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HBr/H_2O_2-mediated formation of C–S bond with thiosulfates

Rongxing Zhang [a], Shengzhou Jin [a], Yuanxing Wan [b], Sen Lin [a,*], Zhaohua Yan [a,*]

[a] College of Chemistry, Nanchang University, Nanchang 330031, PR China
[b] State Key Laboratory of Food Science and Techology, Nanchang University, Nanchang 330031, PR China

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ABSTRACT

A novel, efficient, and green protocol to construct C–S bond has been developed via HBr/H_2O_2-mediated sulfenylation of styrenes and 4-hydroxycoumarins leading to unsymmetrical sulfides. Various unsymmetrical sulfides were prepared in one step with moderate to good yields using environmentally-friendly H_2O_2 as oxidant and HBr as catalyst. Based on the preliminary experimental results, a plausible reaction mechanism was proposed for HBr/H_2O_2-mediated formation of C–S bond with thiosulfates.

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Introduction

The formation of C–S bond has captured growing attention for fundamental field of research in organic synthesis because sulfur-containing compounds widely emerged in various research fields.[1] In particular, unsymmetrical sulfides, have been extensively applied in bioactivator, natural products and medicinal chemistry.[2] (Scheme 1). Therefore, facile and effective methods leading to unsymmetrical sulfides have gained intensive interest from synthetic chemists and pharmacologists.[3]

The traditional strategies for the synthesis of unsymmetrical sulfides are transition metal-catalyzed sulfenylation of arene with thiols or disulfides.[4] In recent years, nonmetal-catalyzed sulfenylation for the formation of C–S bond, especially, iodine-catalyzed sulfenylation of arene with diverse sulfur reagents, has been greatly developed because of these methods with excellent yields, mild conditions, and good selectivity.[5] However, the use of fetid, sensitive, and toxic sulfenylating agents and transition-metal catalysts involved in these methods might hinder their widespread application. As a consequence, the development of efficient, facile, and environmentally-friendly protocol to obtain unsymmetrical sulfides still remains extremely significant and attractive.

Beta-hydroxysulfides and sulfenylated coumarin derivatives are vital unsymmetrical sulfides as intermediates widely found in bioactives and pharmaceutical molecules.[6] Because of their availability and importance, several strategies for the synthesis of beta-hydroxysulfides and sulfenylated 4-hydroxycoumarins have been developed.[7–9] In 2016, Huo reported an auto-oxidative hydroxysulfenylation of alkene to construct C–S bond for beta-hydroxysulfides.[8] Iodine-catalyzed protocol for arylsulfenylation of 4-hydroxycoumarins with thiols was reported by Peddinti group. Lee disclosed a $CuBr/Me_2S$-catalyzed synthesis of arylsulfenylated 4-hydroxycoumarins with arylsulfonylhydrazides.[9]

Although several strategies for the synthesis of beta-hydroxysulfides and arylsulfenylated coumarins have been described, these methods involved in the use of fetid thiols, environmentally malign triphenylphosphine, and metallic reagents. Recently, thiosulfates have gained extensive attention because they are stable, readily available, and environmentally benign, as a result, thiosulfates have been widely applied in the formation of C–S bond.[10] Here, we described a novel, efficient, and green method for the formation of C–S using H_2O_2 as oxidant with environmentally-friendly and HBr as catalyst leading to beta-hydroxysulfides and sulfenylated 4-hydroxycoumarins (Scheme 2).

Results and discussion

We initially optimized the reaction of sodium 4-chlorophenyl thiosulfate **1a** and styrene **2a** in the presence of various catalysts, oxidants and acetonitrile as solvent (Table 1). Bromides catalysts were explored for hydrosulfenylation of syrene **2a** to construct β-hydroxyl sulfide in acetonitrile at 30 °C for 30 min, which afforded desired product **3a** in low yields (Table 1, entries 1–6). Among the catalysts, HBr produced the best result (Table 1, entry 6). Subsequently, we explored the effect of temperature for

* Corresponding authors.
E-mail address: 990831948@qq.com (Z. Yan).

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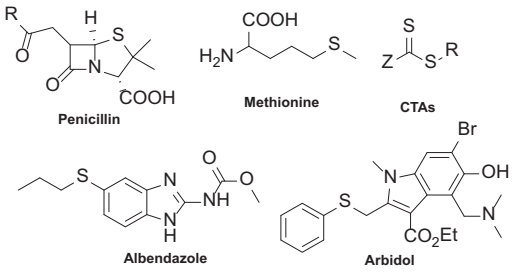
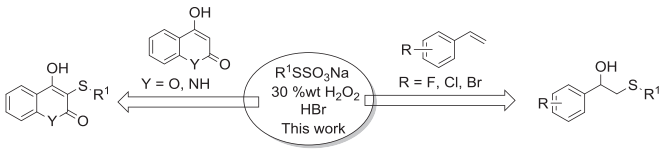


Scheme 1. Unsymmetrical sulfides applied in medicinal chemistry.



