are summarized in Table 3 together with the estimated values of previous calculations based on the substituent effect analysis by

Table 3. The %Migration of X-Substituted Phenyl in the Acetolysis of 2-Phenyl-2-(X-substituted phenyl)ethyl Tosylates (**1**)

Substituent	Percent migration of X-substituted phenyl group		
	Product[a)]	LArSR[b)]	Additivity[c)]
p-MeO	100%	98.3(97.6)%	98.2%
p-Me	82.1%	84.2(83.5)%	84.6%
3-Cl,4-MeO	86.8%	88.4(83.1)%	84.2%
p-F	50.7%	51.8(46.6)%	45.8%
p-Cl	27.0%	28.8(25.2)%	30.7%

a) Product analysis by the ^{13}C-tracer method using ^{13}C NMR spectroscopy (see Experimental). b) $100\times(k_M^X/(k_t^X)_1)$ based on the iterative least-squares method; according to Eq. 8 with fixed $r_N=0.0$ and values in parenthesis with $r_N=0.26$. c) $100\times(k_M^X/(k_t^X)_1)$ based on additivity of rate constants between **1** and **2** systems by Eq. 13.

Eq. 8 and also based on the simple additivity of apparent rates by Eq. 13.

The ratios of aryl migration should be identical to the rate ratios of competing pathways given by the statistical rate analysis. The calculated migration ratios, k_M^X/k_N^X, based on two kinetic analysis methods are in good agreement with experimental ratios from the ^{13}C-tracer product analysis. The ratios from product analysis (Eq. 14) are in better agreement with those from the substituent effect analysis (Eq. 8) than with those from the simple additivity method (Eq. 13), indicating a certain higher order interaction between the substituent effects of the assisting and unassisting aryls. Furthermore, the product ratio in Table 3 may be in close agreement with the corresponding ratios based on the substituent effects using σ^0 as $\bar{\sigma}_N$ rather than with those using σ or even better with that using an average of both parameters. However, the discrepancy or the precision in the logarithmic scale is all within experimental uncertainty.

The product-derived k_M^X and k_N^X values for *p*-Me, (3-Cl,4-MeO), *p*-F, and *p*-Cl derivatives all fall on the respective correlation lines including the points for an unsubstituted one (statistically corrected) as shown by half-closed circles in Fig. 2. In this figure, *m*-Cl, 3,5-di-Cl, and *p*-SO_2Me derivatives are assumed to proceed exclusively through the single (k_N^X) pathway of unsubstituted phenyl migration, to fall on the k_N correlation line. The effects of non-migrating groups are correlated with either σ^0 or σ, implying insignificant electrophilic resonance exaltation, and are just what would be expected for the substituent effect of the unassisting aryl groups at the β-carbon in the phenonium-like transition state ($\mathbf{1}_\Delta^\ddagger$) in Scheme 1. This is consistent also with the negligibly small β-deuterium isotope effect observed for the acetolysis of 2,2-diphenylethyl tosylate.[11)]

In conclusion, the complete agreement between the ratio of aryl-migration products and the relative rate of the competing pathways strongly supports our mechanistic analysis based on dissection of the substituent effects on overall k_t into two composite rates. Further, it is concluded that these solvolyses involve two discrete pathways, k_M^X and k_N^X, which do not cross over. This agreement of experimental migratory aptitudes with the calculated values based on either Eq. 8 or Eq. 13 further manifests that the assumption of the additivity of both substituent effects is practically valid, confirming the simple linear rate-product relationship in the acetolysis of 2,2-diarylethyl tosylates. The dissection of the apparent rate can be used as a precise approximation to analyzing the 2,2-diarylethyl systems where the product analysis is not available.

It should be noted, however, that the calculation based on Eq. 13 sometimes fails to give a proper solution. Simple solutions could not be arrived at in several cases due to a negative figure in the square root in the solution of P in Eq. 12 (e.g., for $\mathbf{1}_{3\text{-Cl,4-MeS}}$ in Table 2). The reason may of course arise from experimental error in the rate data, and also from a finite divergence from simple additivity arising as a result of cross-interaction of substituent effects between assisting and unassisting aryls. The independence of f_M and f_N may not hold very precisely but does only approximately as described above. This point will be discussed in detail in a following paper[12)] for a wide range of substituent changes in the unsymmetrically disubstituted systems. Nevertheless, deviations from the simple additivity are in most cases not very serious, as shown by the good agreement with the product analysis in Table 3, and this approximation based on Eq. 13 is a convenient method to dissect the overall k_t value to the rates for respective pathways in an unsymmetric system.

