and NMR was obtained. All attempts at crystallization were unsuccessful: IR ($CHCl_3$) 3700–3300 (br), 2950–2800 (br), 1725 cm^{-1}; ^1H NMR ($CDCl_3$), composite of Table I and Table II; EIMS m/e (relative intensity) 317 (M^+, 0.6), 148 (10), 139 (15), 138 (89), 135 (22), 105 (17), 94 (42), 93 (100), 80 (24), 77 (17), 57 (44); CIMS m/e (relative intensity) 318 ($M^+ + 1$, 83), 138 (100); high-resolution MS, molecular ion m/e 317.1524, calcd. for $C_{18}H_{23}NO_4$ 317.1628.

9-*O*-[(±)-2-Hydroxy-2-phenylbutyryl]retronecine *N*-Oxide (2a). To a solution of 0.974 g (3.07 mmol) of **2** in 3.75 mL of ethanol was added 1.0 mL of 30% hydrogen peroxide. This mixture was kept at 4 °C in a refrigerator for 2 days. The excess peroxide was destroyed by the addition of MnO_2. The solution was then filtered and the solvent removed in vacuo, leaving a colorless viscous oil. The presence of *N*-oxide was determined by using a Mattocks test.[18] TLC on silica gel with 10% methanol/$CHCl_3$ as the solvent showed a single spot at R_f 0.47 as compared to R_f 0.59 for the free alkaloid. This difference in R_f of 0.1 is typical for pyrrolizidine alkaloid *N*-oxides:[1] ^1H NMR ($CDCl_3$) characteristic peaks δ 0.85 (br t, 3 H, J = 5.0 Hz), 4.69 (br s, 2 H), 5.51 (br s, 1 H), 7.29 (br m, 3 H), 7.47 (br m, 2 H); EIMS m/e (relative intensity) 165 (1), 155 (4), 138 (22), 136 (22), 135 (100), 117 (23), 106 (12), 105 (49), 104 (12); CIMS m/e (relative intensity) 318 (M + 1, 36), 300 (11), 163 (16), 139 (13), 138 (100), 136 (14), 135 (20).

9-*O*-[(*S*)-(+)-2-Hydroxy-2-phenylbutyryl]retronecine (5). A solution of 1,1'-carbonyldiimidazole (0.218 g, 1.35 mmol) and (+)-2-hydroxy-2-phenylbutyric acid (0.212 g, 1.29 mmol) in 15 mL of dry $CHCl_3$ under an argon atmosphere was stirred for 15 min to allow for the complete evolution of CO_2. To this was then added retronecine (0.2058 g, 1.33 mmol), and the solution was stirred for 20 h at room temperature. The $CHCl_3$ was washed with 10 mL of saturated $NaHCO_3$. The aqueous layer was extracted with 10 mL of $CHCl_3$, and the combined $CHCl_3$ extracts were dried ($MgSO_4$), filtered, and reduced in vacuo, leaving 0.3844 g (94%) of a colorless viscous oil: ^1H NMR ($CDCl_3$) see Table I; IR ($CHCl_3$) 3650–3400, 3100–2800, 1725 cm^{-1}; $[\alpha]^{20}_{589}$ +4.6° (c 2.19, MeOH); EIMS m/e (relative intensity) 317 (M^+, 2), 139 (18), 138 (95), 136 (14), 135 (32), 105 (11), 94 (41), 93 (100), 80 (26); CIMS m/e (relative intensity) 318 ($M^+ + 1$, 44), 300 (11), 139 (13), 138 (100), 136 (16), 135 (20); high-resolution MS, molecular ion m/e 317.1588, calcd. for $C_{18}H_{23}NO_4$ 317.1628.

9-*O*-[(*R*)-(−)-2-Hydroxy-2-phenylbutyryl]retronecine (6). The reaction was carried out exactly as described for **5** except that (−)-2-hydroxy-2-phenylbutyric acid was used: ^1H NMR ($CDCl_3$) see Table II; $[\alpha]^{20}_{589}$ + 6.0° (c 3.16, MeOH); EIMS exactly the same as for **5**; high-resolution MS, molecular ion m/e 317.1660, calcd. for $C_{18}H_{23}NO_4$ 317.1628.

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Registry No. (±)-**2a**, 81340-07-0; **3**, 480-85-3; **4**, 315-22-0; (+)-(*S*)-**5**, 81340-08-1; (−)-*R*-**6**, 81370-87-8; (+)-2-hydroxy-2-phenylbutyric acid, 24256-91-5; (−)-2-hydroxy-2-phenylbutyric acid, 3966-31-2.

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Stabilization of Carbanions by Polarization of Alkyl Groups on Nonadjacent Atoms

Frederick G. Bordwell,* George E. Drucker, and Gregory J. McCollum

Chemistry Department, Northwestern University, Evanston, Illinois 60201

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Equilibrium acidities in dimethyl sulfoxide solution have been found to increase along the series Me, Et, *i*-Pr, *t*-Bu for 9-substituted fluorenes when the alkyl group, R, is separated from the fluorene ring by a CH_2, S, or SO_2 moiety. This is a reversal of the effect observed when R is attached directly to the fluorene ring. Separation of the *t*-Bu group from the fluorene ring by a second CH_2 moiety causes the acidifying effect to disappear. A stabilizing, through-space polarization of the alkyl group by the negative charge of the carbanion center is identified as the source of the acid-strengthening effect. Evidence is presented which shows that alkyl groups on nonadjacent carbon atoms stabilize proximate carbanions and thereby may cause acid-strengthening effects also in 9-(2,4,6-trimethylphenyl)fluorene, 9-[(2-methylphenyl)thio]fluorene, 9-[(2-methylphenyl)sulfonyl]fluorene, (alkylthio)acetonitriles, (*tert*-butylsulfonyl)acetonitrile, bis(*tert*-butylthio)phenylmethane, bis(alkylsulfonyl)methanes, alkylthio alkyl sulfoxides, *tert*-butyl methyl sulfone, and *tert*-butyl benzyl sulfone. α-Phenylthio groups are shown to cause substantially larger acidity increases than α-methylthio groups when substituted for a hydrogen atom at the acidic site of fluorene, acetonitrile, or methyl phenyl sulfone. Evidence is presented to show that this is not due to a polarizability effect of phenyl per se, but may be due to enhancement of the polarizability of sulfur by phenyl.

