Oxidation of Thiols with IBX or DMP: One-pot Access to Thiosulfonates or 2-Iodobenzoates and Applications in Functional Group Transformations

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ABSTRACT: Thiosulfonates are accessed by oxidation of feedstock thiols using either DMP in DCM or IBX in MeCN at rt (~30 °C). The protocol gives access to a variety of thiosulfonates in good to excellent yields from both aromatic and aliphatic thiols. The reaction with DMP is found to be better than IBX in terms of reaction rate and conversion, whereas the oxidation with DMP requires lower equivalent than IBX. Benzyl thiols are however found to follow a different reaction pathway when treated with DMP; O-benzyl esters of o-iodobenzoates were isolated. The 1H NMR spectroscopic monitoring studies for the IBX-mediated oxidation of thiol found disulfide as an initial intermediate, which is proposed to undergoes a cascade of oxidations to produce thiosulfonate.

INTRODUCTION

Sulfur-containing compounds, abundant in various natural products,1–2 have potential applications in pharmaceutical,3–4 agricultural,5,6 and chemical synthesis.4 Among the organosulfur compounds, the derivatives with unique S–S bonds are particularly important due to their vast applications; the family includes: disulfides,7–9 thiosulfonates9,10 and thiosulfonates.11,12 In this regard, the protocols that install a new S–S bond is synthetically very important. Among S–S bond containing molecules, thiosulfonates — also known as the S-esters of thiosulfonic acid and sulfonothioates — are a special class, where one of the sulfur of the S–S bond is a dioxide, i.e., SO2, and the other one is a simple sulfide. While the oxidation state of the S-atom in the former is S(VI), the latter has S(II). This polar nature of the asymmetric S–S bond makes the thiosulfonates amphiphilic, where one sulfur atom is electrophilic and the other is nucleophilic. Thus, thiosulfonates can serve as sulfonylation reagents, which is synthetically very useful.4 The above discussion clearly projects thiosulfonates as an efficient sulfonylation reagent, which are considered better compared to disulfides.12,15 Furthermore, when compared with sulfonyl halides, these sulfonylation reagents are more stable and easy to handle.16 Thiosulfonates are also employed as sulfonylation reagents, for example, C–S bonds were installed when treated with compounds bearing active methylene groups.17–19 Apart from synthetic uses, thiosulfonates found to exhibit medicinal properties like antimicrobial, antibacterial, antiviral, antifungal, etc.,4 as well as employed for antiplatelet therapy.20

A number of methodologies have thus far been reported to access thiosulfonates.4,12 Four main strategies followed for their synthesis are: i) from thiols or disulfides in the presence of oxidants with or without metal catalyst,21–23 or without24–28 involvement of transition metals, ii) the addition of disulfides or thiols to sodium sulfonate,29 iii) the reductive coupling of sulfonyl chlorides30,31 and sulfonyl hydrazides with or without metal catalyst,32–34 and iv) the reaction of sulfonyl halides35 with other thiols or thiolates.4,12 In addition, electrochemical methods are also known for the synthesis of thiosulfonates.36,37 Despite the availability of several reagents for the synthesis of thiosulfonates in the literature, only a few are applicable for one-pot direct oxidation of thiols to thiosulfonates.4,20 Most of these methodologies suffer from several drawbacks such as complicated procedures for the synthesis of reagents, the need to activate reagents, use of hazardous chemicals, and expensive techniques.4 Thus, general and facile protocols for direct oxidative transformation of thiols to thiosulfonates remain much sought after.

