HxSFlH, 81536-10-9; 9-l-AdSFlH, 81536-11-0; 9-$PhCH_2SFlH$, 31859-89-9; 9-PhSFlH, 28114-92-3; 9-*o*-MeC_6H_4SFlH, 81536-12-1; 9-*p*-MeC_6H_4SFlH, 31859-88-8; 9-mesSFlH, 81536-13-2; 9-$MeSO_2FlH$, 31859-90-2; 9-$EtSO_2FlH$, 60147-56-0; 9-*i*-$PrSO_2FlH$, 60147-57-1; 9-*t*-$BuSO_2FlH$, 60147-58-2; 9-neopentSO_2FlH, 81536-14-3; 9-$PhSO_2FlH$, 22010-78-2; 9-*o*-$MeC_6H_4SO_2FlH$, 81536-15-4; 9-mesSO_2FlH, 81536-16-5; $MeSCH_2CN$, 35120-10-6; $EtSCH_2CN$, 53250-09-2; *i*-$PrSCH_2CN$, 23178-01-0; *t*-$BuSCH_2CN$, 49827-12-5; 1-$AdSCH_2CN$, 81536-17-6; $PhSCH_2CN$, 5219-61-4; $MeSO_2CH_2Cn$, 2274-42-2; *t*-$BuSO_2CH_2CN$, 81536-18-7; $PhSO_2CH_2CN$, 7605-28-9; $(PrS)_2CHPh$, 60595-12-2; (*t*-BuS)$_2$CHPh, 23837-50-5; $(MeSO_2)_2CH_2$, 1750-62-5; $(EtSO_2)_2CH_2$, 1070-92-4; (*i*-$PrSO_2)_2CH_2$, 6330-39-8; (*t*-$BuSO_2)_2CH_2$, 7144-89-0; $MeSCH_2SOMe$, 33577-16-1; $EtSCH_2SOMe$, 72335-08-1; *t*-$BuSCH_2SOBu$-*t*, 52056-68-5; $MeSO_2Me$, 67-71-0; *t*-$BuSO_2Me$, 14094-12-3; $MeSO_2CH_2Ph$, 3112-90-1; *t*-$BuSO_2CH_2Ph$, 20282-89-7; $CH_2(CN)_2$, 109-77-3; $MeCH(CN)_2$, 3696-36-4; *t*-BuCH(CN)$_2$, 4210-60-0; *p*-$MeC_6H_4CH_2CN$, 2947-61-7; *p*-*t*-$BuC_6H_4CH_2CN$, 3288-99-1; $PhCH_2CN$, 140-29-4; *p*-$MeC_6H_4CH_2SO_2Ph$, 19523-24-1; *p*-*t*-$BuC_6H_4CH_2SO_2Ph$, 81536-19-8; $PhCH_2SO_2Ph$, 3112-88-7; neoPen-CH_2SO_2Ph, 81536-20-1.

Brønsted Correlations for Electron Transfer from Carbanions to Halomethyl Phenyl Sulfone and 1,1-Dinitroalkane-Type Acceptors

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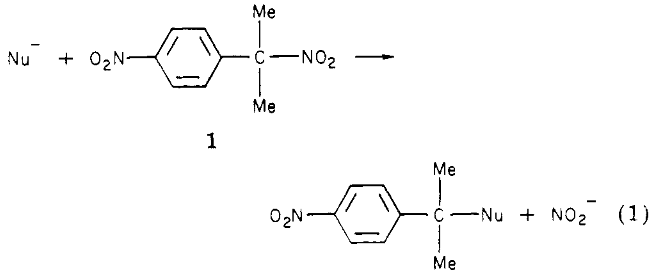
Received July 31, 1981

9-Substituted fluorenyl carbanions, 9-G-Fl$^-$, with G = Ar or Me, have been dimerized to (9-G-Fl)$_2$ by reaction in Me_2SO solution with $PhSO_2CH_2X$ and $R_2C(NO_2)X$ electron acceptors. Rate measurements revealed the following electron-accepting abilities: c-$C_6H_{10}(NO_2)_2$ > $Me_2C(NO_2)_2$ > $PhSO_2CH_2Br$, $PhSO_2CH_2I$ > c-$C_6H_{10}(NO_2)CN$ > c-$C_6H_{10}(NO_2)SO_2C_7H_7$ > $Me_2C(NO_2)SO_2C_7H_7$ > $PhSO_2CH_2Cl$. The rate-limiting step in these reactions is electron transfer from 9-G-Fl$^-$ to the electron acceptor. Plots of log k vs. pK_a of 9-G-FlH are linear with a slope near unity for all seven electron acceptors studied. We conclude that a Brønsted β of unity is characteristic of electron transfer from carbanions to electron acceptors in Me_2SO solution. This is interpreted to mean that the changes in $\Delta G°$ brought about by changes in the basicity of the carbanion are matched by changes in $\Delta G^{\ddagger}$, which correspond to the difference in the energy gap between the HOMO of the donor and the LUMO of the acceptor.

Nucleophiles, Nu$^-$, have been shown to react with electrophiles to form substitution products by a variety of mechanisms when the electrophile contains an atom or group of atoms able to release a weakly basic anion. The most common mechanism is the classical S_N2 pathway, where the electrophile is an alkyl halide, tosylate, or the like. A second mechanism is substitution by electron transfer discovered by Kornblum,[1] where the leaving group may be chloride ion, or a more strongly basic anion, such as NO_2^- (e.g., eq 1).



1

2

(1)

The Kornblum substitution has been shown to occur by a chain mechanism initiated by transfer of an electron from the nucleophile.[2] Nucleophiles of many types have been found to be capable of electron transfer, often, but not always, under photostimulation.[3] However, only a limited number of electron acceptors have been found that can support a chain. In addition to 1, these include $R_2C(NO_2)X$, where X = Cl,[4] Br,[4] NO_2,[3] $PhSO_2$,[3] or CN,[3] and ArX, where X = Br or I.[5]

The chain mechanism involving a nucleophile, Nu$^-$, and an electron acceptor, $R_2C(NO_2)X$, can be represented as occurring by an initiating electron transfer (eq 2), followed by a three-step chain sequence (eq 3–5), any step of which may be rate limiting.[6]

$$Nu^- + R_2C(NO_2)X \rightarrow Nu\cdot + R_2C(NO_2)X^{-}\cdot \qquad (2)$$

$$R_2C(NO_2)X^{-}\cdot \rightarrow R_2CNO_2\cdot + X^- \qquad (3)$$

$$Nu^- + R_2CNO_2\cdot \rightarrow NuC(NO_2)R_2^{-}\cdot \qquad (4)$$

$$NuC(NO_2)R_2^{-}\cdot + R_2C(NO_2)X \rightarrow NuC(NO_2)R_2 + R_2C(NO_2)X^{-}\cdot \qquad (5)$$

Nucleophiles can also be dimerized by electron acceptors. For example, a few 9-substituted fluorenyl anions, 9-G-Fl$^-$, have been shown to react with nitrobenzene to form (9-G-Fl)$_2$ dimers,[7] fluorenyl anion (H-Fl$^-$) has been dimerized by $Me_2C(NO_2)Br$ in Me_2SO to form Fl=Fl,[8] and a variety of other carbanion and enolate ion salts have been dimerized by $R_2C(NO_2)X$ in THF or *t*-BuOH solution.[8] Recently we reported that a number of 9-ArFl$^-$ anions form (9-ArFl)$_2$ dimers in reactions with $R_2C(NO_2)_2$ electron

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[1] Kerber, R. C.; Urry, G. W.; Kornblum, N. *J. Am. Chem. Soc.* **1964**, *86*, 3904–3905; **1965**, *87*, 4520–4528.

