28% yield) of 5-phenylbenzobicyclo[3.1.0]hex-2-ene (**5**) was obtained as a white solid: mp 59–61 °C; NMR ($CDCl_3$) δ 0.68 (t, H(6-endo), 1 H, $J_{1,6\text{-endo}} = 3.8$, $J_{6\text{-endo},6\text{-exo}} = 4.2$), 1.51 (dd, H(6-exo), 1 H, $J_{1,6\text{-exo}} = 8.0$ Hz), 2.71 (ddd, H(1), 1 H, $J_{1,4\text{-endo}} = 1.3$), 3.37 (br d, H(4-endo), 1 H, $J_{4\text{-endo},4\text{-exo}} = 17.0$), 3.47 (d, H(4-exo), 1 H), 7.0–7.4 (m, arom H, 9 H); UV (MeOH) λ_{max} 230 nm (log ε 4.04, sh), 204 (4.58); mass spectrum, *m/e* (relative intensity) 206 (M^+, 100), 191 (15), 178 (14), 165 (24), 128 (18), 92 (33). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.18; H, 6.82; exact mass 206.111 ± 0.003, theory 206.110.

1-Phenyl-1,4-dihydronaphthalene (9). This compound was obtained by reduction of 4-phenyl-2-tetralone[23] to the corresponding alcohol and subsequent dehydration. A mixture (1.4 g) of 1-phenyl-1,2-dihydronaphthalene (**11**) and **9** was obtained. Chromatography on silica with hexane as the eluent followed by an additional purification on HPLC (silica/hexane) yielded **9** as a clear oil: yield 196 mg, corresponding to 14% of the mixture; NMR as reported;[9] mass spectrum, *m/e* (relative intensity) 206 (M^+, 100), 191 (20), 178 (6), 165 (5), 128 (21), 115 (5), 102 (5), 91 (9); exact mass 206.112 ± 0.003, theory 206.110. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.18; H, 6.82.

2-Benzyl-1*H*-indene (16). This compound was synthesized from 2-indanone through a Grignard reaction with benzylmagnesium chloride followed by dehydration using TsOH in toluene in a yield of 30%. After purification on silica with hexane as the eluent a clear oil was obtained which solidified spontaneously into a white solid: mp 47–48.5 °C (lit. mp 46.5–48,[23] 48–49.5,[24] 48 °C[25]); ^1H NMR ($CDCl_3$) δ 3.3 (br s, indene methylenic H, 2 H), 3.8 (br s, benzylic H, 2 H), 6.5 (br s, indene olefinic H, 1 H), 6.9–7.4 (m, arom H, 9 H) [the assignment of the protons at 3.3 and 3.8 ppm might be inverted (cf. literature data[24])]; UV (MeOH) λ_{max} 257 nm (log ε 4.17), 206 (4.42); λ_{min} 232 nm (log ε 3.60); mass spectrum (Finnigan), *m/e* (relative intensity) 206 (M^+, 18), 128 (13), 115 (16), 81 (100). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.09; H, 6.91.

2-Benzylideneindan (17). This compound was obtained in 81% yield as an oil by irradiation of **16** for 1 h at 254 nm: ^1H NMR ($CDCl_3$) δ 3.9 (vbr, methylene H, 4 H), 6.6 (quintet, olefinic H, 1 H), 6.9–7.5 (m, arom H, 9 H); mass spectrum, *m/e* (relative intensity) 208 (M^+, 100), 191 (10), 128 (13), 91 (17). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.05; H, 6.95.

2-Phenyl-1,4-dihydronaphthalene (20). This compound was isolated as a clear oil from a product mixture obtained after flash vacuum pyrolysis of 5-phenylbenzobicyclo[3.1.0]hex-2-ene (**5**) at 700 °C:[8] ^1H NMR ($CDCl_3$) δ 3.5–3.7 (m, methylene H at C(4), 2 H), 3.7–3.9 (m, methylene H at C(1), 2 H), 6.3 (m, olefinic H, 1 H), 7.1–7.6 (m, arom H, 9 H); NMR spectrum similar to reported one in CCl_4;[11] mass spectrum (Finnigan), *m/e* (relative intensity) 206 (M^+, 35), 128 (30), 115 (20), 91 (100).

Registry No. **3**, 82645-20-3; *exo*-**4**, 85803-90-3; **5**, 85803-91-4; *endo*-**6**, 67504-58-9; *exo*-**6**, 67504-57-8; **9**, 13387-49-0; **16**, 16274-93-4; **17**, 23114-34-3; **20**, 40650-73-5.

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Steric and Electronic Effects in S_N2 Reactions of 9-Substituted Fluorenyl and α-Cyano Carbanions with Benzyl Chloride in Dimethyl Sulfoxide Solution

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Rates of reactions of $PhCH_2Cl$ with carbanions derived from six α-cyano carbon acids of varied structure with pK_a values ranging over 16 units have been measured. When placed on a log *k* vs. pK_a plot the points fit near to the extended Brønsted line obtained earlier for the 9-(methoxycarbonyl)fluorenyl ion family, $9\text{-}CO_2MeFl^-$, reacting with $PhCH_2Cl$. It is concluded that differences in shape, size, charge concentration, solvation, or aromaticity play no obvious part in determining the reactivity of these carbanions, all of these effects being incorporated into a single parameter, basicity. Substitution of H by Me in 9-R-Fl^- ions causes no steric effect on reactivity, even toward *i*-PrBr, despite the fact that Me is attached directly to the donor site. Alkyl functions of the type RCH_2 or related functions such as RS, which protrude on one side only of the flat fluorenyl anion, cause only small rate retardations, relative to Me (at the same basicity). Alkyl groups such as *i*-Pr, *t*-Bu, *o*-MeC_6H_4, and $2,4,6\text{-}Me_3C_6H_2$ (Mes) which protrude on both sides of the fluorenyl ion cause sizable steric rate retardations. An equation is derived that allows a reactivity factor, *r*, to be calculated for 9-G-Fl^- ions reacting with $PhCH_2Cl$ in Me_2SO solution. The *r* values relative to a 9-MeFl^- ion of comparable basicity are as follows: CN, 0.45; CO_2Me, 0.45; Me, (0.0); *t*-$BuCH_2$, –0.10; PrS, –0.15; Et, –0.17; *i*-PrS, –0.18; *t*-BuS, –0.18; $PhSO_2$, –0.25; PhO, –0.49; MesS, –0.54; Ph, –0.58; Me_3Si, –1.2; *i*-Pr, –1.5; *o*-MeC_6H_4, –2.2; *t*-Bu, –2.6; Mes, –3.1. Comparison of *r* values with $S°$ steric parameters derived for 2-alkylpyridines[5c] shows some marked differences. These are due in part to the utilization of an electron pair in a p orbital by the carbanion as contrasted with an electron pair in an sp^2 orbital by the pyridine.

There have been many studies of steric effects in S_N2 reaction caused by increasing the size and branching in the alkyl halide but relatively few quantitative studies where steric effects in the nucleophile have been examined. The retardation of alkylation rates caused by *o*-alkyl groups in pyridines were among the first effects of this type to be observed, and these have received most subsequent attention.[1–5] In their pioneering studies of steric effects on equilibria and rates,[3] Brown and his students found that rates of reactions of 2-alkylpyridines with CH_3I in nitro-

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benzene were retarded by 2–3-fold for the changes H to Me, Me to Et, or Et to *i*-Pr. A much greater retardation, 306-fold, occurred from *i*-Pr to *t*-Bu. An abrupt increase in rate retardation such as this has come to be looked on as typical of a steric effect. The smaller alkyl groups are able to minimize steric effects in the transition state by suitable C–R rotations, but this is not possible for the *t*-Bu group.[3b] (A similar effect has been observed for changing R in RCH_2X electrophiles, where the average retarding effects are 30 from H to Me, 2–3 from Me to Et, 13 from Et to *i*-Pr, and 3000 from *i*-Pr to *t*-Bu.[6] In *t*-$BuCH_2X$ every approach of the nucleophile to the backside of the carbon atom holding the halogen atom has been blocked.) These rate changes do not correlate with 2-alkylpyridinium ion pK_a values in water (H, 5.17; Me, 5.97; Et, 5.97; *i*-Pr, 5.83; *t*-Bu, 5.76[3c]) or with heats of 2-alkylpyridine reactions with CH_3SO_3H.[3d] They do correlate, however, with heats of 2-alkylpyridine reactions with BF_3 in nitrobenzene,[3e] which provide a better model for the steric effects encountered in the methylation reaction.

Substitution of a second *o*-methyl group into 2-methylpyridine causes a much larger rate retardation in the reaction with CH_3I than does the first (11-fold vs. 2-fold).[3f] It was suggested that the first methyl group can bend out of the way of the electrophile, but in 2,6-dimethylpyridine this bending action is inhibited by a methyl–methyl interaction, causing the steric effect to increase from about 0.4 to 1.8 kcal/mol.

