Nucleophilic Displacements on Halogen Atoms. VII.[1] Reactions of α-Halo Sulfones with Sodium Arenesulfinates

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A Hammett correlation (using σ^- constants) for the reactions of α-bromo- and α-iodobenzyl phenyl sulfones with sodium arenesulfinates in aqueous dimethylformamide has yielded ρ values of +6.20 and +6.27, respectively. A similar study of the reactions of α-bromo- and α-iodo-*p*-cyanobenzyl phenyl sulfones with substituted sodium arenesulfinates showed that the logarithms of the second-order rate constants gave linear correlations with σ^+ constants to yield ρ values of −2.57 and −1.69, respectively. The order of reactivity in the reactions of sodium benzenesulfinate with the α-halo-*p*-nitrobenzyl phenyl sulfones is $k_{Br} > k_I \gg k_{Cl}$, but α-iodobenzyl phenyl sulfone reacts significantly faster than α-bromobenzyl phenyl sulfone with the nitrogen nucleophile 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN).

The reactions of α-halobenzyl phenyl sulfones with triarylphosphines in aqueous dimethylformamide (DMF) have been investigated in detail.[2,3] This reaction (eq 1) can be characterized as a bimolecular nucleophilic displacement by the phosphine on the halogen atom in **1** to yield a carbanion–halophosphonium ion pair (**3**) which subsequently is rapidly hydrolyzed by water to give the observed products (eq 1).

$$\underset{\mathbf{1}}{\mathrm{ArCHXSO_2Ph}} + \underset{\mathbf{2}}{\mathrm{Ar'_3P}} \xrightarrow{\text{slow}} \underset{\mathbf{3}}{[\mathrm{ArCHSO_2Ph}]^-[\mathrm{Ar'_3PX}]^+}$$

$$\xrightarrow[\mathrm{H_2O}]{\text{fast}} \underset{\mathbf{4}}{\mathrm{ArCH_2SO_2Ph}} + \mathrm{Ar'_3PO} + \mathrm{HX} \qquad (1)$$

Reaction 1 is characterized by several interesting features which distinguish it from normal nucleophilic displacement reactions: (a) k_{Br}/k_I ratios are greater than one;[2-4] (b) the Hammett ρ values associated with the reactions of triphenylphosphine with **1** correlate with σ^- constants and for X = Br and X = I are quite large (ca. +6);[2] (c) the Hammett ρ values associated with **2** in reaction 1 correlate with σ constants and for **1**, Ar = *m*-$\mathrm{CNC_6H_4}$, X = Br and I, the ρ's are ca. −3.[3] These data indicate that this reaction is very sensitive to changes in the substituents on both the nucleophile and the electrophile; this sensitivity was attributed to the high degree of bond making and bond breaking in the transition state of the first step in reaction 1.[2-4]

α-Halo sulfones react with a variety of nucleophiles in protic solvents via nucleophilic attack on the halogen atom to give the reduced sulfones **4**, but to date only triarylphosphines have been studied extensively. We now report on the kinetics of the reactions of the α-halo sulfones **1** with arenesulfinates in aqueous DMF. These reactions (eq 2) follow a pathway similar to eq 1, but in eq 2, the reaction involves nucleophilic displacement on a halogen atom by a sulfur nucleophile.

$$\underset{\mathbf{1}}{\mathrm{ArCHXSO_2Ph}} + \underset{\mathbf{5}}{\mathrm{Ar'SO_2^-}} \xrightarrow{\text{slow}}$$

$$[\mathrm{ArCHSO_2Ph}]^-\mathrm{Ar'SO_2X} \xrightarrow[\mathrm{H_2O}]{\text{fast}} \mathbf{4} + \mathrm{Ar'SO_3^-} + \mathrm{HX} \qquad (2)$$

Results and Discussion

The reactions of sodium benezenesulfinate (**5**, Ar′ = Ph) with the α-halo sulfones were run in 90% (v/v) aqueous DMF, and the rates were measured by titration for liberated halide ion. The kinetic data are given in Tables I and II. The reactions were shown to follow second-order kinetics, first order each in sulfone and benzenesulfinate. The presumed benzenesulfonyl halide intermediates were shown to react under the reaction conditions at rates much greater than those associated with the sulfones **1** (see Experimental Section). The α-chloro sulfones (**1**, X = Cl) reacted considerably slower with sodium benzenesulfinate, and only rate data for α-chloro-*p*-nitrobenzyl phenyl sulfone were determined.

