### Rapid and Effective Synthesis of Diarylsulfur Diimides from Substituted Anilines and Sulfur Monochloride

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**Abstract:** A one-pot and effective procedure has been developed for the synthesis of symmetrical diarylsulfur diimides from anilines, sulfur monochloride, and DABCO in good yields (70–90%). A plausible mechanism for this transformation has been proposed.

Key words: amines, dimerization, imides, anilines, diarylsulfur diimides, sulfur monochloride

Sulfur monochloride is an important reagent for the synthesis of alicyclic and, in particular, heterocyclic compounds.<sup>1</sup> The main feature of this substance is that it can add not only two sulfur atoms to the molecule, as it might be expected from its structure, but also one, three, four, five, or even more atoms.<sup>2</sup> The reactions of anilines with sulfur monochloride have also been investigated and the synthesis of benzofused 1,2,3-dithiazolium (Herz) salts **1** from anilines with the position *ortho* to the amino group unsubstituted using sulfur monochloride is a well-known and widely used procedure.<sup>3</sup> Recently we reported that 2methyl-3,5-dinitroaniline, which contains a methyl group *ortho* to the amino group, can be also reacted with sulfur monochloride to give benzothiazole **2** in high yield.<sup>4</sup>

We attempted to broaden the scope of this reaction, but we found that other anilines containing a methyl or other groups *ortho* to the amino group behave in an entirely different way that led not to ring closure, but to the formation of acyclic sulfur diimides.

Treatment of anilines with a mixture of sulfur monochloride and DABCO (1,4-diazabicyclo[2.2.2]octane) in chloroform followed by heating under reflux gave symmetrical diarylsulfur diimides **3** in high yields (Table 1).

Anilines containing two or more electron-withdrawing groups in the benzene ring, such as 2,4-dinitroaniline, 4-methyl-3,5-dinitroaniline, and 4-nitro-3-(trifluorometh-

yl)aniline, did not react with a mixture of sulfur monochloride and DABCO and the substrates were quantitatively isolated from the reaction mixtures.

We attempted to extend these sulfur monochloride reactions to nitrogen heterocycles with no success. 4-Amino-3,5-dimethylpyridine, 2-aminopyrimidine, and 3-amino-1,2,4-triazine were found to be inert towards sulfur monochloride and DABCO mixtures. The reaction of 4H-1,2,4triazol-4-amine **4** under these conditions unexpectedly gave tetrasulfur tetranitride in moderate yield (Scheme 2). Numerous methods are known for the synthesis of tetrasulfur tetranitride. The closest is the reaction between ammonia and sulfur monochloride in diethyl ether.<sup>7</sup>

$$N = N + S_2CI_2 + DABCO + CHCI_3 + S_4N_4$$

**Scheme 2** Reaction of 4*H*-1,2,4-triazol-4-amine **4** with sulfur monochloride and DABCO

To gain some insight into the mechanism of the formation of diarylsulfur diimides, a few anilines were treated with a smaller amount of sulfur monochloride (1 equiv) and DABCO (2 equiv) in chloroform at low temperature (–20 °C); bis(arylamino) disulfides **5** were isolated in high yields (Scheme 3). Recently a similar method for the synthesis of bis(arylamino) disulfides from anilines, sulfur monochloride, and pyridine in diethyl ether was described.<sup>8</sup>

Bis(arylamino) disulfides 5 were investigated further with the aim of obtaining diarylsulfur diimides. They were found to be inert in the reaction with excess DABCO in chloroform under reflux for four hours, but they were readily transformed into diarylsulfur diimides 3 in high





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Scheme 3 Synthesis of bis(arylamino) disulfides 5 from anilines

Table 1 Synthesis of Diarylsulfur Diimides 3 from Anilines<sup>a</sup>



Diarylsulfur diimide 3						Yield (%)	mp (°C)
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>		
3a	Н	Н	Н	Н	Н	74	oil
3b	Me	Н	Н	Н	Н	70	oil
3c	Me	Н	NO <sub>2</sub>	Н	Н	83	132–134
3d	Me	Н	Н	Н	NO <sub>2</sub>	90	159–161
3e	Me	NO <sub>2</sub>	Н	Н	Н	70	126–128
3f	Me	Н	Me	Н	Me	72	oil
3g	Н	NO <sub>2</sub>	Me	Н	Н	72	112–114
3h	NO <sub>2</sub>	Н	Me	Н	Н	84	127–129
3i	Н	Н	NO <sub>2</sub>	Н	Н	85	188–190
3j	NO <sub>2</sub>	Н	Н	Н	Н	75	125–127
3k	Н	Н	Cl	Н	Н	81	64–65

<sup>a</sup> Satisfactory physical and spectroscopic data was obtained for all new compounds; for known compounds  $3a,b,k^5$  and  $3f,i,k^6$  this data was comparable to that in the literature.

yields on treatment with sulfur monochloride (2 equiv) and DABCO (4 equiv) under reflux in chloroform for one hour (Scheme 4).

