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A Direct Relationship between Nucleophilicity and Basicity in S_N2 Reactions of Fluorenyl Anions with Benzyl Chloride in Dimethyl Sulfoxide Solution

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The rates of reactions for nine 9-substituted fluorenyl anions, 9-G-Fl$^-$ (G = CN, CO_2Me, $PhSO_2$, PhS, Ph, PhO, $PhCH_2$, Me, *t*-Bu), reacting with benzyl chloride in Me_2SO solution have been measured. For 9-CN-Fl$^-$ the rates increased with solvent in the order *N*-methylpyrrolidin-2-one (NMP) < Me_2SO < MeOH < EtOH < *t*-BuOH. By the introduction of substituents into the 2- and 2,7-position(s) of the fluorene ring for 9-CO_2Me-Fl$^-$ and 9-Me-Fl$^-$ anions and into the meta and para positions of the Ph rings in 9-$PhSO_2$-, 9-PhS-, and 9-Ph-Fl$^-$ anions, five families were prepared where steric effects were kept constant within the family. Brønsted-type plots of log k vs. pK_a for these five families gave parallel lines with slopes (β_{Nu}) near 0.3. Judging from the degree of displacement of the family lines from the CO_2Me family line, the steric effects of G in the 9-G-Fl$^-$ anions in these S_N2 reactions increase in the order: CO_2Me < Me < PhS < $PhSO_2$ < Ph ≪ *t*-Bu. The rate–equilibrium data for the five families can be described by the equation $\log (k/k_0) = \beta_{Nu}(\Delta pK_a - c)$, which reveals a direct relationship between nucleophilicity and basicity. The β_{Nu} values remain constant over a range of about 20 kcal/mol in $\Delta G°$, which is contrary to the predictions of the Leffler–Grunwald rate–equilibrium equation and the Hammond postulate. It is concluded that the extent of C–C bond making in the transition state for these S_N2 reactions remains constant for large changes in the basicity of the nucleophile.

The hypothesis of Leffler that a transition state (TS) will resemble more closely the less stable reactants in a chemical equilibrium[1] and the hypothesis of Hammond that the TS will be structurally similar to high-energy species, such as carbanions, carbonium ions, radicals, etc., if such occur along the reaction coordinate,[2] have been used by organic chemists for the past 25 years. In their incisive treatment of rates and equilibria of organic reactions Leffler and Grunwald attempted to quantify and generalize these postulates in the form of a rate–equilibrium relationship (eq 1).[3]

$$\delta\Delta G^{\ddagger} = \alpha\delta\Delta G° \tag{1}$$

In eq 1, α is assumed to vary between the limits of 0 to 1 and to be related to the position of the TS along the reaction coordinate. For an exoenergetic reaction α approaches zero and for an endoenergetic reaction α approaches 1.0. The α in eq 1 can be equated with the Brønsted α in base-promoted deprotonation of carbon acids, and changes in α can be interpreted in terms of changes in the extent of H–C bond breaking in the TS.[3] Often, however, α is constant for large changes in $\Delta G°$, and one must conclude that TS structures change gradually, if at all.[4-6] When curvature is observed in Brønsted plots for carbon acids, it is usually accompanied by changes in the nature of the donor atom in the base,[7-9] and the possibility arises that the curvature may be caused by changes in solvation rather than changes in the extent of H–C bond breaking.[9] When H–C bond breaking is accompanied by extensive structural reorganization, as in the deprotonation of nitroalkanes, α may be outside the limits of 0 and 1. Since deprotonations of carbon acids usually involve more or less structural reorganization, this complicates the interpretation.[10] For proton transfers involving O–H and N^+–H acids, Brønsted plots usually show curvature over rather small ranges of $\Delta G°$.[7] The proton transfers in these reactions have been represented as occurring in two[7] or three[8] steps, and it is uncertain which step is rate determining. Since interpretation in terms of eq 1 must be restricted to a single TS,[3,11] it is questionable whether eq 1 is applicable. It is conceivable that even proton transfers from carbon acids may sometimes involve an intermediate,[10] which would negate interpretation by eq 1[11] and would account for anomalous Brønsted coefficients.[12] In addition to these problems, we note that the hydrogen atom in these reactions is involved both in bond making and in bond breaking. The size of α is usually related to the extent of H–C bond breaking, but the extent of bond making between the base and the hydrogen atom must also be considered. How does this affect the size of α? In view of these complications, we have turned our attention to rate–equilibrium relationships in S_N2 reactions as a guide to TS structures.

In S_N2 reactions the central atom, carbon, is bonding to two different ligands, the nucleophile and the leaving group, in the TS. The extensive evidence accumulated on the mechanism of the S_N2 reaction appears to be best interpreted in terms of a trigonal bipyramidal TS,[14] although strong stabilizing influences may in certain instances allow an intermediate to be formed.[15] Brønsted-

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(1) Leffler, J. E. *Science* **1653**, *117*, 340–341.

(2) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.

(3) Leffler, J. E.; Grunwald, E. "Rates and Equilibria in Organic Reactions"; Wiley: New York, 1964; 156–168. As pointed out by Hudson[16] and by Dewar and Dougherty,[11] the rate–equilibrium equation was first devised (independently) by Bell and by Evans and M. Polanyi. Leffler and Grunwald were the first to attempt a general application to organic reactions, however.

(4) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 511–512.

(5) Johnson, C. D. "The Hammett Equation"; Cambridge Press: Cambridge, England, 1973.

(6) Kemp, D. S.; Casey, M. L. *J. Am. Chem. Soc.* **1973**, *95*, 6670–6680.

(7) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1–19.

(8) Kreevoy, M. M.; Oh, S.-W. *J. Am. Chem. Soc.* **1973**, *95*, 4805–4810. Hassid, A. I.; Kreevoy, M. M.; Laing, T.-M. *Symp. Faraday Soc.* **1975**, *No. 10*, 69.