A comparison of the rate data in Table II with those reported earlier for the reaction of **1** with triphenylphosphine in 90% aqueous DMF[2] shows that triphenylphosphine reacts ca. 10^2 times faster with the α-bromo sulfones and ca. 10 times faster with the α-iodo sulfones than does sodium benzenesulfinate. α-Chloro-*p*-nitrobenzyl phenyl sulfone reacts 13 times faster with triphenylphosphine than with sodium benzenesulfinate in 90% aqueous DMF at 25 °C.

Hammett $\sigma\rho$ plots of the data in Table II give good correlations with σ^- constants which is consistent with the intermediacy of a carbanion (eq 2) and agrees with the data reported previously for the reactions of **1** with triphenylphosphine.[2] The ρ values for the bromides and iodides for reaction 2 are +6.27 (r = 0.996) and +6.20 (r = 0.997), respectively. They are comparable to those ρ values reported for the reactions of **1** with triphenylphosphine: (Br) ρ = +5.97 and (I) ρ = +6.29.[2] The $\Delta H^{\ddagger}$'s for reaction 2 (see Table II) are about 6–8 kcal/mol higher than the $\Delta H^{\ddagger}$'s associated with reaction 1; however, the $\Delta S^{\ddagger}$'s are about 10–15 eu less negative for reaction 2 than reaction 1. This increase in $\Delta S^{\ddagger}$ for reaction 2 (cf. reaction 1) is expected since in reaction 1 charges are being created in the transition state (hence a high ordering of the polar solvent molecules),[5] whereas in reaction 2, the charge is being dispersed in the transition state.

As in the reactions with triarylphosphines,[2-4] the α-bromo sulfones proved to be more reactive than the α-iodo sulfones toward sodium benzenesulfinate. The absolute difference in reactivity between the bromides and iodides for reactions 1 and 2 are remarkably similar (ca. an order of magnitude) which is surprising in view of the difference in nucleophiles. The diminished reactivity of the iodides (cf. the bromo sulfones) is probably due to the weak sulfur–iodine bond (cf. the significantly stronger sulfur–bromine bond) being formed in the transition state.[6] This implies that the use of a nucleophile in which the incipient nucleophile–iodine bond being formed differs little in strength from the analogous nucleophile–bromine bond might lead to a "normal" order of reactivity, i.e., the iodides reacting faster than the bromides.[7] The bond dissociation energies of the nitrogen trihalides[7] suggest that nitrogen nucleophiles might show a different order of reactivity than the phosphines or the sulfinates. However, since amines are significantly harder bases[8] than phosphines or sulfinates,

Table I. Rate Constants for the Reactions of α-Halobenzyl Phenyl Sulfones, $YC_6H_4CHXO_2Ph$, with Sodium Benzenesulfinate in 90% Aqueous DMF

