

The Substituent Effect. XIII. Solvolysis of 1-(7-Substituted 2-Fluorenyl)-ethyl Chlorides and Alkaline Hydrolysis of Ethyl 7-Substituted 2-Fluorencarboxylates

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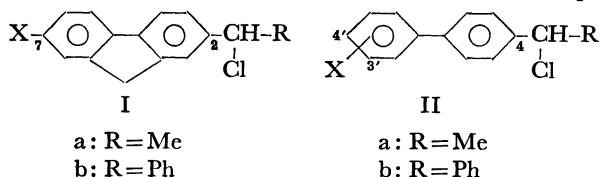
Two sets of rate constants for (i) solvolysis of 1-(7-substituted 2-fluorenyl)ethyl chlorides in both 90 and 80% aqueous acetone and (ii) alkaline hydrolysis of ethyl 7-substituted 2-fluorencarboxylates in 85% aq EtOH have been determined. Both substituent effects could be correlated excellently with the LArSR relationship; the resulting r^+ values (0.82 and 0.47, respectively) were comparable with the r^+ 's in the corresponding biphenyl system under the same conditions. The comparison of ρ_π^+ values clearly indicates a more efficient transmission of the π -electronic effect in the fluorenyl than in the biphenyl system (1:0.75). This can be attributed to a factor of twisting in the latter π -system. The attenuation of the transmission of the π effect was found to be characteristic of the intervening π -systems independent of reactions: 1.00(4-X-1-phenyl), 0.55(6-X-2-naphthyl), 0.35(7-X-2-fluorenyl), and 0.25(4'-X-4-biphenyl).

In previous papers of this series, we demonstrated successful applications of the LArSR relationship (Eq. 1), which is based on reactivities in the phenyl system, to reactivities in some extended π -systems, such as 4-biphenyl¹⁾ and 1-naphthyl systems.²⁾

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

We have been interested further in substituent effects in the fluorenyl system from the viewpoint of the structural similarity in the biphenyl system,¹⁾ but disregarding the problem of planarity.³⁾ It can then, be expected that comparisons of substituent effects between fluorenyl and biphenyl systems under the same conditions can provide important information on the transmission of electronic effects, especially the π -electronic effect, across these π -systems, if Eq. 1 is generally valid.

Although fragmentary data on the pK_a values for some fluorenols and fluorenylamines are available,^{4,5)} systematic studies of substituent effects in the fluorenyl system have been scarcely reported. Available is only a set of reactivity data for detritiation in CF_3COOH , coupled with biphenyl data.⁶⁾ The reactivity range covered is, however, too limited to estimate and compare the π -electronic effects for our present purposes because of the use of a strongly acidic solvent.⁹⁾ Two typical electrophilic reactions in 7-substituted 2-fluorenyl systems with very different amounts of resonance exaltation have been chosen. The one is solvolysis of 1-(2-fluorenyl)ethyl chlorides (Ia), while the other is alkaline hydrolysis of ethyl 2-fluorencarboxylates. Just before this article was to be submitted, another set of solvolysis data appeared in the literature:^{6b)} a pair of substituent effects in α -(2-fluorenyl)benzyl chlorides (Ib) and α -(4-biphenyl)benzyl chlorides (IIb) in 9:1 EtOH-acetone. Our systematic substituent-effect data coupled



with those in the literature show clearly the characteristics of the intervening fluorenyl and biphenyl systems.

Results and Discussion

The rates for the solvolysis of seven 1-(7-substituted 2-fluorenyl)ethyl chlorides Ia in 90% (v/v) aqueous acetone were determined at convenient temperatures by means of the usual acid-base titration method. First-order rate constants, k_1 (s⁻¹), at various temperatures and the relative rates in 2-fluorenyl system with respect to substituents at the 7-position at 25 °C are listed in Table 1, together with some activation parameters; for the MeO, CN, and NO₂ derivatives, the k_1 values at 25 °C were extrapolated from those at other temperatures by means of the Arrhenius equation. Further, the rates for the solvolysis of the same chlorides in 80% (v/v) aq acetone were also determined for the

TABLE 1. SOLVOLYSIS RATES OF 1-(7-X-2-FLUORENYL)-ETHYL CHLORIDES IN 90% (v/v) AQ ACETONE

X	Temp (°C)	10 ⁵ k ₁ (s ⁻¹)	log k/k ₀ (at 25°C)	ΔH [‡] (kcal/mol)	ΔS [‡] (e.u.)
MeO	0.0	4.29			
	10.0	15.8			
	20.0	44.4			
	25.0 ^{a)}	78.7 ^{a)}	1.426 ^{a)}	18	-12
C ₂ H ₅	25.0	9.81	0.522		
H	25.0	2.95	0.000		
Cl	25.0	1.14	-0.413		
Br	25.0	0.997	-0.471		
CN	65.0	5.04			
	55.6	2.16			
	45.0	0.731			
	25.0 ^{a)}	0.0828 ^{a)}	-1.552 ^{a)}	20.0	-19.3
NO ₂	86.0	20.2			
	75.0	8.34			
	64.2	3.00			
	25.0 ^{a)}	0.0495 ^{a)}	-1.775 ^{a)}	20.4	-19.0

a) Extrapolated from other temperatures.

