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Disproportionate Coupling Reaction of Sodium Sulfinates Mediated by BF_3·OEt_2: An Approach to Symmetrical/Unsymmetrical Thiosulfonates

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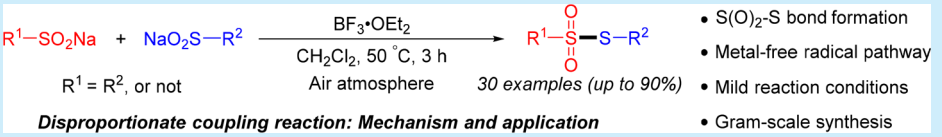
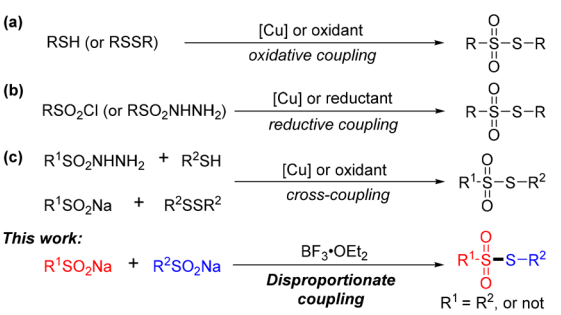
Supporting Information



ABSTRACT: The BF_3·OEt_2-mediated disproportionate coupling reaction of sodium sulfinates was found for the first time. In this reaction, various S−S(O)$_2$ bonds can be formed, efficiently giving thiosulfonates in moderate to excellent yields. As a convenient protocol for the synthesis of symmetrical and unsymmetrical thiosulfonates, its reaction mechanism involves the formation of a thiyl radical and sulfonyl radical via a sulfinyl radical disproportionation. What is more, this transformation can also be applied practically as a gram-scale reaction and to the two-step synthesis of sulfone and sulfonamide in one pot in situ using thiosulfonate as an intermediate.

Organosulfur compounds have attracted considerable attention because of their interesting medicinal, material, and agrochemical applications in recent years.[1] Among them, thiosulfonates are of particular interest, for they have shown a broad spectrum of pharmaceutical and clinical properties such as bactericidal, antimicrobial and fungicidal activities.[2] In addition, thiosulfonates have been widely used as reagents or intermediates in laboratory and industrial organic chemistry due to many advantages, including much better reactivity and stability than commonly used sulfenyl halides and disulfides.[3] Thus, considerable efforts have been made in the development of synthetic protocols for thiosulfonates (Scheme 1). The oxidation of thiols or disulfides is frequently employed for the synthesis of symmetric thiosulfonates (Scheme 1a).[4] In contrast, the reductive coupling of sulfonyl chlorides or hydrazides has also been reported (Scheme 1b).[5] Recently, the cross-coupling reaction of sulfonyl hydrazides with thiols (or sodium sulfinates with disulfides) has been developed for the preparation of unsymmetrical thiosulfonates with the help of transitional metal catalysts (Scheme 1c).[6] In short, for the synthesis of symmetrical/unsymmetrical thiosulfonates in the reported methods, some special additives (oxidants or reductants), toxic reagents (e.g., RSH), or harsh conditions are still demanded for these transformations. Hence, the development of more efficient and environmentally friendly metal-free reaction systems to achieve the thiosulfonates is still highly essential.

Scheme 1. Different Methods for the Synthesis of Symmetrical/Unsymmetrical Thiosulfonates



Sodium sulfinates[7] and sulfoxides[8] are also important organosulfur compounds. Meanwhile, 2(5*H*)-furanone chemistry has recently become a hot research topic.[9] Being interested in the reaction system of sodium sulfinates (**I**), 2(5*H*)-furanones (**II**), and sulfoxides (e.g., DMSO, **III**, Scheme 2),[10] we have already reported the construction of C−C and C−S bonds by the metal-catalyzed reaction of 3,4-dihalo-2(5*H*)-furanones with sodium arylsulfinates and sulfoxides, respectively. Some metal-free sulfonylations using

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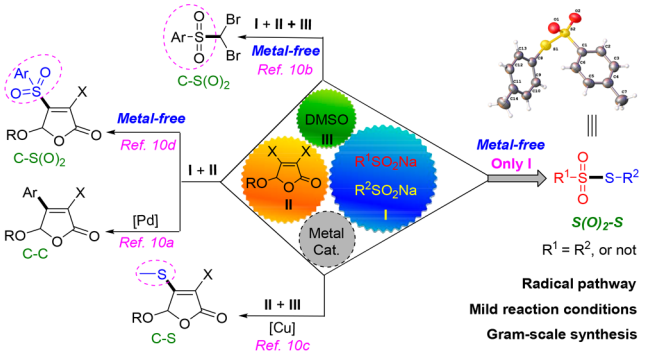
Org. Lett. XXXX, XXX, XXX−XXX