(9) Hupe, D. J.; Wu, D. *J. Am. Chem. Soc.* **1977**, *99*, 7653–7639.

(10) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3108–3113.

(11) Dewar, M. J. S.; Dougherty, R. G. "The PMO Theory of Organic Chemistry"; Plenum: New York, 1975; Chapter 5.[12]

(12) The difficulty in finding a one-step proton-transfer reaction to which eq 1 can be applied with certainty becomes apparent when one sees that the very reaction used by Dewar and Dougherty for illustration, the base-catalyzed decomposition of nitramide, does not involve rate-limiting deprotonation of H_2NNO_2, as they suggest, but rather deprotonation of an intermediate, $HH{=}NO_2H$.[13] The latter reaction could involve a rate-limiting deprotonation to form a hydrogen-bonding carbanion intermediate, $B{-}H\cdots{}^-N{=}NO_2H$, or could involve a concerted E2 elimination, i.e., $B^- + HN{=}NO_2H \rightarrow BH + N{\equiv}N^+{-}O^- + OH^-$.

(13) Bell, R. P. "The Proton in Chemistry", Cornell University Press: Ithaca, NY: 1st ed, 1959; 2nd ed., 1973.

(14) Lowry, T. H.; Richardson, K. H. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; Chapter 4.

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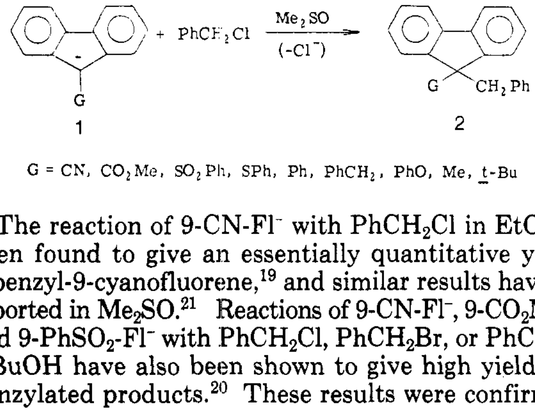
type relationships have been shown to hold for reactions of a series of nucleophiles with a variety of alkylating agents, and β_{Nu} has been shown to fall in the range of about 0.1 to 0.37.[16] It has been suggested that the size of β_{Nu} can be related to the extent of bond making in the TS. However, in a recent study of the reactions of 3- and 4-substituted pyridines with EtI, MeI, $EtOSO_2F$, and $MeOSO_2F$ in Me_2CHNO_2, the relative sensitivities of the alkylating agents to changes in the basicities of the pyridines were shown to remain constant despite changes in rates of as much as 10^6.[17] Also, for a greater than 10^4 variation in rates with $MeOSO_2CH_3$, MeOTs, $(MeO)_2SO_2$, MeI, $MeOSO_3F$, and MeO_3SCF_3 reacting with ArS^- in sulfolane, log $(k_H/k_{p\text{-}NO_2})$ rate ratios varied but little (2.06–2.44).[18] In the present paper we report similar results for a study of the rates of reactions of benzyl chloride with 9-substituted fluorenyl anions, 9-G-Fl$^-$, with variation in basicities of 10^{16} in Me_2SO solution.

Reactions of several 9-G-Fl$^-$ anions with $PhCH_2Cl$ and with other alkylating agents have been studied previously. 9-Cyanofluorenyl ion has been shown to react with MeI, EtI, *i*-PrI, *i*-PrBr, $PhCH_2Cl$, and $PhCH_2Br$ in EtOH solution to give high yields of substitution products. The kinetics, solvent effects, and salt effects are all consistent with an S_N2 mechanism involving free 9-CN-Fl$^-$ anions.[19] A study of the reactions of 9-CN-Fl$^-$, 9-CO_2Me-Fl$^-$, and 9-$PhSO_2$-Fl$^-$ with excess $PhCH_2Cl$ in *t*-BuOH also showed precise first-order behavior to at least 90% completion. Here the evidence pointed to S_N2 reactions involving free ions and ion pairs as nucleophiles.[20]

Results

The reactions of a series of nine 9-substituted fluorenyl anions, 9-G-Fl$^-$, with benzyl chloride in dimethyl sulfoxide have been examined (eq 2).



(2)

1 2

G = CN, CO_2Me, SO_2Ph, SPh, Ph, $PhCH_2$, PhO, Me, t-Bu

The reaction of 9-CN-Fl$^-$ with $PhCH_2Cl$ in EtOH has been found to give an essentially quantitative yield of 9-benzyl-9-cyanofluorene,[19] and similar results have been reported in Me_2SO.[21] Reactions of 9-CN-Fl$^-$, 9-CO_2Me-Fl$^-$, and 9-$PhSO_2$-Fl$^-$ with $PhCH_2Cl$, $PhCH_2Br$, or $PhCH_2F$ in *t*-BuOH have also been shown to give high yields of 9-benzylated products.[20] These results were confirmed in the present study by the isolation of over 90% yield of 9-$PhSO_2$-9-$PhCH_2$-Fl, mp 203–204 °C (lit.[20] mp 203 °C), from the reaction of 9-$PhSO_2$-Fl$^-K^+$ with $PhCH_2Br$ in Me_2SO: NMR δ 7.0–7.4 (8 H, m), 6.4–6.8 (10 H, m), 3.8 (2 H, s). A comparable yield of 9-Ph-9-$PhCH_2$-Fl, mp 139–140 °C (lit.[22] mp 140–141 °C), was obtained in a similar reaction: NMR δ 6.2–7.5 (18 H, m), 3.8 (2 H, s).