[2] Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5660–5662. Russell, G. A.; Danen, W. C. *Ibid.* **1966**, *88*, 5663–5665.

[3] Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734–745.

[4] Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1968**, *90*, 347–353.

[5] Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413–420.

[6] The symbol, $S_{RN}1$, which is often used for this chain sequence, is misleading since it implies that the first step in the sequence (eq 3) is rate limiting. Since this is actually the *least* likely step in the chain to be rate limiting, we urge that this symbolism be abandoned.

[7] Guthrie, R. D.; Wesley, D. P.; Pendygraft, G. W.; Young, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 5870–5877.

[8] Russell, G. A.; Jawdosiuk, M.; Makosza, M. *J. Am. Chem. Soc.* **1979**, *101*, 2355–2359.

0022-3263/82/1947-2510$01.25/0

acceptors in dimethyl sulfoxide solution (eq 6).[9]

$$\text{9-ArFl}^- + R_2C(NO_2)NO_2 \xrightarrow{Me_2SO} (\text{9-ArFl})_2 + (R_2CNO_2)_2 + NO_2^- \quad (6)$$

These reactions were found to have several noteworthy features. Firstly, kinetic and electrochemical evidence indicated that electron transfer from 9-ArFl$^-$ to the electron acceptor occurred as the rate-limiting step. Secondly, Brønsted plots of log k vs. pK_a of 9-ArFlH gave slopes near unity, and, finally, there was no evidence for the formation of the substitution product, 9-ArFl-C(NO$_2$)R$_2$. The failure of the latter to be produced in the reaction of 9-ArFl$^-$ with R$_2$C(NO$_2$)$_2$ was puzzling since it could be formed either by a chain process (eq 3–5) or as a cross product in the coupling of the 9-ArFl· and R$_2$CNO$_2$· radicals formed by eq 7 and 8. (Coupling of these radicals is a possible source of the symmetrical dimers shown in eq 6.)

$$\text{9-ArFl}^- + R_2C(NO_2)_2 \rightarrow \text{9-ArFl}\cdot + R_2C(NO_2)_2^{-}\cdot \quad (7)$$

$$R_2C(NO_2)_2^{-}\cdot \rightarrow R_2CNO_2\cdot + NO_2^- \quad (8)$$

Coupling of radicals is known to approach the diffusion-controlled rate limit unless the radicals are sterically hindered and delocalized (i.e., "persistent"), like the triphenylmethyl radical.[10] The 9-ArFl· radical is likely to be persistent, but the R$_2$CNO$_2$· radical (R$_2$ = Me$_2$ or cyclohexyl) is not. If the (9-ArFl)$_2$ dimer (eq 6) is formed by coupling of 9-Ar-Fl· radicals, as seems likely,[9] why does this radical not couple also with the R$_2$CNO$_2$· radical, which is presumed to be the radical source of the (R$_2$CNO$_2$)$_2$ dimer in eq 6? Also, why do 9-ArFl$^-$ carbanions not react with R$_2$CNO$_2$· radicals to produce 9-ArFlC(NO$_2$)R$_2$ products by a chain mechanism, as is know to happen with carbanions derived from malonic ester, β-cyano esters, β-cyano ketones, and malononitrile?[11] The reaction scheme outlined below appeared to offer an answer to these questions.

First let us assume that the R$_2$CNO$_2$· radical formed via eq 7 and 8 is rapidly scavenged by 9-ArFl$^-$ anion to produce R$_2$C=NO$_2^-$ anion and ArFl· (eq 9). (A reaction of this type has been proposed earlier without experimental evidence.[8]) The R$_2$C=NO$_2^-$ anion thus produced could then also scavenge the R$_2$CNO$_2$· radical (eq 10). As a consequence, R$_2$CNO$_2$· radicals would never be present in high enough concentration to couple with the ArFl· radical which is also present in low concentration.

$$\text{9-ArFl}^- + R_2CNO_2\cdot \xrightarrow{\text{fast}} \text{9-ArFl}\cdot + R_2C{=}NO_2^- \quad (9)$$

$$R_2C{=}NO_2^- + R_2CNO_2\cdot \xrightarrow[(-e)]{\text{fast}} (R_2CNO_2)_2 \quad (10)$$

(via a chain reaction[12])

$$\text{9-ArFl}\cdot + \text{9-ArFl}\cdot \rightarrow (\text{9-ArFl})_2 \quad (11)$$

Additional experiments have now been carried out that strongly support this proposed reaction sequence (eq 7–11).

Results and Discussion

Formation of Cyclohexanenitronate Ion from 9-Phenylfluorenyl Carbanion and 1,1-Dinitrocyclohexane (c-C$_6$H$_{10}$(NO$_2$)$_2$). The key step in the proposed reaction sequence in eq 7–11 is the formation of R$_2$C=NO$_2^-$ in eq 9. When the concentration of this anion builds up sufficiently, it can compete with 9-PhFl$^-$ for R$_2$CNO$_2$· radicals and generate the (R$_2$CNO$_2$)$_2$ dimer by a chain sequence.[12]

$$R_2C{=}NO_2^- + R_2CNO_2\cdot \rightleftarrows (R_2CNO_2)_2^{-}\cdot \quad (12)$$

$$(R_2CNO_2)_2^{-}\cdot + R_2C(NO_2)_2 \rightarrow (R_2CNO_2)_2 + R_2C(NO_2)_2^{-}\cdot \quad (13)$$

$$R_2C(NO_2)_2^{-}\cdot \rightarrow R_2CNO_2\cdot + NO_2^- \quad (14)$$

If this scheme is correct we would expect to find the R$_2$C=NO$_2^-$ anion among the products. This expectation was verified by experiment. When the reaction of the 9-PhFl$^-$ anion was carried out with 63% of 1 equiv of c-C$_6$H$_{10}$(NO$_2$)$_2$, 55% of the nitrocyclohexyl moiety was found as the (c-C$_6$H$_{10}$NO$_2$)$_2$ dimer and 35% as the c-C$_6$H$_{10}$=NO$_2^-$ anion. Under these conditions the 9-PhFl$^-$ and c-C$_6$H$_{10}$=NO$_2^-$ anions are evidently competing about equally for the c-C$_6$H$_{10}$NO$_2$· radical. This is understandable since they are of exactly the same basicity in Me$_2$SO.[13] Why, then, does one of these reactions lead to a chain reaction while the other does not? The answer may be that a radical anion intermediate is formed reversibly in each instance, but the radical anion generated from 9-PhFl$^-$ and c-C$_6$H$_{10}$NO$_2$· has a second mode of decomposition (compare eq 12 and 15). If the equilibria in eq 15 lie to the right, a lower concentration of radical anion will be present and this may not be sufficient to propagate the chain.

$$\text{9-PhFl}^- + c\text{-}C_6H_{10}NO_2\cdot \rightleftarrows (\text{9-PhFl-}c\text{-}C_6H_{10}NO_2)^{-}\cdot \rightleftarrows \text{9-PhFl}\cdot + c\text{-}C_6H_{10}{=}NO_2^- \quad (15)$$

Since 9-PhFl$^-$ and c-C$_6$H$_{10}$=NO$_2^-$ anions have the same basicity, the position of the equilibria in eq 15 will depend on the relative reactivities of the radicals. We conclude that the 9-PhFl· radical is less reactive than the c-C$_6$H$_{10}$NO$_2$· radical, which causes the equilibria in eq 15 to shift to the right. In the reaction of the 9-PhFl$^-$ anion with Me$_2$C(NO$_2$)$_2$ the equilibria comparable to those shown in eq 15 will be shifted farther to the right, since the basicity of the Me$_2$C=NO$_2^-$ anion is 1 pK unit lower than that of the 9-PhFl$^-$ anion.[13] Presumably here too the concentration of the radical-anion intermediate is too low to permit chain propagation.