Stabilization of alkoxide ions in the gas phase increases along the series MeO^-, EtO^-, *i*-PrO^-, *t*-BuO^- because the alkyl groups become better able to stabilize the negative charge by polarization as they increase in size.[1,2] These effects dictate the acidity order MeOH < EtOH < *i*-PrOH < *t*-BuOH in the gas phase. In solution this acid-strengthening polarizability effect is overshadowed by other effects. For example, in the dipolar nonhydroxylic solvent dimethyl sulfoxide the acidity decreases progressively along the series MeOH, EtOH, *i*-PrOH, *t*-BuOH by a total of about 2.4 pK_a units.[3] Here the acidity order is believed to be dictated primarily by a progressive decrease in specific solvation of the alkoxides with increasing size of the alkyl group, augmented by an electron-releasing

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inductive destabilization effect.[2]

For nitroalkanes, RCH_2NO_2, acidities in solution also decrease as the size of the alkyl groups increases along the series Me, Et, *i*-Pr, *t*-Bu. In Me_2SO solution the decrease from Me to *t*-Bu is 1.4 pK_a units, and in 50% $MeOH/H_2O$ it is 1.8 pK_a units.[4] Analysis of alkyl effects for these carbon acids is complicated by their small size and variable nature and by the necessity of considering the effect of alkyl substitution on both the stability of the undissociated acid and its conjugate base. A similar order of acidities for this alkyl series has been observed for 9-alkylfluorenes, 9-R-FlH. In Me_2SO/H_2O there is a decrease in acidity from Me to *t*-Bu of 1.6 pK_a units,[5a] in cyclohexylamine the decrease is 2.0 (ion pair) pK_a units,[5b] and in Me_2SO it is 2.0 pK_a units.[6] If we assume the stabilizing (or destabilizing) effect will be larger in the anion than in the neutral acid, the factors that ordinarily may contribute to this order include progressive changes of the following types:[4] (a) an increase in steric inhibition of solvation (acid weakening), (b) an increase in polar (inductive) electron release (acid weakening), (c) a decrease in hyperconjugation (acid weakening), and (d) an increase in polarizability (acid strengthening). A progressive increase in restrictions to bond rotations causes an additional acid-weakening effect in 9-alkylfluorenes. Examination of space-filling molecular models shows that the methyl group in the 9-Me-Fl^- anion fits snugly between the peri hydrogen atoms in the 1- and 8-positions of the fluorene ring but is free to rotate. On the other hand, the methyl group in the 9-$MeCH_2$-Fl^- anion must protrude in front of the fluorene ring and rotation around the Et–C bond is impeded by the peri hydrogen atoms. Rotations around the *i*-Pr–C and *t*-Bu–C bonds are further restricted and so too are rotations around the Me–C bonds in these groups. Restrictions of bond rotations also occur along this series in the neutral acids, 9-R-FlH, but these restrictions are enhanced in the anions and could cause a progressive decrease in acidity.

When the R group in 9-R-FlH is separated from the fluorene ring by an additional group, i.e., 9-RCH_2-FlH, there is a striking reversal in the effects of R. Now, the change along the series Me, Et, *i*-Pr, *t*-Bu results in a progressive *increase* in acidity in Me_2SO solution.[7] Instead of a 2.0 pK_a unit decrease in acidity from Me to *t*-Bu, there is a 2.3 pK_a unit increase. Remarkably similar effects were observed for changes in R for 9-(alkylthio)fluorenes and for 9-(alkylsulfonyl)fluorenes (Table I). For 9-RS-FlH the increase in acidity from Me to *t*-Bu is 2.1 units and for 9-RSO_2-FlH it is 2.2 units. Furthermore, the size of the progressive increases are similar, i.e., 0.41, 0.61, and 1.27 for 9-RCH_2-FlH, 0.50, 0.62, and 0.97 for 9-RS-FlH, and 0.46, 0.61, and 1.14 for 9-RSO_2-FlH.

The interposition of CH_2, S, or SO_2 between R and the fluorene would be expected to diminish two of the acid-weakening effects, the polar effect of R and hyperconjugation. Examination of space-filling molecular models shows, however, that steric inhibition of solvation should increase since R is now required to lie close to the face of the carbanion center. Indeed, when R = *t*-Bu, one side of the carbanion center will be screened completely from the solvent. Apparently, because of its close proximity to the carbanion center, the *t*-Bu group can exert an internal solvation effect large enough not only to compensate for exclusion of the Me_2SO solvent but also to overshadow other destabilizing effects on the anions. This internal solvation effect increases with increasing size of R along the series Me, Et, *i*-Pr, *t*-Bu, leading to a progressive increase in acidity.

Table I. Equilibrium Acidities in Dimethyl Sulfoxide Solution for 9-R and 9-RX Fluorenes

	pK_a,[a] 9-substituted fluorene			
alkyl group	R[c]	RCH_2[c]	RS[c,e]	RSO_2[c,e]
Me	22.34	22.62	18.00	12.76
Et	22.62	22.21	17.50	12.30
i-Pr	23.18	21.60	16.88	11.69
t-Bu	24.35	20.33	15.91	10.55
neoPent	20.33	22.53		12.53
c-hexyl			16.90	
1-Ad[b]			16.05	
$C_6H_5CH_2$	21.36	22.06	17.22	
C_6H_5	17.92	21.36	15.40	11.55
o-MeC_6H_4	18.78[d]		15.30	11.23
p-MeC_6H_4	18.32[d]		15.71	
2,4,6-$Me_3C_6H_2$	18.55[d]		17.40	12.38

[a] Average of measurements made by two three-point titrations, each against two or three standard acids or indicators; standard deviations were ±0.05 or less. [b] 1-Adamantyl. [c] Unless otherwise noted the pK_a values for these compounds have been reported in ref 6 and 7. [d] See the Experimental Section. [e] See Table III for the physical properties of these compounds.