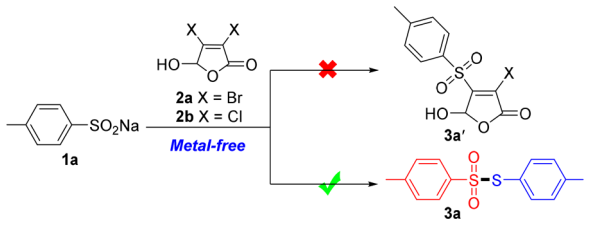
Scheme 2. Tunable Synthesis by the Combination of Sodium Sulfinates, 2(5*H*)-Furanones, DMSO (Solvent), and Catalyst



sodium arylsulfinates as reagents have also been developed. Herein, we report the construction of S−S(O_2) bonds only starting from sodium sulfinates (**I**) based on the systematical investigations on the tunable reaction system of different compounds (**I**, **II**, and **III**, Scheme 2).

Of course, this work is also a surprising discovery, much like our previous reports.[10b,c] During the examination on the scope of sulfonylation on the sodium arylsulfinates, when using mucobromic acid as 2(5*H*)-furanone (**II**), we did not obtain the expected C−S(O_2) bond product but simply observed a single byproduct. It is thiosulfonate **3a**, which was confirmed by single-crystal X-ray diffraction analysis (Scheme 2 or Figure S1, see the Supporting Information (SI) for details).[11] This shows that the substrate mucobromic acid may act as an acid and does not participate in the reaction, and the product thiosulfonate **3a** should be obtained by a disproportionate coupling reaction (Scheme 3). Thus, this reaction may be

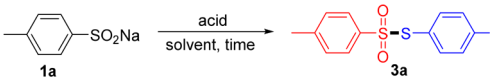
Scheme 3. Reaction of *p*-Toluenesulfinate 1a with Mucobromic Acid 2a (or Mucochloric Acid 2b)



designed to synthesize thiosulfonates without any metal catalysts and extra oxidants (or reductants). The systematical investigation proved this indeed.

Initially, we attempted the disproportionate coupling reaction of *p*-toluenesulfinate **1a** as a model to examine various reaction parameters. The results are summarized in Table 1. Not only treating **1a** with mucobromic acid **2a** (1 equiv) in acetone as solvent at 50 °C for 3 h can give the product **3a** in 46% yield (entry 1), but also using mucochloric acid **2b** (Scheme 3) can obtain the desired product **3a** with a yield of 46% (entry 2). Afterward, we examined the type of acid (entries 3−6). The results show that BF_3·OEt_2 can give a better yield of 51% (entry 3). The control experiments show that acid is essential for this transformation, and while weak acid can significantly promote the reaction, strong acid (e.g., HCl and H_2SO_4) is not conducive to the reaction. Various polar solvents, such as C_2H_5OH, THF, CH_2Cl_2, and CH_3CN,

Table 1. Optimization of Reaction Conditions[a]



entry	acid (*x* equiv)	temp (°C)	solvent	yield[b] (%)
1	**2a** (1)	50	acetone	46
2	**2b** (1)	50	acetone	46
3	BF_3·OEt_2 (1)	50	acetone	51
4	HCl (1)	50	acetone	0
5	H_2SO_4 (1)	50	acetone	0
6		50	acetone	0
7	BF_3·OEt_2 (1)	50	C_2H_5OH	<10
8	BF_3·OEt_2 (1)	50	THF	25
9	BF_3·OEt_2 (1)	50	CH_2Cl_2	83
10	BF_3·OEt_2 (1)	50	CH_3CN	67
11	BF_3·OEt_2 (2)	50	CH_2Cl_2	86
12	**BF_3·OEt_2 (3)**	**50**	**CH_2Cl_2**	**88**
13	BF_3·OEt_2 (4)	50	CH_2Cl_2	86
14	BF_3·OEt_2 (3)	r.t.	CH_2Cl_2	66
15[c]	BF_3·OEt_2 (3)	50	CH_2Cl_2	88

[a]Reaction conditions: all reactions were performed with **1a** (0.50 mmol), acid (*x* equiv) and solvent (3.0 mL) at the designed oil bath temperature under air. [b]Isolated yield. [c]5 h.

were subsequently screened (entries 7−10). To our delight, using CH_2Cl_2 as solvent can give 83% yield (entry 9). We also examined the amount of BF_3·OEt_2 (entries 9, 11−13). It can be found that 3 equiv of BF_3·OEt_2 can give the best yield (entry 12). Furthermore, there is no improvement when the reaction temperature or time is altered (entries 14 and 15). In short, we can achieve the disproportionate coupling reaction of sodium sulfinate **1a** to synthesize thiosulfonate **3a** under mild conditions (entry 12).