The key steps in the formation of diarylsulfur diimides **3** may be explained by the consecutive addition of two anilines to sulfur monochloride with the formation of bis(arylamino) disulfides **5** and addition of a further molecule of sulfur monochloride to give 3,6-diaryl-1,2,4,5,3,6-tetrathiadiazines **6** followed by extrusion of three sulfur atoms to produce sulfur diimides **3** (Scheme 5).

To the best of our knowledge 3,6-diaryl-1,2,4,5,3,6-tetrathiadiazines are not known compounds, although dialkyl derivatives of these heterocycles were prepared by the reaction of alkylamines with sulfur monochloride in diethyl ether.<sup>9</sup>



Scheme 4 Synthesis of diarylsulfur diimides 3 from bis(arylamino) disulfides 5

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Scheme 5 A plausible mechanism for the formation of diarylsulfur diimides 3 from anilines

In conclusion, we have developed a direct and effective synthesis of symmetrical diarylsulfur diimides from commercial available anilines and sulfur monochloride. Diarylsulfur diimides are of special interest because of their high reactivity and from a practical point of view as precursors for the preparation of the corresponding anions, which display a rich coordination chemistry to various metals.<sup>10</sup> Several methods for the preparation of diarylsulfur diimides are known from: (1) hardly available *N*-sulfenylamines,<sup>11</sup> and (2) anilines and sulfur tetrafluoride,<sup>6,12</sup> sulfur dichloride,<sup>13</sup> or sulfur.<sup>14</sup> However a simple, effective synthesis of diarylsulfur diimides from commercially available reagents remains desirable.

Reagents and solvents were analytically pure grade and were used without purification. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Specord M-80 instrument in KBr pellets. <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75.5 MHz) NMR were recorded on a Bruker AM 300 in the solvents indicated. Mass spectra were recorded on a Finnigan MAT INCOS 50 instrument using electron impact ionization.

#### Diarylsulfur Diimides 3; General Procedure

 $S_2Cl_2$  (0.16 mL, 2.0 mmol) was added dropwise to a stirred soln of the aniline (1.0 mmol) and DABCO (0.45 g, 4.0 mmol) in CHCl<sub>3</sub> (15 mL) at -30 °C. The mixture was stirred for 1 h at r.t., refluxed for 1 h, and cooled to 20 °C. It was then filtered and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel Merck 60, hexane to hexane-CH<sub>2</sub>Cl<sub>2</sub> mixtures).

#### **1,3-Bis(2-methyl-4-nitrophenyl)-2\lambda^4-diazathia-1,2-diene (3c)** Orange solid; yield: 138 mg (83%); mp 132–134 °C.

IR (KBr): 1282 and 1099 cm<sup>-1</sup> (N=S=N).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.41 (s, 6 H, CH<sub>3</sub>), 7.49 (d, *J* = 8.8 Hz, 2 H, CH), 7.97 (d, *J* = 8.8 Hz, 2 H, CH), 8.11 (s, 2 H, CH).

 $^{13}C$  NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 18.7 (CH<sub>3</sub>), 122.0, 122.0, and 125.9 (3 CH), 133.3, 145.7, and 148.5 (3 sp<sup>2</sup> C).

MS (EI, 70 eV): m/z (%) = 332 (M<sup>+</sup>, 38), 315 (50), 285 (68), 181 (100), 152 (40), 135 (92), 122 (39), 76 (40), 64 (45).

Anal. Calcd for  $C_{14}H_{12}N_4O_4S$  (332.06): C, 50.60; H, 3.64; N, 16.86; S, 9.65. Found: C, 50.42; H, 3.42; N, 16.54; S, 9.85.

#### 1,3-Bis(2-methyl-6-nitrophenyl)- $2\lambda^4$ -diazathia-1,2-diene (3d)

Yellow crystalline solid; yield: 150 mg (90%); mp 159–161 °C. IR (KBr): 1261 and 1101 cm<sup>-1</sup> (N=S=N).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.29 (s, 6 H, CH<sub>3</sub>), 6.99 (m, 2 H, CH), 7.37 (d, *J* = 7.3 Hz, 2 H, CH), 7.53 (d, *J* = 8.1 Hz, 2 H, CH).

