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Dual Roles of Rongalite: Reductive Coupling Reaction to Construct Thiosulfonates Using Sulfonyl Hydrazides

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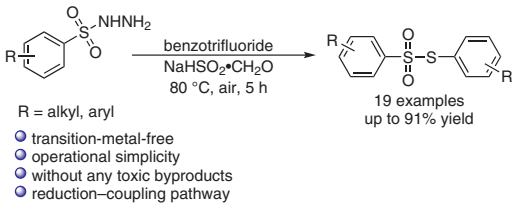

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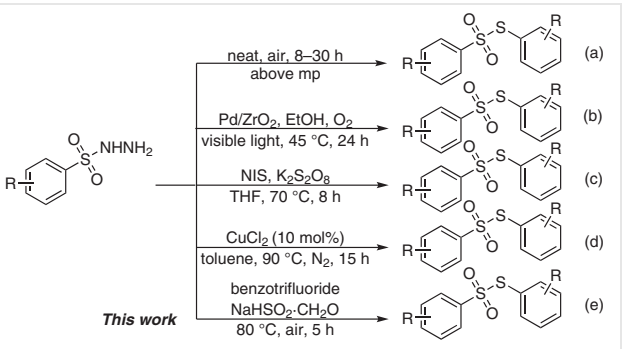
Abstract A tunable and practical transformation of structurally diverse sulfonyl hydrazides into thiosulfonates in the presence of Rongalite ($NaHSO_2{\cdot}CH_2O$) was developed. Transition-metal-free conditions, operational simplicity, and readily available reagents are the striking features of this protocol. It is the first example for the synthesis of thiosulfonates using sulfonyl hydrazides with the assistance of reductant. Additionally, the mechanistic studies revealed that this transformation probably undergoes via a reducing–coupling pathway.

Key words sulfonyl hydrazides, Rongalite, thiosulfonates, transition-metal-free, reductive coupling

Sulfur-containing organic compounds, due to their unique properties, are widely used in material, medicinal, agrochemical applications, and other fields.[1] Notably, thiosulfonates have attracted significant attention for their expressions of a broad spectrum of clinical and pharmaceutical properties, including antimicrobial, antifungal, and antiviral agents.[2] Besides, thiosulfonate derivatives have shown widespread applications in both polymer production and photographic processes.[3] Moreover, they are powerful electrophilic sulfenylating agents in synthetic organic chemistry because of their superior reactivity and stability.[4] In the light of the aforementioned applications, preparation of the thiosulfonate derivatives has been pursued for a long time by researchers.

Initially, the most practically methods for the synthesis of symmetrical thiosulfonates were the direct oxidation of disulfides, thiosulfinates, or thiols via various oxidants.[5] Another common protocol was based on the reductive dimerization of sulfonyl chlorides or coupling with thiols to synthesize symmetrical/unsymmetrical thiosulfonates.[6] Besides, an alternative approach for the synthesis of thiosulfonates comprised a nucleophilic substitution of alkyl halides with alkali-metal thiosulfonates,[7] and coupling of alkali-metal sulfinates with disulfides by means of a promoter to activate the sulfur–sulfur bond.[8] Unfortunately, many of these methods encounter several blemishes, such as to require the use of transition metals or stoichiometric amounts of oxidants, toxic reagents, harsh reaction conditions, or limited substrate scope, etc.[9]

Sulfonyl hydrazides, easily accessible and stable solids, were diffusely used as convenient sulfur nucleophiles or electrophiles in organic synthesis.[10] In 1972, Meier and coworkers first reported the preparation of thiosulfonates via thermal decomposition of arenesulfonyl hydrazides, upon heating above their melting point (Scheme 1a).[11] Guo utilized a catalytic system based on Pd/ZrO_2 nanocomposite photocatalyst to obtain thiosulfonates in moderate to good yield (Scheme 1b).[12] Another approach discovered by the group of Wei delivers thiosulfonates in high yields in the presence of $NIS/K_2S_2O_8$/THF at 70 °C (Scheme 1c).[13] Very recently, Kim et al. developed the $CuCl_2$-promoted decomposition of sulfonyl hydrazides to access diverse symmetrical thiosulfonates with various functional groups (Scheme 1d).[14]

