DOI: 10.1002/adsc.201600633
Advanced Synthesis & Catalysis

Tunable and Practical Synthesis of Thiosulfonates and Disulfides from Sulfonyl Chlorides in the Presence of Tetrabutylammonium Iodide

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Received: June 19, 2016; Revised: August 15, 2016; Published online: ■■ ■■, 0000

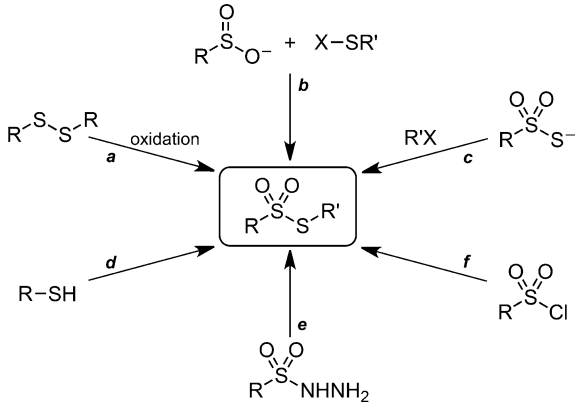
Abstract: A tunable and practical synthesis of electrophilic sulfenylating reagents, thiosulfonates and disulfides, from inexpensive and easily available sulfonyl chlorides, has been developed. By appropriate choice of solvents, the reaction of sulfonyl chlorides and tetrabutylammonium iodide gave the target products in good to excellent yields, respectively. These transformations probably proceed through a reducing–coupling pathway.

Keywords: chemoselectivity; disulfides; reductive coupling; sulfonyl chlorides; thiosulfonates

Organosulfur compounds have received considerable attention in recent years.[1] The development of organosulfur synthetic methodology is an important field in organic synthesis.[2] Among various organosulfur compounds, thiosulfonates are of particular interest, as they have shown a broad spectrum of biological activities such as bactericidal and fungicidal activity.[3] They can block the normal metabolism of microorganisms by sulfenylation of the thiol groups of enzymes. Moreover, thiosulfonates have a wide range of industrial applications both in polymer production and in photographic processes.[4] Thiosulfonates have also been widely used as electrophilic sulfenylating reagents in laboratory and industrial organic chemistry.[5] They are more reactive than the commonly used disulfides and more stable than the very reactive sulfenyl halides.

Because of the widespread application of thiosulfonates, considerable effort has been made in the development of synthetic methods for these compounds. The frequently employed methods involve the oxidation of disulfides, normally symmetrical disulfides (Scheme 1a),[6] and sulfenylation of sulfinic acid salts (Scheme 1b).[7] However, both of these methods need the use of sulfenylating reagents. Another common approach is the reaction of sodium/potassium thiosulfonates with alkyl halides (Scheme 1c).[8] Recently, new protocols have been developed from commercially available or easily prepared substrates. The most convenient method is the one-pot synthesis of thiosulfonates by oxidation of thiols (Scheme 1d).[9] This transformation proceeds *via* the disulfide intermediate. Very recently, the decomposition of sulfonyl hydrazides has been reported for the preparation of thiosulfonates (Scheme 1e).[10] Compared to the above strategies, the reduction of sulfonyl chlorides has been less studied (Scheme 1f),[11] in spite of the fact that this strategy has the advantages of readily available starting materials and relatively mild reaction conditions.

Sulfonyl chlorides are inexpensive and readily available compounds. They have been used for more than a century in organic synthesis, materials science,



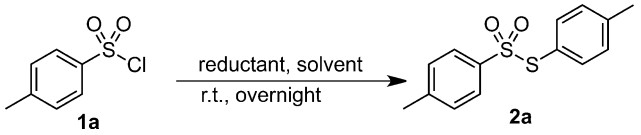
Scheme 1. Different strategies for the synthesis of thiosulfonates.

and medicinal chemistry.[12] The reaction of sulfonyl chlorides and thiols to give thiosulfonates is difficult, owing to the fast nucleophilic attack of the thiol on the initially formed thiosulfonate whereby disulfides are formed.[13] As a consequence, the exploitation of other methods for the transformation of sulfonyl chlorides to thiosulfonates is highly desirable. Several groups have developed the synthesis of "symmetrical" thiosulfonates by reduction of sulfonyl chlorides with potassium iodide in anhydrous acetone/pyridine,[11a] acetyl chloride-activated zinc,[11b] or samarium powder in DMF.[11c] Herein, we would like to disclose an alternative reduction of sulfonyl chlorides with tetrabutylammonium iodide for the preparation of "symmetrical" and "unsymmetrical" thiosulfonates. Moreover, the reaction of sulfonyl chlorides with tetrabutylammonium iodide in DMF to afford disulfides is presented.