Kinetic Measurements. A. Preparation of Solutions. Preparation of solutions of the fluorenes and the halides in Me_2SO were made in advance of the kinetic measurements. The preparation of solutions of solid compounds is described in ref 36. Solutions of liquids were prepared as follows. A 10–20-mL reservoir sealed with a three-way stopcock was degassed repeatedly by evacuating to less than 50 μm and purging with dry argon. After the empty reservoir was tared, a sample of the liquid was introduced via syringe. After the liquid was degassed by three freeze–pump–thaw cycles with intermediate argon flushings, the reservoir was weighed again to determine the amount of liquid introduced. Then, 5–15 mL of Me_2SO was added, and the cell was weighed.

Me_2SO itself is a weak nucleophile, reacting slowly with benzylic chlorides,[23a,b] bromides,[23a,b,c] tosylates,[23d] and iodides,[23b] so solutions of the halides were used immediately after preparation. When stored frozen, the Me_2SO solutions of the benzyl halides kept for several days, giving the same results as the fresh solutions. However, prolonged storage when frozen or short-term storage (2–3 days) at room temperature caused acidic impurities to form in the solutions that interfered with the kinetic measurements.

B. Rate Measurements. Rate measurements were made in standard 1-cm Pyrex spectrophotometric cuvettes closed on top with a three-way stopcock. All rates were followed by monitoring the decrease in absorbance of the fluorenyl anion at a fixed wavelength in the visible region, using a Cary 14 spectrophotometer. The cell compartment of the spectrophotometer was kept at 25 ± 0.1 °C with a Beckman recirculating water bath.

Pseudo-First-Order Rates. For rates slower than 30 $M^{-1}\ s^{-1}$, a 10–100-fold excess of the benzyl halide over the fluorenyl anion was used to make the reaction follow pseudo-first-order kinetics. The procedure was as follows. (1) The spectrophotometric cell was degassed, tared, charged with 2–3 mL of Me_2SO and weighed. (2) A 0.01–0.2-g sample of the stock $CH_3SOCH_2^-K^+$ solution was added and weighed, making the base concentration in the cuvette between 1.5×10^{-4} and 3×10^{-3} M. The cuvette was placed in the spectrophotometer, the appropriate wavelength was dialed, and the absorbance was adjusted to zero. (3) A slight excess of the fluorene solution was added and weighed. The complete deprotonation of the fluorene by $CH_3SOCH_2^-K^+$ occurred within seconds. The wavelength had been chosen so that the anion absorbance would be between 1.0 and 1.5. (4) After equilibration for 15 min at 25 °C in the cuvette holder, a solution of the halide (also at 25 °C) was added, and the decrease in absorbance was monitored. (5) After the reaction was complete, the cuvette was again weighed to determine the exact amount of halide added.

The slope (i.e., pseudo-first-order rate constant) of a plot of ln (A_0/A) vs. time was determined by using a least-squares program on an Olivetti 6060 minicomputer. In all cases, the plots were straight for 3 to 4 half-lives, with correlation coefficients (R^2) of between 0.999 and 0.99999. Division of the slope by the halide concentration gave the second-order rate constant. The halide concentration was varied from run to run to ensure that each reaction was following second-order kinetics. Between 3 and 5 runs were

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[15] Forbus, T. R.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5057–5059.

[16] Hudson, R. F. "Chemical Reactivity and Reaction Paths"; Klopman, G., Ed.; Wiley-Interscience: New York, 1974; Chapter 5.

[17] Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1978**, *100*, 2930–2931.

[18] Lewis, E. S.; Vanderpool, S. H. *J. Am. Chem. Soc.* **1978**, *100*, 6421–6424.

[19] Bowden, K.; Cook, R. S. *J. Chem. Soc. B* **1968**, 1529–1533.

[20] Bethell, D.; Fairclough, C. S.; Wilkinson, R. G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1090–1097.

[21] Groutas, V. Ph.D. Thesis, University of Kentucky, 1973; *Diss. Abstr. B* **1974**, *34*, 5384.

[22] Bachmann, W. E. *J. Am. Chem. Soc.* **1930**, *52*, 3290–3292.

[23] (a) Nace, H. R.; Monagle, J. J. *J. Org. Chem.* **1959**, *24*, 1792–1793. (b) Johnson, A. P.; Pelter, A. *J. Chem. Soc.* **1964**, 520–522. Kornblum, N.; Powers, J. W.; Anderson, G. J.; Jones, W. J.; Larson, H. O.; Levand, O.; Weaver, W. M. *J. Am. Chem. Soc.* **1957**, *79*, 6562. (d) Kornblum, N.; Jones, W. J.; Anderson, G. J. *Ibid.* **1959**, *81*, 4113–4114.

Table I. Acidities of 9-Substituted Fluorenes and Rates of Reaction of Their Conjugate Bases with Benzyl Chloride in Dimethyl Sulfoxide Solution at 25 °C

fluorene	pK_a[a]	10^3k_2, M^{-1} s^{-1} [b]
9-CN	8.3	6.19
9-CO_2Me	10.35	26.8
9-$PhSO_2$	11.55	13.0
9-PhS	15.4	248
9-Ph	17.9	610
9-PhO	19.9	2800
9-$PhCH_2$	21.3	19500
9-Me	22.3	49400
9-*t*-Bu	24.35	471

[a] These indicators have been used to establish the acidity scale in Me_2SO; see ref 36. [b] Standard deviations are ±3% or less based on 3-5 runs.

