Pergamon

Tetrahedron 55 (1999) 10243–10252

TETRAHEDRON

Preparation of *N*-Aryl-*S,S*-diphenylsulfilimines by Nucleophilic Attack of *N*-Lithio-*S,S*-diphenylsulfilimine on Aromatic Compounds

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Received 31 March 1999; revised 1 June 1999; accepted 17 June 1999

Abstract: *N*-Aryl-*S,S*-diphenylsulfilimines with unusual substitution patterns have been prepared by reacting the novel nitrogen nucleophile *N*-lithio-*S,S*-diphenylsulfilimine with a range of activated aromatic substrates. *N*-Lithio-*S,S*-diphenylsulfilimine is not only able to displace chloro groups in conventional aromatic nucleophilic substitution reactions, but also, unlike *S,S*-diphenylsulfilimine itself, can attack at hydrogen-bearing positions in 'vicarious' aromatic nucleophilic substitutions of hydrogen.

Keywords: Arenes; Substitution; Sulfilimines

In a previous paper[1] we reported that the nitrogen nucleophile *S,S*-diphenylsulfilimine **1** could be used to prepare *N*-aryl-*S,S*-diphenylsulfilimines by displacing halo groups from activated halogenoaromatic compounds (Equation 1). The kinetic and mechanistic aspects of this reaction were also studied.[2]

$$ArX + 2Ph_2S{=}NH \rightarrow ArN{=}SPh_2 + Ph_2SNH_2X \qquad (1)$$

This method differs from conventional sulfilimine preparations in that a carbon-nitrogen bond is formed at the final stage rather than a sulfur-nitrogen double bond.[3] In this paper we describe the preparation and use of the lithiated analogue of *S,S*-diphenylsulfilimine, *N*-lithio-*S,S*-diphenylsulfilimine **2**.

$Ph_2S{=}NH$	$Ph_2S{=}NLi$	$Ph_3P{=}NH$	$Ph_3P{=}NLi$
1	**2**	**3**	**4**

By using *N*-lithio-*S,S*-diphenylsulfilimine **2** instead of *S,S*-diphenylsulfilimine **1**, the scope of the *N*-aryl-*S,S*-diphenylsulfilimine preparation may be extended in two ways. *N*-lithio-*S,S*-diphenylsulfilimine is a negatively charged nitrogen nucleophile, and so, in common with a small group of other negatively charged nitrogen nucleophiles such as sulfenamide anions[4] and 4-amino-1,2,4-triazole anions,[5] it may be capable of attacking at hydrogen-bearing aromatic positions.[6] These reactions are sometimes referred to as 'vicarious' nucleophilic aromatic substitutions of hydrogen, because the hydrogen does not leave as a hydride ion, but as part of some other species.[7] Although many carbanions have been used as nucleophiles in nucleophilic aromatic

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PII: S0040-4020(99)00550-5

substitution of hydrogen, few nitrogen species have been used as nucleophiles in these reactions.[8] The use of *N*-lithio-*S,S*-diphenylsulfilimine **2** should also extend the scope of *N*-aryl-*S,S*-diphenylsulfilimine preparations by reacting at chlorine-bearing positions in some substrates which were insufficiently activated to react with *S,S*-diphenyl-sulfilimine **1**.[1]

N-Lithiated sulfilimine nucleophiles, prepared by reacting *N*-unsubstituted sulfilimines with one equivalent of butyl lithium,[9] have been used to displace halide ions from a range of inorganic substrates,[10] but have not been used in aromatic nucleophilic substitutions. The phosphorus analogues[11] of sulfilimines **1** and **2**, *i.e.* tri-phenylphosphinimine **3** and *N*-lithio-triphenylphosphinimine **4**, have been prepared by reacting a triphenyl-aminophosphonium salt with two equivalents of butyl lithium (Equation 2),[12] and used as nucleophiles in aliphatic nucleophilic substitutions.[13]

$$Ph_3PNH_2Br + 2BuLi \rightarrow Ph_3P{=}NLi + LiBr + 2BuH \qquad (2)$$

Results and Discussion

Preparation of *N*-lithio-*S,S*-diphenylsulfilimine

The literature preparations of *N*-lithiated sulfilimines and phosphinimines referred to above suggested that *N*-lithio-*S,S*-diphenylsulfilimine could be prepared by reacting either the unsubstituted sulfilimine **1** or a diphenylaminosulfonium salt with butyl lithium. Both of these approaches were investigated. Unsubstituted sulfilimine **1** may exist as a monohydrate (having a melting point of 70-71 °C) or as the hygroscopic 'free' sulfilimine (having a melting point of 59-61 °C).[14,15] With appropriate quantities of butyl lithium, it was found that both forms of sulfilimine **1** could be used to prepare *N*-lithiated sulfilimine **2** (Equations 3 and 4). These reactions were carried out in anhydrous THF under nitrogen at room temperature, the conditions used in the literature preparation of *N*-lithio-triphenylphosphinimine **4**.[12]

