The Substituent Effect. XII. Solvolysis of 3'- and 4'-Substituted 1-(4-Biphenylyl)ethyl Chlorides

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Rate constants of solvolysis of 3'- and 4'-substituted 1-(4-biphenylyl)ethyl chlorides were measured in 80% (v/v) aqueous acetone. The effect of substituents could be correlated excellently with the LArSR relationship.

$$\log k/k_0 = -1.56(\sigma^0+0.84\Delta\bar{\sigma}_R^+)$$

The ρ and r^+ values are smaller than those in the corresponding phenyl system under identical conditions ($\rho=-4.95$, $r^+=1.15$). The difference of the r^+ values is interpreted in terms of twisting of the two phenyls around the pivot bond in biphenyl. The same treatment has been applied successfully to other sets of reactivity data; solvolysis, protodesilylation, alkaline hydrolysis, and piperidinodebromination. The results indicate a consistently reduced effectiveness of *pi*-electronic transmission in biphenylyl relative to phenyl system in all reactions studied.

In our continuing interest in substituent effects, the LArSR relationship, Eq. 1,[1,2] has been investigated in order to apply it to reactivities for the *pi*-systems beyond the phenyl system; extensive rate studies have already been performed in the solvolysis of substituted 1-phenylethyl chlorides.[2]

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

In the substituted 1-naphthyl system,[3] the substituent effect was successfully separated into a reaction-independent inductive (*I*) effect and a reaction-dependent *pi*-electronic (*Pi*) effect.

To check the general applicability of the LArSR Eq. 1 to substituent effects in the biphenylyl system and to compare the resulting substituent-effect parameters with those of the corresponding phenyl system,[2] we have studied the solvolysis of 3'- and 4'-substituted 1-(4-biphenylyl)ethyl chlorides. The present paper discusses (i) the LArSR treatment for the biphenylyl reactivities, where the different types of electrophilic and nucleophilic reactions available[4a] are included, and (ii) the comparisons of the resulting parameters with those obtained in the phenyl systems under the same conditions. These results must reflect the characteristic features of the intervening biphenylyl *pi*-system between substituents and the reaction center.

Results and Discussion

Rate constants for the solvolysis of nine 3'- and 4'-substituted 1-(4-biphenylyl)ethyl chlorides were determined in 80% (v/v) aqueous acetone at convenient temperatures to give moderate rates which were followed with the usual acid-base titration method. All kinetic runs followed accurately the first-order kinetic law. The reproducibility of the rate constants from repeated runs was within ±1.5%. The 4'-substituted derivatives were confirmed to be of 99—100% purity, based on their infinity readings, while the 3'-halogeno derivatives, which were used for kinetic measurements immediately after the evaporation of solvent and without purification, were estimated to be of *ca.* 97% purity.

The rate constants at various temperatures and the relative rates with respect to substituents are listed in Table 1,[4b] together with the activation parameters. The activation entropies obtained are quite constant at -11.8 ± 1.5 eu (10.7 ± 0.3 log A unit) over the range of substituent, suggesting the operation of a constant mechanism throughout the series.[2] Logarithms of the relative rates at 45 °C are linearly correlated in excellent precision (corr coeff, $r=0.9997$, $s=\pm0.016$) with those at 25 °C, giving a slope of 0.950. The temperature change provides a negligibly small effect on the ρ value with a change of only a few percent. As anticipated from the intervention of the second phenyl group between substituents and the reaction center, apparent substituent effects in the biphenylyl system are much smaller than those in the corresponding phenyl system, for the electronic effects of substituents are transmitted across a longer distance or a larger number of bonds to the reaction center.

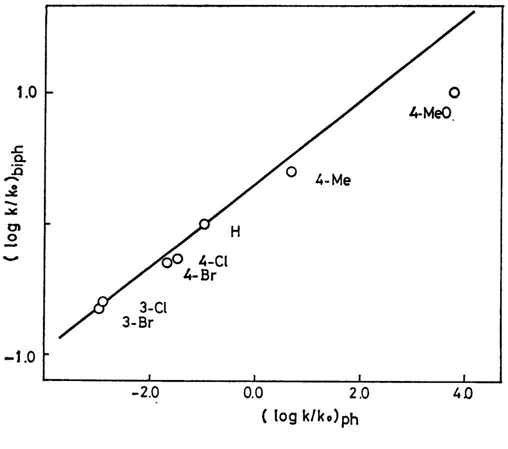

Fig. 1. The log-log plot of biphenylyl *vs.* phenyl system in the present solvolysis.