Our research group is active in the development of oxidation protocols using o-iodoxybenzoic acid (IBX)38–41 and
modified IBXs, and Oxone. In 2016, we have reported a facile protocol to access sulfonic acids using Oxone or KBrO3. During the study, oxidation of thioles with hypervalent iodanes like phenyl iodo bis(trifluoroacetate) (PIFA, $\lambda^3$-iodane), o-iodoxybenzoic acid (IBX, $\lambda^5$-iodane) and NaIO4 ($\lambda^3$-iodane), afforded the disulfide in 84–93% yields at rt. When a higher equivalent of the oxidant will be employed, the in situ generated disulfides should further be oxidized into symmetrical thiosulfonates in one-pot. We thus employed organo-$\lambda^5$-iodanes, namely, IBX and Dess-Martin periodinane (DMP), for this tandem transformation of thioles to thiosulfonates. This hypervalent iodine (V) oxidants are well-known for their mild, user- and eco-friendly attributes, and are capable of executing myriad of transformations. As anticipated, the reactions of both DMP (1.2 equiv) and IBX (2.0 equiv) were found to serve the facile conversion of thioles to thiosulfonates at rt. For benzyl thioles, the reaction with DMP led to the formation of o-iodobenzoate, which were successfully and selectively converted to valuable functional groups such as aldehyde and alcohol. The detailed study and mechanistic insights are discussed below.

**RESULTS AND DISCUSSION**

In our previous report, the oxidation p-bromothiophenol with organo-iiodanes PIDA (1.0 equiv in CHCl3, 3 h) or IBX (1.0 equiv in MeCN, 2h) afforded the homo-coupled product, i.e., disulfide, in 84 and 92% yields, respectively. PIDA is a $\lambda^3$-iodane with iodine at +3 oxidation state, whereas the iodine is at +5 oxidation state for IBX. Considering the oxidation states, the oxidation with more electron-deficient $\lambda^5$-iodane, i.e., IBX, should be superior to the PIDA, and one can expect further oxidation of disulfide to thiosulfonates. However, while the reactivities of both iodosanes remained similar that produced disulfide selectively, nothiosulfonate was observed from the reaction of IBX and thiol. It might be due to the poor solubility of IBX and its reduced product, i.e., o-iodosobenzoic acid (IBA, $\lambda^3$-iodane). It is worth mentioning that IBX is not soluble in common organic solvents except polar and high-boiling DMSO. To facilitate further oxidation of the in situ generated disulfide to thiosulfonate in common organic solvents, we carried out reactions with the soluble triacetate derivative of IBX, i.e., DMP. The oxidation of p-bromothiophenol (1b), as a representative case, was optimized using DMP in different solvents like DCM, dichloroethane (DCE), AcOH, acetone, MeOH, DMSO and DMF, at rt (~30 °C), cf. Table 1. The reactions with DMP (1.2 equiv) in DCM and DMF gave the desired thiosulfonate 2b in ~81% yield (entries 2 and 10, respectively), whereas in other solvents, bis(4-bromophenyl) disulfide (3b) was obtained as the major product. The reaction with only 1.2 equiv of DMP suggests that the in situ produced $\lambda^3$-iodane, from the reduction of DMP, also participates in the oxidation process. The reaction in methanol clearly indicates that the reduced $\lambda^3$-iodane from DMP can promote oxidation of thiol to disulfide and/or thiosulfonate (entry 6). It is also noteworthy that no over-oxidation products, i.e., sulfonal sulfoxide and/or disulfone, were formed when higher equivalents of DMP (2.4 equiv) was employed (entry 4).

**TABLE 1. Optimization of the conversion of p-bromothiophenol (1b) to thiosulfonate 2b using DMP in various solvents.**

<table>
<thead>
<tr>
<th>entry</th>
<th>DMP (equiv)</th>
<th>solvent</th>
<th>time (h)</th>
<th>yields (%)b</th>
<th>2b</th>
<th>3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2</td>
<td>DCE (4)</td>
<td>18</td>
<td>20</td>
<td>61</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>DCM (4)</td>
<td>18</td>
<td>88</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>DCM (4)</td>
<td>14</td>
<td>20</td>
<td>56</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>2.4</td>
<td>DCM (4)</td>
<td>18</td>
<td>86</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
<td>CHCl3 (5)</td>
<td>20</td>
<td>33</td>
<td>49</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>MeOH (5)</td>
<td>36</td>
<td>10</td>
<td>74</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>1.2</td>
<td>AcOH (1)</td>
<td>14</td>
<td>12</td>
<td>56</td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>1.2</td>
<td>acetone (2)</td>
<td>18</td>
<td>40</td>
<td>41</td>
<td>--</td>
</tr>
<tr>
<td>9</td>
<td>1.2</td>
<td>DMSO (1)</td>
<td>12</td>
<td>26</td>
<td>55</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>1.2</td>
<td>DMF (1)</td>
<td>18</td>
<td>81</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

