

# SYNLETT Spotlight 238

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

Compiled by Bárbara Vasconcellos da Silva



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

Bárbara Vasconcellos da Silva was born in Rio de Janeiro, Brazil in 1981. She received her Chemistry degree from Universidade Federal do Rio de Janeiro in 2007 and she is currently working toward her Ph.D. in organic synthesis under the supervision of Dr. Angelo da Cunha Pinto at the same university. Her research interests focus on the synthesis of isatins and oxindole derivatives.

Centro de Tecnologia, Bloco A, Instituto de Química, Universidade Federal do Rio de Janeiro, 21941-590 Rio de Janeiro, Brazil  
E-mail: barbara.iq@gmail.com

### 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

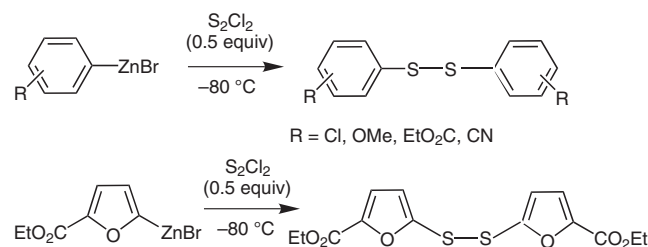
S<sub>2</sub>Cl<sub>2</sub> is synthesized by partial chlorination of elemental sulfur<sup>9</sup> and is also commercially available.



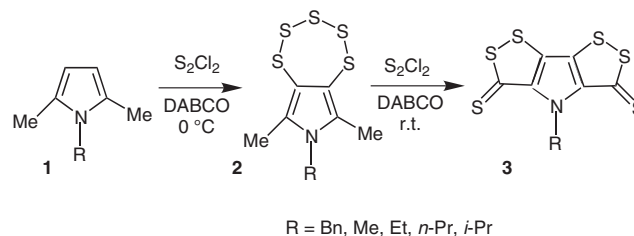
Scheme 1

### Abstracts

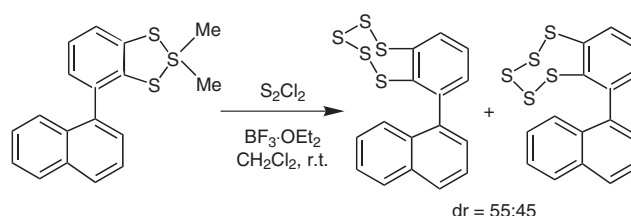
(A) Korn and Knochel<sup>2</sup> have described the use of S<sub>2</sub>Cl<sub>2</sub> to achieve functionalized aryl and heteroaryl disulfides from functionalized zinc organometallics. All the reactions were carried out at -80 °C, producing within ten minutes the expected disulfide in 62–99% yield.



(B) An equilibrated equimolar 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>



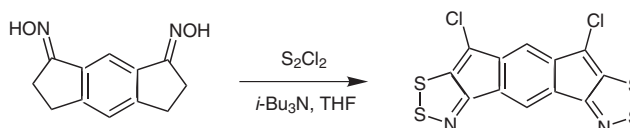
(C) Chiral benzopolysulfides are rarely described in the literature. Sato and co-workers<sup>5</sup> have reported the synthesis of axially chiral benzopentathiepins by treatment of dithiastannole with  $S_2Cl_2$ .



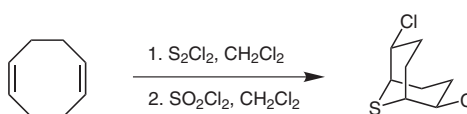
(D) Reaction of a diol with  $S_2Cl_2$  resulted in the first example of a stable and fully characterized cyclic dialkoxy disulfide under mild conditions.<sup>11</sup>



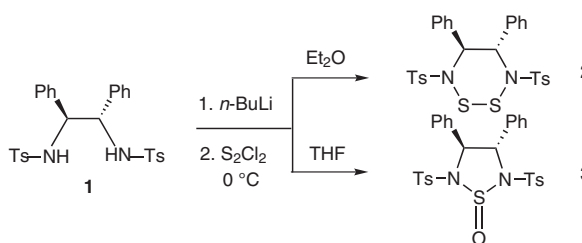
(E)  $S_2Cl_2$  was reacted with 1,7-s-hydrindacenedione dioximes leading to the first example of bis[1,2,3]dithiazolo-s-indacene.<sup>12</sup> In this example,  $S_2Cl_2$  has also been found as a chlorinating agent.



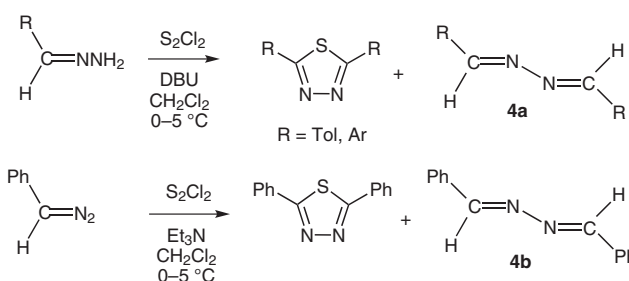
(F) Treatment of 1,5-cyclooctadiene with  $S_2Cl_2$ , followed by reaction with sulfuryl chloride ( $SO_2Cl_2$ ) provides high yields of 2,6-dichloro-9-thiabicyclo[3.3.1]nonane in a robust and convenient manner. This product may be used as connector and as a chiral scaffold through nucleophilic substitution 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<sub>2</sub>O 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<sub>3</sub>N gave 1,3,4-thiadiazoles in good to moderate yields. The azines **4a** and **4b** were obtained as side products.<sup>15</sup>



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