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Iodine/Manganese Dual Catalysis for Oxidative Dehydrogenation Coupling of Amines with Thiols

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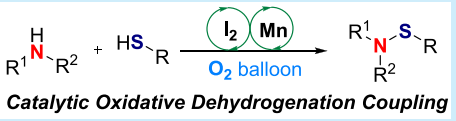
Supporting Information

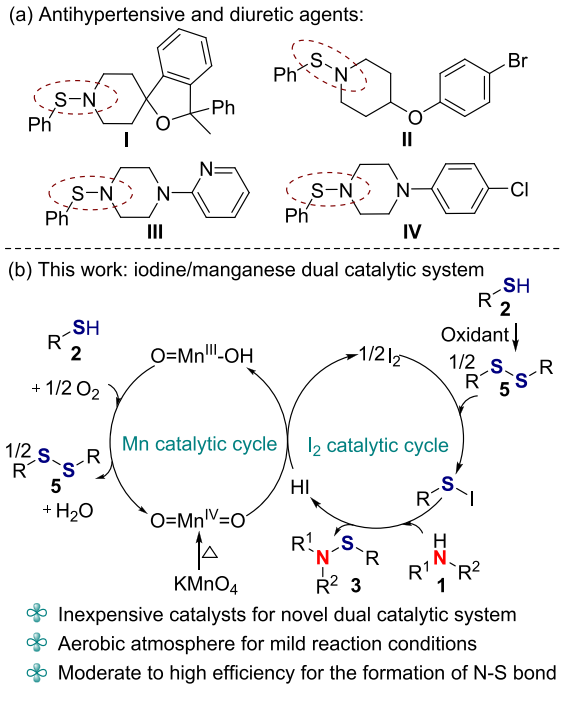
ABSTRACT: A novel dual catalytic system of iodine and manganese is used for the first time for oxidative dehydrogenation coupling of amines with thiols during aerobic oxidation. Sulfenamides are synthesized via this approach with moderate to high efficiencies. The mechanistic studies indicate that activated MnO_2 is an electron transfer bridge for assisting iodine in completing the catalytic cycle.



Catalytic Oxidative Dehydrogenation Coupling

Sulfenamides are recognized as important compounds and are broadly applied in pharmaceuticals, agrochemicals, and industrial utilizations.[1] In particular, the sulfenamides, which possess the structure of arylpiperazine or piperidine, exhibit high antihypertensive or diuretic activities (Scheme 1a).[1c] Sulfenamides also serve as crucial reagents in several organic transformations, such as oxidation, amination, and sulfuration.[2] Considering the significance of sulfenamide derivatives, a variety of classic methods for the synthesis of sulfenamides have been documented. For instance, sulfenamides can be constructed by the reaction of amines with disulfides,[3] sulfenyl chlorides,[2i,4] sulfenyl thiocyanates,[5] thiolsulfonates,[6] *N*-(phenylthiol)phthalimides,[7] or thiols;[8] synthesized by the cross-coupling of *N*-chloroamines[9] or *N*-chlorosuccinimides[10] with metal thiolates; or formed by the reaction of lithium dialkylamides with disulfides.[11] Among them, oxidative dehydrogenation coupling of amines with thiols is the most intriguing strategy for the formation of N−S bonds under an aerobic atomosphere due to the atom and step economy. Copper-catalyzed oxidative coupling reactions of amines with thiols for forming sulfenamides as the only catalytic example have been reported.[8b] However, a systematic and profound investigation of a simple, inexpensive, ligand-free, and efficient catalytic system for accessing sulfenamides via the dehydrogenation coupling of amines with thiols has not been explored. Herein, we describe an iodine/manganese dual catalytic system for this transformation during aerobic oxidation, generating sulfenamides with moderate to high yields (Scheme 1b).