TABLE 2. SOLVOLYSIS RATES OF 1-(7-X-2-FLUORENYL)-ETHYL CHLORIDES IN 80% (v/v) AQ ACETONE

X	Temp (°C)	$10^5 k_1$ (s ⁻¹)	$\log k/k_0$ (at 25 °C)	ΔH^* (kcal/mol)	ΔS^* (e.u.)
MeO	25.0 ^{a)}	1.44×10^3 ^{a)}	1.49 ^{a)}		
C ₂ H ₅	0.0	6.48			
	15.0	45.1			
	25.0	147	0.500	19.6	-5.6
H	0.0	1.94			
	15.0	13.2			
	25.0	46.5	0.000	19.9	-6.9
Cl	25.0	16.1	-0.461		
Br	15.0	3.97			
	25.0	13.5	-0.537	20.3	-8.1
CN	25.0	1.04	-1.650		
NO ₂	25.0	0.516	-1.955		

a) Extrapolated from a linear free-energy relation between rates in 80 and 90% aq acetone (see Text).

sake of comparison. In the latter solvent, apparent substituent effects in the fluorenyl system can be directly compared with those in biphenyl and phenyl systems under identical conditions.^{1,7)} Table 2 contains the kinetic data in 80% aq acetone obtained in the same manner as those in 90% aq acetone.

The k_1 for 7-MeO-2 derivative in 80% aq acetone was extrapolated from the following linear $\log k/k_0$ - $\log k/k_0$ correlation between substituent effects in 80 and 90% aq acetone with a high precision (corr coeff, $r=0.9996$, $s=\pm 0.031$, $n=6$):

$$(\log k/k_0)_{80\%} = 1.065(\log k/k_0)_{90\%} - 0.029.$$

The minor solvent change from 80 to 90% causes only a small change in the ρ value, but none in the r^+ value of Eq. 1.⁸⁾

On the other hand, the rates for the alkaline hydrolysis of seven ethyl 7-substituted 2-fluorencarboxylates in 85% (w/w) aq EtOH at 50 °C were measured by means of usual conductivity and/or titration methods. The second-order rate constants, k_2 (s⁻¹ M⁻¹), and the logarithmic relative rates are listed in Table 3. Unfortunately, we could not get a k_2 for the NO₂ derivative in this ester hydrolysis because the solubility was insufficient to measure it.

TABLE 3. RATES OF ALKALINE HYDROLYSIS OF ETHYL 7-X-2-FLUORENecARboxylates IN 85% (w/w) AQ EtOH AT 50 °C

X ^{a)}	$10^3 k_2$ (s ⁻¹ M ⁻¹)	Method ^{b)}	$\log k/k_0$
MeO	2.06	C	-0.259
C ₂ H ₅	2.82	T	-0.123
H	3.74	C,T	0.000
Cl	4.87	C,T	0.115
Br	5.04	C	0.130
COMe	7.46	C	0.300
CN	10.8	C	0.461

a) We could not get a k_2 of the NO₂ deriv. because of the solubility problem. b) T: titration method, C: conductivity method.

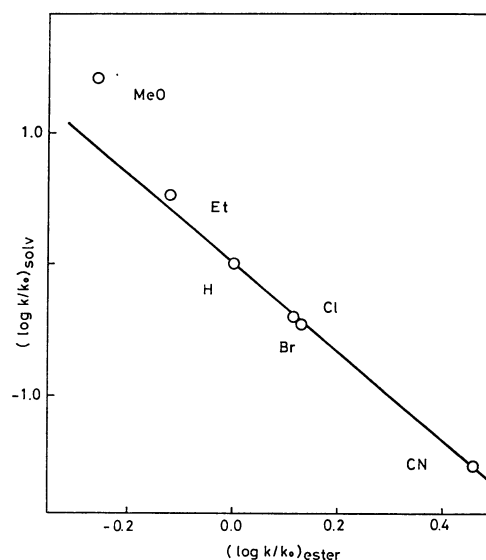


Fig. 1. A plot of $\log k/k_0$ for the solvolysis A (90% acetone, 25 °C) vs. the ester hydrolysis D (85% EtOH, 50 °C) in the present 7-X-2-fluorenyl system.

