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Rate–Equilibrium Relationships for Reactions of Families of Carbanion Nucleophiles with *N*-Benzyl-*N*,*N*-dimethylanilinium Cations and with Alkyl Chlorides, Bromides, and Iodides

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Abstract: Rates of reaction of a family of 9-methylfluorenide anions, 9-MeFl$^-$, with 15 substituted *N*-benzyl-*N*,*N*-dimethylanilinium cations, $GC_6H_4CH_2N(Me)_2C_6H_4Y^+$, were measured in a 0.8 M KNO_3 solution of Me_2SO at 25 °C. Substitution in the benzyl moiety produced a U-shaped Hammett plot, with *m*-CN reacting 9- to 15-fold faster than H and *p*-MeO reacting 1.5- to 3-fold faster than H, depending on the basicity of the 9-RFl$^-$ ion. Brønsted β_{Nu} values obtained by varying nucleophile basicity in the 9-MeFl$^-$ ion family were 0.28 for *N*-(*p*-methoxybenzyl)-*N*,*N*-dimethylanilinium ion, 0.33 for *N*-benzyl-*N*,*N*-dimethylanilinium ion, and 0.39 for *N*-(*m*-cyanobenzyl)-*N*,*N*-dimethylanilinium ion. These β_{Nu} values were unaffected by substitution in the aniline portion of the substrate. Hammett ρ_{Lg} values were obtained by substitution of *m*-Cl, *p*-Br, H, *p*-Me and *p*-MeO groups (Y) in the dimethylaniline leaving group; ρ_{Lg} values were all near 2.0 and were insensitive to the basicity of the attacking nucleophile and the substituent G in the benzyl group of the substrate. β_{Nu} values for families of 9-RFl$^-$ ions reacting with $ArCH_2X$, *n*-BuX, and $CNCH_2X$ also remained constant as the leaving group, X, was changed (Cl, Br, and I) for a given substrate and when the donor atom was changed along the series C$^-$, N$^-$, O$^-$, and S$^-$. These results indicate that there is no direct relationship between the size of β_{Nu} and the extent of bond making or bond breaking in the transition state for S_N2 reactions, as has been generally assumed in theoretical attempts to rationalize the effects of structural variations on rate. It is suggested that S_N2 reactions occur in two stages. The size of β_{Nu} is determined in the first stage where an ion–dipole complex is formed. The rate is determined largely in the second stage where bonds are formed and cleaved and where molecular and solvent reorganization occurs.

The relationship between rates and equilibria, or the lack thereof, has intrigued chemists for over half a century. In 1935 Eyring developed the absolute rate theory, hypothesizing that, in terms of thermodynamics, the transition state (TS) could be treated as a separate chemical entity possessing free energy ($G^‡$), enthalpy ($H^‡$), and entropy ($S^‡$). The TS was postulated to be in equilibrium with starting materials, so the rate of reaction was related to the difference in free energy of starting materials and the TS, $\Delta G^‡$.[1] In the same year Hammett pointed out that the Brønsted catalysis law (eq 1) could be considered to be an example

$$\log k = \beta \log K_a + c \qquad (1)$$

of numerous relationships between rates and equilibria,[2] thereby anticipating the relationship between rates and equilibria in meta- and para-substituted benzenoid substrates, which later formed the basis for the Hammett equation.

At the same time, Evans and Polanyi suggested that the influence of a structural variable, χ, on the reaction rate could be approximated if its influence on the free energy of activation was intermediate to that of the free energy relating the initial and final states.[3] Bell came to the same conclusion at about the same time for proton transfer ($H^+{}_T$) reactions for which he represented the TS as corresponding to the intersection of potential energy curves representing initial and final states.[4] To facilitate a molecular interpretation Bell and Polanyi wrote the Brønsted equation in a differential form (eq 2) where $\Delta G°$ is the standard free-energy change for the reaction, $\Delta G^‡$ is the free energy of activation, and the operator δ represents chemical modifications in the catalyst.

$$\delta(\Delta G^‡) = \beta\delta(\Delta G°) \qquad (2)$$

These ideals of Bell and Polanyi lay dormant for 20 years until revived and extended by Hammond[5] and by Leffler and Grunwald.[6] The latter authors adopted eq 2 and suggested that the coefficient, β, could be used as a measure of the position of the TS along the reaction coordinate, a value approaching zero indicating a reactant-like TS, characteristic of an exergonic reaction, and a value approaching unity indicating a product-like TS, characteristic of an endergonic reaction. For proton-transfer reactions the size of β could then be related to the extent of transfer of the proton in the TS. They cited the observation of Bell and Lidwell[7] that for reactions of a family of RCO_2^- bases with a series of β-diketone, β-keto ester, and ketone acid substrates, the Brønsted β values increased from 0.4 to 0.9 as the reactions become more endoenergetic as support for these postulates. The marked changes in steric and electronic effects at the acidic sites of these substrates make this example suspect, however. Although a few examples of curvature in Brønsted plots have been "fairly definitely established,"[4c] compelling experimental evidence for curvature is difficult to obtain because of the necessity of using more than one family of bases, often with different donor atoms, to construct extended plots in hydroxylic solvents.[8] Also, a recent compilation of β values for proton transfer reactions fails to support the assumption that there is a correlation between the size of β and the overall thermodynamics of the reaction.[8b]

Adherence of an S_N2 reaction to the Brønsted equation (1) was first demonstrated by Hammett[2] by plotting log *k* for reactions of meta- and para-substituted *N*,*N*-dimethylanilines with CH_3I in aqueous acetone[9] vs. pK_a for $GC_6H_4NHMe_2^+$ ions in water. More recent examples include reactions of RCO_2^- ions with $ClCH_2CO_2^-$ in water,[10a] pyridines with EtI in a variety of solvents,[10b] and *p*-$XC_6H_4S^-$ ions with benzyl bromides, *p*-$GC_6H_4CH_2Br$ in MeOH.[11] In the latter study it was observed that the Brønsted β_{Nu} value increased progressively as the character of *G* was changed from electron donor to electron ac-

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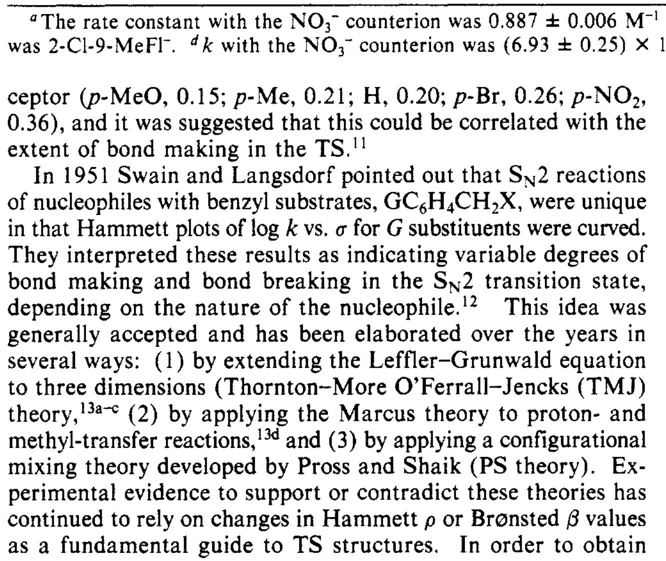
Table I. Second-Order Rate Constants for Reaction of 9-Substituted Fluorenide Ions, 9-GFl⁻, with *N*-Benzyl-*N*,*N*-dimethylanilinium Bromides in 0.8 M KNO_3–Dimethyl Sulfoxide Solution at 25 °C ($M^{-1}\ s^{-1}$)

	Y group of substrates				
anion	*p*-MeO	*p*-Me	H	*p*-Br	*m*-Cl
			A. Substrate $C_6H_5CH_2NMe_2C_6H_4Y^+Br^-$		
9-MeFl⁻	0.818 ± 0.043[a]	1.18 ± 0.03	2.25 ± 0.10[b]	7.23 ± 0.05	16.34 ± 0.82[e]
2-Br-9-MeFl⁻			0.440 ± 0.013[c]		2.62 ± 0.13[e]
2,7-Br_2-9-MeFl⁻	(2.13 ± 0.04) × 10^{-2}	(3.37 ± 0.11) × 10^{-2}	(6.95 ± 0.2) × 10^{-2}[d]	0.258 ± 0.003	0.396 ± 0.017[e]
			B. Substrate *m*-$CNC_6H_4CH_2NMe_2C_6H_4Y^+Br^-$		
9-MeFl⁻	12.11 ± 0.34	23.3 ± 0.60	40.5 ± 2.7	121.4 ± 7.3	266 ± 16
2-Br-9-MeFl⁻			4.55 ± 0.19		24.4 ± 0.4
2,7-Br_2-9-MeFl⁻	0.197 ± 0.003	0.366 ± 0.010	0.616 ± 0.018	2.02 ± 0.045	3.61 ± 0.34
2-Br-9-(PhS)Fl	(2.92 ± 0.12) × 10^{-3}	(4.74 ± 0.08) × 10^{-3}	(8.58 ± 0.22) × 10^{-3}	(2.66 ± 0.10) × 10^{-2}	(7.20 ± 0.55) × 10^{-2}
			C. Substrate *p*-$MeOC_6H_4CH_2NMe_2C_6H_4Y^+Br^-$		
9-MeFl⁻	1.21 ± 0.07	1.94 ± 0.072	4.47 ± 0.17	14.3 ± 0.3	27.2 ± 0.6
2-Br-9-MeFl⁻			1.23 ± 0.06		
2,7-Br_2-9-MeFl⁻	(5.38 ± 0.04) × 10^{-2}	(8.61 ± 0.15) × 10^{-2}	0.241 ± 0.006	0.727 ± 0.03	1.2 ± 0.09

[a] The rate constant with the NO_3^- counterion was 0.887 ± 0.006 $M^{-1}\ s^{-1}$ at 25.3 °C. [b] *k* with the NO_3^- counterion was 2.37 ± 0.08. [c] The anion was 2-Cl-9-MeFl⁻. [d] *k* with the NO_3^- counterion was (6.93 ± 0.25) × 10^{-2}. [e] With NO_3^- counterion.

ceptor (*p*-MeO, 0.15; *p*-Me, 0.21; H, 0.20; *p*-Br, 0.26; *p*-NO_2, 0.36), and it was suggested that this could be correlated with the extent of bond making in the TS.[11]

In 1951 Swain and Langsdorf pointed out that S_N2 reactions of nucleophiles with benzyl substrates, $GC_6H_4CH_2X$, were unique in that Hammett plots of log *k* vs. *σ* for *G* substituents were curved. They interpreted these results as indicating variable degrees of bond making and bond breaking in the S_N2 transition state, depending on the nature of the nucleophile.[12] This idea was generally accepted and has been elaborated over the years in several ways: (1) by extending the Leffler–Grunwald equation to three dimensions (Thornton–More O'Ferrall–Jencks (TMJ) theory,[13a–c] (2) by applying the Marcus theory to proton- and methyl-transfer reactions,[13d] and (3) by applying a configurational mixing theory developed by Pross and Shaik (PS theory). Experimental evidence to support or contradict these theories has continued to rely on changes in Hammett *ρ* or Brønsted *β* values as a fundamental guide to TS structures. In order to obtain additional data of this type with which to evaluate these theories, we present in this paper a study of 9-substituted fluorenide carbanions reacting with *N*-benzyl-*N*,*N*-dimethylanilinium cations (eq 3) and with various alkyl halide substrates.