Under the optimized conditions, the disproportionate coupling reaction of various sodium arylsulfinates was examined to establish the scope and generality of this protocol. The results are summarized in Scheme 4. As expected, many sodium arylsulfinates **1** bearing electron-donating (e.g., alkyl and methoxy) and electron-withdrawing (e.g., halogen and trifluoromethyl) substituents can be transformed into the corresponding symmetrical thiosulfonates **3a**−**i** in moderate to excellent yields. Generally, the sodium arylsulfinates **1** containing electron-donating groups perform better than those with electron-withdrawing groups (**3a** vs **3i**). This reaction is insensitive to the substrates bearing *meta*-substituent fluorine groups (**3j** vs **3f**). For methyl-substituted sodium arylsulfinates **1**, though the number or position of methyl is different, all work well under mild conditions, giving the desired products in good to excellent yields (**3k**−**m** vs **3a**). Furthermore, polycyclic substituted sodium sulfinates **1** can be transformed into the corresponding products in good yields (**3n** and **3o**). To our delight, heteroaryl sodium sulfinate may be also suitable in the protocol with satisfactory results (**3p**).

To further improve the scope of this protocol, this disproportionate coupling method was also applied to the preparation of unsymmetrical thiosulfonates when two different sodium sulfinates were subjected to the standard reaction conditions. The results are shown in Scheme 5. To our delight, the BF_3·OEt_2-mediated disproportionate cross-coupling reaction of sodium alkylsulfinates and sodium arylsulfinates is major, giving unsymmetrical thiosulfonate products in moderate to good yields (**4a**−**h**). It is worth noting that

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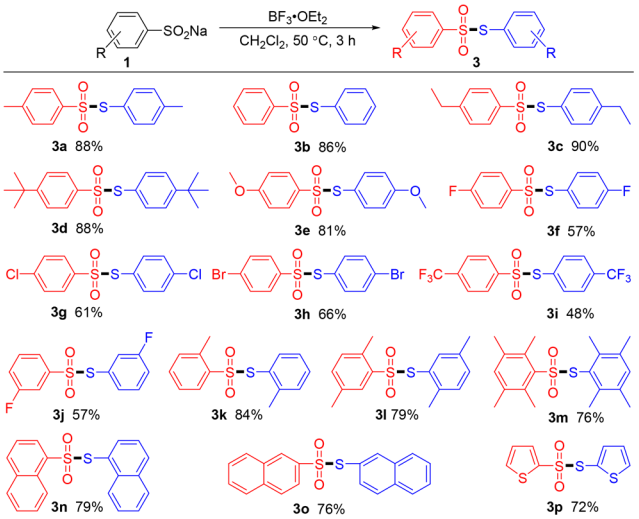
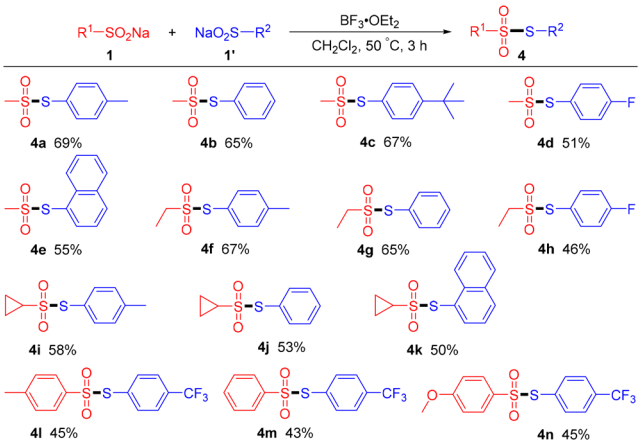
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 4. Synthesis of Symmetrical Thiosulfonates from Sodium Sulfinates 1[a,b]



[a]Reaction conditions: all reactions were performed with **1** (0.50 mmol), $BF_3{\cdot}OEt_2$ (3 equiv), and CH_2Cl_2 (3.0 mL) at 50 °C for 3 h under air unless otherwise noted. [b]Yields of isolated products are given.