Additional insights into steric effects of 2-substituted pyridines, 2-GC_5H_4N and 2-RC_5H_4N, have been obtained from more recent quantitative studies.[4,5] Correlation with Taft E_s constants of rates of reaction with CH_3I for the 2-α-alkyl series (Me, Et, *i*-Pr, *t*-Bu) have been confirmed and extended to other nitrogen heterocycles, but deviations for the 2-β-alkyl series (CH_2R and CH_2Ph) have been reported and explained in terms of conformational effects.[5a] Deviations from a Brønsted plot of $\log(k_G/k_H)$ for rates of reactions of 3- and 4-GC_5H_4N with CH_3I in a variety of dipolar nonhydroxylic solvents vs. pK_a values for 3- and 4-$GC_5H_4NH^+$ ions in water have been observed for 2-substituted pyridine analogues. The extent of these deviations has been used to define a new set of steric constants ($S°$) for alkyl groups, aryl groups, CN, CO_2Me, etc.[5c] An attempt has also been made to use reactivities of 2-substituted pyridines toward CH_3I vs. $CH_3OSO_2CF_3$ to test the position of the S_N2 transition state along the reaction coordinate,[5b] but the results do not agree with those from later studies with 3- and 4-substituted pyridines.[7]

Small rate-retarding effects (1.5–2-fold) have been observed for *o*-Me substitution in reactions of phenoxide ions with CH_3OSO_3Na in water[8] and for the reactions of thiophenoxide ions with *n*-BuCl in Me_2SO,[9] but no systematic study of the effect of increasing alkyl size appears to have been made.

The relative reactivities of a few strongly basic carbanions have been determined by competiton studies. For example, in one study carbanions of the type $PhC(R)CN^-$ (Na^+ cation), where R = H, Me, $PhCH_2$, Et, *i*-Pr, and Ph, were allowed to compete in liquid NH_3 for a limited amount of CH_3I.[10] The rates relative to H were as follows: Me, 1.37; Et, 2.28; Bu, 2.22; *i*-Pr, 1.28; $PhCH_2$, 1.01; 3-pentyl, 0.26; Ph, 0.011. The conclusion was drawn that the steric effects of the alkyl groups are small and are usually overshadowed by polar effects. We now know, however, that $PhC(Me)CN^-$ is more basic than $PhC(H)CN^-$ in Me_2SO solution by 1.1 p*K* units,[11] which should cause over a 2-fold accelerating effect (assuming a Brønsted of about 0.3) instead of the 1.37-fold effect observed. On the other hand, Ph_2CCN^- is 4.4 pK units less basic than $PhCHCN^-$ in Me_2SO,[12] which should cause about a 20-fold rate retardation, compared to the 91-fold retardation observed. This analysis suggests, therefore, that both Me and Ph may be exerting steric effects, relative to H. In any event, it is clear that the effects of basicity must be taken into account if the size of steric effects in carbanion reactions is to be assessed. This can be accomplished with the aid of Brønsted correlations.

In an earlier study, we measured rates of reactions of 9-substituted fluorenyl carbanions (9-G-Fl^-) with $PhCH_2Cl$ in Me_2SO solution. The reactions gave excellent second-order kinetics and high yields of 9-benzylated fluorenes were obtained. Families of 9-G-Fl^- carbanions gave essentially parallel lines in Brønsted plots[13] for G = CO_2Me, $PhSO_2$, PhS, Ph, and Me. Basicities in each family were varied by introducing substituents into 2- and 2,7-positions of the fluorene ring or meta and para positions of a phenyl group in G. The data were accommodated quite well by eq 1.

$$\log(k/k_0) = \beta(\Delta pK_a - c) \qquad (1)$$

Equation 1 allows the reactivity (*k*) of any carbanion to be expressed relative to that of 9-CN-Fl^- (k_0) in terms of (a), β, the slope of the Brønsted line, (b) ΔpK_a, the acidity of the conjugate acid of the 9-G-Fl^- ion, relative to that of 9-CN-FlH, and (c) a parameter, *c*. The latter represented the horizontal distances between the parallel Brønsted lines, which were believed to measure the steric interactions in the S_N2 reaction. This idea has now been tested by making structural changes in the carbanions to increase or decrease steric effects in the S_N2 reactions with $PhCH_2Cl$.

Results and Discussion

The discussion that follows is divided into ten sections. First, we establish that the steric effects inhibited by 9-G-Fl^- ions in S_N2 reactions are small and that this is typical of large, flat, delocalized carbanions. Next, we show that 9-HFl^- and 9-$MeFl^-$ ions differ but little in reactivity and adopt the 9-$MeFl^-$ ion family line as a reference standard that has minimum steric demands. In the third section we use this reference line to define quantitative reactivity (*r*) values for alkyl groups in 9-R-Fl^- ions. The *r* values reveal that alkyl groups such as CH_2R (R = Me, *t*-Bu, Ph), where R protrudes from only one side of the fluorenyl ion, exhibit only slight steric effects compared to *i*-Pr and *t*-Bu groups, where the methyl groups protrude on both sides. In subsequent sections we show by comparisons of *r* values of alkyl groups with those of groups containing heteroatoms that electronic as well as steric effects are operative in the latter. Finally, a comparison of *r* values with corresponding literature $S°$ values, which have been derived

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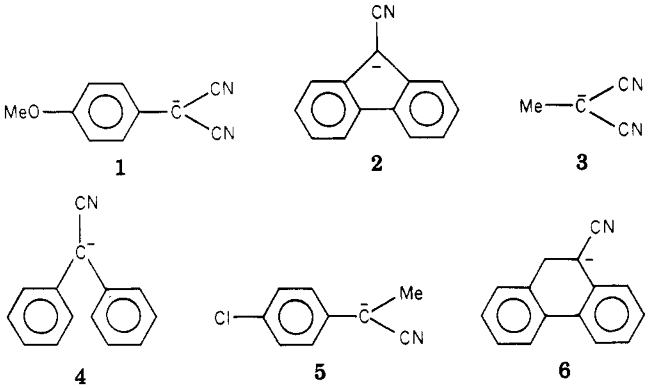
Chart I



for reactivities of 2-substituted pyridines, reveals some similarities and some striking differences.

Effect on Carbanion Nucleophilicity of Changing the Shape, Size, and Charge Distribution in S_N2 Reactions with $PhCH_2Cl$. Nucleophiles (Nu^-) commonly used in quantitative studies of S_N2 reactions cover a basicity range of about 16 pK_a units. For example, representative pK_a values of NuH in Me_2SO solution are as follows: Cl^-, 2.1; pyridine, 3.4; N_3^-, 7.7; PhS^-, 10.3; AcO^-, 12; CN^-, 12.9; PhO^-, 18.0. These nucleophiles differ markedly in S_N2 reactivites, not only because of the large differences in their basicities but also because of differences in the nature of their donor atoms. Nucleophiles utilizing second-row (or higher) donor atoms such as Cl^- or PhS^- have been shown to react at rates several powers of ten faster than do anions of comparable basicity utilizing first-row donor atoms.[14] Steric hindrance in the approach to the electrophile is a third factor expected to influence nucleophilic reactivity.[15] In a recent paper we have shown that 9-$MeFl^-$ ions appear to be remarkably insensitive to structural changes in the electrophile that are expected to increase steric hindrance effects. Thus, the relative S_N2 rate decreases for 9-$MeFl^-$ ions reacting with alkyl bromides in the series n-BuBr, i-BuBr, i-PrBr, and c-$C_6H_{11}Br$ in Me_2SO solution were found to be as small or smaller than those for I^- or N_3^- ions.[16] In order to see whether or not this behavior was typical of large, flat, delocalized carbanions, we compared the rates of S_N2 reactions with $PhCH_2Cl$ of the α-cyano carbanions 1–6 (Chart I), which vary in basicity by over 16 pK units, with those of the 9-$MeFl^-$ and 9-CO_2MeFl^- ion families. The CN function was chosen because its effective size was expected to be close to that of Me or CO_2Me since 9-CN-Fl^- ion fits (fortuitiously) on the 9-CO_2MeFl^- ion family line. The 9-$MeFl^-$ and 9-CO_2MeFl^- ion family lines give parallel Brønsted plots that are only slightly displaced from one another.[13]

The cylindrical cyano function combines a minimum of steric demands with a near-maximum polar effect for an uncharged substituent ($\sigma_I = 0.56$). The delocalizing ability of CN is substantial ($\sigma_{R^-} = 0.33$) but smaller than the polar factor, leading to a σ_I/σ_{R^-} ratio of 1.7.[17] This ratio is similar in size to that for $PhSO_2$ but large compared to that for $COCH_3$ or CO_2CH_3 (0.60 and 0.40, respectively). As a consequence, the charge density on α-cyano carbanions is high, and the charge is therefore unusually susceptible to delocalizing effects. This accounts for the wide range in the basicities of 1–6. The most weakly basic of these carbanions, 1, has the negative charge delocalized into a benzene ring ($\rho = 4.1$ for $ArCH(CN)_2$ acidities[18]) and the two cyano groups. Replacement of the p-$MeOC_6H_4$ ring in 1 by a Me group to form 3 increases the basicity by 6.8 pK units (Table I). Delocalization of the negative charge in 5 is extensive, as shown by the Hammett ρ of 5.7 for acidities of $ArCH_2CN$ in Me_2SO,[18] and must also be extensive in 4 and 6. Delocalization is still greater in 2 ($\rho \simeq 7.5$ for 2-substituted fluorene acidities[19]). When these

Table I. Rates of Reactions of α-Cyano Carbanions with $PhCH_2Cl$ in Me_2SO and Equilibrium Acidities of Their Conjugate Acids in Me_2SO at 25 °C

carbon acid	pK_a[a]	$10k$,[f] M^{-1} s^{-1}	k_{rel}
p-$MeOC_6H_4CH(CN)_2$ (1)	5.68[b]	0.0174	(1.00)
9-cyanofluorene (2)	8.3	0.0619	3.56
$MeCH(CN)_2$ (3)	12.50	1.52	87.4
Ph_2CHCN (4)	17.5[c]	11.3	649.0
p-$ClC_6H_4CH(Me)CN$ (5)	21.73[d]	1240.0	7130.0
9-cyano-9,10-dihydrophenanthrene (6)	21.92[e]	1600.0	92000.0

[a] Reproducible to ±0.1 pK_a unit or less. [b] Branca, J. C. Ph.D. Dissertation, Northwestern University, 1979. [c] Reference 12. [d] Measured by A. H. Clemens. [e] Measured by R. D. Press. [f] Reproducible to ±5% or less.