At the outset, we attempted the reduction of 4-methylbenzenesulfonyl chloride (**1a**) as a model reaction (Table 1). Treatment of **1a** with KI (3.0 equiv.) in CH_3CN at room temperature gave the desired product **2a** in 18% yield (entry 1). To our delight, switching the reductant to $(n\text{-Bu})_4NI$ could increase the yield to 43% (entry 2). No **2a** was detected in the presence of $(n\text{-Bu})_4NBr$ or $(n\text{-Bu})_4NCl$, which indicated that the iodide anion was essential for this transformation (entries 3 and 4). Intriguingly, a significant solvent effect was observed (entries 5–13). Among the common organic solvents, only acetone led to a slightly higher yield (entry 8), whereas other solvents including THF, EtOAc, CH_2Cl_2, and DMSO were less effective (entries 5–7 and 10). It was noteworthy that di(4-methyl)phenyl disulfide was isolated when the reaction was performed in DMF (entry 9). The binary solvent mixture was proven to be beneficial for this reaction, and CH_3CN/acetone (5:1) was the ideal solvent system giving **2a** in 81% yield (entries 11–13). Finally, the yield reached up to 87% by extending the reaction time to 20 h (entry 14).

With the optimized reaction conditions in hand (Table 1, entry 14), the reduction of various aryl- and alkylsulfonyl chlorides was examined to explore the scope of the present protocol (Table 2). Arylsulfonyl chlorides bearing electron-donating and moderately electron-withdrawing substituents (**1a–n**) were transformed to the corresponding thiosulfonates in high yields. When very strongly electron-withdrawing groups were present (4-NO_2 and 4-CN), the disulfides were produced instead. Steric hindrance had no obvi-

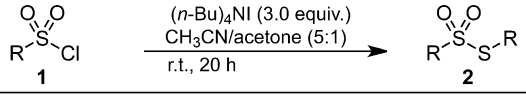
Table 1. Optimization of ther reaction conditions.[a]