Registry no.	X	Y	Temp, °C (±0.1°)	$10^3 k_2$, $M^{-1} s^{-1}$
41037-81-4	Br	m-Cl	80.0	0.576 ± 0.049
			90.0	1.29 ± 0.04
			100.0	3.47 ± 0.13
41037-82-5	Br	m-CN	60.0	1.63 ± 0
			70.0	4.20 ± 0.01
			80.0	10.9 ± 0.03
56571-78-9	Br	p-CH_3SO_2	30.0	1.12 ± 0.01
			40.0	3.35 ± 0.12
			50.0	9.67 ± 0.29
41037-83-6	Br	p-CN	20.0	0.840 ± 0.040
			30.0	2.56 ± 0.16
			40.0	7.55 ± 0.01
41037-84-7	Br	p-NO_2	10.0	123 ± 4
			0.0	43.9 ± 1.0
			−10.00	13.4 ± 0.2
41037-86-9	I	m-Cl	70.0	0.194 ± 0.003
			80.0	0.723 ± 0.016
			90.0	1.56 ± 0.02
41037-87-0	I	m-CN	60.0	0.443 ± 0.017
			70.0	1.28 ± 0.01
			80.0	4.47 ± 0.35
58311-76-5	I	p-CH_3SO_2	30.0	0.617 ± 0.03
			40.0	2.05 ± 0.04
			40.0	6.06 ± 0.05
41037-88-1	I	p-CN	30.0	1.01 ± 0.05
			40.0	5.41 ± 0.47
			50.0	10.3 ± 0
41037-89-2	I	p-NO_2	0.0	10.3 ± 1.4
			10.0	33.4 ± 1.5
			20.0	82.4 ± 0.2
7693-38-1	Cl	p-NO_2	80.0	0.833 ± 0.003
			90.0	1.55 ± 0.04
			100.0	4.69 ± 0.07

Table II. Rate Constants and Activation Parameters for the Reaction of α-Halobenzyl Phenyl Sulfones, $YC_6H_4CHXSO_2Ph$, with Sodium Benzenesulfinate in 90% Aqueous DMF at 25 °C

X	Y[a]	k_{25}, $M^{-1} s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Br	m-Cl	1.16×10^{-6}	22.9 ± 1.2	−12.0 ± 3.3
	m-CN	3.14×10^{-5}	21.6 ± 0.3	−9.7 ± 1.0
	p-SO_2CH_3	6.21×10^{-4}	20.4 ± 0.3	−7.7 ± 1.0
	p-CN	1.49×10^{-3}	19.4 ± 0.4	−9.1 ± 1.4
	p-NO_2	5.41×10^{-1}	15.8 ± 0.3	−9.0 ± 1.0
I	m-Cl	6.84×10^{-7}	25.3 ± 0.3	−5.3 ± 0.7
	m-CN	3.54×10^{-6}	26.4 ± 1.0	+1.9 ± 3.0
	p-SO_2CH_3	3.35×10^{-4}	21.6 ± 0.1	−4.1 ± 0.3
	p-CN	6.27×10^{-4}	22.1 ± 0.5	−1.9 ± 1.5
	p-NO_2	1.37×10^{-1}	16.0 ± 1.1	−9.3 ± 3.7
Cl	p-NO_2	2.15×10^{-6}	22.0 ± 0.2	−14.0 ± 0.9

[a] The σ^- constants used in the Hammett plots are those derived from the ionization of phenols except for the p-CH_3SO_2 group. The σ^- values for the p-CH_3SO_2 group is 0.82 which was obtained from a related study (see ref 1).

typical amines are unreactive in this type of reaction, although some vicinal dihalides may undergo dehalogenation via nucleophilic displacement on an iodine[9] or bromine[10] atom by nitrogen nucleophiles.[11] We have found that the bicyclic amidines such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) are considerably more reactive in reactions involving nucleophilic displacements on halogen atoms than are typical amines; this increased reactivity is probably due to the enhanced polarizability of the bicyclic amidines.[12] The α-iodo sulfones reacted considerably faster than the α-bromo sulfones with DBN. Thus, at ambient temperatures, the reaction of DBN with α-iodobenzyl phenyl sulfone in 90% aqueous DMF was complete within 3 h to give the reduced sulfone 4 (Ar = Ph), while under these conditions, α-bromobenzyl phenyl sulfone gave only recovered starting material. However, at 40° the more reactive α-bromo-m-cyanobenzyl phenyl sulfone did react with DBN to give the reduced sulfone 4. The degree of bond making between the nitrogen and halogen atoms in the transition state for this reaction is no doubt less[9] than the corresponding degree of bond making for the transition states of step one in reactions 1 and 2,[2-4] and this in part accounts for the divergent behavior of DBN vs. the phosphine and sulfinate nucleophiles.[13]