Logarithms of the relative rates for the solvolysis (90% aq acetone) in the fluorenyl system are plotted against those for the ester hydrolysis in Fig. 1. The $-R$ (π -donor) substituents deviate upward from the line made with CN and H substituents, for which no exaltation of resonance might be expected. The more electron-releasing the $-R$ substituent at such a conjugative position, the larger the upward deviation. The deviations indicate that the contribution of through-conjugation between substituents and the reaction center for the solvolysis is much more important to the apparent substituent effects than those for the ester hydrolysis, at least at the conjugative (7-)position in the 2-fluorenyl system. Similar upward deviations had also been obtained in the biphenyl system on the log-log plot of the relative rates between the corresponding solvolysis and ester hydrolysis.¹⁾

An interesting feature which we found in this study is that there exists an excellent linearity (Fig. 2) of the solvolysis rates (25 °C) between fluorenyl (90%) and biphenyl (80%) systems, covering a range of substituents from MeO to NO₂ ($r=0.9998$, $s=\pm 0.026$, $n=7$):

$$(\log k/k_0)_{\text{Fluo}} = 1.362(\log k/k_0)_{\text{Biph}} - 0.028.$$

The linearity suggests that the blends of the π -electronic (π) effect and the inductive (I) effect are practically equivalent in the two systems for the present solvolysis.

Eaborn *et al.* first observed this kind of behavior in detritiation and pointed out that the effects of 7-substituents in the 2-fluorenyl are similar to those of 4'-substituents in the 4-biphenyl system;⁹⁾ a correlation analysis of their detritiation data in CF₃COOH at 70 °C provides high precision with this relation: $(\log k/k_0)_{\text{Fluo}} = 1.11 (\log k/k_0)_{\text{Biph}}$ ($r=0.9986$, $s=\pm 0.08$, $n=6$). Even though the detritiation has been established as a typical electrophilic exalted resonance reaction, since it inevitably contains serious solvent-substituent interaction, MeO derivatives in both π -systems are less reactive than Me ones; therefore, the reactivity range is limited for only

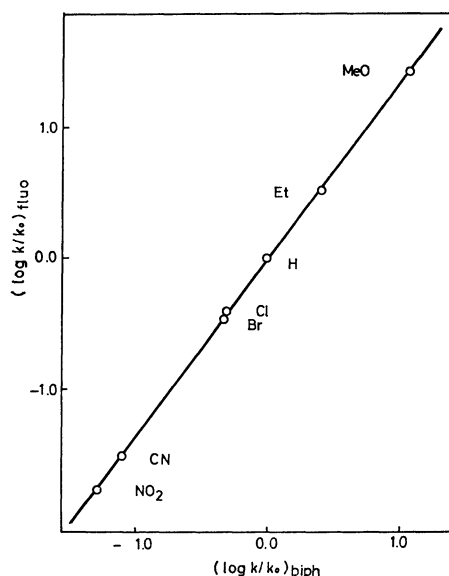


Fig. 2. The linear $\log k/k_0 - \log k/k_0$ plot between fluorenyl (90% acetone, 25 °C) and biphenyl (80% acetone, 25 °C) in the present solvolysis A (Ia vs. IIa).

weakly conjugating substituents.⁹ Bolton and Burley have recently observed a similar linearity between the solvolyses of Ib and IIb (with a slope of 1.45, $r=0.999$), which covers nearly the same range of substituents as ours.

As another example for comparison between the fluorenyl and the biphenyl systems, the present data of ester hydrolysis are correlated linearly with Berliner's

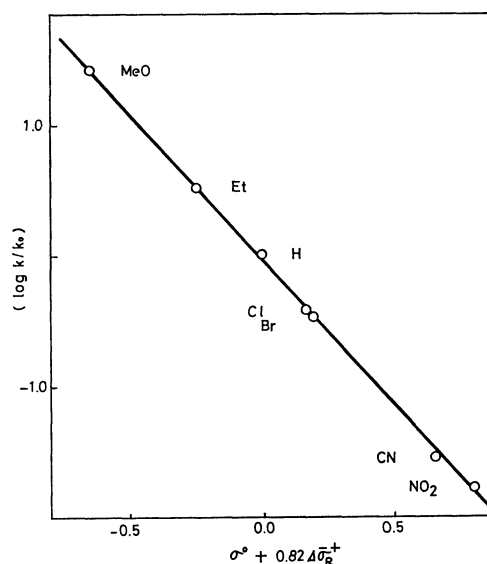


Fig. 3. The LArSR plot for the solvolysis A of 1-(7-X-2-fluorenyl)ethyl chlorides (90%, 25 °C).

data on the alkaline hydrolysis of ethyl biphenylcarboxylates¹⁰ ($r=0.9935$, $n=5$); since the rates are not very sensitive to substituent changes in either system, it is hard to ascertain whether or not their P_i effects relative to I effects are different. From the findings in the above reactions, the linear relationships of the substituent effects between the fluorenyl and the biphenyl systems seem to be quite general.