Reactions of Fluorenyl Anions with α,p-Dinitrocumene (α,p-DNC). The failure of the 9-PhFl$^-$ anions to react with R$_2$CNO$_2$· radicals to form radical anions in sufficient concentration to propagate a chain was attributed in the previous section to rapid decomposition of the radical anion to 9-PhFl· and R$_2$C=NO$_2^-$. It was of interest in this connection to examine the reaction of 9-PhFl$^-$ anion with p-NO$_2$C$_6$H$_4$C(CH$_3$)$_2$NO$_2$ (α,p-DNC). The reaction sequence expected if a chain reaction results is that shown in eq 16–19.

$$\text{9-PhFl}^- + \alpha,p\text{-DNC} \rightarrow \text{9-PhFl}\cdot + \alpha,p\text{-DNC}^{-}\cdot \quad (16)$$

$$\alpha,p\text{-DNC}^{-}\cdot \rightarrow \alpha,p\text{-NC}\cdot + NO_2^- \quad (17)$$

$$\text{9-PhFl}^- + \alpha,p\text{-NC}\cdot \rightarrow \text{9-PhFl-}\alpha,p\text{-NC}^{-}\cdot \quad (18)$$

$$\text{9-PhFl-}\alpha,p\text{-NC}^{-}\cdot + \alpha,p\text{-DNC} \rightarrow \text{9-PhFl-}\alpha,p\text{-NC} + \alpha,p\text{-DNC}^{-}\cdot \quad (19)$$

The question here is whether the (9-phenylfluorenyl)-p-nitrocumyl radical anion 9-PhFl-α,p-NC$^{-}\cdot$, will be present in large enough concentration to propagate the chain (eq

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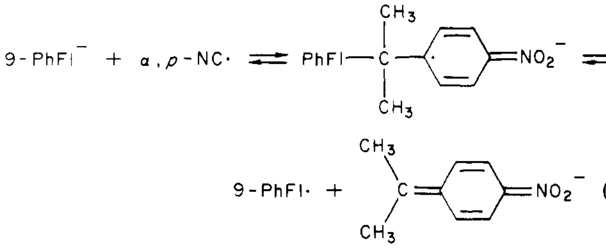
[10] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *8*, 13–19.

[11] Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1968**, *90*, 347–353. Russell, G. A.; Norris, R. K.; Panek, E. J. *Ibid.* **1971**, *93*, 5839–5845.

[12] Kornblum, N.; Boyd, S. D.; Stuchal, F. W. *J. Am. Chem. Soc.* **1970**, *92*, 5783–5784. Kornblum, N.; Boyd, S. D. *Ibid.* **1970**, *92*, 5784–5785.

[13] Both 9-PhFlH and c-C$_6$H$_{11}$NO$_2$ have pK_a values of 17.9 in Me$_2$SO; that of Me$_2$CHNO$_2$ is 16.9 (see Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3113–3116).

17–19) or whether its decomposition to 9-PhFl· (eq 20) will deplete its concentration to a point where a chain sequence is not viable.



(20)

Experiment showed that the reaction of 9-PhFl$^-$ with α,p-DNC occurred rapidly to give an essentially quantitative yield of p-$NO_2C_6H_4C(CH_3)_2$-Fl-Ph (9-PhFl-α,p-NC; eq 21). A similar result was obtained with 9-PhSFl$^-$ (eq 22).

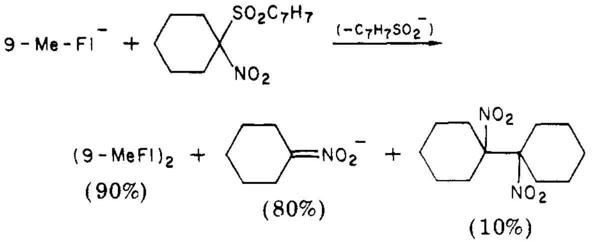
$$\text{9-PhFl}^- + \alpha,p\text{-DNC} \rightarrow \text{9-PhFl-}\alpha,p\text{-NC} + NO_2^- \qquad (21)$$

$$\text{9-PhSFl}^- + \alpha,p\text{-DNC} \rightarrow \text{9-PhSFl-}\alpha,p\text{-NC} + NO_2^- \qquad (22)$$

As will be brought out shortly, there is evidence that the products formed in eq 21 and 22 result from a chain sequence (e.g., eq 16–19). This indicates that either the p-nitrocumyl carbanion is not formed in eq 20 or that it is formed reversibly. The equilibria shown in eq 20 are likely to be shifted to the left, relative to those in eq 15, since the $(CH_3)_2CC_6H_4NO_2^-$ nitronate ion in eq 20 is more basic than the c-$C_6H_{10}NO_2^-$ nitronate ion in eq 15 by about 2 pK units.[14] (The relative stabilities of the radicals, α,p-NC· and 9-PhFl·, in eq 20 are not known.) The reactions of 9-G-Fl$^-$ anions with α,p-DNC did not follow a simple rate law. This was anticipated since the reactions are occurring by a chain sequence (eq 17–19). Reactions with 9-ArFl$^-$ and α,p-DNC started immediately, but that with (the less basic) 9-PhSFl$^-$ anion had an induction period of 10–30 s. The induction period increased progressively as the basicity of the carbanion decreased: 10–30 s for 9-PhSFl$^-$ (pK_a for 9-PhSFlH = 15.4), 20–50 s for 9-(p-BrC_6H_4S)Fl$^-$ (pK_a = 14.8), 100–200 s for 2-Br-9-PhSFl$^-$ (pK_a = 13.2), and 1000–2000 s for 2,7-Br_2-9-PhSFl$^-$ (pK_a = 11.15). Also, addition of as little as 5 mol % of di-*tert*-butyl nitroxide radical, t-Bu_2NO·, caused 67% rate retardation in the reaction of α,p-DNC with 9-(p-BrC_6H_4S)Fl$^-$. The reaction of α,p-DNC with the more basic 9-(m-ClC_6H_4)Fl$^-$ anion could be similarly retarded (63%), although 125 mol % of t-Bu_2NO· was now required. (Reactions of 9-m-ClC_6H_4Fl$^-$ or 9-PhSFl$^-$ anions with c-$C_6H_{10}(NO_2)_2$ showed little or no retardation in the presence of 125 mol % of t-Bu_2NO·.)