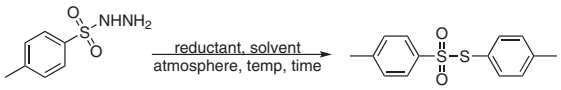


Scheme 1 Synthesis of thiosulfonates using sulfonyl hydrazides

To the best of our knowledge, synthesis of thiosulfonates using sulfonyl hydrazides with the assistance of reductant has not been explored. Herein, we report a tunable and practical transformation of structurally diverse sulfonyl hydrazides into thiosulfonates in the presence of Rongalite as reductant (Scheme 1e).

Initial optimization of the reaction was performed with 4-methylbenzenesulfonohydrazide (**1a**) as a model substrate (Table 1). When the reaction mixture of **1a** (0.2 mmol) and $NaHSO_2{\cdot}CH_2O$ (0.2 mmol) in EtOH (2.0 mL) was stirred at 80 °C under air for 5 h, only 13% yield of the desired 4-methylbenzenesulfonothioate (**2a**) product was isolated (entry 1). Encouraged by this initial result, we performed a further screening of the reaction conditions with respect to the reductant. The examination indicated that the performance of $NaHSO_2{\cdot}CH_2O$ was superior to that of other reductants (entries 1–5). It was noteworthy that ethyl 4-methylbenzenesulfinate was isolated when the reaction used $NaHSO_3$ as reductant (entry 5). Control experiment confirmed that reductant was essential for the transformation to proceed (entry 6). Among the examined solvents, such as $CHCl_3$, toluene, CH_3CN, ethyl acetate and benzene, benzotrifluoride exhibited the highest efficiency in this transformation (entries 7–13). Intriguingly, the efficiency of this transformation was significantly affected by the polarity of solvents, and the weak polarity solvent is superior to the strong polarity. A yield of 86% was achieved after increasing the amount of $NaHSO_2{\cdot}CH_2O$ to 2.0 equiv, while a further increase in $NaHSO_2{\cdot}CH_2O$ quantity decreased the yield (entries 14 and 15). The output was also strongly governed by the reaction temperature; the yield decreased significantly upon lowering (60 °C) as well as increasing (100 °C) the reaction temperature (entries 18 and 19).

Table 1 Optimization of Reaction Conditions



1a (0.2 mmol) **2a**

Entry	Reductant	mmol	Solvent	mL	Temp (°C)	Atmosphere	Time (h)	Isolated yield (%)
1	$NaHSO_2{\cdot}CH_2O$	0.2	EtOH	2.0	80	air	5	13
2	Na_2SO_3	0.2	EtOH	2.0	80	air	5	<5
3	$Na_2S_2O_3{\cdot}5H_2O$	0.2	EtOH	2.0	80	air	5	trace
4	$Na_2S_2O_4$	0.2	EtOH	2.0	80	air	5	<5
5[a]	$NaHSO_3$	0.2	EtOH	2.0	80	air	5	81
6	–	0.2	EtOH	2.0	80	air	5	0
7	$NaHSO_2{\cdot}CH_2O$	0.2	$CHCl_3$	2.0	80	air	5	60
8	$NaHSO_2{\cdot}CH_2O$	0.2	toluene	2.0	80	air	5	75
9	$NaHSO_2{\cdot}CH_2O$	0.2	EtOAc	2.0	80	air	5	47
10	$NaHSO_2{\cdot}CH_2O$	0.2	CH_3CN	2.0	80	air	5	48
11	$NaHSO_2{\cdot}CH_2O$	0.2	THF	2.0	80	air	5	54
12	$NaHSO_2{\cdot}CH_2O$	0.2	benzotrifluoride	2.0	80	air	5	82
13	$NaHSO_2{\cdot}CH_2O$	0.2	benzene	2.0	80	air	5	73
14	$NaHSO_2{\cdot}CH_2O$	2.0	benzotrifluoride	2.0	80	air	5	86
15	$NaHSO_2{\cdot}CH_2O$	4.0	benzotrifluoride	2.0	80	air	5	67
16	$NaHSO_2{\cdot}CH_2O$	0.2	benzotrifluoride	2.0	80	air	3	77
17	$NaHSO_2{\cdot}CH_2O$	0.2	benzotrifluoride	2.0	80	air	7	86
18	$NaHSO_2{\cdot}CH_2O$	0.2	benzotrifluoride	2.0	60	air	5	72
19	$NaHSO_2{\cdot}CH_2O$	0.2	benzotrifluoride	2.0	100	air	5	75
20	$NaHSO_2{\cdot}CH_2O$	0.2	benzotrifluoride	1.0	80	air	5	91
21	$NaHSO_2{\cdot}CH_2O$	0.2	benzotrifluoride	3.0	80	air	5	73
22	$NaHSO_2{\cdot}CH_2O$	0.2	benzotrifluoride	2.0	80	N_2	5	87
23	$NaHSO_2{\cdot}CH_2O$	0.2	benzotrifluoride	2.0	80	O_2	5	83

