was added and washed three times with pentane. After the last wash, the remaining pentane was removed by vacuum. After the cell was weighed again to determine the KH weight, Me_2SO was added and the cell was weighed to produce a solution of $CH_3SOCH_2^-K^+$ of known concentration. A solution of the fluorene (see ref 36) was then made (ca. 0.5 g in 5-10 mL of Me_2SO). $CH_3SOCH_2^-K^+$ (1 equiv) was added to the fluorene solution by syringe, producing the brightly colored fluorenyl anion. Then, 1 equiv of a degassed sample of the benzylic halide was added dropwise with shaking until the anion color disappeared. The solution was poured into water and extracted with ether. After the solution was washed with water and dried with $MgSO_4$, the ether was evaporated in vacuo to give the 9-benzylated product. Each product was recrystallized once before spectra and melting points were taken.

Acknowledgment. We thank the following for preparing and purifying samples used in this study: A. Streitwieser, 9-benzylfluorene; N. R. Vanier, 9-phenoxyfluorene; J. C. Branca, 9-phenyl-2-(phenylsulfonyl)fluorene; D. L. Singer, 9-((*p*-methylphenyl)thio)-2-(phenylsulfonyl)fluorene and the corresponding sulfone; A. H. Clemens, 9-((*p*-bromophenyl)thio)fluorene, 2-bromo-9-(phenylthio)fluorene and their corresponding sulfones; and G. J. McCollum, 2-chlorofluorenone. We are grateful to the National Science Foundation for support.

Registry No. 9-CN-Fl, 1529-40-4; 9-CO_2Me-Fl, 3002-30-0; 9-$PhSO_2$-Fl, 22010-78-2; 9-PhS-Fl, 28114-92-3; 9-Ph-Fl, 789-24-2; 9-PhO-Fl, 59431-16-2; 9-$PhCH_2$-Fl, 1572-46-9; 9-Me-Fl, 2523-37-7; 9-*t*-Bu-Fl, 17114-78-2; 9-CO_2Me-2,7-Br_2-Fl, 73838-62-7; 9-CO_2Me-2-Br-Fl, 73838-63-8; 9-*p*-$MeC_6H_4SO_2$-2-$PhSO_2$-Fl, 73838-64-9; 9-$C_6H_5SO_2$-2-Br-Fl, 73838-65-0; 9-*p*-$BrC_6H_4SO_2$-Fl, 73838-66-1; 9-*p*-MeC_6H_4S-2-$PhSO_2$-Fl, 73838-67-2; 9-C_6H_5S-2-Br-Fl, 29800-84-8; 9-*p*-BrC_6H_4S-Fl, 73855-17-1; 9-CN-Fl^-, 12564-43-1; 9-CO_2Me-Fl^-, 12565-94-5; 9-$PhSO_2$-Fl^-, 71805-74-8; 9-PhS-Fl^-, 71805-72-6; 9-Ph-Fl^-, 31468-22-1; 9-PhO-Fl^-, 73838-68-3; 9-$PhCH_2$-Fl^-, 53629-11-1; 9-Me-Fl^-, 31468-21-0; 9-*t*-Bu-Fl^-, 73838-69-4; 9-CO_2Me-2,7-Br_2-Fl^-, 73838-70-7; 9-CO_2Me-2-Br-Fl^-, 73838-71-8; 9-*p*-$MeC_6H_4SO_2$-2-$PhSO_2$-Fl^-, 73838-72-9; 9-$C_6H_5SO_2$-2-Br-Fl^-, 73838-73-0; 9-*p*-$BrC_6H_4SO_2$-Fl^-, 73838-74-1; 9-*p*-MeC_6H_4S-2-$PhSO_2$-Fl^-, 73838-75-2; 9-C_6H_5S-2-Br-Fl^-, 73838-76-3; 9-*p*-BrC_6H_4S-Fl^-, 73838-77-4; benzyl chloride, 100-44-7.

Hammett and Brønsted-Type Relationships in Reactions of 9-Substituted Fluorenyl Anions with Benzyl Halides

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The rates of reaction of 9-substituted fluorenyl anions, 9-G-Fl^- (G = CN, Ph, Me), with substituted benzyl chlorides (*p*-MeO, *p*-Me, *m*-Me, *p*-F, *p*-Cl, *m*-Cl, *m*-CF_3, *m*-NO_2) in Me_2SO solution have been measured. A "U-shaped" Hammett plot was obtained for 9-CN-Fl^- ($\rho_{meta} \simeq 1.3$), but a "normal" Hammett plot was obtained with 9-Ph-Fl^- ($\rho = 1.8$), which is 9.6 p*K* units more basic. Brønsted-type plots of log *k* vs. pK_a obtained for three 9-G-Fl^- families (9-$PhSO_2$, 9-PhS, and 9-Ph) reacting with *m*-$CF_3C_6H_4CH_2Cl$ gave slopes (β_{Nu}) near 0.4. The β_{Nu} values for the 9-Ph-Fl^- family reacting with $ArCH_2Cl$ were increased by the presence of electron-accepting substituents, *p*-MeO (0.30), H (0.365), *m*-CF_3 (0.45), *m*-NO_2 (0.485). The small increases in Hammett ρ values and β_{Nu} values caused by electron-withdrawing substituents in $ArCH_2Cl$ are interpreted to mean that there is a small increase in the negative charge density on the benzylic carbon atom and/or chlorine atom in the transition state. Rates for the reaction of $PhCH_2Br$ with eight 9-G-Fl^- anions were measured. For 9-CN-Fl^- the k^{Br}/k^{Cl} rate ratio was found to be 4 times larger in Me_2SO than in EtOH. The reactivity-selectivity principle is discussed and the conclusion drawn that it should be abandoned.