The present solvolysis of the Ia fluorenyl system

TABLE 4. CORRELATION PARAMETERS BY MEANS OF THE LArSR Eq. 1

Reaction	Substituted(X) <i>pi</i> -system ^{a)}	Solv ^{b)} (%)	Temp (°C)	ρ	r^+	R^f	$\pm s^g$	n^h	Ref.
A: Solvolysis ArCHMeCl	3,4-X-1-Ph	80A	45	-4.95	1.15	0.999	0.040	16	7
		80A	25	-5.15	(1.15)				7
		90A	45	-4.75	1.18	0.999	0.033		12
	7-X-2-Fluo	90A	25	-2.23	0.82	0.999	0.053	7	c)
		80A	25	-2.38	(0.82)			6	c)
	3',4'-X-4-Biph	80A	45	-1.56	0.84	0.999	0.023	9	1
		80A	25	-1.63	0.86				1
	3,4-X-1-Naph	80A	45	-5.12	1.04	0.999	0.116	10	2
B: Solvolysis ArCH(Ph)Cl	6-X-2-Naph	80A	45	-3.35	0.84	0.999	0.025	5	13
	3,4-X-1-Ph	100E	25	-4.13	1.17	0.998	0.125		36
	7-X-2-Fluo	9: 1EA	25	-1.98	0.73	0.997	0.08	6	6b
	3',4'-X-4-Biph	9: 1EA	25	-1.30	0.75	0.995	0.06	12	6b
	3,4-X-1-Ph	90A	25	-4.54	1.00 (by definition)				d)
	3',4'-X-4-Biph	90A	25	-1.39	0.67	0.999	0.024	6	d)
C: Solvolysis ArCMe ₂ Cl	6-X-2-Naph	95A	30	-2.92	0.70	0.999	0.032	5	14
	3,4-X-1-Ph	85E	25	2.58	0.25	0.997	0.069	16	15
	7-X-2-Fluo	85E	50	0.63	0.47	0.999	0.011	7	c)
D: Hydrolysis ArCOOEt	3',4'-X-4-Biph	90E	25	0.58	0.34	0.999	0.005	8	d)
	3,4-X-1-Naph	85E	50	2.19	0.27	0.999	0.03	10	2
	4-X-1-Naph ^{e)}	85M	30	1.97	0.27	0.989	0.084	6	14
	6-X-2-Naph ^{e)}	70D	25	1.72	0.17	0.995	0.08	7	16
	6-X-2-Naph ^{e)}	85M	30	1.22	0.26	0.996	0.04	9	14

a) Ph(phenyl), Fluo(fluorenyl), Biph(biphenyl), and Naph(naphthyl) *pi*-systems. b) A (acetone), E (ethanol), EA (EtOH: acetone), M (methanol), and D (dioxane). c) Present study. d) Taken from Table 2 of Ref. 1. e) Methyl esters instead of ethyl esters. f) Correlation coefficient. g) Standard deviation. h) Number of substituents included.

correlates linearly with a single set of neither σ^0 nor σ^+ , as has been discussed in the biphenyl system.¹⁾ The application of the LArSR Eq. 1 to the data Ia in 90% aq acetone (25 °C) gives an excellent correlation (Fig. 3) with the correlation coefficient of 0.9993 and the standard deviation of ± 0.053 ($n=7$), providing nearly the same r^+ value (0.82) as that in the biphenyl system (0.84):¹⁾

$$(\log k/k_0)_{\text{Fluo}}^{\text{Solvo}} = -2.231(\sigma^0 + 0.815\Delta\sigma_R^+) - 0.050.$$

Further, the substituent effects on the alkaline hydrolysis of ethyl 2-fluorencarboxylates can be accommodated simply with neither σ^0 nor σ , but can be accommodated successfully with the LArSR Eq. 1:¹¹⁾

$$(\log k/k_0)_{\text{Fluo}}^{\text{Ester}} = 0.628(\sigma^0 + 0.470\Delta\sigma_R^+).$$

The results of correlation analysis for the present and the related reactivity data available under closely similar conditions are summarized in Table 4, covering three solvolyses and ester hydrolysis. For comparisons of representative *pi*-systems through which the effects of substituents are effectively transmitted, the table also includes some naphthyl systems as well as the fluorenyl and biphenyl ones. From nearly perfect fits in every case (Table 4), it may be concluded that substituent effects from conjugative positions in any extended *pi*-systems for any reactions can generally be described by means of the LArSR Eq. 1, at least in electrophilic exalted resonance reactions.

Table 4 shows clearly that substituent effects depend greatly on the structures of the intervening *pi*-systems. The ρ values decrease systematically in the following order: phenyl > (1-naphthyl) > 2-naphthyl > 2-fluorenyl > 4-biphenyl. The ρ values relative to that in the phenyl system (see Table 5) appear to remain constant for the other systems: phenyl (1.00), 2-naphthyl (0.65), 2-fluorenyl (0.46), and 4-biphenyl (0.32); slight deviations from such a quantitative regularity are found only in the fluorenyl and biphenyl systems for ester hydrolysis (*ca.* 0.25 and 0.20 respectively). The relative ρ values for 1-naphthyl can not be fairly compared, because their ρ 's are usually subject to variation with the steric effects of peri-hydrogen; *e.g.*, on solvation at the reaction center.