The log *k*-log *k* plot of the solvolysis rates between the biphenylyl and the phenyl systems under identical conditions does not show a linear relation (Fig. 1). All *-R*(*pi*-donor) 4'-substituted derivatives deviate downward from the line drawn through the 3'-substituted and unsubstituted derivatives, suggesting not only a far smaller ρ value but also a smaller r^+ value for the 4-biphenylyl system than for the phenyl system ($\rho=$

Table 1. Solvolysis rates of 3′- and 4′-substituted 1-(4-biphenylyl)ethyl chlorides in 80% (v/v) aq acetone

Subst.	Temp (°C)	10^5k_1 (s^{-1})	$\log k/k_0$ (45 °C)[4b]	$\log k/k_0$ (25 °C)[4b]	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
4′-MeO	39.65	47.0				
	30.00	16.0				
	20.00	5.35				
	45.00	79.8[a]	1.024		19.5	−11.4
	25.00	9.41[a]		1.086		
4′-Me	55.00	54.3				
	49.75	30.3				
	39.65	10.7				
	45.00	18.9[a]	0.399		20.8	−10.3
	25.00	1.95[a]		0.402		
H	55.00	20.7				
	49.75	13.0				
	39.65	4.16				
	45.00	7.55[a]	0.000		20.9	−11.9
	25.00	0.772[a]		0.000		
4′-Cl	59.85	20.3				
	49.75	6.58				
	39.65	2.27				
	45.00	4.08[a]	−0.263		21.8	−10.3
	25.00	0.378[a]		−0.310		
4′-Br	59.85	17.6				
	49.75	6.05				
	39.65	2.10				
	45.00	3.74[a]	−0.305		21.1	−12.5
	25.00	0.372[a]		−0.317		
3′-Cl	59.85	9.48				
	49.75	3.11				
	39.65	1.02				
	45.00	1.87[a]	−0.606		22.2	−10.5
	25.00	0.166[a]		−0.668		
3′-Br	59.85	7.94				
	49.75	2.66				
	39.65	0.904				
	45.00	1.63[a]	−0.666		21.6	−12.6
	25.00	0.154[a]		−0.700		
4′-CN	81.75	26.8				
	75.00	14.5				
	65.00	5.48				
	45.00	0.664[a]	−1.056		21.9	−13.4
	25.00	0.0608[a]		−1.104		
$4'$-NO_2	81.75	19.6				
	75.00	10.3				
	65.00	3.92				
	45.00	0.461[a]	−1.214		22.2	−13.3
	25.00	0.0409[a]		−1.276		

a) Extrapolated or interpolated from other temperatures.

-4.95, $r^+=1.15$).[2]

A plot of the biphenylyl data at 45 °C against Brown's σ^+ [5,8] appears to give a good linear relation with a ρ^+ value of -1.46 ($r=0.9988$, $s=\pm0.037$, $n=9$); the dotted line in Fig. 2. An unfavorable deviation is seen for the unsubstituted point; this amounts to 0.08 log-unit, which corresponds to a 20% change in the rate constant obtained. Such an error should not be expected for the rate measurements.

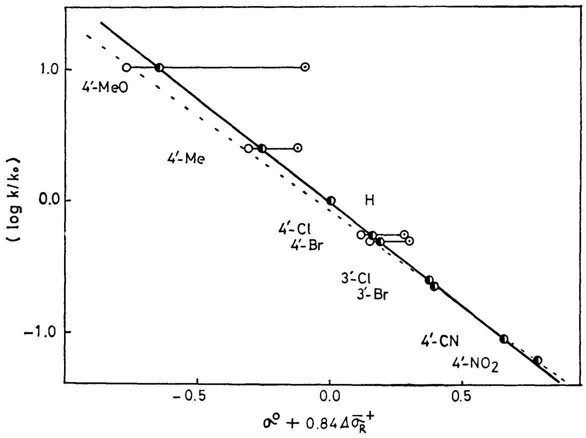

Fig. 2. The LArSR plot for the solvolysis of 1-(4-biphenylyl)ethyl chlorides at 45 °C (◐). A dotted line shows Brown's σ^+ correlation; ○ and ⊙ indicate σ^+ and σ° plots for $-R$ substituents, respectively.