In the previous paper we showed that linear Brønsted-type plots were obtained for families of 9-substituted fluorenyl anions, 9-G-Fl^-, reacting with benzyl chloride in Me_2SO solution when the basicity of the anions was changed by remote substitution.[1] A series of parallel lines was obtained, all of which had slopes (β_{Nu}) near 0.3. The constancy of β_{Nu} for changes of $\Delta G°$ of as much as 20 kcal/mol was interpreted to mean that the extent of C–C bond making in the transition state (TS) for these reactions is essentially constant. In this paper we examine the effects on the rates of introducing meta and para substituents into the Ph group of $PhCH_2Cl$ and analyze the results with the aid of Hammett plots and Brønsted-type plots.

Previous work on the reaction of the 9-CN-Fl^- anion with $ArCH_2Cl$ in EtOH showed that this reaction gave a "U-shaped" Hammett plot similar to those that have frequently been observed for the reactions of benzyl halides with other types of nucleophiles.[2] Also, an earlier study of the reactions of *p*-ArS^- anions with *p*-$GC_6H_4CH_2Br$ in MeOH solution showed that in these reactions there was a tendency for β_{Nu} derived from Brønsted-type plots to

Table I. Rates of Reaction of the Conjugate Bases of 9-Cyanofluorene (1), 9-Phenyl-2-(phenylsulfonyl)fluorene (2), 9-Phenylfluorene (3), and 9-Methylfluorene (4) with Meta- and Para-Substituted Benzyl Chlorides, $GC_6H_4CH_2Cl$, in Me_2SO at 25 °C[a]

G	10^3k_2 (1)	10^3k_2 (1)[b]	10^3k_2 (2)	10^3k_2 (3)	10^3k_2 (4)
p-MeO	30.4	5.65	259	1870	76500
p-Me	9.13		56.0	677	46600
m-Me	9.43		54.0	1020	60300
H	6.19	1.62	38.2	610	49400
p-F	13.2		-	1700	-
p-Cl	15.2		115	2510	172000
m-Cl	15.3		105	3410	241000
m-CF_3	22.7		141	6060	-
m-NO_2	54.0	21.6	409	31900	-
p-NO_2			710		-

[a] $M^{-1}\ s^{-1}$; the results of 3-5 runs with standard deviations of ±3% or less in most instances. [b] In NMP solvent.

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(1) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.*, preceding paper in this issue.

(2) Bowden, K.; Cook, K. S. *J. Chem. Soc.* 1968, 1529-1533.

0022-3263/80/1945-3320$01.00/0

Table II. Equilibrium Acidity Constants of Substituted Fluorenes (pK_a) and Second-Order Rate Constants (10^3k_2) for Reactions of Anions Derived Therefrom with *m*- and *p*-$XC_6H_4CH_2Cl$ or with $PhCH_2Br$ in Me_2SO at 25 °C[a]

(a) 9-$PhSO_2$-Fluorene Family

fluorene	pK_a	$10^3k_2^{m\text{-}CF_3}$	$10^3k_2^{PhCH_2Br}$
9-*p*-$MeC_5H_4SO_2$-2-$PhSO_2$	8.6	6.11	860
9-$C_6H_5SO_2$-2-Br	9.6	11.9	1250
9-*p*-$BrC_6H_4SO_2$	10.9	43.6	
9-$C_6H_5SO_2$	11.6	68.3	4770

(b) 9-$PhSO_2$-Fluorene Family

fluorene	pK_a	$10^3k_2^{m\text{-}CF_3}$
9-*p*-MeC_6H_4S-2-$PhSO_2$	11.9	57.5
9-C_6H_5S-2-Br	13.2	263
9-*p*-BrC_6H_4S	14.8	970
9-C_6H_5S	15.4	1760

(c) 9-Ph-Fluorene Family

fluorene	pK_a	$10^3k_2^{m\text{-}CF_3}$	$10^3k_2^{m\text{-}NO_2}$	$10^3k_2^{p\text{-}MeO}$	$10^3k_2^{PhCH_2Br}$
9-C_6H_5-2-$PhSO_2$	13.8	141	409	259	13 890
9-*p*-$MeSO_2C_6H_4$	15.2	394	1490	294	28 000[b]
9-*m*-ClC_6H_4	16.8	1910	7580	901	100 000[b]
9-C_6H_5	17.9	6060	31900	1870	189 000[b]
9-*p*-MeC_6H_4	18.3	10050			

(d) 9-Me-Fluorene Family

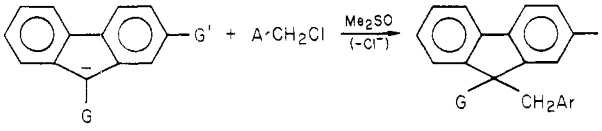
fluorene	pK_a	$10^3k_2^{m\text{-}Cl}$
9-Me-2,7-Br_2	17.7	6 120
9-Me-2-Cl	20.05	42 100
9-Me	22.3	241 000

[a] $M^{-1}\ s^{-1}$; reproducible to 3%, or less, based on 3-5 runs, unless otherwise noted. [b] Reproducible to ±5-10%.

increase in size as G became more electron withdrawing.[3,4] We have confirmed and extended both of these observations for reactions of 9-G-Fl^- anions.

Results

The rate data for the reactions of 9-CN-Fl^- (1), 9-Ph-2-$PhSO_2$-Fl^- (2), 9-Ph-Fl^- (3), and 9-Me-Fl^- (4) with meta and para substituted benzyl chlorides in Me_2SO (eq 1) are summarized in Table I.



(1)

G = CN, Ph, Me; G' = H
G = Ph; G' = $PhSO_2$

In agreement with the results reported in the preceding paper,[1] the yields in these reactions were found to be high, and excellent second-order kinetics were observed to at least 90% reaction.

Rate measurements were also carried out for reactions between a number of 9-G-Fl^- anions in which substituents were present in the phenyl ring of G or in the 2- or 2,7-position(s) of the fluorene nucleus and selected benzyl chlorides or benzyl bromide. The rate constants (k_2) and equilibrium acidities of 9-G-FlH (pK_a) are summarized in Table II.