On the other hand, each solvolysis gives nearly equal apparent r^+ values for the 2-fluorenyl, 4-biphenyl, and 2-naphthyl systems in spite of the different ρ values, while the ester hydrolysis offers an apparently larger r^+ in the fluorenyl system. However, it is worth noting that the resonance contribution given by ρr^+ is clearly larger for the 2-fluorenyl than for the 4-biphenyl system in all the reactions listed (Table 4). As long as the parameters of σ^0 and $\Delta\sigma_R^+$ derived from the original phenyl system are utilized for the present LArSR analysis in the fluorenyl and biphenyl systems, the comparison of ρr^+ is much more reasonable than that of simple r^+ as a measure of the resonance contribution in such extended *pi*-systems.³⁷⁾ The larger ρr^+ values are exactly in line with the concept of the planar-fluorenyl and nonplanar-biphenyl systems.

In previous papers,²⁾ we demonstrated the validity of a more fundamental LSFE Eq. 2 for separating substituent effects into *Pi* and *I* effects in variously substitut-

ed 1-naphthyl systems. As the LSFE treatment has been much more useful,^{2,18,38)} especially in extended *pi*-systems beyond original phenyl systems, it is actually very important to get reliable ρ_i and ρ_π parameters:

$$\log k/k_0 = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ + \rho_\pi^-\sigma_\pi^-. \quad (2)$$

Only when a given set of substituent-effect data covers a sufficient range of reactivity and sufficient numbers of substituents for both $-R$ and $+R$ classes of substituents, we can get reliable ρ_i , ρ_π^+ , and ρ_π^- values statistically.³⁸⁾ In the case of the present data sets, which contain only a few $+R$ substituents, it is, however, perhaps rather dangerous to use statistical ρ_π^- values and then ρ_π^+ values for discussions because of the too limited number of substituents. If it is assumed that ρ_π^- is equal to ρ_i (as in the LArSR treatment), and if σ_i' is provided as $\sigma_i + \sigma_\pi^-$ for $+R$ substituents in electrophilic reactions (and $\sigma_i' = \sigma_i$ for $-R$ substituents), then Eq. 2 should be rewritten as

$$\log k/k_0 = \rho_i\sigma_i' + \rho_\pi^+\sigma_\pi^+,$$

for both $-R$ and $+R$ groups. Consequently, the statistically derived ρ_i and ρ_π^+ values (on the basis of the σ_i' and σ_π^+ correlations) should cover the same range of substituents and should have the same accuracy as in the LArSR treatment. Usually, a data set of an electrophilic reaction involves a few $+R$ substituents such as NO_2 and CN . Therefore, it is recommended in practice that the substituent effects be separated into *Pi* and *I* effects by interconversions of the LArSR parameters to the LSFE parameters, instead of by a direct determination from the LSFE Eq. 2. Based on the definitions of $\sigma^0 = \sigma_i + \sigma_\pi^+$ and $\sigma_\pi^+ = 0.415 \Delta\sigma_R^+$, the LSFE parameters hold the following mathematical relations with the LArSR parameters:¹⁹⁾

$$\rho_i = \rho, \quad \rho_\pi^+ = \rho(1 + r^+/0.415). \quad (3)$$

The ρ_i and ρ_π^+ values can be evaluated by means of Eq. 3 from the ρ and r^+ values in Table 4. Table 5 illustrates the ρ_i , ρ_π^+ values relative to those in the phenyl system; these values show the corresponding

TABLE 5. RELATIVE ρ_i AND ρ_π^+ VALUES IN SOME *pi*-SYSTEMS

Reaction ^{a)}	<i>Pi</i> -system ^{a)}	Relative ^{b)} ρ_i	Relative ^{b)} ρ_π^+
A: Solvolysis ArCHMeCl	Ph	1.00	1.00
	2-Naph	0.68	0.54
	Fluo	0.46	0.36
	Biph	0.32	0.25
	1-Naph	(1.03)	(0.96)
B: Solvolysis ArCH(Ph)Cl	Ph	1.00	1.00
	Fluo	0.48	0.35
	Biph	0.31	0.23
C: Solvolysis ArCMe ₂ Cl	Ph	1.00	1.00
	2-Naph	0.64	0.51
	Biph	0.31	0.23
D: Hydrolysis ArCOOEt + OH ⁻	Ph	1.00	1.00
	2-Naph	0.66	0.58
	Fluo	0.24	0.32
	Biph	0.22	0.25
	1-Naph	(0.85)	(0.87)

a) Taken from Table 4. b) Both relative values are calculated by using ρ and r^+ in Table 4 and Eq. 3.