1 + 2 → 4 + 3 (3)

The rates of reaction 3 can be controlled and varied systematically by remote substitution in three ways: (a) the nucleophilicity of the carbanion base (**1**) can be varied by changing X and X′ while keeping steric effects, solvation, and the nature of the donor atom constant, (b) the electrophilicity of the substrate (**2**) can be varied by changing *G*, and (c) the leaving group ability of **4** can be varied by changing Y, without changing the nature of the C–Lg bond being broken. In this paper we describe how the rates of this reaction are affected by each of these variables and compare the results with predictions of the TMJ and PS theories.

Results

Kinetics. The rates were measured by following the decay of the colored fluorenide anion at a fixed wavelength when reacted with a large excess of the anilinium salt, as described previously.[14,15] The reactions were run in 0.8 M KNO_3–dimethyl sulfoxide solution in order to eliminate salt effects. The rates of reaction of 9-R-fluorenide ions reacting with *N*-benzyl-*N*,*N*-dimethylanilinium ions are shown in Table I.

The counterion for the anilinium salts was Br⁻ in most cases. This can cause difficulties since Br⁻ is fairly nucleophilic in Me_2SO and can form $ArCH_2Br$ by reaction with **2**. After the solutions had aged several hours, they caused an immediate drop in the fluorenide ion absorbance when added to the anion solution due to the reaction with $PhCH_2Br$. This was followed by a slow decay (caused by the reaction with the anilinium salt), which is about 10^4 slower than the reaction with $PhCH_2Br$. For this reason the solutions of the salts were prepared just prior to use to prevent buildup of $ArCH_2Br$. As a check on the counterion effect, nitrate and bromide salts of $PhCH_2{}^+N(Me)_2Ph$ were prepared and the rates measured with 9-MeFl⁻ and 2,7-Br_2-9-MeFl⁻ ions. No difference in rates was observed in runs with the different counterions. Attempted synthesis of other nitrates often resulted in oils or resins that could not be crystallized. Consequently, the rates for the majority of anilinium salts were measured with Br⁻ as counterion.

Product Studies. The S_N2 substitution product from 9-G-fluorenide ion and the displaced *N*,*N*-dimethylanilines were each recovered in about 90% yield from the following reactions: (1) 9-PhFl⁻ ion with *N*-benzyl-*N*,*N*-dimethyl-*p*-methylanilinium bromide; (2) 9-MeFl⁻ ion with *N*-(*m*-cyanobenzyl)-*N*,*N*-dimethyl-*p*-methylanilinium bromide; (3) 9-MeFl⁻ ion with *N*-(*m*-cyanobenzyl)-*N*,*N*-dimethyl-*p*-methoxyanilinium bromide; (4) 9-MeFl⁻ ion with *N*-(*p*-methoxybenzyl)-*N*,*N*-dimethyl-*p*-chloroanilinium bromide; and (5) 9-MeFl⁻ ion with *N*-benzyl-*N*,*N*-dimethylanilinium nitrate. No other products were observed from NMR analyses of the crude materials. The fluorene products from the reaction with the two *m*-cyanobenzyl compounds were not solids, however. The oils obtained were purified by bulb-to-bulb distillation to give solids, which were crystallized. HPLC analysis of the crude fluorene product from the reaction of 9-MeFl⁻ ion with *N*-(*m*-cyanobenzyl)-*N*,*N*-dimethyl-*p*-methoxyanilinium bromide showed no starting material, but two impurities of about 3% and 5% were present. The crude amine isolated from this

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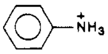
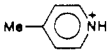
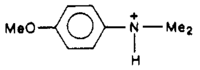
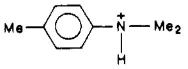
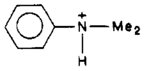
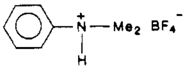
Table II. Acidities of Protonated Nitrogen Bases in Dimethyl Sulfoxide Solution at 25 °C

compd	indicator (pK_a)	pK_a	av pK_a
	MDNPH (4.59)[a] CDNPH (3.56)[b]	3.58 ± 0.05 3.59 ± 0.05	3.59 ± 0.05 (3.6)[c]
	MDNPH (4.59) CDNPH (3.56)	3.99 ± 0.04 4.05 ± 0.03	4.02 ± 0.05
	MDNPH (4.59) CDNPH (3.56)	3.55 ± 0.03 3.60 ± 0.04	3.57 ± 0.05
	MDNPH (4.59) CDNPH (3.56)	2.96 ± 0.01 2.97 ± 0.03	2.96 ± 0.03
	CDNPH (3.56)	2.41 ± 0.02	2.44 ± 0.05
	CDNPH (3.56)	2.47 ± 0.03	

[a] MDNPH = 6-methyl-2,4-dinitrophenol. [b] CDNPH = 4-chloro-2,6-dinitrophenol. [c] Kolthoff, I. M.; Chantooni, M. K.; Bhowmik, S. O. *J. Am. Chem. Soc.* **1968**, *90*, 23–28.

reaction was pure, however, melting at 46–47 °C [lit.[16] mp 48 °C]. Spectral data and melting points for the products are given in the Experimental Section.

Reaction with the methyl group instead of the benzyl group was ruled out by measuring the rate of reaction of 9-MeFl$^-$ ion with $PhNMe_3^+$. The methylation reaction was $>10^3$ slower than the benzylation reaction with $PhCH_2NMe_2Ph^+$.

Acidity Measurements. The acidities of the dimethylanilinium ions in Me_2SO solution were measured by equilibrating the amine with an indicator (HIn) of known pK_a (eq 4) and measuring the absorbance of the indicator anion (In$^-$) formed. Further details are given in the Experimental Section.

$$HIn + R_3N: \overset{K_{eq}}{\rightleftharpoons} In^- + R_3N^+H \tag{4}$$

The acidities of the conjugate acids of several nitrogen bases in Me_2SO solution are listed in Table II. The pK_a of 3.59 measured for $PhNH_3^+$ agrees well with literature reports of 3.6,[18] 3.7,[17] and 3.72[19] As a further check on the method, $PhNMe_2H^+BF_4^-$ was prepared and the pK_a measured by the normal technique described in ref 20 and 21. The acidities determined by the two methods agreed within 0.06 pK_a unit, and the average value of 2.44 agreed well with the value of 2.51 measured by Benoit.[19]

The results with the indicator 2,4-dinitro-1-naphthol (pK_a = 2.12[21]) were not consistent, varying about 0.5 pK_a unit within a single titration. To obtain a pK_a for these highly acidic compounds, the exact pK_a of the indicator must be known so that the [H$^+$] due to its autoionization can be precisely determined. We were not able to measure a pK_a with a precision <±0.03 pK_a unit for 2,4-dinitro-1-naphthol and were consequently unable to measure anilinium ion pK_a values of less than 2.

A comparison of acidities of five protonated nitrogen cations in water, 50% EtOH–water, 70% Me_2SO–water,[22a] and Me_2SO is shown in Table III. The *N*,*N*-dimethylanilinium ions are about 2 units more acidic in Me_2SO than in water, and the 4-picolinium ion and anilinium ion are 1.4 and 0.6 pK_a units, respectively, more acidic in Me_2SO compared to water. Cox and Parker[22b] have estimated the free energy of transfer of the proton from water to Me_2SO to be −4.5 kcal/mol (3.3 pK_a units), yet several attempts to measure the acidity of Me_2SOH^+ in water have given inconsistent results ranging from −2.8 to +1.0.[21] Differences in solvation of the amine and ammonium ion between water and Me_2SO also contribute to the ΔpK_a observed between the two solvents.

The Hammett ρ values for the acidities of substituted *N*,*N*-dimethylanilinium ions are 3.43 in water and 3.87 in 70% Me_2SO/water (33 mol % Me_2SO/water).[22] Only three substituted *N*,*N*-dimethylanilinium ions were measured in Me_2SO, giving a rough ρ value of 4.5. This increase in ρ values in Me_2SO compared to water is probably caused by lesser solvation (no H-bond donation) of the anilinium cation in Me_2SO solution.

Leaving Group Effects in S_N2 Reactions with Alkyl Halides. Reactions of 9-CO_2MeFl$^-$ and 9-MeFl$^-$ ion families with $PhCH_2X$, *n*-BuX, and $CNCH_2X$ halides (X = Cl, Br, and I) were carried out in order to examine the effect of the leaving group and substituents on the rate and the size of β_{Nu} (Tables IV–VI).

Comparison of the rate constants in Table IV shows that the k^{Br}/k^{Cl} leaving group effects are large, being in the range 300–400 for $PhCH_2X$, 500–600 for *n*-BuX, and 100–200 for $CNCH_2X$. These effects are as much as an order of magnitude larger than those in hydroxylic solvents. Parker has explained these large effects in terms of a greater differential in the solvation of the incipient chloride and bromide ions in the dipolar non-hydrogen bonding solvents.[23] The I/Br ratios are also for the most part larger, apparently for the same reason, but they are relatively small (<20) in either type of solvent.

The β_{Nu} values in Table V are for the most part derived from three-point plots and are not highly accurate. They are remarkably consistent, however, in showing no change with changing leaving group.

The β_{Nu} values for benzyl halides, $GC_6H_4CH_2X$, increase as the electron-withdrawing nature of G increases,[15] but once again remain constant for changes in the nature of the leaving group (Table VI). There is also a progressive increase in the rate constant as G is made more electron withdrawing. For example, in the $ArCH_2Cl$ series the relative rates for along the series G = H, *m*-Cl, and *m*-NO_2 are (1.0), 2.5, and 8.7, respectively, and in the $ArCH_2Br$ series they are (1.0), 3.1, and 11.0, respectively.

Polarizability Effects and a Search for a Charge-Transfer (CT) Complex. We examined rates of reaction of 9-RFl$^-$ ions with 2-$MeC_6H_4CH_2Cl$, 2,4,6-$Me_3C_6H_2CH_2Cl$, and 9-chloromethylanthracene, 9-$AnCH_2Cl$ (Table VII) in order to determine the effect of polarizability and to search for the presence of a CT complex.

Examination of Table VII shows that, with 9-PhSFl$^-$ ion, 2-methylbenzyl chloride reacts 2.5-fold faster than does $PhCH_2Cl$ and 2,4,6-trimethylbenzyl chloride reacts 5-fold faster. These rate increases are not due to electronic effects alone, since 4-methylbenzyl chloride reacts only 10% faster with 9-PhFl$^-$ than does benzyl chloride.[15] Similar but larger effects have been observed earlier. With I$^-$ ion in acetone rate enhancements of 11- and 290-fold were observed for 2-Me and 2,4,6-$Me_3C_6H_2CH_2Cl$, respectively, relative to $PhCH_2Cl$;[24] with PhS$^-$ ion in MeOH a 5.2-fold enhancement for 2-Me was reported.[25] Both sets of authors attributed the accelerations to polarizability effects of the ortho methyl groups. This explanation is reasonable also for the present results. The β_{Nu} value for the 9-(PhS)Fl$^-$ family reacting with 2-$MeC_6H_4CH_2Cl$ is 0.31, the same within experimental error as that with $PhCH_2Cl$,[14] but β_{Nu} for 2,4,6-$Me_3C_6H_2CH_2Cl$ is only 0.24. This appreciable drop in β_{Nu} is similar to, but larger than, that observed for 4-$MeOC_6H_4CH_2Cl$ (0.30),[15] which suggests that a sizable stabilization of the positive charge is developing on the benzylic carbon atom.