Experimental Section

The pK_a and kinetic measurements and the product studies were carried out by the method described in the preceding paper.[1] The product isolated in over 90% yield from the reaction of 9-Ph-Fl^- with *m*-$NO_2C_6H_4CH_2Cl$ had the following: mp 153–154 °C; NMR δ 7.0–7.5 (17 H, m), 3.8 (2 H, s). Microanalysis by the usual combustion method gave satisfactory analyses for hydrogen and nitrogen, but the % C was low by 0.56. Reanalysis using a Carlo Erba CHN analyzer which operates at a higher combustion temperature (1050 to 1100 °C) gave good agreement with the calculated results.

Anal. Calcd for $C_{26}H_{19}NO_2$: C, 82.73; H, 5.04; N, 3.71. Found: C, 82.43; H, 5.05; N, 3.67.

(Microanalyses were by Microtech, Skokie, IL.)

The product from the reaction of 9-Me-Fl^- with *p*-$MeOC_6H_4CH_2Cl$ had mp 120–121 °C and NMR δ 7.0–7.5 (8 H, m), 6.4 (4 H, s), 3.6 (3 H, s), 3.0 (2 H, s), 1.5 (3 H, s). Again, ordinary microanalysis gave a low % C (by 0.74). Analysis using the Carlo Erba analyzer gave good agreement.

Anal. Calcd for $C_{22}H_{20}O$: C, 87.95; H, 6.72. Found: C, 87.80; H, 6.75.

Mass spectra in each instance gave parent peaks of low-abundance and high-abundance peaks corresponding to the loss of a benzyl fragment. Presumably the low carbon analyses are caused by incomplete combustion.

Benzyl Halides. Benzyl bromide, benzyl chloride, *m*- and *p*-chlorobenzyl chlorides, *m*- and *p*-methylbenzyl chlorides, *p*-fluorobenzyl chloride, and *m*-(trifluormethyl)benzyl chloride were commercially available liquids and were distilled under vacuum once or twice through a 10-cm Vigreux column; *m*- and *p*-nitrobenzyl chloride were commercially available solids and both were recrystallized twice from hexane.

p-Methoxybenzyl chloride was made from *p*-methoxybenzyl alcohol and thionyl chloride by the method of Swain and Langsdorf;[5] bp 120–122 °C (8 mm) [lit.[5] bp 92.5 °C (1.5 mm)].

Discussion

Hammett Correlations. The failure of the reactions of anionic nucleophiles with benzyl halides to follow a well-defined Hammett relationship has long been known. Young and Jencks have recently reviewed the literature in this area and have concluded that much or most of the curvature observed in these U-shaped Hammett plots can be accounted for by assuming a balance of opposing electron-donor resonance and electron-acceptor polar effects by substituents, rather than a change in mechanism (from S_N2 to S_N1 or ion pair) or a change in structure of the transition state (TS) with different balances of bond

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(3) Hudson, R. F.; Klopman, G. J. *J. Chem. Soc.* **1962**, 1062–1067.

(4) Hudson, R. F. "Chemical Reactivity and Reaction Paths"; G. Klopman, Ed.; Wiley-Interscience: New York, 1974; Chapter 4.

(5) Swain, C. G.; Langsdorf, W. P. *J. Am. Chem. Soc.* **1951**, *73*, 2813–2831.

Table III. Changing Substituent Patterns for the Relative Rates of Reactions of 9-G-Fl⁻ with G′-$C_6H_4CH_2Cl$ in Me_2SO at 25 °C

G′	9-CN-Fl⁻ (EtOH)[a]	9-CN-Fl⁻	9-Ph-2-$PhSO_2$-Fl⁻	9-Ph-Fl⁻	9-Me-Fl⁻
H	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
p-Me	1.8_5	1.5	1.5	1.1	0.9
m-Me	1.8_5	1.5	1.4	1.7	1.2
p-F		2.1		2.8	
p-MeO		4.9	6.8	3.0	1.5
p-Cl		2.4	3.0	4.0	3.5
m-Cl	2.1	2.5	2.8	5.7	4.9
m-CF_3		3.7	3.7	9.9	
m-NO_2	8.6	8.7	10.7	53	
p-NO_2			19		

[a] Data of Bowden and Cook at 20 °C (ref 2).

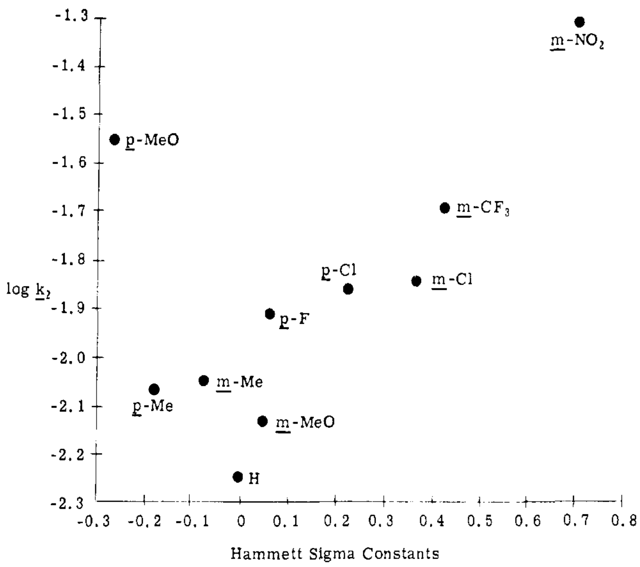

Figure 1. Plot of log k_2 vs. Hammett σ constants for the reactions of 9-cyanofluorenyl anion with benzyl chlorides in Me_2SO solution at 25 °C. (The point for *m*-$MeOC_6H_4CH_2Cl$ is estimated from the rate data in EtOH reported in ref 2. Hammett σ's were used except for $\sigma_{m\text{-MeO}}$ for which $\sigma = 0.04$ has been found to be more suitable in Me_2SO solvent. See: Bordwell, F. G.; Cornforth, F. J. *J. Org. Chem.* **1978**, *43*, 1763–1768.

