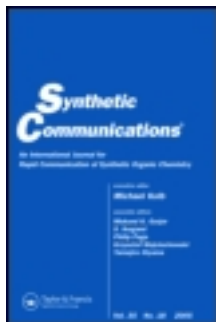


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### Hypervalent Iodine in Synthesis XXI: A Facile Method for the Preparation of Thiosulfonic S-Esters by the Oxidation of Diaryl Disulfides or Thiophenols with Phenyliodine (III) bis(Trifluoroacetate)

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**HYPERVALENT IODINE IN SYNTHESIS X X I ; A FACILE  
METHOD FOR THE PREPARATION OF THIOSULFONIC  
S-ESTERS BY THE OXIDATION OF DIARYL DISULFIDES  
OR THIOPHENOLS WITH PHENYLIODINE ( III )  
BIS(TRIFLUOROACETATE)**

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**Abstract:** Phenyliodine ( III ) bis (trifluoroacetate) can be used to readily oxidize diaryl disulfides or thiophenols to corresponding thiosulfonic S-esters with good yields under very mild conditions.

Thiosulfonic S-esters have been reported<sup>[1]</sup> to be powerful sulfonylating agents which react faster and more completely than disulfides; in addition, they are more stable and easier to handle than sulfinyl chlorides. They have also been found to be useful for temporary blocking of mercapto groups in protein chemistry<sup>[2]</sup>. Unfortunately, the synthetic application of thiosulfonic

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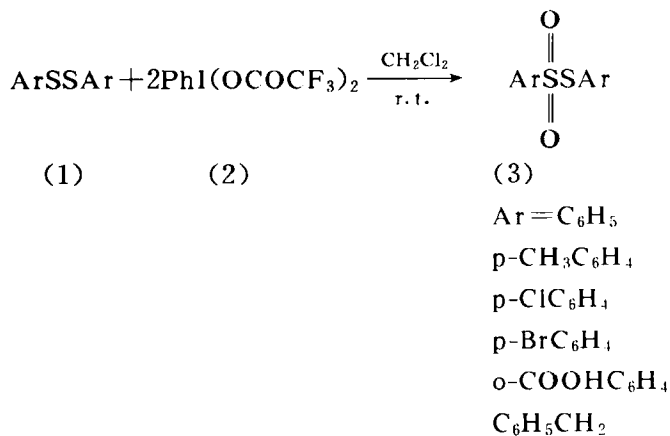
Ⓐ To whom correspondence should be addressed.

S-esters has hitherto been limited by their somewhat difficult preparation. Although there exist some methods of preparation, e. g. 1-hydroxypyridine-2 (1H)-thione with arenesulfinyl chlorides<sup>[3]</sup>, arenesulfonyl chlorides with potassium iodide in anhydrous acetone under catalytic amounts of pyridine<sup>[4]</sup>, sulfonic acid reduction by stannous chloride<sup>[5]</sup>, sulfinyl chlorides with activated Zn refluxing in benzene<sup>[6]</sup>, thiosulfonates with NaIO<sub>4</sub><sup>[7]</sup>, thiophenols with N<sub>2</sub>O<sub>4</sub><sup>[8]</sup>, disulfides with H<sub>2</sub>O<sub>2</sub>/AcOH<sup>[9]</sup>, etc. Most of them need high requirements of reaction conditions, long reaction time, toxic and unstable reagents. Therefore, it is still necessary to find out a facile method for preparation of thiosulfonic S-esters.

Following our findings that phenyliodine (III) bis (trifluoroacetate), PIB, could oxidize the diaryl ditellurides to afford the arenetellurinic mixed anhydrides<sup>[10]</sup> and the diaryl diselenides to afford the areneseleanyl trifluoroacetates<sup>[11]</sup>, these prompted us to examine the reaction of PIB with diaryl disulfides, since S, Se and Te are members of the same family. We found that the oxidation of diaryl disulfides with PIB readily occurred in a single step which provides a facile method for the preparation of thiosulfonic S-esters. (Scheme 1)

To the stirred solution of the appropriate diaryl disulfides in methylene chloride was slowly added the solution of PIB in methylene chloride at room temperature. Then, simple stirring of the mixture for 15 minutes gave, after workup and isolation, the corresponding thiosulfonic S-esters in good yields, as shown in Table 1.