Scheme 1. Sulfenamides for Drugs and a Strategy for the Synthesis of Sulfenamides



A large number of X−S (X = C, N, O, S, or P) bond formation reactions have been developed through metal, photoredox, small molecule, or iodine catalysis.[12,13] Iodine is one of the economical and green catalysts that has been increasingly applied in the construction of X−S bonds.[12c] As a single catalyst, iodine could be regenerated by a terminal oxidant such as TBHP, H_2O_2, $K_2S_2O_8$, or molecular oxygen.[14] Despite the fact that oxygen is the most ideal oxidant, a higher temperature is usually required in the transformations.[15] To overcome this kinetically unfavorable effect, Iida and colleagues reported a subtle strategy with regard to the catalytic couple of iodine and flavin-catalyzed sulfenylation of indoles with thiols using oxygen as the oxidant.[16] Flavin was used as an electron transfer bridge between iodine and oxygen to form C−S bonds. However, pre-preparation and the high

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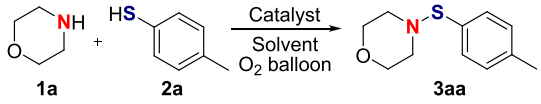
cost of flavin limited organic transformations. Therefore, a commercially available and cheaper catalyst is desired. Actually, $KMnO_4$ is an inexpensive inorganic compound and is often used as a strong oxidant rather than a catalyst because of its highest oxidation state. Even though $KMnO_4$ itself cannot be an electron transfer bridge, it can be heated to liberate activated MnO_2, which has an intermediate oxidation state for single-electron transfer (SET). Thus, we wonder whether a catalytic amount of $KMnO_4$ could cooperate with iodine to realize the oxidative dehydrogenation coupling of amines with thiols under mild reaction conditions (Table 1).

Table 1. Optimization of Reaction Conditions[a]



1a 2a 3aa

entry	catalyst (mol %)	yield (%)[b]
1	I_2 (10)/$KMnO_4$ (10)	80
2	I_2 (10)	trace
3	$KMnO_4$ (10)	trace
4	–	–
5	I_2 (10)/$KMnO_4$ (10)	70[c]
6	I_2 (10)/$KMnO_4$ (10)	78[d]
7	I_2 (10)/$KMnO_4$ (10)	75[e]
8	I_2 (10)/$KMnO_4$ (10)	43[f]
9	I_2 (10)/$KMnO_4$ (10)	75[g]

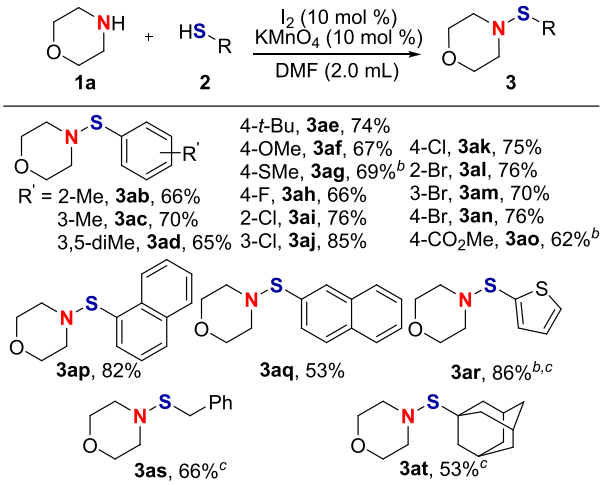
[a]Reaction conditions: **1a** (0.5 mmol, 1 equiv), **2a** (0.5 mmol, 1 equiv), catalyst (10 mol %), DMF (2.0 mL), 80 °C, 12 h, oxygen balloon. [b]Isolated yields. [c]At 60 °C. [d]At 100 °C. [e]At 120 °C. [f]For 6 h. [g]Under an air atmosphere.