$$Ph_2S{=}NH.H_2O + 2BuLi \rightarrow Ph_2S{=}NLi + LiOH + 2BuH \qquad (3)$$

$$Ph_2S{=}NH + BuLi \rightarrow Ph_2S{=}NLi + BuH \qquad (4)$$

$$Ph_2SNH_2Cl + 2BuLi \rightarrow Ph_2S{=}NLi + LiCl + 2BuH \qquad (5)$$

Diphenylaminosulfonium chloride was used to prepare *N*-lithio-*S,S*-diphenylsulfilimine **2** (Equation 5). Although sulfilimine **2** was not isolated or spectroscopically characterised, three pieces of evidence suggested that it was present in the THF solutions. All three products (Equations 3 to 5) gave deep yellow solutions on addition of butyl lithium, suggesting that the same product had formed in each case. Deeply coloured solutions are characteristic[6] of anionic species in THF; *e.g.* lithiated phosphinimine **4** was deep orange in THF solution and its presence was confirmed by ^{31}P nmr.[12] When each of the solutions was exposed to air, it became colourless and was shown, by removal of THF and separation of the organic and inorganic fractions by $CHCl_3$ extraction, to contain sulfilimine **1** and a white solid. The white solid was alkaline, gave a brown precipitate with silver nitrate solution, and a carmine-red flame test; hence we conclude that it was lithium hydroxide. *N*-Aryl-*S,S*-diphenylsulfilimines were prepared by adding one equivalent of aromatic substrate to a solution of *N*-

lithio-*S,S*-diphenylsulfilimine **2** in THF, and stirring for twenty-four hours at room temperature. The results of these experiments are summarised in the Table. Two experiments were carried out where one equivalent of aromatic substrate was added to a THF solution of *N*-lithio-triphenylphosphinimine **4** prepared according to the literature method.[12] For the purposes of comparison, results of previous experiments[1] involving *S,S*-diphenylsulfilimine **1** are also included in the Table where relevant.

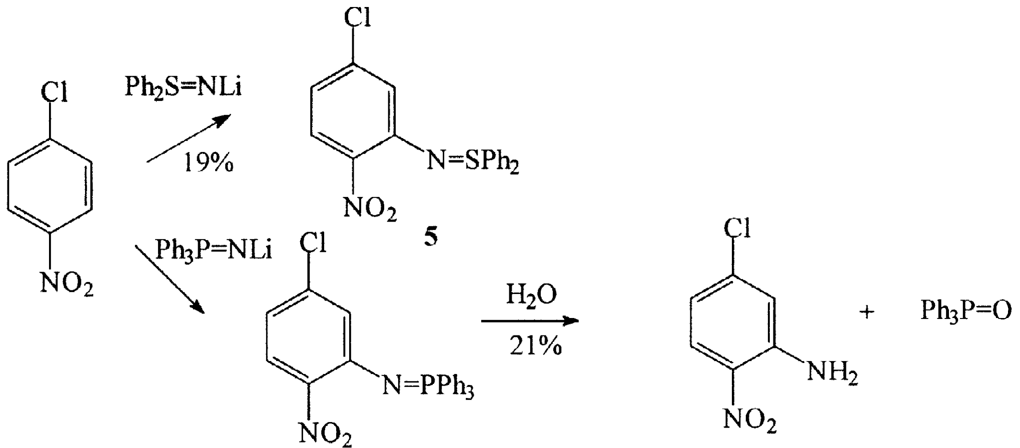
Preparation of *N*-aryl-*S,S*-diphenylsulfilimines

Substrate	Nucleophile	Product(s), yield(s) and comments
1-Chloro-4-nitrobenzene	$Ph_2S{=}NLi$	Sulfilimine **5** (19%)
1-Chloro-4-nitrobenzene	$Ph_2S{=}NH$	No reaction after 24 hrs / Δ / butan-1-ol
1-Chloro-4-nitrobenzene	$Ph_3P{=}NLi$	1-Chloro-3-amino-4-nitrobenzene **6** (21%)
1,3-Dinitrobenzene	$Ph_2S{=}NLi$	Sulfilimines **7** (20%) and **8** (14%)
2-Chloro-3-nitropyridine	$Ph_2S{=}NLi$	Sulfilimines **9** (34%) and **10** (49%)
2-Chloro-3-nitropyridine	$Ph_2S{=}NH$	Sulfilimine **9** (76%) after 7 hrs / Δ / EtOH
2-Chloro-5-nitropyridine	$Ph_2S{=}NLi$	Sulfilimines **11** (4%) and **12** (trace)
2-Chloro-5-nitropyridine	$Ph_2S{=}NH$	Sulfilimine **13** (81%) after 4 hrs / Δ / THF
Chloropyrazine	$Ph_2S{=}NLi$	Sulfilimine **14** (12%)
Chloropyrazine	$Ph_2S{=}NH$	No reaction after 24 hrs / Δ / butan-1-ol
Chloropyrazine	$Ph_3P{=}NLi$	No reaction
2-Chloropyridine	$Ph_2S{=}NLi$	No reaction
2,4-Dichloro-6-*n*-propoxy-1,3,5-triazine	$Ph_2S{=}NLi$	Sulfilimines **15** (9%) and **16** (3%)
2,4-Dichloro-6-*n*-propoxy-1,3,5-triazine	$Ph_2S{=}NH$	Sulfilimine **15** (11%) after 3 hrs / RT / THF