a All reactions were carried out using 0.53 nmol of p-bromothiophenol (1b) with DMP in different solvents at rt (~30 °C). Isolated yield. Encouraged by the facile oxidation with DMP, the oxidation of thioles with IBX in common organic solvent was re-investigated. It is worth mentioning that IBX is a very mild oxidant that remains unreactive towards various electron-rich and oxidizable groups like aldehyde, ketone, alkene, alkyne, pyridine, sulfide, thiophene, furan, iodoarene, acetal, N-Boc, O-Bz, etc. Thus, the oxidation protocol could be very beneficial in terms of functional group tolerance. When the reaction of thiol with IBX (1.0 equiv) in MeCN was conducted at rt, after 24h, both disulfide 3d and thiosulfonate 2d were isolated in 18 and 75% yields, respectively (entry 4, Table 2). Hence, with a longer reaction time of 24h than the previous report of 2h, the in situ generated disulfides can be further oxidized into thiosulfonates (entries 8 vs 4). IBX was then employed in an excess amount to facilitate the oxidation and to reduce the reaction time. To our delight, with 2.0 equiv of IBX in a mixture of solvents, i.e., t-BuOH:H2O or MeCN:H2O, the oxidation of p-methoxythiophenol (1d) led to the corresponding thiosulfonate 2d selectively in respectable isolated yields (entries 1-2, Table 2). When the same reaction was performed in MeCN with 2.0 equiv of IBX, the reaction was over in 12h and the yield of the corresponding thiosulfonate 2d was increased to...
The oxidation of aliphatic thiol, namely, 2-ethylthiophenol, was found to be slower, where the desired thiosulfonates were obtained in relatively lower yields. When 3 equiv of IBX was employed, the product was isolated in a similar yield (entry 5), and no over-oxidation products were isolated from the reaction. As discussed earlier, with 1.0 equiv of IBX, the yield of thiosulfonate 2d was decreased to 75\% (entry 4). It clearly indicates that the reaction required more than 1.0 equiv of oxidant for the complete conversion of thiol 1d to thiosulfonates 2d. Although the reaction worked in other solvents like DCE and DCM, it took a longer duration for completion (entries 6–7). Thus, the reaction conditions with 1d (0.71 mmol) and IBX (2.0 equiv) in MeCN (10 mL) were considered as the best (Table 2, entry 3), and it was further implemented to access thiosulfonates from thiols.

**TABLE 2.** Optimization of the conversion of p-methoxythiophenol (1d) to thiosulfonate 2d using IBX in various solvents.

<table>
<thead>
<tr>
<th>entry</th>
<th>IBX (equiv)</th>
<th>solvent</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>2d</th>
<th>3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>BuOH:H2O (5 mL, 4:1 v/v)</td>
<td>24</td>
<td>71</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>MeCN:H2O (5 mL, 4:1 v/v)</td>
<td>24</td>
<td>68</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>MeCN (10 mL)</td>
<td>12</td>
<td>91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>MeCN (10 mL)</td>
<td>24</td>
<td>75</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>MeCN (10 mL)</td>
<td>12</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.0</td>
<td>DCE (10 mL)</td>
<td>16</td>
<td>87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.0</td>
<td>DCM (10 mL)</td>
<td>16</td>
<td>84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>MeCN (10 mL)</td>
<td>2</td>
<td>0</td>
<td>92</td>
<td></td>
</tr>
</tbody>
</table>

a All reactions were carried out using ca. 0.71 mmol of the p-methoxythiophenol (1d) at rt (~30 °C). b Isolated yield. c Ref. 52.

