Kinetics and mechanism of the reaction of *S,S*-diphenylsulfilimine with a series of aryl halides

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The stoichiometry, rate constants and order of reaction have been determined for the reaction of *S,S*-diphenylsulfilimine with the substrates 1-fluoro-2,4-dinitrobenzene, 1-chloro-2,4-dinitrobenzene, 2-chloro-3-nitropyridine, 2-chloro-5-nitropyridine and 2-chloro-3,5-dinitropyridine. Arrhenius parameters and solvent effects have also been determined for some of these reactions. The results demonstrate that the reaction is a typical nucleophilic aromatic substitution process with no measurable base catalysis. A high reactivity of the sulfilimine reagent is observed and accounted for in terms of the contribution of the ylid form to the overall structure.

The first observation that *N*-unsubstituted *S,S*-diarylsulfilimines undergo nucleophilic substitution reactions with activated aryl halides was by Tamura *et al*.,[1] who showed that diphenylsulfilimine reacted with 1-fluoro-2,4-dinitrobenzene in ethanol as solvent over a period of 10 minutes at room temperature to give the corresponding *N*-(2,4-dinitrophenyl)-*S,S*-diphenylsulfilimine. Under these conditions 1-chloro-2,4-dinitrobenzene failed to react. Much more recently Vlasova *et al*.[2] have demonstrated that *S,S*-diphenylsulfilimine will also react with various heterocycles *e.g.* furazans, furoxans, pyrazines or triazines, displacing a chloro or nitro group. Like Tamura they assumed that 1-chloro-2,4-dinitrobenzene would not react under their conditions (dichloromethane solvent, room temperature, 48 h) although 1,2,4-trinitrobenzene does in fact do so.

At first sight both the stability and nucleophilicity of these sulfilimines seems unusual, particularly if formulated as containing a $R_2S{=}NH$ grouping. The chemistry of carbon based imines is dominated by addition and condensation reactions and nitrogen atoms hybridised sp^2 are generally less basic (by a factor of at least 1000[3]) than those hybridised sp^3.

Azide ion is 4000 times less reactive than the methoxide ion towards nucleophilic displacement of fluorine in 4-nitrofluorobenzene,[4] although the difference is much less marked for iodine displacement. In turn, methoxide ion is considerably less reactive than an amide ion[5a] although there are obviously many factors concerned in a comparison of azide ion with amide ion other than a simple change in hybridisation. The nucleophilic behaviour of the sulfilimine may well be enhanced by the strong contribution[6] of the ylid form to the resonance hybrid.

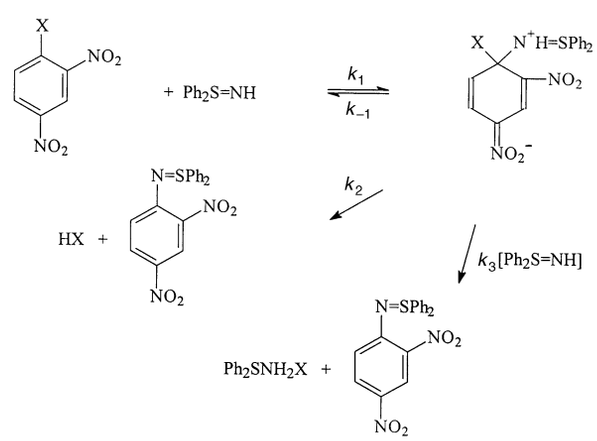
$$R_2S{=}NH \longleftrightarrow R_2S^+{-}N^-H$$

There is much physical evidence for the importance of this ylid structure,[6] although most exists for *N*-substituted dialkyl- and diaryl-sulfilimines rather than *N*-unsubstituted compounds, *e.g.* the electric dipole moments of some *N*-aryl-*S,S*-dimethylsulfilimines suggest 40–60% ionic character in the S–N bond.[7] On the other hand, shorter than expected S–N bonds in many *N*-tosylsulfilimines may be held[6] to demonstrate the contribution of the double bonded form, as well as the possibility of back donation of the electron pair on nitrogen into a vacant d-orbital on sulfur. Also in favour of a strong ylid contribution is the magnitude of the pK_a of *S,S*-diphenylsulfilimine which at 8.56[8] is comparable to the pK_a values of typical aliphatic sp^3 hybridised nitrogen bases ranging *e.g.* from piperidine (11.12), a frequently used nucleophile, to trimethylamine (9.81). Characteristically, sp^2 hybridised nitrogen bases such as pyridine (5.25) or quinoline (4.88) have much lower pK_a values. It seems probable that nucleophilicity towards carbon may be similarly affected since there is usually a strong correlation between basicity and nucleophilicity.[9] Clearly it is of interest to investigate the extent to which diarylsulfilimines behave in an analogous manner to a neutral nucleophile such as piperidine, or whether they resemble more an anionic species such as azide or methoxide ion.

