and the solution was stirred for 16 h. The reaction mixture was added to Florisil and evaporated. The resulting powder was transferred to a Florisil chromatography column (15 × 2 cm). Chromatography with petroleum ether–ethyl acetate (10:1) lead to a product/educt mixture.

After a second chromatography (silica gel 60, 20 × 2 cm, petroleum ether–ethyl acetate (10:1)) the pure ether **17** (500 mg, 1.9 mmol, 80% yield) was obtained as a colorless oil. The yields depend critically upon the purity of the educts. ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.7 (C-1,4), 24.4 (C-5,7), 17.4 (C-6), 87.4 (C-8), 143.6 and 143.4 (C ipso); 128.0, 127.7, 126.9, 126.6, 122.8 (aromatic C). Absolute mass: 264.1511, calcd for $C_{19}H_{20}O$ 264.1514.

Protonation of 5. A THF-d_8 solution of 30 mg of 2,3-benzo-8-*anti*-methoxy-8-phenylbicyclo[3.2.1]octene (**17**) (0.11 mmol) was placed in contact with activated lithium within a sealed NMR tube. The reaction was monitored NMR spectroscopically. The signals of the methyl ether **15** disappeared while new signals (particularly the signals of a benzyllithium structure) grew out of the noise (data are given in Table II). When the reaction was complete, the NMR tube was broken under an argon atmosphere (−78 °C) and quenched with water. The hydro derivative 2,3-benzo-8-*anti*-phenylbicyclo[3.2.1]octene (**18**) remained as a colorless oil after filtration on silica gel and evaporation of the solvent (80% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (1 H, m), 1.05 (1 H, m), 1.24 (2 H, br), 1.81 (2 H, m), 3.53 (3 H, br), 7.16 (5 H, m), 7.33 (4 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.1 (C-1,4), 146.7 (C-2,3), 22.6 (C-5,7), 18.2 (C-6), 52.8 (C-8), 140.8, 128.5, 126.5, 125.5, 122.4 (aromatic C).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Supplementary Material Available: Ortep drawing of **10** and tables of fractional atomic coordinates, thermal parameters, bond lengths, and bond angles for **10** (5 pages). Ordering information is given on any current masthead page.

Nucleophilic Aromatic Substitution Reactions with Carbanions and Nitranions in Dimethyl Sulfoxide Solution

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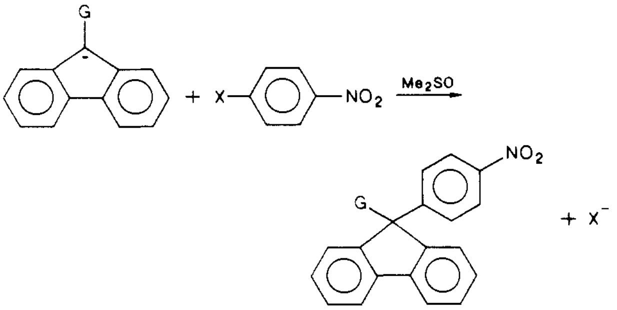
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received February 11, 1986*

Abstract: Rate constants for S_NAr reactions between families of substituted fluorenide carbanions and phenothiazinide nitranions and p-$NO_2C_6H_4X$ (X = F, Cl, Br, I, and PhO) have been measured in Me_2SO solution and compared with literature data for S_NAr reactions of families of oxanion and thianion nucleophiles. The Brønsted β_{Nu} values for S_NAr reactions are in the range 0.5–0.7, distinctly larger than those for S_N2 reactions (0.2–0.5) but not so large as to indicate an electron-transfer mechanism ($\beta_{Nu} \simeq 1$). Although the size of β_{Nu} is believed to be associated with the extent of charge transfer and bonding in the transition state, no charge-transfer (CT) bands were observed in the carbanion reactions. For anions at the same basicity the order of donor-atom effects was observed to be $S^- \gg C^- > O^- > N^-$. This order is the same as that usually observed in S_N2 reactions, but the spread in reactivity is of the order of 10^9 compared to 10^5. The larger spread is believed to be associated with a larger steric effect. For S_NAr reactions, increasing steric effects in G of 9-GFl^- (Fl^- = fluorenide) ions along the series 9-$MeFl^-$ < 9-$(PhS)Fl^-$ > 9-$(C_6H_5)Fl^-$ < 9-$(o\text{-}MeC_6H_4)Fl^-$ caused a rate retardation of 10^5 compared to $10^{2.4}$ for S_N2 reactions. No evidence for a buildup of a carbanion intermediate, $Nu(X)C_6H_4NO_2^-$, was observed in instances where the basicities of Nu^- and X^- are nearly equal.

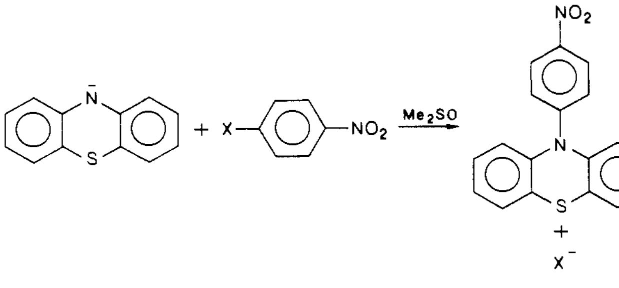
In studies in Me_2SO solution of S_N2 reactions at saturated carbon with families of carbanions, nitranions, oxanions, and thianions, we have found that when solvation, steric, and donor-atom effects are held constant, the rates of the reactions depend on only two factors: (1) the relative basicity of the anion as measured by the acidity of its conjugate acid, pK_{HA}, and (2) the sensitivity of the anion to changes in basicity, as measured by the Brønsted β of its family.[1] This has allowed us to determine donor-atom effects at the same basicity, which for S_N2 reactions generally follow the order $S^- \gg C^- > O^- > N^-$.[2] The β_{Nu} values in these studies range from 0.2 to 0.5. We now report the results of an investigation of substitution reactions at aromatic carbon, primarily with p-nitrohalobenzenes, designed to see if these observations are applicable for nucleophilic attack at sp^2 carbon as well as sp^3 carbon.

Results

Families of 9-substituted fluorenide carbanions, 9-GFl^- (G = Me, Ar, or ArS, Fl^- = fluorenide), and substituted phenothiazinide nitranions, GPz^- (G = H, 2-Cl, and 3,7-Br_2, Pz^- = phenothiazinide), were reacted with p-nitrohalobenzenes, p-$NO_2C_6H_4X$ (X = F, Cl, Br, and I), in Me_2SO solution to form substitution products in over 90% yields (eq 1 and 2). Rate constants for these and analogous reactions are summarized in Table I.



(1)



(2)

Discussion

Mechanism. There is strong eveidence to indicate that most S_NAr substitutions of this kind occur by addition–elimination

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[1] (a) Bordwell, F. G.; Hughes, D. L. J. *Org. Chem.* **1980**, *45*, 3314–3220; (b) **1980**, *45*, 3320–3325, (c) **1982**, *47*, 3224–3232; (d) **1983**, *48*, 2207–2215; (e) **1983**, *48*, 2216–2222.