At one time we considered as an alternative explanation the possibility that the acid-strengthening alkyl effects might be caused by steric relief of strain in forming the anion.[7] A study of the models reveals that the 9-*t*-$BuCH_2$-FlH molecule is crowded and that there are some restrictions to rotation around both the *t*-Bu–CH_2 and CH_2–FlH bonds. In the anion the restrictions to rotation around the *t*-Bu–CH_2 bond are largely removed, but this effect is balanced by a sharp increase in the restriction to rotation around the CH_2–Fl^- bond. In 9-$EtCH_2$-FlH there is no crowding and there is free rotation around both the Et–CH_2 and CH_2–FlH bonds. In the anion, however, there is restricted rotation around the CH_2–Fl^- bond. Here the steric argument predicts that the change from CH_3 to $EtCH_2$ will cause a decrease in acidity rather than the 0.13 pK_a unit increase observed. This interpretation is therefore ruled out.

We have now examined the effect of further changes in the structure of R on the acidities of fluorenes to test the polarizability interpretation and have also sought and found similar effects in open-chain analogues.

Results and Discussion

Alkyl Stabilization of Fluorenyl Anions by Polarizability Effects. The results reported previously for 9-CH_2-, 9-RS-, and 9-RSO_2-substituted fluorenes with R equal to Me, Et, *i*-Pr, and *t*-Bu are reproduced in Table I. Acidity data for other 9-substituted fluorenes have been added in order to test the effect of (a) interposing an additional CH_2 moiety between the *t*-Bu group and the fluorene nucleus, (b) increasing the bulk of R, (c) MeS vs. PhS, and (d) *o*-methyl substitution in the benzene rings of 9-Ph, 9-PhS, and 9-$PhSO_2$ substituents.

The change from 9-*t*-$BuCH_2$-FlH to 9-*t*-$BuCH_2CH_2$-FlH increases the bulk and polarizability of R but at the same time moves the *t*-Bu group farther from the carbanion center in the fluorenyl anion. The result is a 2.2 pK_a unit decrease in acidity. Now the acid-strengthening effect of this more remote *t*-Bu group is *less* than that of a com-

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parable methyl group, i.e., 9-*t*-BuCH$_2$CH$_2$-FlH is 0.3 pK_a unit less acidic than 9-MeCH$_2$CH$_2$-FlH. Nearly the same result, a 2.0 pK_a unit decrease in acidity, is observed on interposing an additional CH$_2$ moiety between *t*-Bu and SO$_2$ in 9-*t*-BuSO$_2$-FlH. Once again the *t*-Bu effect becomes less than that of Me, i.e., 9-*t*-BuCH$_2$SO$_2$-FlH is a weaker acid than 9-MeCH$_2$SO$_2$-FlH by 0.23 unit. Proximity of the *t*-Bu group to the carbanion center is clearly an essential feature of its acid-strengthening effect. This is consistent with polarizability being the dominant factor since such effects are known to fall off rapidly with distance.[2]

Examination of Table I shows that 9-PhS-FlH is more acidic than 9-MeS-FlH by 2.6 pK_a units. Is this marked increase caused by polarization of phenyl? We think not. Replacement of Me by Ph will increase the inductive effect, but this effect will be relatively small. If the difference is due to a polarizability effect, the same difference should be observed for replacing Me by Ph in the carbon analogue. Instead, we see by examining Table I that the difference in acidities between 9-MeCH$_2$-FlH and 9-PhCH$_2$-FlH is only 1.26 pK_a units. This is about the difference we would expect for an inductive effect. Interposing another CH$_2$ group between Ph and the fluorene ring causes the Ph effect to decrease to 0.7 (compare 9-PhCH$_2$CH$_2$-FlH with 9-MeCH$_2$CH$_2$-FlH). Again this is the order of magnitude one would expect for an inductive effect. We conclude that polarization of phenyl is not a significant factor here and that polarization of phenyl per se is not a significant factor in causing PhS to be more strongly acidifying than MeS.

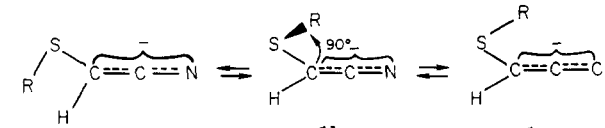
The conclusion that it is the proximity of the group rather than its bulk that is the more important factor is supported by the results with 9-(cyclohexylthio)fluorene and 9-(1-adamantylthio)fluorene. We see that c-C$_6$H$_{11}$S-FlH has an acidity comparable to 9-*i*-PrS-FlH. Evidently the five methylene carbon atoms in the cyclohexyl ring can provide no more stabilization to the 9-c-C$_6$H$_{11}$S-Fl$^-$ anion than the two methyl groups in 9-*i*-PrS-Fl$^-$. Also, the adamantyl group, C$_{10}$H$_{16}$, in 9-(1-AdS)-FlH, despite its greater bulk, has about the same acidifying effect as the *t*-Bu group in 9-*t*-BuS-FlH (Table I). Branching of the alkyl group should have an effect e.g., *t*-BuS-FlH should be more acidic than BuS-FlH or *sec*-BuS-FlH, but this point has not been tested experimentally.

Comparison of the acidity data in Table I for 9-C$_6$H$_5$-FlH, 9-*p*-MeC$_6$H$_4$-FlH, and 9-*o*-MeC$_6$ H$_4$-FlH shows that *p*-Me caused a 0.40 acidity decrease and *o*-Me a 0.86 unit decrease. The *p*-Me effect is attributable to destabilization of the anion by polar electron release. There is no evidence for stabilization of the anion by the *o*-methyl group. This is not surprising since examination of models shows that the *o*-Me group restricts rotation around the Ar–C bond, causing an increase in the dihedral angle between the plane of the benzene ring and that of the fluorene ring. The resulting steric inhibition of resonance evidently overshadows any acid-strengthening effect of the *o*-Me group. This is likely to be small in any event since, even in the most favorable conformation, the methyl group is not as close to the carbanion center as is the Me group in the 9-MeCH$_2$-Fl$^-$ anion. In the 9-(2,4,6-Me$_3$C$_6$H$_2$)-Fl$^-$ anion the two *o*-Me groups require the plane of the benzene ring to be essentially orthoganol to that of the fluorene ring. Despite the additional steric inhibition of resonance in the anion and the presence of the acid-weakening *p*-Me group 9-(2,4,6-Me$_3$C$_6$H$_2$)-FlH is a *stronger* acid than 9-(2-MeC$_6$H$_4$)-FlH by 0.23 pK_a unit. This could be due to the stabilization of the anion by the two *o*-Me groups that are now fixed above and below the p orbitals of the carbanion. Steric relief of strain in forming the anion may provide an important acid-strengthening effect here, however, since examination of models shows that the mesityl group is even more crowded in the acid than in its anion.