We have therefore undertaken a study of the kinetics of the reaction of *S,S*-diphenylsulfilimine with a series of activated aromatic and heterocyclic chloro-substituted compounds together with 1-fluoro-2,4-dinitrobenzene in order to compare its reactivity with more typical nitrogen nucleophiles. We also hoped to elucidate the mechanism of the substitution reaction.

Results and discussion

The widely accepted S_NAr mechanism as formulated for secondary amines,[10] but with the amine replaced with an imine, may apply (see Scheme 1). Here either the first stage or, more



Scheme 1

rarely, the second stage can be rate-determining with the consequent possibility of base catalysis. Applying the steady state approximation gives eqn. (1).

$$\text{Rate} = k_A[Ph_2S{=}NH][ArX] \qquad (1)$$

where

$$k_A = k_1k_2 + k_1k_3[Ph_2S{=}NH]/(k_2 + k_{-1} + k_3[Ph_2S{=}NH]) \quad (2)$$

If $k_2 + k_3[Ph_2S{=}NH] \gg k_{-1}$, then the observed rate constant, $k_A = k_1$, and the formation of the σ-complex is rate-determining, base catalysis is not observed and the reaction is second order overall. On the other hand, if $k_2 + k_3[Ph_2S{=}NH] \ll k_{-1}$, then k_A has a linear dependence on $[Ph_2S{=}NH]$ and base catalysis is observed. Bunnett and Garst[11] have suggested that a ratio of at least 50 for k_3/k_2 is required to distinguish true base catalysis from solvent effects. If there is no base catalysis, then the observed value of k_A becomes equal to $k_1k_2/(k_{-1} + k_2)$ and there remains the possibility that, if $k_{-1} \gg k_2$, then $k_A = Kk_2$, where $K = k_1/k_{-1}$ and the reaction is second-order overall with the second step rate-limiting.

Stoichiometry of reaction

In line with the scheme, complete reaction of the halogeno substrates required two moles of the sulfilimine to form one mole of the corresponding *N*-aryl compound [reaction (3)]. If the

$$ArCl + 2Ph_2S{=}NH \longrightarrow ArN{=}SPh_2 + Ph_2S^+NH_2\,Cl^- \quad (3)$$

reaction is carried out in tetrahydrofuran as solvent at high concentrations, a 1:2 ratio of 1-chloro-2,4-dinitrobenzene:sulfilimine results in the precipitation of 100 mol% of the *S*,*S*-diphenylaminosulfonium chloride; the salt tends to stay in solution in protic solvents and dimethylsulfoxide (DMSO). In the presence of an at least two-fold excess of the sulfilimine, the yield of *N*-aryl product is almost quantitative and no other products were identified.

Order of reaction

Table 1 contains second-order rate constants determined for the various substrates in the solvents chloroform, methanol and DMSO measured at 32 °C.

The kinetics were determined using absorption spectroscopy in the visible region to follow the formation of the bright yellow products. At the concentrations used, precipitation of the salt did not occur. The reactions were run under pseudo-first-order conditions with a large excess of sulfilimine: good first-order plots were obtained over at least three half-lives and at six different wavelengths. Also, no significant trend was observed in the second-order rate constants over a three-fold variation in sulfilimine concentration and hence we conclude that the reaction is first-order with respect to each reagent and second-order overall. The reaction order was checked most extensively in chloroform solvent with 1-fluoro-2,4-dinitrobenzene, since base catalysis is most often observed in solvents of low polarity and with fluorine displacement,[12] but there was no evidence of any variation, nor was there for any of the substrates in the other solvents. It is clear that there is no evidence of base catalysis and that the first step of the mechanism outlined in Scheme 1 is most probably rate-determining. This is confirmed by examination of the relative rates of loss of fluorine and chlorine from the corresponding 1-halo-2,4-dinitrobenzenes: the rate ratio for F/Cl displacement is 1000, and more or less independent of solvent, indicating that the rate-determining step is N–C bond formation and not the loss of halogen.