TABLE 6. APPLICATION OF THE LArSR Eq. 1 TO ALKALINE HYDROLYSIS IN AQ EtOH

System ^{a)}	Solv (%)	Temp (°C)	ρ	r^+	R^b	n^d	Ref.
ArCOOEt	85E	25	2.58	0.25	0.999	16	15
ArCH ₂ COOEt	85E	25	1.10	0.00 ^{b)}	0.996	10	20
ArCH ₂ CH ₂ COOEt	88E	30	0.64	0.00 ^{b)}	0.998	11	20
			0.64	0.00 ^{b)}	0.998	6	20
Ar(<i>c</i> -C ₃ H ₄)COOEt, <i>trans</i>	88E	30	0.88	0.00 ^{b)}	0.998	8	20
Ar(<i>c</i> -C ₃ H ₄)COOEt, <i>cis</i>	88E	30	1.06	0.00 ^{b)}	0.995	6	21
ArCH=CHCOOEt, <i>trans</i>	85E	25	1.19	0.39	0.999	9	22
	88E	30	1.27	0.31	0.999	6	23
ArCH=CHCOOEt, <i>cis</i>	88E	30	1.12	0.26	0.999	4	23

a) Ar(substituted phenyl), *c*-C₃H₄(cyclopropyl). b) σ^0 values were used for correlation. c) Correlation coefficient. d) Number of substituents.

relative effectiveness through which *Pi* and *I* effects are transmitted.

It is worth emphasizing that there exists a remarkable regularity in the attenuation behavior on the transmission of *Pi* effects. That is, a decrement remains constant for any given *pi*-system independent of the reactions or, more exactly, independent of the varied contributions of *Pi* effects in any type of reaction. The effectiveness of transmission is generally 55% for the 2-naphthyl, 35% for the 2-fluorenyl, and 25% for the 4-biphenyl, as large as that for the phenyl *pi*-system. The variations probably reflect characteristics of the systems.

Because of their geometrical similarity, substituent effects between fluorenyl and biphenyl systems can be compared most interestingly. The ratio of the *Pi* effects, biphenyl/fluorenyl, for the present solvolysis is calculated to be 0.72, reflecting the obviously decreased effectiveness of the transmission across the intervening biphenyl relative to the fluorenyl system. This figure must be well related with the twisting angle of both phenyl rings in biphenyl, because such a twisting is expected to decrease the *Pi* contribution. In the case of ester hydrolysis, the ratio shows a slightly larger value (0.78), probably the result of slight differences in the reaction conditions. Some proper correction will provide a value closer to 0.72. At any rate, the averaged value of 0.75 ± 0.03 is remarkably the same as the previous value obtained on the basis of a different comparison between the biphenyl and phenyl systems.¹⁾ Table 5 also indicates that the 6-X-2-naphthyl system is 1.6 times more effective than 7-X-2-fluorenyl in transmitting the *Pi* effects, although their r^+ values appear to be equal.

On the other hand, we can not get any regularity in the attenuation of relative *I* effects among the systems studied, though a limited regularity probably holds in three solvolyses, A, B, and C, in Table 4, as has been mentioned above. The results of the A solvolysis (ArCHMeCl) show the ρ_i in the fluorenyl system to be larger than that in the biphenyl system. Further, for another solvolysis, B (ArCHPhCl), the same thing is true.

These findings are not consistent with the transmission mode of the *I* effect through a field, since the simplified distance between substituents and the reaction center is equivalent for this pair. As a factor controlling the magnitude of the apparent ρ_i , the nature of the inter-

vening bonds, such as the bond-order in the pivot bond in the biphenyl component, may be incorporated with another factor of distance.¹⁾ The excellent linearity between the 2-fluorenyl and the 4-biphenyl systems may, therefore, imply that the ρ_i is also a function of the interplanar angle. This suggests that the higher the bond-order character of the intervening bond, the larger the ρ_i , even if the simplified distance is equal. This suggestion seems to be consistent with the results shown in Table 6.

The table compares the results of the LArSR treatment for the substituent-effect data available on ester hydrolysis under similar conditions. A major point in which we are interested is the nature of the intervening bond. When the intervening group between a substituted phenyl group and COOEt changes from -CH₂CH₂- to -cyclopropyl- to -CH=CH-, the ρ 's obviously change from 0.6 to *ca.* 0.9, and *ca.* 1.2 respectively. This suggests some operation of intervening bond-order effects on the transmission of the *I* effect.

In summary, it is particularly important to note that the LArSR relationship can be applied equally well to reactivities in extended *pi*-systems such as 7-X-2-fluorenyl and 6-X-2-naphthyl, other than the phenyl system.