making and bond breaking.[6] However, they noted a changing selectivity for the benzyl chlorides *p*-$NO_2C_6H_4CH_2Cl$ vs. $C_6H_5CH_2Cl$ in reactions with anilines. As the basicity of the aniline was increased by 1.8 p*K* units by substitution, i.e., *m*-Cl, *p*-Cl, H, *p*-Me, *p*-MeO, the apparent two-point ρ changed from −0.8 to −0.2. This was accounted for with the aid of a reaction-coordinate-energy contour diagram by assuming that the electron-donor substituents, *p*-Me and *p*-MeO, cause both "anti-Hammond" and "Hammond" effects whereas the electron-attracting substituents, *p*-Cl and *m*-Cl, cause only "Hammond" effects. The latter effects result in more bond making and a more negative ρ. By using 9-G-Fl⁻ anions, we have now examined the effect on benzyl chloride selectivity of changing the basicity of the nucleophile by 14 p*K* units.

The least basic of the 9-G-Fl⁻ anions, 9-CN-Fl⁻, showed a selectivity pattern in reactions with $ArCH_2Cl$ in Me_2SO (Figure 1) similar to that reported for this reaction in EtOH (Table III). Comparison of the selectivity pattern for 9-CN-Fl⁻ with that observed for 9-Me-Fl⁻, which is more basic by 14 p*K* units and has similar steric requirements,[1] showed that rate accelerations by the electron-donor substituents, *p*-Me, *m*-Me, and *p*-MeO, relative to H, had decreased slightly, whereas those for electron-acceptor substituents, *p*-Cl, *m*-Cl, had increased slightly. The same trend was observed for 9-Ph-Fl⁻, which is 9.6 p*K* units more basic than 9-CN-Fl⁻ and more sterically demanding.[1] These changes indicate that in the TS the negative charge density on the benzylic carbon atom and/or chlorine atom has increased slightly for the more basic nucleophiles, causing a small decrease in electron-donor resonance and a small increase in polar electron acceptance.

For the 9-CN-Fl⁻ reactions, the Hammett plot is scattered (Figure 1); the H and meta points for electron-withdrawing substituents appear to fall on one line ($\rho \simeq 1.3$; $R^2 = 0.97$) and the points for *p*-Me, *m*-Me, *p*-F, and *p*-Cl appear appear to fall on a second line ($\rho \simeq 0.6$; $R^2 = 0.95$). The divergence of these lines supports the conclusion that electron-acceptor polar effects ("meta line") and electron-donor resonance effects ("para line") are both effective in stabilizing the TS.[6] Note that the weak electron-donor properties of *p*-Me and *m*-Me are sufficient to make them rate accelerating, relative to H, and that *p*-Cl ($\sigma = 0.23$) is as effective as *m*-Cl ($\sigma = 0.37$) in accelerating the rate. The *p*-MeO point deviates from either line. Its accelerating effect is only moderate, however, since the ρ calculated from the H and *p*-MeO points is only −0.9 (using σ^+ for *p*-MeO).

For the more basic 9-Ph-Fl⁻ anion, the slightly greater negative charge on the benzylic carbon atom and/or chlorine atom in the TS has caused a decrease in the resonance electron-donor effects and an increase in the polar electron-acceptor effects. The result is an essentially "normal" Hammett plot (Figure 2);[7] for the points *p*-Me, *m*-Me, *p*-F, *p*-Cl, *m*-Cl, *m*-CF_3, and *m*-NO_2, $\rho = 1.8$ and $R^2 = 0.953$. The H point deviates from the line, as does the *p*-MeO point, but the other points fall in the prescribed order.

Comparing the "meta line" for 9-CN-Fl⁻ with the "normal" line for 9-Ph-Fl⁻ nucleophiles, we see that ρ has increased from about 1.3 to 1.8 for a change in basicity of 9.6 p*K* units. This change is in the same direction as observed for the changing basicity of aniline on ArS⁻ nucleophiles.[6] These changes in basicity cause only small relative changes in rates, however. For 9-G-Fl⁻ anions reacting with *p*-$MeOC_6H_4CH_2Cl$, the rate change, relative to $PhCH_2Cl$, is only 1.6-fold for a basicity change of $10^{9.6}$ and only 3.3-fold for a basicity change of 10^{14}. For *m*-$NO_2C_6H_4CH_2Cl$, the rate change, relative to $PhCH_2Cl$, is only 6.2-fold for a basicity change of $10^{9.6}$. The assumption of a *slight* increase in the negative charge density on the benzylic carbon atom and/or chlorine atom in TS appears

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[6] Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288–3294.

[7] One cannot expect Hammett σ constants to give precise correlations in systems such as this wherein the geometric relationship of the substituents to the reaction site in the TS differs appreciably from that in the benzoic acid–benzoate ion equilibrium.