After optimizations of the reaction with both DMP and IBX, the scope of the methodology was investigated with various substituted thiols 1a–k, Scheme 1. The oxidation with DMP occurred in a facile manner for both electron-rich (1a and 1c–e) and electron-deficient (1b) thiophenols, where the thiosulfonates 2a–e were obtained in 81–89\% isolated yields. When ortho-substituted thiols 1f–h were employed, the oxidation was found to be slower, where the desired products 2f–h were obtained in relatively lower yields (72–79\%). Furthermore, in the case of sterically hindered 2,4,6-trimethylthiophenol (1j), oxidation using DMP led to an intractable mixture, where isolation of the desired product 2j was not possible. For 3,4-dichlorothiophenol (1i), the corresponding thiosulfonate 2i was isolated in 80\% yield. The oxidation of aliphatic thiol, namely, 2-phenylethanethiol (1k), with DMP was found to proceed more sluggishly, yielding the corresponding thiosulfonate 2k in only 56\% yield.

**SCHÉME 1.** One-pot oxidation of thiols (a: aryl, b: alkyl) to thiosulfonates using IBX in McCN or DMP in dry DCM.

The same series of thiols 1a–k was then subjected to oxidation with IBX in MeCN, Scheme 1. Thiophenols 1a–e with electron-donating and electron-withdrawing substituent, produced the thiosulfonates 2a–e in excellent yields (85–91\%) within 12–36h, Scheme 1a. However, the reaction rates for thiols (1g and 1h) containing electron-withdrawing and ortho-substituents were slower, where the thiosulfonates 2g and 2h were obtained in low yields. Specifically, the reactions of sterically-encumbered thiols were sluggish; while the reaction of o-thiocresol (1f) led to the corresponding thiosulfonate 2f in 73\% yield, 2,4,6-trimethylthiophenol (1j) yielded the corresponding thiosulfonate 2j in an isolated yield of only 20\%. When an aliphatic thiol, namely, 2-phenylethanethiol (1k), was subjected to the reaction condition, the corresponding thiosulfonate 2k was obtained in 79\% yield after 48h, Scheme 1b. It is worth mentioning that, the oxidation of electron-deficient 3-nitrothiophen to thiosulfonate was neither feasible with IBX nor DMP.

Surprisingly, the reactions of benzyl thiols 1l–n with DMP led to benzyl 2-iodobenzoates 4l–n in 69–83\% isolated yields; the reac\ons were found to be very slow (48h). Contrarily, the reaction of 1l with 2.0 equiv of IBX selectively produced S-benzyl benzenesulfonothioate 2l in 73\% yield, Scheme 2. Generally, such benzyl-esterification with λ-
iodane is observed for the reactions of ethynylbenziodoxolones (EBX) with thiiranes and thiethanes, the photochemical-cum-metal-catalyzed reaction of IBA with styrene, and arylacetic acid with several λ^3-iodanes. However, to the best of our knowledge, the transfer of an iodoarene from a hypervalent iodine(V) compound, i.e., λ^3-iodane, is unprecedented. This protocol can thus serve as one-pot functional group transformation of benzyl thiols to alcohols. It is worth mentioning that the conversion of alcohols to thiols is known using Lawesson’s reagent and through Newmann-Kwart rearrangement, however, a methodology that serve for one-pot thiol to alcohol is still at large. Herein, the reactions of benzyl thiols 1l–n with DMP led to benzoate esters 4l–n in 69–78% isolated yield in 48h, Scheme 2. The isolated product 4l was hydrolyzed with aqueous 1M NaOH that offered benzyl alcohol 5l with overall yield with 67%, Scheme 2. Further study on the mechanistic details and their applicability in organic synthesis is going on in our lab. It is to be noted that reaction of benzyl thiol 1l with IBX was consistent with other thiols that offered thiosulfonate 2l in 73% yields; no benzoate ester was observed.