Experimental

Materials. 2-Substituted Fluorenes: 2-Acetylfluorene (mp 127.5–128 °C),²⁴⁾ 2-nitrofluorene (mp 160.5 °C), and 2-ethylfluorene (mp 99–100 °C) were prepared by the standard procedures previously reported.^{25–27)} 2-Chlorofluorene was made as has been described by Sengupta,²⁸⁾ with slight modifications; chlorine gas was passed through a CHCl₃ solution of fluorene under cooling, until the IR absorbance at 764 cm⁻¹ of the product periodically extracted from the reaction mixture became larger than that at 725 cm⁻¹. Although the product (recrystallized from MeOH) was contaminated with dichloro derivative, it was used without purification in the next acetylation step. 2-Bromofluorene was also prepared by bromination. Bromine (100 g) was rapidly added to a dioxane (600 g) solution of fluorene (70 g) at room temperature. After stirring for 3 h and the subsequent decomposition of the excess Br₂, the solution was poured into water and the precipitate was recrystallized from MeOH–benzene, giving 2-bromofluorene in an 85% yield (mp 109–110 °C, lit,²⁹⁾ mp 110–111 °C).

7-Substituted 2-Acetylfluorenes: As has been described by Arene

and Taylor in connection with the preparation of 7-methoxy-2-acetylfluorene,³⁰ 7-ethyl-2-acetylfluorene was obtained by the acetylation of 2-ethylfluorene (with Ac_2O and AlCl_3 in nitrobenzene) in an 85% yield; recrystd from EtOH, mp 125.5–126.5 °C. 7-Chloro- or 7-bromo-2-acetylfluorene was synthesized by the addition of Ac_2O (0.6 mol) to a nitrobenzene solution (800 ml) of the respective halofluorene (0.4 mol) and AlCl_3 (0.83 mol) under cooling. The mixture was stirred for 3 h and then allowed to stand overnight. After a usual work-up, the product was recrystallized from benzene and then CCl_4 ; 7-chloro-2-acetylfluorene (83% yield, mp 141–142 °C) and 7-bromo-2-acetylfluorene (75% yield, mp 144–146 °C). 7-Cyano-2-acetylfluorene (recrystd from EtOH–benzene; mp 117–120 °C) was prepared by the use of CuCN from 7-bromo-2-acetylfluorene (60% yield) according to the method described by Fridmann and Shechter.³¹

7-Nitro-2-acetylfluorene was obtained by the literature method³² in a 72% yield (mp 233–233.5 °C, lit,³² mp 228 °C); however, because of its low solubility, the purification by recrystallization was difficult. The nitro derivative (50.6 g) was reduced with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (226 g) and concd HCl (280 ml) in AcOH (3500 ml). After treatment with aq KOH , 7-amino-2-acetylfluorene was obtained in a 52% yield; mp 221–221.5 °C. The amine was converted to 7-hydroxy-2-acetylfluorene in a 43% yield *via* diazonium sulfate (recrystd from MeOH–acetone, mp *ca.* 140 °C, dec). The methylation of the hydroxy derivative with Me_2SO_4 afforded 7-methoxy-2-acetylfluorene: mp 137–138 °C, lit,³⁰ mp 134–135 °C.

All of the above acetylfluorenes except the NO_2 and CN derivatives (low solubilities) were further purified by column chromatography on Al_2O_3 with a benzene eluent²⁴ and subsequently reduced by appropriate methods to the following alcohols.

1-(7-Substituted 2-Fluorenyl)ethyl Alcohols and Chlorides Ia:

The substituted and unsubstituted 2-acetylfluorenes were converted to the corresponding alcohols by a standard reduction with LiAlH_4 (for the MeO, Et, H, and Cl derivatives) or NaBH_4 (for the Br, CN, and NO_2 derivatives). All the alcohols were recrystallized from benzene–hexane or EtOH–benzene. The physical properties are tabulated in Table 7.

TABLE 7. PHYSICAL CONSTANTS AND ANALYTICAL DATA OF 1-(7-X-2-FLUORENYL)ETHYL ALCOHOLS

X	Mp(°C)	Calcd(Found)	
		C, %	H, %
MeO	147	79.97 (80.08)	6.71 (6.62)
C_2H_5	153–154.5	85.67 (85.61)	7.61 (7.64)
H	131.5–133	85.68 (85.66)	6.71 (6.51)
Cl	110–111	73.63 (73.54)	5.35 (5.57)
Br	155–156	62.30 (62.57)	4.53 (4.50)
CN	151–152	81.68 (81.07)	5.57 (4.80)
NO_2	178–180, dec	70.58 (70.75)	5.13 (5.11)

With the exception of the CN and NO_2 derivatives, the 1-(7-substituted 2-fluorenyl)ethyl chlorides were prepared by passing dry HCl gas through an ether (200 ml) solution of the alcohol (*ca.* 5 g); although the solubility of some alcohols was less sufficient, HCl gas was bubbled in and, as the reaction proceeded, the alcohol was dissolved into a solution. After the treatment as has been described before,⁷ the chlorides were purified by recrystallization from hexane or ether–petroleum ether and used for kinetics immediately after the evaporation of the solvents *in vacuo*. The CN and NO_2 derivatives were made by the SO_2Cl method⁷ and were recrystal-

lized from hexane–benzene.