Table II. Equilibrium Acidity Constants of Substituted Fluorenes (pK_a) and Second-Order Rate Constants (10^3k_2)[a] for the Reactions of Anions Derived Therefrom with Benzyl Chloride in Me_2SO at 25 °C

fluorene	pK_a	10^3k_2
(a) 9-CO_2Me-Fluorene Family		
9-CO_2Me-2,7-Br	6.5	1.82
9-CO_2Me-2-Br	8.2	5.70
9-CO_2Me	10.35	26.8
(b) 9-$PhSO_2$-Fluorene Family		
9-*p*-$MeC_6H_4SO_2$-2-$PhSO_2$	8.6	2.6
9-$C_6H_5SO_2$-2-Br	9.6	3.46
9-*p*-$BrC_6H_4SO_2$	10.9	9.31
9-$C_6H_5SO_2$	11.6	13.0
(c) 9-PhS-Fluorene Family		
9-*p*-MeC_6H_4S-2-$PhSO_2$	11.9	18.9
9-C_6H_5S-2-Br	13.2	56.4
9-*p*-BrC_6H_4S	14.8	168
9-C_6H_5S	15.4	248
(d) 9-Ph-Fluorene Family		
9-C_6H_5-2-$PhSO_2$	13.8	38.2
9-*p*-$MeSO_2C_6H_4$	15.2	64.3
9-*m*-ClC_6H_4	16.8	257
9-C_6H_5	17.9	610
9-*p*-MeC_6H_4	18.3	896
(e) 9-Me-Fluorene Family		
9-Me-2,7-Br_2	17.7	1650
9-Me-2-Cl	20.0_5	8870
9-Me	22.3	49400

[a] M^{-1} s^{-1}; reproducible to ±3% or less based on 3-5 runs.

made for each rate reported, and the rates were generally reproducible to ±3%.

Second-Order Rates. For reactions with rates greater than 30 M^{-1} s^{-1}, only 1.5-5-fold excesses of the halide were used, and the second-order rate equation (eq 3) was used

$$\ln\left\{\frac{[\mathrm{Fl}]_0[\mathrm{RX}]}{[\mathrm{Fl}][\mathrm{RX}]_0}\right\} = ([\mathrm{RX}]_0 - [\mathrm{Fl}]_0)kt \qquad (3)$$

to calculate the rates, where $[\mathrm{Fl}]_0$ and $[\mathrm{Fl}]$ are the fluorenyl anion concentrations at $t = 0$ and time t, respectively, and $[\mathrm{RX}]_0$ and $[\mathrm{RX}]$ are the halide concentrations at $t = 0$ and at time t, respectively.

These runs differ from the pseudo-first-order runs in that the extinction coefficient of the anion must be determined from a Beer's law plot in order to calculate $[\mathrm{Fl}]_0$ and $[\mathrm{Fl}]$. The procedure was as follows.

As outlined in steps 1 and 2 above, the cuvette was tared and then charged with Me_2SO and $CH_3SOCH_2^-K^+$. Then, instead of adding the fluorene solution in excess, it was added in small aliquots such that 4-6 points could be obtained with less total fluorene added than $CH_3SOCH_2^-K^+$ present, and the weight and absorbance for each point were recorded. Plotting absorbance vs. fluorene concentration produced a Beer's law plot, the slope of which gave the extinction coefficient for the fluorenyl anion at the chosen wavelength. Then, a slight excess of the fluorene solution was added, and steps 3 through 5 were completed as outlined above.

The concentration of Fl^- at time t was determined by dividing the absorbance at time t by the extinction coefficient. $[\mathrm{Fl}]_0$ was calculated from the known concentration of the fluorene solution, the extinction coefficient, and the absorbance at the excess point. It was corrected for the small dilution that occurred when the halide solution was added. $[\mathrm{RX}]_0$ was determined gravimetrically. $[\mathrm{RX}]$ could then be calculated from the expression $[\mathrm{RX}]_0 - [\mathrm{RX}] = [\mathrm{Fl}]_0 - [\mathrm{Fl}]$.

The minicomputer was used to calculate all concentrations and to draw the least-squares line of a plot of ln $\{([\mathrm{Fl}]_0[\mathrm{RX}])/([\mathrm{Fl}][\mathrm{RX}]_0)\}$ vs. time. The slope of the line divided by $([\mathrm{RX}]_0 - [\mathrm{Fl}]_0)$ gave the second-order rate constant. Rates up to 227 M^{-1} s^{-1} were determined in this manner.

Rate data for the reaction of 9-G-Fl^- anions with $PhCH_2Cl$ are summarized in Tables I and II.

Additional substitutions were made into the 2-position of the fluorenyl nucleus or into the meta or para position of the phenyl ring for 9-$PhSO_2$-, 9-PhS-, and 9-Ph-fluorenes, in order to obtain carbanions where the basicity had been varied while the steric effects were kept constant. For 9-CO_2Me- and 9-Me-fluorenes this was accomplished by substitution of Cl or Br into the 2-position and Br into the 2,7-positions of the fluorene nucleus.

Discussion

Solvent Effects. Bowden and Cook found that alkylations of 9-CN-Fl^- anions were faster in EtOH than in MeOH and that addition of Me_2SO to the EtOH solvent caused progressive rate retardation. For reaction with $PhCH_2Cl$, the rate-retarding effect was 13-fold when the solvent composition reached 75 mol % Me_2SO.[19] In agreement, we found the rate in pure Me_2SO to be 16 times slower at 25 °C than that reported in EtOH. Also, the rate in a second dipolar nonhydroxylic solvent, *N*-methylpyrrolidin-2-one (NMP), was found to be 57.5 times slower than that reported in EtOH. On the other hand, the rate with the 9-CN-Fl^-Na^+ ion pair is reported to be 1.6 times faster in *t*-BuOH than in EtOH.[20] The rates of reaction increase, therefore, in the order NMP < Me_2SO < MeOH < EtOH < *t*-BuOH. These relative rates are probably dictated on the one hand by the relative ability of these solvents to stabilize the 9-CN-Fl^- anion[19] and on the other by their ability to stabilize the incipient Cl^- anion in the transition state (TS). These effects may complement or oppose one another. The large delocalized 9-CN-Fl^- anion is better stabilized by Me_2SO than by the alcohol solvents, judging from the lower acidity of 9-CN-FlH in MeOH than in Me_2SO by 5.8 pK_a units.[24] The ability of the solvents to stabilize the incipient Cl^- in the TS decreases in the order MeOH > EtOH > *t*-BuOH > Me_2SO > NMP. The order of solvent effects, EtOH > Me_2SO, results from a

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[24] Ritchie, C. D. "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969; Vol. I, Chapter 4.