The application of Eq. 1[1,2] provides an excellent correlation, with a standard deviation of ±0.023 and a correlation coefficient of 0.9996 (Fig. 2).[6]

$$\log k/k_0 = -1.56(\sigma^\circ + 0.84\Delta\bar{\sigma}_R^+) - 0.03$$

In this plot, there is no particular deviation. The $\rho(-1.56)$ obtained is identical with the ρ value determined from the 3′-substituents and $+R$(*pi*-acceptor) 4′-substituents ($\rho=-1.57$, $r=0.9987$, $s=\pm0.028$, and $n=5$). The identity indicates that the effects of 3′-substituents (and $+R$ 4′-ones) in the 4-biphenylyl system can be practically treated just as those of the *meta* (and $+R$ *para*) substituents in the phenyl system.

Inukai has reported[7] that the solvolysis data of 1-(4-biphenylyl)-1-methylethyl chlorides also showed downward deviations for $-R$ substituents on the simple σ^+ plot, although the reaction center was the same as that for the reference reaction of σ^+. It was well understood that such deviations resulted from the r^+ (0.67) value, which was smaller than unity (Table 2, Reaction C). Similarly, the recent results of Bolton and Burley for the substituent effects on α-(4-biphenylyl)benzyl chlorides[27] are also best treated with a r^+ value of 0.75 (Table 2, Reaction B). These facts illustrate the assertion that our LArSR Eq. 1 can describe the solvolyses in the 4-biphenylyl system more precisely than does Brown's treatment. The lower r^+ values indicate that the resonance contribution from $-R$ substituents in 4′-position to the stabilization of the transition state is less effective in the biphenylyl system.

The LArSR treatment has been found to be generally applicable to other reactivities in the biphenylyl systems. The results of the correlation analysis are shown in Table 2, in comparison with those in the phenyl systems under the same conditions for the respective reactivities, although the substituent-effect data available are too limited to check the applicability thoroughly. The table includes six typical electrophilic reactions[4a] (solvolyses of secondary and tertiary chlorides, protodesilylation, alkaline hydrolysis of esters, and acid dissociation) and a typical nucleophilic reaction[16] (piperidinodebromination). It is clear at a glance that the correlation for

Table 2. Application of the LArSR Eq. 1 to reactivities for 3′- and 4′-substituted 4-biphenylyl system

Reaction	Solv[a]	Temp (°C)	System	ρ	r^+	R[g]	$\pm s$[h]	n[i]	Ref.
Electrophilic reactions[4a]									
A: Solvolysis	80A	45	Biph	−1.56	0.84	0.999	0.023	9	b)
$ArCHMeCl$	80A	45	Ph	−4.95	1.15	0.999	0.040	16	2
B: Solvolysis	9: 1EA	25	Biph	−1.30	0.75	0.995	0.057	12	27
$ArCH(Ph)Cl$	100E	25	Ph	−4.13	1.17	0.998	0.125		28
C: Solvolysis	90A	25	Biph	−1.39	0.67	0.999	0.024	6	7
$ArCMe_2Cl$	90A	25	Ph	−4.54	1.00	(by definition)			8
D: Protodesilylation	AcOH-H$^+$	50	Biph	−1.31	0.41	0.999	0.013	6	9
$ArSiMe_3+H^+$	AcOH-H$^+$	50	Ph	−4.99	0.74	0.999	0.068	11	10
E: Alkaline Hydrolysis	88.7E	25	Biph	(0.58)	(0.34)	0.999	0.005	8	11
$ArCOOEt+OH^-$	85E	25	Ph	2.58	0.25	0.997	0.069	16	1c
F: Acid dissociation	50BE	25	Biph	(0.46)	(0.14)	0.978	0.04	8	12
$ArCOOH$	50BE	20	Biph	(0.49)	(0.36)	0.945	0.06	18	c), 13
	50BE	25	Ph	1.43	0.20	0.991	0.09	6	12
Nucleophilic reactions[4a]									
G: Piperidinodebromination $Ar(NO_2)Br+PiP$	100M	50	Biph[d]	0.95	0.36[f]	0.991	0.038	12	14
H: Ammonium Dissociation	50E	20	Biph	(0.64)	(0.1)	0.988	0.035	10	13
$ArNH_3^+$	50E	25	Ph	(3.11)		0.983	0.120	10	e), 15

a) 80A (80% aq acetone), 9: 1EA (9: 1 EtOH: acetone), 100E (100% EtOH), AcOH-H$^+$(AcOH-aq H_2SO_4), 50BE (50% 2-butoxyethanol), and 100 M (100% MeOH). b) Present study. c) The points of 3′-CN, 3′-NO_2, 4′-Ph, and 4′-CN were omitted for calculations because of problems with their solubility and purity. d) The reaction of 3′- and 4′-substituted 3-nitro-4-bromobiphenyls with piperidine. e) The point of *p*-F was omitted. Substituents involved are too limited (from *p*-Me to *m*-Br) to get an accurate ρ. f) For the corresponding phenyl system, the r^- of 0.77 was employed (see Text). g) Correlation coefficient. h) Standard deviation. i) Number of substituents involved.