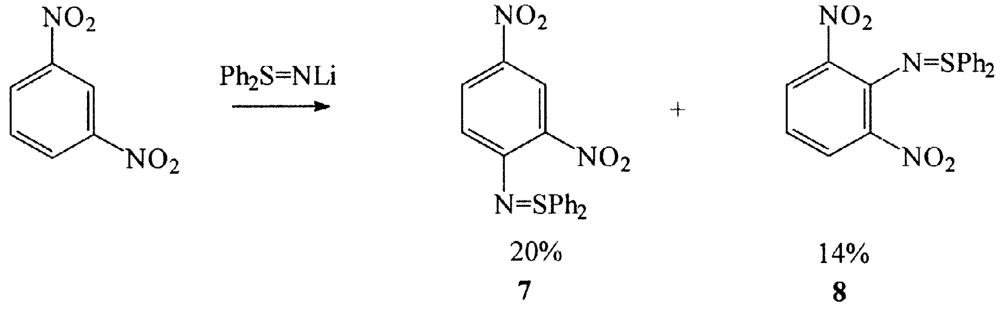
The reactions may be divided into three categories: *N*-aryl-*S,S*-diphenylsulfilimines may be prepared by aromatic nucleophilic substitution of hydrogen, competition between aromatic nucleophilic substitution of hydrogen and chlorine, or aromatic nucleophilic substitution of chlorine only.

a) By aromatic nucleophilic substitution of hydrogen

The chlorine-bearing position in 1-chloro-4-nitrobenzene was insufficiently activated to react with unsubstituted sulfilimine **1**, but *N*-lithiated sulfilimine **2** and *N*-lithiated phosphinimine **4** attacked at the hydrogen-bearing 3 position, activated by an *ortho* nitro group and a *meta* chloro group (Scheme 1). In the reaction between phosphinimine **4** and 1-chloro-4-nitrobenzene, thin layer chromatography showed that a brilliant yellow product was present in solution at the end of the reaction, but during flash column chromatography the product visibly decomposed on the column to a duller yellow product with an R_f value of 0.48 in dichloromethane. This product was identified by its melting point[16] and NMR as amino compound **6**. The presence of both **6** and triphenylphosphine oxide in the methanol column washings suggested that the *N*-aryl-triphenylphosphinimine product had formed, but had then been hydrolysed. Phosphinimines are more vulnerable to hydrolysis than sulfilimines. *N*-Aryl-triphenylphosphinimines are known to be stable in the atmosphere,[17,18] but are rapidly hydrolysed in solution if small quantities of acid or base catalyst are present.[19]



Scheme 1

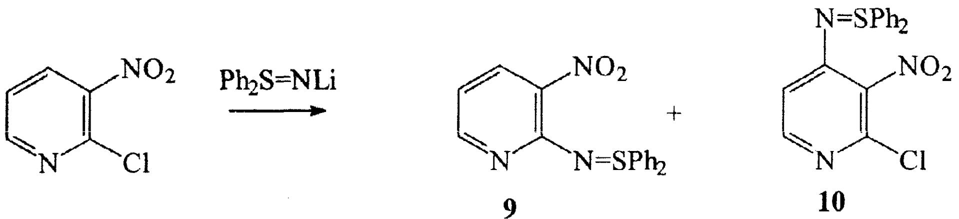


Scheme 2

In the reaction between sulfilimine **2** and 1,3-dinitrobenzene, attack occured at both of the activated hydrogen-bearing positions, giving sulfilimines **7** and **8** as products. Allowing for the statistical factor, the yields suggest that the 2 position (*ortho* to two nitro groups) is comparable in reactivity to the 4 and 6 positions (*ortho* to one nitro group and *para* to one nitro group). Sulfilimine **7** has previously been prepared by displacing a halo group from a 1-halo-2,4-dinitrobenzene.[14,15]

b) By competition between nucleophilic aromatic substitution of hydrogen and chlorine