[2] (a) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1982**, *47*, 169–170. (b) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1984**, *106*, 3234–3239.

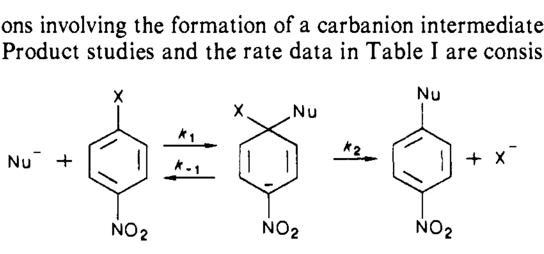
0002-7863/86/1508-5991$01.50/0

Table I. Rate Constants for Reactions of Fluorenide (Fl$^-$) Carbanions and Phenothiazinide (Pz$^-$) Nitranions with *p*-Nitrohalobenzene, *p*-Cyanofluorobenzene, and *p*-Nitrophenyl Phenyl Ether in Me$_2$SO Solution at 25 °C

anion	pK_{HA}^{c}	k, M^{-1} s^{-1d}
(A) *p*-Nitrochlorobenzene Substrate		
2-Br-9-MeFl$^-$	20.05	23.3 ± 1.5
2,7-Br$_2$-9-MeFl$^-$	17.7	0.880 ± 0.05
9-(PhO)Fl^{-a}	19.9	34.4 ± 4.2
9-(*p*-MeC$_6$H$_4$)Fl$^-$	18.33	(1.75 ± 0.12) × 10^{-2}
9-(C$_6$H$_5$)Fl$^-$	17.9	(8.07 ± 0.08) × 10^{-3}
9-(*m*-ClC$_6$H$_4$)Fl$^-$	16.85	(1.82 ± 0.10) × 10^{-3}
9-(*i*-PrS)Fl^{-a}	16.9	(4.45 ± 0.03) × 10^{-3}
9-(C$_6$H$_5$S)Fl^{-a}	15.4	1.11 × 10^{-2}
9-(*p*-BrC$_6$H$_4$S)Fl^{-a}	14.8	(6.39 ± 0.25) × 10^{-3}
2-Br-9-(C$_6$H$_5$S)Fl^{-a}	13.2	(4.46 ± 0.26) × 10^{-4}
Pz^{-b}	22.72	(9.95 ± 0.02) × 10^{-3}
2-ClPz^b	20.79	(4.35 ± 0.20) × 10^{-4}
(B) *p*-Nitrofluorobenzene Substrate		
2,7-Br$_2$-9-MeFl$^-$	17.7	3.09 ± 0.09
Pz$^-$	22.7	0.941 ± 0.02
2-ClPz$^-$	20.79	(9.31 ± 0.02) × 10^{-2}
3,7-Br$_2$Pz$^-$	20.13	(4.50 ± 0.10) × 10^{-2}
9-(*p*-MeC$_6$H$_4$)Fl$^-$	18.33	(9.42 ± 0.10) × 10^{-2}
9-(C$_6$H$_5$)Fl$^-$	17.9	(4.88 ± 0.10) × 10^{-2}
9-(*m*-ClC$_6$H$_4$)Fl$^-$	16.85	(1.29 ± 0.07) × 10^{-2}
9-(*p*-MeSO$_2$C$_6$H$_4$)Fl$^-$	15.25	(1.03 ± 0.01) × 10^{-3}
9-(*o*-MeC$_6$H$_4$)Fl$^-$	18.8	2.58 × 10^{-4} (1 run)
(C) *p*-Nitroiodobenzene Substrate		
2,7-Br$_2$-9-MeFl$^-$	17.7	1.01 ± 0.03
2-Br-9-MeFl$^-$	20.05	30.08 ± 1.35
(D) *p*-Nitrobromobenzene Substrate		
9-(*p*-MeC$_6$H$_4$)Fl$^-$	18.33	(4.25 ± 0.4) × 10^{-2}
9-(C$_6$H$_5$)Fl$^-$	17.9	(1.88 ± 0.03) × 10^{-2}
9-(*m*-ClC$_6$H$_4$)Fl$^-$	16.85	(3.68 ± 0.02) × 10^{-3}
Pz^{-b}	22.72	(9.76 ± 0.24) × 10^{-3}
2-ClPz^{-b}	20.79	(4.5 ± 0.3) × 10^{-4}
(E) *p*-Nitrophenyl Phenyl Ether Substrate		
9-MeFl$^-$	22.35	4.59 ± 0.24
2-Br-9-MeFl$^-$	20.05	0.158 ± 0.02
2,7-Br$_2$-9-MeFl$^-$	17.7	(7.42 ± 0.07) × 10^{-3}
9-(*p*-MeC$_6$H$_4$)Fl$^-$	18.33	6.6 × 10^{-5} (1 run)
2-Br-9-PhCH$_2$Fl$^-$	18.9	(3.03 ± 0.09) × 10^{-2}
9-PhOFl$^-$	19.9	0.30 ± 0.03
Pz^{-b}	22.72	(5.78 ± 0.15) × 10^{-4}
(F) *p*-Cyanofluorobenzene Substrate		
9-MeFl$^-$	22.35	(3.53 ± 0.11) × 10^{-2}
2-Br-9-MeFl$^-$	20.05	(2.66 ± 0.04) × 10^{-3}
2,7-Br$_2$-9-MeFl$^-$	17.7	(2.35 ± 0.02) × 10^{-4}

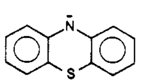
[a] Rate constant calculated from 10–20% of reaction because of interfering absorbance (see Experimental Section). [b] Rate constants calculated from 10–20% of reaction because the absorbance failed to go to zero. [c] Measured in Me$_2$SO solution. [d] Determined spectroscopically by monitoring the decay of the colored anion. The absorbance decays to zero, and the rates were calculated from data obtained over 2–3 half-lives unless otherwise noted (see Experimental Section).

reactions involving the formation of a carbanion intermediate (eq 3).[3] Product studies and the rate data in Table I are consistent with this mechanism and rule out alternative possibilities such as (a) concerted displacement, (b) elimination to form a benzyne intermediate, or (c) an electron-transfer (e$_T$$^-$) mechanism.



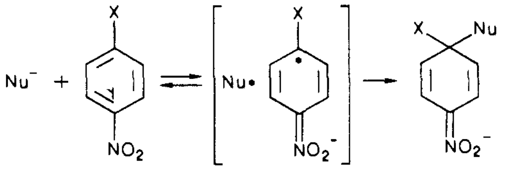
(3)

Table II. Relative Leaving-Group Abilities for the Reactions of Carbanions, Nitranions, Oxanions, and Thianions with *p*-XC$_6$H$_4$NO$_2$ Usbstrates in Me$_2$SO at 25 °C

nu	X	rel rate	k^F/k^{Cl}
2.7-Br$_2$-9-MeFl$^-$	OPh	(1.0)	3.5
	Cl	12	
	I	14	
	F	42	
9-(*p*-MeC$_6$H$_4$)Fl$^-$	OPh	(1.0)	5.3
	Cl	270	
	Br	640	
	F	1430	
	OPh	(1.0)	96
	Cl	17	
	Br	17	
	F	1630	
PhO^{-a}	Cl	(1.0)	260
	Br	1.7	
	I	0.5	
	F	260	
PhS^{-b}	Cl	(1.0)	8.0
	Br	2.5	
	I	1.6	
	F	8.0	

[a] Reference 5; the rate constant for X = Cl is 2.0 × 10^{-3} M^{-1} s^{-1}. [b] Reference 5; the rate constant for X = Cl is 1.3 M^{-1} s^{-1}.