Relative reactivities of *S*,*S*-diphenylsulfilimine and piperidine

It is instructive to compare the relative reactivities of the classic neutral nucleophile piperidine[13,14] and sulfilimine. The rate ratios vary with solvent and departing halogen, ranging from a factor of 250 in favour of piperidine for 1-chloro-2,4-dinitrobenzene to 40 for 1-fluoro-2,4-dinitrobenzene, both in methanol as solvent; in chloroform the figure is 130 for the chloro compound. These figures show a remarkably high relative reactivity for the sulfilimine (compare azide/amide ion mentioned earlier), confirming its ylid character and paralleling its relatively high basicity.

Table 1 Second-order rate constants for the reaction of *S*,*S*-diphenylsulfilimine with various aromatic substrates in the solvents chloroform, methanol and dimethylsulfoxide

	k_A/dm^3 mol^{-1} s^{-1}		
Substrate	$CHCl_3$	MeOH	DMSO
1-Fluoro-2,4-dinitrobenzene (A)	1.15	0.213	28.5
1-Chloro-2,4-dinitrobenzene (B)	1.14×10^{-3}	2.45×10^{-4}	2.97×10^{-2}
2-Chloro-5-nitropyridine (C)	1.08×10^{-4}	5.87×10^{-5}	2.36×10^{-3}
2-Chloro-3-nitropyridine (D)	1.89×10^{-4}	5.07×10^{-5}	6.23×10^{-4}
2-Chloro-3,5-dinitropyridine (E)	9.43	—	—

Solvent effects

The effect of solvents on S_NAr reactions of aromatic halogeno compounds with piperidine has been thoroughly investigated.[13,14] It is generally accepted that the transition state may well resemble the σ-complex, a betaine-type species, involving considerable charge separation (see Scheme 1), formed from the reaction of two dipolar, but neutral molecules. If the case is similar for our nucleophile, then we would expect a considerable acceleration in rate on passing from a solvent of low polarity (chloroform) to a more polar one (DMSO) in which the transition state may be stabilised relative to the ground state. Alternatively, if the ground state nucleophile exhibits considerable ylid character, then the acceleration may be much less marked than for piperidine. We have examined this point for four of the substrates, obtaining rate ratios (DMSO/$CHCl_3$, 32 °C) of 24 ± 2 for the substrates 1-fluoro-2,4-dinitrobenzene, 1-chloro-2,4-dinitrobenzene and 2-chloro-5-nitropyridine. This compares very well with the corresponding factor of 22.3 (25 °C) obtained by Mancini *et al.*[14] for the reaction of piperidine with 1-chloro-2,4-dinitrobenzene, suggesting that the ylid character of the nucleophile does not cause a change in the relative solvation energies of ground and transition states in the two solvents. On the other hand, the acceleration factor for the substrate 2-chloro-3-nitropyridine is only 4.0; this low value perhaps reflects the unique structure of this compound in our series; it is the only one without a nitro group substituted *para* to the site of attack. This absence may well lower the dipolar nature of the transition state, making it more comparable with the dipolar character of the ground state sulfilimine, resulting in only a small accelerative effect.

The effect of the protic solvent methanol on the rate of our reaction is again very similar to that of the alcohols on the corresponding reaction of piperidine studied by Martinez *et al.*[13] The authors observe a decrease in the rate constant by a factor of 6.1 for the substrate 1-chloro-2,4-dinitrobenzene; in our case the effects vary a little with substrate, the decrease ranging from 1.8 for 2-chloro-5-nitropyridine to 5.4 for 1-fluoro-2,4-dinitrobenzene. This lowering is suggested[13] to arise from the efficient solvation by hydrogen bonding of the nitrogen nucleophile compared with the transition state; the slightly lower values in our case may well be a consequence of the lower basicity of the sulfilimine compared with piperidine.