![Scheme 2](image)

**SCHEME 2.** One-pot selective conversion of benzyl thiols to thiosulfonate or benzoate esters, and subsequent transformation of the ester (4l) to benzyl alcohol (5l) and aldehyde (6l) at rt.

**MECHANISM OF OXIDATIONS OF THIOLS**

To reconcile the mechanism of oxidation of thiols to thiosulfonates with IBX, we monitored the reaction by \(^1^H\) NMR spectroscopy to identify possible intermediate(s) en route to the end product(s). For this, the reactions mediated by IBX were considered convenient, as the reaction in CD\(_3\)CN should permit ready identification of the intermediate(s) where the hypervalent iodonanes IBX and IBA, will remain insoluble. \(^1^H\) NMR monitoring reaction was carried out for the oxidation of \(p\)-methoxythiophenol (1d) in CD\(_3\)CN by employing IBX (2.0 equiv), cf. Figure 1. As can be seen, the diagnostic signals (i) corresponding to methoxy and aromatic hydrogens can be readily recognized at 3.76 ppm (OMe) and at 6.85 and 7.26 ppm, respectively. After 2h of the reaction, three new distinguishable signals (ii) appeared at 3.78, 6.90 and 7.42 ppm. These were assigned to the bis(4-methoxyphenyl) disulfide (3d) by comparison of the signals of the independently prepared solution of 3d in CD\(_3\)CN.

As these signals that correspond to the disulfide 3d gradually disappear, one observes the formation of four new signals (iii) at 6.98 and 6.92 ppm as doublets and at 3.86 and 3.82 ppm as singlets. These signals correspond to the S-4-methoxyphenyl 4-methoxybenzenesulfonofluorothioate (2d) as the end product. Thus, \(^1^H\) NMR spectroscopic monitoring clearly reveals that the conversion of thiols to thiosulfonates proceeds via the intermediary formation of disulfides. Unfortunately, none of the other intermediates could be identified, as all other signals are insignificant as to reveal any identity. Although we have already shown the formation of disulfide intermediates during the solvent optimization studies (Table 1), we again treated the disulfide 3d with IBX under similar conditions to verify the formation of thiosulfonate 2d independently, Scheme 4. Indeed, the reaction afforded 2d in 92% isolated yields at rt after 36h. It is worth mentioning that, the formation of \(\alpha\)-iodobenzoic

![Figure 1](image)

**FIGURE 1.** \(^1^H\) NMR monitoring of the reaction of \(p\)-methoxythiophenol (1d) in the presence of IBX in CD\(_3\)CN at 30 °C at different intervals of time: (i) 0h, without addition of IBX; (ii) 2h after the addition of IBX; (iii) 4h; (iv) 6h; (v) 22h; (vi) 45h; (vii) 54h.
acid (IA) was observed during the course of the reaction (cf. Figure 1).\textsuperscript{5} It indicated that IBA is also involved in the oxidation and gets reduced to IA. For instance, the reaction with 1.0 equiv of IBX producing thiosulfonate in 75% and disulfide in 18% clearly indicated that \( \lambda^2 \)-iodane is participating in the oxidation (Table 2, entry 4). In fact, the oxidation with PIFA clearly suggested that the disulfides can be obtained from thiol.\textsuperscript{52} Consolidating the above observations, a plausible reaction mechanism for the conversion of thiols to thiosulfonates with IBX through the intermediary disulfides is shown. It’s needless to mention that the single electron transfer (SET) from \( e^- \)-rich thiols to I(V) species to begin with should lead to the thiol radicals that dimerize to the disulfide,\textsuperscript{52} where IBX is subsequently reduced to IBA (Scheme 3). The reaction might be going through a thioalkoxyperiodinane (TAP) species, similar to the alkoxyperiodinane-adduct formed from the reaction of IBX and alcohol.\textsuperscript{42,62,68} The disulfide may undergo subsequent oxidation with IBX to thiosulfinate by a single electron transfer process. It is worth mentioning that the direct attack of disulfide to the electrophilic hypervalent iodine center is less feasible due to steric hindrance, such an attack of sulfide is found to be energetically unfavorable;\textsuperscript{42,69} the probability of a nucleophilic attack is thus not considered here. The oxidation of disulfides to thiosulfonates with IBX may follow a single electron or oxygen transfer process. The subsequent oxidation of thiosulfinate with IBX may then lead to thiosulfonate.