 $^{13}C$  NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 18.9 (CH<sub>3</sub>), 122.6, 125.1, and 136.1 (3 CH), 132.7, 136.7, and 139.3 (3 sp<sup>2</sup> C).

MS (EI, 70 eV): *m/z* (%) = 332 (M<sup>+</sup>, 13), 286 (23), 166 (43), 164 (55), 152 (100), 150 (90), 135 (42), 106 (52), 97 (62), 91 (85), 64 (97).

Anal. Calcd for  $C_{14}H_{12}N_4O_4S$  (332.06): C, 50.60; H, 3.64; N, 16.86; S, 9.65. Found: C, 50.55; H, 3.41; N, 16.79; S, 9.81.

# **1,3-Bis(2-methyl-3-nitrophenyl)-** $2\lambda^4$ -diazathia-1,2-diene (3e) Yellow crystalline solid; yield: 116 mg (70%); mp 126–128 °C.

IR (KBr): 1287 and 1100 cm<sup>-1</sup> (N=S=N).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.40 (s, 6 H, CH<sub>3</sub>), 7.08 (m, 2 H, CH), 7.34 (d, *J* = 8.1 Hz, 2 H, CH), 7.53 (d, *J* = 8.1 Hz, 2 H, CH).

<sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.6 (CH<sub>3</sub>), 122.1, 125.4, and 126.3 (3 CH), 126.0, 144.9, and 151.2 (3 sp<sup>2</sup> C).

MS (EI, 70 eV): m/z (%) = 332 (M<sup>+</sup>, 55), 317 (100), 285 (64), 181 (89), 135 (67), 90 (30), 77 (30).

Anal. Calcd for  $C_{14}H_{12}N_4O_4S$  (332.06): C, 50.60; H, 3.64; N, 16.86; S, 9.65. Found: C, 50.32; H, 3.50; N, 16.49; S, 9.89.

### **1,3-Bis(4-methyl-3-nitrophenyl)-** $2\lambda^4$ -diazathia-1,2-diene (3g) Yellow crystalline solid; yield: 120 mg (72%); mp 112–114 °C.

IR (KBr): 1281 and 1097 cm<sup>-1</sup> (N=S=N).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.60 (s, 6 H, CH<sub>3</sub>), 7.34 (d, *J* = 8.1 Hz, 2 H, CH), 7.56 (d, *J* = 8.1 Hz, 2 H, CH), 8.03 (s, 2 H, CH).

 $^{13}C$  NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 20.2 (CH<sub>3</sub>), 119.1, 127.4, and 133.3 (3 CH), 132.3, 143.5, and 149.1 (3 sp<sup>2</sup> C).

MS (EI, 70 eV): *m/z* (%) = 332 (M<sup>+</sup>, 56), 317 (100), 285 (34), 271 (33), 182 (48), 136 (33), 108 (47), 77 (50), 65 (73).

Anal. Calcd for  $C_{14}H_{12}N_4O_4S$  (332.06): C, 50.60; H, 3.64; N, 16.86; S, 9.65. Found: C, 50.52; H, 3.49; N, 16.15; S, 9.92.

## **1,3-Bis(4-methyl-2-nitrophenyl)-** $2\lambda^4$ -diazathia-1,2-diene (3h) Yellow crystalline solid; yield: 139 mg (84%); mp 127–129 °C.

IR (KBr): 1252 and 1099 cm<sup>-1</sup> (N=S=N).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.30 (s, 6 H, CH<sub>3</sub>), 6.97 (d, *J* = 8.1 Hz, 2 H, CH), 7.14 (d, *J* = 8.1 Hz, 2 H, CH), 7.59 (s, 2 H, CH).

<sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta = 20.7$  (CH<sub>3</sub>), 123.2, 124.8, and 134.3 (3 CH), 135.8, 136.7, and 139.8 (3 sp<sup>2</sup> C).

MS (EI, 70 eV): *m/z* (%) = 332 (M<sup>+</sup>, 17), 315 (11), 286 (32), 182 (40), 152 (80), 124 (33), 76 (84), 65 (100).