On the basis of the pioneering works about iodine- or manganese-catalyzed reactions,[14−17] we hypothesize that thiol **2** is oxidized by oxidants[18] in the reaction system, affording disulfide **5** that then reacts with I_2 to produce R−S−I via SET. R−S−I subsequently reacts with amine **1** to give the corresponding product **3** and HI via SET.[2i,4,13u,16a] HI is oxidized by MnO_2, leading to regeneration of I_2. MnO_2 is formed in situ through the heating of $KMnO_4$, producing Mn(III) that is then oxidized by O_2 and **2** to give MnO_2 (Scheme 1b).

To verify our hypothesis for the synthesis of sulfenamides, morpholine **1a** and 4-methylbenzenethiol **2a** were employed as the model substrates to optimize the reaction conditions (see the Supporting Information for details). Initially, numerous combinations of catalysts were examined in DMF at 80 °C for 12 h with an oxygen balloon (Table S1). Surprisingly, the catalytic system of I_2 and $KMnO_4$ could efficiently catalyze the oxidative dehydrogenation coupling reaction to provide the corresponding product **3aa** in a ≤80% yield (entry 1). A trace of sulfenamide **3aa** was observed in the presence of I_2 or $KMnO_4$ and not detected in the absence of a catalyst (entries 2−4). Furthermore, diverse solvents were screened for the reaction of **1a** with **2a**, affording **3aa** in 8−73% yields (Table S2). Polar aprotic solvents, especially DMF, presented better effects according to the solvent screening. In addition, changing the temperature and time led to a decrease in the yield of **3aa** (entries 5−8). The transformation could also be carried out under an air atmosphere, yielding **3aa** in 75% yield (entry 9).

With the optimized reaction conditions in hand, the substrate scope of thiols was investigated as shown in Table 2. Aryl thiophenol with various substituents on the phenyl ring

Table 2. Substrate Scope of Thiol[a]



1a 2 3

[a]Reaction conditions: morpholine **1a** (0.5 mmol, 1 equiv), **2** (0.5 mmol, 1 equiv), I_2 (10 mol %), $KMnO_4$ (10 mol %), DMF (2.0 mL), 80 °C, 12 h, isolated yield. [b]For 24 h. [c]**1a** (1.0 mmol, 2 equiv).

was compatible with the N−S bond formation reaction, generating the corresponding products in good to exellent yields. Electron-donating groups such as methyl, *tert*-butyl, methoxy, and methylthio substituents at the *ortho*, *meta*, or *para* position of the aryl ring were tolerented in the reaction, affording products **3ab**−**3ag** in 65−74% yields. Electron-withdrawing groups were also used. Halogen compounds, such as fluoro-, chloro-, and bromo-subsituted aryl thiophenols, smoothly provided the desired products **3ah**−**3an** in 66−85% yields. The aryl thiophenol with an ester group could be employed in the reaction, yielding product **3ao** in 62% yield. In addition, 1-naphthyl-, 2-naphthyl-, and 2-thienyl-substituted products **3ap**−**3ar**, respectively, could be obtained in 53−86% yields. In addition to aryl and heteroaryl groups, alkyl-substituted thiols were also suitable for the transformation. Phenylmethanethiol and adamantane-1-thiol underwent dehydrogenation coupling to afford sulfenamides **3as** and **3at** in 66% and 53% yields, respectively.

After the generality of thiols had been examined, a variety of amines **1** were applied to the oxidative coupling reaction with 4-methylbenzenethiol **2a** (Table 3). Thiomorpholine **1b** was treated with **2a** to provide the corresponding product **3ba** in 60% yield. *tert*-Butoxycarbonyl (Boc)-protected piperazines **1c** and **1d** were successfully converted to sulfenamides **3ca** and **3da** in 65% and 77% yields, respectively. Analogously, benzyloxycarbonyl (Cbz)-substituted piperazine **1e** also reacted well to give product **3ea** in 73% yield. Other piperazines having bis(aryl)methyl substituents did not affect the reaction and were successfully tested, giving products **3fa** and **3ga** in 40% and 51% yields, respectively. The dehydrogeantion coupling of 4-substitued piperidine compounds with **2a** was carried out, affording the desired products in good yields (70% and 75% yields for **3ha** and **3ia**, respectively). Although 9*H*-carbazole decreased the yield of **3ja** (30%), it still showed that aryl amine was also compatible with the catalytic system for forming N−S bonds. Unexpectedly,