Presumably an induction period is needed to allow time for a sufficient concentration of radicals to be produced to initiate the chains. The progressive increase in induction periods with decreasing basicity of the carbanion is consistent with an electron-transfer initiation step since we have seen that thermal electron transfers to electron acceptors are highly sensitive to carbanion basicity.[9]

Reactions of Fluorenyl Anions with 1-Nitro-(p-toluenesulfonyl)cyclohexane (c-$C_6H_{10}(NO_2)$Ts). The nitro sulfone, c-$C_6H_{10}(NO_2)$Ts, has been shown to react with c-$C_6H_{10}{=}NO_2^-$ anion to produce the (c-$C_6H_{10}NO_2)_2$ dimer.[17] Our experiments showed, however, that reactions between c-$C_6H_{10}(NO_2)$Ts and carbanions of the 9-ArFl$^-$ family were too slow at 25 °C for convenient rate measurement. Reactions in a suitable rate range did occur with the more basic 2-Br-9-MeFl$^-$ and 9-MeFl$^-$ anions, however. The sequence of reactions suggested for 9-ArFl$^-$ and c-$C_6H_{10}(NO_2)_2$ should apply here, but a different product distribution should result from the reaction of these more basic fluorenyl anions and the weaker nitro sulfone acceptor. The same nitronate ion, c-$C_6H_{10}NO_2^-$, is produced in each reaction. This anion can compete effectively with the 9-ArFl$^-$ anion for the c-$C_6H_{10}NO_2$· radical but should not be able to compete effectively with the much more basic 9-MeFl$^-$ anion. Furthermore, whereas in the reaction of 9-PhFl$^-$ anion with c-$C_6H_{10}(NO_2)_2$ an electron transfer from the [c-$C_6H_{10}(NO_2)_2]^-$· radical anion can occur to the strong 1,1-dinitro acceptor, only the weak nitro sulfone acceptor is present in the 9-MeFl$^-$ reaction. We predicted, therefore, that only a small amount of (c-$C_6H_{10}NO_2)_2$ dimer would be formed in the 9-MeFl$^-$ reaction, and that the major products would be (9-MeFl)$_2$ and c-$C_6H_{10}{=}NO_2^-$. This was verified by experiment (eq 23).



(23)

Since in this reaction formation of the (c-$C_6H_{10}NO_2)_2$ dimer has been suppressed because the c-$C_6H_{10}{=}NO_2^-$ anion fails to compete effectively with the 9-MeFl$^-$ anion, it follows that most c-$C_6H_{10}NO_2$· radicals react with 9-MeFl$^-$ to give 9-MeFl· radicals (eq 25). These radicals therefore, are being produced from 9-MeFl$^-$ by two reactions (eq 24 and 25), and only a little more than 1 equiv of electron acceptor should be required to dimerize 2 equiv of 9-MeFl$^-$. Experiment showed that 1.25 equiv of c-$C_6H_{10}(NO_2)$Ts was sufficient to dimerize 2 equiv of 9-MeFl$^-$ anion.

$$\text{9-MeFl}^- + \text{c-}C_6H_{10}(NO_2)\text{Ts} \rightarrow \text{9-MeFl}\cdot + \text{c-}C_6H_{10}(NO_2)\text{Ts}^-\cdot \qquad (24)$$

$$\text{9-MeFl}^- + \text{c-}C_6H_{10}NO_2\cdot \rightarrow \text{9-MeFl}\cdot + \text{c-}C_6H_{10}{=}NO_2^- \qquad (25)$$

Reactions of Fluorenyl Anions with 1-Cyano-1-nitrocyclohexane ($C_6H_{10}(NO_2)CN$). In earlier sections we have accounted for the failure of cross products to be formed in reactions of 9-G-Fl$^-$ carbanions with $R_2C(NO_2)X$ electron acceptors (X = NO_2 or Ts) by assuming that R_2CNO_2· radicals are transient in nature because they are scavenged rapidly by the 9-G-Fl$^-$ and $R_2C{=}NO_2^-$ anions present in the solution. The electron acceptor c-$C_6H_{10}(NO_2)CN$ offered a further opportunity to test this rationale since a different result would be expected. This electron acceptor is known to produce the c-$C_6H_{10}(NO_2)CN^-$· radical anion, which loses NO_2^- ion and gives the c-$C_6H_{10}CN$· radical. This radical should not be converted by 9-PhFl$^-$ anion to the strongly basic $C_6H_{10}CN^-$ ion, however, since the equilibrium should lie in the reverse direction (eq 26).[18] It is possible that a cross product could

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(14) The pK_a of p-$NO_2C_6H_4CH_3$ is 20.4 in Me_2SO;[15] the pK_a of p-nitrocumene is not known but is expected to be about 0.3 unit lower by analogy with the relative pK_a values of p-$PhCOC_6H_4CH_3$ (26.9[15]) and p-$PhCOC_6H_4CH(CH_3)_2$ (26.6[16]).

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(16) Drucker, G. E. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1978.

(17) (a) Zeilstra, J. J.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 954–960. (b) Kornblum, N.; Boyd, S. D.; Ono, N. *J. Am. Chem. Soc.* **1974**, *96*, 2580–2582.

Table I. Rates of Reaction of 9-G-Fl⁻ Carbanions with Electron Acceptors in Me_2SO at 25 °C

electron acceptor	G[a]	pK_a[b]	10k[e]	β[f,g]
c-$C_6H_{10}(NO)_2$	C_6H_5	17.9	175 ± 23	1.3[g]
$Me_2C(NO_2)_2$	C_6H_5	17.9	66.0 ± 8.2	1.2[g]
$PhSO_2CH_2Br$	C_6H_5	17.9	3.03 ± 0.12	1.1[g]
$PhSO_2CH_2I$	C_6H_5	17.9	2.81 ± 0.25	1.3[g]
c-$C_6H_{10}(NO_2)CN$	Me	17.7[c]	too slow	
c-$C_6H_{10}(NO_2)CN$	Me	20.0[d]	0.264 ± 0.035	
c-$C_6H_{10}(NO_2)CN$	Me	22.34	47.15 ± 2.79	0.97
c-$C_6H_{10}(NO_2)SO_2C_7H_7$	Me	17.7[c]	too slow	
c-$C_6H_{10}(NO_2)SO_2C_7H_7$	Me	20.0[d]	0.0610 ± 0.002	
c-$C_6H_{10}(NO_2)SO_2C_7H_7$	Me	22.34	18.2 ± 0.9	1.06
$Me_2C(NO_2)SO_2C_7H_7$	Me	17.7[c]	too slow	
$Me_2C(NO_2)SO_2C_7H_7$	Me	20.0[d]	0.0526 ± 0.0012	
$Me_2C(NO_2)SO_2C_7H_7$	Me	22.34	14.3 ± 0.4	1.04
$PhSO_2CH_2Cl$	Me	22.34	0.14 ± 0.01	

[a] In 9-G-Fl⁻. [b] In Me_2SO at 25 °C. [c] 2,7-Br_2-9-MeFlH. [d] 2-Br-9-MeFlH. [e] $M^{-1}\ s^{-1}$. [f] Slope of the Brønsted plot. [g] See ref 9; it is doubtful that β values exceed 1.0 (see text).

be formed if the radical anion formed in eq 27 has sufficient lifetime to propagate a chain.