The effects of substituents on reactivity

By comparison of the appropriate rate constants in chloroform (Table 1) the substituent rate factors (SRFs) for an *ortho*-nitro group (87 000, E/C) and a *para*-nitro group (50 000, E/D) may be calculated. Similarly, the direct comparison E/B gives the SRF for an *ortho*-aza group (8300) showing that the ring nitrogen atom is approximately 10 times less activating than a nitro group in the same position. The corresponding SRFs for a *para*-nitro group in the reactions with methoxide ion in methanol[5a] (50 °C, $\rho = 3.90$) and piperidine in benzene[15] (45 °C,

Table 2 Activation parameters for the reaction of *S*,*S*-diphenylsulfilimine with 1-fluoro- and 1-chloro-2,4-dinitrochlorobenzene in the solvents chloroform and methanol

	Temperature range/°C	No. of points	E_a/kJ mol^{-1}	*A*	Correlation coefficient	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/kJ mol^{-1}
Substrate A							
$CHCl_3$	24–56	10	49.8 ± 2.9	$(3.5 \pm 5.9) \times 10^8$	0.994	47.2 ± 2.6	−90.0 ± 8.2
MeOH	24–56	7	50.9 ± 4.1	$(1.2 \pm 4.7) \times 10^8$	0.987	48.1 ± 4.1	−99.4 ± 13.0
Substrate B							
$CHCl_3$	32–56	11	58.7 ± 6.0	$(1.3 \pm 8.3) \times 10^7$	0.974	55.9 ± 6.1	−118.1 ± 19.1
MeOH	38–59	6	83.5 ± 6.3	$(3.9 \pm 9.9) \times 10^{10}$	0.986	81.0 ± 6.3	−50.3 ± 19.1

$\rho = 4.08$) are 114 000 and 151 000, respectively. While our figure is obviously closer to the one for methoxide ion, the difference between our value and the two literature figures is almost certainly due to the higher overall reactivity of our system. However, Eggiman *et al.*[16] have shown that the introduction of an *ortho*-aza group into 1-chloro-2,4-dinitrobenzene increases the rate constant for the reaction with aniline by a factor of 5870, somewhat less than in our reaction, although the substrates involved are identical.

More significantly, in chloroform as solvent, we observe a greater activating effect for an *ortho*-nitro group compared with one in the *para* position ($k^o/k^p = 1.75$) which is the reverse of the relative activating influence of these two groups for methoxide ion attack ($k^o/k^p = 0.25$–0.5). This is in line with the observations of Bunnett and Morath[17] on the reaction of piperidine with 1-chloro-2-nitro- and 4-nitro-benzenes: they also observe a stronger *ortho* activating affect and suggest it is due to the stabilisation of the developing positive charge on nitrogen in the transition state by the neighbouring nitro group and/or hydrogen bonding between the N–H and a nitro group oxygen atom. Alternatively, it has been argued[18] that the difference arises from repulsion of an incoming negatively charged nucleophile by the *ortho*-nitro group. However, while the observed values of k^o/k^p were greater than unity in both protic and aprotic solvents (59, benzene; 2.2, methanol), our values are not, being 1.75 in chloroform, 0.86 in methanol and 0.26 in DMSO. Again, this may arise from the behaviour of the *S*,*S*-diarylsulfilimine nucleophile being intermediate between that of piperidine and an anionic species. However it may be noted that some earlier measurements[19] using piperidine as nucleophile on C and D in ethanol give a value of k^o/k^p of 0.65, which although greater than typical methoxide ion figures, suggests the resemblance of our nucleophile to a neutral rather than an ionic species.

Effect of temperature

Arrhenius activation energies, pre-exponential factors and enthalpies and entropies of activation and the associated errors are given in Table 2 for the 1-fluoro- and 1-chloro-2,4-dinitrobenzenes in both chloroform and methanol as solvents.

Enthalpies and entropies of activation were calculated directly from the Eyring equation [eqn. (4)] plotting ln (k_A/T)

$$\ln \frac{k_A}{T} = \ln \frac{k}{h} + \frac{\Delta S^{\ominus}}{R} - \frac{\Delta H^{\ominus}}{RT} \qquad (4)$$

versus 1/*T*. The errors given are calculated from the associated standard deviations.