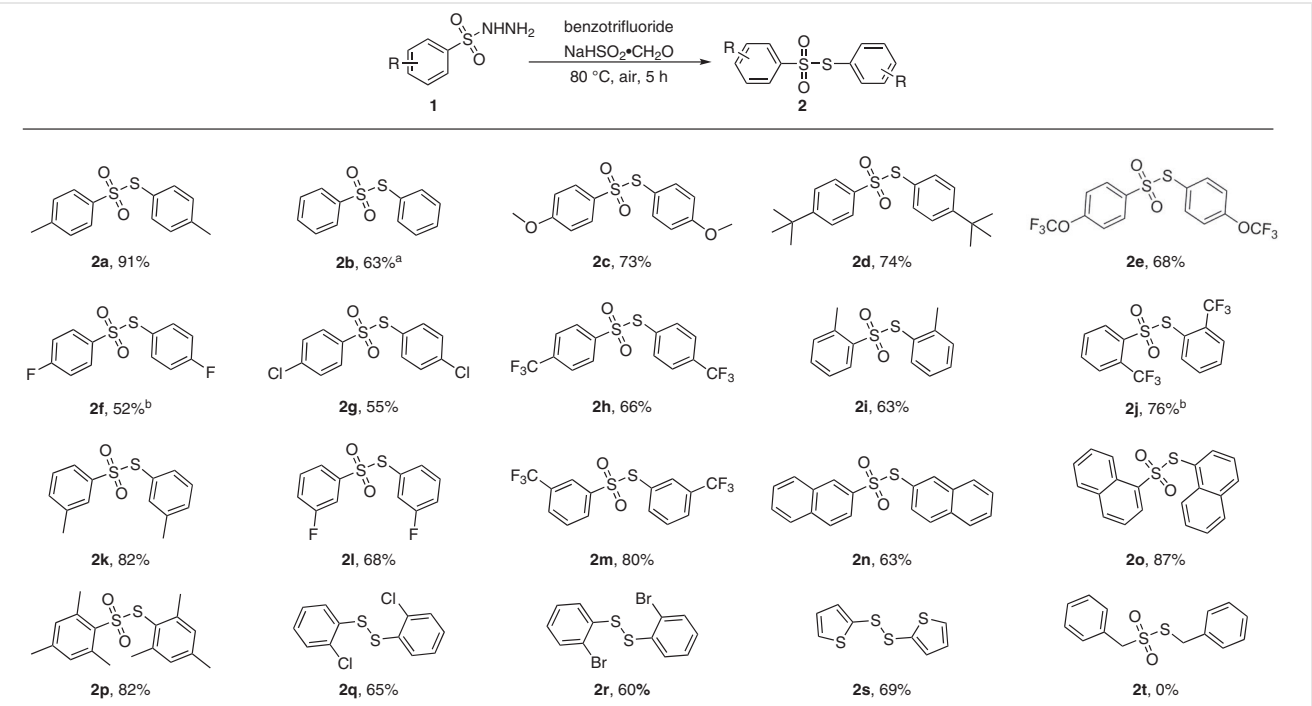
[a] Product was the ethyl 4-methylbenzenesulfinate.