The order of leaving-group effects, F > Br ~ Cl ~ I, shows that C–X bond cleavage is not involved in the rate-limiting step, as required by the concerted mechanism. The rate order 9-GFl$^-$ ≫ Pz$^-$ (Table I) is inconsistent with the benzyne mechanism in view of the reluctance of carbanions, relative to nitranions of the same basicity, to attack hydrogen.[4] The observation of good second-order kinetics is inconsistent with an electron-transfer chain mechanism. It is conceivable, however, that the first step in eq 3 involves a nonchain single-electron transfer (eq 4).



(4)

Leaving-Group Effects. Relative leaving-group effects for the carbanions and nitranions listed in Table I are compared in Table II with those observed for oxanions and thianions by Bartoli and Todesco.[5]

The data in Tables I and II suggest that the order of leaving-group effects for *p*-NO$_2$C$_6$H$_4$X substrates is F > Cl ~ Br ~ I > OPh for reactions with nucleophiles bearing all types of donor atoms. The k^F/k^{Cl} ratios are small for carbanions and thianions (3.5–8.0). They are over an order of magnitude larger for nitranions and oxanions (96–260). The higher reactivity of the aryl fluoride than the other halides is unusual in view of the large C–F bond energy and strongly supports the addition–elimination mechanism (eq 3).[3] Evidently, the strong polarization of the C$^{\delta+}$–F$^{\delta-}$ bond is responsible. The higher reactivity of oxanions and nitranions toward this positively charged carbon atom, relative to carbanions, is similar to the relative donor-atom effects toward positive hydrogen in E2 and 3-butenenitrile isomerization reactions.[4c] (The much lower basicity of PhS$^-$ thianions prevents comparison with the others.)

The relatively low reactivity of the PhO$^-$ ion as a leaving group is not surprising in view of the relatively high basicity of its conjugate acid (pK_{HA} = 18.0 in Me$_2$SO[6]) compared to that of,

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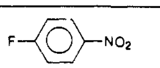
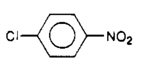
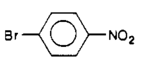
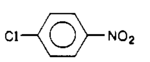
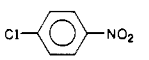
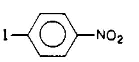
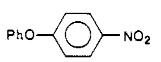
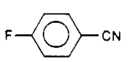
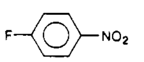
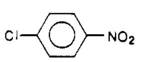
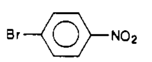
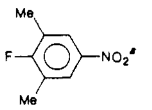
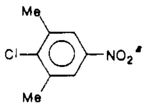
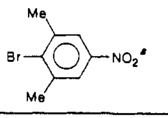
(3) (a) Bunnett, J. F.; Zahler, R. A. *Chem. Rev.* **1951**, *49*, 273–412. (b) Bunnett, J. F. *Q. Rev., Chem. Soc.* **1958**, *12*, 1–16. (c) Bartoli, G.; Todesco, P. E. *Acc. Chem. Res.* **1977**, *10*, 125–132.

(4) (a) Bordwell, F. G.; Mrozack, S. R. *J. Org. Chem.* **1982**, *47*, 4813–4815. (b) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1983**, *48*, 619–621. (c) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem, Soc.* **1985**, *107*, 4737–4744.

(5) (5) Bartoli, G.; Todesco, P. E. *Tetrahedron Lett.* **1968**, 4867–4870.

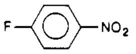
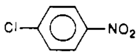
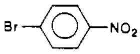
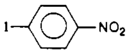
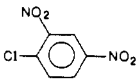
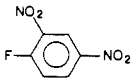
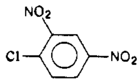
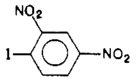
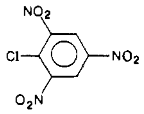
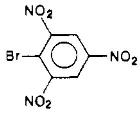
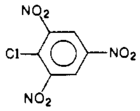
(6) Bordwell, F. G.; McCallum, R. J.; Olmstead, W. N. *J. Org. Chem.* **1984**, *49*, 1424–1427.

Table III. Brønsted β_{Nu} Values for Carbanion, Nitranion, and Oxanion Families Reacting with 4-$XC_6H_4NO_2$ Substrates in Me_2SO Solution at 25 °C

Nu family	substrate	β_{Nu}	R^2[c]
9-PhFl⁻		0.58 (0.62)[b]	0.998 (0.998)[b]
		0.65	0.997
		0.71	0.998
9-(PhS)Fl⁻		0.65	0.992
9-MeFl⁻		0.605	2 pts
		0.63	2 pts
		0.60	0.9988
		0.47	0.9993
phenothiazinide		0.51	0.9998
		0.70	2 pts
		0.70	2 pts
PhO⁻[a]		0.51	0.997, 4 pts
		0.60	0.993, 3 pts
		0.60	0.999, 3 pts

[a] Rate data are from ref 7. [b] Values in parentheses include the 9-(p-$MeSO_2C_6H_4$)Fl⁻ point which was not measured with the other substrates. [c] The square of the correlation coefficient.

Table IV. Brønsted β_{Nu} Values for S_NAr Reactions with Thianion, Amine, and Oxanion Families in Hydroxylic Solvents

Nu family	substrate	solvent	β_{Nu}	ref
ArS⁻		MeOH, 50 °C	0.52	*a*
ArS⁻		MeOH, 50 °C	0.48	*a*
ArS⁻		MeOH, 50 °C	0.55	*a*
ArS⁻		MeOH, 50 °C	0.55	*a*
ArO⁻		MeOH	0.91	*b*
amines		water	0.42	*c*
amines		water	0.52	*c*
amines		water	0.45	*c*
amines		water	0.64	*c*
2-NpCOO⁻		80% MeOH/water	0.56	*d*
ArO⁻		75% EtOH/water	0.67	*e*

[a] Bartoli, G.; DiNunno, L.; Forlani, L.; Todesco, P. E. *Int. J. Sulfur Chem., Part C* **1971**, *6*, 77–84. [b] Leahy, G. D.; Liveris, M.; Miller, J.; Parker, A. J. *Aust. J. Chem.* **1956**, *9*, 382–390. [c] Dixon, J. E.; Bruice, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 2052–2056. [d] Nadar, P. A.; Gnanasekaran, C. *J. Chem. Soc., Perkin Trans. 2* **1978**, 671–673. [e] Ryan, J. J.; Hummfray, A. A. *J. Chem. Soc. B* **1967**, 1300–1305.

say, Cl⁻ ($pK_{HA} \simeq 2$ in Me_2SO). The fact that there is a <20-fold difference in reactivity between p-$NO_2C_6H_4OPh$ and p-$NO_2C_6H_4Cl$ is further support for the mechanism shown in eq 3.