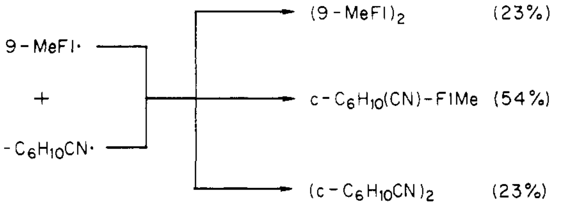
$$9\text{-MeFl}^- + \text{c-}C_6H_{10}CN\cdot \rightleftarrows 9\text{-MeFl}\cdot + C_6H_{10}CN^- \quad (26)$$

$$9\text{-MeFl}^- + \text{c-}C_6H_{10}CN\cdot \rightleftarrows 9\text{-MeFl-c-}C_6H_{10}CN^{-}\cdot \quad (27)$$

Alternatively, if 9-MeFl· and c-$C_6H_{10}CN$· radicals are formed in equal amounts and at comparable rates, a nearly statistical distribution of dimer coupling products should result.[21] This is essentially what was observed. Equations 28–30 are therefore sufficient to account for the results.

$$9\text{-MeFl}^- + \text{c-}C_6H_{10}(CN)NO_2 \xrightarrow{\text{slow}} 9\text{-MeFl}\cdot + \text{c-}C_6H_{10}(CN)NO_2^{-}\cdot \quad (28)$$

$$\text{c-}C_6H_{10}(CN)NO_2^{-}\cdot \xrightarrow{\text{fast}} \text{c-}C_6H_{10}CN\cdot + NO_2^- \quad (29)$$



(30)

The reaction sequence 28–30 differs from that for 9-MeFl⁻ reacting with c-$C_6H_{10}(NO_2)Ts$ in that there is only one step where 9-MeFl⁻ is converted to 9-MeFl·. The sequence therefore predicts that 1 equiv of the electron acceptor, c-$C_6H_{10}(NO_2)CN$, will be needed to dimerize each equivalent of 9-MeFl⁻. In practice, it was observed spectroscopically that >95% of c-$C_6H_{10}(NO_2)CN$ was required to cause complete disappearance of one equivalent of 9-MeFl⁻ carbanion.

It is noteworthy that the less basic anion is lost preferentially from $R_2C(NO_2)X^{-}\cdot$ radical anions, i.e., $C_7H_7SO_2^- \gg NO_2^- \gg CN^-$.[24] The relative stabilities of the radical fragments, c-$C_6H_{10}NO_2$·, c-$C_6H_{10}CN$·, and c-$C_6H_{10}SO_2Ar$·, are not known.

Kinetics. In the reactions between 9-ArFl⁻ carbanions and the electron acceptors, $R_2C(NO_2)X$, described in the previous sections it has been suggested that electron transfer from the carbanion to the acceptor is rate limiting. The kinetics were followed by observing the change in absorbance of the 9-G-Fl⁻ anion reacting with 5–50-fold excess of electron acceptor under pseudo-first-order conditions. Variation of acceptor concentrations showed that in each instance the reactions were first order in donor and acceptor.

With $R_2C(NO_2)_2$ acceptors the proposed reaction scheme (eq 7–14) assumes that the R_2CNO_2· radical will be formed in steady-state concentrations. At the beginning of the reaction the R_2CNO_2· radical will be scavenged immediately by the 9-Ar-Fl⁻ anion, which is present in high concentration. The reaction should then follow the rate law shown in eq 31. After about 2 half-lives, deviation from first-order behavior was observed in that the rate of disappearance of 9-ArFl⁻ decreased. This is consistent with increasing competition between the 9-ArFl⁻ and $R_2C{=}NO_2^-$ ions for the R_2CNO_2· radical as the concentration of 9-ArFl⁻ decreases and that of $R_2C{=}NO_2^-$ builds up (eq 9).

$$-d[9\text{-ArFl}^-]/dt = 2k[9\text{-ArFl}^-][R_2C(NO_2)_2] \quad (31)$$

In the reaction of 9-MeFl⁻ (or 2-Br-9-MeFl⁻) with $R_2C(NO_2)Ts$ the proposed reaction scheme suggests that the $R_2C{=}NO_2^-$ ion, because of its relatively low basicity, will not be able to compete effectively with 9-MeFl⁻ ion for the R_2CNO_2· radical. The reaction should then follow a simpler rate law (eq 32) without much deviation from first-order behavior. In practice, good first-order behavior was observed for as much as 4 half-lives.

$$-d[9\text{-MeFl}^-]/dt = k[9\text{-MeFl}^-][R_2C(NO_2)Ts] \quad (32)$$

In the reaction of 9-MeFl⁻ (or 2-Br-9-MeFl⁻) with $R_2C(NO_2)CN$ we would expect from the proposed reaction scheme that pseudo-first-order kinetics would be observed well beyond 2 half-lives since there is no evidence to in-

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(18) The pK_a of c-$C_6H_{11}CN$ in Me_2SO has not been measured but is likely to be above 33, judging from the pK_a of 31.3 for CH_3CN[19] and the deacidifying effect of alkyl substitution on $CH_2(CN)_2$.[20]

(19) 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.

(20) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3095–3101.

(21) Me_2CCN· radical is reported to dimerize at the diffusion-controlled limit,[22] but the more highly delocalized $(CN)_3C$· radical decays at a considerably slower rate.[23]

(22) Ray, J. C.; Williams, R. R.; Nach, J. R.; Harnill, W. A. *J. Am. Chem. Soc.* **1956**, *78*, 519–521.

(23) Kaba, R. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 523–526.

(24) The pK_a values in Me_2SO for p-$CH_3C_6H_4SO_2H$ (O–H acidity) and HCN (C–H acidity) are 7.4[25] and 12.9,[26] respectively. The comparison should be made between S–H, C–H, and N–H acidities, however, since it is S–C, C–C, and N–C bonds that are being broken. The acidities of the H–$SO_2C_7H_7$ and H–NO_2 acids are unknown, but the acidity order is no doubt H–$SO_2C_7H_7$ ≫ H–NO_2 ≫ H–CN. For example, the pK_a values of H–SC_6H_5, H–NHC_6H_5, and H–$CH_2C_6H_5$ in Me_2SO are 10.2, 30.7, and ~42, respectively.

dicate that the 9-MeFl$^-$ anion can convert the c-$C_6H_{10}CN\cdot$ radical to the corresponding carbanion (eq 26). Nevertheless, deviation form first-order behavior was observed after about 2 half-lives, the rate of disappearance of 9-MeFl$^-$ decreasing in much the same manner as with the $R_2C(NO_2)_2$ acceptor. This suggests that 9-MeFl$^-$ is disappearing by a second route as the reaction enters into its later stages. It is possible, therefore, that in later stages of the reaction formation of the radical anion via eq 27 and formation of 9-MeFl-*c*-$C_6H_{10}CN$ by a chain sequence may achieve some importance.

Brønsted β Values for Electron Transfer Reactions. In our preliminary communication we reported Brønsted β values of near unity for electron-transfer reactions between 9-Ar-Fl$^-$ anions and four electron acceptors, $PhSO_2CH_2Br$, $PhSO_2CH_2I$, $Me_2C(NO_2)_2$, and c-$C_6H_{10}(NO_2)_2$.[9] These studies have now been extended to three additional electron acceptors, $Me_2C(NO_2)Ts$, c-$C_6H_{10}(NO_2)Ts$, and c-$C_6H_{10}(NO_2)CN$ (Table I).