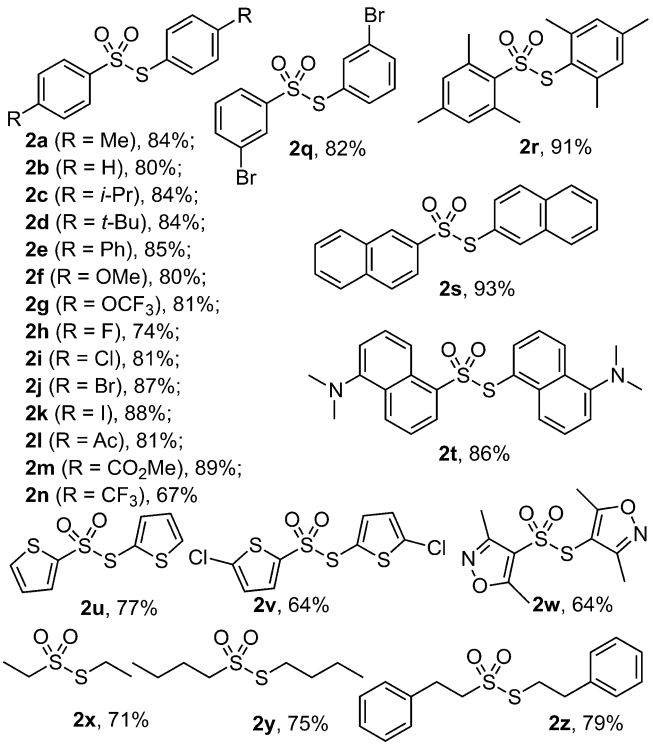


Entry	Reductant	Solvent	Yield [%][b]
1	KI	CH_3CN	18
2	$(n\text{-Bu})_4NI$	CH_3CN	43
3	$(n\text{-Bu})_4NBr$	CH_3CN	0
4	$(n\text{-Bu})_4NCl$	CH_3CN	0
5	$(n\text{-Bu})_4NI$	THF	23
6	$(n\text{-Bu})_4NI$	EtOAc	28
7	$(n\text{-Bu})_4NI$	CH_2Cl_2	trace
8	$(n\text{-Bu})_4NI$	acetone	52
9[c]	$(n\text{-Bu})_4NI$	DMF	78 (73)[d]
10	$(n\text{-Bu})_4NI$	DMSO	0
11	$(n\text{-Bu})_4NI$	CH_3CN/acetone (1:1)	78
12	$(n\text{-Bu})_4NI$	CH_3CN/acetone (5:1)	81
13	$(n\text{-Bu})_4NI$	CH_3CN/acetone (1:5)	54
14[e]	$(n\text{-Bu})_4NI$	CH_3CN/acetone (5:1)	87

[a] *Reaction conditions:* **1a** (0.2 mmol), reductant (0.6 mmol), solvent (1.2 mL), room temperature, overnight.
[b] Yield was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.
[c] Product was the di(4-methyl)phenyl disulfide.
[d] Isolated yield.
[e] 20 h.

Table 2. Synthesis of "symmetrical" thiosulfonates from sulfonyl chlorides.[a]



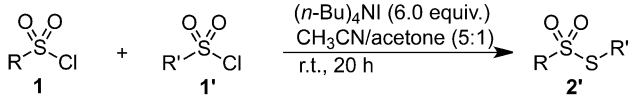


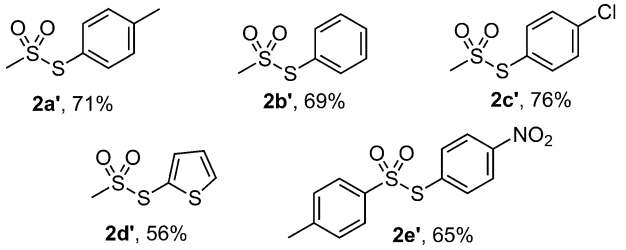
[a] *Reaction conditions:* **1** (1.0 mmol), $(n\text{-Bu})_4NI$ (3.0 mmol), CH_3CN/acetone (5.0 mL/1.0 mL), room temperature, 20 h, isolated yield.

ous impact on the yields, as sulfonyl chlorides **1q–t** with the substituent at different positions on the aromatic ring all proceeded efficiently to afford products **2q–t** in 82–93% yields. Heteroaromatic sulfonyl chlorides (**1u–w**) also served as good substrates. Moreover, this protocol was applicable to the efficient reduction of alkylsulfonyl chlorides (**1x–z**) into the respective products in good yields.

Besides the preparation of "symmetrical" thiosulfonates, this reduction protocol could also be applied to the synthesis of "unsymmetrical" thiosulfonates. As shown in Table 3, two different sulfonyl chlorides were subjected to the standard reaction conditions. Surprisingly, the cross-coupling of two different sulfonyl chlorides was the major reaction, giving "unsymmetrical" thiosulfonates **2′** in good yield. Although the homo-dimerization of sulfonyl chlorides to "symmetrical" thiosulfonates **2** was unavoidable in all cases, this protocol provided a rare example of the selective synthesis of **2′** from the same type of sulfur source.

Table 3. Synthesis of "unsymmetrical" thiosulfonates from sulfonyl chlorides.[a]



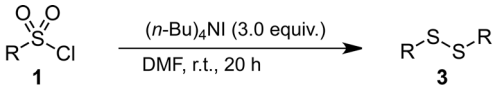


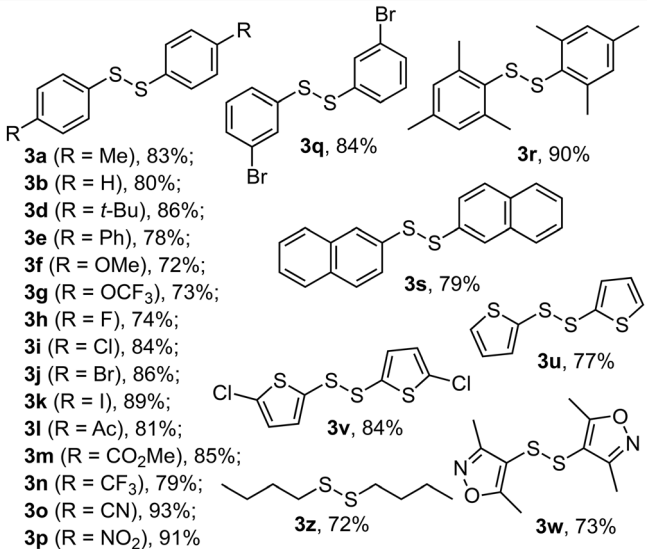
[a] *Reaction conditions:* **1** (0.5 mmol), **1′** (0.5 mmol), (*n*-Bu)$_4$NI (3.0 mmol), CH_3CN/acetone (5.0 mL/1.0 mL), room temperature, 20 h, isolated yield.