These results indicate that the reactivity is controlled predominantly by assisting aryls, implying that the aryl-assisted ionizing step is to be rate-determining. The contribution from the unassisting group should be attributed to an additional effect on this aryl-assisted transition state, because of the small ρ_N value with σ^0. There appears to be no contribution from the stability of an intermediate secondary cation, because the substituent effect on benzylic cation stability should result in σ^+-fit ($r\fallingdotseq 1$) with a large negative ρ value (about -4) for the effect of unassisting groups but not of assisting groups.

Table 4. Physical Data of 2-Phenyl-2-(X-substituted phenyl)ethyl Tosylates

Substituent X	Mp/(°C)	Carbon/%		Hydrogen/%		Nitrogen/%	
		Found	Calcd	Found	Calcd	Found	Calcd
4-OCH_2CH_2-3	78.5—79.5	70.04	70.03	5.71	5.62		
p-MeO	82—83	69.18	69.09	5.83	5.80		
p-MeS	95.5—96.0	66.37	66.30	5.58	5.56		
p-*t*-Bu	71.0—72.0	73.61	73.50	6.98	6.91		
3,4-di-Me	116.0—117.0	72.60	72.60	6.43	6.36		
3,5-di-Me	113.5—114.5	72.56		6.35			
3-Cl,4-MeO	105.5—106.5	63.45	63.38	5.10	5.08		
3-Cl,4-MeS	101.0—102.0	61.02	61.03	4.95	4.89		
3-CN,4-MeO	93—96.0	67.79	67.79	5.28	5.20	3.39	3.44
p-Me	108.6—109.4[a]	72.10	72.03	6.05	6.11		
m-Me	113.0—113.9	72.19		6.04			
p-Br	109.0—110.0	58.45	58.48	4.52	4.44		
m-Br	73.5—74.5	58.42		4.46			
p-CN	122.5—123.0	70.04	70.01	5.17	5.07	3.72	3.71
m-CN	89.5—90.5	69.93		5.19		3.65	
p-F	102.5—103.0	67.99	68.09	5.16	5.17		
p-Cl	101.5—102.5	65.17	65.19	4.96	4.95		
m-Cl	52.0—52.5	65.19		4.96			
3,5-di-Cl	136.5—137.0	59.87	59.86	4.24	4.31		

a) Lit,[6] mp 106 °C.

Table 5. Acetolysis Products of 2-Phenyl-2-(substituted phenyl)ethyl-2-^{13}C Tosylate[a]

Mode	Ar*CHCH$_2$Ph (OAc)	Ph*CHCH$_2$Ar (OAc)	[%Acetates][b]	Ar*CH=CHPh	Ph*CH=CHAr	[%Stilbenes][c]
Ar=*p*-Methoxyphenyl						
CW	0%	100%	[88%]	0%	100%	[12%]
		(57.65)			(106.74)	
Ar=3-Chloro-4-methoxyphenyl						
CW	12.6%	87.4%				
FT	13.2%	86.8%	[87.5%]			[12.5%]
	(55.22)	(55.91)		(106.96)	(107.92)	
Ar=*p*-Methylphenyl						
CW	18.0%	82.0%	[82.0%]	17.7%	82.3%	[18.0%]
FT	17.9%	82.1%	[84.5%]	16.0%	84.0%	[15.5%]
	(57.38)	(57.57)		(108.89)	(107.89)	
Ar=*p*-Fluorophenyl						
CW	49.3%	50.7%				
FT	45.2%	54.8%	[82.4%]	46.0%	54.0%	[17.6%]
	(55.91)	(55.40)		(108.55)	(107.32)	
Ar=*p*-Chlorophenyl						
CW	72.0%	28.0%	[75.6%]	72.3%	27.7%	[24.4%]
FT	73.0%	27.0%	[84.9%]	72.2%	27.8%	[15.1%]
	(56.60)	(57.05)		(107.49)	(109.68)	

a) Initial concentration of 0.02 M of ^{13}C enriched tosylates in AcOH buffered with sodium acetate of 0.022 M. b) %Yield of total acetates. c) %Yield of total stilbenes. d) The numbers in parentheses are ^{13}C chemical shift of asterisk carbon (enriched carbon) in ppm down-field from $*CH_3COOH$ (δ=20.6 from TMS).

Experimental

Materials: The 2-aryl-2-phenylethanols were prepared from 1,1-diphenylethylenes by the hydroboration-oxidation method[13] as described in our foregoing papers.[1,3] 2-Cyanophenyl-2-phenylethanols were prepared from the corresponding bromo compounds by refluxing with CuCN in DMF by the Friedman and Shechter procedure.[14] Most derivatives were purified through a silica-gel column. 2-(*p*-*t*-Butylphenyl)-2-phenylethanol (mp 82 °C; lit,[15] mp 82 °C) and 2-(*p*-cyanophenyl)-2-phenylethanol (mp 94.5—95 °C) were recrystallized from benzene–hexane.