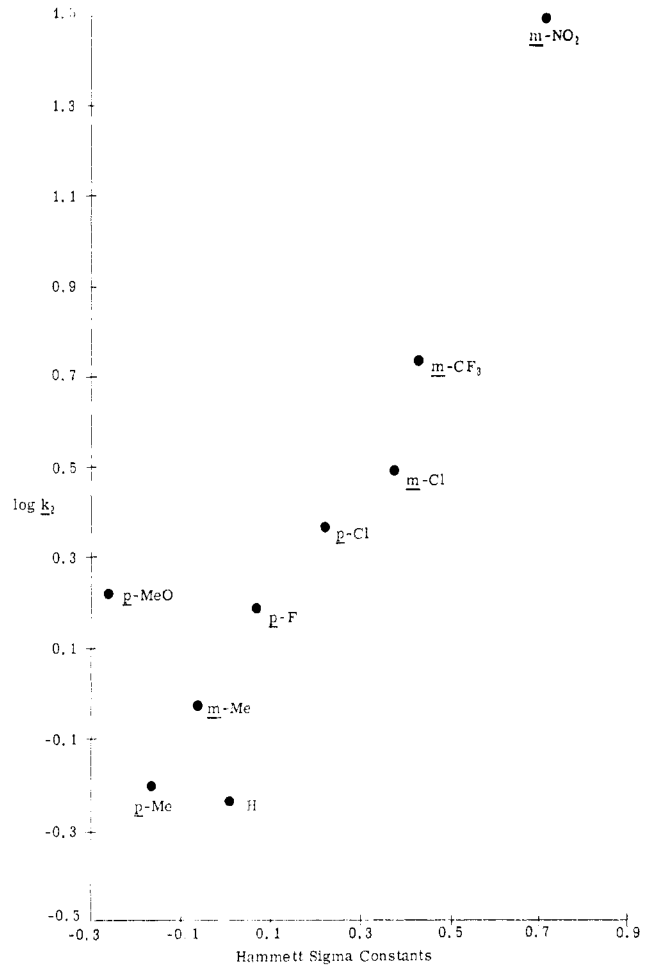

Figure 2. Plot of log k_2 vs. Hammett σ constants for the reactions of 9-phenylfluorenyl anion with benzyl chlorides in Me_2SO solution at 25 °C.

sufficient to account for these results.[6] The evidence presented in the previous paper indicates that the extent of C–C bond making in the TS does not change appreciably for reactions of these 9-G-Fl$^-$ anions with $PhCH_2Cl$ that involve rate changes of as much as 10^4. It seems unlikely, then, that the much smaller rate changes just discussed are due to changes in the extent of bond making.[8]

Variation in β_{Nu} Values with Substituent Changes. The data in Table II allow β_{Nu} to be determined for a number of substituted benzyl chlorides. The Brønsted-type plots in Figure 3 show that for reactions of m-$CF_3C_6H_4CH_2Cl$ with 9-G-Fl$^-$ anions in Me_2SO linear relationships are observed with the 9-$PhSO_2$-Fl$^-$, 9-PhS-Fl$^-$, and 9-Ph-Fl$^-$ families. The β_{Nu} values are near 0.4 and are therefore distinctly higher than the β_{Nu} values near 0.3 obtained for these families reacting with unsubstituted benzyl chloride.[1] The relationship of these lines to one another is comparable to that for these families reacting with $PhCH_2Cl$, and the same equation can be used to relate them (eq 2)[1] with $\beta_{Nu} = 0.4$ instead of 0.3. Presumably

$$\log (k/k_0) = \beta_{Nu}(\Delta pK_a - c) \qquad (2)$$

the displacement of other 9-G-Fl$^-$ families from the line will be similar to those previously observed.[1] If so, the c values will be the same as before, and k_0 can be taken as the rate for 9-CN-Fl$^-$ with m-$CF_3C_6H_4CH_2Cl$.

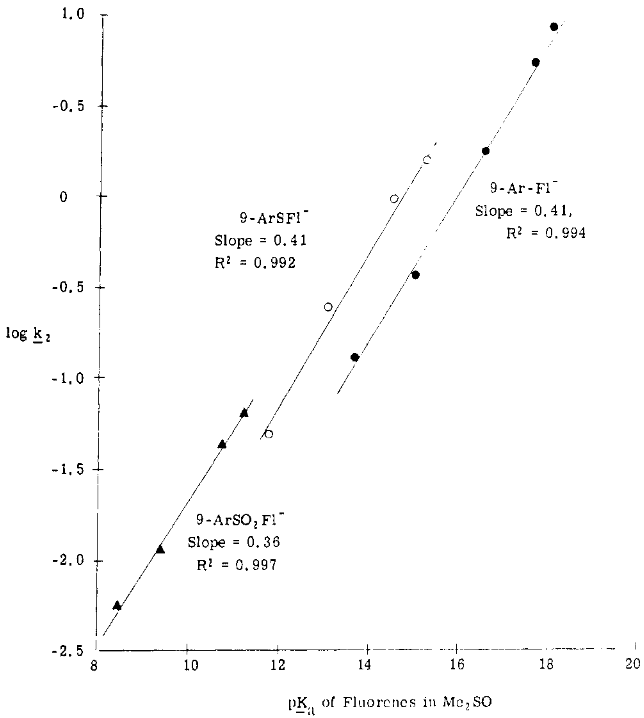

Figure 3. Plots of log k_2 vs. pK_a for the reactions of remotely substituted fluorenyl carbanions with m-$CF_3C_6H_4CH_2Cl$ in Me_2SO at 25 °C. (See Table II for the data.)

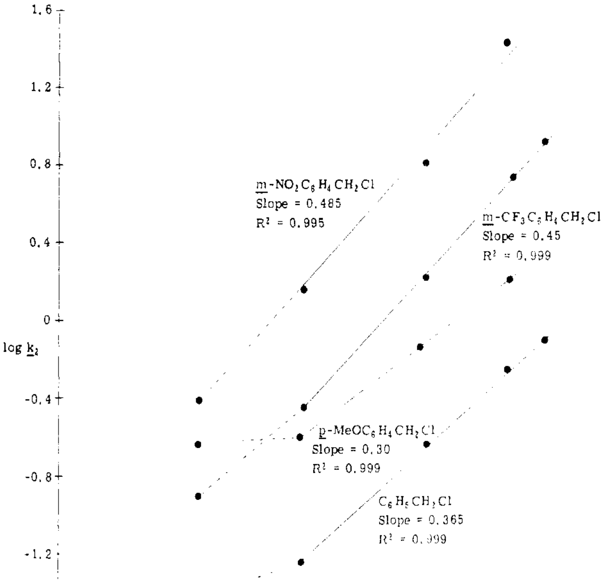

Figure 4. Plots of log k_2 vs. pK_a for 9-Ar-Fl$^-$ anions reacting with $C_6H_5CH_2Cl$, p-$MeOC_6H_4CH_2$, m-$CF_3C_6H_4CH_2Cl$, and m-$NO_2C_6H_4CH_2Cl$. (The 9-Ph-2-$PhSO_2$ points were omitted from the least-squares calculations of the slopes—see the text for a discussion.)