\begin{center}
\textbf{SCHEME 3.} Plausible reaction mechanism for the formation of thiosulfonates from thiols using IBX.
\end{center}

In addition to the support of the proposed mechanism, we have done some of the controlled experiments to confirm the path of the reaction. Interestingly, the oxidation of disulfide 3d using IBX in optimized reaction protocol offered excellent yield of the product 2d, Scheme 4a. In order to prove that the reduced product of IBX, i.e., IBA, is capable to perform the oxidation, thiol 1b was treated with 2 and 4 equiv of IBA. After 24h, the reactions afforded thiosulfonate 2b in >90 isolated yields, While reaction with 4.0 equivalents oxidant gave 2b quantitatively, small amount of disulfide 3b (~5–10%) was obtained for reaction with 2.0 equiv IBX produced Scheme 4b.

\begin{center}
\textbf{SCHEME 4.} Controlled experiment for the oxidation of thiols to thiosulfonates using IBX.
\end{center}

In order to establish a gram-scale protocol, we have performed the oxidation of 1a (1 gram) to 2a Scheme 5. The reaction with DMP and IBX offered 2a in respectable yields.

\begin{center}
\textbf{SCHEME 5.} Reaction of thiophenol to thiosulfonates in gram scale.
\end{center}

**CONCLUSIONS**

A facile methodology for the conversion of thiols to thiosulfonates has been developed employing IBX and DMP. The oxidations can be achieved employing DMP (1.2 equiv)/DCM or IBX (2.0 equiv)/MeCN at rt (30 \( ^\circ \)C), and a variety of thiosulfonates can be accessed. DMP-mediated oxidation of benzyl thiols do not afford thiosulfonates, but lead to esters of \( o \)-iodobenzoic acid. The latter can be further explored for tandem transformations into aldehyde and alcohol. This is the first report of thiol to alcohol conversion using hypervalent iodine reagents. Mechanistic investigation through \( ^1 \)H NMR spectroscopic monitoring reveals that the oxidations proceed through the formation of intermediary disulfides; the latter evidently undergo a cascade of oxidations with either I(V) or I(III) species to furnish thiosulfonates. In view of the fact that thiosulfonates have vast applications, we believe that this methodology will constitute
an invaluable addition to the transformations mediated by hypervalent iodine compounds.

**EXPERIMENTAL SECTION**

**General Aspects:** Column chromatography was conducted with silica gel of 100–200 μ particle size. NMR spectra were recorded with 400 MHz and 500 MHz spectrometers. IR spectra were recorded on an FT-IR spectrophotometer. Mass spectral analyses were carried out with ESI-QTOF instrument.

**General Procedure for the Synthesis of Thiosulfonates using DMP:** To a solution of thiol (0.10 g) in dry dichloromethane (4 mL) slowly added 1.2 equiv of DMP, and the resultant reaction mixture was stirred at rt (−30 °C). The reaction completion was judged by thin layer chromatography (TLC) monitoring. At the end, the reaction mixture was diluted with dichloromethane (20 mL) and washed with an aqueous saturated NaHCO₃ solution. The aqueous layer was separated and washed twice with dichloromethane (10 mL). The combined organic extract was dried over anhyd Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by a short-pad silica gel column chromatography.

