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## Cs<sub>2</sub>CO<sub>3</sub>-promoted cross-dehydrogenative coupling of thiophenols with active methylene compounds†

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A convenient and efficient  $\alpha$ -sulfenylation of carbonyl compounds has been achieved via the halogen-free Cs<sub>2</sub>CO<sub>3</sub>-promoted cross-dehydrogenative coupling (CDC) of thiophenols with active methylene compounds using air as the oxidant under mild conditions. This transformation provides a straightforward route to the construction of carbon–sulfur bonds with wide functional group compatibility, which produces  $\alpha$ -sulfenylated carbonyl compounds in up to 95% yield.

The development of new methods to construct carbon–sulfur bonds has been of particular interest due to the wide applications of organosulfur compounds in biological chemistry and organic synthesis.<sup>1,2</sup> Among them,  $\alpha$ -sulfenylated carbonyl compounds are important intermediates for the synthesis of heterocycles,<sup>3</sup>  $\beta$ -keto sulfones,<sup>4</sup>  $\alpha,\beta$ -unsaturated carbonyl compounds,<sup>5</sup> and others.<sup>6</sup> Therefore,  $\alpha$ -sulfenylation of carbonyl compounds is highly desirable, and a variety of useful synthetic methods have been well documented. The traditional preparation of this class of compounds mainly relies on the use of pre-functionalized substrates including: (1) nucleophilic substitution of  $\alpha$ -halogenated carbonyl compounds with thiols<sup>7</sup> (Fig. 1a) or disulfides<sup>8</sup> (Fig. 1b); and (2) the reactions of carbonyl compounds with thio sources such as sulphenyl halides, disulfides, sulfonothioates, sulfenamides, and *N*-(phenylthio)

succinimide (Fig. 1c).<sup>9</sup> However, these methods are limited because the corresponding starting materials are high-cost and/or temperature- or moisture-sensitive. Thus, the development of a convenient and efficient protocol for the synthesis of  $\alpha$ -sulfenylated carbonyl compounds remains a challenge.

The cross-dehydrogenative coupling (CDC) reactions are powerful methods in organic synthesis that can avoid the use of pre-functionalized substrates.<sup>10</sup> The CDC reactions involving thiols have attracted much attention because this strategy represents more straightforward, efficient, and atom-economic to construct carbon–sulfur and sulfur–heteroatom bonds.<sup>11</sup> The oxidative CDC has also been applied to  $\alpha$ -sulfenylation of carbonyl compounds (Fig. 1d).<sup>12</sup> The coupling of thiols with active methylene compounds in the presence of CBr<sub>4</sub> has been reported by Liang and co-workers.<sup>12a</sup> Yadav and co-workers have reported  $\alpha$ -sulfenylation of monoketones in the presence of NCS.<sup>12b</sup> Recently, Hu, Lei and co-workers developed iodine-catalyzed oxidative coupling of 1,3-diketones with thiophenols using DTPB as the oxidant.<sup>12c</sup> Prabhu and co-workers developed a couple of  $\alpha$ -sulfenylations of monoketones or 1,3-diketones using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or DMSO (in the presence of I<sub>2</sub>) as the oxidant.<sup>12d-f</sup> However, the current oxidative coupling protocols requires the use of halogenated reagents and/or strong oxidants. In this regard, seeking greener oxidants for this CDC reaction is still a significant issue. Molecular oxygen as the greener and more sustainable oxidant has been widely used in organic synthesis.<sup>13</sup> Moreover, inorganic bases have been well utilized for carbon–sulfur and sulfur–heteroatom bond forming reactions.<sup>14</sup> With these backgrounds, we envisioned that  $\alpha$ -sulfenylated carbonyl compounds might be formed through the CDC reaction of thiols with carbonyl compounds using O<sub>2</sub> as the oxidant in the presence of an inorganic base. Herein, we report an efficient halogen-free Cs<sub>2</sub>CO<sub>3</sub>-promoted  $\alpha$ -sulfenylation of active methylene compounds under air.

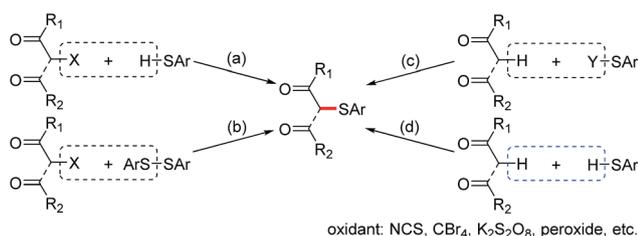


Fig. 1 Strategies for  $\alpha$ -sulfenylation of carbonyl compounds.