The results show that when there are *o*-, *p*-directive groups on the aromatic ring, the reaction can take place readily whereas *m*-directive groups can make the reaction difficult, and even for strong electron-withdrawing group such as -NO<sub>2</sub> the reaction will not occur under this condition.



(Scheme 1)

Table 1. Thiosulfonic S-esters (3) from diaryl disulfides

product (3)	yield (%)	m. p. (°C)	Lit. M. P (°C)	I. R. (KBr) cm <sup>-1</sup>
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> SC <sub>6</sub> H <sub>5</sub>	78	42-44	42-44 <sup>[12]</sup>	1330, 1145
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -p	83	74-76	76-78 <sup>[13]</sup>	1330, 1145
p-ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Cl-p	74	135-136	137-138 <sup>[14]</sup>	1330, 1148
p-BrC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Br-p	73	157-159	160-161 <sup>[14]</sup>	1338, 1148
o-COOHC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> COOH-o <sup>[a]</sup>	51	212-214	210-216 <sup>[15]</sup>	1330, 1148
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> <sup>[b]</sup>	70	68-70	/	1330, 1148
o-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -o	0	/	/	/

[a] o-COOHC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>COOH-o could be available under reflux for 2 hours in MeCN.

[b] C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SO<sub>2</sub>SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> could be available under reflux for 2 hours in CH<sub>2</sub>Cl<sub>2</sub>

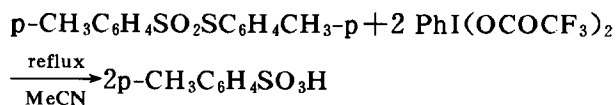
Unlike the reactions of diaryl diselenides and diaryl ditellurides with PIB, which could lead to the cleavage of Se—Se and Te—Te, the reaction of diaryl disulfides with PIB did not result in the cleavage of S—S bond. This result is accordance with the fact that the S—S bond is stronger than Se—Se bond and Te—Te bond. In order to investigate the possibility of S—S bond cleaved by PIB under vigorous conditions, we examined the reaction of  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{SC}_6\text{H}_4\text{CH}_3\text{-}p$  with PIB under reflux in MeCN. (Scheme 2)

We found that under these condition, the S—S bond could be cleaved by further oxidation with PIB. This means under the mild conditions the S—S bond would survive during oxidation.

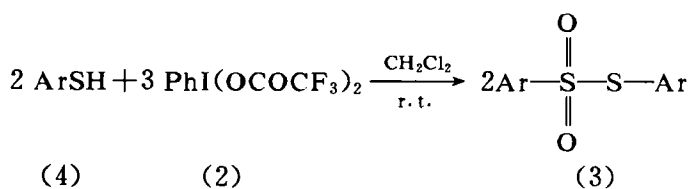
Combined with the fact that, in general, diaryl disulfides can be prepared from thiophenols and phenyliodine(III) diacetate can oxidise thiophenols to diaryl disulfides, we thought it possible to oxidise thiophenols directly to thiosulfonic S-esters with PIB. As expected, when solution of 1.5 equivalent PIB in methylene chloride was added to stirred solution of the appropriate thiophenol in methylene chloride at room temperature, the reaction took place rapidly. After workup and isolation, the corresponding thiosulfonic S-esters in good yields were obtained. (Scheme 3)

Considering [hydroxy(tosyloxy)iodo]benzene,  $\text{PhI}(\text{OH})\text{OTs}$ , is a similar hypervalent iodine oxidant, we examined its reaction with disulfide such as  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SSC}_6\text{H}_4\text{CH}_3\text{-}p$  with the result that it can also oxidise the disulfide to thiosulfonic S-ester. (Scheme 4)