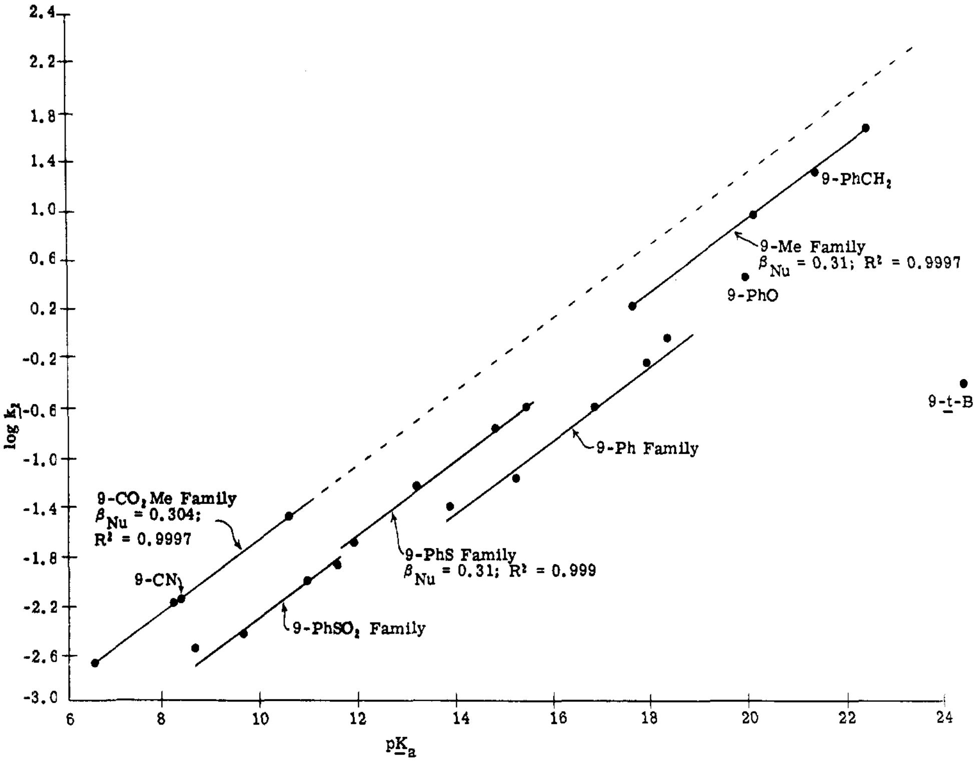

Figure 1. Plot of log k_2 vs. pK_a for reactions of 9-substituted fluorenyl carbanions reacting with benzyl chloride in Me_2SO at 25 °C. See Table II for rate and pK_a data for the various 9-G-Fl⁻ families.

combination of these factors. The latter factor is probably largely responsible for the order MeOH > Me_2SO > NMP, judging from the large differences in the chloride ion free energies of transfer, i.e., 6.2 kcal/mol for MeOH → Me_2SO and 4 kcal/mol for Me_2SO → NMP.[25] This rate order is opposite to that for S_N2 reactions of inorganic anions in these solvents, NMP > Me_2SO ≫ MeOH, which is dictated primarily by the relative abilities of these solvents to stabilize the small anionic nucleophiles.[26]

Rates and Rate–Equilibrium Relationships. Examination of Table I shows that, with two exceptions, the rates increase with increasing basicity of the 9-G-Fl⁻ anion. The exceptions are 9-$PhSO_2$-Fl⁻, which reacts about 4.5 times slower than expected from its basicity, and 9-*t*-Bu-Fl⁻, which reacts about 1000 times slower. It is evident that these rates are being retarded by sizable steric effects. The basicities of the 9-G-Fl⁻ anions increase by 14 pK units from 9-CN-Fl⁻ to 9-MeFl⁻, and this is accompanied by an 8000-fold increase in rate.

A Brønsted-type plot of log k_2 vs. pK_a for the data in Table I gives a curve with considerable scatter, the *t*-Bu point deviating widely. (This is reminiscent of curved Brønsted plots in proton-transfer reactions. For example, curvature is obtained when a log k_2 vs. pK_a plot is made from data of Bell for the deprotonation of a series of ketonic substrates by RCO_2^-,[13] and the changing slope Brønsted β) has been generally interpreted in terms of variation in the extent of C–H bond breaking in the TS.[3,16,27]) When, however, Brønsted-type plots are made with data for the five individual families 9-CO_2Me, 9-$PhSO_2$, 9-PhS, 9-Ph, and 9-Me (Table II), where steric effects have been kept constant by remote substitution, a series of nearly parallel lines is obtained (Figure 1). The appearance of parallel lines in Figure 1 is similar to the behavior often observed for Brønsted plots where a series of bases having similar structures but different steric demands are used. For example, Brønsted plots for the deprotonation of nitramide by a series of primary, secondary, tertiary, and heterocyclic amines give parallel lines,[28] and similar behavior is observed for the deprotonation of various ketones by a series of pyridines (2-Me- and 2,6-diMe-pyridines).[29] In the present instance it is the difference in steric demands of the 9-G substituents that causes the displacement of the lines.