every reaction is excellent ($R>0.99$), except for F reaction, where the biphenylyl system has a very small ρ. Thus, in general, the LArSR treatment is equally applicable to 4-biphenylyl reactivities.

In the comparison between the biphenylyl and phenyl systems, the ratio of ρ values, ρ_{Biph}/ρ_{Ph}, is as a good approximation *ca.* 0.3 in all cases; the ratios of r, r^+_{Biph}/r^+_{Ph}, for A, B, C, and D reaction series (in Table 2) are of the magnitude of 0.5—0.7. For the solvolysis of benzhydryl chlorides, $r^+_{Ph}=1.17$ (in EtOH)[28] was employed for this calculation. The r^+_{Biph} values for E and F series are not quite as reliable as the others, because of the low sensitivities to substituent change ($\rho_{Biph}\simeq 0.5$). In the case of the nucleophilic reaction[4a] of G series, we could not find the substituent-effect data in the phenyl system which corresponded to the same conditions as those in the biphenylyl system. Most recently, we have studied the reactions of 4-substituted 1-chloro-2-nitrobenzenes and 4-substituted 1-fluoro-2-nitrobenzenes with piperidine in MeOH,[17] which could be correlated excellently by means of the LArSR Eq. 1; in the former piperidinodechlorination at 80 °C, $\rho=3.86$, $r^-=0.77$ ($R=0.998$, $s=\pm 0.106$, $n=14$) and in the latter piperidinodefluorination at 25 °C, $\rho=4.02$, $r^-=0.78$ ($R=0.999$, $s=\pm 0.08$, $n=7$). Since the leaving groups of Cl and F gave identical r^- values, it is reasonably estimated that the piperidinodebromination may have a similar amount of nucleophilic resonance exaltation ($r^-=0.77$).[18] Then, the ratio of r^-, r^-_{Biph}/r^-_{Ph}, for G reaction will be of the magnitude of 0.5.

These features of the ratios of r^+ and r^- lead us to the view that there is no simple linear log *k*-log *k* relationship between the biphenylyl and phenyl systems for a reaction with $r^\pm_{Ph}>0.5$. However, if a given reaction shows a smaller contribution from the resonance effect ($r^\pm_{Ph}<0.5$), such a linearity may hold practically within experimental uncertainty; in fact both E and F series belong to this case.[11,12]

As far as the comparison of substituent effects between the biphenylyl and phenyl systems are concerned, the relative ρ can be taken as a measure of the transmission of polar effects (more exactly inductive effects) of substituents in biphenylyl relative to the phenyl system. According to a field effect model by Kirkwood-Westheimer,[19] ρ is derived to be proportional to the reciprocal of the square of the distance R,

$$\rho = A\cos\theta/R^2,$$

where A is a constant under given reaction conditions, θ is the angle between a C–X (substituent) dipole and a distance vector to a reaction center, and R is the distance between them. Since $\cos\theta\simeq 1$ (4′- or *para* position of substituents) and $A_{Biph}/A_{Ph}\simeq 1$ can reasonably be expected, the following relation may hold to a first approximation:

$$\rho_{Biph}/\rho_{Ph} = (A_{Biph}/A_{Ph})(R^2_{Ph}/R^2_{Biph}) \simeq R^2_{Ph}/R^2_{Biph}.$$

The relative ρ values are in good agreement with the respective values calculated by using simplified distances (Table 3); this seems to suggest the importance of the transmission mode through the field, as far as the