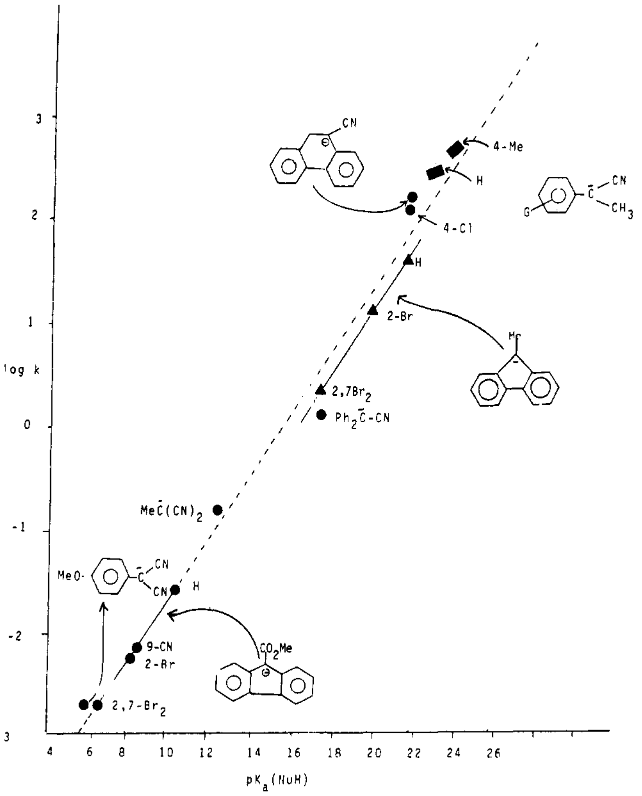


Figure 1. Brønsted lines for the 9-methoxycarbonyl and 9-methylfluorenyl carbanion families (● for 9-CO_2MeFl^- ions and ▲ for 9-$MeFl^-$ ions) reacting with $PhCH_2Cl$ in Me_2SO solution, with points (●) for α-cyano carbanions 1–6 added. The ■ points for p-$GC_6H_4C(CH_3)CN^-$ for G = H and Me are based on rates with n-BuCl, assuming that the rate ratio for $PhCH_2Cl/n$-BuCl observed for G = Cl will hold.

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[15] A fourth factor is solvation, but the Me_2SO solvent used in our work does not hydrogen bond to anions, so solvent effects are limited to differences in electrostatic solvation, which appear to be incorporated into basicity differences.

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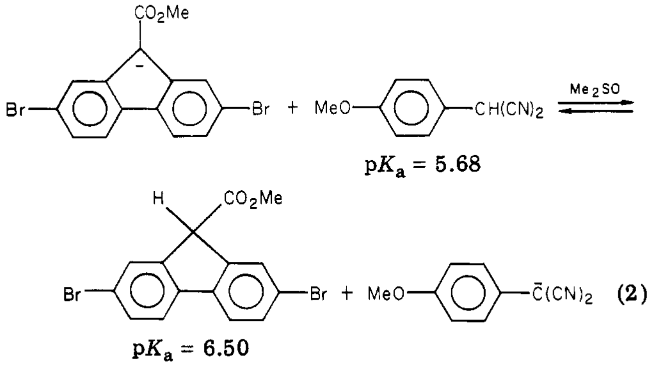
carbanions react with $PhCH_2Cl$, the free electron pair must become at least partially localized in the transition state as the bond to carbon is formed. Rates of reactions of **1**–**6** with $PhCH_2Cl$ in Me_2SO are summarized in Table I.

Figure 1 shows a Brønsted plot for the 9-CO_2MeFl^- family, which covers the pK_a range 6.5–10.35. A dashed extension of the line is shown, and the 9-Me-Fl^- ion family line,[13] which covers the pK_a range 17.7–22.3, has been added for reference. The points for the α-cyano carbanions **1**–**6** have been added to the plot. Examination shows that the point for 9-CN-Fl^- (**2**) fits the 9-CO_2MeFl^- ion line and that the points for α-cyano carbanions **1**, **3**, **5**, and **6** are slightly above the line, while that for Ph_2CCN^- (**4**) is somewhat below the line. It would appear that the size or shape of the α-cyano carbanion is unimportant in determining S_N2 reactivities. Scalar molecular models indicate that the two benzene rings in Ph_2CCN^- cannot be coplanar, which may account for the somewhat lower reactivity of this anion. One might have expected 9-G-Fl^- carbanions to exhibit a lower S_N2 reactivity because of loss of aromaticity of the cyclopentadienyl moiety during bond formation,[20] but this does not happen.

Our conclusion is that the electronic and solvation effects that are controlling relative carbanion basicities are controlling relative carbanion reactivities in exactly the same way. Relative carbanion basicities are calculated from ΔpK_a values. For example, for eq 2, ΔpK_a = 6.5 − 5.7 = 0.8. The assumption is that the position of the equilibrium is determined primarily by the relative thermodynamic stabilities of the (solvated) carbanions, the relative energies of the parent acids playing only a minor role. The fact that pK_a values extending over a range of 16 units can be used to represent carbanion reactivites (when steric effects are absent) shows that this is indeed a very good assumption.



(2)

Table II. Rates of Reactions of 9-G-Fl^- and 1,2-Benzofluorenyl Carbanions with Alkyl Halides in Me_2SO Solution at 25 °C

9-G-Fl^-	pK_a[a]	second-order rate constants[d]		
		$PhCH_2Cl$	i-PrBr	n-BuCl
$MeFl^-$	22.35	49.4	1.80[c]	3.20×10^{-2}
2-Br-$MeFl^-$	20.05	8.87	0.20[c]	
2,7-Br_2-$MeFl^-$	17.7	1.65	0.031[c]	
HFl^-	22.6		1.09	2.8×10^{-2}
2-Br-HFl^-	20.0		0.18	
2,7-Br_2-HFl^-	17.9		2.9×10^{-2}	
1,2-benzo-Fl^-	19.7[b]		0.130	

[a] pK_a of the conjugate acid in Me_2SO (±0.05). [b] Measured by G. E. Drucker. [c] Mrozack, S. R. Ph.D. Dissertation, Northwestern University, 1982. [d] In $M^{-1}\ s^{-1}$; average of three runs reproducible to ±5% or less.

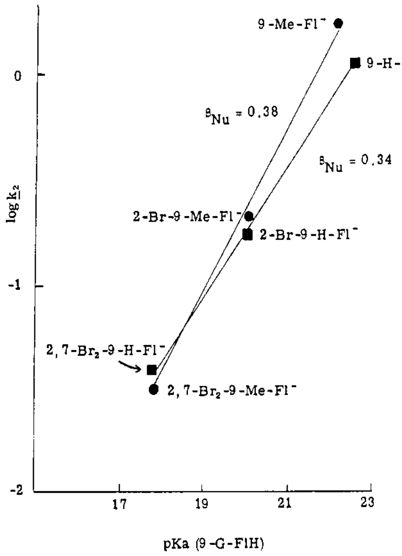


Figure 2. Brønsted lines for fluorenyl and 9-methylfluorenyl carbanion families (■ for HFl^- ions and ● for 9-$MeFl^-$ ions) reacting with $PhCH_2Cl$ in Me_2SO solution.

Reactions of Fluorenyl, 9-Methylfluorenyl, and 1,2-Benzofluorenyl Carbanions with Alkyl Halides. In the following sections we will be examining how steric effects of the groups G in 9-G-fluorenyl anions affect S_N2 reactivity. Before doing so, however, we need to adopt a 9-G-Fl^- family with minimal steric effects as a standard for comparison. We thought initially that the 9-CO_2MeFl^- ion family was the proper choice because its line lay slightly above the 9-$MeFl^-$ ion family line (Figure 1) and other 9-G-Fl^- family lines.[13] To test this hypothesis, we measured the reactivity of the 9-HFl^- family, which should have the least steric demands of all. We anticipated, however, that rate measurements of the fluorenyl ion, HFl^-, with $PhCH_2Cl$ would be complicated by side reactions. The product from this reaction is 9-$PhCH_2FlH$, which is 1.6 pK_a units more acidic than HFlH. (ΔpK_a is statistically corrected for the number of acidic hydrogen atoms.) As a consequence the colored 9-$PhCH_2Fl^-$ ion will soon appear in solution. This ion will not only interfere with measurement of the decay of the HFl^- ion absorbance but will also react with the $PhCH_2Cl$ substrate. To avoid this problem, we turned to i-PrBr as a substrate. Here the product is 9-i-PrFlH, which is 0.3 pK_a unit less acidic than HFlH; also, the 9-i-$PrFl^-$ ion is expected to react much more slowly with i-PrBr than does the HFl^- ion. As a further precaution the rates for the HFl^- ion family reacting with i-PrBr and also with n-BuCl (used as a check) were calculated from absorbance changes occurring during the first 10–20% of the reaction, before much 9-R-Fl^- ion could be formed.