Examination of scalar molecular models shows that the CN function is the only 9-G function listed in Table I that can be rotated freely past the 1 and 8 (peri) hydrogen atoms of the fluorene nucleus. Since the CN point fits on the CO_2Me family line, we conclude that the 9-CO_2Me family has relatively small steric demands and have extended this line with a dashed section in Figure 1 to bring out its relationship with other lines. Comparing this extended line with that of the 9-Me family shows that rates for the latter appear to be slowed by about twofold because of "steric factors".[30] The line for the 9-PhS family is displaced slightly more. There is more scatter for the 9-$PhSO_2$ family; assuming a parallel line for this family, as shown in Figure 1, the rates are slowed by about 4.5-fold relative to the 9-CO_2Me family. In the 9-PhS and 9-$PhSO_2$ families, the steric effects in the TS can be minimized by orientation of the Ph group to the side of the fluorene ring away from $PhCH_2Cl$, as in **3** and **4**. (The protruding oxygen atoms increase the steric effect of the sulfone function.) This is not possible for the 9-Ph family (**5**), where the intervening atom is absent and the π system of

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

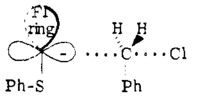
(26) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1–32.

(27) Kosower, E. S. "Physical Organic Chemistry", Wiley: New York, 1968; Chapter 1. Jones, J. R. "The Ionization of Carbon Acids"; Academic Press: New York, 1973; Chapter 8.

(28) Bell, R. P.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1949**, 1288–1297.

(29) Feather, J. A.; Gold, V. *J. Chem. Soc.* **1965**, 1752–1761.

(30) We use this term in a general sense to include all types of rate retardations caused by proximity effects such as repulsions between bonds, repulsions between lone pairs and bonds, restrictions of bond rotations, etc.



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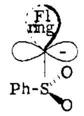

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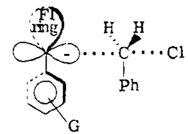

5

the Ph ring overlaps as much as possible with the carbanion p orbital. As a consequence, the increased steric demand causes about a 7.5-fold retardation for the 9-Ph family, relative to the 9-CO_2Me family.

Assuming that remote substitution will produce parallel lines also for the other 9-G functions listed in Table I,[31] the size of the steric effects of the 9-$PhCH_2$, 9-PhO, and 9-*t*-Bu functions can also be assessed. The point for the 9-$PhCH_2$ function fits near the 9-Me line (Figure 1), indicating that the steric effect of Ph has been minimized in the TS by proper orientation, as in **3** and **4**. On the other hand, the 9-PhO point fits about on the 9-Ph family line, indicating a sizable steric effect,[30] presumably caused by repulsions involving the lone pairs on oxygen. Evidently the longer C–S bond reduces the size of such repulsions in the 9-PhS family. There is no way that orientation of the 9-*t*-Bu function can minimize steric repulsions in the TS. The result is a 10^3-fold rate retardation relative to the 9-CO_2Me family line (Figure 1).

Nucleophilicity–Basicity Relationships. The nucleophilicity of 9-CN-Fl^-, the least basic nucleophile in Table I, has been placed on Pearson's n_{CH_3I} scale[32] (eq 4) at 8.59.[19] This means that it is one of the more powerful

$$n_{CH_3I} = \log (k_{Nu}/k_{MeOH}) \qquad (4)$$

nucleophiles known, being more reactive than CN^- (n_{CH_3I} = 6.70) but less reactive than PhS^- (n_{CH_3I} = 9.92).

The relative nucleophilicities of CN^-, 9-CN-Fl^-, and PhS^- in Me_2SO remain to be determined. Judging from the pK_a values in Me_2SO for the conjugate acids (HCN, 12.9;[33] 9-CN-FlH, 8.3; PhSH, 9.98[34]), the nucleophilicities should be in the order $CN^- > PhS^- >$ 9-CN-Fl^-, but nucleophilicities do not usually correlate well with basicities. For example, CN^- is 1.7 p*K* units more basic in water than PhS^-, yet is $10^{3.2}$ times less nucleophilic.[32] A plot of n_{CH_3I} values against pK_a values shows a shotgun pattern.[32] Also, 9-CN-Fl^- reacts with BuBr in Me_2SO at a rate roughly 10^4 times more slowly than does PhS^-, despite a difference in basicities of only 1.7 units.[35] In light of this background, the simple relationship between nucleophilicity and basicity revealed by the near constancy of the β_{Nu} values in Figure 1 is noteworthy. All of the rate data in Tables I and II can be accommodated reasonably well by eq 5,

$$\log (k/k_0) = \beta_{Nu}(\Delta pK_a - c) \qquad (5)$$

where *k* is the rate for a given 9-G-Fl^- nucleophile with $PhCH_2Cl$, k_0 is the rate with 9-CN-Fl^-, $\beta_{Nu} = 0.3$ (Figure 1), $\Delta pK_a = pK_a$(9-G-FlH) − pK_a(9-CN-FlH), and *c* is a constant the size of which is determined by the extent to which steric interactions cause displacement of the 9-G-Fl^- family line from the extended 9-CO_2-Me-Fl^- family line (Figure 1). The values of *c* for the 9-Me, 9-PhS, 9-$PhSO_2$, Ph, and 9-*t*-Bu families are 1.3, 1.8, 2, 3.1, and 10, respectively.

Attempts to define the nucleophilic characteristics of anions on the basis of relative rates of reactivity in S_N2 reactions in hydroxylic solvents by use of linear free-energy relationships have not been very successful. For example, an attempt to estimate n_{CH_3I} values for 15 nucleophiles by Hudson's method using bond energies, ionization potentials, and solvation energies gave poor results, despite the use of three entirely adjustable parameters.[32] Some success has been achieved with organic and inorganic systems with the Edwards equation (eq 6), where E_n is the oxidation potential of Nu, normalized to $E_n = 0$ for Nu = H_2O, S is the solvent, and *H* is the pK_a of the conjugate acid of Nu.[37]

$$\log (k_{Nu}/k_S) = \alpha E_n + \beta H \qquad (6)$$

The nucleophilic characteristics defined by the E_n term are believed to include polarizability[37] and solvation.[26,38] The success of eq 5 in accommodating the data in Tables I and II is no doubt due primarily to the fact that the nature of the donor atom and steric effects within a given 9-G-Fl^- family have been kept constant in this series of reactions. When the nature of the donor atom is changed, the length and strength of the bond being formed are changed. A difference in bond lengths in the TS will result in a difference in steric effects, and a difference in bond strengths will result in a difference in TS energies.