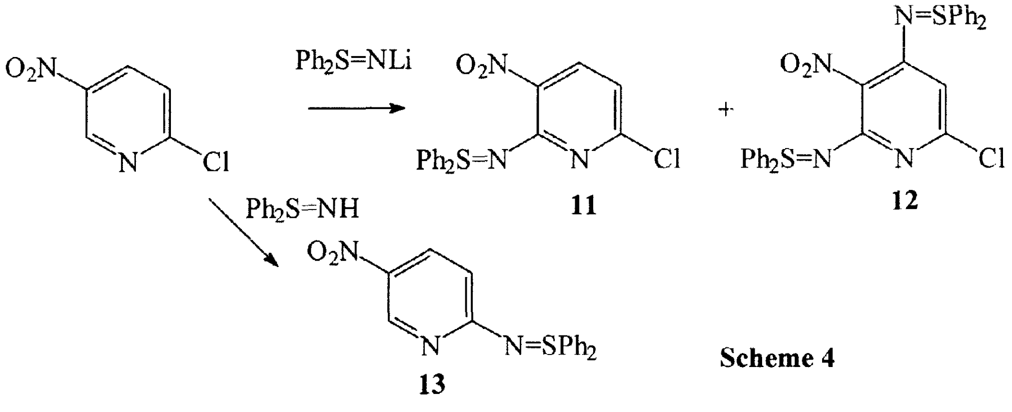
In the reaction between sulfilimine **2** and 2-chloro-3-nitropyridine, the chloro group was displaced giving sulfilimine **9**, and attack took place at a hydrogen-bearing position giving sulfilimine **10** (Scheme 3).



Scheme 3

In contrast, in the reaction between sulfilimine **2** and 2-chloro-5-nitropyridine, the chloro group remains intact, but attack occurs at two hydrogen-bearing positions to give sulfilimine **11** and a trace of a compound provisionally identified as sulfilimine **12** from its ^{1}H nmr and mass spectra, but not completely characterised (Scheme 4).

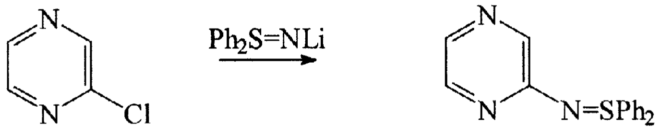
The results in Schemes 3 and 4 suggest that sulfilimine **2** attacks preferentially at positions *ortho* to nitro groups. Since the chloro groups in 2-chloro-3-nitropyridine and 2-chloro-5-nitropyridine show comparable reactivity in their reactions with unsubstituted sulfilimine **1**, the marked preference of sulfilimine **2** to attack at positions *ortho* to nitro groups cannot be rationalised solely in terms of the activating effects of the groups on the pyridine ring. In studies of nucleophilic aromatic substitution of hydrogen in nitroaromatic substrates, the regioselectivity of the reaction has been shown to depend on the solvent.[20,21] If the anionic nucleophiles form loose ion pairs with their counter ions (*e.g.* in DMSO or liquid ammonia), then the *ortho* / *para* ratio depends upon the steric nature of the carbanions. However, if the anionic nucleophiles form tight ion pairs with their counter ions (*e.g.* in THF) then attack occurs exclusively at positions *ortho* to nitro groups. It has been suggested that the metal cations are attracted by the negative charge associated with the nitro oxygens; the fact that exclusive *ortho* attack no longer takes place if an equivalent of an appropriate crown ether is added to the reaction mixture would seem to support this.[20]



Scheme 4

c) By nucleophilic aromatic substitution of chlorine

Chloropyrazine failed to react with unsubstituted sulfilimine **1** and *N*-lithiated phosphinimine **4**, and in the reaction between sulfilimine **2** and chloropyrazine, sulfilimine **14** was obtained (Scheme 5), although no reaction took place between sulfilimine 2 and 2-chloropyridine. 2-Chloropyridine is very much less activated to nucleophilic attack than chloropyrazine; in the reaction with phenoxide ion in methanol at 50 °C, 2-chloropyridine reacts a million times more slowly than chloropyrazine.[22]

