

# SYNLETT Spotlight 238

## Disulfur Dichloride (S<sub>2</sub>Cl<sub>2</sub>)

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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### Introduction

Disulfur dichloride (S<sub>2</sub>Cl<sub>2</sub>), also known as sulfur chloride (S<sub>2</sub>Cl<sub>2</sub>), is widely used in organic synthesis as a sulfurizing and chlorinating agent. Sulfide compounds are found in many natural products and may have useful biological properties.<sup>1</sup> This reagent has been explored for the preparation of heteroaryl disulfides,<sup>2</sup> symmetric aryl di-, tri-, and tetrasulfides,<sup>2,3</sup> episulfides<sup>4</sup> and benzopolysulfides.<sup>5,6</sup> Moreover, S<sub>2</sub>Cl<sub>2</sub> is a suitable substrate for the synthesis of dialkoxy disulfide,<sup>7</sup> or for the Herz reaction.<sup>8</sup> It decomposes into SO<sub>2</sub>, HCl, and S<sub>8</sub> when exposed to wet air due to reaction with water.

S<sub>2</sub>Cl<sub>2</sub> is a smelly, clear, yellowish-red, oily liquid. It should be used with care and proper precautions must be taken because it is toxic, corrosive, and harmful to the environment.

### Preparation

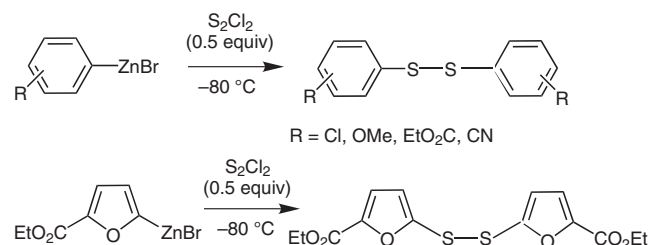
S<sub>2</sub>Cl<sub>2</sub> is synthesized by partial chlorination of elemental sulfur<sup>9</sup> and is also commercially available.



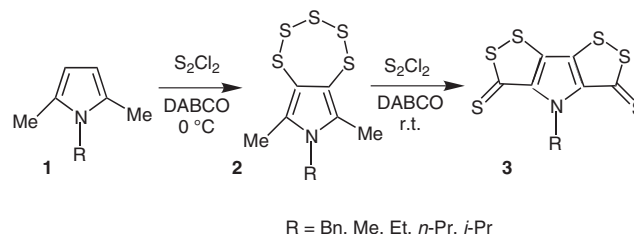
Scheme 1

### Abstracts

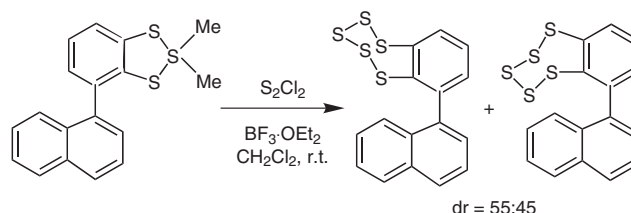
(A) Korn and Knochel<sup>2</sup> have described the use of S<sub>2</sub>Cl<sub>2</sub> to achieve functionalized aryl and heteroaryl disulfides from functionalized zinc organometallics. All the reactions were carried out at –80 °C, producing within ten minutes the expected disulfide in 62–99% yield.



(B) An equilibrated equimolecular mixture of S<sub>2</sub>Cl<sub>2</sub> and DABCO (1,4-diazobicyclo[2.2.2]octane) has been used for treatment of N-substituted 2,5-dimethylpyrroles **1** giving pentathiepinopyrroles **2** in moderate yields. Further reaction of **2** with the same mixture at room temperature has resulted in an extensive reaction cascade, to give bis(dithiolo)pyrrole **3** in high yield.<sup>10</sup>



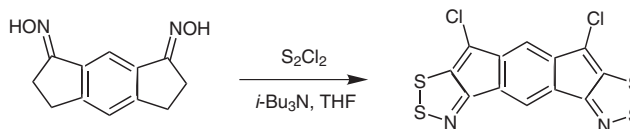
(C) Chiral benzopolysulfides are rarely described in the literature. Sato and co-workers<sup>5</sup> have reported the synthesis of axially chiral benzopentathiepins by treatment of dithiastannole with  $S_2Cl_2$ .



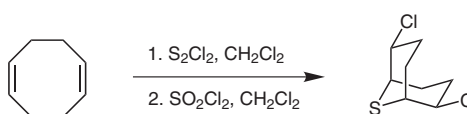
(D) Reaction of a diol with  $S_2Cl_2$  resulted in the first example of a stable and fully characterized cyclic dialkoxo disulfide under mild conditions.<sup>11</sup>



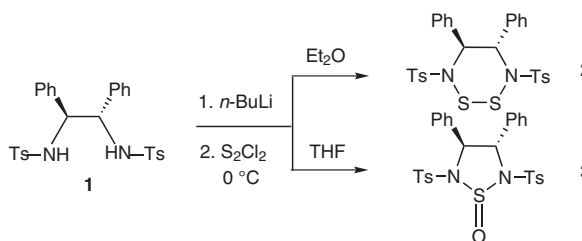
(E)  $S_2Cl_2$  was reacted with 1,7-*s*-hydrindacenedione dioximes leading to the first example of bis[1,2,3]dithiazolo-*s*-indacene.<sup>12</sup> In this example,  $S_2Cl_2$  has also been found as a chlorinating agent.



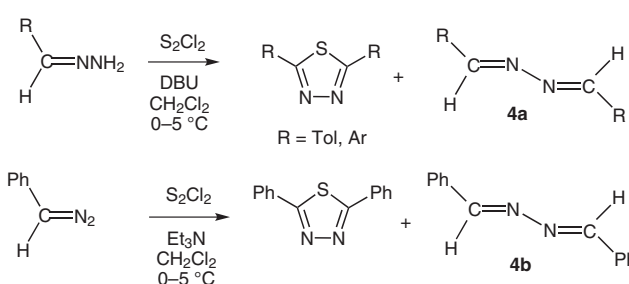
(F) Treatment of 1,5-cyclooctadiene with  $S_2Cl_2$ , followed by reaction with sulfonyl chloride ( $SO_2Cl_2$ ) provides high yields of 2,6-dichloro-9-thiabicyclo[3.3.1]nonane in a robust and convenient manner. This product may be used as connector and as a chiral scaffold through nucleophilic substitution of chloride.<sup>13</sup>



(G)  $S_2Cl_2$  is a very effective reagent for the preparation of nitrogen-substituted thiosulfinyl compounds ( $R_2N)_2S=S$ . When the substituted 1,2-ethylenediamine (**1**) containing electron-withdrawing groups on the nitrogen atoms was treated with *n*-BuLi in  $Et_2O$  and then with  $S_2Cl_2$ , compound **2**, a new heterocyclic system, was obtained in 57% yield. The reaction in THF gave sulfoxide **3** in 27% yield.<sup>14</sup>



(H) The reaction of aldehyde hydrazones or phenyldiazomethane with  $S_2Cl_2$  in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or  $Et_3N$  gave 1,3,4-thiadiazoles in good to moderate yields. The azines **4a** and **4b** were obtained as side products.<sup>15</sup>



## References

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