Extent of Bond Making in S_N2 Transition States. Brønsted-type plots for S_N2 reactions of various alkyl sulfonates and alkyl halides have been observed previously with ArS^-, ArO^-, and pyridine nucleophiles.[16] The size of β_{Nu} derived from these plots has been generally accepted as a measure of the extent of bond making between Nu and carbon in the TS.[16,39] The present results differ from these earlier studies in that the basicities of the nucleophiles have been varied over a much wider range (16 p*K* units, rather than 2–3 p*K* units).

The reaction of 9-CN-Fl^- with $PhCH_2Cl$ in Me_2SO is exoenergetic by about 6.2 pK_a units, judging from the differences in acidities of the conjugate acids of 9-CN-Fl^- and Cl^- in Me_2SO.[40] The constancy of β_{Nu} revealed in Figure 1 for the five 9-G-Fl^- families reacting with $PhCH_2Cl$ shows that a constant fraction of the electron density in the anion, as measured by proton affinity, is utilized for bond making in the TS even when the basicity of the nucleophile is increased by as much as 16 p*K* units. In energetic terms, β_{Nu} remains constant as $\Delta G°$ changes from about −9 kcal/mol to less than −30 kcal/mol. If β_{Nu} is taken as a measure of the extent of C–C bond making in the TS, we must conclude that there is essentially no change in the extent of bond making even for large changes in $\Delta G°$. The same conclusion appears to be emerging from recent studies of leaving-group effects.[17,18] Here the rate changes are larger than those we have observed by about two orders of magnitude, yet changes in β_{Nu} appear to be small. For 3- and 4-substituted pyridines there is no evidence for a change of β_{Nu} for alkylations in Me_2CHNO_2 solution,[17] and for methylations of ArS^- in sulfolane solu-

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[31] This has been verified for the 9-*t*-Bu function (Hughes, D. L., unpublished results).

[32] Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319–326.

[33] Ritchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.* **1967**, *89*, 1721–1725.

[34] Courtot-Coupez, J.; Le Démézet, M. *Bull. Soc. Chim. Fr.* **1969**, 1033–1040.

[35] Based on data for PhS^- reacting with BuBr in DMF[26] and unpublished work of Hughes on the reactions of 9-G-Fl^- anions with BuBr in Me_2SO. We hope to be able to establish a scale of nucleophilicities in Me_2SO solution for carbanions, nitranions, and other anions. The pK_a scale in Me_2SO provides quantitative data on anions ranging in basicities from about 2 to 32.[36]

[36] Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006–7014.

[37] Edwards, J. O. *J. Am. Chem. Soc.* **1954**, *76*, 1540–1547: Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 16–24.

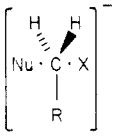
[38] Parker, A. J.; Ko, E. C. F.; Alexander, R.; Broxton, T. J. *J. Am. Chem. Soc.* **1968**, *90*, 5049–5069.

[39] McLennan, D. J. *J. Chem. Soc. B* **1966**, 705–708.

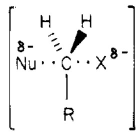
[40] McCallum, C.; Pethybridge, A. D. *Electrochim. Acta* **1975**, *20*, 815–818.

tion β_{Nu} appears to decrease slightly as the reaction becomes more exoenergetic,[18] judging from two-point β_{Nu} values. We conclude that variations in $\Delta G°$ over wide ranges brought about by altering the basicity of either the nucleophile or leaving anion cause little or no changes in β_{Nu} values, contrary to predictions of the rate–equilibrium equation (eq 1). (This corresponds to the constancy of β frequently observed in proton-abstraction reactions.[4–6]) A constant degree of bond making in S_N2 reactions wherein the nature of the donor atom is kept constant seems reasonable. After all, we know that a large amount of energy is required to change bond lengths and that this is the reason that bond lengths between atoms of a particular kind are remarkably constant in molecular structures. Why shouldn't this be true also in transition states? The data suggest that there is an optimum distance of approach for the nucleophilic and the electrophilic carbon atoms in the TS. A closer approach will lead to a sharp increase in potential energy. In retrospect, the commonly made assumption of different degrees of bond making in the TS appears unjustified.

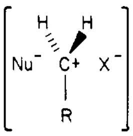
This is contrary to most current thought concerning S_N2 reactions. Most investigators have followed the early lead of Swain and Langsdorf[41] in assuming that TS structures for S_N2 reactions vary appreciably in the degree of bond making and bond breaking depending on the nature of (a) the nucleophile, (b) the substituents attached to the carbon atom, and (c) the leaving group.[14,16,26] Reactions of RCH_2X with powerful nucleophiles (Nu^-) are described as having "tight" (symmetrical) TS structures, with appreciable bond making and relatively little bond breaking (TS 6). Reactions of weak nucleophiles, such as solvents, are described as having "loose" (symmetrical) TS structures, with little bond making and much bond breaking (TS 8). Reactions with moderately active nucleophiles are described as having TS structures with intermediate degrees of bond making and bond breaking (TS 7).