Scheme 2. Method for the synthesis of beta-hydroxysulfides and sulfenylated coumarins via HBr/H_2O_2.

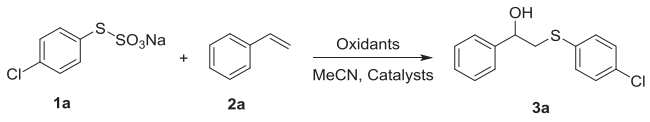
hydrosulfenylation of styrene **2a** with sodium 4-chlorophenyl thiosulfate **1a** (Table 1, entries 7–10), the results showed that 60 °C was the best choice and the corresponding product **3a** was obtained in 72% yield (Table 1, entry 9). The yield was improved when HBr was increased to 0.5 equivalent (Table, entries 10–12). **3a** was not formed when HCl or HI were employed as catalyst (Table 1, entries 13–14). A negative effects emerged when $K_2S_2O_8$, DBHP, and TBHP were employed as oxidants (Table 1, entries 15–17). Thus, the optimized conditions were established as follows: 4-chlorophenyl thiosulfate **1a** (1.2 equiv), styrene **2a** (1.0 equiv), HBr (50 mol%) as catalyst, H_2O_2 (2.0 equiv) as oxidant, and nitrile as the solvent for 30 min at 60 °C in a sealed tube.

Various thiosulfates and styrene derivatives were employed to construct bata-hydroxysulfides under the optimized reaction conditions (Table 2). When sodium *s*-(4-methylphenyl) thiosulfate and sodium *s*-(4-chlorophenyl) thiosulfate were respectively subjected to hydroxysulfenylation with syrene **2a** (Table 2, **3a**–**3b**), the results showed that the desired products were obtained in good yields. A bad result was gained when sodium butylthiosulfate (Table 2, **3c**), and *s*-benzylthiosulfate were used as the substrates under optimized condition, However, an interesting phenomenon was discovered when the temperature was increased to 100 °C for *s*-benzylthiosulfate, the corresponding product was detected in 65% yield (Table 2, **3da**) for 30 min and beta-acetamidosulfide was gained in moderate yield for 10 h (Table 2, **3db**). A class of styrene derivatives with groups (F, Cl, Br) were conducted to hydroxysulfenylation with *s*-(4-chlorophenyl) thiosulfate and desired products were obtained in moderate to good yields (Table 2, **3e**–**3i**). Unfortunately, hydroxysulfenylation of cyclohexene did not work under the optimized reaction conditions (Table 2, **3j**).

To further extend the substrate scope of this method, alkenes **4**, were next investigated and results showed that the corresponding thioethers containing five-membered ether and lactone were produced in good to excellent yields (Table 3, **5a**–**5c**).

Likewise, the method is suitable for the synthesis of sulfenylated aromatic derivatives under this system. First we conducted sulfenylation of 4-hydroxycoumarin which is important pharmaceutical intermediate[6c,d] and the positive results were described when reaction temperature was increased to 100 °C for 10 h (Table 4). The reactions of 4-hydroxycoumarin and a series of thiosulfates afforded sulfenylated 4-hydroxycoumarins and desired products were obtained in good yields (Table 4, **7a**–**7f**). Next, we turned our attention to sulfenylation of 4-hydroxyquinolin-2(1*H*)-one and cyclohexane-1,3-dione structurally similar to 4-hydroxycoumarin with thiosulfates and positive results have been obtained (Table 4, **7g**–**7h**). However,

Table 1
Optimization of reaction conditions for beta-hydroxy sulfides.



Entry	Catalysts (mol%)	Oxidants (equiv.)	Temp (°C)	Yield[b] (%)
1	–(20)	H_2O_2 (2.0)	30	N.R.
2	NBS (20)	H_2O_2 (2.0)	30	12
3	NaBr (20)	H_2O_2 (2.0)	30	20
4	TBAB (20)	H_2O_2 (2.0)	30	15
5	Br_2 (10)	H_2O_2 (2.0)	30	23
6	HBr (20)	H_2O_2 (2.0)	30	32
7	HBr (20)	H_2O_2 (2.0)	40	54
8	HBr (20)	H_2O_2 (2.0)	50	63
9	HBr (20)	H_2O_2 (2.0)	60	72
10	HBr (20)	H_2O_2 (2.0)	80	68
11	HBr (30)	H_2O_2 (2.0)	60	78
12	HBr (50)	H_2O_2 (2.0)	60	85
13	HCl (50)	H_2O_2 (2.0)	60	N.R.
14	HI (50)	H_2O_2 (2.0)	60	N.R.
15	HBr (50)	$K_2S_2O_8$ (2.0)	60	N.R.
16	HBr (50)	DBHP (2.0)	60	Trace
17	HBr (50)	TBHP (2.0)	60	32

[a]Reaction conditions: **1a** (0.24 mmol), **2a** (0.20 mmol), oxidants (0.40 mmol), MeCN (1.0 mL), 47% wt HBr (0.10 mmol), 30 min, in a sealed tube.
[b] Yield of isolated product.

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