Brønsted β_{Nu} Values. Brønsted plots of log k vs. pK_{HA} (both in Me_2SO solution) were constructed for fluorenide carbanions, phenothiazinide ions, and phenoxide oxanions reacting with p-$NO_2C_6H_4Cl$ and p-$NO_2C_6H_4F$ from the data in Tables I and II (Figures 1 and 2). The slopes of the lines (β_{Nu}) for these plots and those for related reactions with thianions, oxanions, and amine nucleophiles in hydroxylic solvents are summarized in Table III and IV.

The β_{Nu} values in Tables III and IV, which range for the most part between 0.5 and 0.7, are distinctly larger than those for S_N2 reactions, which range from 0.2 to 0.5. β_{Nu} measures the sensitivity of the rates to changes in the basicity of the nucleophile. Its size appears to be associated with the extent of charge transfer in the transition state for the rate-limiting step (or steps). In single-electron-transfer reactions from carbanions, where charge transfer is essentially complete, β_{Nu} is near unity.[8] In these S_NAr reactions, where its size is determined by the bonding between the nucleophile and a partially positively charged sp^2 carbon atom, β_{Nu} is large but not near unity. One would expect the β_{Nu} size to increase as the positive charge increases, e.g., when more nitro groups are added to the electrophile. The data in Tables I, III, and IV lend some support for this view. For example, β_{Nu} for amines reacting with 2,4,6-$(NO_2)_3C_6H_2Cl$ is 0.12 unit larger than for 2,4-$(NO_2)_2C_6H_3Cl$ (Table IV), and β_{Nu} for p-$NO_2C_6H_4F$ reacting with 9-MeFl⁻ family ions is 0.11–0.15 unit larger than for p-CNC_6H_4F reacting with 9-ArFl⁻ family ions (Table III). Similar increases in β_{Nu} values are also observed in S_N2 reactions with $GC_6H_4CH_2Cl$ electrophiles as G is made more electron withdrawing[1b] and also in GCH_2X electrophiles as G is changed from n-Pr to CN.[9]

The increase in β_{Nu} for p-$NO_2C_6H_4F$ vs. p-CNC_6H_4F is accompanied by a 13 000-fold increase in rate for reactions with the 2,7-Br_2-9-MeFl⁻ ion. Since the β_{Nu} values are different, the rate ratio will change somewhat as the basicity of the anion is changed, but NO_2 clearly stabilizes the transition state more than does CN. The 13 000-fold rate difference is equivalent to a $\delta\Delta G^{*}$ of 5.7 kcal/mol. The $\delta\Delta G^{\circ}$ for the bond-forming, rate-determining step can be approximated by the difference in basicities of the intermediates **1** and **2**. These can be estimated from the pK_{HA} values of $PhC^{-}HNO_2$ (12.3) and $PhC^{-}HCN$ (21.9). This difference of 9.6 pK units is equivalent to a $\delta\Delta G^{\circ}$ between the two reactions of 13 kcal/mol, suggesting that the transition state is experiencing

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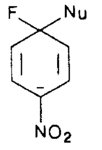
(7) Bartoli, G.; Ciminale, F.; Todesco, P. E. *J. Org. Chem.* **1975**, *40*, 872–874.

(8) (a) Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1981**, *46*, 1035–1037; (b) **1982**, *47*, 2510–2516. (c) Bordwell, F. G.; Clemens, A. H.; Smith, D. E.; Begemann, J. *J. Org. Chem.* **1985**, *50*, 1151–1156.

(9) Hughes, D. L. Ph.D. Dissertation, Northwestern University, 1981.



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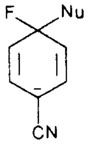

2

5.7/13 ($\delta\Delta G^{\ddagger}/\delta\Delta G^{\circ}$) of the charge-density difference existing in the product anion ground state. Thus, in S_NAr reactions, the transition-state energy is highly responsive to changes in the ground-states energy of the reactants (basicity), as represented by β_{Nu} values of 0.47–0.62, and also to changes in the ground-state energy of the product anions, as represented by β_{Pr} = 0.44.

β_{Nu} Values as a Function of X in *p*-$NO_2C_6H_4X$. Examination of Tables III and IV indicates that β_{Nu} is but little affected by the nature of X. The only apparent trend is toward a smaller β_{Nu} value when X is F. The latter values range from 0.51 to 0.58 in Table III, whereas the range when X = Br, Cl, I, and PhO is from 0.60 to 0.70. Since no bond cleavage occurs in the rate-determining step, the role of X can only be an electrostatic or steric effects., Apparently, these effects do not differ greatly for these leaving groups. It is noteworthy that even in S_N2 reactions, where C–X bond breaking *does* occur in the transition state of the rate-limiting step, β_{Nu} is insensitive to the nature of the leaving group.[9,10]

β_{Nu} Values as a Function of the Nature of the Donor Atom in the Nucleophile. The β_{Nu} values for a given subtrate vary somewhat with the nature of the donor atom in the nucleophile, but no trends emerge (Table III). For example, in the reaction with *p*-$NO_2C_6H_4F$, the β_{Nu} for the carbanion family (9-$PhFl^-$) is larger than β_{Nu} for the nitranion and oxanion families, whereas with *p*-$NO_2C_6H_4Cl$, the β_{Nu} for the nitranion family is larger than those for the carbanion and oxanion families. Variations in β_{Nu} with changes in the nature of the donor atom are also small in S_N2 reactions.[4]

Nucleophile Donor-Atom Effects in S_NAr Reactions. Since the Brønsted plots in Figures 1 and 2 have about the same slope, the lines can be extended in order to compare rates of families with different donor atoms at the same basicity. Table V presents relative rates for thianions, carbanions, oxanions, and nitranions of the same basicity reacting with *p*-$NO_2C_6H_4Cl$, *p*-$NO_2C_6H_4OPh$, *p*-$NO_2C_6H_4F$, and $C_6H_5CH_2Cl$.

The order of donor-atom effects for all four substrates is $S^- \gg C^- > O^- > N^-$, the same as in S_N2 reactions, but the difference in donor-atom effects appears to be substantially larger in the S_NAr reactions. (The much greater rate for azide than phenothiazinide nitranions gives notice that these rate comparisons of the donor-atom effects for highly delocalized anions may not hold for more localized anions.)

Measures of intrinsic basicities of anions with different donor atoms toward carbon have recently been calculated from gas-phase equilibrium data by using a method developed by Hine and Weimar.[12] These calculations show that, at the same hydrogen basicity, the intrinsic basicity order toward carbon is $C^- > S^-$, $N^- > O^-$.[13] This order shows that the relatively high nucleophilicity of thianions in S_NAr and S_N2 reactions is not an intrinsic property. (The high polarizability of these "soft" anions is the generally accepted explanation.) On the other hand, the high nucleophilicity of carbon in these reactions may well have a thermodynamic origin.