Scheme 5. Synthesis of Unsymmetrical Thiosulfonates from Sodium Sulfinates 1 and 2[a,b]

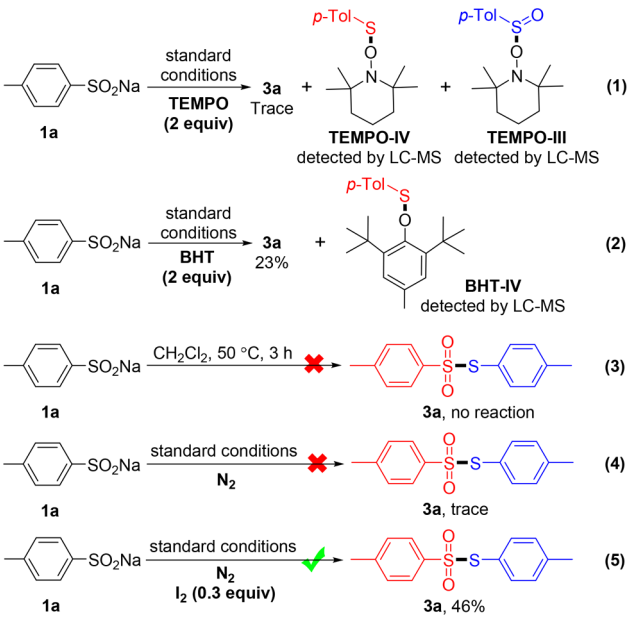


[a]Reaction conditions: all reactions were performed with **1** (0.25 mmol), **1′** (0.25 mmol), $BF_3{\cdot}OEt_2$ (3 equiv), and CH_2Cl_2 (3.0 mL) at 50 °C for 3 h under air unless otherwise noted. [b]Yields of isolated products are given.

sodium cyclopropanesulfinates are also a suitable reaction partner for this novel transformation, and they can react with different sodium arylsulfinates (**4i–k**). On the other hand, two different sodium arylsulfinates also can be subjected to the desired cross-coupling products in moderate yields (**4l–n**). Though the homocoupling of sodium sulfinates to symmetrical thiosulfonates **3** was unavoidable, their yields are very low, and the maximum yield of homocoupling products was no more than 20%. Thus, this method may provide a rare example for the selective synthesis of unsymmetrical thiosulfonates **4** from the same type of sodium sulfinates to form new S–S(O_2) bonds.

The disproportionate reaction is one of the most useful and powerful methods for organic synthesis.[12] Encouragingly, starting from only thiols, a simple and efficient radical cross-coupling reaction was reported to construct unsymmetrical disulfide via a electrochemical pathway recently.[13] On the other hand, $BF_3{\cdot}OEt_2$ is commonly used as Lewis acid with high activity in many synthetic procedures.[14] However, the $BF_3{\cdot}OEt_2$-mediated disproportionate coupling reaction of sodium sulfinates for the synthesis of thiosulfonates has been rarely reported. Thus, in order to understand the reaction mechanism, a series of control experiments were carried out (Scheme 6).

Scheme 6. Control Experiments



Initially, we conducted the radical trapping experiments by adding 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) into the model reaction under the standard conditions. As expected, the reaction is completely suppressed (eq 1 in Scheme 6), while the capture of thiyl radical (**IV**) and sulfinyl radical (**III**) by TEMPO can be detected by LC–MS. Similarly, the formation of product **3a** is inhibited upon the addition of the radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the reaction (eq 2), and the BHT adduct (BHT-**IV**) is also detected by LC–MS (see Figure S2). Therefore, both cases indicate that a radical pathway should be involved in this process with the existence of thiyl and sulfinyl radical intermediates. The control experiment also implies that $BF_3{\cdot}OEt_2$ is essential for this transformation (eq 3). In addition, it can be found that an N_2 atmosphere is markedly disadvantageous for the reaction (eq 4) compared with the air atmosphere. If I_2 is added under the N_2 atmosphere, a yield of 46% can be obtained (eq 5). These results suggest that air may play an important role in the transformation.