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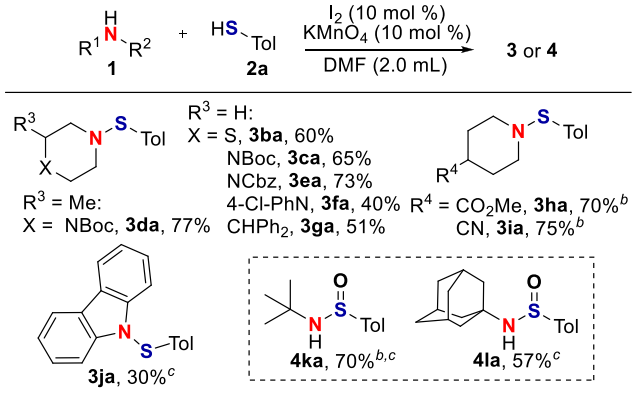
Table 3. Substrate Scope of Amine[a]

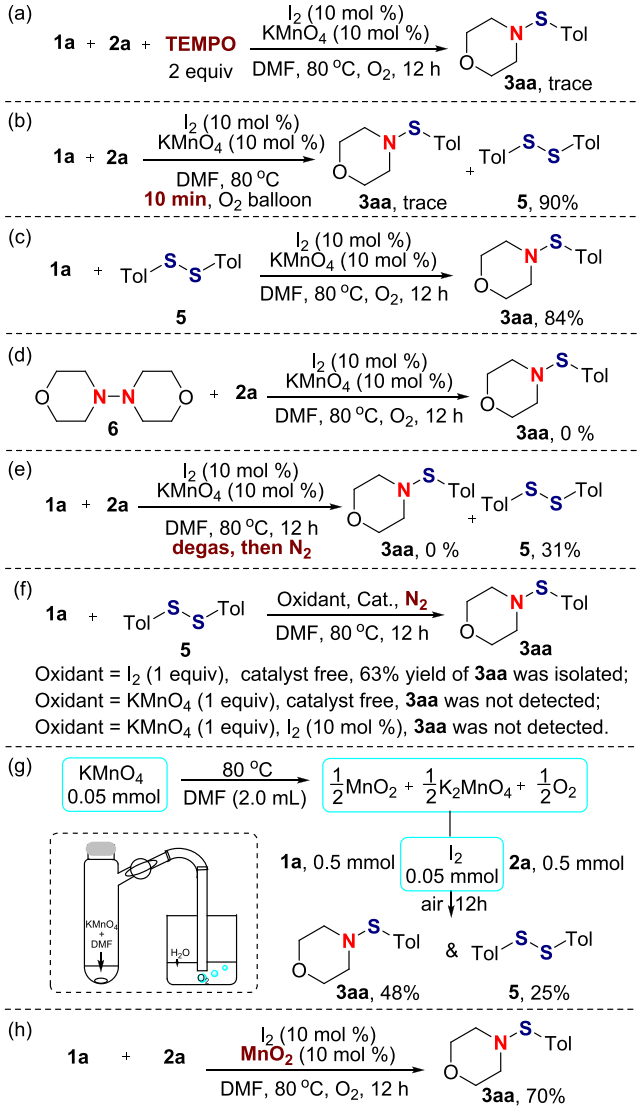


[a]Reaction conditions: amine **1** (0.5 mmol, 1 equiv), **2a** (0.5 mmol, 1 equiv), I_2 (10 mol %), $KMnO_4$ (10 mol %), DMF (2.0 mL), 80 °C, 12 h, isolated yield. [b]**1** (1.0 mmol, 2 equiv). [c]For 24 h.

when using primary amines **1k** and **1l** as the coupling partner of 4-methylbenzenethiol **2a**, sulfinamide derivatives were generated in moderate to good yields (70% and 57% yields for **4ka** and **4la**, respectively). The primary amines were convered to sulfinamides rather than sulfenamides, which can presumably be attributed to the reactivity of primary amines being higher than that of secondary amines.