Steric Effects in S_NAr Reactions. Studies with 9-GFl^- carbanions in S_N2 reactions with $PhCH_2Cl$ in Me_2SO have revealed an order of steric effects at the same hydrogen basicity of 9-(*o*-MeC_6H_4)Fl^- ≫ 9-(C_6H_5)Fl^- > 9-(C_6H_5S)Fl^-, 9-(*i*-PrS)Fl^- > 9-$MeFl^-$, 9-($PhCH_2$)Fl^-.[1d,e] Table VI shows the relative rates of these carbanions reacting with *p*-$NO_2C_6H_4F$, *p*-$NO_2C_6H_4Cl$, *p*-$NO_2C_6H_4OPh$, and $PhCH_2Cl$ electrophiles.

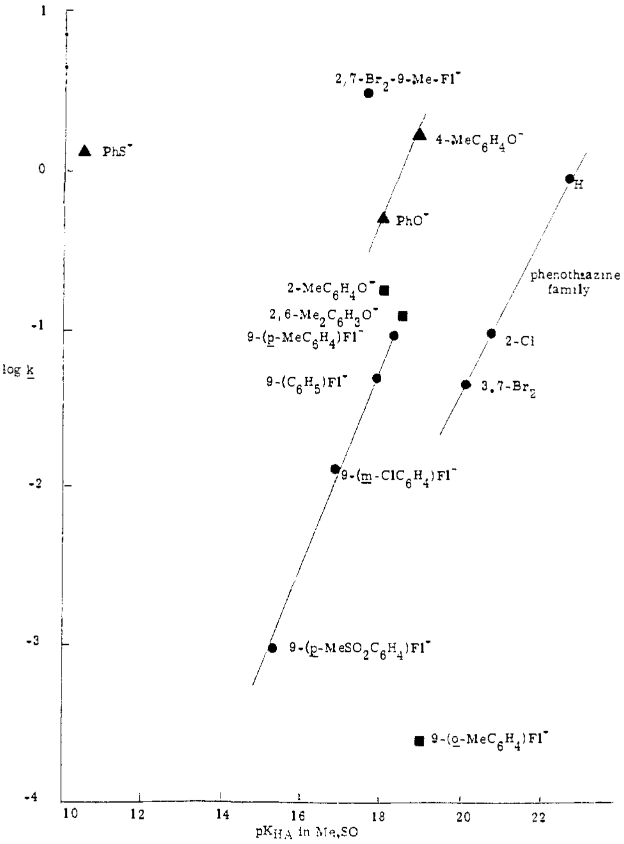

Figure 1. Brønsted plot of the log of the rate constants of reactions with *p*-nitrofluorobenzene of carbanions, nitranions, and oxanions in Me_2SO at 25 °C vs. the pK_{HA} values of their conjugate acids. The slopes of the lines are given in Table III. Rate data for the triangular points (oxanions and thianion) are from ref 7. Points for sterically hindered anions are represented by squares.

Examination of Table VI shows that steric effects of the 9-G groups are in the same order for both aliphatic and aromatic substitution reactions but that the magnitude of the steric effect is increased in the reactions with the aromatic substrates. For example, the spread in rates from the least to the most sterically encumbered carbanion, 9-$MeFl^-$ vs. 9-(*o*-MeC_6H_4)Fl^-, is 10^5 for *p*-$NO_2C_6H_4F$ compared to 250 for $PhCH_2Cl$. The rate difference for 9-$MeFl^-$ vs. 9-$PhFl^-$ is 10^2–10^3-fold in S_NAr reactions vs. only 5-fold in S_N2 reactions. Also noteworthy in this connection is the high nucleophilicity of the linear azide ion, which reacts 20000-fold faster with *p*-$NO_2C_6H_4F$, at the same basicity, than does the large, flat phenothiazinide ion. In S_N2 reactions, azide ion is 60-fold and 2500-fold more nucleophilic in Me_2SO toward *n*-PrOTs and *n*-BuI, respectively, than is a carbazolide ion of equal basicity.[9]

In Figure 1 the vertical displacement downward of about 4 log units for the square point for the 9-(*o*-MeC_6H_4)Fl^- ion from the 9-(C_6H_5)Fl^- family line represents the size of the steric effect of an ortho methyl group. Similarly, the upward displacement of about 2 log units for the square point for the 2,7-Br_2-9-$MeFl^-$ ion represents the difference in the steric effects of Me and Ph. In S_N2 reactions the steric effects of C_6H_5 vs. Me and of *o*-MeC_6H_4 vs. C_6H_5 amount to only about 0.6 and 2.2 log units, respectively.[1e] The deviations of the 2-$MeC_6H_4O^-$ and 2,6-$Me_2C_6H_3O^-$ points from the PhO^- ion family lines in Figures 1 and 2 show that the steric effects for ortho methyl groups are much smaller in these ions.

The increased steric effects may explain, in part, the larger spread in S^-, C^-, O^-, and N^- rate differences in S_NAr than S_N2 reactions (Table V). Since bond lengths decrease in the order C–S > C–C > C–N > C–O, we can expect crowding in the transition state to increase along the series. This trend will be exaggerated if bonding increases. We have seen that β_{Nu} increases for S_NAr reactions, relative to S_N2 reactions. If this increase is associated with increased bonding, steric effects should increase,

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[10] Bordwell, F. G.; Branca, J. C.; Cripe, T. A. *J. Isr. Chem.* **1985**, *26*, 357–366.

[11] Miller, J.; Parker A. J. *J. Am. Chem. Soc.* **1961**, *83*, 117–123.

[12] Hine, J.; Weimar, R. D., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 3387–3396.

[13] Cripe, T. A. Ph.D. Dissertation, Northwestern University, Sept., 1985.

Table V. Relative Rates of Carbanion, Nitranion, Oxanion, and Thianion Nucleophiles of the Same Basicity Reacting with p-$XC_6H_4NO_2$ and $PhCH_2Cl$ in Me_2SO Solution at 25 °C

	substrate			
Nu family	k(rel(p-$NO_2C_6H_4Cl$))[a]	k(rel(p-$NO_2C_6H_4OPh$))	k(rel(p-$NO_2C_6H_4F$))[a,b]	k(rel($C_6H_5CH_2Cl$))[c]
phenothiazinide	(1.0)	(1.0)	(1.0)	(1.0)
ArO^-	10^2		10^2	3
9-$MeFl^-$	10^5	10^4	10^3	30
N_3^-			10^4	
PhS^-	10^9		10^6	4×10^5

[a] Rates for ArO^- and PhS^- taken from ref 7. [b] Rates for N_3^- taken from ref 11. [c] Reference 4.