Experiment showed that the HFl^- ion, despite a 0.3 pK unit greater basicity, was 1.1 times less reactive than 9-$MeFl^-$ toward n-BuCl and was 1.6 times less reactive toward i-PrBr (Table II). These small differences are not significant, however, because the relative reactivities depend on the basicities chosen for comparison. For example, the Brønsted β is slightly larger for the reaction of the 9-$MeFl^-$ ion family with i-PrBr (0.38) than for the reaction with the HFl^- ion family (0.34). As a result, whereas the 9-$MeFl^-$ ion is more reactive toward i-PrBr than the HFl^- ion, its 2-Br derivative is of about the same reactivity, and its 2,7-Br_2 derivative is less reactive than the 2,7-Br_2 derivative of the HFl^- ion (Figure 2).

The near equality of the rates of 9-$MeFl^-$ and HFl^- ions of equal basicity in S_N2 reactions with i-PrBr and n-BuCl

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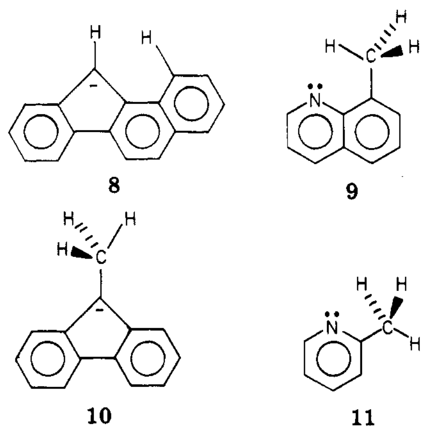
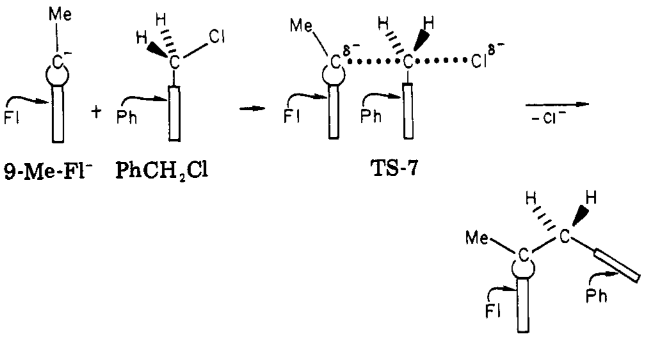
[20] The resonance energy of the cyclopentadienyl moiety in the fluorene ring has been estimated from acidity measurements to be about 14–15 kcal/mol. see: Bordwell, F. G.; Drucker, G. E.; Fried, H. E. *J. Org. Chem.* 1981, *46*, 632–635.

Chart II



shows that these reactions are remarkably insensitive to steric effects produced by substitution near the reaction site in the nucleophile, since Me is known to have a much larger steric effect than H. For example, E_s values derived from acid-catalyzed ester hydrolyses for H, Me, and Et are 1.24, 0, and −0.07, respectively.[21] Furthermore, recent calculations estimate that replacement of H in a CH_3X substrate by Me in S_N2 reactions introduces 6.2 kcal/mol of strain energy in the transition state,[22] and the average rate retardation produced by this substitution is 30-fold.[6] The absence of a Me vs. H effect in 9-R-Fl⁻ ions must mean that in the transition state the Me group is bent away from the substrate (TS-7). The reaction of the 9-MeFl⁻ ion with $PhCH_2Cl$ can be pictured as one where the fluorenyl and phenyl rings come face to face, perhaps forming a complex by overlap of the π systems, as is believed to occur in some charge-transfer complexes.[23] As partial bonding between the carbanion and electrophilic centers occurs, the C-9-Me in the 9-MeFl⁻ ion and the methylene hydrogen atoms in $PhCH_2Cl$ bend away from one another to remove steric repulsions, giving TS-7. (Rectangles are used to represent fluorenyl or phenyl rings.)



9-Me-Fl⁻ $PhCH_2Cl$ TS-7

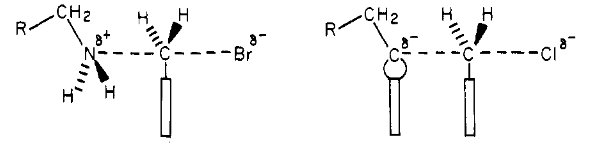
9-Me-9-$PhCH_2$Fl

Substitution of an HC= moiety at C-1 in the HFl⁻ ion also fails to produce a steric effect since the rate of reaction of the 1,2-benzo-HFl⁻ ion (8, Chart II) with *i*-PrBr was such as to cause this point to fit the line for the HFl⁻ family in Figure 2.

The absence of a steric effect in 8 contrasts with the 1000-fold rate retardation in 8-methylquinoline (9), relative to quinoline.[4a] Similarly, the absence of a steric effect in the 9-MeFl⁻ ion (10) contrasts with the steric effect caused by Me in 2-methylpyridine (11) where the methyl group is one atom further removed from the donor center. It seems likely, therefore, that the nitrogen nucleophiles utilize lone-pair electrons in the S_N2 reaction, as suggested previously,[5] rather than the p electrons in the pyridine ring, whereas carbanions must utilize p electrons. Steric effects should be less in the latter instance. This interpretation is supported by Brown's observation that steric effects for S_N2 reactions of 2-alkylpyridines correlate with their heats of reaction with BF_3.[3e]

Since the reactivity of a fluorenyl ion appears to be about equal to that of a 9-MeFl⁻ ion of the same basicity and about 2.5 times *less* than that of a 9-CO_2MeFl⁻ ion of the same basicity, these relative rates cannot be controlled by steric factors. Instead, the greater reactivity of 9-CO_2MeFl⁻ and 9-CN-Fl⁻ ions must be due to an electronic factor, as will be brought out later. Henceforth we plan to use an extension of the 9-MeFl⁻ ion family line as a reference line for reactions wherein both steric and electronic effects are minimal, rather than the 9-CO_2MeFl⁻ ion family line.

Steric Effects of Alkyl Groups in the Reactions of 9-Alkylfluorenyl Ions with Benzyl Chloride. In the previous two sections we have seen that electronic effects of α-cyano carbanions on basicities lead to corresponding effects on S_N2 reactivities toward $PhCH_2Cl$ and that neither a methyl group at C-9 nor a HC= group at C-1 in a fluorenyl ion produces an observable steric effect in S_N2 reactions with *i*-PrBr or *n*-BuCl. It was of interest in the latter connection to determine the size of steric effects caused by alkyl groups on S_N2 reactivities in 9-R-Fl⁻ ions as the size of R is changed further along the series H, Me, Et, $PhCH_2$, *i*-Pr, *t*-Bu, and Ph. The steric effects for alkyl groups as assessed from rates of acid-catalyzed ester hydrolyses (Taft E_s constants) are as follows: H, 1.24; Me, (0.0); Et, −0.07; $PhCH_2$, −0.38; *i*-Pr, −0.47; *t*-Bu, −1.54; *t*-$BuCH_2$, −1.74.[21] Taft showed that the relative S_N2 reactivities of 2-alkylpyridines toward CH_3I in nitrobenzene could be correlated with E_s values, and this has been amply supported by recent work.[5] Recently, relative S_N2 reactivities of primary amines, RNH_2, with $CH_2{=}CHCH_2Br$ in benzene have been correlated with RCH_2 E_s values.[22] The transition state for the latter reaction (e.g., TS-12) can be considered to resemble that with RCH_2Fl^- ions (e.g., TS-13). (Rectangles are used to represent fluorenyl or phenyl rings or C=C bonds.)



($CH_2{=}CHCH_2Br$) TS-12 (9-RCH_2Fl⁻) ($PhCH_2Cl$) TS-13

Analysis of the data for the rates of reactions of $PhCH_2Cl$ with 9-R-Fl⁻ ions of the same basicity can be accomplished with the aid of Brønsted plots. In view of the earlier observation of parallel Brønsted lines for reactions of 9-G-Fl⁻ ions with $PhCH_2Cl$ when G is CO_2Me, PhS, or Me,[13] it seems safe to assume that the lines will also be parallel for Brønsted plots with 9-R-Fl⁻ ions. We can then use eq 3, a modified version of eq 1, to compare

$$r = \beta(\Delta pK_a) - \log(k^{Me}/k^{G}) \qquad (3)$$

S_N2 reactivities of 9-R-Fl⁻ ions, relative to Me. A graphical representation is given in Figure 3.

The vertical displacements downward of the points from the 9-PhS-Fl⁻ ion and 9-MeFl⁻ ion family lines in Figure

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[21] (a) Taft, R. W. "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13. (b) MacPhee, J. A.; Panaye, A.; Dubois, J.-E. *Tetrahedron* **1978**, *34*, 3553–3562.

[22] DeTar, D. F. *J. Org. Chem.* **1980**, *45*, 5174–5176.

[23] Mulliken, R. S.; Person, W. B. "Molecular Complexes, a Lecture and Reprint Volume"; Wiley-Interscience: New York, 1969; Chapter 5.

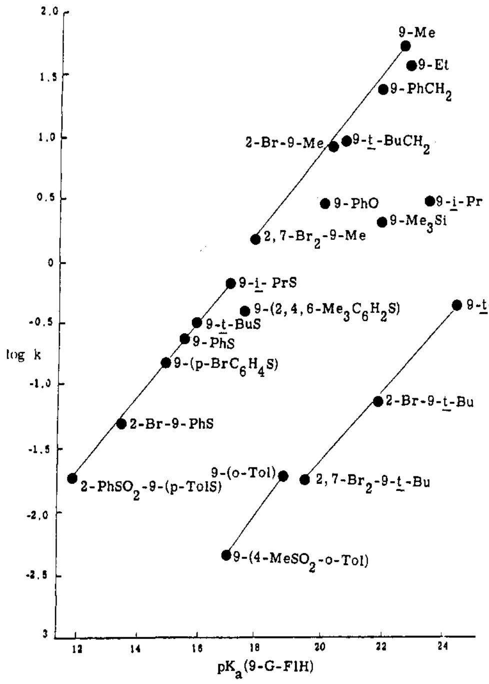


Figure 3. Logarithm of second-order rate constants (k) for reactions of 9-alkyl-, 9-(alkylthio)-, 9-aryl-, and 9-(arylthio)-fluorenyl ions reacting with $PhCH_2Cl$ in Me_2SO plotted against the pK_a constants for their conjugate acids. The lines for the 9-MeFl$^-$ ion and 9-PhS-Fl$^-$ ion families[13] are used as references.