The β values reported in Table I are not of high precision for several reasons. Firstly, the unit slope means that the rate changes by an order of magnitude for each change of 1 p*K* unit in basicity. This high sensitivity of rate to basicity limits the range of basicities that can be studied by our kinetic method. For example, the three members of the 9-MeFl$^-$ family cover a basicity range of 4.6 p*K* units, corresponding to $10^{4.6}$ in rates. As a consequence, rates with only two of the family bases are in a convenient range for rate measurements with nitro sulfone and nitro nitrile electron acceptors (Table I). With 1,1-dinitro electron acceptors three-point β values could be obtained, but here the rates show larger standard deviations because the reaction course changes (see the section on kinetics). We believe that the most reliable β values are those obtained using the $PhSO_2CH_2Br$, $Me_2C(NO_2)Ts$, and c-$C_6H_{10}(NO_2)Ts$ electron acceptors where the β values are 1.1, 1.04, and 1.06, respectively. These reactions could be followed well beyond 2 half-lives and the standard deviations in the rate constants were ±5% or less. We conclude from these and other results[27] that *a β of unity is characteristic of electron transfer from carbanions to electron acceptors in Me_2SO solution.* This conclusion is of interest since, although linear free-energy relationship are commonly observed in plots of log *k* vs. one-electron oxidation (or reduction) potentials of donors (or acceptors), the slopes are considerably less than unity.[29,30] This has provoked some discussion.[29,31]

The observation of $\beta = 1.0$ lends itself to a simple interpretation if we assume that formation of the initial donor-acceptor complex, $D + A \rightleftarrows D\cdots A$, is followed by irreversible electron transfer. For example, we can assume that in the reaction 9-Ar-Fl$^-$ with $PhSO_2CH_2X$ the electron is transferred from the carbanion donor into an antibonding orbital of the C–X bond with the formation of a three-electron bond, which can be represented as a "half bond" (eq 33).[32] This bond is stabilized by the presence of an electron-withdrawing function on carbon.[33] The $PhSO_2$ group therefore plays a dual role in the reaction, on the one hand sterically discouraging "backside approach" to carbon, which would lead to an S_N2 reaction, and on the other hand encouraging "frontside approach" to the halogen and transfer of an electron from the carbanion to the C–X bond (eq 33). The $\beta = 1$ corresponds to complete electron transfer in the transition state.

$$\text{9-ArFl}^- + \text{X–CH}_2\text{SO}_2\text{Ph} \rightarrow$$
$$\text{9-ArFl}\cdot + [\text{X}\dot{-}\text{CH}_2\text{SO}_2\text{Ph} \leftrightarrow \dot{\text{X}}\cdot\dot{\text{C}}\text{H}_2\text{SO}_2\text{Ph}]^- \quad (33)$$

According to FMO theory there must be a proper energy matchup between the HOMO of the donor and the LUMO of the acceptor. Experiment shows that at room temperature in Me_2SO this is achieved with a 9-*m*-$ClC_6H_4Fl^-$ donor and a $PhSO_2CH_2X$ acceptor where X is Br or I.[9] When we change to the 9-$C_6H_5Fl^-$ donor, which is 1.1 p*K* units more basic ($\Delta G° = 1.5$ kcal/mol), the $\beta = 1.0$ requires that the HOMO–LUMO energy gap (ΔG^*) be decreased by a like amount. (Note that the basicity of 9-ArFl$^-$ anion is changed by remote substitution so that steric effects, as well as solvent effects, are kept constant.) This interpretation is supported by the observation that the relative reduction potentials (irreversible) of $PhSO_2CH_2X$, with X = I, Br, and Cl (–0.5, –0.6, and –1.5 V, respectively), correlate at least roughly with the relative rates ($k^I \simeq k^{Br}$ <<sor 10^6k^{Cl}). Also, the oxidation potentials for 9-ArFl$^-$ anions (Ar = *m*-ClC_6H_4, C_6H_5, and *p*-MeC_6H_4) plot linearly with pK_a of 9-ArFlH (in kilocalories/mole) with a slope near unity.[34]

Comparison of the rate data (Table I) shows that the relative rates for 9-PhFl$^-$ reacting with the electron acceptors $PhSO_2CH_2I$, $PhSO_2CH_2Br$, $Me_2C(NO_2)_2$, and c-$C_6H_{10}(NO_2)_2$ are (1.0), 1.1, 23.5, and 62, respectively. Extrapolation, assuming $\beta = 1.0$, shows that 9-Me-Fl$^-$, which is 4.4 p*K* units more basic, should react with these electron acceptors about 3×10^4 times faster. The observed rate for 9-MeFl$^-$ reacting with $PhSO_2CH_2Cl$ (Table I) is, therefore, almost 10^6 slower than the extrapolated rate for $PhSO_2CH_2Br$. The relative rates for $R_2C(NO_2)X$ reacting with 9-MeFl$^-$ anions (observed or extrapolated) are as follows: $Me_2C(NO_2)SO_2C_7H_7$ (1.0) < c-$C_6H_{10}(NO_2)SO_2C_7H_7$ (1.3 < *c*-$C_6H_{10}(NO_2)CN$ (3.3) < $Me_2C(NO_2)NO_2$ (1.8×10^6) < c-$C_6H_{10}(NO_2)NO_2$ (4.8×10^6). These data suggest that the LUMOs in the 1,1-dinitro electron acceptors are at energy levels about 8.5–9 kcal/mol below those of the nitro sulfone and nitro nitrile electron acceptors. ($PhSO_2CH_2Br$ and $PhSO_2CH_2I$ are slightly weaker electron acceptors than $R_2C(NO_2)_2$.) It is not clear whether the electron from the donor enters a σ^* orbital in the C–X or C–NO_2 bond or a π^* orbital in the NO_2 function in these acceptors.

Summary and Conclusions. Two 9-substituted fluorenyl carbanion families, 9-G-Fl$^-$ (G = Ar or Me), covering a basicity range of 5.5 p*K* units have been found to react in Me_2SO solution with electron acceptors of the type $PhSO_2CH_2X$ (X = Br or I) and $R_2C(NO_2)X$ (X = NO_2, SO_2Ar, or CN) by rate-determining single electron transfer. The 9-G-Fl$\cdot$ radicals produced thereby dimerize to $(\text{9-G-Fl})_2$ in a nonchain process. The rates of these reactions vary over a range of about 10^6, depending on the basicity of the carbanion and the structure of the electron acceptor. The rate differences provide a measure of rel-

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[34] We are indebted to Professor Donald E. Smith and John Begemann for assistance with the electrochemistry. Those studies will be published separately.

ative electron accepting ability. Plots of log k vs. pK_a of 9-G-FlH give Brønsted β values near unity for seven different electron acceptors. If $\beta = 1$ proves to be general for reactions of anions with electron acceptors, as seems likely,[27] this may provide a simple kinetic method for distinguishing reactions of anions with electrophiles where electron transfer is the rate-limiting step from related reactions occurring by other mechanisms. For example, reactions of delocalized carbanions, nitranions, oxanions, and thianions with $PhCH_2Cl$ in Me_2SO that occur by S_N2 mechanisms have been found to have β values of 0.30–0.52.[35] Furthermore, if we adopt the view of Pross and Shaik that electron transfer can be considered to be a principal contributor to the wave function describing the energy of the transition state for S_N2 reactions,[36] $\beta = 1.0$ may provide a benchmark by which the extent of the electron transfer contribution can be judged.