When β_{Nu} values were compared for a series of benzyl chlorides reacting with the 9-Ph-Fl$^-$ nucleophile family (Figure 4), a progressive increase was observed as the electron-acceptor capacity of the substituent increased: p-MeO (0.30) < H (0.365) < m-CF_3 (0.45) < m-NO_2 (0.485). β_{Nu} follows the same trend as the Hammett ρ (Figure 2), with a slightly smaller sensitivity ($\rho_{\beta_{Nu}} \simeq 1.2$). This suggests that when an electron-acceptor substituent is present

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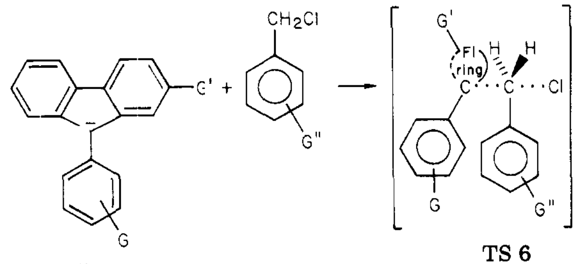
[8] A referee has argued that the data can be interpreted with the aid of a reaction-coordinate-energy contour diagram like that used by Young and Jencks.[6] This is true, but we see no need to invoke combinations of "anti-Hammond" and "Hammond" effects to account for small changes in rates when β_{Nu} values indicate that "Hammond" effects are absent for much larger changes in rates.[1]

in the benzene ring to stabilize a negative charge a *slightly* larger fraction of the charge is transferred from the nucleophile to the benzylic carbon atom and/or chlorine atom in the TS. This increased charge transfer does not necessarily require an increase in bond making in the TS.

The β_{Nu} plots in Figure 4 include only the points for the 9-Ph-Fl$^-$ family where substitution was made in the Ph ring (*p*-Me, H, *m*-Cl, *p*-MeSO$_2$). The point for the 2-PhSO$_2$ substituent in the fluorene ring was omitted because it appeared to deviate. Examination of Figure 4 shows that the extent of deviation increases with decreasing electron-acceptor ability of the substituent in the benzyl chloride, i.e., *m*-NO$_2$ < *m*-CF$_3$ < H < *p*-MeO. These deviations are in the direction of rate enhancement. The data show that substitution in the 2-position of the fluorene ring produces a slightly different electronic effect than substitution in the Ph ring. This is understandable when one compares the structural features of the anion **5** and the TS **6**.



5

TS **6**

The stability of fluorenyl anions is known to be highly sensitive to substitution in the fluorene ring ($\rho_{K_a} \simeq 7.5$).[9] Furthermore, the 2-position has some para character,[9] and the 2-PhSO$_2$ group will therefore display some σ_p^- character in stabilizing **5**. Substitution in the Ph ring has a much smaller effect (ρ_{K_a} for 9-Ar-FlH $\simeq$ 2.2[10]). The Ph ring is twisted out of the plane of the fluorenyl ring because of steric interactions with the 1 and 8 ("peri") hydrogen atoms,[10] but the *p*-MeSO$_2$ group will no doubt still exhibit some σ_p^- character in stabilizing **5**. In TS **6** the 9-GC$_6$H$_4$ ring has moved to the side of the fluorene ring opposite to the incoming electrophile and an appreciable fraction of the negative charge density has shifted away from the 9-carbon atom. The substituents G and G′ are now exerting their influence, not only on the 9-carbon atom but also by through-space electrostatic interactions on the developing C–C bond and on the negatively charged benzylic carbon atom. It is not surprising, then, that the relative effects of the G and G′ atoms on the stabilities of **5** and **6** are different.

Leaving-Group Effects. According to the picture emerging from considerations of Brønsted-type β_{Nu} values and Hammett relations for the reactions of 9-G-Fl$^-$ anions with ArCH$_2$Cl in Me$_2$SO solution, the TS is one where a constant amount of C–C bond making occurs for wide ranges of 9-G-Fl$^-$ basicities and a small increase in negative charge develops on the benzylic carbon atom. This picture seems to require that the progressive increase in rate observed with increased basicity be accompanied by a progressive increase in charge density on chlorine, which may correspond to a progressive increase in the extent of C–Cl bond breaking. We attempted to obtain some information bearing on this point by comparing the rates of reaction of 9-G-Fl$^-$ anions with PhCH$_2$Br to those with PhCH$_2$Cl.

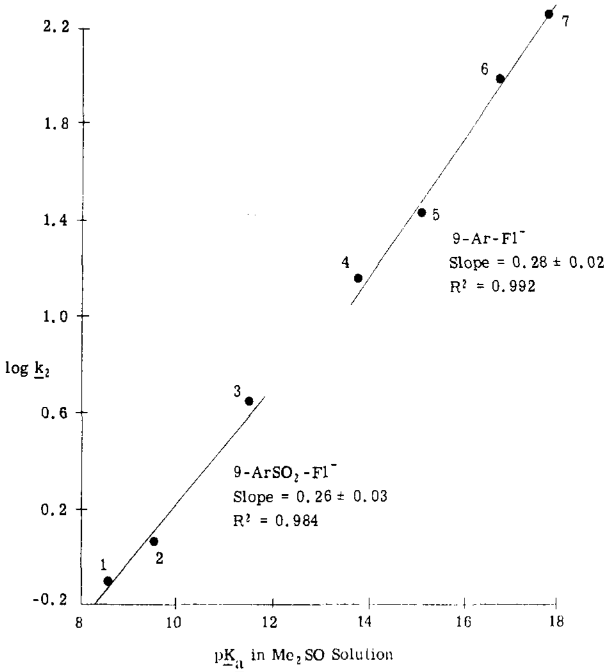


Figure 5. Plots of log k_2 for the reactions of 9-PhSO$_2$-Fl$^-$ and 9-Ph-Fl$^-$ carbanions with C$_6$H$_5$CH$_2$Br in Me$_2$SO at 25 °C. Points 1 (2-PhSO$_2$-9-PhSO$_2$), 2 (2-Br-9-PhSO$_2$), 3 (9-PhSO$_2$), 4 (2-PhSO$_2$-9-Ph), 5 (9-*p*-MeSO$_2$C$_6$H$_4$), 6 (9-*m*-ClC$_6$H$_4$), 7 (9-C$_6$H$_5$).