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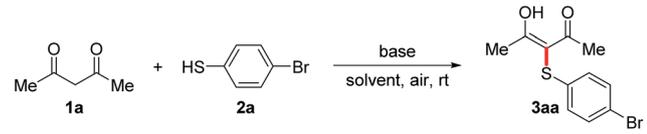
The reaction conditions were tested by using a model reaction of acetylacetone **1a** with 4-bromo-thiophenol **2a** in solvents under air atmosphere at room temperature, and the results were shown in Table 1. Initially, no reaction occurred when the reaction of **1a** with **2a** in CH<sub>3</sub>CN in the absence of bases under air was carried out (entry 1). To our delight, when Cs<sub>2</sub>CO<sub>3</sub> (1 equiv.) was added, the reaction proceeded smoothly to afford the desired product 3-(4-bromophenylthio)pentane-2,4-dione **3aa** in 82% yield (entry 2). When the reaction of **1a** with **2a** was carried out under N<sub>2</sub>, only trace amounts of **3aa** were detected (entry 3). This result demonstrates that the reaction involved an aerobic oxidative cross-coupling. We then turned to screen other bases (entries 4–9), and found that Cs<sub>2</sub>CO<sub>3</sub> was the optimal base. The increase or decrease of Cs<sub>2</sub>CO<sub>3</sub> amount did not improve the yield (entries 10–14). Notably, the use of catalytic amounts of Cs<sub>2</sub>CO<sub>3</sub> also led to the formation of **3aa** in moderate yields (entries 13 and 14). Switching the solvent from CH<sub>3</sub>CN to THF, dioxane, DMSO, EtOH, or H<sub>2</sub>O decreased the yield of **3aa** (entries 15–19), while the use of DMF afforded the desired product in 98% yield (entry 20). It is noteworthy that disulfide **4a**, which was generated *via* an aerobic oxidative homocoupling of thiol **2a**,<sup>14a</sup> was observed in all cases under air.

We then set out to explore the generality of the CDC reaction of thiols with active methylene compounds. We first applied the optimized conditions to the coupling of various thiols **2** with

acetylacetone **1a** (Table 2). Pleasingly, the results showed that thiophenol substrates bearing different groups such as electron-withdrawing halogen groups (Br, Cl and F) and electron-donating groups (alkyl, OMe, OH and NH<sub>2</sub>) at the *para*, *meta* or *ortho* or at both positions of aromatic rings, as well as the bulky 2-naphthalenethiol, were all well tolerated. The corresponding **3aa–3as** were isolated in moderate to excellent yields, indicating that the electronic and steric effects were not evident in this reaction. The scale-up reaction was also attempted. When we increased the scale of the reaction from 0.4 to 4 mmol, the yield of **3ad** only slightly decreased (from 86% to 79%). We then turned our attention to aliphatic thiols. Unfortunately,  $\alpha$ -sulfenylation of **1a** with benzylthiol or cyclohexylthiol failed to give the desired **3at** or **3au**.

Next, the coupling of 4-bromo-thiophenol **2a** with a variety of active methylene compounds **1** under the optimized conditions was examined, and the results are illustrated in Table 3. 1,3-Diketones bearing methyl, ethyl, isopropyl and phenyl groups were all applicable to the CDC reaction, leading to the formation of **3ba–3da** in 68–85% yields. When ethyl acetoacetate was employed, the reaction also proceeded smoothly to afford **3ea** in 82% yield. In addition, dialkyl malonates were also well tolerated, and the desired products **3fa** and **3ga** were obtained in good yields. We then turned to  $\alpha$ -sulfenylation of monosubstituted malonates, and the reaction of **2a** with  $\alpha$ -alkylmalonates led to the corresponding **3ha** and **3ia** in 84% and 89% yield, respectively.

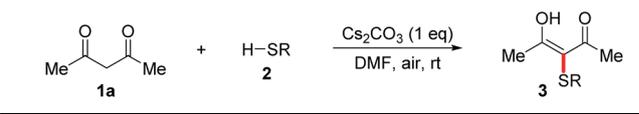
Table 1 Optimization of reaction conditions<sup>a,b</sup>

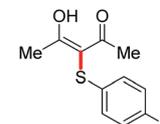
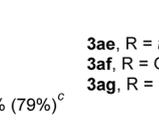
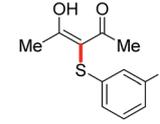
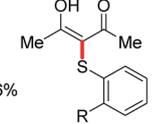
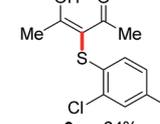
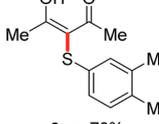
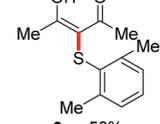
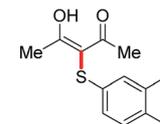
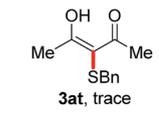
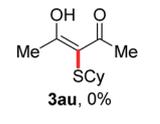