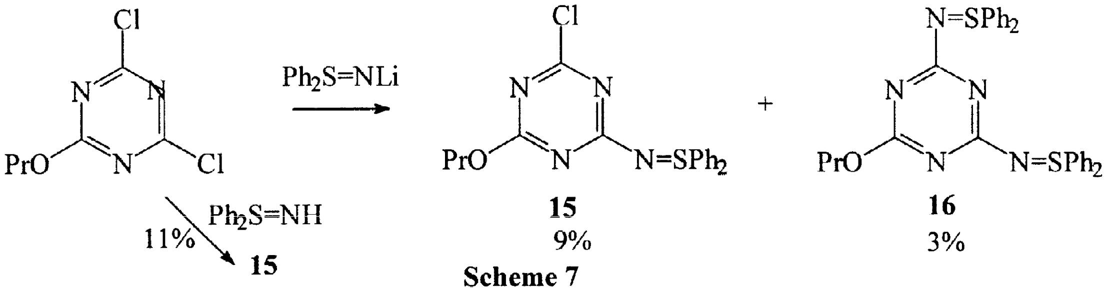


Scheme 5 **14**

These results show that *N*-lithio-*S,S*-diphenylsulfilimine **2** can be used to prepare *N*-aryl-*S,S*-diphenylsulfilimines from some substrates insufficiently activated to react with *S,S*-diphenylsulfilimine **1**. The results also show that *N*-lithio-*S,S*-diphenylsulfilimine **2** is a more powerful nucleophile than its phosphorus analogue *N*-lithio-triphenylphosphinimine **4**. This result is consistent with studies of the nature of the sulfur-nitrogen bond in sulfilimines and the phosphorus-nitrogen bond in phosphinimines. Both sulfilimines and phosphinimines may be depicted as ylids[17,23] (Scheme 6). The electric dipole moments of some *N*-aryl-*S,S*-diphenylsulfilimines suggest as much as 40-60% ionic character in the sulfur-nitrogen bond,[24] and in kinetic studies[2] *S,S*-diphenylsulfilimine **1** was shown to have a significantly higher reactivity than that of comparable neutral nitrogen nucleophiles. Bond length data[25] and thermochemical data[26] showing phosphinimines to have appreciable resonance energy suggests that the ylid form makes less of a contribution in phosphinimines than in sulfilimines, and thus phosphinimines are the weaker nucleophiles.

$$\mathrm{Ph_2S{=}NR} \longleftrightarrow \mathrm{Ph_2S^{+}{-}\!\!\!-\overset{-}{N}R}$$
$$\mathrm{Ph_3P{=}NR} \longleftrightarrow \mathrm{Ph_3P^{+}{-}\!\!\!-\overset{-}{N}R}$$

Scheme 6



Scheme 7

In the reaction between sulfilimine **2** and 2,4-dichloro-6-*n*-propoxy-1,3,5-triazine, monosubstituted sulfilimine **15** and disubstituted sulfilimine **16** were obtained (Scheme 7), showing that sulfilimine **2** may be used to prepare poly-*S,S*-diphenylsulfilimino compounds from substrates highly activated to nucleophilic attack.

Conclusion

N-Lithio-*S,S*-diphenylsulfilimine **2** has been shown to extend the scope of *N*-aryl-*S,S*-diphenylsulfilimine preparations in that it permits nucleophilic substitutions to be achieved in positions on the aromatic ring not bearing halogen substituents, thus increasing the diversity of products and removing the requirement for suitably substituted halogeno precursors to be available. Also its significantly greater nucleophilicity compared with the parent sulfilimine gives access to a much wider range of substrates, particularly making an activated chloro substituent a useful leaving group compared to the more expensive fluoro.

In certain cases the above advantages may be offset by the reduction in yields through side reactions between the aromatic substrate and various strongly basic species present in the reaction vessel such as *N*-lithio-*S*,*S*-diphenylsulfilimine **2** itself or a slight excess of unchanged butyl lithium. It is known that anionic bases may attack at both substituted and unsubstituted positions in aromatic rings[27] to form anionic σ-complexes, which, instead of decomposing to a product (as in a typical S_NAr reaction), may remain as stable deeply coloured species.[28] The base may also abstract a proton from the aromatic ring,[29] which sometimes results in rearrangement reactions which change the substitution pattern.[30]

Experimental

Melting points were measured on a Gallenkamp Apparatus and are uncorrected. ^{1}H nmr spectra were recorded on either a Bruker AC-250 or AC-300 spectrometer. Chemical shifts are quoted in parts per million and coupling constants (*J*) are quoted to the nearest 0.5 Hz. Multiplicities are described as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), multiplet (m) and broad (br). In beam electron impact (EI) mass spectra were obtained using a Kratos Analytical Profile MS and a Shimadzu GC-14A. Accurate masses were obtained by peak matching. IR spectra where taken were consistent with the proposed structure. Microanalyses were carried out by Butterworth Laboratories Ltd of Teddington, Middlesex, UK. Columns were packed with Kieselgel 60 flash silica (Merck) and retention factors are quoted for t.l.c. plates pre-coated with Kieselgel 60 F-254 (Merck). All starting materials were purchased from Aldrich (with the exception of 2,4-dichloro-6-*n*-propoxy-1,3,5-triazine, which was purchased from Lancaster) and their purity was checked by running ^{1}H nmr spectra. Diethyl ether, THF and petrol (40-60 °C) were distilled over sodium, methanol was distilled over magnesium and dichloromethane was distilled over calcium hydride.

Typical *in situ* preparations of *N*-lithio-*S*,*S*-diphenylsulfilimine

From S,S-diphenylsulfilimine. To a deoxygenated solution of *S*,*S*-diphenylsulfilimine (0.248 g, 1.23 mmol) in anhydrous THF (15 cm^3) under nitrogen was added butyl lithium (0.49 cm^3 of a 2.5 M solution in hexane, 1.23 mmol). The mixture immediately turned deep yellow and was stirred at room temperature for 30 mins.

From S,S-diphenylsulfilimine monohydrate. To a deoxygenated solution of *S*,*S*-diphenylsulfilimine monohydrate (0.270 g, 1.23 mmol) in anhydrous THF (15 cm^3) under nitrogen was added butyl lithium (0.98 cm^3 of a 2.5 M solution in hexane, 2.46 mmol). The mixture immediately turned deep yellow and was stirred at room temperature for 30 mins.