With the increase of solvent volume, poor yields of **2a** were observed, but a decrease of the solvent volume could give the target product in 91% yield (Table 1, entries 20 and 21). A decreased yield was obtained when the reaction was carried out under N_2 or O_2 (entries 22 and 23). Therefore, the optimal reaction conditions were found to include 4-methylbenzenesulfonohydrazide (**1a**, 0.2 mmol), $NaHSO_2{\cdot}CH_2O$ (2.0 equiv) in benzotrifluoride (1.0 mL) at 80 °C under air for 5 h.

With the optimized reaction conditions in hand, we next probed the substrate scope of the present protocol (Scheme 2). With respect to arenesulfonyl hydrazides, a wide range of functionalities substituted on the benzene ring was compatible with the present reductive coupling reaction, including alkyl, fluoro, chloro, methoxy, trifluoromethyl, and trifluoromethoxy. Hence, a series of novel thiosulfonates were readily accessed in yields ranging from moderate to good (**2a**–**p**, 52–91%). 4-Methylbenzenesulfonohydrazide (**1a**) exhibited the highest reactivity to afford the corresponding 4-methylbenzenesulfonothioate (**2a**) in 91% yield. For methyl-substituted arenesulfonyl hydrazides, though the position or number of methyl is different, all work well under standard reaction conditions, giving the target products in good to excellent yields (**2a**,**i**,**k**,**p**). Moreover, polycyclic aromatic sulfonyl hydrazides proved to be suitable reactants, affording **2n** and **2o** in moderate yields.

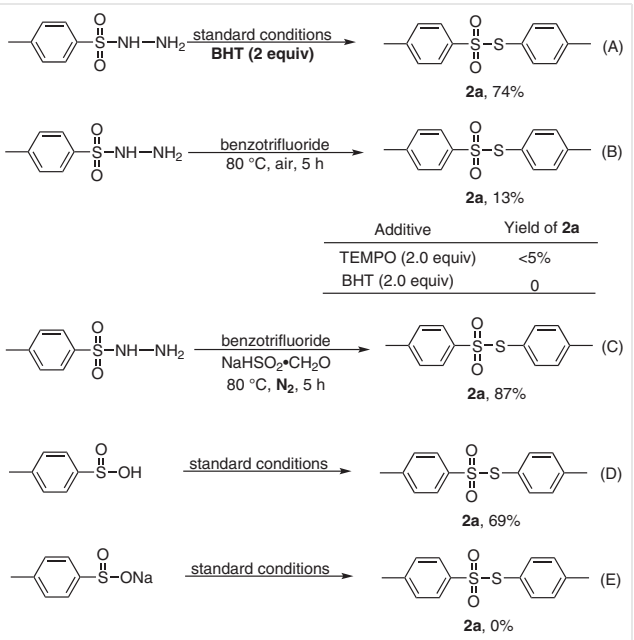
It was worth noting that the reduction of arenesulfonyl hydrazides with *o*-Cl, *o*-Br, and thiophene-2-sulfonohydrazide **1s** produced the corresponding disulfides instead. We suspected that the corresponding thiosulfonates were easily further reduced to disulfides by the Rongalite. To our disappointment, the reduction of phenylmethanesulfonohydrazide **1t** did not proceed well.

To gain insight into the mechanism of this transformation, a series of preliminary experiments were performed. When 2.0 equiv of 2, 4-di-*tert*-butyl-4-methylphenol (BHT) was introduced under the standard reaction conditions, the yield of **2a** was not significantly affected, which points away from a radical pathway (Scheme 3A). Apparently, the reductant was essential for this reaction, as the reaction without reductant participation only generated small amounts of the desired product (13% yields for **2a**). The reaction was completely suppressed when the radical scavengers 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and BHT were added in the reaction conditions without reductant, suggesting that a radical pathway might be the minor process in this reaction (Scheme 3B). Besides, the reaction under N_2 atmosphere was found to be uninfluenced, leading to excellent yield (87% yield for **2a**, Scheme 3C). On the basis of the relevant literature reports,[15] we speculated that the 4-methylbenzenesulfinic acid or sodium 4-methylbenzenesulfinate might be an intermediate for this reaction. Subsequently, two crucial control experiments were performed to further study the reaction mechanism. 4-Methyl-



Scheme 2 Scope of the synthesis of the thiosulfonates. *Reagents and conditions*: Arenesulfonyl hydrazide **1** (0.2 mmol), $NaHSO_2{\cdot}CH_2O$ (2.0 equiv), benzotrifluoride (1.0 mL) at 80 °C under air for 5 h. Isolated yield. [a] Toluene (1.0 mL). [b] Arenesulfonyl hydrazides 1 (0.4 mmol).