TABLE 3. RELATIVE ρ, q_r^+ (q_r^-), AND RELATED VALUES

Reaction[a)]	$\rho_{\mathrm{Biph}}/\rho_{\mathrm{Ph}}$	$R^2_{\mathrm{Ph}}/R^2_{\mathrm{Biph}}$	$q^{\pm}_{r,\mathrm{Biph}}/q^{\pm}_{r,\mathrm{Ph}}$
A: ArCHMeCl	0.32	0.33	0.80
B: ArCHPhCl	0.31	0.33	0.74[b)]
C: $ArCMe_2Cl$	0.31	0.33	0.77
D: $ArSiMe_3$	0.26	0.25	0.71
E: ArCOOEt	0.22	0.33	
F: ArCOOH	0.32	0.36	
G: $Ar(NO_2)Br$	(0.2)	0.25	0.73[c)]
H: $ArNH_3^+$	(0.2)	0.33	

a) See Table 2. b) $r^+_{\mathrm{Ph}}=1.17$ was used (see Text). c) $r^-_{\mathrm{Ph}}=0.77$ was used (see Text).

present comparisons are concerned.

Dewar and Grisdale assumed that the factor controlling the inductive effect in ΔpK_a of substituted naphthoic and biphenylcarboxylic acids is solely the electrostatic field effect, the magnitude of which is expressed by a function of the reciprocal of the distance.[20a)] As summarized in Tables 2 and 3, the data sets accumulated for biphenylyl reactivities and the results properly analyzed have come to show that the $1/R^2$ approximation is likely to be a more precise description of the ρ (inductive effect) than the Dewar approximation. An alternative mode based on successive polarizations through intervening bonds, however, is not completely ruled out. The transmission factor per one phenyl ring is calculated to be 0.31, as an average of A and C reactions. This figure results in a transmission factor of 0.63[20b)] per a sp^2 carbon unit, which is slightly smaller than the values estimated from 1-naphthyl[3)] and other side chain reactivities.[4c)]

Comparisons of r values in both biphenylyl and phenyl systems also give us interesting facts concerning the loss of resonance in the intervening *pi*-electronic system. Since the apparent substituent constants can be rewritten in terms of σ_i and σ_π,[1)] the use of the relative q_r value, instead of the relative r, is reasonable for a net comparison of *pi*-electronic effect.

$$\bar{\sigma} = \sigma^0 + r^+\Delta\bar{\sigma}_R^+ + r^-\Delta\bar{\sigma}_R^- = \sigma_i + q_r^+\sigma_\pi^+ + q_r^-\sigma_\pi^-, \qquad (2)$$

where $q_r^+=1+r^+/0.415$ and $q_r^-=1+r^-/0.73$. The relative q_r values, as tabulated in Table 3, reflect the effectiveness of resonance in the biphenylyl relative to the phenyl system and show nearly a constant value of 0.76 ± 0.04. The q_r^+ ratios obtained from the four electrophilic exalted resonance reactions,[4a)] A, B, C, and D, agree quite well with the q_r^- ratio of the nucleophilic exalted resonance reaction,[4a)] G. It should be noted here that the same type of treatment can be successfully performed with the $+R$ class of substituents in nucleophilic exalted reactions. The resulting relative q_r^- is just equivalent with the well-examined relative q_r^+'s in the electrophilic cases. It is then concluded that the relative effectiveness of *pi*-electronic transmission in the biphenylyl to the phenyl system remains constant in spite of the quite different types of reactions.

In the usual approximation, the reduced effectiveness may be explained in terms of a twisting of two phenyls around the pivot bond in biphenyl.[21)] If the total reduced effect is to be caused only by the factor of twisting, the angle can be calculated to be *ca.* 30° from the relation of $\cos^2\theta=0.75$. The angle in a solution has been estimated to be around 35° from some sources.[22)] Then the two phenyl rings in biphenyl probably act as if the twisting angle remains nearly the same in all reactions.

The reactivity difference between the present biphenylyl and phenyl derivatives may also be considered as a factor affording lower r^+ values for the biphenylyl system: in the present solvolysis, the former is *ca.* 10 times more reactive than the latter. The increased stabilization of the transition state by the second phenyl ring in biphenylyl should cause a decreased demand for the electron releasing resonance contribution from 4'-substituents. This may predict a lower r^+ value. If this is the case, a much lower r^+ value would be expected in the corresponding fluorenyl system because of the coplanarity of the second phenyl ring. Our experimental results[4c)] show clearly that this is not the major factor. A more detailed discussion on the twisting should be done with an alternative comparison between the biphenylyl and fluorenyl systems.

Finally, it is worth particular emphasis that the LArSR relationship, which is based on reactions in the phenyl system, applies equally excellently to reactivities in the other *pi*-system of biphenylyls.