The large positive ρ values associated with the α-bromo and α-iodo sulfones in reaction 2, $Ar'SO_2^- = PhSO_2^-$, are indicative of a carbanion-like transition, i.e., nearly complete carbon–halogen bond cleavage.[2] In order to ascertain the degree of sulfur–halogen bond making in the transition state, a study of the variation of rates with a change in

Table III. Kinetic Data for the Reactions of α-Halo-*p*-cyanobenzyl Phenyl Sulfones, $p\text{-}NCC_6H_4CHXSO_2Ph$, with Sodium Arenesulfinates, $YC_6H_4SO_2Na$, in 90% Aqueous DMF

X	Y	Temp, °C (±0.1°)	$10^3 k_2$, $M^{-1} s^{-1}$
Br	*p*-Cl	50.0	1.52 ± 0.07
		60.0	3.88 ± 0.14
		70.0	12.4 ± 0.19
Br	*p*-CH_3	20.0	0.510 ± 0.018
		30.0	1.53 ± 0.09
		40.0	4.13 ± 0.18
Br	*p*-$CH_3C(=O)NH$	30.0	10.7 ± 0.6
		40.0	30.6 ± 1.2
		50.0	62.1 ± 1.8
Br	*p*-CH_3O	30.0	9.55 ± 0.08
		40.0	26.7 ± 0.7
		50.0	65.3 ± 1.8
I	*p*-Cl	50.0	1.69 ± 0.01
		60.0	4.17 ± 0.15
		70.0	10.4 ± 0.4
I	*p*-CH_3	20.0	0.346 ± 0.034
		30.0	1.52 ± 0.15
		40.0	5.92 ± 0.17
I	*p*-$CH_3C(=O)NH$	30.0	4.23 ± 0.18
		40.0	12.1 ± 0.2
		50.0	27.5 ± 0.3
I	*p*-CH_3O	20.0	2.24 ± 0.01
		30.0	8.71 ± 0.12
		40.0	21.3 ± 0

structure of the arenesulfinates was undertaken (Tables III and IV). The data in Table IV give good Hammett plots and show significantly better correlations with σ^+ values[14] compared with normal σ^- values: 1 (Ar = $p\text{-}CNC_6H_4$; X = Br), $\rho_{\sigma^+} = -2.57$ ($r = 0.999$), $\rho_\sigma = -4.18$ ($r = 0.931$);[15] 1 (Ar = $p\text{-}CNC_6H_4$; X = I), $\rho_{\sigma^+} = -1.69$ ($r = 0.998$), $\rho_\sigma = -2.78$ ($r = 0.945$).[15] These ρ values can be contrasted with those associated with reaction 1 in which the substituents were varied on the ring positions of the triarylphosphines.[3] These latter ρ values (eq 1) are ca. −3 with the one associated with the α-iodo sulfone being slightly larger than the ρ value for the α-bromo sulfone. Where these two systems differ significantly is that for the phosphines (eq 1), the change in rates correlates better with the normal Hammett σ constants, whereas for eq 2 the change in rates with a change in the aryl substituents in the arenesulfinates correlates with σ^+ constants much better than with normal σ values (vide supra).