Table III. Comparison of Steric Effects of Hydrocarbon Functions on Equilibria and Rates for Reactions of 9-R-Fl$^-$ Carbanions with $PhCH_2Cl$ in Me_2SO Solution at 25 °C

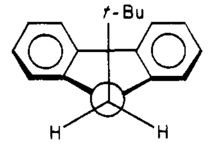
R	pK_a(9-R-FlH)^a	k^b	r^d
Me	22.34	49.4	(0.0)
Et	22.62	40.5	−0.17
$PhCH_2$	21.35	19.5	−0.10
i-Pr	23.18	2.96	−1.5
t-Bu	24.35	0.471	−2.6
t-$BuCH_2$	20.33	9.47	−0.11
C_6H_5	17.92	0.610	−0.58
o-tolyl	18.78	0.0201	−2.2
2-Me-4-$MeSO_2C_6H_3$	16.95	0.00452	−2.3
Mes	18.55	0.00244^c	−3.1

^{a} Reference 24. ^{b} In M^{-1} s^{-1}; average of three runs reproducible to ±5%. ^{c} Calculated from the rate with $PhCH_2Br$ (k = 0.756 M^{-1} s^{-1}) by dividing by 310, the k^{Br}/k^{Cl} value for 9-PhFl$^-$ reacting with $PhCH_2X$.[13] ^{d} Calculated from eq 3.

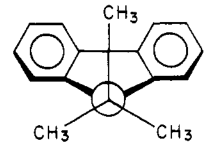
3 are represented in eq 3 by r, the relative reactivities at equal basicities of 9-G-Fl$^-$ ions with $PhCH_2Cl$ in Me_2SO solution. When G is an alkyl group, r represents the steric retardation relative to methyl, assuming that electronic effects are absent or constant. The difference in basicities is given by ΔpK_a = [pK_a(9-MeFlH) − pK_a(9-G-FlH)], a term allowing comparison of reactivities at equal basicities. The size of β, the slope of the line, provides a measure of the sensitivity of the reactivities to changes in basicity. The size of β is known to be substrate dependent.[13] For reactions of the 9-MeFl$^-$ ion family, β increases from 0.31 for $PhCH_2Cl$ to 0.38 for *i*-PrBr to 0.42 for *c*-$C_6H_{11}Br$.[16] The increase in β values suggests that the sensitivity of the reaction to basicity may increase with increasing steric demands in the substrate.

For alkyl groups of the type RCH_2, r values show that steric effects are small and nearly constant: HCH_2, (0.0); $MeCH_2$, −0.17; $PhCH_2$, −0.10; *t*-$BuCH_2$, −0.11 (Table III). The small size of these steric effects is consistent with the absence of a steric effect between H and Me and is understandable since R moieties in the 9-RCH_2Fl^- ions protrude from only one side of the flat fluorenyl ion and do not inhibit approach of the electrophile from the other side (TS-13). The near equality of the steric effect in 9-R-Fl$^-$ ions when R is ethyl or neopentyl is striking. The rate of reaction of $PhCH_2Cl$ with the 9-*t*-$BuCH_2Fl^-$ ion is 5.2 times slower than that with the 9-MeFl$^-$ ion, whereas that with the 9-EtFl$^-$ ion is only 1.2 times slower (Table III). Most of the rate-retarding effect of the *t*-$BuCH_2$ group is caused, however, by a 2 pK unit lower basicity. On the other hand, rate retardation for the 9-EtFl$^-$ ion occurs despite a 0.28 pK unit increase in basicity. When the rate effects are calculated at the same basicity, the steric effect of *t*-$BuCH_2$ appears to be slightly smaller than that of Et (r = −0.11 and −0.17, respectively).

In contrast to 9-RCH_2Fl^- ions, 9-*i*-PrFl$^-$ and 9-*t*-BuFl$^-$ ion reactivities are strongly retarded (16.7- and 105-fold, respectively, relative to 9-MeFl$^-$). Whereas the *t*-Bu group in the 9-*t*-$BuCH_2Fl^-$ ion fits snugly over one side of the carbanion center (see Newman projection 14), thus allowing its methyl groups to internally solvate that side of the carbanion,[24] the methyl groups in the 9-*t*-BuFl$^-$ ion protrude from both sides of the fluorenyl ion, thus blocking approach from either side (15). (In 14 and 15 the lobes of the carbanion p orbital, which extend above and below the plane of the fluorene ring, have been omitted.)



14 (9-*t*-$BuCH_2Fl^-$)



15 (9-*t*-BuFl$^-$)

Correlation of the Acidities of 9-(Arylthio)- and 9-(Alkylthio)fluorenes with the Reactivities of their Conjugate Bases with $PhCH_2Cl$. In a recent paper we showed that 9-RCH_2FlH and 9-RSFlH compounds exhibit a remarkably similar and unexpected equilibrium acidity pattern as R was changed along the series Me, Et, *i*-Pr, and *t*-Bu.[24] In each instance the acidities increased progressively along the series, which is the *reverse* of what happens when R is attached directly to the fluorene ring. The unexpected acidity increases were explained in terms of increases in the stabilities of the corresponding carbanions. In conformations like 14, the R groups are held close to one side of the carbanion center. The same is true for R groups in 9-RS-Fl$^-$ ions. These R groups exclude solvent from this side of the ion but provide stabilization through an intramolecular polarizability effect that increases in magnitude with increasing alkyl size. In the preceding section we saw that the unusual acidity pattern for 9-alkylfluorenes, *t*-$BuCH_2$ > Me > Et ≫ *i*-Pr > *t*-Bu, was mimicked by their reactivities toward $PhCH_2Cl$. Now we find by examination of Figure 3 that this is true also for 9-(arylthio)- and 9-(alkylthio)fluorenes. The 9-ArS-FlH family, which includes members where acidities have been changed by introducing remote substituents into either the Ar or fluorene rings, have acidities in the 12–15.4 pK_a range, about 6 pK_a units lower than the range for the 9-MeFlH family. The lower acidity of this family is mimicked by a corresponding lower reactivity of their conjugate bases toward $PhCH_2Cl$. Despite the large differences in acidities of the two families and in the basicities of their conjugate bases, the two Brønsted lines are parallel and displaced from one another by only about 0.2 log unit.

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(24) Bordwell, F. G.; Drucker, G. E.; McCollum, G. J. *J. Org. Chem.* **1982**, *47*, 2504–2510.

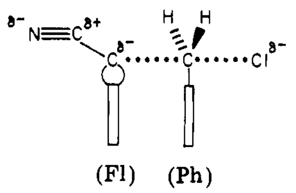
Table IV. Steric and Electronic Effects of Functions Containing Heteroatoms in 9-G-Fl⁻ Carbanions

G	pK_a	k[a]	r[b]	G	pK_a	k[a]	r[b]
CN	8.3	0.00619	0.45	*i*-PrS	16.9	0.683	−0.18
CO_2Me	10.35	0.0268	0.45	*t*-BuS	15.9	0.326	−0.18
Me	22.34	49.4	(0.0)	$PhSO_2$	11.55	0.0130	−0.25
PhS	15.4	0.248	−0.15	PhO	19.9	2.80	−0.49
MesS	17.4	0.417	−0.54	Me_3Si	21.7	~2[c]	−1.2

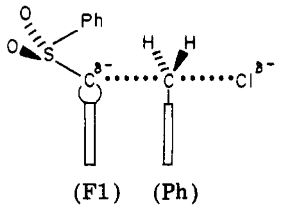
[a] In $M^{-1}\ s^{-1}$; average of three runs reproducible to ±5% at 25 °C, unless otherwise noted. [b] Reactions of 9-G-Fl⁻ with $PhCH_2Cl$ in Me_2SO at 25 °C (calculated from eq 3). [c] ±15%.

Once again we see that acidity differences can be explained in terms of relative carbanion thermodynamic stabilities and that these cause corresponding differences in carbanion reactivities. This holds also for 9-*t*-BuS-Fl⁻ ion. The lesser reactivity of 9-*t*-BuS-Fl⁻ ion is not caused by a steric effect but by its lower basicity; both the 9-*t*-BuS-Fl⁻ and 9-*i*-PrS-Fl⁻ ion points fit on the 9-ArS-Fl⁻ ion family line (Figure 3). Furthermore, extension of this line would include the points for the 9-*t*-$BuCH_2Fl^-$, 9-$PhCH_2Fl^-$, and 9-Et-Fl⁻ ions. In other words, the *r* values for most 9-ArS-Fl⁻ ion points are about −0.2 (Table IV). The lone exception is the point for 9-MesS-Fl⁻ where *r* is decreased to −0.54 for steric reasons.