TS 6
("tight")



TS 7
("intermediate")



TS 8
("loose")

Attempts have been made to use these qualitative representations to accommodate a vast array of data for nucleophiles possessing a wide range of basicities and different types of donor atoms, electrophiles, RX, with many types of structural variations in R, and leaving groups X with different types of acceptor atoms and wide ranges of basicity of X^-. In addition, the explanations often encompass data in different solvents (hydroxylic, dipolar nonhydroxylic, nonpolar) with different counterions, M^+. The present study has focused attention on only one structural variation, the basicity of a nucleophile that has a single type of donor atom, namely, carbon. The data obtained are not consistent with this qualitative picture in that we see no evidence for changes in the extent of bond making in the TS even for large changes in the basicity of Nu^-. We can anticipate, however, that a change in the nature of the donor atom *will* cause a change in the extent of bond making in the TS because the length and strength of the bond being formed will change. This will cause a change in the optimum bond length in the TS. In future papers we will examine the effect of changing the nature of the donor atom, as well as the effects of structural changes in R and in the leaving group X.

Experimental Section

General. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian T-60 spectrometer in $CDCl_3$. Melting points are uncorrected and were determined by using a Thomas-Hoover Unimelt capillary melting-point apparatus. High-performance LC analyses were obtained on a Waters 600 instrument. The purification of Me_2SO[36] and the preparation of $CH_3SOCH_2^-K^+$[36,42] have been described elsewhere. Reference 36 describes the procedure for measuring acidities in Me_2SO and also describes the general procedures used to prevent the carbanion solutions from coming into contact with air.

Fluorenes. The syntheses of 9-methylfluorene,[36] 9-*tert*-butylfluorene,[36] 9-phenylfluorene,[36] 9-(phenylthio)fluorene,[36] 9-(phenylsulfonyl)fluorene,[43] 9-cyanofluorene,[43] 9-phenyl-2-(phenylsulfonyl)fluorene,[43] 9-((*p*-methylphenyl)thio)-2-(phenylsulfonyl)fluorene, 9-((*p*-methylphenyl)sulfonyl)-2-(phenylsulfonyl)fluorene,[43] and 9-phenoxyfluorene[44] have been described elsewhere.

2,7-Dibromo-9-methylfluorene. 9-Methylfluorene (0.55 g, 0.0032 mol) was dissolved in 5 mL of $CHCl_3$ and 1.15 g (0.0072 mol) of Br_2 was added dropwise over a 30-min period. After the mixture was stirred overnight, the chloroform was evaporated in vacuo to give a brown solid. Three recrystallizations from ethanol afforded a white solid: mp 138–140 °C (lit.[45] mp 137–138 °C); NMR ($CDCl_3$) δ 1.5 (3 H, d), 3.8 (1 H, q), 7.3–7.5 (6 H, m).

9-(*m*-Chlorophenyl)fluorene was prepared by the method of Cockerill.[46] Several recrystallizations from hexane gave white crystals, mp 98–99 °C (lit.[46] mp 96 °C).

2-Chloro-9-methylfluorene. Methylmagnesium iodide was prepared by normal Grignard procedures from 0.74 g (0.032 mol) of magnesium turnings and 4.05 g (0.028 mol) of methyl iodide in 20 mL of dry ether. 2-Chlorofluorenone (1.3 g, 0.006 mol) dissolved in 25 mL of 60:40 (v/v) ether/benzene was added over a 10-min period and the mixture was refluxed for an additional 1.5 h. The mixture was poured into aqueous NH_4Cl, and the ether layer was separated, washed with water, dried with Na_2SO_4, and evaporated in vacuo to give a brown product. After recrystallization from hexane/ethyl acetate, 2-chloro-9-hydroxy-9-methylfluorene, mp 146–147 °C, was obtained.

Hydrogen iodide prepared in situ was used to reduce the carbinol. A solution of 1 g (0.004 mol) of iodine, 2 mL of 50% H_3PO_2, and 50 mL of acetic acid was heated to reflux and 0.7 g (0.003 mol) of the alcohol dissolved in 12 mL of acetic acid was added dropwise over a 1.5-h period. The solution was refluxed for another 30 min after complete addition, cooled, poured into 100 mL of water, and extracted with ether. After the solution was washed with water and dried over $MgSO_4$, the ether was evaporated in vacuo to yield a yellow oil. Bulb-to-bulb distillation at 155 °C (0.3 mmHg) and recrystallization from MeOH gave 2-chloro-9-methylfluorene as a white solid, mp 54–55 °C. High-performance LC analysis (100% hexane eluant, μ-CN column, 0.7 mL/min flow rate) showed only one peak.

9-(*p*-(Methylsulfonyl)phenyl)fluorene. A sample of 9-(*p*-$MeSC_6H_4$)-9-OH-fluorene was made from the Grignard of *p*-$MeSC_6H_4Br$ and fluorenone and then reduced with HI/HOAc to give 9-(*p*-$MeSC_6H_4$)-fluorene. The sulfide (0.20 g, 0.0007 mol) was dissolved in 5 mL of $CHCl_3$ and cooled to 0 °C. A solution of 0.33 g (0.002 mol) of *m*-chloroperoxybenzoic acid in 5 mL of $CHCl_3$ was added dropwise with stirring over a 20-min period. After complete addition, the solution was allowed to warm to room temperature and was stirred for 24 h. The solution was filtered, washed with $NaHSO_3$, $NaHCO_3$, and water, dried with $MgSO_4$, and evaporated. Recrystallization from ethanol produced flaky, colorless crystals, mp 165–166 °C.

General Procedure for the Product Studies. A liquid cell (see above) was degassed and tared, and KH (20% in mineral oil)

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[41] Swain, C. G.; Langsdorf, W. P. *J. Am. Chem. Soc.* **1951**, *73*, 2813–2821.

[42] Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.*, accompany paper in this issue.

[43] McCollum, G. J. Ph.D. Thesis, Northwestern University, 1977.

[44] Vanier, N. R. Ph.D. Thesis, Northwestern University, 1976.

[45] Sieglitz, A. *Ber.* **1920**, *53*, 2241–2249.

[46] Cockerill, A. F.; Lamper, J. E. *J. Chem. Soc. B* **1971**, 503–506.

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

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

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

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

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Received March 26, 1979

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

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

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

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

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

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

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

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

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