Experimental

Materials. 4-Methyl-, 4-chloro-, 4-bromo-, and 3-chlorobiphenyls were prepared by the Gomberg-Bachmann reaction.[23)] 4-Methoxybiphenyl was made by methylation of commercial 4-hydroxybiphenyl in an alkaline solution with slight modifications of the standard Hier's method[24)] (87% yield). 3-Bromobiphenyl was prepared as directed by Mowry from 2-aminobiphenyl *via* 2-amino-5-bromobiphenyl.[25)]

Almost all 4-acetylbiphenyls were obtained by the usual Friedel-Crafts acetylation of the above monosubstituted biphenyls. 3-Bromo-4'-acetylbiphenyl was prepared by following a slight modification of Berliner's directions.[12)] After decomposition of the complex produced, the simple procedure of cooling its solution, instead of successive extraction procedures, gave crude crops (mp 36—37 °C) in 64% yield (recrystd from ligroin; mp 40.5—41 °C). 4-Cyano-4'-acetylbiphenyl was prepared from 4-bromo-4'-acetylbiphenyl by using CuCN in DMF[26)] (50% yield, mp 117—120 °C). 4-Nitro-4'-acetylbiphenyl (mp 150—151 °C) was obtained in 27% yield by an acetylation ($AlCl_3$, Ac_2O, nitrobenzene solvent) of 4-nitrobiphenyl. Melting and boiling points of all monosubstituted biphenyls and substituted 4-acetylbiphenyls prepared were equal or very close to the literature values[12,25)] and the elemental analysis data agreed with the calculated values.

The acetylbiphenyls were reduced with lithium aluminium hydride or sodium borohydride (especially for the CN and NO_2 derivatives) to the corresponding 1-(4-biphenylyl)ethanol by standard methods. Except for the CN and NO_2 derivatives, every chloride was prepared with dry HCl gas in dry ether as described before.[2)] After evaporation of the solvent, crude crops of chlorides were purified by recrystallization from appropriate solvents. 3'-Chloro and 3'-bromo derivatives (liquid) were employed for kinetics without purification; the respective alcohols were purified and, just before kinetics, they were converted into the chlorides for rate measurements. 4'-Cyano and 4'-nitro substituted chlorides were made by the

TABLE 4. PHYSICAL CONSTANTS OF SUBSTITUTED 1-(4-BIPHENYLYL)ETHANOLS AND THEIR CHLORIDES

Subst.	Mp or bp of alcohol(°C)	Mp of chloride(°C)
H	95.5—96a)	52.5—53b)
4′-MeO	119—119.5	117—118
4′-Me	99—99.5	97—97.5
4′-Cl	107—108	98.5—99.5
4′-Br	148—148.5	118—119
3′-Cl	33.5—34 (160—165/0.75 mmHg)	c)
3′-Br	136—140/0.2 mmHg	c)
4′-CN	135	83.5—84
4′-NO_2	107—108	107—110

a) Lit,2) mp 97 °C. b) Lit,2) mp 52.0—52.5 °C.
c) Used without purification.

method of thionyl chloride2) and purified by recrystallization from hexane–benzene. The physical constants are listed in Table 4.

Solvent and Kinetic Measurements. The 80% (V/V) aqueous acetone was prepared by mixing 4 volumes of purified acetone and 1 volume of distilled water at room temparature (*ca.* 20 °C). Different batches of the solvent in this study were found to give an identical solvolysis rate for the 4′-chloro (or 4′-bromo) derivative within experimental errors; the interpolated rate for the unsubstituted derivative at 45 °C reasonably agreed with the previous rate measured at 45 °C.2) The determination of the first-order rate constants in 80% aq acetone followed the method described previously;2) Bromothymol Blue was used as an indicator. Temperatures were controlled within ±0.02 °C.

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4) a) The term "electrophilic reaction" is used to characterize the reaction in which *pi*-donor($-R$) substituents show an electrophilic exalted resonance effect. On the other hand, the term "nucleophilic reaction" refers to the reaction where *pi*-acceptor($+R$) substituents show a nucleophilic exalted resonance effect. The authors wish to express their thanks to Prof. J. Shorter for his kind comment on these terms.1d) b) At 45 °C, apparent substituent effects for the present solvolysis can be directly compared with those in the phenyl system under the same conditions. At 25 °C, the effects can be compared with those in the fluorenyl system.4c) c) Y. Tsuno, Y. Tairaka, M. Sawada, T. Fujii, and Y. Yukawa, *Bull. Chem. Soc. Jpn.*, **51**, 601 (1978).

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