7-Substituted 2-Fluorenicarboxylic Acids³³ and Their Ethyl Esters: The 7-methoxy-, 7-ethyl-, 7-chloro-, 7-bromo-, and unsubstituted 2-acetylfluorenes were moderately oxidized to the respective 7-substituted 2-fluorenicarboxylic acids by the use of iodine in pyridine (20–89% yields) using a method similar to that described by Barnett *et al.*³⁴ The 7-nitro-2-acetylfluorene was converted to the corresponding acid by following the procedure of Weisburger *et al.*⁵ The acid hydrolysis of 7-cyano-2-acetylfluorene gave 7-acetyl-2-fluorenicarboxylic acid (80% yield).

All of the ethyl 7-substituted 2-fluorenicarboxylates were prepared by the esterification of the corresponding acids or acid chlorides with EtOH, except in the case of ethyl 7-cyano-2-fluorenicarboxylate, which was obtained from the bromo derivative (39% yield) in the same manner as was used for 7-cyano-2-acetylfluorene. Every ester was purified by column chromatography on Al_2O_3 with a benzene eluent and by subsequent recrystallization from hexane or hexane–EtOH. The physical properties and analytical data of the esters are given in Table 8.

TABLE 8. PHYSICAL CONSTANTS AND ANALYTICAL DATA OF ETHYL 7-X-2-FLUORENICARBOXYLATES

X	Mp(°C)	Calcd(Found)	
		C, %	H, %
MeO	142–143	76.10 (76.00)	6.01 (6.01)
C_2H_5	109–109.5	81.17 (80.95)	6.81 (6.89)
H	85–85.5 ^a	80.65 (80.76)	5.92 (5.95)
Cl	131.5–132	70.46 (70.61)	4.80 (4.59)
Br	137–138	60.59 (60.54)	4.13 (3.96)
COMe	149–149.5	77.12 (76.90)	5.75 (5.70)
CN	187–188	77.55 (77.53)	4.98 (4.90)
NO_2	200.5	67.84 (67.62)	4.63 (4.46)

a) Lit,³⁵ mp 81–82 °C.

The proton NMR spectra for the esters, chlorides, and their precursors (the alcohols and ketones) were consistent with the respective assigned structures.

Kinetics and Solvents. *Solvolysis:* The 80% (V/V) and 90% (V/V) aqueous acetones were prepared by mixing nominal volumes of each component at 25 °C. Kinetics were carried out in the concentration of each chloride at *ca.* 0.02 M^{-1} , and the reaction was followed by titration with aq NaOH (*ca.* 0.02 M^{-1}), using Bromothymol Blue or Bromocresol Green as an indicator. All the kinetic runs accurately obeyed the first-order kinetic law, and the determination of $k_1(\text{s}^{-1})$ followed the method which we have previously described.⁷ The reproducibility of the rate constants from repeated runs was within $\pm 1\%$.

Alkaline Hydrolysis: The 85% (w/w) aqueous EtOH was prepared by mixing 4000 ml of abs EtOH and 545 ml of water at 25 °C;¹⁵ this gave $d_4^{25} = 0.826_6$ by means of a pycnometer. A NaOH solution (*ca.* 0.08 M^{-1}) in the solvent was made by dissolving sodium in the solvent and then standardizing it with benzoic acid. The temperature was controlled at 50 ± 0.02 °C.

A polyethylene cell equipped with Pt plates was employed for the conductivity measurements. Bromothymol Blue was used as an indicator for the titration method. The $k_2(\text{s}^{-1}\text{M}^{-1})$ values from the equimolar reactions of the ester and the OH^- were determined by the method which will be described elsewhere.¹⁵ No initial concentration effects could be detected in the concentration range of 0.012–0.036 M^{-1} of the ester

and the OH^- . Ethyl 7-nitro-2-fluorencarboxylate showed a low solubility (less than 0.005 M^{-1}), and so the determination of an accurate k_2 value was given up in the present study. The titration and conductivity methods gave the same k_2 . The reproducibility of the rate constants from repeated runs was within $\pm 1\%$.

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$$-\Delta\Delta G_p = \rho r^+ \Delta\bar{\sigma}_R^+ 2.3RT = \rho(\sigma - \sigma^0) 2.3RT.$$

Since the parameters of $(\sigma^0)_{\text{Fluo}}$ and $(\Delta\bar{\sigma}_R^+)_{\text{Fluo}}$ derived from the fluorenyl system are not utilized for the present analysis, the ρr^+ obtained does not correspond to the through-conjugation in the fluorenyl system.

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