Substitution of an *o*-methyl group into 9-C$_6$H$_5$S-FlH causes a 0.10 pK_a unit increase in acidity. Examination of molecular models shows that there is severe restriction of rotation around the S–Fl bond in the 9-C$_6$H$_5$S-Fl$^-$ anion but not around the C$_6$H$_5$–S bond. Introduction of the *o*-methyl group causes little in the way of further restrictions. Rotation around the 2-MeC$_6$H$_4$–S bond in the 9-(2-MeC$_6$H$_4$S)-Fl$^-$ anion can position the methyl group either near or far from the carbanion center and a combination of rotations around the Ar–S and S–Fl bonds can position the methyl group over either one or the other of the two lobes of the carbanion p orbital. Perhaps the stabilizing polarizability effect of the *o*-methyl group operative in some conformations is balanced by a destabilizing polar effect operative in others. Introduction of an additional *o*-methyl and a *p*-methyl group results in about a 2 pK_a unit decrease in acidity. The models show that the second *o*-methyl group greatly increases restriction to bond rotations. Evidently the favored conformations of the 9-(2,4,6-Me$_3$C$_6$H$_2$S)-FlH$^-$ anion are those in which the Me groups are exerting destabilizing polar effects on the anion. Similar effects are observed in the 9-(arylsulfonyl)fluorenes. Here a single *o*-methyl group causes a 0.32 pK_a unit acidity increase, but the three methyl groups in 9-(2,4,6-Me$_3$C$_6$H$_2$SO$_2$)-FlH cause an 0.83 unit acidity decrease.

Polar and Polarizability Effects of Alkyl Groups on Acidities of Open-Chain Carbon Acids. In the previous section we have seen that alkyl groups in 9-substituted fluorenes can cause sizable acid-strengthening effects when restrictions of bond rotations require the alkyl group to be in close proximity to one of the p orbitals of the carbanion. It was of interest to see whether similar effects could be observed in open-chain analogues where steric restrictions to rotations are much less severe.

The (alkylthio)acetonitriles, RSCH$_2$CN, appeared to offer a good testing ground for alkyl effects since, although the charge in RSCHCN$^-$ carbanions is delocalized to nitrogen, there is reason to believe that the charge density on carbon is relatively high compared to, say, that on carbon in an *aci*-nitroalkane or enolate ion.[6] The alkyl group can adopt a variety of orientations relative to the carbanion as in conformations **1a–1c**.



1a **1b** **1c**

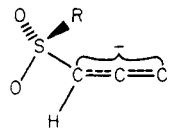
In conformation **1b** the R group is placed directly over the face of the carbanion, an orientation required in 9-RS-Fl$^-$ anions. Examination of Table II reveals that the acidities of RSCH$_2$CN compounds increase as R changes along the series Me, Et, *i*-Pr, *t*-Bu in the same manner as for 9-RS-FlH compounds. The acidity increase from Me to *t*-Bu for RSCH$_2$CN compounds is 1.40 pK_a units, not as large as for 9-RS-FlH compounds (2.09 units), but there is a progressive increase in ΔpK_a along the series (0.30, 0.38, 0.72) just as there is in the 9-RS-FlH series, i.e., 0.50, 0.62, 0.97. We conclude that here too the alkyl groups are exerting an acid-strengthening effect by virtue of their ability to stabilize RSCHCN$^-$ anions by polarization. In this series, however, the acidity when R is 1-adamantyl is near that of MeSCH$_2$CN rather than that of *t*-BuSCH$_2$CN. Evidently the bulky adamantyl group dictates a confor-

Table II. Acidities of (Alkylthio)- and (Alkylsulfonyl)acetonitriles and of Bis(alkylsulfonyl)methanes and Related Compounds

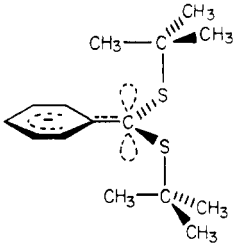
compd	pK_a[a]	compd	pK_a[a]
$MeSCH_2CN$	24.26		
$EtSCH_2CN$	23.96	$MeSCH_2SOMe$	29.0
i-$PrSCH_2CN$	23.58	$EtSCH_2SOEt$	28.7
t-$BuSCH_2CN$	22.86	t-$BuSCH_2SO$-t-Bu	18.0 ± 0.1
1-$AdSCH_2CN$	23.31	$MeSO_2CH_3$	31.1
$PhSCH_2CN$	20.85	t-$BuSO_2CH_3$	30.3 ± 0.2
$MeSO_2CH_2CN$	13.58	$MeSO_2CH_2Ph$	25.39
t-$BuSO_2CH_2CN$	12.79	t-$BuSO_2CH_2Ph$	24.88
$PhSO_2CH_2CN$	12.04	$CH_2(CN)_2$	11.08
$(PrS)_2CHC_6H_5$	29.18	$MeCH(CN)_2$	12.44
$(t$-$BuS)_2CHC_6H_5$	27.46	t-$BuCH(CN)_2$	13.22
$(MeSO_2)_2CH_2$	15.01	p-$MeC_6H_4CH_2CN$	22.88
$(EtSO_2)_2CH_2$	14.42	p-t-$BuC_6H_4CH_2CN$	22.65
$(i$-$PrSO_2)_2CH_2$	14.10	$C_6H_5CH_2CN$	21.91
$(t$-$BuSO_2)_2CH_2$	13.70	p-$MeC_6H_4CH_2SO_2Ph$	24.11
		p-t-$BuC_6H_4CH_2SO_2Ph$	24.05
		$C_6H_5CH_2SO_2Ph$	23.43

[a] pK_a values given with four significant figures are averages of runs against two indicators and have standard deviations of less than ±0.05 unit. Other pK_a values have standard deviations of ±0.05 unit unless otherwise noted.

mation for the 1-AdSCHCH$^-$ anion where its polarizability effect is diminished (e.g., **1a**). Comparison of the acidities of $MeSO_2CH_2CN$ and t-$BuSO_2CH_2CN$ shows an effect similar to that for $MeSCH_2CN$ vs. t-$BuSCH_2CN$, but the polarizability effect is less (0.79 pK_a unit vs. 1.40 units). This may be due in part to the larger C–S bond angle in conformation **2b** of the tetrahedral sulfone function (~109°) than in conformation **1b** of the sulfide function (~90°) and in part to the greater inherent polarizability of sulfur in the sulfide vs. sulfone function.