Table VI. Relative Rates of 9-GFl^- Carbanions of the Same Basicity Reacting with p-$XC_6H_4NO_2$ and $PhCH_2Cl$ in Me_2SO Solution at 25 °C

Nu	k(rel(p-$FC_6H_4NO_2$))	k(rel(p-$ClC_6H_4NO_2$))	k(rel(p-$PhOC_6H_4NO_2$))	k(rel($PhCH_2Cl$))[a]
9-(o-Tol)Fl^-	(1.0)			(1.0)
9-$PhFl^-$	10^3	(1.0)	(1.0)	60
9-(ArS)Fl^-		50		160
9-(i-PrS)Fl^-		100		160
9-$MeFl^-$	10^5	200	10^3	250
9-($PhCH_2$)Fl^-			10^3	200

[a] Reference 1.

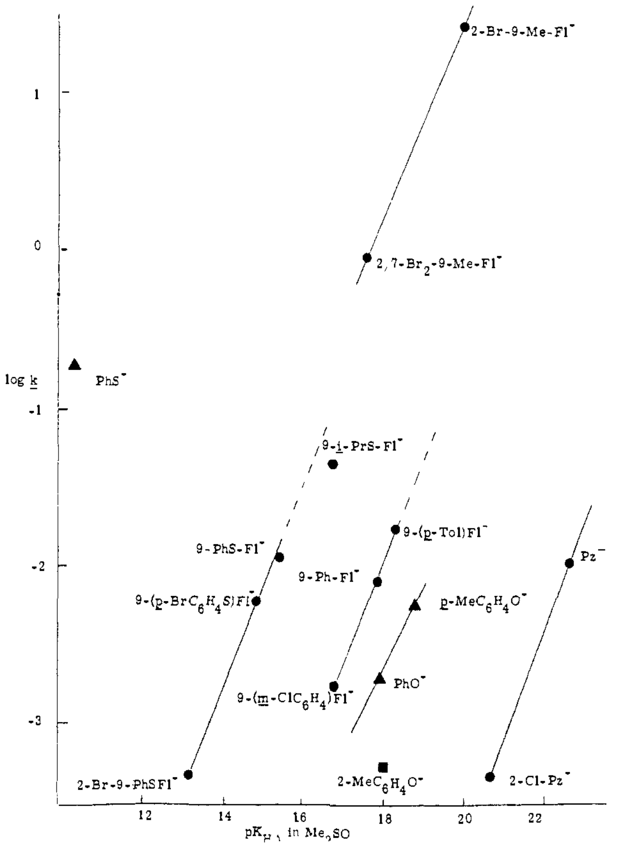
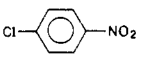
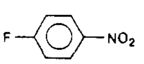


Figure 2. Brønsted plot of the log of the rate constants of reactions of carbanions, nitranions, and oxanions with p-nitrochlorobenzene vs. the pK_{HA} values of their conjugate acids in Me_2SO solution at 25 °C. The slopes of the lines are given in Table III. The triangular points for the oxanions and thianion are based on rate data from ref 7. Points for sterically hindered anions are represented by squares.

which would account for the increased spread in donor-atom effects. Looked at from another point of view, the apparent increase in steric effects and the larger β_{Nu} values for S_NAr than S_N2 reactions can be considered to be indicative of a higher degree of bond formation in the S_NAr transition state.

Activation Parameters. One of the remarkable aspects of the S_NAr reaction is that substrates with strongly basic leaving groups, such as PhO^- and F^-, react at rates comparable to those of substrates with leaving groups such as I^-, Br^-, and Cl^-, which are less basic by about 15 pK_a units. It wouldn't be surprising to find a difference in mechanism for electrophiles with leaving groups of such widely different basicities. For example, in the reaction with the 9-$PhFl^-$ ion one would expect the k_2/k_1 ratio in eq 3 to be large when Cl^- is the leaving group and near unity when F^- is the leaving group, on the basis of pK_{HA} values for Cl^-, F^-, and 9-$PhFl^-$ of 2, >14, and 17.9, respectively. In the latter instance there would be a buildup of the carbanion intermediate. Activation parameters were measured for these two reactions to see whether evidence for a difference in mechanisms might emerge. The data are summarized in Table VII.

Table VII. Rate Constants for Reactions of 9-Phenylfluorenide Ion with p-$FC_6H_4NO_2$ at 35 and 45 °C in Me_2SO Solution and the Activation Parameters for These Reactions

substrate	k, M^{-1} s^{-1} (T, °C)[a]	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
	$(1.55 \pm 0.02) \times 10^{-2}$ (35.5) $(2.99 \pm 0.06) \times 10^{-2}$ (46.0)	11.15 ± 0.25	-30.7 ± 0.8
	$(8.48 \pm 0.42) \times 10^{-2}$ (35.0) 0.147 ± 0.002 (44.8)	10.0 ± 0.2	-31.0 ± 0.5

[a] Rate constants at 25 °C are given in Table I.

The activation parameters are similar for the two reactions, with the rate difference between the two substrates showing up in the $\Delta H^\ddagger$ term. The near equality of the $\Delta S^\ddagger$ term indicates that the mechanism and timing of the two reactions must be similar; the substrate having the more basic leaving group (F^-) reacts no differently than the one having the less basic leaving group (Cl^-). This conclusion was supported by attempts to observe the formation of the carbanion intermediates in eq 3. (See the discussion of σ-complexes in the Experimental Section.)

The $\Delta S^\ddagger$ term (−31 eu) for the S_NAr reactions with 9-$PhFl^-$ ion is slightly more negative than the values obtained for the S_N2 reactions of 9-$PhFl^-$ ion with $PhCH_2Cl$ (−25 eu).[9] This is consistent with the S_NAr reactions having a rate-determining step in which only bond formation is occurring, since this transition state is more organized than that in the S_N2 reactions of aliphatic substrates, where some bond breaking is occurring.

The $\Delta S^\ddagger$ values in Me_2SO observed for fluorenide carbanions in S_NAr reactions are more negative than those reported in the literature. For example, Miller reports $\Delta S^\ddagger$ values ranging from −6 to −22 eu for N_3^-, MeO^-, MeS^-, and PhS^- reacting with p-$NO_2C_6H_4F$ and p-$NO_2C_6H_4I$ in MeOH.[14] This suggests that reactions in Me_2SO with delocalized anions are more highly organized than those for more localized anions in hydroxylic solvents. As pointed out by a referee, release of the more tightly

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[14] Ho, K. C.; Miller, J.; Wong, K. W. *J. Chem. Soc. B* **1966**, 310–324.

bound MeOH solvent from the smaller ions should augment the entropy of activation.

Experimental Section

Materials. The syntheses and/or purifications of the nucleophiles used in this study have been described previously.[1] The aromatic substrates were all commerically available and were purified by distillation or recrystallization.