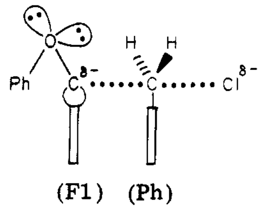
Electronic and Steric Effects of Functions Containing Heteroatoms on Fluorene Acidities and Fluorenyl Ion Reactivities. 9-Substituted fluorenes vary in acidities over 16 pK_a units (from 8.3 for 9-CN-FlH to 24.3 for 9-*t*-BuFlH) for electronic and steric reasons. The large acidifying effect of the CN group is primarily electrostatic in nature, the resonance factor being secondary ($\sigma_I/\sigma_{R^-} = 1.7$).[17] The reverse is true for the slightly smaller effect of CO_2Me (pK_a = 10.35; $\sigma_I/\sigma_{R^-} = 0.6$). Despite the differences in origin of these electronic effects, the point for the 9-CN-Fl⁻ ion fits on the 9-CO_2MeFl⁻ ion family line (Figure 1). The *r* values for CN and CO_2Me are each 0.45 unit more positive than that of Me (Table IV). This cannot be a steric effect since we have seen that there is no steric difference between the 9-MeFl⁻ and HFl⁻ ions, and the CN and CO_2Me groups certainly have larger steric demands than hydrogen. In going from the initial state to the transition state, the highly delocalized negative charge in the 9-G-Fl⁻ ion must become more localized at C-9 in order to effect partial bonding with the electrophile. The transition state will therefore be stabilized by electron-withdrawing groups at C-9, e.g., 9-CO_2Me or 9-CN (TS-18). (An opposite effect is observed for a 2-CN function in pyridine nucleophiles where a positive charge develops on the donor atom in the transition state.[4]) The $PhSO_2$ group has an electronic effect very similar to that of CN,[17] but its steric demands are much larger, since it is tetrahedral whereas the CN group is linear.[25] The small negative *r* value for $PhSO_2$ indicates that the steric effects of the Ph ring (or the protruding oxygen atoms) in TS-19 overshadow the electronic effect. The PhO function causes a destabilizing effect in the S_N2 reaction (*r* = −0.5) presumably because of increased interaction of the localized charge with the oxygen lone pairs (TS-20).



TS-18



TS-19



TS-20

The longer C–S and C–Si bonds in 9-(mesitylthio)- and 9-(trimethylsilyl)fluorenyl ions, 9-MesS-Fl⁻ and 9-Me_3Si-Fl⁻, account for the modest steric effects indicated by their *r* values (−0.6 and −1.2, respectively) as compared to the larger steric effects indicated for their carbon analogues (Table III).

Steric Effects for Reactions of 9-*t*-BuFl⁻ Ions, β Values, and Leaving Group Effects. The rates of reactions of the 9-*t*-BuFl⁻ ion and its 2-Br and 2,7-Br_2 derivatives with $PhCH_2Cl$, $PhCH_2Br$, and *m*-$CF_3C_6H_4CH_2Cl$ are summarized in Table V, along with k^{Br}/k^{Cl} leaving group effects and β values. The β value of 0.29 for the reaction with $PhCH_2Cl$ is slightly lower than that for the reaction with the 9-MeFl⁻ ion family (0.31). A further decrease in β to 0.21 was observed for the reaction of the 9-*t*-BuFl⁻ ion family with $PhCH_2Br$. On the other hand, increased steric hindrance in the substrate in the series *n*-BuBr, *i*-PrBr, *c*-$C_6H_{11}Br$ appears to cause small increases in β. The values are 0.365, 0.38, and 0.42, respectively.[16] Also, β increases from 0.29 to 0.34 for reactions of the 9-*t*-BuFl⁻ ion family when a *m*-CF_3 group is substituted into $PhCH_2Cl$ (Table V). This electronic effect on β is similar to that observed for reactions of other 9-G-Fl⁻ ions with substituted benzyl chlorides.[13] We will defer comment as to possible causes for these changes in β except to note the consequences of these changes on Br/Cl leaving group ratios.

The greater sensitivity of the reaction of $PhCH_2Cl$ than $PhCH_2Br$ with 9-*t*-BuFl⁻ ions (β = 0.29 and 0.21, respectively) means that the $PhCH_2Cl$ rates will decrease much more rapidly than the $PhCH_2Br$ rates as the basicity of the nucleophile is lowered. As a consequence, the Br/Cl rate ratio increases from 357 to 670 as the basicity of the 9-*t*-BuFl⁻ ion is decreased by 5 p*K* units (Table V). A similar increase was observed earlier for reactions of $PhCH_2Br$ and $PhCH_2Cl$ with 9-ArFl⁻ ions where the Br/Cl rate ratio increased from 310 to 465 when the basicity of the 9-ArFl⁻ ion was decreased by 2.7 p*K* units.[13] Traditionally the size of leaving group rate ratios in S_N2 reactions has been taken as a measure of the extent of C–X bond breaking in the transition state. The present results indicate, however, that leaving group effects will vary with the basicity of the nucleophile if the two substrates exhibit different sensitivities to basicity changes. For example, the increase in Br/Cl leaving group effect from 357 to 670 with a decrease in basicity of the 9-*t*-BuFl⁻ ion by 5 p*K* units is unlikely to be associated with a change in the extent of C–X bond breaking.

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(25) In the accompanying paper we show from the acidities of 9-substituted xanthenes and the reactivities of their conjugated bases that steric demands increase in the order CN < CO_2Me < Ar < SO_2Ph.

Table V. Rates of Reactions of Substituted 9-*t*-BuFl$^-$ Carbanions with $C_6H_5CH_2Cl$, *m*-$CF_3C_6H_4CH_2Cl$, and $C_6H_5CH_2Br$ in Me_2SO Solution at 25 °C

9-*t*-BuFl$^-$	pK_a[a]	10^2k ($ArCH_2X$)[b]	k^{Br}/k^{Cl}	β
t-BuFl$^-$	24.37	47.1 ($PhCH_2Cl$)		
2-Br-*t*-BuFl$^-$	21.7	7.7 ($PhCH_2Cl$)		
2,7-Br_2-*t*-BuFl$^-$	19.4	1.7 ($PhCH_2Cl$)		0.29
t-BuFl$^-$		12100 ($PhCH_2Br$)	357	
2-Br-*t*-BuFl$^-$		3120 ($PhCH_2Br$)	401	
2,7-Br_2-*t*-BuFl$^-$		1160 ($PhCH_2Br$)	670	0.21
t-BuFl$^-$		479 (*m*-$CF_3C_6H_4CH_2Cl$)		
2-Br-*t*-BuFl$^-$		64.8 (*m*-$CF_3C_6H_4CH_2Cl$)		0.34
2,7-Br_2-*t*-BuFl$^-$		9.88 (*m*-$CF_3C_6H_4CH_2Cl$)		

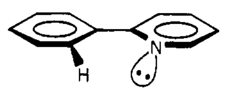
[a] pK_a of the conjugate acid in Me_2SO (±0.05). [b] In M^{-1} s^{-1}; average of three runs reproducible to ±5% or less.

Steric Effects for 9-Arylfluorenyl Ions. The *r* value of −0.58 for Ph (Table III) shows that the rate with the 9-PhFl$^-$ ions is retarded appreciably, relative to the 9-MeFl$^-$ ion. This is suggestive of a steric factor, which is consistent with evidence for twisting of the Ar ring in 9-arylfluorenyl ions.[26] One would expect an *o*-Me group to increase the angle of twist since interference with the peri hydrogen atoms is increased substantially. Experiment showed that the rate for the 9-*o*-$CH_3C_6H_4Fl^-$ ion is retarded by 30-fold, relative to that of the 9-PhFl$^-$ ion, despite a 0.86 p*K* unit increase in basicity.[27] The result is an *r* value of −2.2, indicating strong steric retardation. A further 8.2-fold rate decrease was observed for the 9-MesFl$^-$ ion. Here the second *o*-Me group leads to a decrease in basicity of only 0.17 p*K* unit, despite the presence of a *p*-Me group, which should have increased the basicity by 0.4 unit.[27] The *r* value is now increased to −3.1, larger than that for the 9-*t*-BuFl$^-$ ion (−2.6).

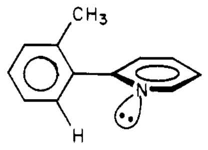
Comparison of *r* Values with *S*° Values. As pointed out in the introduction, steric parameters (*S*°) purported to be free of electronic effects have recently been derived for 33 2-substituted pyridines on the basis of deviations from a Brønsted plot for 3- and 4-substituted pyridines.[5c] Since both *r* and *S*° measure, at least in part, the effect of steric hindrance in the nucleophile on relative reactivities in S_N2 reactions carried out in dipolar nonhydroxylic solvents, one might have expected to find a correlation between the two. Comparison shows, however, that the differences are more striking than the similarities. The use of pK_a values in water in deriving *S*° values is a possible source of some of the differences. It is known that rates of N-methylation of 3-substituted pyridines in Me_2SO give good Brønsted correlations with pK_a values in water,[4] suggesting that at least remote electronic effects can be correlated reasonably well when different solvents are used for log *k* and pK_a. For 2-substituted pyridines, however, differences in steric hindrance to solvation are likely to be greater in water than in dipolar nonhydroxylic solvents. Two other factors also contribute to the differences: (a) 2-substituted pyridines use the lone electron pair on nitrogen, which is in the plane of the ring, to bond to the electrophile in the transition state whereas 9-G-Fl$^-$ ions use an electron pair in a p orbital perpendicular to the ring; (b) in the pyridines the substituent is bonded to a carbon atom adjacent to the reaction site, whereas in 9-G-Fl$^-$ it is bonded directly to the reaction site. The latter differences together with the presence of the two benzene rings fused to the cyclopentadienyl moiety in 9-G-Fl$^-$ ions gives rise to differences in conformational effects.