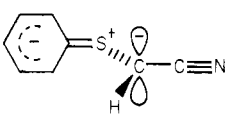
2b



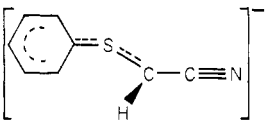
3

Comparison of the acidities of $(PrS)_2CHC_6H_5$ and $(t$-$BuS)_2CHC_6H_5$ reveals that here too the larger polarizability of t-Bu than Pr causes an appreciable increase in acidity (ΔpK_a = 1.72). The effect is larger than that in $RSCH_2CN$ compounds (ΔpK_a = 1.10 for t-Bu vs. Et) despite the extensive delocalization of the negative charge into the benzene ring. This suggests that the preferred conformation is one where the t-Bu groups are positioned at each lobe of the p orbital of the carbanion, as in **3**.

(Phenylthio)acetonitrile is more acidic than (methylthio)acetonitrile by 3.41 pK_a units. Similarly, $PhSCH_2SO_2Ph$ is more acidic than $MeSCH_2SO_2Ph$ by 3.10 pK_a units.[8] In an earlier section we pointed out a similar effect for 9-PhS-FlH vs. 9-MeS-FlH (ΔpK_a = 2.6) and addressed the question of how much of this difference is due to the inductive effect of Ph vs. Me and how much, if any, might be due to a polarizability effect. Comparison showed that in the carbon analogues, 9-$PhCH_2$-FlH and 9-$MeCH_2$-FlH the acidity difference was smaller (ΔpK_a = 1.26). It was concluded that this is about the size expected from the difference in inductive effects of Ph vs. Me. This conclusion can be supported by a Taft analysis of the data for $PhSCH_2CN$ vs. $MeSCH_2CN$. By using a two-point Taft plot derived from the pK_a values for $Me_3{}^+NCH_2CN$ vs. $MeCH_2CN$, we can estimate $\rho_I \simeq 17$ for this substrate.[8] Multiplying ρ_I by the difference in σ_I values of Ph and Me (0.14) gives 2.4 pK_a units, which is the acid-strengthening effect of Ph vs. Me if the groups were attached directly at the acidic site. This pK_a difference can be expected to be reduced by at least one-half by the intervening sulfur atom (larger "fall-off" factors than 2 are commonly used). The maximum enhancement due to the inductive effect of Ph is thus calculated to be 1.2 pK_a units in $PhSCH_2CN$, leaving 2.2 pK_a units to be accounted for in some other way. A similar calculation for $PhSCH_2SO_2Ph$ leaves 1.9 pK_a units to be accounted for. These enhancements may be due to a polarizability effect or a conjugative effect. We have seen that Ph in PhS does not exert a polarizability effect per se and that R in RS does not enhance the polarizability of S, but it is possible that Ph may enhance the polarizability of S by virtue of its ability to delocalize its electrons (**4a**). It is difficult, however, to distinguish a polarizability effect of this kind from some kind of a conjugative effect, which may be represented by **5a**.



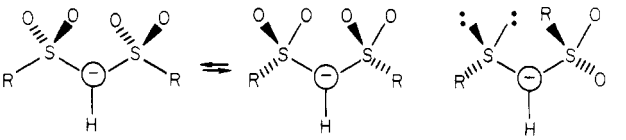
4a



5a

The Ph group in $PhSO_2CH_2CN$ enhances the acidity by 1.5 pK_a units relative to the Me group in $MeSO_2CH_2CN$. This is probably not significantly different from the 1.2 unit difference calculated for the difference in Ph and Me inductive effects. We conclude that the Ph group does not enhance the polarizability or conjugative ability of the sulfone function.

The alkyl groups in the anions derived from bis(alkylsulfonyl)methanes, $(RSO_2)_2CH_2$, or alkylthio alkyl sulfoxides, $RSCH_2SOR$, can also assume various conformations, e.g., **6a**, **6b**, and **7**. In these structures the circles represent the p orbitals of the carbanions, the lobes of which protrude out and back from the plane of the paper.



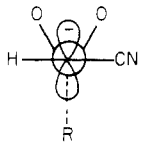
6a **6b** **7**

Conformations **6b** and **7**, where the each R group is positioned near to one of the lobes of the carbanion p orbital, appear to be most favorable to the maximization of the polarizability effects of the alkyl groups. These polarizability effects do appear to be important since the acidities of $(RSO_2)_2CH_2$ compounds increase progressively as R is changed along the series Me, Et, i-Pr, t-Bu. The acidity increase from Me to t-Bu is 1.31 pK_a units, which compares with 1.40 observed in the $RSCH_2CN$ series, but in the bis sulfones the effect is larger between Me and Et (0.59) than between Et and i-Pr (0.32) or i-Pr and t-Bu (0.40). The polarization effects of R in $RSCH_2SOR$ are slightly smaller than those in $(RSO_2)_2CH_2$ (ΔpK_a for Me vs. t-Bu = 1.0 compared to 1.3).

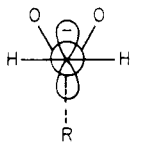
Polarizability effects are evident also for RSO_2CH_3 and RSO_2CH_2Ph acids, but the effects are small, like those for

(8) Bordwell, F. G.; Van Der Puy, M.; Vanier, N. R. *J. Org. Chem.* **1976**, *41*, 1885–1886. In this paper we estimate $\rho_I \cong 14.5$ for G-CH_2CN; more recent data support a $\rho_I \cong 17$.

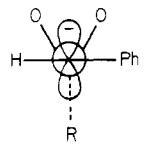
RSO_2CH_2CN (ΔpK_a for Me vs. *t*-Bu = 0.8, 0.5, and 0.8, respectively). In an earlier paper we have summarized evidence that shows that α-sulfonyl carbanions are planar and exist preferentially in a conformation in which the p orbital of the carbanion is flanked by the oxygen atoms of the sulfonyl group, as in **8**, **9**, and **10**.[9] In these drawings the circle represents the sulfur atom.