Kinetics. The reactions were followed to 2–3 half-lives by monitoring the decay of the colored anion at a fixed wavelength, as described previously.[1] The rate constants were found to be first order in both nucleophile and substrate, and the second-order rate constants were usually reproducible to less than ±7%. Occasionally, colored byproducts were formed that interfered with the kinetics. For example, in the reactions of the 9-(PhO)Fl$^-$ ion and of the 9-(PhS)Fl$^-$ family ions with p-$ClC_6H_4NO_2$, a blue color formed as the reaction proceeded so that the absorbance of the indicator anion did not go to zero. The absorbance of the interfering species was factored out by assuming its rate of production was first order and occurring at the same rate as the decay of the anion. (This behavior was observed for the 9-(PhO)Fl$^-$ ion, where the rise in blue color was monitored at $\lambda = 650$ nm.) In these instances the rates were calculated by using only the first 10–20% of the reaction, before significant buildup of the interfering absorbance had occurred. Nevertheless, these rates must be viewed with caution since the initially formed substitution product may have undergone further reaction (see below). For the reactions of phenothiazinide nitranions with p-$ClC_6H_4NO_2$, p-$BrC_6H_4NO_2$, and p-$PhOC_6H_4NO_2$ electrophiles, the absorbance again failed to go completely to zero, but here there was no color change. The rates were again calculated from the first 10–20% of reaction.

Attempts to measure the rates with carbazolenide nitranion or 2-naphthoxide oxanion families failed because the absorbance increased, instead of decreasing, upon addition of the electrophile, probably as a result of charge transfer. A product study with carbazolenide nitranion reacting with p-$FC_6H_4NO_2$ gave the substitution product.

σ-Complexes. In 1960 and 1961 Miller, Parker, and Bolton reported that the reaction of N_3^- with p-$NO_2C_6H_4F$ in dry DMF gave a σ-complex corresponding in structure to the carbanion intermediate in eq 3, which did not decompose until water was added.[15] However, 2 years later they retracted this report because they were unable to reproduce the results.[16] We looked further into the matter. As was brought out in the Discussion, an anion σ-complex of this type should have a pK_{HA} value similar to that of $PhCHNO_2^-$ ($pK_{HA} = 12.3$). Thus the σ-complex would be less basic than the leaving group in the case of PhO$^-$ ($pK_{HA} = 18.0$) or F$^-$ ($pK_{HA} \geq 13$–14).[17]

For reactions of 9-(m-ClC_6H_4)Fl$^-$ or 9-(p-$MeSO_2C_6H_4$)Fl$^-$ ions with p-$NO_2C_6H_4F$, a new absorbance of $\lambda_{max} = 434$ nm grew in as the reaction proceeded and remained constant long after the reactant anion absorbance had completely decayed. We thought this colored species might be a σ-complex. Addition of $PhSO_2NHPh$ ($pK_a = 11.95$) quenched the color, as expected for a species with a pK_{HA} of about 12.3. An equivalent of $PhSCH(SO_2Et)_2$ ($pK_a = 7.1$) also essentially quenched the color. The basicity of the solution from a reaction of equivalent amounts of 9-(m-ClC_6H_4)Fl$^-$ ion with p-$NO_2C_6H_4F$, measured after complete decay of the indicator anion, was about 13. This estimate was arrived at because the solution was not basic enough to deprotonate 9-(m-ClC_6H_4)FlH ($pK_a = 16.8$) but did deprotonate 2-($PhSO_2$-9-(p-MeC_6H_4S)FlH ($pK_a = 11.9$), giving a curved Beer's law plot. This consistent with the presence of either the σ-comples or F$^-$ ion. As a further test, 2-Br-9-($PhCH_2$)Fl$^-$ ion ($pK_{HA} = 18.9$) was reacted with 1 equiv of p-$NO_2C_6H_4OPh$. Here the pK_{HA} of the PhO$^-$ ion leaving group (18.0) is much higher than that of the expected σ-complex ($\sim$12.3). Again, after the reaction was completed, a new band at $\lambda_{max} = 435$ nm remained. However, addition of more indicator anion ($pK_{HA} = 18.9$) produced the colored 2-Br-9-($PhCH_2$)Fl$^-$ ion, showing that the PhO$^-$ ion, was the major species present. We conclude that substitution products, not σ-complexes, are the final products formed in these reactions. The absorbance bands in the $\lambda = 400$ nm region are apparently caused by colored byproducts.

Charge-Transfer Complexes. Transient charge-transfer (CT) complexes are formed in many organic reactions,[18] including S_NAr reactions. For example, in the reaction of aniline with 2,4-dinitrochlorobenzene in ethanol, kinetic, as well as spectral, evidence for CT was obtained.[19] Thus, the second-order rate constants decreased as the aniline concentration increased (27% for a 5-fold concentration change), showing that an intermediate was present in more than steady-state amounts. However, we have found no evidence for CT formation in S_NAr reactions with fluorenide carbanions. The 9-(p-MeC_6H_4)Fl$^-$ ion has maxima at λ = 526, 494, 460, 399, and 377 nm in Me_2SO solution. Upon addition of about 3 equiv of p-$NO_2C_6H_4Cl$, the resulting spectrum was superimposable upon the spectrum of the anion itself down to 400 nm, where p-$NO_2C_6H_4Cl$ began to absorb. The same behavior was observed for 9-(p-$MeSO_2C_6H_4$)Fl$^-$ and 9-(m-ClC_6H_4)Fl$^-$ ions reacting with p-$NO_2C_6H_4F$; here addition of the substrate did not alter the ion spectrum at all. Also, the reaction kinetics were always second order, first order in each reactant. The substrate was in large excess, but the excess was altered by 3- to 5-fold (e.g., from a 10-fold to a 30- and 50-fold excess) to ensure that the reaction was second order. The rate constants were generally reproducible to ±5%.

Product Studies. The product studies were carried out as described in earlier publications.[1] Details concerning individual reactions are summarized below.

Reactions with 9-Phenylfluorenide Ion. Reactions with p-$NO_2C_6H_4X$ with X = F, Cl, Br, and I gave an identical product, 9-phenyl-9-(p-nitrophenyl)fluorene: mp 177–178 °C (EtOH); NMR ($CDCl_3$) δ 7.0–7.4 (13 H, m, fluorene and Ph), 7.6–8.1 (4 H, m, $C_6H_4NO_2$ ring); mass spectrum (relative intensity), m/e 363 (M^+, 100%), 317 (14.7%, loss of NO_2), 241 (42.8%, loss of $NO_2C_6H_4$). The yields were 90% for X = F, Cl, and Br. Chromatography of the product for X = I on silica gave 10% of 9-PhFlH and 30% of substitution product. The remaining product, eluted with ether, was a yellow solid, mp 150–170 °C. No further characterization was attempted.

Reactions with 9-Benzylfluorenide Ion. Reactions with p-$NO_2C_6H_4X$ with X = I and PhO each gave an identical product in over 90% yield: mp 163–165 °C; NMR ($CDCl_3$) δ 3.7 (2 H, s, CH_2Ph), 6.2–8.1 (17 H, m, aromatic H); mass spectrum (relative intensity), m/e 377.2 (M^+, 10%), 286 (100%, loss of $PhCH_2$), 246 (25%, loss of $PhCH_2$ and NO_2), 91 (25%, $PhCH_2$).

Reaction with p-cyanofluorobenzene for 3.5 h gave a mixture containing 30% recovered starting material and 70% 9-benzyl-9-(p-cyanophenyl)fluorene, separated by crystallization from ether; pp 233–236 °C; NMR δ 3.7 (2 H, s, CH_2Ph), 6.2–7.6 (17 H m, aromatic H); mass spectrum (relative intensity), m/e 357 (M^+, 7.4%), 266 (100%, loss of $PhCH_2$).