For both types of nucleophiles reactivity values become more negative along the series Me, Et, *i*-Pr, and *t*-Bu, but *r* values (0, −0.17, −1.5, −2.6) are smaller than *S*° values (−0.73, −1.08, −1.44, −3.94), and only the latter correlate with E_s. The *S*° value for Ph (−1.82) is more negative than that for *i*-Pr whereas the reverse is true for the *r* value for Ph (−0.58). The *S*° and *r* values for $PhCH_2$ (−1.16 and −0.10) are both less than the respective values for Ph, however. There is a striking reversal in the relative Ph, *o*-tolyl, and Mes *S*° and *r* values. The *S*° values become progressively less negative (−1.82, −0.77, and −0.23) whereas the *r* values become progressively more negative (0.58, −2.2, and −3.1). There is a reversal in sign of *r* and *S*° for CN and CO_2Me effects, which are mildly accelerating for 9-G-Fl$^-$ ion reactions (*S*° = −0.89 and −1.04, respectively).

The less negative *r* than *S*° value for *t*-Bu suggests that bonding of the electrophile to the (larger) p orbital of the 9-*t*-BuFl$^-$ carbanion in the transition state occurs at a greater distance than bonding to the lone-pair orbital on nitrogen in 2-*t*-BuC_5H_4N. The equality of *r* values for H and Me (*r*'s = 0.0) compared to the *S*° values (0.0 for H and −0.73 for Me) may stem from a similar cause, together with a more facile deformation of Me in the carbanion reaction (TS-7). In 2-$RCH_2C_5H_4N$ the approach of the electrophile to the lone-pair electrons on nitrogen is partially blocked by R from most conformations whereas the electrophile can minimize steric hindrance by approaching the lobe of the carbanion p orbital from the side of the 9-RCH_2Fl^- ion opposite to the side where R is constrained to reside (e.g., opposite to *t*-Bu in 14). The result is a much smaller *r* than *S*° value for $PhCH_2$ (−0.10 vs. −1.16). The large *S*° value for Ph (−1.82) suggests that 2-PhC_5H_4N is reacting via a conformation where the two aromatic rings are nearly coplanar (21); here a C-2 hydrogen atom in the benzene ring impedes approach of the electrophile. The benzene ring in 2-*o*-tolylC_5H_4N (22) is twisted relative to the pyridine ring for steric reasons, however, and the impedance to electrophile approach to N is greatly reduced. The presence of two *o*-Me groups in 2-$MesC_5H_4N$ causes further twisting, resulting in still less impedance.



21



22

In 9-*o*-Tol- and 9-Mes-Fl$^-$ ions the benzene rings are constrained to a position orthoganol to the fluorene ring by the peri hydrogen atoms at C-1 and C-8 (as in 22), but this causes an opposite effect since it impedes approach

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[26] Cockerill, A. F.; Lamper, J. E. *J. Chem. Soc. B* 1971, 503–507. These authors have estimated the angle of twist to be 39° on the basis of an analysis of the effect of substituents in the phenyl ring on acidity of the 9-arylfluorenes. There is still substantial overlap between the carbanion p orbitals and the π system of the phenyl group, however, since 9-PhFlH is 5 pK_a units more acidic than HFlH.

[27] Twisting of the ring should decrease the acidity of 9-*o*-MeC_6H_4FlH because of poorer overlap of the π system of the 9-Ar ring with that of the fluorenyl ring in the anion and the electron-releasing effect of the *o*-Me group. These effects are partially overshadowed by the ability of the *o*-Me group to stabilize the carbanion by internal solvation.[24]

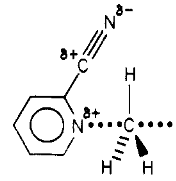
Table VI. Physical Properties of the Products of Carbanions Reacting with $PhCH_2Cl$ in Me_2SO Solution

product	reaction time[a]	yield, %	mp, °C	MS, *m/e* (relative intensity, assignment)	NMR ($CDCl_3$), δ
9-$PhCH_2$-9-CO_2Me-FlH	6 h	92	104–105[b]	314 (76.3, M^+), 255 (16.2, 9-$PhCH_2Fl\cdot$), 233 (100, 9-COOMeFl·), 91 (50.3, $PhCH_2\cdot$)	3.48 (2 H, s, CH_2Ph), 3.55 (3 H, s, CH_3O), 6.5–7.6 (13 H, m, aromatic)
9-$PhCH_2$-9-*t*-Bu-FlH	1 h	95	104–106	312 (23.7, M^+), 255 (100, 9-$PhCH_2Fl\cdot$), 221 (13, 9-*t*-BuFl·), 165 (27, Fl·)	1.0 (9 H, s, $C(CH_3)_3$), 3.5 (2 H, s, CH_2Ph), 6.3–6.8 (5 H, m, phenyl H), 7.0–7.6 (8 H, m, fluorenyl H)
9-$PhCH_2$-9-*o*-Tol-FlH	12 h	91	165–166	346 (81.1, M^+), 255 (100, 9-*o*-tolFl·), 91 (9.0, $PhCH_2\cdot$)	1.1 (3 H, s, CH_3), 3.7 (2 H, s, CH_2Ph), 6.0–6.2, 6.5–7.5, 7.9–8.1 (17 H, m, aromatic H)
$Ph_2C(CN)CH_2Ph$	10 min	93	127–128 (lit.[c] 129)		3.6 (2 H, s, CH_2Ph), 6.7–7.3 (15 H, m, aromatic H)
$PhC(CH_2Ph)(CH_3)CN$	5 min	100	oil, distilled at 160–165 °C, (20 μm) (lit.[d] 40–42 °C)		1.6 (3 H, s, CH_3), 3.0 (2 H, s, CH_2Ph), 6.7–7.2 (10 H, m, aromatic H)[e]

[a] Reactant concentrations were both about 0.1 M. [b] Reference 31. [c] Reference 32. [d] Reference 10. [e] The NMR matches that given in ref 10.

of the electrophile to either lobe of the carbanion p orbital. The result is a reversal of relative effects on reactivity of Ph, *o*-Tol, and Mes substitutions into the 9-position of the fluorenyl carbanion and the 2-position of the pyridine ring.

The negative $S°$ value for the CN function (−0.89) is likely to have its origin in an electronic effect as well as a steric effect. For the S_N2 reaction of the $2\text{-}CNC_5H_4N$ with CH_3I the inductive effect of the CN function will inhibit the development of the positive charge on nitrogen in the transition state (**TS-23**) whereas the opposite is true for concentration of the negative charge on carbon in the 9-CN-Fl^- ion in the S_N2 reaction with $PhCH_2Cl$ (**TS-18**). The same is true for other symmetrical functions like Cl ($S°$ = −0.54) or Br ($S°$ = −0.82); for larger, planar functions like CO_2Me the larger steric effect gives rise to a more negative value ($S°$ = −1.05).



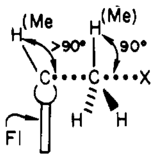
TS-23

We conclude that steric effects in nucleophiles are inexorably combined with electronic effects and that no one set of reactivity values, such as *r* or S°, can be expected to have general validity.

Comparison of Steric Effects Caused by Alkyl Groups in Nucleophiles and Electrophiles. In the introduction we cited evidence to show that steric effects in S_N2 reactions are characterized by an abrupt increase when it becomes impossible for the reactants to minimize repulsions by orientation of alkyl groups through conformational changes. This was observed for 2-alkylpyridines reacting with CH_3I where rate retardations increased by only 2–3-fold as R was changed along the series H, Me, Et, and *i*-Pr but increased by 306-fold between *i*-Pr and *t*-Bu.[3] A similar pattern was cited for changing R in RCH_2X, the rate retarding effects for an "average" nucleophile being 30, 2.5, 13, and 3000, respectively, for changes in R along the series H, Me, Et, *i*-Pr, and *t*-Bu.[6] (Carbanion nucleophiles were not included in determining these average values, but recent work indicates that 9-MeFl$^-$ ions respond to changes in α- or β-alkyl substitution in RX electrophiles in the same manner as do I^- and N_3^- nucleophiles.[16]) In this paper we have seen that reactions of 9-G-Fl$^-$ ions with $PhCH_2Cl$ conform to these same steric patterns. Thus, (a) there is no steric effect when G is changed from H to Me because in the transition state Me can bend away from the electrophile, (b) there is a minimal steric effect when G is CH_2R or SR, irrespective of the size or degree of branching in R, because in the transition state R can be positioned on the opposite side of the fluorene ring from that becoming attached to the electrophile, and (c) a sizable steric effect sets in when G protrudes on both sides of the fluorene ring so that repulsions with the electrophile cannot be avoided.

The steric effects when G in 9-G-Fl$^-$ is *t*-Bu or *o*-tolyl appear to be smaller than comparable alkyl effects in the electrophile, where the change from HCH_2X to *t*-$BuCH_2X$ causes about a 3×10^6 rate retardation. A recent calculation suggests that these steric effects may be much larger than indicated by the rate data, amounting of 6.2 kcal/mol for merely changing from HCH_2X to $MeCH_2X$, corresponding to a rate retardation of 3.5×10^4-fold.[22] The 10^3 times smaller rate retardation observed than calculated was explained by assuming that Me substitution causes a compensating rate acceleration of 320-fold due to a "bonding effect" (stabilization of R^+ in the $Nu^{\delta-}\cdots R^+\cdots X^{\delta-}$ transition state by Me). In 9-G-Fl$^-$ nucleophiles there is no compensating "bonding effect" in changing from H to Me, yet there is no evidence that Me substitution introduces a steric effect. Presumably the difference between the effect of Me substitution in the nucleophile and electrophile is that in the transition state a Me attached to the nucleophile can bend away from the electrophile whereas a Me attached to the electrophile encounters the leaving X group when it tries to bend away from the nucleophile (**TS-24**).