Entry	Base (equiv.)	Solvent	Yield of <b>3aa</b> (%)
1		CH <sub>3</sub> CN	0
2	Cs <sub>2</sub> CO <sub>3</sub> (1)	CH <sub>3</sub> CN	82
3 <sup>c</sup>	Cs <sub>2</sub> CO <sub>3</sub> (1)	CH <sub>3</sub> CN	Trace
4	K <sub>2</sub> CO <sub>3</sub> (1)	CH <sub>3</sub> CN	65
5	Na <sub>2</sub> CO <sub>3</sub> (1)	CH <sub>3</sub> CN	0
6	NaOAc (1)	CH <sub>3</sub> CN	0
7	K <sub>3</sub> PO <sub>4</sub> (1)	CH <sub>3</sub> CN	45
8	CsF (1)	CH <sub>3</sub> CN	16
9	Et <sub>3</sub> N (1)	CH <sub>3</sub> CN	<10
10	Cs <sub>2</sub> CO <sub>3</sub> (3)	CH <sub>3</sub> CN	74
11	Cs <sub>2</sub> CO <sub>3</sub> (2)	CH <sub>3</sub> CN	82
12	Cs <sub>2</sub> CO <sub>3</sub> (1.5)	CH <sub>3</sub> CN	75
13	Cs <sub>2</sub> CO <sub>3</sub> (0.5)	CH <sub>3</sub> CN	61
14	Cs <sub>2</sub> CO <sub>3</sub> (0.2)	CH <sub>3</sub> CN	48
15	Cs <sub>2</sub> CO <sub>3</sub> (1)	THF	73
16	Cs <sub>2</sub> CO <sub>3</sub> (1)	Dioxane	50
17	Cs <sub>2</sub> CO <sub>3</sub> (1)	DMSO	57
18	Cs <sub>2</sub> CO <sub>3</sub> (1)	EtOH	25
19	Cs <sub>2</sub> CO <sub>3</sub> (1)	H <sub>2</sub> O	0
20	Cs <sub>2</sub> CO <sub>3</sub> (1)	DMF	98

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), base, solvent (1 mL), room temperature, open air, 6 h. <sup>b</sup> Yield based on **1a** was determined by <sup>1</sup>H NMR analysis of crude products using an internal standard. <sup>c</sup> The reaction was carried out under N<sub>2</sub>.

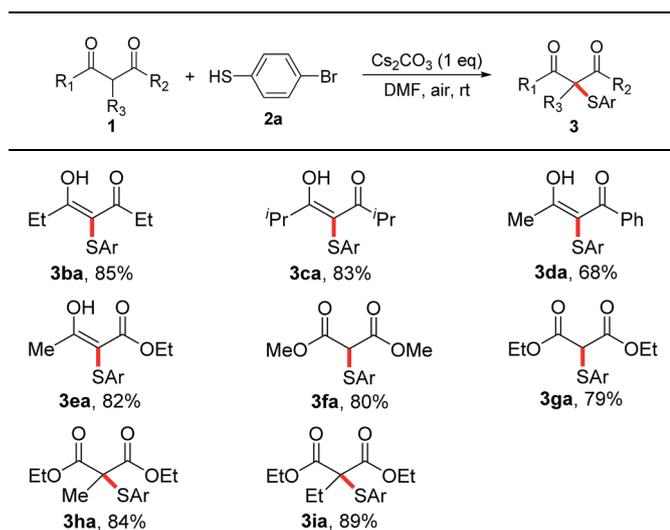
Table 2 Scope of thiols<sup>a,b</sup>



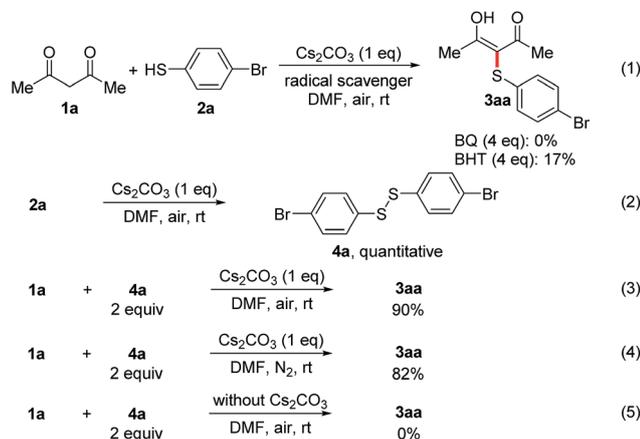
 <b>3aa</b> , R = Br, 93% <b>3ab</b> , R = Cl, 62% <b>3ac</b> , R = F, 75% <b>3ad</b> , R = Me, 86% (79%) <sup>c</sup>	 <b>3ae</b> , R = <i>t</i> -Bu, 87% <b>3af</b> , R = OH, 50% <b>3ag</b> , R = NH <sub>2</sub> , 53%
 <b>3ah</b> , R = Br, 61% <b>3ai</b> , R = Cl, 80% <b>3aj</b> , R = F, 89% <b>3ak</b> , R = OMe, 76%	 <b>3al</b> , R = Br, 94% <b>3am</b> , R = Cl, 72% <b>3an</b> , R = F, 80% <b>3ao</b> , R = Me, 76%
 <b>3ap</b> , 64%	 <b>3aq</b> , 73%
 <b>3ar</b> , 58%	 <b>3as</b> , 95%
 <b>3at</b> , trace	 <b>3au</b> , 0%