Reaction of Phenothiazinide Ion with p-Nitrochlorobenzene. A 93% yield of N-(p-nitrophenyl)phenothiazine, mp 157–158 °C (EtOH), was obtained [lit.[20] mp 157 °C]: mass spectrum (relative intensity), m/e 320 (M^+, 100%).

Reaction of Carbazolenide Ion with p-Nitrofluorobenzene. An 88% yield of N-(p-nitrophenyl)carbazole, mp 208–209 °C (EtOH/EtOAc), was obtained [lit.[21] mp 209–211 °C].

Reaction of Thiophenoxide Ion with p-Nitrochlorobenzene. A 57% yield of p-nitrophenyl phenyl sulfide, mp 55–56 °C, was obtained [lit.[22] mp 55 °C].

Reaction of 9-(Phenylthio)fluorenide Ion with p-Nitrochlorobenzene. Reacting equivalent amounts on a 1-mmol scale (0.28 and 0.16 g, respectively) for 24 h followed by pouring the mixture into water and extracting it with CH_2Cl_2 gave 0.33 g of an orange resin. The mass spectrum showed only a very small peak at m/e 395, the parent peak of the substitution product. Prominent peaks occurred at m/e 287, 273, and 231. The first corresponds to the parent peak for 9-(p-$NO_2C_6H_4$)FlH and the second to the loss of 9-(PhS)Fl$^-$. It seems likely that the substitution product, 9-(PhS)-9-(p-$NO_2C_6H_4$)Fl, undergoes nucleophilic attack on sulfur by 9-(PhS)Fl$^-$ to form 9,9-$(PhS)_2$Fl and 9-(p-$NO_2C_6H_4$)Fl$^-$ ion since comparable reactions of 9-GFl$^-$ ions with 9-(PhS)-9-PhFl have been observed.[23]

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Registry No. p-$ClC_6H_4NO_2$, 100-00-5; p-$FC_6H_4NO_2$, 350-46-9; p-$IC_6H_4NO_2$, 636-98-6; p-$BrC_6H_4NO_2$, 586-78-7; p-$PhOC_6H_4NO_2$, 620-88-2; p-FC_6H_4CN, 1194-02-1; 2-Br-9-MeFl$^-$, 81255-42-7; 2,7-Br_2-9-MeFl$^-$, 73872-46-5; 9-(PhO)Fl$^-$, 73838-68-3; 9-(p-MeC_6H_4)Fl$^-$, 42730-14-3; 9-(C_6H_5)Fl$^-$, 31468-22-1; 9-(m-ClC_6H_4)Fl$^-$, 73872-45-4; 9-(i-

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(17) After KF was dried overnight at 100 °C, the salt readily deprotonated an indicator of $pK_a = 13$ in Me_2SO but would barely deprotonate 9-(PhS)FlH ($pK_a = 15.4$). The effective pK_a is therefore estimated to be 13–14 in Me_2SO. This is higher than the actual pK_a, however, since hydrogen bonding by the HF produced will greatly stabilize F$^-$ and increase the acidity.

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PrS)Fl$^-$, 85535-30-4; 9-(C_6H_5S)Fl$^-$, 71805-72-6; 9-(p-BrC_6H_4S)Fl$^-$, 73838-77-4; 2-Br-9-(C_6H_5S)Fl$^-$, 73838-76-3; Pz$^-$, 76069-04-0; 2-ClPz$^-$, 79990-93-5; 3,7-Br$_2$Pz$^-$, 79990-94-6; 9-(p-MeSO$_2$C$_6$H$_4$)Fl$^-$, 73872-44-3; 9-(o-MeC$_6$H$_4$)Fl$^-$, 85535-26-8; 9-MeFl$^-$, 31468-21-0; 2-Br-9-PhCH$_2$Fl$^-$, 103422-01-1; 9-PhCH$_2$Fl$^-$, 53629-11-1; 9-phenyl-9-(p-nitrophenyl)fluorene, 103437-36-1; 9-benzyl-9-(p-nitrophenyl)fluorene, 103422-02-2; 9-benzyl-9-(p-cyanophenyl)fluorene, 103422-03-3; N-(p-nitrophenyl)phenothiazine, 19606-94-1.

Absence of Stereoelectronic Control in Hydrolysis of Cyclic Amidines

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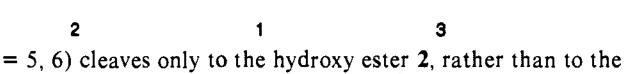
Abstract: According to Deslongchamps' theory of stereoelectronic control, preferential cleavage of a tetrahedral intermediate occurs when there are two lone pairs antiperiplanar to the leaving group. For reasons presented (Perrin and Arrhenius, *J. Am. Chem. Soc.* **1982**, *104*, 2839), product studies of hydrolysis of cyclic amidines can test this theory, and initial results supported it. However, those results are ambiguous, owing to a mismatch of leaving abilities. We now find that hydrolysis of three six-membered ring amidines bearing matched leaving groups produces predominantly aminoamide, the product of ring cleavage, and only 3–9% lactam, as expected from the theory. In contrast, hydrolysis of three five- or seven-membered ring amidines produces substantial (ca. 50%) lactam. Despite attempts to accommodate these results to the theory, it is concluded that there is no general requirement for two lone pairs antiperiplanar to the leaving group and that stereoelectronic control, even in six-membered ring amidines, contributes less than 2 kcal/mol.

According to Deslongchamps'[1] theory of stereoelectronic control, preferential cleavage of a tetrahedral intermediate occurs when there are two lone pairs antiperiplanar to the leaving group. This is certainly a plausible theory, supported by MO calculations,[2] X-ray data (from acetal derivatives),[3] and the Principle of Least Motion.[4] The experimental evidence is contained in a notable series of papers by Deslongchamps and his co-workers.[5] The key result is the observation (eq 1)[6] that a cyclic hemiorthoester (**1**, n = 5, 6) cleaves only to the hydroxy ester **2**, rather than to the lactone **3**. Recently we have concluded[7] that this evidence is ambiguous, both because it requires an unwarranted[8] assumption that conformational interconversion even in the five-membered ring is slower than cleavage and because the observation can be rationalized more simply on the basis of the well-known[9] instability of lactones and E esters. The many other observations claimed[10] as evidence for stereoelectronic control can likewise be attributed[7] to this instability. Deslongchamps[1,11] has referred to this instability as a "secondary stereoelectronic effect," but this begs the question of whether there is any "primary" effect. Although the theory has been generally accepted,[12] and there is good evidence[13] for stereoelectronic control at the aldehyde level of oxidation (but considerable controversy[14] for stereoelectronic control in reactions at phosphorus), only few objections have been raised,[15] most notably Capon and Grieve's reinvestigation[16] of the hydrolysis of **1**, where they found substantial formation of **3**.



2 **1** **3**

In view of the importance of the theory for permitting the selective creation or destruction of a chiral center[17] and for en-

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