For 9-PhFl$^-$ and 9-(CN)Fl$^-$ ions reacting with 9-(chloromethyl)anthracene, rate enhancements of 122- and 61-fold, re-

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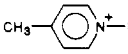
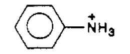
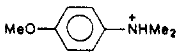
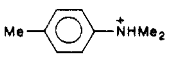
Table III. Acidities of Protonated Nitrogen Bases in Several Solvents

compd	pK_a[a] (water)	pK_a[a] (50% EtOH/water)	pK_a[b] (70% Me_2SO/water)	pK_a[c] (Me_2SO)	ΔpK_a (Me_2SO–water – 0.6)[d]
	6.02			4.02	1.4
	4.58		3.41	3.6	0.6
		5.15		3.6	
	5.63	4.94	3.57	2.95	2.1
PhN^+HMe_2	5.06	4.21, 4.09	2.00	2.45	1.9

[a] Jencks, W. P.; Regenstein, J. *Handbook of Biochemistry and Molecular Biology*; 2nd ed.; Sober, H. A., Ed.; Chemical Rubber Co.: Cleveland, 1970; pp J150–J189. [b] Yates, K.; Welch, G. *Can. J. Chem.* **1972**, *50*, 474–478. [c] This study. [d] Subtraction of 0.6 accounts for the difference in molarities of the solvents: log (55/14) = 0.6.

Table IV. Rate Constants, k (M^{-1} s^{-1}), and β_{Nu} Values for Reactions with 9-Substituted Fluorenide Ion Families, 9-RFl⁻, with Alkyl Chlorides, Bromides, and Iodides in S_N2 Reactions in Me_2SO Solution at 25 °C

		k for G =		
9-RFl⁻ or 9-GFl⁻	pK_{HA}	H	m-Br	m-NO_2
		For Benzyl Bromides, $GC_6H_4CH_2Br$		
9-CO_2MeFl⁻	10.35	9.39 ± 0.37	29.4 ± 0.1	103.6 ± 0.1
2-Br-9-CO_2MeFl⁻	8.2	2.12 ± 0.089	6.28 ± 0.05	17.75 ± 0.05
2,7-Br_2-9-CO_2MeFl⁻	6.5	0.629 ± 0.032	1.17 ± 0.03	2.64 ± 0.01
		For n-BuI		
9-CO_2MeFl⁻	10.35	0.136 ± 0.029		
9-(CN)Fl⁻	8.3	(2.04 ± 0.03) × 10^{-2}		
2,7-Br_2CO_2Me	6.5	(4.05 ± 0.24) × 10^{-3}		
		For n-BuBr		
9-MeFl⁻	22.35	15.6 ± 0.33		
2-Br-9-MeFl⁻	20.05	2.03 ± 0.06		
2,7-Br_2-9-MeFl⁻	17.7	0.310 ± 0.006		
		For n-BuCl		
9-MeFl⁻	22.35	(3.20 ± 0.04) × 10^{-2}		
2-Br-9-MeFl⁻	20.05	(3.71 ± 0.26) × 10^{-3}		
2,7-Br_2-9-MeFl⁻	17.7	(5.4 ± 0.3) × 10^{-4}		
		For $CNCH_2I$		
9-CO_2MeFl⁻	10.35	12.85 ± 0.19		
2,7-Br_2-9-CO_2MeFl⁻	6.5	0.131 ± 0.001		
		For $CNCH_2Br$		
9-CO_2MeFl⁻	10.35	6.83		
2-Ph-9-CO_2MeFl⁻	8.2	0.592		
2,7-Br_2-9-CO_2MeFl⁻	6.5	0.0607		
		For $CNCH_2Cl$		
9-CO_2MeFl⁻	10.35	(3.76 ± 0.03) × 10^{-2}		
2-Br-9-CO_2MeFl⁻	8.2	3.1 × 10^{-3}		
2-Br-9-(CN)Fl⁻	8.3	(6.82 ± 0.17) × 10^{-3}		
9-(p-MeC_6H_4)Fl⁻	18.33	15.7 ± 0.55		
9-C_6H_5Fl⁻	17.90	8.52 ± 0.19		
9-(m-ClC_6H_4)Fl⁻	16.85	2.45 ± 0.04		
9-(p-$MeSO_2C_6H_4$)Fl⁻	15.2	0.338 ± 0.014		
9-(PhS)Fl⁻	15.4	1.63 ± 0.02		
9-(p-BrC_6H_4S)Fl⁻	14.8	0.927 ± 0.04		
2-Br-9-(PhS)Fl⁻	13.2	0.131 ± 0.006		
2-$PhSO_2$-9(p-MeC_6H_4S)Fl⁻	11.9	(1.39 ± 0.04) × 10^{-2}		
2,7-Br_2-9-(PhS)Fl⁻	11.15	(1.33 ± 0.03) × 10^{-2}		

spectively, were observed, relative to $PhCH_2Cl$. For 9-(o-MeC_6H_4)Fl⁻, a 22-fold rate retardation (relative to 9-PhFl⁻) occurs with $PhCH_2Cl$ because of steric hindrance in Nu⁻, but a 171-fold rate enhancement occurs with 9-(chloromethyl)anthracene, relative to $PhCH_2Cl$, despite the presence of the two peri hydrogen atoms in the anthracene moiety, which might have been expected to augment the steric effect of the 2-methyl moiety. (In a similar study with I⁻ ion in acetone, a 73-fold acceleration for 9-$AnCH_2Cl$ vs. $PhCH_2Cl$ has been observed.[26]) One reason for the enhanced rate for 9-$AnCH_2Cl$ may be that the peri hydrogen atoms lock the chloromethyl group into a conformer with the CH_2–Cl bond positioned for backside displacement by the Nu⁻ approaching over the face of the anthracene moiety. (The 2-Me and 2,6-Me_2 groups in 2-$MeC_6H_4CH_2Cl$ and 2,4,6-$Me_3C_6H_2CH_2Cl$ may play similar roles.) Since the 9-$AnCH_2Cl$/$PhCH_2Cl$ ratio is similar, and not smaller, with the more hindered 9-(o-MeC_6H_4)Fl⁻ ion there is apparently no increase in steric hindrance in the S_N2 TS for 9-$AnCH_2Cl$ vs. $PhCH_2Cl$.

No evidence for the formation of a charge-transfer (CT) complex was observed with 9-$AnCH_2Cl$, which might have been expected to be an electrophile prone to CT. The visible spectrum

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[26] Fierens, P. J. C.; Hannaert, H.; van Rysselberge, J.; Martin, R. H. *Helv. Chim. Acta* **1955**, *38*, 2009–2021.

Table V. Summary of β_{Nu} Values

substrate	family	β_{Nu}[a]	substrate	family	β_{Nu}[a]
$PhCH_2Cl$	$9\text{-}CO_2MeFl^-$	0.31[b]	$PhCH_2Br$	$9\text{-}CO_2MeFl^-$	0.305
	$9\text{-}ArS\text{-}Fl^-$	0.31[b]			
	$9\text{-}MeFl^-$	0.31[b]			
	$2\text{-}NpO^-$	0.32[b]			
	carbazolide$^-$	0.32[b]			
	$9\text{-}ArFl^-$	0.365[b]			
$n\text{-}BuCl$	$9\text{-}MeFl^-$	0.38	$n\text{-}BuBr$	$9\text{-}MeFl^-$	0.365
	ArS^-	0.40[c]	$n\text{-}BuBr$	ArS^-	0.38[d]
	$2\text{-}NpO^-$	0.36	$n\text{-}BuI$	$9\text{-}CO_2MeFl^-$	0.395
	carbazolide$^-$	0.35	$n\text{-}BuI$	carbazolide$^-$	0.35
$CNCH_2Cl$	$9\text{-}CO_2MeFl^-$	0.51[d]	$CNCH_2Br$	$9\text{-}CO_2MeFl^-$	0.53
	$9\text{-}(ArS)Fl^-$	0.50[e]	$CNCH_2I$	$9\text{-}CO_2MeFl^-$	0.52
	$2\text{-}NpO^-$	0.445			
	$9\text{-}ArFl^-$	0.53[f]			

[a] Derived unless otherwise noted from three-point plots with R^2 values of 0.99 or better (R^2 is the square of the least-squares correlation coefficient). [b] References 15 and 37. [c] Reference 8a. [d] Two-point plot. [e] Five-point plot. [f] Four-point plot.

Table VI. β_{Nu} Values for Benzyl Chlorides and Bromides

Nu^- family	$ArCH_2X$	β_{Nu}[a]	(R^2)[b]
$9\text{-}CO_2MeFl^-$	$C_6H_5CH_2Cl$[a]	0.304	0.9997
$9\text{-}CO_2MeFl^-$	$C_6H_5CH_2Br$	0.305	0.9999
$9\text{-}MeFl^-$	$m\text{-}ClC_6H_4CH_2Cl$	0.35	0.9999
$9\text{-}CO_2MeFl^-$	$m\text{-}BrC_6H_4CH_2Br$	0.36	0.992
$9\text{-}ArFl^-$	$m\text{-}NO_2C_6H_4CH_2Cl$[a]	0.455	0.995
$9\text{-}CO_2MeFl^-$	$m\text{-}NO_2C_6H_4CH_2Br$	0.41	0.992

[a] Reference 14; note that the β_{Nu} value for the $9\text{-}ArFl^-$ ion family is slightly larger than those for the other families (Table V). [b] R^2 is the square of the least-squares coefficient.

Table VII. Comparison of the Rate Constants for Reactions of $9\text{-}GFl^-$ Ions, with 2-Methyl- and 2,4,6-Trimethylbenzyl Chlorides and with 9-(Chloromethyl)anthracene ($9\text{-}AnCH_2Cl$) with Benzyl Chloride (BzCl) in Me_2SO at 25 °C

		rate const k, $M^{-1}\ s^{-1}$[a]			
$9\text{-}GFl^-$	pK_a	BzCl	2-MeBzCl	2,4,6-Me_3BzCl	9-$AnCH_2Cl$
$9\text{-}o\text{-}MeC_6H_4$	18.8	2.0×10^{-2}			3.43
$9\text{-}C_6H_5$	17.9	0.61	1.55		74.6
$9\text{-}C_6H_5S$	15.4	0.248	0.626	1.11	
$9\text{-}Br\text{-}9\text{-}C_6H_5S$	13.2	0.0564	0.152	0.392	
$2\text{-}PhSO_2\text{-}9\text{-}(o\text{-}MeC_6H_4)$	11.9	0.0189	0.0505		
$2,7\text{-}Br_2\text{-}9\text{-}C_6H_5S$	11.15			0.110	
9-CN	8.3	6.2×10^{-3}			0.38

[a] Reproducible to ±5% or better.

of the $9\text{-}(CN)Fl^-$ ion was unchanged upon addition of $9\text{-}AnCH_2Cl$, and the spectrum of $9\text{-}AnCH_2Cl$ was likewise unaffected by addition of $9\text{-}(CN)Fl^-$ ion. No new peaks were observed, and the ϵ values for both reactants stayed constant over wide ranges of λ when the other reactant was added. Since the formation of CT complex formation has been shown to be highly sensitive to steric effects,[27] we searched further for evidence of CT formation by examining the effect on rates of introducing a *p-tert*-butyl group into both the nucleophile and electrophile (Table VIII). The presence of the *p-t*-Bu moieties should hinder CT complex formation and should lead to rate retardation if the CT complex is on the reaction coordinate. Examination of Table VIII shows that, with both the $9\text{-}CO_2MeFl^-$ and *p-tert*-butyl anions, $p\text{-}t\text{-}BuC_6H_4CH_2Cl$ reacts slightly faster than does $PhCH_2Cl$. These slight rate increases are similar to those observed for $p\text{-}MeC_6H_4CH_2Cl$ with similar anions and offer no support for the presence of a CT complex.