It has been pointed out[5c] that one of the more marked distinctions between neutral and anionic nucleophiles is that the values of $\Delta S^{\ominus}$ for reactions of neutral nucleophiles with neutral substrates are much more negative than those for reactions of anionic nucleophiles. A typical value for the reaction of piperidine with 1-chloro-2,4-dinitrobenzene is −126 J K^{-1} mol^{-1} while that for *p*-nitrophenoxide ion reaction is −56 J K^{-1} mol^{-1}. Similar differences have been observed in both protic and aprotic solvents although there is at least one report[20] in which values of $\Delta S^{\ominus}$ for amines only differ a little from those of anionic reagents. For 1-fluoro-2,4-dinitrobenzene in both chloroform and methanol, our values of $\Delta S^{\ominus}$ are intermediate between the typical values for neutral and anionic reagents; however the corresponding figure for the chloro compound in chloroform is somewhat higher (though possibly not significantly), whereas in methanol it appears to be significantly lower. At present we have no clear explanation for the marked sensitivity to temperature for the rate constant for this substrate in methanol. However, one difference between the chloro and fluoro substrates in methanol may be the ability of the partially negatively charged halogen group in the transition state to hydrogen bond to the solvent more strongly in the case of fluorine. This may lower the activation energy of the fluoro compound relative to that of its chloro analogue in methanol, and likewise make for a larger decrease in the entropy term for the fluoro than for the corresponding chloro substrate. The difference between the two substrates would be much lower in the very weakly hydrogen bonding solvent chloroform. This argument is based on the premise that the activation energy for the reaction of the fluoro compound in methanol would be higher than that observed without the stabilising effect of possible hydrogen bond formation. The difference between the activation energies for F and Cl displacement is usually larger in protic than in aprotic solvents.

We conclude that the behaviour of the sulfilimine nucleophile most closely resembles that of a typically reactive amine such as piperidine rather than a species formulated as containing an sp^2 hybridised nitrogen atom.

Experimental

All melting points were measured on a Gallenkamp Melting Point Apparatus and are uncorrected. ^{1}H NMR spectra were obtained using a Bruker AC-300 spectrometer; chemical shift are given in ppm, *J* values in Hz. UV spectra were obtained using a Perkin-Elmer Lambda-5 UV–VIS spectrophotometer and mass spectra were obtained using a Kratos Analytical Profile MS and a Shimadzu GC-14A. Columns were packed with Kieselgel 60 flash silica (Merck) and retention factors are quoted for TLC plates pre-coated with Kieselgel 60 F-254 (Merck).

Materials

S,*S*-Diphenylsulfilimine (Aldrich) was left to stand in air for four days in order to convert it to *S*,*S*-diphenylsulfilimine monohydrate (mp 70–71 °C),[1] since in this form it was stable and non-hygroscopic. At the concentrations used, the amount of water involved had no measurable solvent effect, nor did it react with the substrates. 1-Fluoro-2,4-dinitrobenzene, 1-chloro-2,4-dinitrobenzene, 2-chloro-5-nitropyridine, 2-chloro-3-nitropyridine and 2-chloro-3,5-dinitropyridine were all purchased from Aldrich, and their purity was checked by running ^{1}H NMR spectra ($CDCl_3$, 300 MHz). Spectrophotometric grade chloroform and anhydrous DMSO were purchased from Aldrich. Methanol was dried by distillation over magnesium, dichloromethane was distilled over calcium hydride and THF and petrol (bp 40–60 °C) were distilled over sodium.

Typical procedure for the preparation of *N*-aryl-*S*,*S*-diphenylsulfilimines

2-(*S*,*S*-Diphenylsulfilimino)-3,5-dinitropyridine. To a solution of *S*,*S*-diphenylsulfilimine monohydrate (0.947 g, 4.32 mmol) in THF (20 cm^3) was added 2-chloro-3,5-dinitropyridine (0.439 g, 2.16 mmol) and the mixture was refluxed for 30 min. THF was removed *in vacuo* and the crude product was purified by flash column chromatography [1:2 v/v dichloromethane–light petroleum (40–60 °C), gradient to 100% dichloromethane] to give the desired product as a crystalline yellow solid in quantitative yield; mp 171–173 °C, $R_f = 0.52$ (CH_2Cl_2); λ_{max}($CHCl_3$)/nm 366; δ_H(300 MHz, $CDCl_3$) 7.45–7.52 (6 H, m, Ar*H*), 7.86–7.93 (4 H, m, Ar*H*) and 8.90–8.94 (2 H, 2 d, Ar*H*); *m/z* (EI) 368 (M^+, 12%), 243 (M–SOPh, 10), 213 (M–SOPh–NO, 8), 202 (15), 186 (SPh_2, 100), 154 (Ph_2, 12), 109 (SPh, 20) and 77 (Ph, 22) ($C_{17}H_{12}N_3SO_4$ requires 368.0579; found 368.0588; dev. 2.2 ppm).