From S,S-diphenylaminosulfonium chloride. To a deoxygenated solution of *S*,*S*-di-phenylaminosulfonium chloride (0.292 g, 1.23 mmol) in anhydrous THF (15 cm^3) under nitrogen was added butyl lithium (0.98 cm^3 of a 2.5 M solution in hexane, 2.46 mmol). The mixture immediately turned deep yellow and was stirred at room temperature for 30 mins.

Nucleophilic aromatic substitution reactions of *N*-lithio-*S*,*S*-diphenylsulfilimine and *N*-lithio-triphenylphosphinimine

1-Chloro-3-(S,S-diphenylsulfilimino)-4-nitrobenzene **5** To a solution of *N*-lithio-*S*,*S*-diphenylsulfilimine **2** (5 mmol) in anhydrous THF (15 cm^3) was added a solution of 1-chloro-4-nitrobenzene (0.788 g, 5 mmol) in anhydrous THF (5 cm^3). The mixture turned brown and was stirred under nitrogen for 24 hrs at room temperature. THF was removed *in vacuo* and the crude product was purified by flash column chromatography (1:2 v/v CH_2Cl_2 - 40-60 °C petrol) and 1-chloro-3-(*S*,*S*-diphenylsulfilimino)-4-nitrobenzene **5** was obtained as a yellow oil in 19% yield; Rf = 0.47 (CH_2Cl_2); Found: C, 60.06; H, 3.57; N, 7.90. $C_{18}H_{13}N_2SClO_2$ requires C, 60.58; H, 3.67; N, 7.85%; δ_H ($CDCl_3$, 250 MHz) 6.56-6.60 (1H, dd, ArH, *J* = 10 Hz, 2.5 Hz) 6.94-6.95 (1H, d, ArH, *J* = 2.5 Hz) 7.49-7.52 (6H, m, ArH) 7.69-7.73 (1H, d, ArH, *J* = 10 Hz) 7.83-7.88 (4H, m, ArH); m/z (EI) 356, 358 (M^+, 1%, 0.3%) 186 (SPh_2, 100), $^{12}C_{18}{}^{1}H_{13}{}^{14}N_2{}^{32}S^{35}Cl^{16}O_2$ requires 356.038628, found: 356.03771, dev. 2.5 ppm.

Attempted preparation of 1-chloro-3-triphenylphosphinimino-4-nitrobenzene. To a solution of *N*-lithiotriphenylphosphinimine **4** (1.12 mmol) in anhydrous THF (15 cm^3) under nitrogen was added a solution of 1-chloro-4-nitrobenzene (1.12 mmol) in anhydrous THF (5 cm^3). The solution turned black, and the mixture was stirred under nitrogen for 24 hrs at room temperature. THF was removed *in vacuo* and the components of the mixture were separated by flash column chromatography (1:5 v/v CH_2Cl_2 - 40-60 °C petrol). A solid, later identified as lithium bromide, was not soluble in the column solvent system, and was removed by filtration. The desired product was not obtained, but 5-chloro-2-nitroaniline **6** was obtained as a yellow solid (0.04 g, 21%), 1-chloro-4-nitrobenzene was recovered in 68% yield, and the methanol column washings were shown to contain triphenylphosphine oxide. 5-Chloro-2-nitroaniline **6**; m.p. 129-130 °C (lit.,[16] 128-129 °C); Rf = 0.48 (CH_2Cl_2); δ_H ($CDCl_3$, 250 MHz) 5.90-6.20 (2H, br s, NH_2) 6.82-6.83 (1H, d, ArH, *J* = 2.5 Hz) 6.67-6.71 (1H, dd, ArH, *J* = 8 Hz, 2.5 Hz) 8.06-8.09 (1H, d, ArH, *J* = 8 Hz); m/z (EI) 172, 174 (M^+, 100%, 33%) 126, 128 (M-NO_2).

1-(S,S-Diphenylsulfilimino)-2,4-dinitrobenzene **7** *and 1,3-dinitro-2-(S,S-diphenyl-sulfilimino)-benzene* **8** To a solution of *N*-lithio-*S,S*-diphenylsulfilimine **2** (0.38 mmol) in anhydrous THF (10 cm^3) was added 1,3-dinitrobenzene (0.38 mmol). The mixture was stirred under nitrogen for 24 hrs at room temperature and THF was removed *in vacuo*. The crude product was purified by flash column chromatography (1:5 v/v CH_2Cl_2 - 40-60 °C, gradient to 100% CH_2Cl_2). 1-(*S,S*-Diphenylsulfilimino)-2,4-dinitrobenzene **7** was obtained as a yellow solid in 20% yield (for characterisation see Ref. 2) and 1,3-dinitro-2-(*S,S*-diphenylsulfilimino)benzene **8** was obtained as a red oil in 14% yield; Rf = 0.47 (CH_2Cl_2); Found: C, 58.67; H, 3.19; N, 11.79. $C_{18}H_{13}N_3SO_4$ requires C, 58.85; H, 3.56; N, 11.45%; δ_H ($CDCl_3$, 300 MHz) 6.62-6.68 (1H, t, ArH, *J* = 9 Hz) 7.44-7.52 (6H, m, ArH) 7.69-7.72 (2H, d, ArH, *J* = 9 Hz) 7.73-7.79 (4H, m, ArH); m/z (EI) 367 (M^+, 7%) 337 (M-NO, 1) 284 (2) 242 (2) 186 (SPh_2, 100) 109 (SPh, 7) 77 (Ph, 13). The starting material 1,3-dinitrobenzene was recovered in 64% yield.