Discussion

Comparison of Predictions of Variable-Transition-State Theories with Experimental Results Based on β_{Nu} and β_{Lg} Values. In Table IX we have summarized predictions based on the Thornton–More O'Ferrall–Jencks (TMJ) theory[13a-c,28] and the Pross–Shaik (PS) theory[29] of the effects on bond making and bond breaking in S_N2 reactions of benzyl substrates caused by (a) an increase in leaving group ability, (b) an increase in nucleophilicity, and (c) an increase in the electron-withdrawing or electron-donating power of G in $GC_6H_4CH_2X$.

Table VIII. Rate Constants ($M^{-1}\ s^{-1}$) for S_N2 Reactions of $9\text{-}CO_2MeFl^-$ and $p\text{-}t\text{-}BuC_6H_4O^-$ ions with $PhCH_2Cl$ and $p\text{-}t\text{-}BuC_6H_4CH_2Cl$ in Me_2SO at 25 °C

anion	$k(PhCH_2Cl)$	$k(p\text{-}t\text{-}BuC_6H_4CH_2Cl)$	$k(p\text{-}t\text{-}Bu)/k(PhCH_2Cl)$
$9\text{-}CO_2MeFl^-$	2.68×10^{-2}	$5.0 \pm 0.01 \times 10^{-2}$	1.8
$p\text{-}t\text{-}BuC_6H_4O^-$	0.61 ± 0.04	0.76 ± 0.05	1.2

Examination of Table IX shows that the two theoretical approaches are at odds on most counts. Furthermore, if it is assumed that Brønsted β values can be used as measures of the extent of bond making and bond breaking, we see that the β_{Nu} and β_{Lg} values determined for reactions obtained by varying R, X, G, and Y substituents in eq 3 fail to agree with most of the predictions. In the following three sections we will examine the experimental evidence presented by the authors to support these predictions and discuss possible reasons for the divergence between theory and experiment.

Effect of Increasing Leaving Group Ability on the Extent of Bond Making. The TMJ theory predicts that an increase in leaving group ability should result in a decrease in bond making.[13,28a] Experimental support for this prediction, as applied to solvolyses of benzyl substrates, has been summarized by Harris, namely (a) larger α-deuterium isotope effects, (b) higher k_{OTs}/k_{Cl} ratios, (c) higher Grunwald–Winstein m values, and (d) smaller k_E/k_W ratios (the selectivity for displacement by EtOH vs. H_2O).[28b] The changes in these parameters are complex, however, and other interpretations are possible.[30]

In the present study we have examined the effect on β_{Nu} of changing the leaving group moiety in $GC_6H_4CH_2N(Me)_2C_6H_4Y^+$ cations (**2**) by changing Y along the series *p*-MeO, *p*-Me, H, *p*-Br, and *m*-Cl. Rates with the $9\text{-}MeFl^-$ ion family, $9\text{-}MeFl^-$, $2\text{-}Br\text{-}9\text{-}MeFl^-$, and $2,7\text{-}Br_2\text{-}9\text{-}MeFl^-$, were measured for each of these variations in Y for substrates with G = *p*-MeO, H, and *m*-CN. The β_{Nu} values obtained from plots of log k vs. pK_{HA} for each of these 15 substrates reacting with the three members of the $9\text{-}MeFl^-$ ion family are given in Table X, and the Brønsted plots, including also the point for the $2\text{-}Br\text{-}9\text{-}(PhS)Fl^-$ ion, for reactions of $m\text{-}CNC_6H_4N(Me)_2C_6H_4Y^+$ cations are shown in Figure 1. Examination of Table X shows that the β_{Nu} values change with the nature of the substituent (G) in the benzyl ring but *remain constant for any given G substituent.* The rates in this study span a range of about 10^4 (Table I). This observation of a constant β_{Nu} with changing leaving group abilities is supported by the results of a similar study by Kneir and Jencks, who observed a constant β_{Nu} of 0.14 over a 50-fold rate range for aliphatic amines reacting with $CH_3OCH_2N(Me)_2C_6H_4Y^+$ cation substrates in water, with Y = *m*-NO_2, *p*-Br, and H.[31]

Westaway and Ali have carried out a similar study with $p\text{-}XC_6H_4S^-$ ions (X = OCH_3, CH_3, H, and Cl) reacting with $GC_6H_4CH_2N(Me)_2C_6H_4Y^+$ cations in DMF, where Y = *p*-OCH_3, H, and *p*-Cl.[32a] Pross and Shaik[29a] calculated three-point ρ_{Nu}

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(27) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 2783–2791.

(28) (a) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288–3294. (b) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295–3300.

(29) (a) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702–3709. (b) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363–370. (c) Pross, A. *J. Org. Chem.* **1984**, *49*, 1811–1818.

(30) (a) Johnson, C. D. *Chem. Rev.* **1975**, *7*, 755–765. (b) Roberts, I.; Johnson, C. D. *Tetrahedron* **1977**, *80*, 1306–1310. (c) Rappoport, Z.; Ta-Shma, R. *J. Org. Chem.* **1982**, *47*, 5207–5209.

(31) Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789–1798.

(32) (a) Westaway, K. C.; Ali, S. F. *Can. J. Chem.* **1979**, *57*, 1089–1097. (b) Westaway, K. C.; Poirier, R. A. *Can. J. Chem.* **1975**, *53*, 3216–3226. (c) Westaway, K. C.; Ali, S. F. *Can. J. Chem.* **1979**, *57*, 1354–2367. (d) Westaway, K. C.; Waszczylo, Z. *Can. J. Chem.* **1982**, *60*, 2500–2520.

Table IX. Changes in Bond Making and Bond Breaking Predicted by the Thornton–More O'Ferrall–Jencks (TMJ) and Pross–Shaik (PS) Theories for Reactions of 9-RFl$^-$ Ions with $GC_6H_4CH_2NMe_2C_6H_4Y^+$ Cations Compared to Experimental Observations

	TMJ theory[a,b]		PS Theory[c]		
change in exptl parameter	bond making	bond breaking	bond making	bond breaking	exptl results
increase in leaving group ability	decrease[a,b]	decrease[a,b]	increase[d]	increase	const β_{Nu}[e,f]
increase in nucleophilicity	const[a,b]	decrease[a,b]	increase	increase[d]	const β_{Nu};[f] const ρ_{Lg}[g]
increase in electron-acceptor power of G	increase[a,b]	decrease[a,b]	increase	increase	increased β_{Nu};[h] const β_{Lg}[h]
increase in electron-donor power of G	decrease	increase	decrease	decrease	decreased β_{Nu};[h] const β_{Lg}[h]

[a] Reference 13. [b] Reference 28. [c] Reference 29a. [d] A more recent analysis by Pross (private communication, Aug 1984) suggests that this prediction should be "little change." The other predictions remain as indicated (ref 29b,c). [e] Slopes of the Brønsted plots for reaction 3 in which Y in the $NMe_2C_6H_4Y$ leaving group is varied for reactions with a family of 9-MeFl$^-$ carbanions (Table X and Figure 1). [f] Slopes of various Brønsted plots (Table XI) and slopes of the Brønsted plots for families of 9-RFl$^-$ ions reacting with $PhCH_2Cl$ (ref 14). [g] Slopes of the Hammett plots for the reactions of 9-RFl$^-$ ions with $GC_6H_4CH_2NMe_2C_6H_4Y^+$ cations (Table XII and Figure 2). [h] Slopes of Brønsted plots where G in $GC_6H_4CH_2NMe_2C_6H_4Y^+$ cations is varied (Table X. See also ref 15).

Table X. Brønsted β_{Nu}[a] Values for the 9-MeFl$^-$ Anion Family Reacting with $GC_6H_4CH_2NMe_2C_6H_4Y^+$ Cations in Me_2SO at 25 °C

Y	β_{Nu} (G = *p*-MeO)	β_{Nu} (G = H)	β_{Nu} (G = *m*-CN)
p-MeO	0.29	0.34	0.39
p-Me	0.29	0.33	0.39
H	0.27	0.33	0.39
p-Br	0.28	0.32	0.38
m-Cl	0.29	0.34	0.40

[a] Slopes of the Brønsted plots of log *k* for the reactions vs. pK_a of $GC_6H_4CH_2NHMe_2^+$ ions.

Table XI. Brønsted β_{Nu} Values for Reactions of Nucleophiles with Substrates Containing Different Leaving Groups

nucleophiles	substrates	solvent	β_{Nu}	ref
amines	$CH_3OCH_2NMe_2C_6H_4Y^+$	H_2O	0.14	31
RCO_2^- family	$ClCH_2CO_2^-$; $BrCH_2CO_2^-$	H_2O	0.20	10
inorganic oxoanions	$MeONO_2$; $MeOSO_2Ph$; $MeOClO_3$	H_2O	0.24	34
pyridine family	MeI; $MeOSO_2F$	Me_2CHNO_2	*a*	35
$C_6H_5S^-$; $NO_2C_6H_4S^-$	$MeOSO_2CH_3$; $MeOSO_2F$; $MeOSO_2CF_3$; MeI	sulfolane	~0.4–0.5[b]	38
9-CO_2MeFl$^-$ family	$PhCH_2Cl$; $PhCH_2Br$	Me_2SO	0.31	*c*
9-MeFl$^-$ family	*n*-BuCl; *n*-BuBr; *n*-BuI	Me_2SO	0.37	*c*
9-CO_2MeFl$^-$ family	$PhCOCH_2Cl$; $PhCOCH_2Br$	Me_2SO	0.40	37
9-CO_2MeFl$^-$ family	$ClCH_2CN$; $BrCH_2CN$; ICH_2CN	Me_2SO	0.52	*c*

[a] Plots of log *k* vs. pK_a values for pyridines in water or the gas phase were reported to be linear. [b] log ($k_H/k_{p\text{-}NO_2}$) rates for $XC_6H_4S^-$ ions ranged from 2.0 to 2.4; assuming the ΔpK_a between *p*-NO_2 and H is the same as in Me_2SO (4.8 units[15]), *β* ranges from 0.42 to 0.50 for a two-point plot. [c] Present work.

values from these data of 1.73, 1.91, and 2.14 for X = Cl, H, and Me, respectively, and cited the increase along the series as experimental support for their prediction that the extent of bond making increases as the leaving group ability increases.[33] It seems doubtful, however, that this change in *ρ* is significant in view of the contrary results reported in Table V.