2-Aryl-2-phenylethanols were converted into the tosylates by the Tipson procedure[16] and were recrystallized from appropriate solvents. The physical data for tosylates are listed in Table 4.

^{13}C-Labeled Compounds: Substituted benzophenones-carbonyl-^{13}C were synthesized by the Friedel–Crafts reaction of benzoyl-carbonyl-95%-^{13}C chloride with appropriate substituted benzenes in CS_2. *p*-Chlorobenzophenone-

carbonyl-^{13}C was obtained from *p*-chlorobenzoyl-carbonyl-^{13}C chloride. 1-Aryl-1-phenylethylenes-1-^{13}C were prepared by the dehydration with $KHSO_4$ from 1-aryl-1-phenylethanols-1-^{13}C, which were synthesized by the Grignard reaction of the substituted benzophenones-carbonyl-^{13}C with methylmagnesium iodide in the same way as for nonlabeled compounds.

The 2-aryl-2-phenylethanols-2-^{13}C prepared from 1,1-diphenylethylenes-1-^{13}C by the hydroboration-oxidation method[13] were converted into the 2-^{13}C labeled tosylates, recrystallized from benzene–hexane; *p*-MeO derivative, mp 83.0—83.5 °C; *p*-Me, mp 107 °C; 3-Cl,4-MeO, mp 117—118 °C; *p*-F, mp 102—103 °C; *p*-Cl, mp 102 °C.

Solvent: Commercial glacial acetic acid was purified as described before.[1,3] The purity was estimated to be >99.9% from the freezing point test. Acetolysis solvent with 0.022 M sodium acetate was prepared from this purified acetic acid and dried sodium acetate (special reagent grade) using a volumetric flask at 25 °C.

Kinetic Measurements: Acetolysis rates were titrimetrically measured by the ampoule technique as described in the foregoing papers.[1,3] All kinetic runs were followed to 2.5 half-lives reaction and indicated excellent first-order behavior. All the first-order rate constants were reproducible from repeated run within 3%.

Product Analysis. ^{13}C-Labeled 2-phenyl-2-(substituted phenyl)ethyl tosylates (0.1 M) in acetic acid containing of 0.12 M sodium acetate were sealed in an 8-mm diameter NMR tube and were allowed to react for an appropriate time at 90.10 °C in a thermostatted bath. The reaction was stopped by rapid cooling and the ^{13}C NMR spectrum was recorded at 35 °C. Rates estimated from the ^{13}C NMR measurement agree well with the titrimetric one. The reaction was followed over ten half-lives and the migrating product composition was found to be constant for the whole reaction. The precise product composition was analyzed after longer than 10 half-lives of the reaction under the same conditions as rate measurements. In the sealed ampoule, the 0.02 M solution of ^{13}C-labeled tosylates in acetic acid (50 cm^3) buffered with 0.022 M NaOAc was allowed to react over 10 half-lives at 90.10 °C in a thermostatted bath. After evaporation of acetic acid under reduced pressure, the residue was dissolved in CCl_4. The CCl_4 extract was washed with 10% aq $NaHCO_3$, sat. NaCl, dried over $MgSO_4$, and evaporated. The residue in about 1 cm^3 of CCl_4 was used for the ^{13}C NMR measurement.

The proton-decoupled ^{13}C NMR spectra were obtained by using a Hitachi Perkin–Elmer R-22 FT NMR Spectrometer operating at 22.63 MHz.[17] The peak intensities of acetolysis products were measured under the conditions of data point 16K and sweep spectral width 200—20 ppm using a HITAC-10II computer.[17] The results are summarized in Table 5. Most peak intensities were considered to be proportional to the product concentration within the two similar labeled carbon atoms of secondary acetates or within the olefinic carbons of the stilbene in the present tracer study. However, the ^{13}C label peaks of the *p*-F derivative became broad due to long-range coupling with *p*-F atom. Therefore, the two peaks of the alkyl carbons of migrating acetates were also accumulated in CW mode under the conditions of sweep time 25 s for sweep width 40 Hz. Except for *p*-F, the ratios of peak intensities obtained by the CW mode agreed with those by FT mode within experimental error. The ratios of migrated acetates obtained in CW mode for *p*-F were used to give better result for the dissection of apparent rates. The ratio of peak intensities of the olefin carbons of stilbene was less reliable than that of acetate because the former was a minor component and their peaks overlapped the peaks of benzene ring carbons of natural abundance but was in satisfactory agreement with the value obtained from the migrated acetates. All data of ^{13}C-label distribution were summarized in Table 5.

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