Spectroscopic characterization of products

1-(*S*,*S*-Diphenylsulfilimino)-2,4-dinitrobenzene. Mp 128 °C (lit.[1] 134 °C); $R_f = 0.36$ (CH_2Cl_2); λ_{max}($CHCl_3$)/nm 383; δ_H(300 MHz, $CDCl_3$) 6.94 (1 H, d, *J* 15, Ar*H*), 7.51–7.56 (6 H, m, Ar*H*), 7.82–7.86 (4 H, m, Ar*H*), 8.03–8.07 (1 H, dd, Ar*H*) and 8.66 (1 H, d, *J* 3, Ar*H*); *m/z* (EI) 367 (M^+, 5%) and 186 (SPh_2, 100).

2-(*S*,*S*-Diphenylsulfilimino)-5-nitropyridine. Mp 141–143 °C; $R_f = 0.27$ (CH_2Cl_2); λ_{max}($CHCl_3$)/nm 318; δ_H(300 MHz, $CDCl_3$) 6.84 (1 H, d, *J* 18, Ar*H*), 7.45–7.52 (6 H, m, Ar*H*), 7.72–7.81 (4 H, m, Ar*H*), 8.05–8.12 (1 H, dd, Ar*H*) and 8.87 (1 H, d, *J* 3, Ar*H*); *m/z* (EI) 323 (M^+, 33%), 277 (M–NO_2, 1) 214 (M–SPh, 8), 202 (20), 186 (SPh_2, 100), 154 (Ph_2, 15), 109 (SPh, 32) and 77 (Ph, 32) ($C_{17}H_{13}N_3SO_2$ requires 323.0729; found 323.0731; dev. 2.2 ppm).

2-(*S*,*S*-Diphenylsulfilimino)-3-nitropyridine. Mp 132–134 °C; $R_f = 0.20$ (CH_2Cl_2); λ_{max}($CHCl_3$)/nm 425; δ_H(300 MHz, $CDCl_3$) 6.46–6.50 (1 H, dd, Ar*H*), 7.45–7.48 (6 H, m, Ar*H*), 7.88–7.91 (4 H, m, Ar*H*), 8.06–8.08 (1 H, dd, Ar*H*) and 8.15–8.19 (1 H, dd, Ar*H*); *m/z* (EI) 323 (M^+, 7%), 293 (M–NO, 1), 214 (M–SPh, 1), 186 (SPh_2, 100), 109 (SPh, 9) and 77 (Ph, 14) ($C_{17}H_{13}N_3SO_2$ requires 323.0729; found 323.0716; dev. 3.7 ppm).

Kinetics

The kinetics were determined under conditions where the nucleophile was in a 10- to 1000-fold excess over the substrate. The increase in absorbance was measured at six wavelengths covering a range of ±30 nm on either side of the peak maximum associated with the brilliant yellow *N*-aryl-*S*,*S*-diphenylsulfilimine product. The positions of the absorption maxima for the four products were determined by preparing and characterizing the compounds (as described above) and taking their UV spectra. The colourless starting materials had been shown to absorb at significantly lower wavelengths (210 nm), and thus a concentration range of 1.0×10^{-3}–0.1 mol dm^{-3} for the nucleophile could be used, depending on substrate reactivity. Substrate concentrations were chosen to generate a final absorbance of not greater than 2.5 (*ca.* 0.1–1.0×10^{-4} mol dm^{-3}). A Perkin-Elmer Lambda-5 UV–VIS spectrophotometer with a thermostatted cell compartment was used. Pseudo-first-order rate constants were obtained by processing the absorbance–time data for each of the six wavelengths using a non-linear least squares method.[21] Root mean square errors between calculated and observed absorbances smaller than 1×10^{-3} indicated a good first-order fit. The mean of the six pseudo-first-order rate constants was divided by the appropriate concentration of nucleophile to obtain the second-order rate constant k_A. Reactions were started by adding 10 or 20 μl of aryl halide solution to a 1 cm quartz UV cell containing 3 ml of *S*,*S*-diphenylsulfilimine solution. The spectrum was back-corrected before the addition of the aryl halide solution.

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