2-Chloro-3-nitro-4-(S,S-diphenylsulfilimino)pyridine **10** To a solution of *N*-lithio-*S,S*-diphenylsulfilimine **2** (1.23 mmol) in anhydrous THF (15 cm^3) was added 2-chloro-3-nitropyridine (0.195 g, 1.23 mmol). The mixture was stirred under nitrogen for 24 hrs at room temperature and the THF was removed *in vacuo*. The crude product was purified by flash column chromatography (1:3 v/v CH_2Cl_2 - 40-60 °C petrol, gradient to 100% CH_2Cl_2). Substitution at the chlorine-bearing position had taken place giving 2-(*S,S*-diphenylsulfilimino)-3-nitropyridine **9** as a yellow solid in 34% yield (for characterisation see Ref. 2) and substitution at the 4-position had taken place giving 2-chloro-3-nitro-4-(*S,S*-diphenylsulfilimino)pyridine **10** as a yellow solid in 49% yield; Rf = 0.15 (CH_2Cl_2); δ_H ($CDCl_3$, 300 MHz) 6.75-6.80 (1H, d, ArH, *J* = 15 Hz) 7.40-7.55 (6H, m, ArH) 7.63-7.73 (4H, m, ArH) 7.85-7.90 (1H, d, ArH, *J* = 15 Hz); m/z (EI) 357, 359 (M^+, 5%, 2%) 186 (SPh_2, 100) 125 (M-SPh_2-NO_2, 12) 77 (Ph, 24), $^{12}C_{17}{}^{1}H_{12}{}^{14}N_3{}^{32}S^{35}Cl^{16}O_2$ requires 357.033877, found: 357.03237, dev. 4.2 ppm.

2-Chloro-5-nitro-6-(S,S-diphenylsulfilimino)pyridine **11** To a solution of *N*-lithio-*S,S*-diphenylsulfilimine **2** (2.50 mmol) in anhydrous THF (15 cm^3) was added 2-chloro-5-nitropyridine (0.396 g, 2.50 mmol). The mixture was stirred under nitrogen for 24 hrs at room temperature and the THF was removed *in vacuo*. The crude product was purified by flash column chromatography (1:3 v/v CH_2Cl_2 - 40-60 °C petrol, gradient to 100% CH_2Cl_2) and 2-chloro-5-nitro-6-(*S,S*-diphenylsulfilimino)pyridine **11** was obtained as a yellow solid in 4% yield; Rf = 0.53 (CH_2Cl_2); δ_H ($CDCl_3$, 300 MHz) 6.42-6.47 (1H, d, ArH, *J* = 15 Hz) 7.40-7.53 (6H, m, ArH) 7.83-7.99 (4H, m, ArH) 8.11-8.16 (1H, d, ArH, *J* = 15 Hz); m/z (EI) 357, 359 (M^+, 1%, 0.3%) 232, 234 (M-PhSO, 1, 0.3) 202 (2) 186 (SPh_2, 100) 152 (7) 109 (SPh, 7) 77 (Ph, 17), $^{12}C_{17}{}^{1}H_{12}{}^{14}N_3{}^{32}S^{35}Cl^{16}O_2$ requires

357.033877, found: 357.03301, dev. 2.4 ppm. A trace of a disubstituted product 2,4-di(*S,S*-diphenylsulfilimino)-3-nitro-6-chloropyridine **12** was obtained as a yellow solid; Rf = 0.62 (CH_2Cl_2); δ_H ($CDCl_3$, 300 MHz) 6.70 (1H, s, ArH) 7.49-7.60 (12H, m, ArH) 7.89-7.96 (8H, m, ArH); m/z (EI) 354 (M-$OSPh_2$, 5) 277 (M-Ph-$OSPh_2$, 4) 218 (Ph_2SO_2, 19) 186 (SPh_2, 100) 170 (18) 152 (10) 109 (SPh, 9) 77 (Ph, 35).