Hammett $\sigma\rho$ studies of arenesulfinates have consistently shown better correlations with σ constants rather than σ^+ constants. Those studies reported in the literature include bimolecular nucleophilic displacements (SN2 reactions) on carbon[16] and oxygen[17] atoms, Michael additions to acrylonitrile,[18] and correlation of S–O stretching frequencies in the ir spectra of substituted sodium arenesulfinates.[19] In all these studies, the ρ values are ca. −1 indicating that they are not as sensitive to substituent changes as are the reactions we are reporting. Although additional Hammett type studies of SN2 reactions on halogen atoms with arenesulfinate nucleophiles have not been reported, several studies dealing with the reactivity of meta- and para-substituted thioanisoles toward *N*-chloro sulfonamides[20] and molecular bromine[21] (reactions which involve nucleophilic displacement by a sulfur atom on a halogen atom) have been reported. These ρ values were found to be on the order of −3.5 and were derived from a correlation of rates with normal σ constants rather than σ^+ constants. Although the sulfinate anion in these cited studies does not appear to function as an electron-accepting group (via resonance), the sulfonyl group in sulfones under suitable conditions can operate as a strong resonance accepting group.[22] For example, for a series of para-substituted aryl sulfones, the square root of the integrated intensities of the symmetric and asymmetric S–O bond stretching frequencies correlate with σ^+ constants.[23] Since we are suggesting that the transition state for reaction 2 lies very close to complete sulfur–halogen bond formation, it is reasonable that a structure–reactivity correlation might resemble more closely those observed for sulfones (and sulfonyl halides) than those associated with arenesulfinates.

Experimental Section

The syntheses of the α-halo sulfones have been reported previously.[2] The sodium arenesulfinates were prepared by the method of Smiles and Bere[24] and were recrystallized from ethanol. The kinetic procedure followed that reported earlier[2] except that the final concentrations of the sulfones were 0.001 M, and the concentrations of the sodium arenesulfinates ranged from 0.01 to 0.2 M. Aliquots (ca. 5 ml) of sample were quenched with water[25] and titrated against standard silver nitrate solutions using a Sargent-Welch recording titrator Model D equipped with a Corning Silver billet and Sargent calomel electrodes which were interposed by a potassium nitrate–agar salt bridge. Preparative runs for reaction 2 were made for the reactions of α-chloro-, α-bromo-, and α-iodo-*p*-nitrobenzyl phenyl sulfones with sodium benezenesulfinate at ca. 80 °C for 1 half-life. Upon workup, each reaction mixture yielded a solution which was shown by NMR spectroscopy to be a 50:50 mixture of starting α-halo sulfone 1 and reduced sulfone 4. The sulfones were isolated by preparative TLC (silica gel, methylene chloride) and identified by ir, melting point, and mixture melting point.

Reaction of α-Bromo-*m*-cyanobenzyl Phenyl Sulfone with 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN). To a solution of 1.00 g (2.98 mmol) of the α-halo sulfone in 40 ml of 90% aqueous DMF was added 0.40 g (3.22 mmol) of DBN (Aldrich) in 2 ml of 90%

Table IV. Rate Constants and Activation Parameters for the Reaction of α-Halobenzyl Phenyl Sulfones, $p\text{-}CNC_6H_4CHXSO_2Ph$, with Sodium Arenesulfinates, $YC_6H_4SO_2Na$, in 90% Aqueous DMF at 25 °C

Registry no.	X	Y[a]	k_2, $M^{-1} s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
14752-66-0	Br	*p*-Cl	7.11×10^{-5}	22.5 ± 1.0	−1.8 ± 0.8
824-79-3		*p*-CH_3	8.89×10^{-4}	18.5 ± 0.4	−10 ± 1.5
15898-43-8		*p*-$CH_3C(=O)NH$	6.95×10^{-3}	16.5 ± 0.6	−13 ± 1.9
6462-50-6		*p*-CH_3O	1.60×10^{-2}	16.9 ± 0.3	−7.7 ± 0.9
873-55-2		*p*-H	1.49×10^{-3}	19.4 ± 0.4	−9.1 ± 1.4
	I	*p*-Cl	1.23×10^{-4}	19.4 ± 0.4	−11 ± 1
		p-CH_3	7.33×10^{-4}	25.3 ± 0.9	12 ± 3
		p-$CH_3C(=O)NH$	2.62×10^{-3}	17.6 ± 0.4	−11 ± 1
		p-CH_3O	4.31×10^{-3}	20.0 ± 0.1	−2.1 ± 0.1
		p-H	6.27×10^{-4}	22.1 ± 0.5	−1.9 ± 1.7