On the basis of the above experimental results and previous reports,[15–18] a possible reaction pathway is proposed, as shown in Scheme 7 (for the unsymmetrical thiosulfonate **4**, its plausible mechanism based on Scheme 7 can be seen in the SI). First, an oxygen-centered radical **I** is produced through the oxidation of sodium sulfinate **1** by air upon heating, and radical **I** can be resonance-stabilized with a sulfonyl radical **II**.[15,16] Self-coupling of the radical **II** can generate the intermediate disulfone **B**[16] (some intermediates **B**, e.g., **5a** and **5b**, have been isolated, and their characterization data, especially some

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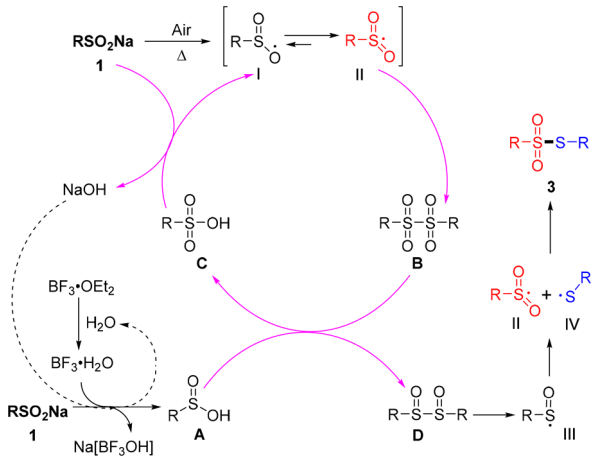
Org. Lett. XXXX, XXX, XXX–XXX

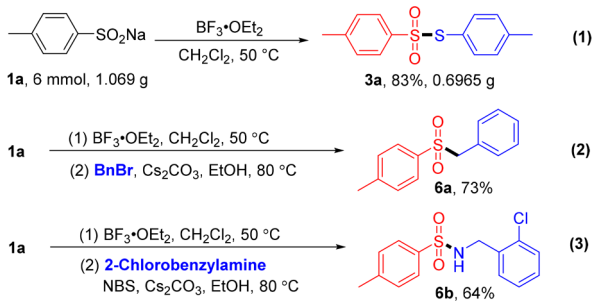
Scheme 7. Proposed Reaction Mechanism for the Formation of Thiosulfonate 3



discussion on the verification experiments based on these intermediates **B** can be seen in the SI). On the other hand, $BF_3{\cdot}H_2O$ can be produced in situ from $BF_3{\cdot}OEt_2$ in the case of a trace amount of water[17] under open-flask conditions (the discussions on air as a dual role can be seen in the SI). Then $BF_3{\cdot}H_2O$ generates sodium sulfinate **1**, which is neutralized to form intermediate sulfinic acid **A**. Subsequently, **B** may be reduced by **A** to give the corresponding disulfoxide **D** and sulfonic acid **C**.[18] In the circle, intermediate **C** can oxidize reactant **1** through free-radical intermediates to produce intermediate **B** participating in the next reaction.[16,18b] Finally, the homolytic cleavage of unstable intermediate **D** takes place under heating, and the generated radical **III** may easily disproportionate into radical **II** and radical **IV**, which can be combined into the desired thiosulfonate.[15]

To demonstrate the practicability of this protocol, a scaled-up experiment was performed with *p*-toluenesulfinate **1a**. As shown in Scheme 8, the disproportionate coupling reaction of

Scheme 8. Practical Application Experiments



1a on gram-scale can give thiosulfonate **3a** in a yield 83% (eq 1). More importantly, the versatile synthetic utility of the obtained thiosulfonate as intermediate[3,19] in situ was also investigated. For example, once *p*-toluenesulfinate **1a** in dichloromethane is treated with $BF_3{\cdot}OEt_2$ for 3 h, only simple removal of the solvent gives a residue, and then the addition of benzyl bromide can afford the corresponding sulfone product **6a** in a yield of 73% (eq 2). Similarly, a one-pot, two-step synthesis of sulfonamide **6b** can also be achieved (eq 3), and the remaining halogen may be further derivatized.

In summary, we found a $BF_3{\cdot}OEt_2$-mediated radical disproportionate coupling reaction of sodium sulfinates for the first time. The simple and mild conditions make it a convenient procedure for the synthesis of thiosulfonates in good yields. This practical protocol has good tolerance to different functional groups and can also be applied for the preparation of unsymmetrical thiosulfonates. In addition, the gram-scale protocol can be further developed as a one-pot, two-step reaction avoiding the isolation and purification of the intermediate thiosulfonate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01808.

Experimental section, characterization data of all compounds, ^1H, ^{13}C, and ^{19}F NMR and MS spectra for all compounds, data for single-crystal X-ray analysis, experimental spectra used in discussions, and discussions on the reaction mechanism (PDF)

Accession Codes

CCDC 1849386 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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