To investigate the reaction mechanism for the iodine/manganese-catalyzed oxidative dehydrogenative coupling, a series of reactions were performed (see the Supporting Information for details). Initially, stoichiometric (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) was added to the treatment of **1a** with **2a** under the standard reaction conditions, giving a trace of **3aa** (Scheme 2a). The result revealed that the radical species might be involved in the reaction. When the transformation was carried out for only 10 min, a trace of **3aa** was observed and a 90% yield of disulfide **5** was isolated, suggesting that the generation of **5** from **2a** was rapid (Scheme 2b). Disulfide **5** was reacted with **1a** and **2a** was reacted with hydrazine (**6**), giving product **3aa** in 84% and 0% yields, separately (reactions c and d, respectively, of Scheme 2). When the reaction of **1a** with **2a** was performed under a N_2 atmosphere, **3aa** could not be observed and a 31% yield of **5** was isolated (Scheme 2e). The discoveries indicated that disulfide **5** was a crucial intermediate, hydrazine **6** was not an intermediate, and oxygen was a key terminal oxidant for the reaction. Sequentially, two coupling transformations of **1a** with **5** were independently performed in the presence of the different oxidants and catalysts under a N_2 atmosphere (Scheme 2f). Sulfenamide **3aa** was obtained in 63% yield when using I_2 as the oxidant, and no product was detected with an equivalent amount of $KMnO_4$. Combined with the result of entry 4 in Table 1, the data further confirmed our assumption that both iodine and manganese were indispensable for achieving the catalytic cycle and molecular oxygen was the terminal oxidant. In addition, a facile reaction apparatus was set up to explore the active manganese species (Scheme 2g). $KMnO_4$ was heated in DMF, and oxygen bubbles could be observed in a beaker of water, implying that activated MnO_2 might be produced. After the bubbling of oxygen had ceased, 10 mol % I_2, **1a**, and **2a** were added to the reaction tube with a manganese catalyst under an air atmosphere. Sulfenamide **3aa** and disulfide **5** were independently obtained in 48% and 25% yields, respectively, after 12 h. Furthermore, freshly prepared

Scheme 2. Experiments for Mechanistic Studies

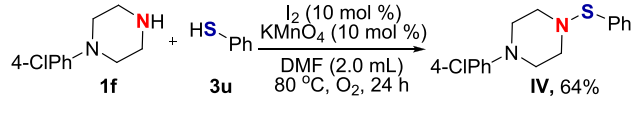


MnO_2 was introduced into the reaction mixture, giving **3aa** in 70% yield (Scheme 2h). These two reactions confirmed that MnO_2 was an active species in the catalytic cycle. An exhaustive study of the reaction mechanism is underway.

Additionally, this iodine/manganese dual catalysis gave a straightforward approach to sulfenamide **IV**, which possessed antihypertensive activity (Scheme 3). **IV** could be readily prepared in 64% yield by the oxidative dehydrogenation coupling reaction of piperazine **1f** with thiophenol **3u** (see the Supporting Information for details).

In conclusion, a dual catalytic system of iodine/manganese-catalyzed oxidative dehygenative coupling of amines with thiols under mild reaction conditions has been established, producing various sulfenamides in moderate to high yields. The reaction

Scheme 3. Synthesis of Antihypertensive Activity Derivative IV



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mechanism research suggested that single-electron transfer might be involved in this transformation, and both iodine and manganese are indispensable for accomplishing the catalytic cycle. This protocol also provided an economic and efficient methodology for synthesizing potential drugs that contained the sulfenamide building blocks. Further exploitation of this process for pharmaceutical preparation or industrial application is occurring through this approach in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02545.

Experimental procedures, characterization data, and NMR spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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