**General Procedure for the Synthesis of Thiosulfonates using IBX:** To a solution of thiol (0.10 g) in 10 mL of acetonitrile was added 2.0 equiv of IBX and the reaction mixture was stirred at rt (−30 °C). The progress of the reaction was monitored by TLC analysis. The reaction mixture was worked up and purified similar to the above DMP procedure.

**bis(4-Bromophenyl)disulfide (3b)**
White solid; ¹H NMR (CDCl₃, 400 MHz) δ 7.32 (d, J = 8.7 Hz, 4H), 7.41 (d, J = 8.7 Hz, 4H).

**bis(4-Methoxyphenyl)disulfide (3d)**
Yellowish liquid; ¹H NMR (CDCl₃, 400 MHz) δ 3.78 (s, 6H), 6.82 (d, J = 8.5 Hz, 4H), 7.38 (d, J = 9.1 Hz, 4H).

**S-Phenyl benzencesulphoniothioate (2a)**
Pale Liquid; Yield: 96 mg (85%) (with IBX) and 98 mg (86%) (with DMP); ¹H NMR (CDCl₃, 400 MHz) δ 7.29–7.35 (m, 4H), 7.38–7.48 (m, 3H), 7.56 (t, J = 8.2 Hz, 3H).

**S-4-Bromophenyl 4-bromobenesulphoniothioate (2b)**
White solid; Yield: 93 mg (86%) (with IBX) and 95 mg (88%) (with DMP); ¹H NMR (CDCl₃, 400 MHz) δ 7.23 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H).

**S-4-Tolyl 4-methylbenzenesulfoniothioate (2c)**
White solid; Yield: 100 mg (90%) (with IBX) and 90 mg (81%) (with DMP); ¹H NMR (CDCl₃, 400 MHz) δ 2.36 (s, 3H), 2.40 (s, 3H), 7.12 (d, J = 7.7 Hz, 2H), 7.18–7.23 (m, 4H), 7.44 (d, J = 8.7 Hz, 2H).

**S-4-Methoxyphenyl 4-methoxybenzenesulfoniothioate (2d)**
White solid; Yield: 100 mg (91%) (with IBX) and 98 mg (89%) (with DMP); ¹H NMR (CDCl₃, 400 MHz) δ 3.80 (s, 3H), 3.84 (s, 3H), 6.81–6.86 (m, 4H), 7.24 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H).

**S-4-tert-Butylphenyl 4-tert-butilbenzenesulfoniothioate (2e)**
Brown Solid; Yield: 97 mg (90%) (with IBX) and 91 mg (84%) (with DMP); ¹H NMR (CDCl₃, 400 MHz) δ 1.29 (s, 9H), 1.31 (s, 9H), 7.26 (d, J = 9.6 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H).

**S-2-Tolyl 2-methylbenzenesulfoniothioate (2f)**
Colorless Liquid; Yield: 81 mg (73%) (with IBX) and 80 mg (72%) (with DMP); ¹H NMR (CDCl₃, 400 MHz) δ 2.14 (s, 3H), 2.67 (s, 3H), 7.06–7.12 (m, 2H), 7.17–7.22 (m, 2H), 7.29–7.32 (m, 2H), 7.38 (d, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H).

**S-2-Bromophenyl 2-bromobenesulfoniothioate (2g)**
White solid; Yield: 84 mg (78%) (with IBX) and 42 mg (79%) (with DMP); mp. 120–122 °C; IR (KBr) cm⁻¹ 3085, 1570, 1445, 1327, 1149, 775, 593; ¹H NMR (CDCl₃, 500 MHz) δ 7.26–7.30 (m, 2H), 7.33 (td, J = 7.5 Hz, J = 1.4 Hz, 1H), 7.41 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.53 (dd, J = 7.9 Hz, J = 1.4 Hz, 1H), 7.57 (dd, J = 7.9 Hz, J = 1.7 Hz, 1H), 7.69 (dd, J = 7.6 Hz, J = 1.7 Hz, 1H), 7.78 (dd, J = 6.4 Hz, J = 1.1 Hz, 1H); βC NMR (CDCl₃, 125 MHz) δ 121.3, 127.2, 128.3, 129.2, 131.2, 131.4, 133.0, 133.6, 134.6, 136.1, 140.1, 142.1; ESI-MS: m/z calcld for C₁₂H₁₁BrO₃S₂ 406.8405 [M+H]⁺ found 406.8419.