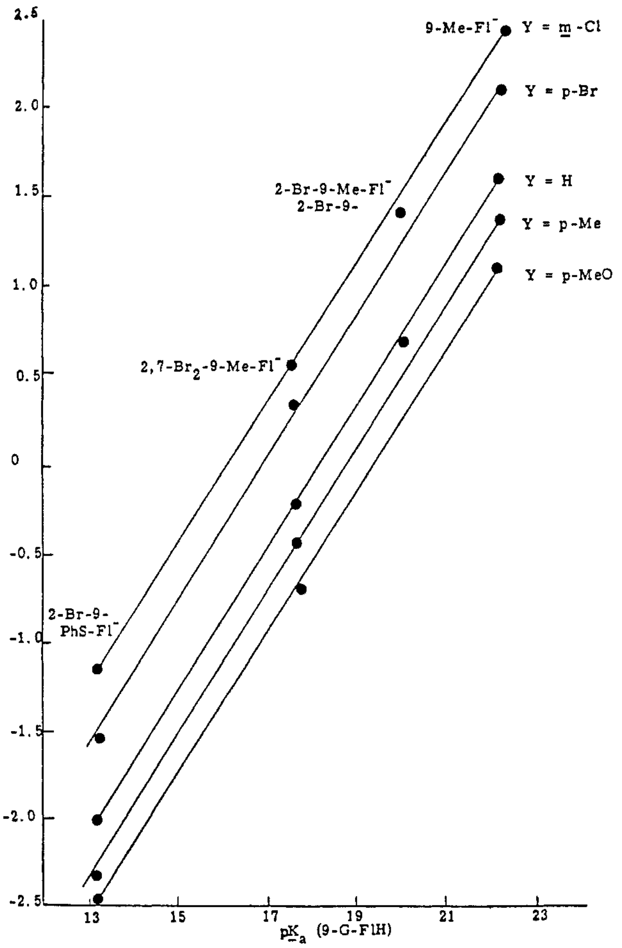

Figure 1. Brønsted plots for 9-substituted fluorenide carbanions, 9-GFl$^-$, reacting with *m*-$CNC_6H_4CH_2NMe_2C_6H_4Y^+$ cations in which Y is varied. A 2-Br-9-(PhS)Fl$^-$ ion point has been used to extend the 9-MeFl$^-$ family line. (In Brønsted plots of data for S_N2 reactions of $PhCH_2Cl$ with 9-GFl$^-$ ions the 9-MeFl$^-$ ion family line has been shown to essentially join the 9-(PhS)Fl$^-$ family line when extended.)

The conclusion that β_{Nu} values remain constant for changes in leaving group abilities is supported further by data given in Table XI for S_N2 reactions in which structural variations are made in leaving groups of alkyl halides (Cl, Br, and I) and alkyl esters of organic and inorganic acids. In Koskikallio's study, β_{Nu} remained constant at 0.24 for changes in the leaving group from ONO_2 to OSO_2Ph to $OClO_3$ in reactions with inorganic ions that spanned a p*K* range of 11 units.[34] In Arnett's study[35] β_{Nu} remained constant for changes in leaving groups that caused changes in rates of about $10^{5.5}$,[36] and in the present study β_{Nu} remained constant with five different RX electrophiles where X was changed along the series Cl, Br, and I.[37] In a study of leaving group abilities covering 10^5 in rates, Lewis[38] found a small decrease in

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[33] The Hammett plots are derived from data covering only about 2 pK_a units, and the rate constants for the same reactions reported in ref 32b and 32c differ by 17–47%.

[34] Koskikallio, J. *Acta Chem. Scand.* **1972**, *26*, 1201–1208.

[35] Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1978**, *100*, 2930–2931; **1980**, *102*, 5892–5901.

[36] Young and Jencks[28] have rationalized the findings of Arnett and Reich that methylations of pyridine have a constant β_{Nu} over a 10^5 range in leaving group ability by arguing that the methyl carbocation is so unstable that the left top corner of the contour energy diagram will be very high in energy so that only small shifts could occur in the perpendicular direction. However, this argument will not explain the unchanging β_{Nu} values in the benzyl system (Table V) or the results in their $CH_3OCH_2NMeC_6H_4Y^+$ system[31] where a much more stable cation ($PhCH_2^+$ or $MeOCH_2^+$) would make the left top corner low in energy. For these cases large perpendicular shifts should occur, but the constant β_{Nu} values when the leaving group ability changes fail to support this prediction.

[37] Hughes, D. L. Ph.D. Dissertation, Northwestern University, 1981.

Table XII. Hammett ρ_{Lg} Values for 9-R-Fluorenide Anions Reacting with $GC_6H_4CH_2NMe_2C_6H_4Y^+$ Cations in 0.8 M KNO_3–Dimethyl Sulfoxide Solution at 25 °C

anion	pK_a	G	ρ_{Lg}[a]
9-MeFl⁻	22.35	H	2.05 ± 0.09, R^2 = 0.994
2,7-Br_2-9-MeFl⁻	17.7	H	2.06 ± 0.10, R^2 = 0.992
9-MeFl⁻	22.35	*m*-CN	2.03 ± 0.09, R^2 = 0.994
2,7-Br_2-9-MeFl⁻	17.7	*m*-CN	1.96 ± 0.09, R^2 = 0.994
2-Br-9-(PhS)Fl⁻	13.2	*m*-CN	2.13 ± 0.12, R^2 = 0.990
9-MeFl⁻	22.35	*p*-MeO	2.14 ± 0.03, R^2 = 0.9992
2,7-Br_2-9-MeFl⁻	17.7	*p*-MeO	2.13 ± 0.12, R^2 = 0.991

[a] Y groups were *p*-MeO, *p*-Me, H, *p*-Br, and *m*-Cl.

β_{Nu} with increasing leaving group abilities, but the trend is slight and the β_{Nu} values are based on only two points. Note that these studies (Table XI) encompass S_N2 reactions in several solvents wherein (a) neutral nucleophiles react with cation substrates, (b) anionic nucleophiles react with anionic substrates, (c) anionic nucleophiles react with neutral substrates, (d) neutral nucleophiles react with neutral substrates, and (e) anionic nucleophiles react with cationic substrates. In summary, our results and most of those in the literature give no support to the predictions of the TMJ and PS theories that increasing leaving group ability changes the extent of bond making in the S_N2 transition state.

Effect of Increasing Nucleophilicity on the Extent of Bond Breaking. In the last section we focused attention on nucleophile bonding and noted that, contrary to predictions (Table IX), increasing the leaving group ability failed to increase or decrease the extent of bond making, as judged by the constancy of β_{Nu} values. In this section we will focus on the effect of nucleophilicity on leaving group cleavage and show that, contrary to the predictions in Table IX, our data fail to support the idea that increased nucleophilicity causes a decrease[28] (TMJ) or an increase[29a] (PS) in bond breaking, as judged by the constancy of β_{Lg}.

Harris[28b] supported his prediction that increased nucleophilicity will cause a decrease in bond breaking (Table IX) by reference to two examples where experimental data appear to show that increased nucleophilicity caused a decrease in leaving group rate ratios, e.g., he refers to a decrease in the $PhCH_2Br/PhCH_2Cl$ rate ratio in aminolysis reactions as nucleophile reactivity increases.[12] Young and Jencks suggest that increased basicity of an aniline reacting with benzyl chloride will cause both parallel and perpendicular shifts in transition-state structure (Hammond and anti-Hammond effects).[28a] The resulting vector turns out to be at a 45° angle to the reaction coordinates, which leads to the conclusion that there will be less bond breaking, but no change in bond making, in agreement with Harris. Pross and Shaik support their prediction that increased nucleophilicity will increase in bond making by reference to the work of Westaway and Ali[32] discussed above.

In the present study Hammett ρ_{Lg} values determined in Me_2SO solution from rates of reactions of 9-RFl⁻ anions with *N*-benzyl-*N*,*N*-dimethylanilinium cations, $GC_6H_4CH_2N(Me)_2C_6H_4Y^+$ (Y = *p*-MeO, *p*-Me, H, *p*-Br, and *m*-Cl), were used to evaluate the effect of changes in nucleophilicity on the extent of bond breaking. Rate measurements were made with (a) 9-MeFl⁻ and 2,7-Br_2-9-MeFl⁻ ions for G = H; (b) 9-MeFl⁻, 2-Br-9-MeFl⁻, and 2-Br-9-(PhS)Fl⁻ ions for G = *m*-CN, and (c) 9-MeFl⁻ and 2,7-Br_2-9-MeFl⁻ ions for G = *p*-MeO (Table XII). The total range of nucleophile basicities covered was 9 p*K* units. Hammett plots of log *k* vs. σ for the Y substituents in the dimethylaniline leaving group for these reactions (eq 3) are presented in Figure 2. The slopes provide ρ_{Lg} values, which are all near 2.0; the data are given in Table XII. For reasons discussed earlier,[8b] Brønsted β values are usually more precise than Hammett ρ values. This is not true in the present instance, however, because pK_a values could be measured in Me_2SO solution for only three of five *N*,*N*-dimethylanilinium ions (see the Results section). The rough β_{Lg} values calculated from ρ_{Lg}/ρ_{pK_a} range from 0.44 to 0.48.

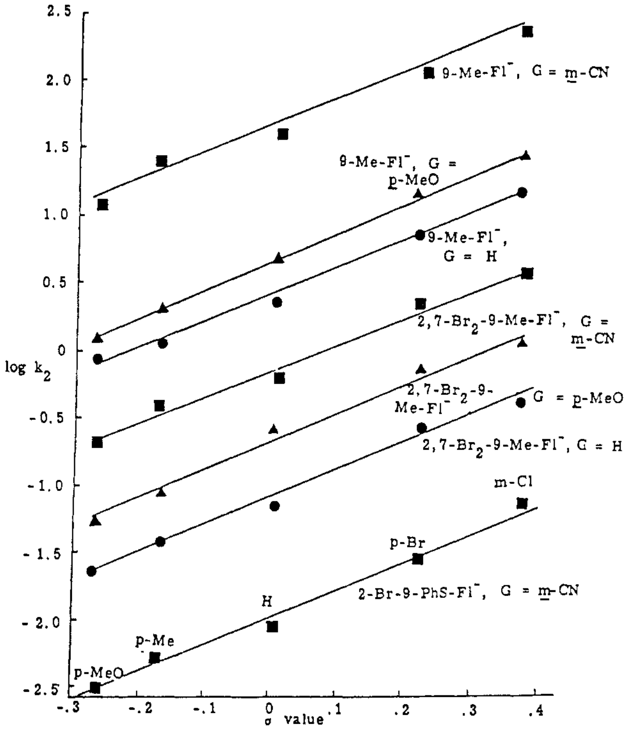

Figure 2. Plots of the logarithm of the rate constants for reactions of 9-substituted fluorenide carbanions, 9-RFl⁻, with $GC_6H_4CH_2NMe_2C_6H_4Y^+$ cations vs. the Hammett σ value of the Y substituent. (■) G = *m*-CN; (●) G = H; (▲) G = *p*-MeO. (The slopes of the lines are listed in Table IX.)

The point in question here is whether or not ρ_{Lg} (or β_{Lg}) varies as the strength of the nucleophile is increased. As shown in Figure 2 and Table XII, the ρ_{Lg} values remain essentially constant when the basicity of the nucleophile is varied by 9 p*K* units, from 9-MeFl⁻ (pK_{HA} = 22.35) to 2-Br-9-(PhS)Fl⁻ (pK_{HA}) = 13.2). (The rate constants change by a factor of 5000-fold in these studies.) If we accept the assumption that β_{Lg} measures the extent of bond breaking in the transition state, these results point toward no change in the extent of bond breaking when the nucleophilicity is increased, in conflict with both the PS and TMJ theories.