8a $(RSO_2CHCN)^-$

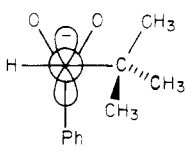


9a $(RSO_2CH_2)^-$

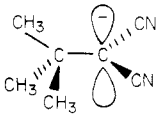


10a $(RSO_2CHPh)^-$

In **8a**, **9a**, and **10a** with R = *t*-Bu, the methyl groups on *t*-Bu can rotate directly into the bottom lobe of the p orbital of the carbanion. Polarization of these methyl groups is the source of the anion stabilization that gives rise to the acid-strengthening effect of *t*-Bu. These *t*-Bu effects contrast sharply with the acid-weakening effects of *t*-Bu vs. Me observed when the R group is attached directly at the acidic site, as in RCH_2SO_2Ph or $RCH(CN)_2$, rather than on a nonadjacent atom (Table II). In the anions derived from RCH_2SO_2Ph or $RCH(CN)_2$ acids the methyl groups in *t*-Bu are directed nearly parallel to the p orbital of the carbanion, as shown in **11a** and **12a**. In



11a



12a

this orientation the polarizability effects are small and are evidently completely overshadowed by acid-weakening polar and solvation effects since changing R from H to Me causes a 1.36 pK_a unit decrease in acidity in $RCH(CN)_2$, and replacement of Me by *t*-Bu causes a further 0.78 unit decrease.[10] The results with alkyl malononitriles can be considered to be analogous to those obtained with the alcohols, ROH.[1,2] The $[RC(CN)_2]^-$ carbanions are relatively small compared to, say, fluorenyl carbanions and are therefore much more subject to specific solvation effects. The change from Me to *t*-Bu causes a larger decrease in acidity for the oxygen acid (ROH) than for the carbon acid (2.4 pK_a units vs. 0.78 pK_a unit in Me_2SO) because specific solvation effects are stronger at the more electronegative oxygen atom.

The acidities of p-$RC_6H_4CH_2CN$ and p-$RC_6H_4CH_2SO_2Ph$ compounds given in Table II allow a comparison of the effect of Me vs. *t*-Bu groups situated para to the carbanion center. Here the polarizability effect should be diminished appreciably since the negative charge density on the adjacent ring carbon is relatively low and the orientation of the methyl groups in *t*-Bu with respect to this carbanion center is unfavorable. We see that p-$MeC_6H_4CH_2CN$ is a weaker acid than $C_6H_5CH_2CN$ by 0.97 pK_a unit and that p-*t*-$BuC_6H_4CH_2CN$ is weaker by 0.74 unit; for the p-$RC_6H_4CH_2SO_2Ph$ series the corresponding ΔpK_a values are 0.68 and 0.62 unit, respectively. These differences in *p*-Me and *p*-*t*-Bu effects are within, or only slightly outside, the experimental errors in the measurements and the size of the acid-weakening effects is about that expected for an electron-releasing polar effect for R. There is no evidence for a polarizability effect.

Summary and Conclusions

Evidence has been presented to show that alkyl groups separated from a C–H acidic site by a CH_2, S, or SO_2 moiety increase its acidity in the order Me < Et < *i*-Pr < *t*-Bu. The effects range in size for *t*-Bu vs. Me from 0.5 to 2.4 pK_a units in Me_2SO solution. The acid-strengthening effects are attributed to a through-space stabilization of the carbanion by the alkyl group. These polarizability effects are particularly strong in 9-substituted fluorenes because of conformational restrictions, but they occur also in open-chain substrates such as $RSCH_2CN$. It seems likely that stabilization of an anion, A^-, by a polarizable group, G, separated from A^- by a methylene group, as in GCH_2A^-, or by a like moiety, such as S, SO_2, Se, O, should be a general phenomenon in solution. These polarizability effects are relatively weak, however, being of the order of 3 kcal/mol, or less, when G is an alkyl group. As such, they are often overshadowed by other effects and have hitherto been largely overlooked in solution.[2] In fact, they may be difficult to observe in hydroxylic solvents because of strong specific solvation of A^- by hydrogen bonding. We anticipate that additional examples will be forthcoming in dipolar nonhydroxylic solvents,[11] but even in these solvents alkyl polarizability effects may be overshadowed by acid-weakening alkyl effects of steric or electrostatic origin, as is evident from the acidity order $HCH(CN)_2$ > $MeCH(CN)_2$ > *t*-$BuCH(CN)_2$, which prevails in both Me_2SO and H_2O solution. Polarizability effects of R groups one atom removed from the carbanionic center are much more effective at stabilizing carbanions in solution, for geometric reasons, than are R groups attached directly to the carbanion center. It seems likely that polarization of the H–C bonds in the alkyl group by the carbanion center, i.e., $C^-\cdots H^{\delta+}-C^{\delta-}$, may be the principal stabilizing factor. This electrostatic representation is equivalent to stabilization by hydrogen bonding between the carbanion and the alkyl group suggested by Schlosser to account for the high *Z*/*E* ratio at equilibrium for $CH_3CH{=}CHCH_2K$ (*Z*/*E* = 96/4 in hexane, 99.2/0.8 in THF) and for $CH_3CH_2CH{=}CHCH_2K$ (*Z*/*E* = 94.6 in hexane).[16]

Experimental Section

Equilibrium acidity measurements were carried out by the method described earlier.[6]

9-Alkylfluorenes were prepared by three methods: (a) direct alkylation,[17] (b) alkylation of 9-(methoxycarbonyl)fluorene followed by saponification and decarboxylation,[18] and (c) reaction

(9) Bordwell, F. G.; Branca, J. C.; Johnson, C. R.; Vanier, N. R. *J. Org. Chem.* **1980**, *45*, 3884–3889.

(10) Similar results were obtained in the RCH_2SO_2Ph series where pK_a values with R = H, Me, Et, *i*-Pr, and *t*-Bu of 29.0, 31.0, 31.0, 30.7, and 31.2, respectively, have been observed in Me_2SO solution. The latter four results probably have standard deviations of ±0.3 pK_a unit or more, however, since they are in a high pK_a range where measurements are difficult, and they were made at an early stage in the development of our pK_a scale. It is clear, nevertheless, that the *t*-Bu group does not have an acid-strengthening effect and there is no evidence for a polarizability effect here.