Experimental Section

General Procedures. NMR spectra were obtained with either a Varian T-60 or EM-360 spectrometer. Mass spectra were run by Ms. H. L. Hung on an HP5984 GC/MS system. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. The purification of Me_2SO and preparation of $CH_3SOCH_2^-K^+$ stock solution are described elsewhere.[19,37] Microanalyses were by Micro-Tech Laboratories, Inc., Skokie, IL.

Syntheses. The syntheses of 9-methylfluorene,[19] 2,7-dibromo-9-methylfluorene,[35] 9-(*p*-tolyl)fluorene,[38] 9-phenylfluorene,[19] 9-(*m*-chlorophenyl)fluorene,[38] 9-(phenylthio)fluorene,[19] 9-(carbomethoxy)fluorene,[19] and 9-cyanofluorene[19] have all been described elsewhere.

2-Bromo-9-methylfluorene was prepared by the method used to synthesize 2-chloro-9-methylfluorene.[35]

2-Bromo-9-(phenylthio)fluorene. 2,9-Dibromofluorene was prepared from 2-bromofluorene as previously described.[38,39] Anhydrous methanol (25 mL) and sodium (92 mg, 0.004 mol) were placed in a N_2-flushed flask. After reaction was complete the stirred solution was flushed with N_2 for a further 5 min, and thiophenol (0.45 mL, 0.0045 mol) and then 2,9-dibromofluorene (1.3 g, 0.004 mol) were added. The solution was stirred overnight under a positive pressure of N_2 and then poured into H_2O and extracted with ether. The ether extracts were washed with 2 N NaOH, H_2O, and brine, dried with $MgSO_4$, and evaporated to give a white solid. Recrystallization from ether gave 1.3 g (93%) of 2-bromo-9-(phenylthio)fluorene: mp 114–115 °C; NMR ($CDCl_3$) δ 5.1 (1 H, s), 6.9–7.5 (12 H, m); mass spectrum (70 eV), *m/e* 354 (M^+), 245. Anal. Calcd for $C_{19}H_{13}BrS$: C, 64.60; H, 3.71; Br, 22.62. Found: C, 64.60; H, 3.79; Br, 22.39.

9-[(*p*-Bromophenyl)thio]fluorene was prepared in a similar way in 87% yield from reaction of 9-bromofluorene with *p*-(bromothio)phenol. It had the following: mp 108 °C; NMR ($CDCl_3$) δ 5.2 (1 H, S), 6.9–7.4 (12 H, m); mass spectrum (70 eV), *m/e* 354 (M^+), 165.

2,7-Dibromo-9-(phenylthio)fluorene was prepared in 90% yield by the reaction of 2,7,9-tribromofluorene with thiophenol. It had the following: mp 117–118 °C; NMR ($CDCl_3$) δ 5.1 (1 H, s), 7.1 (5 H, s), 7.3 (4 H, s), 7.5 (2 H, s); mass spectrum (70 eV) *m/e* 431.9 (M^+), 353, 322.8.

2,2-Dinitropropane and 1,1-dinitrocyclohexane were prepared in 85% and 88% yields, respectively, by the method of Kaplan and Schechter.[40]

***α,p*-Dinitrocumene, 2-nitro-2-(*p*-toluenesulfonyl)propane, and 1-cyano-1-nitrocyclohexane** were kindly donated by Dr. N. Kornblum.

1-Nitro-1-(*p*-toluenesulfonyl)cyclohexane was prepared by the method of Kornblum.[41]

Bromoacetonitrile was obtained from Aldrich, distilled once, and used without further purification.

Kinetic Measurements. Preparation of Me_2SO solutions of solid compounds was carried out as described earlier.[19] The Me_2SO solution of the low-melting 1,1-dinitrocyclohexane was prepared by the method normally used for liquids.[35] The 9-G-Fl$^-$ anions were generated by addition of $CH_3SOCH_2^-K^+$ solution and rate measurements made as detailed previously.[35] It was found that the Me_2SO solutions of all the electron acceptors used in this work could be stored frozen for 2–3 weeks, giving the same results as freshly made solutions. Normally, however, the solutions were used shortly after preparation.

In the course of this work, some experiments were carried out which required slight modifications of the general kinetic measurement technique.

Trapping experiments performed on the reactions of 9-*m*-ClC_6H_4-Fl$^-$ anion and 9-*p*-BrC_6H_4S-Fl$^-$ anion with *α,p*-dinitrocumene were carried out in the usual pseudo-first-order way[35] except that a calculated amount of a freshly prepared Me_2SO solution of *t*-$Bu_2NO\cdot$ was added to the 9-G-Fl$^-$ anion solution. The absorbance of the 9-G-Fl$^-$ anion was not affected even when the *t*-$Bu_2NO\cdot$ was present at higher concentrations. The solution was left to equilibrate for 15 min, excess of *α,p*-dinitrocumene added, and the reaction monitored in the usual way.

Several mechanistic probes were made by running reactions in which the electron acceptor was present in concentrations equal to or less than that of the 9-G-Fl$^-$ anion. These runs were treated as second-order reactions and the ratio of initial electron-acceptor concentration to initial 9-G-Fl$^-$ anion concentration was calculated as described earlier.[35] The reactions were run initially with ~50% equivalent of electron acceptor and allowed to proceed until the 9-G-Fl$^-$ anion absorbance had completely levelled off, at which time a little more electron acceptor was added and the reaction allowed to proceed until the 9-G-Fl$^-$ anion absorbance levelled off once more. This process was continued until zero absorbance had been reached, which was taken as the equivalence point. This method was used to study the reactions of 9-PhFl$^-$ anion with $PhSO_2CH_2Br$, of 9-Me-Fl$^-$ anion with c-$C_6H_{10}(NO_2)(SO_2C_7H_7)$, and of 9-Me-Fl$^-$ anion with c-$C_6H_{10}(NO_2)_2$.

General Product Study Procedure. A stronger stock solution of $CH_3SOCH_2^-K^+$ (200–800 mM) was used for product study work than for kinetic work. It was prepared in the usual way[19] except 3–8 times the amount of potassium hydride was used. At these concentrations the solutions of $CH_3SOCH_2^-K^+$ are pale yellow.

A Me_2SO solution of 1 mM of 9-G-fluorene was made up in the usual way. One equivalent of $CH_3SOCH_2^-K^+$ was added from the stock solution and deprotonation occurred rapidly to generate the 9-G-Fl$^-$ anion. An amount of electron acceptor solution was then added such that it was just sufficient to react with all the 9-G-Fl$^-$ anion. The solution was stirred until the anion color disappeared and then poured into H_2O (50 mL) and extracted with ether (3 × 50 mL). The combined extracts were washed with H_2O, dried with $MgSO_4$, and evaporated to give the crude product mixture. An NMR spectrum was then taken, and since the mixture usually consisted of only two compounds each with a charateristic NMR absorbance, the relative amounts could be ascertained to within ±10%. The product mixture was then absorbed onto silica gel (Grade 950, mesh size 60–200), and the products were separated by column chromatography. Hexane used for column chromatography was purified by distillation over $CaSO_4$. Mallinckrodt anhydrous ether was used directly from its container. Unless otherwise stated, an 80–90% material balance was obtained.