Furthermore, the transformation of sulfonyl chlorides to disulfides was also investigated. The results are summarized in Table 4. The reduction of aryl-, heteroaryl-, and alkylsulfonyl chlorides **1** with (*n*-Bu)$_4$NI in DMF proceeded smoothly and the corresponding disulfides **3** were obtained in good to excellent yields. Various functional groups including ether, ketone, ester, halide, cyano, and nitro were well tolerated. Compared to common methods employed for the reductive coupling of sulfonyl chlorides,[11c,14] the current one avoids the use of metal reagents and/or high reaction temperatures.

Next, we explored the synthesis of unsymmetrical disulfides under the standard conditions. The reaction of sulfonyl chlorides **1b** and **1l** as a representative example is shown in Scheme 2. Three different disulfides **3b**, **3a′**, and **3l** were isolated in low yields, which indicated that the selectivity of this reaction was poor.

Table 4. Reductive coupling of sulfonyl chlorides to disulfides.[a]

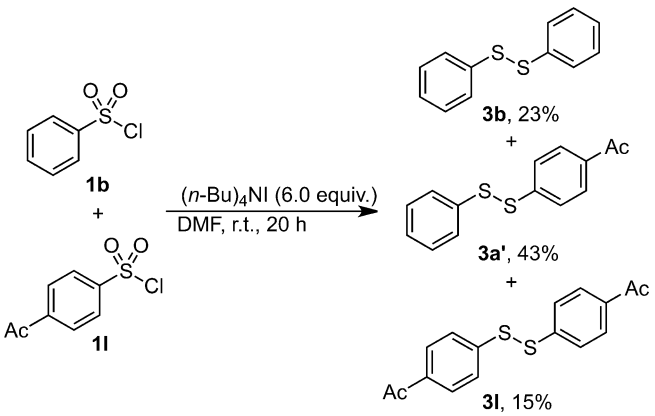




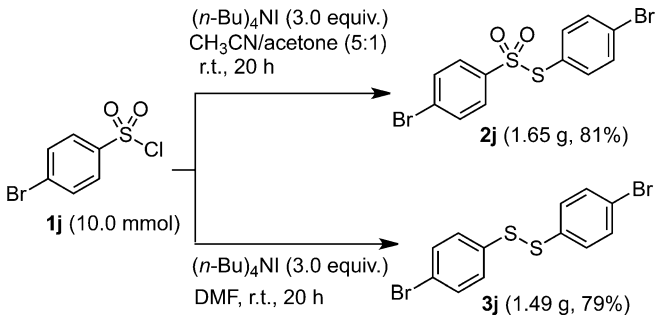
[a] *Reaction conditions:* **1** (1.0 mmol), (*n*-Bu)$_4$NI (3.0 mmol), DMF (6.0 mL), room temperature, 20 h, isolated yield.

To demonstrate the practical usefulness of these protocols, gram-scale experiments were performed with sulfonyl chloride **1j**. As shown in Scheme 3, the reductive coupling of **1j** on a 10.0 mmol scale gave thiosulfonate **2j** and disulfide **3j** in 81% and 79% yields, respectively.