Table IV. Summary of Leaving-Group Effects for Substituted Fluorenyl Carbanions Reacting with PhCH$_2$Br and PhCH$_2$Cl in Me$_2$SO at 25 °C[a]

substituent	pK_a	k^{Br}/k^{Cl}
9-CN	8.3	351[b]
9-*p*-MeC$_6$H$_4$SO$_2$-2-PhSO$_2$	8.6	330
9-C$_6$H$_5$SO$_2$-2-Br	9.6	361
9-C$_6$H$_5$SO$_2$	11.6	367
9-C$_6$H$_5$-2-PhSO$_2$	13.8	364
9-*p*-MeSO$_2$C$_6$H$_4$	15.2	435
9-*m*-ClC$_6$H$_4$	16.8	389
9-C$_6$H$_5$	17.9	310

[a] Second-order rate constants with PhCH$_2$Cl are reproducible to ±3%; those with PhCH$_2$Br are reproducible to ±5–10%, the errors increasing as k_2 increases. [b] In NMP the ratio is 580.

In EtOH at 25 °C PhCH$_2$Br reacts with 9-CN-Fl$^-$ at a rate ~80 times faster than does PhCH$_2$Cl.[2] In Me$_2$SO, the k^{Br}/k^{Cl} ratio increases to 351. This substantial difference is no doubt caused primarily by the difference in the relative abilities of Me$_2$SO and EtOH to solvate the incipient Cl$^-$ and Br$^-$ ions in the TS. Note, for example, that single-ion free energies of transfer of Cl$^-$ and Br$^-$ from MeOH to Me$_2$SO show that Br$^-$ solvation is favored over Cl$^-$ solvation by 1.8 kcal M^{-1}.[11]

The data for the 9-PhSO$_2$-Fl$^-$ and 9-Ph-Fl$^-$ families give satisfactory Brønsted-type plots for reactions with PhCH$_2$Br (Figure 5). The β_{Nu} values are smaller in each instance for PhCH$_2$Br than for PhCH$_2$Cl. The reason for this is not clear as yet, since the size of β_{Nu} values appears to depend not only on the extent of C–C bond making in the TS but also on electronic effects of substituents in the Ph ring of ArCH$_2$X. It is possible, therefore, that differing electronic effects of Cl and Br may influence the size of β_{Nu}.[15]

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(9) Bordwell, F. G.; McCollum, G. J. *J. Org. Chem.* **1976**, *41*, 2391–2395. The ρ_{K_a} for 2-substitution into the fluorene ring of 9-Ar-FlH will be smaller than 7.5 because of delocalization of the negative charge in the anion into the Ar ring (resonance-saturation effect).

(10) Cockerill, A. G.; Lamper, J. E. *J. Chem. Soc. B* **1971**, 503–507.

(11) Cox, B. G.; Hedwig, G. R.; Parker, A. J.; Watts, D. W. *Aust. J. Chem.* **1974**, *27*, 477–501.

Focusing attention on the 9-Ph-Fl$^-$ family, where the data are likely to be more reliable, we find that β_{Nu} decreases from 0.31 for PhCH$_2$Cl to 0.28 for PhCH$_2$Br. This change can have a substantial effect on the $k^{\mathrm{Br}}/k^{\mathrm{Cl}}$ rate ratios as may be seen by comparing the ratios 435, 389, and 310 in the 9-Ph-Fl$^-$ family for the *p*-MeSO$_2$, *m*-Cl, and H substituents, respectively (Table IV).

Interpretation of $k^{\mathrm{Br}}/k^{\mathrm{Cl}}$ leaving-group effects is rendered difficult because of the large differences (a) in Cl and Br electronegativities, (b) in C–Cl and C–Br bond lengths and bond strengths, and (c) in solvation of the incipient Cl$^-$ and Br$^-$ ions. We hope to obtain additional information concerning leaving-group effects in S$_{\mathrm{N}}$2 reactions by studying systems where the nature of the atoms in the bond broken is kept constant.

The Reactivity–Selectivity Principle (RSP). A controversy has arisen recently over the validity of the so-called reactivity–selectivity principle (RSP), which states that a more reactive species will be less selective in choosing its reaction partner and vice versa.[12] The data in Table III contain many exceptions to RSP. For example, 9-Me-Fl$^-$ reacts with PhCH$_2$Cl over 8000 times as rapidly as does 9-CN-Fl$^-$.[1] According to RSP, the highly reactive 9-Me-Fl$^-$ ion should be less selective in choosing *m*-ClC$_6$H$_4$CH$_2$Cl vs. PhCH$_2$Cl than will the less reactive 9-CN-Fl$^-$ ion. We see from Table III, however, that in a competition for equal amounts of these reagents 9-Me-Fl$^-$ would choose *m*-ClC$_6$H$_4$CH$_2$Cl over PhCH$_2$Cl in a ratio of 4.9 to 1.0, compared to 2.5 to 1.0 for 9-CN-Fl$^-$. The constancy of β_{Nu} for large changes in $\Delta G°$ brought about by increased nucleophile basicities or decreased leaving-group basicities, which was discussed in the previous paper,[1] constitutes an even greater challenge to RSP. It must be remembered that RSP has its origin in the Leffler–Grunwald rate–equilibrium relationship.[13] The experimental support for RSP rests primarily, therefore, on the observation of a variation of Brønsted β's in proton-transfer reactions, i.e., curved Brønsted plots, and a variation in β_{Nu} in Brønsted-type plots for S$_{\mathrm{N}}$2 reactions.[14] We have argued elsewhere that curved Brønsted plots are at least as likely to arise from failure to keep steric effects constant and the use of different kinds of donor and acceptor atoms (causing solvation effects of change) as from changes in the extent of bond making and bond breaking in the TS.[1] The failure to observe curvature in Brønsted-type plots for S$_{\mathrm{N}}$2 reactions[1] supports this view. We agree with the conclusion that RSP should be abandoned.[6]

Acknowledgment. We are grateful to the National Science Foundation for the support of this work.