S,S-Diphenylsulfiliminopyrazine **14** To a solution of *N*-lithio-*S,S*-diphenyl-sulfilimine **2** (6.25 mmol) in anhydrous THF (15 cm^3) was added a solution of chloropyrazine (0.716 g, 6.25 mmol) in THF (5 cm^3). The mixture turned brown after 1 hr and was stirred under nitrogen for 24 hrs at room temperature. THF was removed *in vacuo* leaving a white solid suspended in a brown oil. The crude product was mixed with chloroform, allowing the oil to dissolve and the white solid to remain in suspension. The white solid was removed by filtration and chloroform was removed from the filtrate *in vacuo* leaving the brown oil. The white solid was alkaline in aqueous solution and gave a brown precipitate of silver oxide (I) with silver nitrate solution, suggesting that it was lithium hydroxide. The brown oil was purified by flash column chromatography (1:1 v/v Et_2O - 40-60 °C petrol, gradient to 100% Et_2O) giving *S,S*-diphenylsulfiliminopyrazine **14** as a brown solid (0.201g, 12%); m.p. 104-106 °C; Rf = 0.18 (Et_2O); Found: C, 68.49; H, 4.43; N, 14.98. $C_{16}H_{13}N_3S$ requires C, 68.79; H, 4.69; N, 15.04%; δ_H ($CDCl_3$, 300 MHz) 7.45-7.49 (6H, m, ArH) 7.68-7.69 (1H, d, ArH, *J* = 3 Hz) 7.73-7.78 (5H, m, ArH) 8.31-8.32 (1H, d, ArH, *J* = 3 Hz); m/z (EI) 279 (M^+, 15%) 202 (M-Ph, 4) 186 (SPh_2, 100) 170 (M-SPh, 15) 109 (SPh, 12) 92 (8) 77 (Ph, 16), $^{12}C_{16}{}^{1}H_{13}{}^{14}N_3{}^{32}S$ requires 279.08302, found: 279.08398, dev. 3.4 ppm. The starting material chloropyrazine was recovered in 16% yield.

Attempted preparation of triphenylphosphiniminopyrazine. To a solution of *N*-lithio-triphenylphosphinimine **4** (1.12 mmol) in anhydrous THF (15 cm^3) under nitrogen was added a solution of chloropyrazine (0.128 g, 1.12 mmol) in anhydrous THF (5 cm^3). The mixture was stirred under nitrogen at room temperature for 24 hrs and THF was removed *in vacuo*. T.l.c. and the ^1H nmr spectrum of the crude product showed that no reaction had taken place.

Attempted preparation of 2-(S,S-diphenylsulfilimino)pyridine. To a solution of *N*-lithio-*S,S*-diphenylsulfilimine **2** (1.23 mmol) in anhydrous THF (15 cm^3) was added 2-chloropyridine (0.140 g, 1.23 mmol). The mixture was stirred under nitrogen for 24 hrs at room temperature. At the end of the reaction, a white solid was suspended in a colourless solution. The white solid was removed by filtration and identified as lithium hydroxide. THF was removed from the filtrate *in vacuo* and ^1H nmr spectroscopy on the crude product showed that the only pyridine species present was the starting material, 2-chloropyridine.

2-Chloro-4-(S,S-diphenylsulfilimino)-6-n-propoxy-1,3,5-triazine **15** *and 2,4-di(S,S-diphenylsulfilimino)-6-n-propoxy-1,3,5-triazine* **16.** To a solution of *N*-lithio-*S,S*-diphenylsulfilimine **2** (1.23 mmol) in anhydrous THF (15 cm^3) was added 2,4-dichloro-6-*n*-propoxy-1,3,5-triazine (0.256 g, 1.23 mmol). The mixture was stirred under nitrogen for 24 hrs at room temperature. At the end of this time, a thick white solid had formed on the side of the flask. The white solid was removed by filtration and identified as lithium chloride. THF was removed from the filtrate *in vacuo* giving a yellow solid which was purified by flash column chromatography (1:5 v/v Et_2O - 40-60 °C petrol, gradient to 100% Et_2O). The monosubstituted product 2-chloro-4-(*S,S*-diphenylsulfilimino)-6-*n*-propoxy-1,3,5-triazine[1] **15** was obtained as a colourless oil in 9% yield and the disubstituted product 2,4-di(*S,S*-diphenylsulfilimino)-6-*n*-propoxy-1,3,5-triazine **16** was obtained as a brown solid in 3% yield; Rf = 0.03 (Et_2O); δ_H ($CDCl_3$-CD_3OD, 250 MHz) 0.88-0.95 (3H, t, CH_3, *J* = 7.2 Hz) 1.62-1.75 (2H, m, CH_2) 4.20 (2H, t, OCH_2, *J* = 6.2 Hz) 7.36-7.47 (12H, m, ArH) 7.71-7.76 (8H, m, ArH); m/z (EI) 537 (M^+, 4%) 428 (M-SPh, 2) 353 (1) 277 (2) 218 (10) 186 (SPh_2, 100) 152 (7) 109 (SPh, 28) 77 (Ph, 23), $^{12}C_{30}{}^{1}H_{27}{}^{14}N_5{}^{32}S_2{}^{16}O$ requires 537.165706, found: 537.16664, dev. 1.2 ppm.

Acknowledgements

We thank the DERA for the award of a research studentship (to CT). © British Crown Copyright 1998/DERA Farnborough, Hants. UK. Published with the permission of the Controller of Her Britannic Majesty's Stationery Office.

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