In **TS-24**, the H–C–X angle is only 90°, so replacement of H by Me will cause severe crowding. On the other hand,



TS-24

the H–C–C angle can be greater than 90° because H (or Me) can bend away as the nucleophile approaches.

Summary and Conclusions. The S_N2 reactivities of various 9-G-Fl$^-$ carbanions toward $PhCH_2Cl$ have been compared with the aid of Brønsted correlations. The 9-CN-Fl$^-$ ion and other flat α-cyano carbanions of various sizes show similar reactivities, indicating that bonding distances in S_N2 transition states between carbanion p orbitals and the $PhCH_2Cl$ electrophile are relatively long. As a consequence, steric effects are surprisingly small unless G is bulky [e.g., 9-MeFl$^-$ and 9-HFl$^-$ ions show nearly the same reactivities); the reactivity of the 9-CN-Fl$^-$ ion, which is about 14 p*K* units less basic, is found to be slightly enhanced (for electronic reasons) when reactivities are compared at the same basicity. Steric effects on reactivities become appreciable with 9-G-Fl$^-$ ions when parts of G protrude on both sides of the fluorene ring, as when G = *t*-Bu or *o*-Tol, but steric effects are small for large groups such as *t*-$BuCH_2$ or *t*-BuS where the *t*-Bu group is confined to one side of the fluorene ring. Steric effects on reactivities of 2-substituted pyridines, where the nitrogen lone electron pair is involved, may be appreciably different from those on reactivities of 9-G-Fl$^-$ ions, where the carbanion p orbital is involved. For example, in the series G = Ph, *o*-Tol, and Mes, S_N2 reactivities decrease substantially along the series for 2-GC_5H_4, but the reverse is true for 9-G-Fl$^-$ ions.

Experimental Section

Rates were measured by following the decrease in absorbance of the colored anions at fixed wavelength.[13] For the noncolored anion $MeC(CN)_2^-$ the rate was measured as described in ref 9.

Acidities were measured as described previously.[28]

Materials. The alkyl halides were commercially available and distilled before use. Diphenylacetonitrile, fluorene, 1,2-benzofluorene, and 2-bromofluorene were commercially available and recrystallized before use. 9-Cyano-9,10-dihydrophenanthrene was a gift from F. D. Lewis, Northwestern University; (*p*-methoxyphenyl)malononitrile was a gift from O. Webster at Du Pont. 9-*tert*-Butylthiofluorene, 9-isopropylthiofluorene, and 9-(mesitylthio)fluorene were prepared by Drucker;[24] 9-phenoxyfluorene and 9-(trimethylsilyl)fluorene were prepared by Vanier.[29] The preparation or source of the 9-(phenylthio)fluorene family, the 9-arylfluorene family, the 9-methylfluorene family, the 9-(methoxycarbonyl)fluorene family, and 9-cyanofluorene have been given earlier.[13] 9-Benzylfluorene was prepared by the method of Durst and Gokel.[30] 9-Alkylfluorenes were prepared by the methods described previously.[24] The following appear to be new compounds.

2-Bromo-9-*tert*-butylfluorene: mp 137–139 °C (EtOH); NMR ($CDCl_3$) δ 0.9 (9 H, s, $C(CH_3)_3$) 3.6 (1 H, s, 9-H proton), 7.0–7.5 (7 H, m, Ar protons); TLC on silica (hexane) showed one spot; mass spectrum, *m/e* (relative intensity) 300 (10, M^+ with ^{79}Br), 302 (10, M^+ with ^{81}Br), 244 (15.6, loss of *t*-Bu group), 165 (38.6, Fl·), 57 (100, *t*-Bu·). Anal. Calcd for $C_{17}H_{17}Br$: C, 67.77; H, 5.65. Found: C, 68.10; H, 5.86.

2,7-Dibromo-9-*tert*-butylfluorene: mp 159–159.5 °C (EtOH); NMR ($CDCl_3$) δ 0.9 (9 H, s, $C(CH_3)_3$) 3.6 (1 H, s, 9-H proton), 7.4–7.6 (6 H, m, aromatic protons); TLC on silica (hexane) showed one spot; mass spectrum, *m/e* (relative intensity) 378 (15.8, M^+ with $^{79}Br^{79}Br$), 380 (29.2, M^+ with $^{79}Br^{81}Br$), 382 (15.8, M^+ with $^{81}Br^{81}Br$), 57 (100, *t*-Bu·). Anal. Calcd for $C_{17}H_{16}Br_2$: C, 53.68; H, 4.21. Found: C, 53.66; H, 4.23.

2-Bromo-9-methylfluorene: mp 61–63 °C (MeOH); NMR ($CDCl_3$) δ 1.4 (3 H, d, CH_3) 3.8 (1 H, q, 9-H proton), 7.0–7.6 (7 H, m, aromatic protons); TLC on silica (hexane) showed one spot; mass spectrum, *m/e* (relative intensity) 258 (19, M^+ with ^{79}Br), 260 (19, M^+ with ^{81}Br), 179 (100, 9-MeFl·). Anal. Calcd for $C_{14}H_{11}Br$: C, 64.86; H, 4.25. Found: C, 64.53; H, 4.26.

Product Studies. In addition to the four product studies reported earlier for 9-G-Fl$^-$ anions reacting with $ArCH_2X$,[13] five more product studies have confirmed that substitution products are formed cleanly in high yields. The procedure has been outlined earlier.[13] Physical properties for the products are given in Table VI.

Acknowledgment. This investigation was supported by the National Science Foundation.

Registry No. 1, 85535-17-7; 1 conjugate acid, 33534-87-1; **2**, 12564-43-1; **2** conjugate acid, 1529-40-4; **3**, 78232-00-5; **3** conjugate acid, 3696-36-4; **4**, 18802-83-0; **4** conjugate acid, 86-29-3; **5**, 85535-18-8; **5** conjugate acid, 2184-88-5; **6**, 85535-19-9; **6** conjugate acid, 56666-55-8; $PhCH_2Cl$, 100-44-7; *i*-PrBr, 75-26-3; *n*-BuCl, 109-69-3; 9-Me-Fl$^-$, 31468-21-0; 2-Br-9-Me-F$^-$, 81255-42-7; 2,7-Br_2-9-Me-F$^-$, 73872-46-5; HFl$^-$, 12257-35-1; 2-Br-HFl$^-$, 85535-20-2; 2,7-Br_2-HFl$^-$, 85535-21-3; 1,2-benzo-F$^-$, 85535-22-4; 9-Et-Fl$^-$, 85535-23-5; 9-$ChCH_2$-Fl$^-$, 53629-11-1; 9-*i*-Pr-Fl$^-$, 85535-24-6; 9-*t*-Bu-Fl$^-$, 73838-69-4; 9-*t*-$BuCH_2Fl^-$, 85535-25-7; 9-C_6H_5-Fl$^-$, 31468-22-1; 9-*o*-tolyl-Fl$^-$, 85535-26-8; 9-(2-Me-4-$MeSO_2C_6H_3$)-Fl$^-$, 85535-27-9; 9-Mes-Fl$^-$, 85535-28-0; 9-CO_2Me-Fl$^-$, 12565-94-5; 9-PhS-Fl$^-$, 71805-72-6; 9-MesS-Fl$^-$, 85535-29-1; 9-*i*-PrS-Fl$^-$, 85535-30-4; 9-*t*-BuS-Fl$^-$, 85535-31-5; 9-$PhSO_2$-Fl$^-$, 71805-74-8; 9-PhO-Fl$^-$, 73838-68-3; 9-MesSi-Fl$^-$, 85535-32-6; $PhCH_2Br$, 100-39-0; *m*-$CF_3C_6H_4CH_2Cl$, 705-29-3; 9-*t*-Bu-FlH, 17114-78-2; 2-Br-9-*t*-Bu-Fl$^-$, 85535-33-7; 2,7-Br_2-9-*t*-Bu-Fl$^-$, 85535-34-8; 9-$PhCH_2$-9-CO_2Me-FlH, 57643-29-5; 9-$PhCH_2$-9-*t*-Bu-FlH, 85535-35-9; 9-$PhCH_2$-9-*o*-tolyl-FlH, 85535-36-0; $Ch_2C(CN)CH_2Ph$, 5350-82-3; CHC-$(CH_2Ph)(CH_3)CN$, 5558-92-9; 9-Me-FlH, 2523-37-7; 2-Br-9-Me-FlH, 85535-37-1; 2,7-Br_2-9-Me-FlH, 73872-42-1; HFlH, 86-73-7; 2-Br-HFlH, 1133-80-8; 2,7-Br_2-HFlH, 16433-88-8; 1,2-benzo-FlH, 238-84-6; 9-CO_2Me-FlH, 3002-30-0; 9-PhS-FlH, 28114-92-3; 9-MesS-FlH, 81536-13-2; 9-*i*-PrS-FlH, 60147-54-8; 9-*t*-BuS-FlH, 60147-55-9; 9-$PhSO_2$-FlH, 22010-78-2; 9-PhO-FlH, 59431-16-2; 9-Me_3Si-FlH, 7385-10-6; 2-Br-9-*t*-Bu-FlH, 85535-38-2; 2,7-Br_2-9-*t*-Bu-FlH, 85535-39-3; $PhCH_2SMe_2^+$, 45809-04-9.

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