Effect of Increasing the Electron-Acceptor Power of the Substituent G in the Benzyl Moiety of $GC_6H_4CH_2X$ Substrates. Analysis of the data for the reactions of 9-GFl⁻ ion families with benzyl substrates using the Brønsted relationship shows that β_{Nu} values increase as the electron-withdrawing power of G in $GC_6H_4CH_2X$ increases (Tables VI and X). If β_{Nu} is indicative of the amount of bond making in the TS, these results are in accord with the predictions of both the TMJ and PS theories (Table IX). However, they are puzzling because (1) this is the only case where our experimental results appear to agree with the predictions of the two theories, (2) as discussed above, large changes in nucleophilicity and leaving group ability (10^5 rate variation) cause no change in β_{Nu}, yet the small rate changes caused by differing G substituents cause a large change in β_{Nu}, and (3) a change in the G substituent causes a change in β_{Nu} but no change in β_{Lg} (Table X), which implies that bond making is changing in the TS but bond breaking is not (in contrast to the TMJ prediction, Table IX).

Factors Affecting the Size of β_{Nu} and an Interpretation of β_{Nu} Changes in Terms of Electrostatic Effects. The absolute meaning of β_{Nu} is not clear, but changes in β_{Nu} must have mechanistic significance. For families of nucleophiles where steric and solvent effects are kept constant and basicity is changed by remote substitution, as in our present studies, β_{Nu} can be defined as the sensitivity of rates to changes in basicity. Application of the Brønsted relationship to S_N2 reactions has shown that β_{Nu} remains remarkably constant for (a) changes in Nu⁻ basicity over a range of as much as 20 kcal/mol;[14] (b) changes in the nature of the donor atom in Nu⁻ (e.g., from C⁻ in 9-GFl⁻ ions, to N⁻ in carbazolide

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[38] Lewis, F. S.; Vanderpool, S. H. *J. Am. Chem. Soc.* **1978**, *100*, 6421-6424.

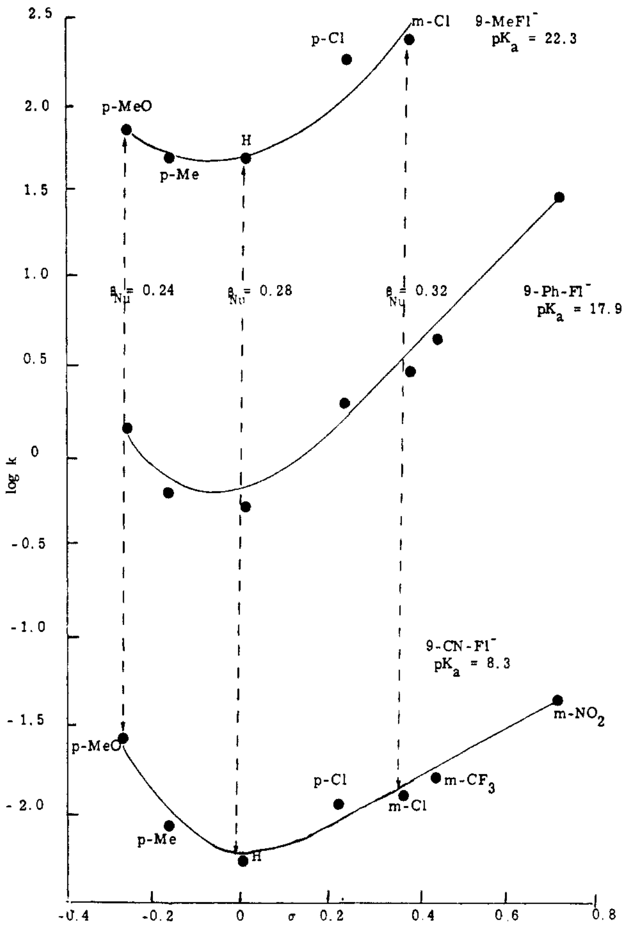

Figure 3. Hammett plots for 9-RFl⁻ ions reacting with $GC_6H_4CH_2Cl$ chlorides in Me_2SO solution at 25 °C; log k vs. σ for the G substituent. (Data taken from ref 15.)

or phenothiazinide ions, to O⁻ in 2-naphthoxide ions, and to S⁻ in ArS⁻ (Table V);[39] and (c) changes in the nature of the leaving group along the series Cl, Br, I, and $N(Me)_2Ar^+$ (Tables V, VI, and X).[40]

There are two structural changes that cause β_{Nu} (or ρ_{Nu}) to increase: (1) the introduction of electron-withdrawing groups into the electrophile and (2) a decrease in the extent of delocalization of charge in the anionic nucleophile. The increase in β_{Nu} (or ρ_{Nu}) with increases in the electron-withdrawing groups in *m*- and *p*-$GC_6H_4CH_2X$ substrates has been known for many years;[11,12,15,28a] further examples are given in Tables VI and X. Similar increases have been observed for GCH_2X substrates (Tables V and XI). The increase in β_{Nu} with decreased delocalization in the Nu⁻ has been observed for the phenoxide ion vs. the 2-naphthoxide ion families (0.4 vs. 0.3) and[37] the acetanilide family, ArN=C(O⁻)CH$_3$, vs. the anilide family, ArNR⁻[42] and for the placement of substituents in the Ar vs. the fluorene ring in 9-ArFl⁻ ions.[43] Effects of both changes are observable in the reactions of 9-GFl⁻ ions with $G'C_6H_4CH_2Cl$ chlorides.[15] As G′ is changed from *p*-MeO to H to *m*-Cl, β_{Nu} increases from about 0.24 to 0.28 to 0.32 because of the increase in electron-withdrawing effects in the electrophiles. But at the same time the slope of the curve for donors tends to decrease and that for acceptors to increase as the basicities of the Nu⁻ families increase from 9-(CN)Fl⁻ to 9-PhFl⁻ to 9-MeFl⁻, i.e., as the extent of delocalization of the negative charge in Nu⁻ decreases. In other words, the substituents in the electrophile exert a polarization effect on Nu⁻, which increases in effectiveness as the charges in the anions become more localized. The result is curved Hammett plots (Figure 3).

The failure of changes in the nature of the donor atom in the anion along the series C⁻, N⁻, O⁻, S⁻ to affect the size of β_{Nu} shows that it is the nature of the charge that is important and not the length or strength of the Nu–C bond (C–C, N–C, O–C, or S–C) being formed. Nor does the nature of the bond being broken (C–Cl, C–Br, C–I, or $C–N(Me_2)Ar^+$) affect the size of β_{Nu}. Yet these structural changes can lead to large changes in the reaction rates. At the same time the relatively large increases in β_{Nu} associated with the presence of electron-withdrawing groups in electrophiles can cause either small rate increases (e.g., $GC_6H_4CH_2X$ substrates) or sizable rate increases (e.g., $CNCH_2X$ substrates). It would appear that these changes in β_{Nu} are associated with an electrostatic effect that is not directly related to the principal kinetic barrier. Formation of a charge-transfer (CT) or ion–dipole complex comes to mind. Since a search for a CT complex proved negative (see the Results section), we believe that the changes in β_{Nu} values discussed above are most likely associated with electrostatic effects in the formation of ion–dipole complexes. Studies of anions reacting with methyl halides in the gas phase have shown that, on contact, an ion–dipole complex is formed in a potential well.[44] Recent calculations on the effect of solvent on the gas-phase S_N2 identity reaction of Cl⁻ with CH_3Cl have shown that water eliminates the potential well, but the ion–dipole minimum is still clearly apparent in DMF (eq 5).[45] Similarly, association of Cl⁻ ion with benzyl substrates has been shown to occur in acetonitrile solution.[46]

$$\mathrm{Nu^- + R^{\delta+}{-}X^{\delta-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Nu^{\delta-}\cdots R^{\delta+}{-}X^{\delta-} \xrightarrow{k_2} Nu{-}R + X^-} \tag{5}$$

We suggest that the size of β_{Nu} gives a rough measure of the strength of the ion–dipole interaction occurring in the first stage of the S_N2 reaction in Me_2SO solution, that in which the ion–dipole complex is formed. This is consistent with the relative insensitivity of β_{Nu} to changes in size, shape, or basicity of the nucleophile or the nature of its donor atom. It is also consistent with the increase in β_{Nu} caused by electron-withdrawing substituents, G, in $GC_6H_4CH_2X$ and GCH_2X, since these substituents will increase the positive charge on carbon in the C–X bond in the ion–dipole. On the other hand, the positive charge can be dispersed into ortho methyl groups in benzyl substrates leading to a decrease in β_{Nu} (see Results section). An increase in β_{Nu} also occurs as delocalization of the charge in Nu⁻ is made less effective, leading to more charge transfer. Evidently the differences in the dipole moments for Cl, Br, or I leaving groups are too small to affect the size of β_{Nu} appreciably, and Y in $GC_6H_4CH_2N^+(Me)_2C_6H_4Y$ is too remote to have an effect. The lack of correlation of β_{Nu} with rates of reactions noted earlier is understandable since the rate in S_N2 reactions is controlled principally by the necessity to overcome the large barrier caused by solvent and molecular reorganization associated with the breaking of the C–X bond and the formation of the Nu–C bond. The size of β_{Lg} is associated with the size of this barrier, which explains why β_{Lg} is insensitive to the basicity of the nucleophile and why changes in the electron-withdrawing power of substituents G in $GC_6H_4CH_2X$ can affect β_{Nu} without affecting β_{Lg}.

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(39) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1984**, *106*, 3234–3239.

(40) The observation that the sensitivities within a family of nucleophiles (β_{Nu}) remain constant for changes in X of GCH_2X electrophiles is similar to the observation of Ritchie that relative nucleophilicities (N_+ values) of groups of orphan nucleophiles (e.g., N_3^-, CN⁻, and CH_3O^-) remain constant for reactions with a number of different highly delocalized cation electrophiles.[41]

(41) (a) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348–354. (b) Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 3573–3578. (c) Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 7313–7318.

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(45) Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 3049–3950. (b) *J. Am. Chem. Soc.* **1985**, *107*, 154–163. (c) Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 2974–2975.

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Summary and Conclusions

Evidence is presented to show that Brønsted β_{Nu} values for S_N2 reactions remain constant for reactions of families of delocalized anion nucleophiles for (a) changes in basicity over a range of over 20 kcal/mol, (b) changes in the nature of the donor atom in the anion from carbon to nitrogen to oxygen to sulfur, and (c) changes in the nature of the leaving group along the series Cl, Br, I, and $N^+(Me_2)Ar$. On the other hand, β_{Nu} values increase (a) when G in the $GC_6H_4CH_2X$ or GCH_2X electrophile becomes more electron withdrawing or (b) when the charge in the anion nucleophile becomes less delocalized. These observations are not accommodated by theories that assume that β_{Nu} (and/or β_{Lg}) provides a measure of the extent of bond making (and/or bond breaking) in the transition state of a single-step reaction. They can be accommodated, however, by the assumption that the size of β_{Nu} is determined by the strength of the ion–dipole interaction occurring in the formation of an ion–dipole complex in the initial stage of a two-stage reaction. Since the major part of the bond making and bond breaking process occurs in the second stage of the reaction, there need be no direct correlation between the size of β_{Nu} and the rates of these reactions and no direct connection between β_{Nu} and β_{Lg}. We can expect several factors to play significant roles in determining the size of k_2, which will usually be mainly responsible for determining the size of the kinetic barrier for the overall S_N2 reaction. These include (a) the redox potentials of Nu^- and RX, (b) the strengths of the bonds being formed and broken, and (c) the energy required for molecular and solvent reorganization.