(11) We have observed evidence for acid-strengthening polarizability effects for *o*-Me and *o*-*t*-Bu groups in phenols in Me_2SO solution.[12]

(12) Olmstead, W. N.; Stark, M. E., unpublished results.

(13) The order and very existence of polar electron release from alkyl groups in anions is still a matter of controversy. Ritchie pointed out several years ago that σ^* for all alkyl groups and for hydrogen can be considered to be zero in many Taft plots.[14] Recent analyses, including gas-phase data, have supported electron release for R vs. H in the original order, i.e., *t*-Bu > Et > Me,[2] but a recent statistical analysis of solution data supports the assignment of a zero polar effect to R.[15]

(14) Ritchie, C. D. *J. Phys. Chem.* **1961**, *65*, 2091–2093.

(15) DeTar, D. F. *J. Org. Chem.* **1980**, *45*, 5166–5174.

(16) Schlosser, M.; Hartmann, *J. Am. Chem. Soc.* **1976**, *98*, 4674–4676. This study differs from ours, however, in that K^+ is intimately associated with the carbanion and may influence the equilibrium position.

(17) Murphy, W. S.; Hauser, C. R. *J. Org. Chem.* **1966**, *31*, 85–88.

(18) Anet, F. A.; Bavin, P. M. G. *Can. J. Chem.* **1956**, *34*, 991–1005.

Table III. Physical Properties for Sulfides and Sulfones in Tables I and II

compd[a]	mp (or bp/mm), °C	NMR spectral data (δ relative to Me_4Si)
9-EtSFlH	46.5-47[e]	0.90 (3 H, t), 1.96 (2 H, q), 4.88 (1 H, s), 7.2-7.8 (8 H, m)
9-*i*-PrSFlH	63-63.5	0.96 (6 H, d), 2.32-2.80 (1 H, m), 4.84 (1 H, s), 7.1-7.9 (8 H, m)
9-*t*-BuSFlH[b]	133.5-135	1.42 (9 H, s), 4.76 (1 H, s), 7.1-7.8 (8 H, m)
9-$PhCH_2$SFlH	67.5-68.5[f]	3.3 (2 H, s), 5.0 (1 H, s), 7.0-8.0 (13 H, m)
9-1-AdSFlH	217-218.5	1.75 (6 H, m), 2.0 (9 H, m), 4.8 (1 H, s), 7.1-7.8 (8 H, m)
9-c-HexSFlH	66-67.5	0.8-1.7 (10 H, m), 2.2 (1 H, s), 4.9 (1 H, s), 7.0-7.8 (8 H, m)
9-*o*-MeC_6H_4SFlH	54.5-55	2.40 (3 H, s), 5.3 (1 H, s), 7.1-7.8 (12 H, m)
9-MesSFlH	102-102.5	2.3 (3 H, s), 2.4 (1 H, s), 6.9-7.7 (10 H, m)
9-$MeSO_2$FlH	187.5-188.5[g]	
9-$EtSO_2$FlH	170.5-171.5[h]	0.94 (3 H, t), 2.2 (2 H, q), 5.2 (1 H, s), 7.2-8.0 (8 H, m)
9-*i*-$PrSO_2$FlH	125-126	0.80 (6 H, d), 2.6 (1 H, m), 5.25 (1 H, s), 7.2-8.2 (8 H, m)
9-*t*-$BuSO_2$FlH[c]	166.5-167.5	0.82 (9 H, s), 5.36 (1 H, s), 7.3-8.3 (8 H, m)
9-$BuSO_2$FlH	96.5-97[i]	
9-neoPenSO_2FlH	132.5-133.5	0.9 (9 H, s), 1.95 (2 H, s), 5.05 (1 H, s), 7.1-8.0 (m)
9-*o*-$MeC_6H_4SO_2$FlH	178.0-178.5	2.35 (3 H, s), 5.45 (1 H, s), 6.9-7.8 (12 H, m)
9-MesSO_2FlH	194-195.5	
t-$BuSCH_2CN$	112.5-112.8/36[j]	1.38 (9 H, s), 3.32 (2 H, s)
i-$PrSCH_2CN$	32-40/1[k]	1.3 (6 H, d), 3.2 (1 H, m), 3.3 (2 H, s)
$EtSCH_2CN$	99-102/45[l]	1.35 (3 H, t), 2.75 (2 H, q), 3.35 (2 H, s)
1-$AdSCH_2CN$	78.0-79.0	
$(t\text{-BuS})_2CHPh$[d]	48.5-49	1.26 (18 H, s), 5.02 (1 H, s), 7.1-7.6 (5 H, m)
t-$BuSO_2CH_2CN$	140-141	1.55 (9 H, s), 3.95 (2 H, s)
$MeSO_2CH_2CN$	80.5-81.5[m]	
neoPenCH_2SO_2Ph	59-60	0.9 (9 H, s), 1.4-1.8 (2 H, m), 2.95-3.3 (2 H, m), 7.5-8.1 (5 H, m)

[a] All compounds were purified by standard methods until they gave one spot by TLC. [b] Anal. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.13. Found: C, 80.48; H, 7.05. [c] Anal. Calcd for $C_{17}H_{18}O_3S$: C, 71.30; H, 6.3. Found: C, 71.53; H, 6.34. [d] Anal. Calcd for $C_{15}H_{24}S_2$: C, 67.10; H, 9.01. Found: C, 67.24; H, 9.04. [e] Reference 20. [f] Lit.[21] mp 66-76 °C. [g] Lit.[22] mp 187.5-188.5 °C. [h] Lit. mp 168 °C. [i] Reference 23. [j] Reference 24. [k] Lit.[25] bp 88-90 °C (23 mm). [l] Lit.[26] bp 104-105 °C (50 mm). [m] Lit.[27] mp 84 °C.