**S-2-Chlorophenyl 2-chlorobenesulfoniothioate (2h)**
White solid; Yield: 92 mg (83%) (with IBX) and 86 mg (78%) (with DMP); ¹H NMR (CDCl₃, 400 MHz) δ 7.20–7.30 (m, 2H), 7.33–7.40 (m, 2H), 7.49–7.58 (m, 3H), 7.65 (dd, J = 7.7 Hz, J = 1.5 Hz, 1H).

**S-3,4-Dichlorophenyl 3,4-dichlorobenzencesulphoniothioate (2i)**
White solid; Yield: 96 mg (89%) (with IBX) and 88 mg (81%) (with DMP); mp. 108–110 °C; IR (KBr) cm⁻¹ 3084, 1562, 1453, 1345, 1155, 819, 618; ¹H NMR (CDCl₃, 400 MHz) δ 7.22–7.25 (m, 1H), 7.40 (dd, J = 8.4 Hz, J = 1.8 Hz, 2H).
1H), 7.46-7.49 (m, 2H), 7.55 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 2.3 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 126.4, 126.9, 129.3, 131.0, 131.5, 133.8, 134.0, 135.3, 137.2, 137.7, 139.2, 142.0; ESI-MS+ m/z calcd for C21H16ClNO3S2: 343.0892 [M+NH4]+; found 343.0909.

S-Mesityl 2,4,6-trimethylbenzenesulfonothioate (2j)31

White solid; Yield: 22 mg (20%) (with IBX); 1H NMR (CDCl3, 400 MHz) δ 2.14 (s, 6H), 2.26 (s, 2H), 2.28 (s, 3H), 2.34(s, 6H), 6.87 (s, 2H), 6.88 (s, 2H).

S-(2-Phenylethyl) 2-phenylethane-1-sulfonothioate (2k)35

Colorless semisolid; Yield: 175 mg (72%) (with IBX); 1H NMR (CDCl3, 400 MHz) δ 7.37, 131.0, 131.5, 133.8, 134.0, 135.3, 137.2, 137.7, 139.2, 141.3, 142.0, 166.2; ESI-MS+ m/z calcd for C13H13ClNO3S2: 370.0315 [M+NH4]+; found 343.0909.

Benzy1 alcohol (5i)

Colourless liquid; Overall yield 58 mg (67%, with DMP); 1H NMR (CDCl3, 400 MHz) δ 2.72 (s, 1H), 4.61 (s, 2H), 7.27-7.37 (m, 5H).

Benzaldehyde (6i)

Colourless liquid; Overall yield 52 mg (91%, with IBX); 1H NMR (CDCl3, 400 MHz) δ 7.52 (t, J = 7.5 Hz, 2H), 7.62 (tt, J = 7.4 Hz, J = 1.4 Hz, 1H), 7.87 (dd, J = 8.2 Hz, J = 1.4 Hz, 2H), 10.01 (s, 1H).

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org/doi/10.xxxxxxxx.

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Author Contributions

The major contribution was done by the first corresponding author (AQ) throughout the project. The authors, NY and SP have the almost equal contribution prioritically. The manuscript was written with few additional experiments by the last corresponding author (KNP).

Notes

The authors declare no competing financial interest

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Oxidation of Thiols with IBX or DMP: One-pot Access to Thiosulfonates or 2-Iodobenzoates and Applications in Functional Group Transformations

Graphic for TOC

- One-pot conversion of thiols to thiosulfonates
- First report of one-pot benzyl thiols to 2-iodobenzoates
- One-pot conversion of benzyl thiols to alcohols/alddehydes