Anal. Calcd for  $C_{14}H_{12}N_4O_4S$  (332.06): C, 50.60; H, 3.64; N, 16.86; S, 9.65. Found: C, 50.28; H, 3.39; N, 16.67; S, 9.87.

#### Bis(arylamino) Disulfides 5; General Procedure

 $S_2Cl_2$  (0.16 mL, 2.0 mmol) was added dropwise to a stirred soln of the aniline (2.0 mmol) and DABCO (0.45 g, 4.0 mmol) in CHCl<sub>3</sub> (15 mL) at -30 °C. The mixture was stirred at -20 °C for 0.5 h and poured into H<sub>2</sub>O (20 mL). The organic layer was washed with H<sub>2</sub>O and dried (MgSO<sub>4</sub>). Solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography (silica gel Merck 60, hexane to hexane-CH<sub>2</sub>Cl<sub>2</sub> mixtures).

#### *N*,*N*'-Dithiobis(2-methylaniline) (5b)

Yellow gum; yield: 251 mg (91%).

IR (KBr): 3377 cm<sup>-1</sup> (NH).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.17 (s, 6 H, CH<sub>3</sub>), 5.17 (s, 2 H, NH), 6.90 (d, *J* = 7.3 Hz, 2 H, CH), 7.14 (m, 4 H, 2 CH), 7.34 (d, *J* = 8.1 Hz, 2 H, CH).

<sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 17.4 (CH<sub>3</sub>), 115.1, 121.1, 127.1, and 130.7 (4 CH), 124.9 and 143.5 (2 sp<sup>2</sup> C).

MS (EI, 70 eV): m/z (%) = 276 (M<sup>+</sup>, 12), 227 (20), 136 (62), 107 (100), 94 (56), 77 (80), 65 (31).

Anal. Calcd for  $C_{14}H_{16}N_2S_2$  (276.08): C, 60.83; H, 5.83; N, 10.13; S, 23.20. Found: C, 60.69; H, 5.72; N, 10.04; S, 23.45.

#### N,N'-Dithiobis(2-methyl-3-nitroaniline) (5e)

Yellow crystalline solid; yield: 289 mg (79%); mp 119–121 °C. IR (KBr): 3396 (NH), 1520 and 1343 cm<sup>-1</sup> (NO<sub>2</sub>).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.24 (s, 6 H, CH<sub>3</sub>), 5.40 (s, 2 H, NH), 7.10 (m, 2 H, CH), 7.29 (d, *J* = 8.1 Hz, 2 H, CH), 7.37 (d, *J* = 8.1 Hz, 2 H, CH).

 $^{13}C$  NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 12.7 (CH<sub>3</sub>), 116.7, 118.8, and 126.9 (3 CH), 118.9, 145.4, and 151.6 (3 sp<sup>2</sup> C).

MS (EI, 70 eV): *m/z* (%) = 366 (M<sup>+</sup>, 9), 199 (50), 182 (43), 165 (30), 151 (100), 135 (34), 76 (26).

Anal. Calcd for  $C_{14}H_{14}N_4O_4S_2$  (366.06): C, 45.89; H, 3.85; N, 15.29; S, 17.50. Found: C, 45.72; H, 3.75; N, 15.14; S, 17.78.

#### N,N'-Dithiobis(4-methyl-3-nitroaniline) (5g)

Yellow crystalline solid; yield: 245 mg (67%); mp 190–192 °C. IR (KBr): 3325 cm<sup>-1</sup> (NH).

<sup>1</sup>H NMR (300 MHz, pyridine- $d_5$ ):  $\delta = 2.40$  (s, 6 H, CH<sub>3</sub>), 7.02 (d, J = 8.1 Hz, 2 H, CH), 7.29 (d, J = 8.1 Hz, 2 H, CH), 7.87 (s, 2 H, CH), 9.62 (s, 2 H, NH).

<sup>13</sup>C NMR (75.5 MHz, pyridine- $d_5$ ):  $\delta = 19.6$  (CH<sub>3</sub>), 111.7, 121.4, and 133.5 (3 CH), 124.7, 147.1, and 149.6 (3 sp<sup>2</sup> C).

MS (EI, 70 eV): m/z (%) = 366 (M<sup>+</sup>, 9), 199 (12), 167 (13), 152 (100), 135 (62), 76 (82).

Anal. Calcd for  $C_{14}H_{14}N_4O_4S_2$  (366.05): C, 45.89; H, 3.85; N, 15.29; S, 17.50. Found: C, 45.69; H, 3.72; N, 15.18; S, 17.42.

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**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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