of fluorene with a Grignard or alkyllithium reagent followed by hydrogenolysis of the resulting alcohol.[19] Method a was found to be satisfactory only for 9-*i*-PrFlH where dialkylation is not a serious problem. Method b was used to prepare 9-*tert*-butylfluorene.[18] Method c was found to be the best general method. It was used for 9-Me-, 9-Et-, 9-Pr-, 9-*i*-Bu-, 9-$((CH_3)_3CCH_2)$-, and 9-$((CH_3)_3CCH_2)CH_2$-substituted fluorenes. (Reaction of *i*-BuMgBr with fluorenone gave fluorenol and isobutylene, but 9-*i*-BuFlOH was obtained readily by reaction of $CH_2{=}C(Me)CH_2MgCl$ with fluorenone followed by catalytic hydrogenation.) The reduction of the 9-alkyl-9-fluorenols was carried out (after purification) by the following modification of the literature method.[19] Iodine (1 g, 0.0004 mol) and acetic acid (50 mL were stirred together in a flask fitted with a reflux condenser and dropping funnel. Hypophosphorous acid (2 mL of 50%, 0.0156 mol) was added and the mixture warmed to reflux. A solution of 1–2 g of 9-alkyl-9-hydroxyfluorenol in 10 mL of acetic acid was then added slowly to the boiling mixture over a period of 1–2 h. When addition was complete, the mixture was stirred for an additional hour, cooled, diluted with water, and extracted with hexane. The hexane layer was washed thoroughly, dried ($MgSO_4$), and evaporated to leave the 9-alkylfluorene. All 9-alkylfluorenes had NMR spectra consistent with the assigned structures and melting points agreed with literature values.[5,18]

9-(*o*-Tolyl)-, 9-mesityl-, and 9-(3,3-dimethylbutyl)fluorenes appear to be new compounds.

9-(*o*-Tolyl)fluorene was purified by crystallization from ethanol: mp 92–94.5 °C; NMR ($CDCl_3$, Me_4Si) δ 1.1 (s, 1.2 H), 2.6 (s, 1.8 H), 4.9 (s, 4 H), 5.3 (s, 6 H), 6.1–7.8 (m, 12 H).

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.00; H, 6.17.

(9-Alkylfluorenes frequently give low analytical values for carbon. The present results were obtained with a Carlo Erba furnace to effect complete combustion.)

9-Mesitylfluorene was purified by column chromatography over silica gel and triturated to remove 9,9′-bifluorene: mp 85–87.5 °C; NMR ($CDCl_3$, Me_4Si) δ 1.2 (s, 3 H), 2.4 (s, 3 H), 2.7 (s, 3 H), 5.6 (s, 1 H), 6.6–7.8 (m, 10 H). The sharp methyl singlets contrast with the broad bands for the methyl and methine protons in 9-(*o*-tolyl)fluorene.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.86, H, 7.15.

9-(3,3-Dimethylbutyl)fluorene was crystallized from ethanol: mp 56–57 °C; NMR ($CDCl_3$, δ Me_4Si) 0.8–1.2 (m, 11 H), 1.85–2.3 (m, 2 H), 3.95 (t, J = 5 Hz, 1 H), 7.1–7.9 (m, 8 H).

9-(Alkylthio)- and 9-(Alkylsulfonyl)fluorenes. 9-(Alkylthio)fluorenes were prepared from 9-Br-FlH by the method of Bavin[22] and purified by crystallization until a single spot was obtained by TLC. Oxidation to sulfones was carried out with *m*-chloroperoxybenzoic acid. Melting points and NMR peaks are given in Table III.

(Alkylthio)acetonitriles were prepared from RSNa and $ClCH_2CN$ in ethanol (Table III). Oxidation with *m*-chloroperoxybenzoic acid gave the corresponding sulfones.

Bis(alkylsulfonyl)methanes and alkylthio alkyl sulfoxides were prepared by literature methods.

Acknowledgment. We are grateful to the National Science Foundation for support of this investigation. The samples of 9-(*o*-tolyl)- and 9-mesitylfluorene were synthesized by Daniel Campbell. One of us (F.G.B.) expresses his appreciation to the John Simon Guggenheim Memorial Foundation for a fellowship and to Professor Manfred Schlosser of the University of Lausanne for his hospitality during part of the period when this paper was written.

Registry No. 9-*o*-MeC_6H_4FlH, 18181-25-4; 9-*p*-MeC_6H_4FlH, 18153-43-0; 9-mesFlH, 18153-40-7; 9-MeSFlH, 59431-17-3; 9-EtSFlH, 60147-53-7; 9-*i*-PrSFlH, 60147-54-8; 9-*t*-BuSFlH, 60147-55-9; 9-c-

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

Frederick G. Bordwell* and Anthony H. Clemens

Chemistry Department, Northwestern University, Evanston, Illinois 60201

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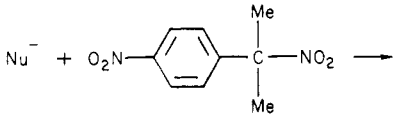
9-Substituted fluorenyl carbanions, 9-G-Fl$^-$, with G = Ar or Me, have been dimerized to (9-G-Fl)$_2$ by reaction in Me$_2$SO solution with PhSO$_2$CH$_2$X and R$_2$C(NO$_2$)X electron acceptors. Rate measurements revealed the following electron-accepting abilities: c-C$_6$H$_{10}$(NO$_2$)$_2$ > Me$_2$C(NO$_2$)$_2$ > PhSO$_2$CH$_2$Br, PhSO$_2$CH$_2$I > c-C$_6$H$_{10}$(NO$_2$)CN > c-C$_6$H$_{10}$(NO$_2$)SO$_2$C$_7$H$_7$ > Me$_2$C(NO$_2$)SO$_2$C$_7$H$_7$ > PhSO$_2$CH$_2$Cl. 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$_2$SO 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$_N$2 pathway, where the electrophile is an alkyl halide, tosylate, or the like. A second mechanism is substitution by electron transfer discovered by Kornblum,[1] where the leaving group may be chloride ion, or a more strongly basic anion, such as NO$_2^-$ (e.g., eq 1).



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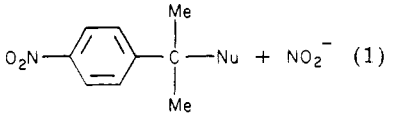

2

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$_2$C(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$_2$C(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]

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

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

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

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

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$_2$C(NO$_2$)Br in Me$_2$SO to form Fl=Fl,[8] and a variety of other carbanion and enolate ion salts have been dimerized by R$_2$C(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$_2$C(NO$_2$)$_2$ electron

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