Experimental Section

Rate Measurements. These were made in 0.8 M KNO_3 solution of Me_2SO at 25 °C by monitoring the decrease in absorbance of the colored fluorenyl anion at a fixed wavelength as described previously.[14]

Acidity Measurements. The measurements of the dimethylanilinium ions were made by equilibrating the amine with an indicator whose anion was colored. The procedure is described below. (1) A Beer's law titration of the indicator anion (In^-) was made by adding weighed aliquots of the indicator (HIn) solution to a solution of piperidine in Me_2SO in a cuvette. The absorbance of In^- was measured for each aliquot, and the slope of a plot of Abs. vs. [In^-] gave ϵ. (2) After the cuvette was cleaned, 2 mL of Me_2SO was added and the cuvette weighed. A solution of the amine of unknown pK_a was then added and the cuvette weighed. (Enough amine was added to make its concentration about 2 mM in the cuvette.) Several aliquots of the indicator solution were added to establish the equilibrium in eq 4. After each addition, the cuvette was weighed to determine the amount of HIn that had been added and the absorbance measured in order to determine In^- concentration. From the weights of aliquots added and ϵ, the equilibrium constant for equation was determined; from the known pK_a of HIn, the pK_a of R_3N^+H could then be determined. Further details of the method, including Debye–Hückel corrections, have been described elsewhere.[21,27]

Procedure for Product Studies. Approximately 1 mmol of the 9-substituted fluorene was placed in a small flask and degassed 3 times by evacuating to 50 μm and flushing with argon. Five milliliters of dry, degassed Me_2SO was added to the flask via syringe through a three-way stopcock. One equilivalent of $CH_3SOCH_2^-K^+$ solution was then added, producing the colored fluorenide anion. Next, 1 equiv of the *N*-benzyl-*N*,*N*-dimethylanilinium salt in Me_2SO solution was added. The disappearance of the anion color signaled complete reaction, at which time the reaction mixture was poured into water and extracted with ether. The ether layer was washed twice with dilute HCl to remove the dimethylaniline. This acid layer was separated, neutralized with NaOH, and then extracted with ether. The ether layer was washed 3 times with water and once with brine, dried over $MgSO_4$, and then rotary evaporated to yield the dimethylaniline. An NMR was taken of the crude material to verify the identity of the aniline. The ether layer from above which contained the fluorene S_N2 product was washed 3 times with water and once with brine, dried over $MgSO_4$, and then rotary evaporated in a tarred flask. This flask containing the product was placed in a vacuum oven to remove the last traces of water and solvent and then weighed to determine the crude yield of the reaction. An NMR of the crude material was taken. One recrystallization generally provided pure material. Spectral data and physical constants for each product study are given below.

Reaction of 9-PhFl$^-$ Ion with $PhCH_2NMe_2C_6H_4Me$-*p*$^+$ in Me_2SO. Reaction time: 12 h. Yield: 73%. Crude mp: 136–138 °C [lit.[14] mp 139–140 °C]. NMR ($CDCl_3$): δ 3.8 (2 H, s, CH_2), 6.5–7.3 (9 H, m, aromatic protons). NMR ($CDCl_3$) of the isolated aniline: δ 2.2 (3 H, s, CH_3Ar), 2.8 (6 H, *s*, $(CH_3)_2N$), 6.4–7.0 (4 H, m, aryl protons). This is superimposable on an NMR taken on commercially available *p*-methyl-*N*,*N*-dimethylaniline.

Reaction of 9-MeFl$^-$ Ion with *m*-$NCC_6H_4CH_2NMe_2C_6H_4Me$-*p*$^+$ in Me_2SO. Reaction time: 5 min. Yield: 94%. Mp (hexane): 73–74 °C for the fluorene product. NMR ($CDCl_3$) of the fluorene product: δ 1.6 (3 H, s, CH_3), 3.1 (2 H, s, CH_2Ph), 6.5–7.5 (12 H, m, aryl protons). NMR of the aniline: same as that for the previous product study.

Reaction of 9-MeFl$^-$ Ion with *m*-$CNC_6H_4CH_2NMe_2C_6H_4OMe$-*p*$^+$ in Me_2SO. Reaction time: 10 min. Yield: 93%. Mp (hexane): 74–75 °C for the fluorene product. The fluorene NMR was the same as that reported previously.[14] Aniline NMR: δ 2.8 (6 H, s, $N(CH_3)_2$), 3.7 (3 H, s, OCH_3), 6.6 (4 H, s, aryl protons). Crude mp 46–47 °C [lit.[16] mp 48 °C]. HPLC analysis of the crude fluorene product showed two impurities of about 3% and 5%.

Reaction of 9-MeFl$^-$ Ion with *p*-$MeOC_6H_4CH_2NMe_2C_6H_4Cl$-*m*$^+$ in Me_2SO. Reaction time: 2 min. Yield: 100%. Mp (EtOH/water): 119–121 °C [lit.[14] mp 120–121 °C]. The fluorene NMR was identical with that reported previously.[14] The amine NMR [δ 2.8 (6 H, s, $N(CH_3)_2$), 6.3–7.1 (4 H, m, aryl protons)] was identical with that from a known sample of *m*-chloro-*N*,*N*-dimethylaniline.

Reaction of 9-MeFl$^-$ Ion with $C_6H_5CH_2NMe_2C_6H_5^+$ in Me_2SO. Reaction time: 15 min. Yield: 92%. Mp (MeOH): 70–71 °C. Fluorene NMR ($CDCl_3$): δ 1.5 (3 H, s, CH_3), 3.0 (2 H, s, CH_2Ph), 6.4–7.4 (13 H, m, aromatic protons). The NMR of the aniline product was identical with that of a known sample: δ 2.8 (6 H, s, $N(CH_3)_2$), 6.6–7.4 (5 H, m, aryl protons).

Materials. The syntheses of the 9-G-fluorenes have been described earlier.[14] *p*-Methoxybenzyl bromide,[47] *m*-$ClC_6H_4NMe_2$,[48] and *p*-$MeOC_6H_4NMe_2$[48] were made as described in the literature. The other anilines and benzyl bromides were commercially available.

***N*,*N*-Dimethylanilinium Hydrotetrafluoroborate.** This compound was prepared by adding equivalent amounts of *N*,*N*-dimethylaniline and 48% HBF_4 to *i*-PrOH and boiling off the alcohol. Recrystallization from *i*-PrOH/ether gave a solid, mp 58–62 °C [lit.[49] mp 54–56 °C]. Neutralization equivalent = 208.0; theoretical 209.0.

The *N*-benzyl-*N*,*N*-dimethylanilinium salts were prepared according to the directions of Westaway and Poirier.[32] One equivalent of $ArCH_2Br$ and 1.1 equiv of the appropriate aniline were stirred in dry benzene from 2 h to 3 days. The salts were recrystallized from *i*-PrOH/ether. The nitrate salts were also prepared from the directions of Westaway and Poirier.[28b] Further characterization of each salt is given below.

***N*-Benzyl-*N*,*N*-dimethylanilinium Bromide.** Reaction time: 24 h. Mp: 149–151 °C [lit.[28b] mp 150–152 °C]. NMR: δ 3.6 (6 H, s, CH_3), 5.1 (2 H, s, CH_2Ph), 6.8–7.9 (10 H, m, aryl protons).

***N*-Benzyl-*N*,*N*-dimethylanilinium Nitrate.** Mp: 157–158 °C [lit.[31] mp 157–158 °C].

***N*-Benzyl-*N*,*N*-dimethyl-4-methylanilinium Bromide.** Reaction time: 24 h. Mp: 172–174 °C. NMR (CD_3SOCD_3): δ 2.4 (3 H, s, CH_3Ar), 3.5 (6, H, s, $(CH_3)_2N$), 5.0 (2 H, s, CH_2Ar), 6.8–7.7 (9 H, m, aryl protons).

***N*-Benzyl-*N*,*N*-dimethyl-3-chloroanilinium Nitrate.** Reaction time: 36 h. Mp: 116.5–117 °C. NMR (CD_3SOCD_3): δ 3.5 (6 H, s, CH_3), 5.0 (2 H, s, CH_2Ph), 6.8–8.0 (9 H, m, aryl protons).

***N*-Benzyl-*N*,*N*-dimethyl-4-bromoanilinium Bromide.** Reaction time: 72 h. Mp: 145–146 °C. NMR (CD_3SOCD_3): δ 3.5 (6 H, s, $(CH_3)_2N$), 5.0 (2 H, s, CH_2Ph), 6.8–7.3 (5 H, m, unsubstituted phenyl protons), 7.7 (4 H, s, para-substituted phenyl protons).

***N*-Benzyl-*N*,*N*-dimethyl-4-methoxyanilinium Bromide.** Reaction time: 24 h. Mp: 128–130 °C. NMR (CD_3SOCD_3): δ 3.5 (6 H, s, $(CH_3)_2N$), 3.7 (3 H, s, CH_3O), 5.0 (2 H, s, CH_2Ph), 6.8–7.8 (9 H, m, aryl protons).

***N*-(3-Cyanobenzyl)-*N*,*N*-dimethylanilinium Bromide.** Reaction time: 36 h. Mp: 138–139 °C dec. nNMR (CD_3SOCD_3): δ 3.6 (6 H, s, $(CH_3)_2N$), 5.0 (2 H, s, CH_2Ar), 7.2–7.8 (9 H, m, aryl protons).

***N*-(3-Cyanobenzyl)-*N*,*N*-dimethyl-4-methylanilinium Bromide.** Reaction time: 6 h. Mp: 153–154 °C. NMR (CD_3SOCD_3): δ 2.4 (3 H, *s*, CH_3Ar), 3.6 (6 H, s, $CH_3)_2N$), 5.1 (2 H, s, CH_2Ar), 7.1–7.8 (8 H, m, aryl protons).

***N*-(3-Cyanobenzyl)-*N*,*N*-dimethyl-3-chloroanilinium Bromide.** Reaction time: 1 week. Mp: 119–120 °C. NMR (CD_3SOCD_3): δ 3.6 (6 H, s, $(CH_3)_2N$), 5.0 (2 H, s, CH_2Ar), 7.2–8.0 (8 H, m, aryl protons).

***N*-(3-Cyanobenzyl)-*N*,*N*-dimethyl-4-bromoanilinium Bromide.** Reaction time: 48 h. Mp: 122–123 °C. NMR (CD_3SOCD_3): δ 3.6 (6 H, s, $(CH_3)_2N$), 5.0 (2 H, s, CH_2Ar), 7.2–7.7 (8 H, m, aryl protons).

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***N*-(3-Cyanobenzyl)-*N*,*N*-dimethyl-4-methoxyanilinium Bromide.** Reaction time: 12 h. Mp: 150–152 °C. NMR (CD_3SOCD_3): δ 3.6 (6 H, s, $(CH_3)_2N$), 3.8 (3 H, s, CH_3O), 5.1 (2 H, s, CH_2Ar), 6.9–7.9 (8 H, m, aryl protons).

***N*-(4-Methoxybenzyl)-*N*,*N*-dimethylanilinium Chloride.** Reaction time: 48 h. Mp: 105–106 °C. NMR (CD_3SOCD_3): δ 3.6 (6 H, s, $(CH_3)_2N$), 3.7 (3 H, s, CH_3O), 5.0 (2 H, s, CH_2), 6.7–7.9 (9 H, m, aryl protons).