[a] The σ^+ constants used in the Hammett plots are given in ref 14 except for the acetamido group. The σ^+ constant for CH_3CONH is reported by S. Clementi and P. Linda, *J. Chem. Soc., Perkin Trans. 2,* 1887 (1973).

aqueous DMF. The solution was heated at 40 °C for 10 h. The addition of water resulted in the formation of a brown precipitate. The precipitate was redissolved in methylene chloride and the solution dried ($MgSO_4$) and decolorized with neutral Norit. Methylene chloride was removed in vacuo and crystallization from methylene chloride–hexane gave 631 mg (83%) of *m*-cyanobenzyl phenyl sulfone. The product identification was made by comparison with an authentic sample.[2]

Reaction of α-Iodo- and α-Bromobenzyl Phenyl Sulfones with DBN. To 200 mg (0.56 mmol) of α-iodobenzyl phenyl sulfone in 6 ml of 90% aqueous DMF at room temperature was added 200 mg (1.01 mmol) of DBN. The reaction was followed by TLC (silica gel, methylene chloride). After 3 h the reaction was complete. Water was added, and the mixture was extracted twice with 20-ml portions of methylene chloride, washed once with water, and dried ($MgSO_4$). The solvent was removed in vacuo. Crystallization from methylene chloride–hexane gave 80 mg (62%) of benzyl phenyl sulfone. Identification was made by comparison with an authentic sample.[2] Under similar conditions, α-bromobenzyl phenyl sulfone gave only recovered starting material.

Reaction of Benzenesulfonyl Halides in Aqueous DMF. Solutions of benzenesulfonyl chloride and benzenesulfonyl bromide (~0.001 M) in 90% aqueous DMF were monitored in a Freas conductivity cell with conductance readings taken with a Barnstead conductivity bridge, Model PM-70CB.[2] The rate of increase in conductivity for the bromide was too fast to follow at 25 °C and crude data for benzenesulfonyl chloride showed that it reacted $>10^3$ times faster than α-chloro-*p*-nitrobenzyl phenyl sulfone reacted with 0.2 M sodium benzenesulfinate in 90% aqueous DMF at 25 °C.

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Registry No.—1,5-Diazabicyclo[4.3.0]non-5-ene, 3001-72-7; α-iodobenzyl phenyl sulfone, 41037-85-8; α-bromobenzyl phenyl sulfone, 15296-88-5.

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(11) We take this opportunity to note that dehalogenations are not always as straightforward as they might appear. Some time ago, one of us (B.B.J.) attempted to dehydrohalogenate *meso*-1,2-dibromo-1,2-diphenylethane with sodium ethoxide in ethanol–dioxane cosolvent. Unless the reagent grade dioxane had been purified, this reaction led to *trans*-stilbene as the major product. If the dioxane was purified carefully, the normal product, (*E*)-1,2-diphenylbromoethane, was obtained.
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(25) Originally the aliquots were quenched with water–acetone–nitric acid (1:1:1); however, electrode response was significantly better with water alone.

Displacement of the Nitro Group of Substituted Nitrobenzenes—a Synthetically Useful Process

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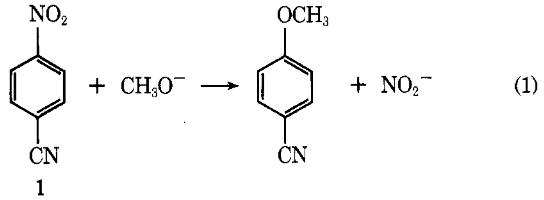
Nitrobenzenes substituted by a variety of electron-withdrawing groups readily undergo nucleophilic displacement of the nitro group at 25°C if the reaction is conducted in hexamethylphosphoramide (HMPA). The yields of pure products are excellent.

Nucleophilic displacement of a nitro group from a benzene ring carrying only one activating group, e.g., the process of eq 1, has, in the past, rarely been observed.[1] Recently, however, Beck and his colleagues[2] have shown that when a dipolar aprotic solvent (DMF) is employed the displacement of a nitro group by mercaptide ions occurs readily at room temperature and that processes such as that of



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(1)