Reactions of Nitro Electron Acceptors with 9-G-Fl$^-$ Anions. The product mixture from reaction of 1 equiv of 9-Ph-Fl$^-$ anion with 63% of 1 equiv of 1,1-dinitrocyclohexane was separated by elution with 98% hexane/2% ether to give $(9\text{-Ph-Fl})_2$ and with 93% hexane/7% ether to give 1,1′-dinitro-1,1′-bicyclohexane, mp 216 °C, identical with an authentic sample prepared as described previously.[42] However, this accounted for only 55% of the ni-

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trocyclohexyl material. A further 35% was found as the cyclohexane nitronate anion in the aqueous layer by the following procedure. The aqueous layer was treated with a 50–100-fold excess of buffered solution made of equimolar amounts of sodium acetate and acetic acid in H_2O and stirred rapidly for several min. Ether (AR grade) was added and stirring continued for a further 15 min. The ether layer was then collected and the aqueous layer extracted twice more with AR ether. The combined extracts were washed with saturated $NaHCO_3$ solution and then brine and dried with $MgSO_4$. After careful removal of ether by distillation, nitrocyclohexane remained as a pale-yellow liquid identical by NMR with an authentic sample.[42]

To test the efficiency of this process, we dissolved 100 mg of $c\text{-}C_6H_{10}NO_2^-K^+$ in 50 mL of H_iO and treated the solution with buffered acid as described above. This led to isolation of 92% of the original nitrocyclohexyl anion as nitrocyclohexane. This technique was less successful in extracting the 2-nitropropyl anion from H_2O. In a similar test only 15% of the theoretical amount was recovered as 2-nitropropane. This explained the low material balance (<50%) of nitro compound obtained from product studies involving 2,2-dinitropropane and 2-nitro-2-(*p*-toluenesulfonyl)propane.

The product mixture of reaction between 9-Ph-Fl$^-$ and 2,2-dinitropropane led to isolation of $(9\text{-Ph-Fl})_2$ by elution with 98% hexane/2% ether and 2,3-dinitro-2,3-dimethylbutane by elution with 93% hexane/7% ether. The latter had the following: mp 214 °C (lit.[43] mp 210–212 °C); NMR ($CDCl_3$) δ 1.7 (s); it accounted for only 45% of the nitropropyl moiety.

The reaction between 9-PhS-Fl$^-$ anion and 1 equiv of α,*p*-dinitrocumene led to an essentially quantitative yield of substitution product. Recrystalization from ethanol gave 9-(phenylthio)-9-*p*-nitrocumyl)fluorene as white crystals: mp 197 °C; NMR ($CDCl_3$) δ 1.6 (s, 6 H), 6.4 (m, 5 H), 6.8 (M, 12 H); mass spectrum (70 eV), *m/e* 437 (M^+) 273, 164. Anal. Calcd for $C_{28}H_{23}NO_2S$: C, 76.89; H, 5.30; N, 3.20. Found: C, 76.78; H, 5.33; N, 3.08.

Similarly, the reaction of 9-Ph-Fl$^-$ with 1 equiv of α,*p*-dinitrocumene gave 9-phenyl-9-(*p*-nitrocumyl)fluorene as white crystals: mp 158–159 °C; NMR ($CDCl_3$) δ 1.3 (s, 3 H), 1.7 (s, 3 H), 6.7–7.5 (m, 17 H); mass spectrum (70 eV), *m/e* 405 (M^+), 241, 164.

The product mixture resulting from reaction of 9-Me-Fl$^-$ anion with 65% of 1 equiv of 1-nitro-1-(*p*-toluenesulfonyl)cyclohexane was adsorbed onto a silica gel column and separated by elution with 95% hexane/5% ether to give $(9\text{-MeFl})_2$ and with 90% hexane/10% ether to bring through 1,1′-dinitro-1,1′-bicyclohexane. Nitrocyclohexane was formed by treating the aqueous layer as above.

The product mixture obtained from reaction between 9-Me-Fl$^-$ anion and 1 equiv of 1-cyano-1-nitrocyclohexane required elution with 95% hexane/5% ether to bring through 9-methyl-9-(cyanocyclohexyl)fluorene as a colorless oil: NMR ($CDCl_3$) δ 6.4–7.1 (m, 8 H), 0.7–2.5 (m, 13 H); mass spectrum (70 eV), *m/e* 287 (M^+), 179, 108. Elution with 93% hexane/7% ether gave a mixture which on further chromatography was resolved into $(9\text{-MeFl-})_2$ by elution with 95% hexane/5% ether and 1,1′-dicyano-1,1′-bicyclohexane, mp 223–224 °C (lit.[44] mp 224–225 °C) by elution with 93% hexane/7% ether. Dimethyl-9,9′-bifluorene, $(9\text{-Me-Fl})_2$ had the following: mp 207–208 °C (lit.[45] mp 209–210 °C); NMR ($CDCl_3$) δ 1.7 (6 H, s), 6.4–7.3 (16 H, m); mass spectrum (70 eV), *m/e* 358 (M^+, 1.1) 179 (9-MeFl$^+$, 100).

The reaction of 9-CO_2Me-Fl$^-$ anion with 1 equiv of bromoacetonitrile led to only one product. Recrystallization from ethanol gave 9-(carbomethoxy)-9-(cyanomethyl)fluorene as white crystals: mp 124–125 °C; NMR ($CDCl_3$) δ 3.1 (s, 2 H), 3.6 (s, 3 H), 7.1–7.5 (m, 8 H); mass spectrum (70 eV), *m/e* 263 (M^+), 204. Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.56; H, 4.98; N, 5.32. Found: C, 77.42; H, 5.04; N, 5.31.

Acknowledgment. We are indebted to Professor Nathan Kornblum and Allen S. Erickson not only for their sage advice but also for supplying us with samples of several electron acceptors. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for financial support. One of us (F.G.B.) expresses appreciation to the John Simon Guggenheim Memorial Foundation for a fellowship.

Registry No. 9-(*p*-BrC_6H_4S)Fl$^-$, 73838-77-4; 2-Br-*9*-PhSFl$^-$, 73838-76-3; 2,7-Br_2-9-PhSFl$^-$, 81245-84-3; 9-(*m*-ClC_6H_4)Fl$^-$, 73872-45-4; 9-(*p*-MeC_6H_4)Fl$^-$, 42730-14-3; 9-Ph-Fl$^-$, 31468-22-1; 9-PhS-Fl$^-$, 71805-72-6; α,*p*-DNC, 3276-35-5; 9-Me-Fl$^-$, 31468-21-0; 9-CO_2Me-Fl$^-$, 12565-94-5; $BrCH_2CN$, 590-17-0; *c*-$C_6H_{10}(NO_2)_2$, 4028-15-3; $Me_2C(NO_2)_2$, 595-49-3; $PhSO_2CH_2Br$, 19169-90-5; $PhSO_2CH_2I$, 65492-21-9; *c*-$C_6H_{10}(NO_2)CN$, 58102-55-9; *c*-$C_6H_{10}(NO_2)SO_2C_7H_7$, 41774-12-3; $Me_2C(NO_2)SO_2C_7H_7$, 21272-86-6; $PhSO_2CH_2Cl$, 7205-98-3; 2,7-Br_2-9-MeFl$^-$, 73872-46-5; 2-Br-9-MeFl$^-$, 81255-42-7.

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