Registry No. **1**, 1529-40-4; **1** anion, 12564-43-1; **2**, 73636-50-7; **2** anion, 73872-40-9; **3**, 789-24-2; **3** anion, 31468-22-1; **4**, 2523-37-7; **4** anion, 31468-21-0; 9-*p*-MeC$_6$H$_4$SO$_2$-2-PhSO$_2$-Fl, 73838-64-9; 9-C$_6$H$_5$SO$_2$-2-Br-Fl, 73838-65-0; 9-*p*-BrC$_6$H$_4$SO$_2$-Fl, 73838-66-1; 9-C$_6$H$_5$SO$_2$-Fl, 22010-78-2; 9-*p*-MeC$_6$H$_4$S-2-PhSO$_2$-Fl, 73838-67-2; 9-C$_6$H$_5$S-2-Br-Fl, 29800-84-8; 9-*p*-BrC$_6$H$_4$S-Fl, 73855-17-1; 9-C$_6$H$_5$S-Fl, 28114-92-3; 9-*p*-MeSO$_2$C$_6$H$_4$-Fl, 73872-41-0; 9-*m*-ClC$_6$H$_4$-Fl, 32377-11-0; 9-*p*-MeC$_6$H$_4$-Fl, 18153-43-0; 9-Me-2,7-Br$_2$-Fl, 73872-42-1; 9-Me-2-Cl-Fl, 73872-43-2; 9-*p*-MeC$_6$H$_4$SO$_2$-2-PhSO$_2$-Fl$^-$, 73838-72-9; 9-C$_6$H$_5$SO$_2$-2-Br-Fl$^-$, 73838-73-0; 9-*p*-BrC$_6$H$_4$SO$_2$-Fl$^-$, 73838-74-1; 9-C$_6$H$_5$SO$_2$-Fl$^-$, 71805-74-8; 9-*p*-MeC$_6$H$_4$S-2-PhSO$_2$-Fl$^-$, 73838-75-2; 9-C$_6$H$_5$S-2-Br-Fl$^-$, 73838-76-3; 9-*p*-BrC$_6$H$_4$S-Fl$^-$, 73838-77-4; 9-C$_6$H$_5$S-Fl$^-$, 71805-72-6; 9-*p*-MeSO$_2$C$_6$H$_4$-Fl$^-$, 73872-44-3; 9-*m*-ClC$_6$H$_4$-Fl$^-$, 73872-45-4; 9-*p*-MeC$_6$H$_4$-Fl$^-$, 42730-14-3; 9-Me-2,7-Br$_2$-Fl$^-$, 73872-46-5; 9-Me-2-Cl-Fl$^-$, 73872-47-6; *p*-MeOC$_6$H$_4$CH$_2$Cl, 824-94-2; *p*-MeC$_6$H$_4$CH$_2$Cl, 104-82-5; *m*-MeC$_6$H$_4$CH$_2$Cl, 620-19-9; C$_6$H$_5$CH$_2$Cl, 100-44-7; *p*-FC$_6$H$_4$CH$_2$Cl, 352-11-4; *p*-ClC$_6$H$_4$CH$_2$Cl, 104-83-6; *m*-ClC$_6$H$_4$CH$_2$Cl, 620-20-2; *m*-CF$_3$C$_6$H$_4$CH$_2$Cl, 705-29-3; *m*-NO$_2$C$_6$H$_4$CH$_2$Cl, 619-23-8; *p*-NO$_2$C$_6$H$_4$CH$_2$Cl, 100-14-1; PhCH$_2$Br, 100-39-0.

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(14) Following the original suggestion of Leffler and Grunwald,[13] comparisons of rate and product data from solvolysis reactions have often been used in support of RSP. The mechanistic complexity of these reactions, wherein products can arise from at least two types of ion pairs, as well as free cations, renders them unsuitable, however, as a testing ground for RSP.[12a]

(15) **Note Added in Proof.** Additional work with these and other substrates suggests that, in general, the β_{Nu} values for RCl and RBr do not differ significantly.

Acidities of Indene and Phenyl-, Diphenyl-, and Triphenylindenes

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Equilibrium acidities in Me$_2$SO for indene and 2-phenyl-, 3-phenyl-, 1,3-diphenyl-, 2,3-diphenyl-, and 1,2,3-triphenylindenes are reported. The pK_{a} values for indene and 1,3-diphenylindene agree reasonably well with literature values once the latter are corrected to an absolute basis. It is urged that henceforth acidities of weak acids in Me$_2$SO or other dipolar nonhydroxylic solvents be referred to an absolute base rather than an arbitrary reference standard. 2-Phenylindene was found to be only 0.7 pK_{a} unit more acidic than indene, and 2-Ph substitution into 3-phenyl- and 1,3-diphenylindenes caused a decrease in acidity for steric reasons. The 7.6 pK_{a} units greater acidity of 1,3-diphenylindene, relative to indene, is attributed mainly to charge delocalization in the anion.

Phenyl substitution for hydrogen has been found to increase the acidity of carbon acids in solution substantially. In the absence of steric effects, the size of the phenyl acidifying effect has been shown to decrease with a decrease in the size of the negative charge on the carbon atom to which the phenyl group is attached (resonance-saturation effect).[1] When phenyl groups are substituted successively for hydrogen, there is a progressive decrease in the size of the acidifying effects. For example, in the gas phase, phenyl substitution into methane increases the

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