<sup>a</sup> Reaction conditions: **1a** (0.4 mmol), **2** (0.8 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (0.4 mmol) in DMF (2 mL) stirring at room temperature under air for 6–12 h. <sup>b</sup> Isolated yield based on **1a**. <sup>c</sup> The reaction was performed in a 4 mmol scale.

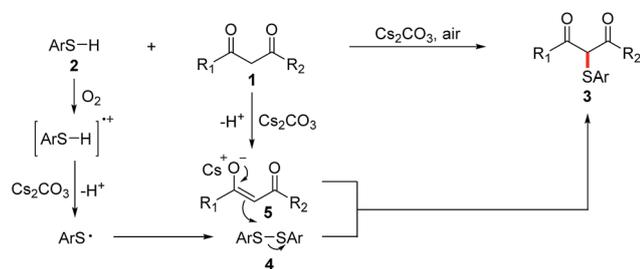


Table 3 Scope of active methylene compounds<sup>a,b</sup>

<sup>a</sup> Reaction conditions: **1** (0.4 mmol), **2a** (0.8 mmol), and  $\text{Cs}_2\text{CO}_3$  (0.4 mmol) in DMF (2 mL) stirring at room temperature under air for 6–12 h. <sup>b</sup> Isolated yield based on **1**.



Scheme 1 Mechanistic studies.



Scheme 2 Proposed mechanism.

To gain more insight into the mechanism of the CDC reaction, a series of control experiments were conducted (Scheme 1). When radical scavenger BQ and BHT was introduced into the reaction,

the yield of **3aa** reduced from 93% to 0% and 17%, respectively (eqn (1)), suggesting that this transformation might proceed *via* a radical pathway. In consideration of the generation of disulfides in all cases, the reaction of thiol **2a** with  $\text{Cs}_2\text{CO}_3$  under air was carried out, leading to the formation of disulfide **4a** in quantitative yield (eqn (2)). The above results suggest that  $\text{Cs}_2\text{CO}_3$  could increase the oxidation rate of thiols with dioxygen and disulfide was produced *via* a thiyl radical homocoupling.<sup>14a,15</sup> In addition, the reaction of **1a** with disulfide **4a** under the standard conditions gave **3aa** in good yields regardless of the presence of air (eqn (3) and (4)), which demonstrates that disulfide might be an intermediate in the CDC reaction. Moreover, the reaction of **1a** with **4a** in the absence of  $\text{Cs}_2\text{CO}_3$  failed to give **3aa** (eqn (5)), which indicates  $\text{Cs}_2\text{CO}_3$  is indispensable in this reaction.

According to the literatures and our observations, a plausible reaction mechanism is outlined in Scheme 2. Initially, thiyl radical is generated from the autoxidation of thiol **2** in the presence of  $\text{Cs}_2\text{CO}_3$  and dioxygen, and thiyl radical undergoes homocoupling to produce disulfide **4**.<sup>14a,14a,15,16</sup> Meanwhile, active methylene compound **1** reacts with  $\text{Cs}_2\text{CO}_3$  to form intermediate **5**. Finally, the nucleophilic attack of the *in situ*-generated enolate **5** on disulfide **4** affords  $\alpha$ -sulfenylated carbonyl compound **3**.

## Conclusions

In conclusion, we have developed the  $\text{Cs}_2\text{CO}_3$ -promoted cross-dehydrogenative coupling (CDC) of thiophenols with active methylene compounds, which provides a highly convenient and efficient protocol for the synthesis of  $\alpha$ -sulfenylated carbonyl compounds with wide functional group compatibility under mild conditions. To the best of our knowledge, this finding is the first example of aerobic CDC reaction of thiols with carbonyl compounds. We envision that the reaction mode outlined here will have potential applications in organic synthesis.

## Conflicts of interest

There are no conflicts to declare.

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