In conclusion, we have provided a facile method for the preparation of thiosulfonic S-esters from diaryl disulfides and thiophenols which has some advantages over the existing ones such as easily accessible starting materials, mild reaction conditions, simple procedure, and avoiding the use of toxic and haz-

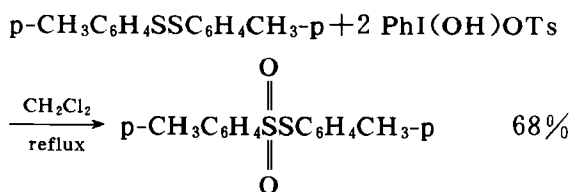


(Scheme 2)



Ar	yield (%)
$\text{C}_6\text{H}_5$	79
p- $\text{CH}_3\text{C}_6\text{H}_4$	81
p- $\text{ClC}_6\text{H}_4$	76
$\text{C}_6\text{H}_5\text{CH}_2$	74

(Scheme 3)



(Scheme 4)

ardous reagents. Moreover, the range of application of hypervalent iodine in organic synthesis has been extended.

## Experimental Section

### 1. General procedure of the preparation of thiosulfonic S-esters from diaryl disulfides :

Under stirring, the solution of 2 mmol (0.86g)  $\text{PhI}(\text{O-COCF}_3)_2$  in 20 ml  $\text{CH}_2\text{Cl}_2$  was added to the solution of 1 mmol diaryl disulfides in 5 ml  $\text{CH}_2\text{Cl}_2$  at the room temperature. After 15 minutes, the mixture was washed with 5% NaOH 10ml and then washed with 10 ml water. The  $\text{CH}_2\text{Cl}_2$  layer was dried by anhydrous magnesium sulphate. After removal of the most solvent, the residue was isolated by TLC with the petroleum ether (b. p. 30–60°C) and  $\text{CH}_2\text{Cl}_2$  in the ratio of 2 to 1 as the developer to give the thiosulfonic S-esters and purified by recrystallization from  $\text{CH}_3\text{OH}$ . The products were identified by comparison of melting points with literature values and by IR spectral data.

### 2. General procedure of the preparation of thiosulfonic S-ester from thiophenols :

Under stirring, the solution of 1.5 mmol (0.645g)  $\text{PhI}(\text{O-COCF}_3)_2$  in 20 ml  $\text{CH}_2\text{Cl}_2$  was added to the solution of 1 mmol thiophenols in 5 ml  $\text{CH}_2\text{Cl}_2$  at room temperature. After reaction for 30 minutes, the products was isolated as the above procedure.

### 3. Further oxidation of S-(p-toluenyl)-p-toluenesulfonate with PIB :

Under stirring, the solution of 2 m mol (0.86g)  $\text{PhI}(\text{O-COCF}_3)_2$  in 20ml MeCN was added to the solution of 1m mol (0.28 g) p- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{SC}_6\text{H}_4\text{CH}_3$ -p in 5 ml MeCN. After reflux for about 2 hours, the solvent was removed under reduced pressure. The residue was added some petroleum ether (b. p 60–90°C) to give p-toluenesulfonic acid 0.27 g with yield 78%, m. p. 99°C (Lit. 102°C) I. R. (KBr),  $1330\text{cm}^{-1}$ ,  $1140\text{cm}^{-1}$ .



**4. S-(p-toluenyl)- p-toluenesulfonate from  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SSC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-p with [hydroxy(tosyloxy)iodo]benzene :**

Under stirring, the suspended solution of 2m mol (0.50g) PhI(OH)OTs in 20 ml CH<sub>2</sub>Cl<sub>2</sub> was added to the solution of 1m mol (0.246g) p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SSC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-p in 5ml CH<sub>2</sub>Cl<sub>2</sub>. After re-flux for about 1 hour until the solution became clear, the mixture was isolated as above procedure 1 to give S-(p-toluenyl) p-toluenesulfonate 0.19g, yield 68%, M. P. 70–72°C (Lit. 76–78°C) IR(KBr) 1330cm<sup>-1</sup>, 1145cm<sup>-1</sup>.

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