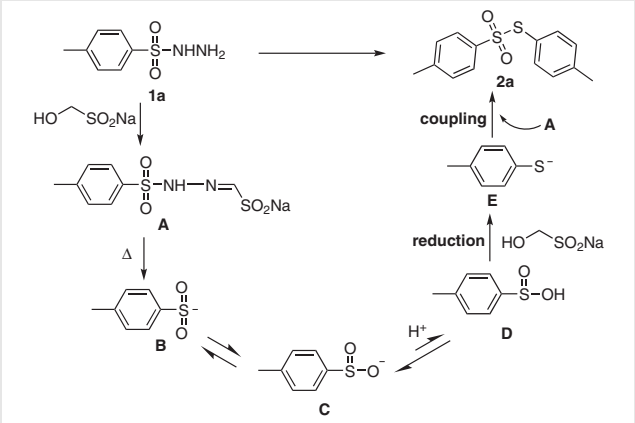
benzenesulfinic acid, instead of 4-methylbenzenesulfonohydrazide (**1a**), was used to react with Rongalite under the standard reaction conditions, and afforded the target product **2a** in 69% yield, which demonstrated that 4-methylbenzenesulfinic acid might be an intermediate for this reaction (Scheme 3D). However, no desired product **2a** was obtained in this reaction, when sodium 4-methylbenzenesulfinate with Rongalite was reacted under the same standard reaction conditions (Scheme 3E).



Scheme 3 Controlled experiments for mechanism study

On the basis of previous reports and the results of the control experiments,[11–14,16] we try to postulate a probable mechanism as shown in Scheme 4. Initially, intermediate A was generated by the reaction of 4-methylbenzenesulfonohydrazide (**1a**) with $NaHSO_2{\cdot}CH_2O$. Subsequently, intermediate **A** underwent thermal decomposition to afford sulfinyl anion **B**, which can resonate with the sulfur-centered anion **C**.[17] Next, species **C** is trapped by H^+ to form key intermediate sulfinic acid **D**, which was further reduced to thiolate **E** by $NaHSO_2{\cdot}CH_2O$. Finally, nucleophilic substitution reaction of thiolate **E** with intermediate **A** occurred to attain target product **2a**.

In summary, we have developed an efficient and general method for the highly selective construction of thiosulfonate frameworks via a $NaHSO_2{\cdot}CH_2O$-promoted reducing–coupling reaction.[18] This synthetic method has many advantages such as simple starting materials, mild reaction conditions, without any transition-metal catalyst, additive, ligand, and moreover without any toxic byproducts. In this protocol, $NaHSO_2{\cdot}CH_2O$ acts not only as the accelerant but also as the reductant for this transformation. In addition, a



Scheme 4 Proposed mechanism

possible reaction mechanism was proposed to explicate the product formation. Further studies on this original approach are ongoing in our laboratory.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707310.

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(18) ***S*-(*p*-Tolyl) 4-Methylbenzenesulfonothioate (2a): Typical Procedure**

A mixture of **1a** (0.2 mmol), $NaHSO_2{\cdot}CH_2O$ (0.4 mmol, 47.2 mg), and benzotrifluoride (1.0 mL) in a 15 mL flask was heated at 80 °C under air for 5 h. The reaction mixture was cooled to room temperature, poured into H_2O (10 mL) and extracted with EtOAc (20 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to yield **2a** as a white solid; yield: 51mg (91%).

^1H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.3 Hz, 2 H), 7.29–7.20 (m, 4 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 2.43 (s, 3 H), 2.39 (s, 3 H).^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.56, 142.01, 140.43, 136.45, 130.17, 129.33, 127.56, 124.56, 124.56, 21.63, 21.45. HRMS (EI-TOF): *m/z* calcd for $C_{14}H_{14}O_2S_2$: 278.0435; found: 278.0466.