***N*-(4-Methoxybenzyl)-*N*,*N*-dimethyl-4-methylanilinium Bromide.** Reaction time: 3 h. Mp: 149–150 °C. NMR (CD_3SOCD_3): δ 2.4 (3 H, s, CH_2Ar), 3.6 (6 H, s, $(CH_3)_2N$), 3.7 (3 H, s, CH_3O), 4.9 (2 H, s, CH_2Ar), 6.8–7.7 (8 H, m, aryl protons).

***N*-(4-Methoxybenzyl)-*N*,*N*-dimethyl-3-chloroanilinium Bromide.** Reaction time: 3 days. Mp: 116–118 °C. NMR (CD_3SOCD_3): δ 3.6 (6 H, s, $(CH_3)_2N$), 3.7 (3 H, s, CH_3O), 5.0 (2 H, s, CH_2Ar), 6.6–7.6 (8 H, *m*, aryl protons).

***N*-(4-Methoxybenzyl)-*N*,*N*-dimethyl-4-bromoanilinium Bromide.** Reaction time: 12 h. Mp: 139–140 °C. NMR (CD_3SOCD_3): δ 3.6 (6 H, s, $(CH_3)_2N$), 3.7 (3 H, s, CH_3O), 5.0 (2 H, s, CH_2Ar), 6.6–7.1 (4 H, m, aryl protons from *p*-MeO phenyl ring), 7.7 (4 H, s, aryl protons from *p*-Br phenyl ring).

***N*-(4-Methoxybenzyl)-*N*,*N*-dimethyl-4-methoxyanilinium Bromide.** Reaction time: 3 days. Mp: 150–151 °C. NMR (CD_3SOCD_3): δ 3.5 (6 H, s, $(CH_3)_2N$), 3.7 (3 H, s, CH_3O), 3.8 (3 H, s, CH_3O), 4.9 (2 H, s, CH_2Ar), 6.7–7.7 (8 H, m, aryl protons).

Product Studies. These were carried out in Me_2SO solution as previously described.[14]

Reaction of 9-CO_2MeFl$^-$ with $ClCH_2CN$ for 3 h gave 88% of 9-CO_2Me-9-CH_2CNFl. Mp: 124–125 °C (MeOH). NMR ($CDCl_3$): δ 3.1 (2 H, s, CH_2) 3.6 (3 H, s, CH_3) 7.1–7.7 (8 H, m).

Reaction of 9-(2-methylphenyl)fluorenide ion with $PhCH_2Cl$ for 12 h gave 91% of 9-(2-MePh)-9-$PhCH_2$Fl. Mp: softens 158 °C, melts at 165–166 °C. NMR ($CDCl_3$): δ 1.1 (3 H, s, CH_3) 3.7 (2 H, s, CH_2) 6.0–6.2, 6.5–7.5, 7.9–8.1 (17 H, m, aryl protons). UV: λ_{max} 266, 270, 294, 306 nm. Mass spectrum (70 eV): *m/e* 346 (8.1%, M^+) 255 (100%, loss of 9-$PhCH_2^•$ or 9-(2-$CH_3Cl_6H_4^•$), 91 (9.0%, $PhCH_2^•$).

Reaction of 9-PhFl$^-$ with $PhCH_2N^+(Me_2)C_6H_4Me$-*p* for 12 h gave 73%. Mp: 136–138 °C [lit.[14] mp 139–140 °C]. NMR ($CDCl_3$): δ 3.8 (2 H, s, CH_2) 6.5–7.3 (9 H, m, aryl protons). The NMR of the amine product was superimposable on that of a sample of *p*-$MeC_6H_4NMe_2$.

Reaction of 9-MeFl$^-$ with *m*-$CNC_6H_4CH_2N^+(Me_2)C_6H_4Me$-*p* for 5 min gave 95% 9-Me-9-*m*-CNC_6H_4Fl. Mp: 73–74 °C (hexane). NMR: δ 1.6 (3 H, s, CH_3), 3.1 (2 H, s, CH_2Ph), 6.5–7.6 (12 H, m, aryl protons). The NMR of the aniline product was identical with that of *p*-$MeC_6H_4NMe_2$. Mass spectrum (70 eV): *m/e* 295 (9.3%, M^+), 179 (100%, 9-MeFl$^•$), 116 (20%, $CNC_6H_4CH_2^•$).

Reaction of 9-MeFl$^-$ with *m*-$CNC_6H_4N(Me_2)C_6H_4OMe$-*p* for 10 min gave 93% 9-Me-9-*m*-CNC_6H_4Fl, identical with the sample prepared in the previous experiment.

Reaction of 9-MeFl$^-$ with *m*-$MeOC_6H_4CH_2N^+C_6H_4Cl$-*m* for 2 min gave 100% 9-Me-9-(*p*-$MeOC_6H_4$)Fl. Mp: 119–121 °C (EtOH/H_2O) [lit.[14] mp 120–121 °C]. NMR identical with the product prepared from 9-MeFl$^-$ and *p*-$MeOC_6H_4CH_2Cl$.

Reaction of 9-MeFl$^-$ with $PhCH_2N^+(Me_2)C_6H_5$ for 15 min gave 92% 9-Me-9-$PhCH_2$Fl. NMR identical with that from the product obtained from 9-MeFl$^-$ and $PhCH_2Cl$.

Reaction of 9-CO_2MeFl$^-$ with 9-(chloromethyl)anthracene (9-$AnCH_2Cl$) for 1 h gave 92% 9-CO_2Me-9-$AnCH_2$Fl as yellow needles (EtOH, hexane). Mp: 195 °C (softens at 189 °C). NMR ($CDCl_3$): δ 3.4 (3 H, s, CH_3), 4.5 (2 H, s, CH_2), 6.8–8.0 (16 H, m, aromatic), 8.3 (1 H, br s, aromatic H). Mass spectrum: *m/e* 4/4 (7.5%, M^+), 191 (100%, $ArCH_2^•$).

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Registry No. 1 (R = CO_2Me; X = X′ = H), 12565-94-5; **1** (R = CO_2Me; X = H; X′ = Br), 73838-71-8; **1** (R = CO_2Me; X = X′ = Br), 73838-70-7; **1** (R = CN; X = X′ = H), 12564-43-1; **1** (R = Me; X = X′ = H), 31468-21-0; **1** (R = Me; X = H; X′ = Br), 81255-42-7; **1** (R = Me; X = X′ = Br), 73872-46-5; **1** (R = CO_2Me; X = H; X′ = Ph), 104292-29-7; **1** (R = CN; X = H; X′ = Br), 104292-30-0; **1** (R = *p*-MeC_6H_4; X = X′ = H), 42730-14-3; **1** (R = Ph; X = X′ = H), 31468-22-1; **1** (R = *m*-ClC_6H_4; X = X′ = H), 73872-45-4; **1** (R = *p*-$MeSO_2C_6H_4$; X = X′ = H), 73872-44-3; **1** (R = SPh; X = X′ = H), 71805-72-6; **1** (R = *p*-BrC_6H_4S; X = X′ = H), 73838-77-4; **1** (R = SPh; X = H; X′ = Br), 73838-76-3; **1** (R = *p*-$MeC_{H4}S$; X = H; X′ = SO_2Ph), 73838-75-2; **1** (R = SPh; X = X′ = Br), 81245-84-3; **1** (R = *o*-MeC_6H_4; X = X′ = H), 85535-26-8; **1** (R = Me; X = H; X′ = Cl), 73872-47-6; **2**·Br^- (G = H; Y = *p*-OMe), 104292-31-1; **2**·NO_3^- (G = H; Y = *p*-OMe), 58247-36-2; **2**·Br^- (G = H; Y = *p*-Me), 97788-15-3; **2**·Br^- (G = H; Y = H), 23145-45-1; **2**·NO_3^- (G = H; Y = H), 2484-09-5; **2**·Br^- (G = H; Y = *p*-Br), 104292-32-2; **2**·NO_3^- (G = H; Y = *m*-Cl), 104292-34-4; **2**·Br^- (G = *m*-CN; Y = *p*-OMe), 104292-35-5; **2**·Br^- (G = *m*-CN; Y = *p*-Me), 104322-37-4; **2**·Br^- (G = *m*-CN; Y = H), 104292-36-6; **2**·Br^- (G = *m*-CN; Y = *p*-Br), 104292-37-7; **2**·Br^- (G = *m*-CN; Y = *m*-Cl), 104292-38-8; **2**·Br^- (G = *p*-OMe; Y = *p*-OMe), 104292-39-9; **2**·Br^- (G = *p*-OMe; Y = *p*-Me), 104292-40-2; **2**·Br^- (G = *p*-OMe; Y = H), 28949-78-2; **2**·Cl^- (G = *p*-OMe; Y = H), 104292-44-6; **2**·Br^- (G = *p*-OMe; Y = *p*-Br, 104292-41-3; **2**·Br^- (G = *p*-OMe; Y = *m*-Cl), 104322-38-5; **3** (R = Ph; G = X = H), 35377-96-9; **3** (R = Me; G = *m*-CN; X = H), 104292-42-4; **3** (R = Me; G = *p*-OMe; X = H), 104292-43-5; **3** (R = Me; G = X = H), 61076-90-2; **3** (R = *o*-C_6H_4Me; G = X = H), 85535-36-0; **4** (Y = *p*-Me), 99-97-8; **4** (Y = *p*-OMe), 701-56-4; **4** (Y = *m*-Cl), 6848-13-1; **4** (Y = H), 121-69-7; **4** (Y = *p*-Br), 586-77-6; $PhCH_2Br$, 100-39-0; *m*-$NCC_6H_4CH_2Br$, 28188-41-2; *p*-$MeOC_6H_4CH_2Cl$, 824-94-2; *p*-$MeOC_6H_4CH_2Br$, 2746-25-0; $ClCH_2CN$, 107-14-2; $PhCH_2Cl$, 100-44-7; $PhNH_3^+$, 17032-11-0; *p*-$MeOC_6H_4NHMe_2^+$, 17251-79-5; *p*-$MeC_6H_4NHMe_2^+$, 45795-44-6; $PhNHMe_2^+$, 17835-98-2; BuCl, 109-69-3; BuBr, 109-65-9; BuI, 542-69-8; $NCCH_2Br$, 590-17-0; $NCCH_2I$, 624-75-9; *m*-$ClC_6H_4CH_2Cl$, 620-20-2; *m*-$BrC_6H_4CH_2Br$, 823-78-9; *m*-$O_2NC_6H_4CH_2Cl$, 619-23-8; *m*-$O_2NC_6H_4CH_2Br$, 3958-57-4; 2-MeBzCl, 552-45-4; 2,4,6-Me_3BzCl, 1585-16-6; 9-$AnCH_2Cl$, 24463-19-2; *p*-*t*-$BuC_6H_4O^-$, 28528-33-8; *p*-*t*-$BuC_6H_4CH_2Cl$, 19692-45-6; 9-CO_2Me-9-CH_2CNFl, 104292-45-7; 9-CO_2Me-9-$AnCH_2$Fl, 104292-46-8; $PhNMe_2 \cdot H^+ \cdot BF_4^-$, 22533-76-2; 4-methylpyridine conjugate acid, 16950-21-3.