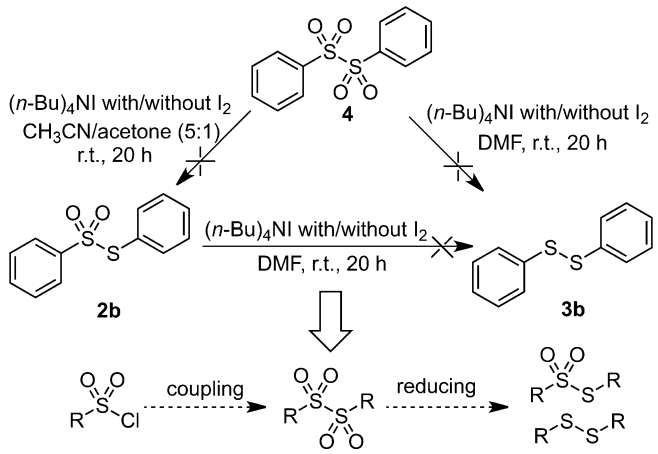
Finally, several control experiments were carried out to elucidate the mechanism of this reaction (Scheme 4). Treatment of disulfone **4** with (*n*-Bu)$_4$NI and I_2 in either CH_3CN/acetone or DMF could not give the products **2b** and **3b**, and the reduction of



Scheme 2. Synthesis of unsymmetrical disulfide **3a′**.



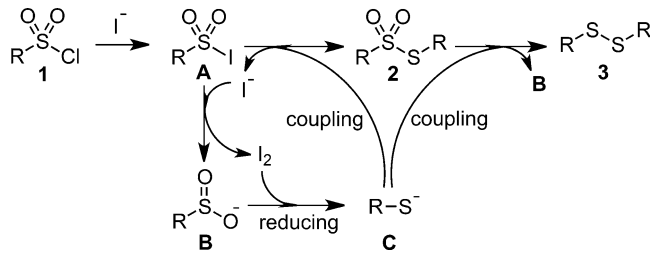
Scheme 3. Gram-scale reactions.



Scheme 4. Mechanistic investigations.

thiosulfonate **2b** with $(n\text{-Bu})_4NI$ and I_2 in DMF did not take place. These results excluded the coupling–reducing pathway.[11c]

From the above investigations, the reaction mechanism involves most likely a reducing–coupling process (Scheme 5). First, the nucleophilic attack of iodide anion to sulfonyl chloride **1** gave sulfonyl iodide **A**, which underwent another nucleophilic attack by iodide anion to afford sulfinate **B**. The sulfinate **B** was then reduced to thiolate **C** by I_2.[15] Finally, the reaction of sulfonyl iodide **A** with thiolate **C** produced thiosulfonate **2**. When the reaction was performed in DMF, a weak reducing agent,[16] the reduction step was accelerated to give more thiolate **C** in the reaction mixture, thus leading to the formation of disulfide **3**.



Scheme 5. Proposed reaction mechanism.

In conclusion, we have developed a chemoselective reductive coupling of sulfonyl chlorides for the practical synthesis of thiosulfonates and disulfides, respectively. This protocol could also be applied for the preparation of "unsymmetrical" thiosulfonates. The high efficiencys, cost-effectiveness, and mild conditions make this protocol attractive for the preparation of these two types of sulfur-containing compounds.

Experimental Section

General Procedure for the Synthesis of Thiosulfonates from Sulfonyl Chlorides

To a solution of sulfonyl chloride **1** (1.0 mmol) in CH_3CN/acetone (2.5/0.5 mL), $(n\text{-Bu})_4NI$ (1.11 g, 3.0 mmol) in CH_3CN/acetone (2.5/0.5 mL) was slowly added by a syringe. After stirring at room temperature for 20 hours, the solvents were evaporated. The residue was purified by silica gel column chromatography to afford the corresponding thiosulfonate **2**.

General Procedure for the Synthesis of Disulfides from Sulfonyl Chlorides

To a solution of sulfonyl chloride **1** (1.0 mmol) in DMF (3.0 mL), $(n\text{-Bu})_4NI$ (1.11 g, 3.0 mmol) in DMF (3.0 mL) was slowly added by a syringe. After stirring at room temperature for 20 hours, aqueous $NaHCO_3$ and aqueous $Na_2S_2O_3$ were added. Then, the reaction mixture was extracted with Et_2O. The organic phase was washed with H_2O and brine, dried by Na_2SO_4, concentrated under vacuum. The residue was purified by silica gel column chromatography to afford the corresponding disulfide **3**.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21502215, 21421002, 21332010, 21272036), the National Basic Research Program of China (2012CB21600), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20020000), and the Youth Innovation Promotion Association CAS (No. 2016234).

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6 Tunable and Practical Synthesis of Thiosulfonates and Disulfides from Sulfonyl Chlorides in the Presence of Tetrabutylammonium Iodide

Adv. Synth. Catal. **2016**, *358*, 1 – 6

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