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Synthesis and Nano-Pd catalyzed chemoselective oxidation of symmetrical and unsymmetrical sulfides

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A highly chemoselective, efficient and nano-Pd catalyzed protocol for the rapid construction of sulfoxides and sulfones *via* the oxidation of symmetrical and unsymmetrical sulfides using H_2O_2 as an oxidant has been developed, respectively. The ready availability of starting materials, easy recovery and reutilization of the catalyst, wide substrate scope, and high yields make this protocol an attractive alternative. The process also involves the metal-free and microwave-promoted synthesis of symmetrical diarylsulfides, and FeCl₃-mediated preparation of symmetrical diaryldisulfides through the reaction of arenediazonium tetrafluoroborates with Na₂S-9H₂O as a sulfur source. In addition, unsymmetrical sulfides were generated *via* the K₂CO₃-mediated reaction of arenediazonium tetrafluoroborates with symmetrical disulfides.

Introduction

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Aromatic organosulfur molecules such as thioethers, disulfides, sulfoxides and sulfones are widely present in nature, and are often found in biologically and pharmaceutically active compounds, as well as organic materials. They commonly serve as useful synthetic intermediates in organic reactions, too. Therefore, the development of novel, efficient and environmentally benign methodologies for the construction of these molecules is very important.

Symmetrical diaryl thioethers are commonly prepared via the metal-catalyzed reactions of aryl halides with different sulfur surrogates in the presence of a base.¹ However, these methods typically require high temperature and are restricted to the existence of a metal catalyst and base. An interesting alternative synthesis of these compounds via the metalcatalyzed deoxygenation reduction of sulfoxides was documented.² Recently, it has been demonstrated that thionyl chloride (SOCl₂) and triphenylphosphine (Ph₃P) can also be used to finish the reaction without the use of any metal.³ However, the approach is limited to the use of stoichiometric amount of SOCl₂. Despite the value of these methods, it is highly appealing to develop greener and simpler methods for constructing various diaryl thioethers. Microwave irradiation has been widely recognized as an efficient synthetic tool.⁴ To date, nevertheless, no report was observed for the synthesis of symmetrical diaryl thioethers involving the use of microwave.

The traditional method utilized to generate symmetrical diaryl disulfides is the oxidative coupling of thiols in the

presence of an oxidant.⁵ However, readily oxidizable, foulsmelling, and less available arenethiols were required in these procedures. Although some homocouplings of sodium arenesulfinates have been disclosed, complex reaction system, narrow substrate scope and low yields were unavoidable.6 Recently, some improvements have been directed to the use of sulfur transfer reagents and aryl halides as coupling partner.⁷ Additionally, arenediazonium tetrafluoroborates could be transferred into diary disulfides by employing CS₂ as a sulfer source,⁸ and the use of Na₂S as an efficient sulfur transfer reagent has also been observed for the synthesis of alkyl disulfides.9 Despite these achievements, to the best of our knowledge, a successful example for the synthesis of diaryl of arenediazonium disulfides through the reaction tetrafluoroborates with Na₂S·9H₂O remains unknown.

So far, considerable efforts have been paid to develop efficient synthetic strategies for the formation of unsymmetrical arylsulfides¹⁰ such as deoxygenation of thioetherification12 sulfoxides11, decarbonylative and sulfenylation of organic reagents with arylsulfonyl chlorides or sodium arylsulfinates¹³. Among them, the cross couplings of aryl halides with thiols are proven to be more prominent.14 Especially, Pd, Cu, Ni, Co, Fe and Rh-based catalytic systems have been extensively studied.¹⁵ However, these processes are limited to the use of thiols, ligands or transition metals. Although the coupling of two aromatic substrates is also proven to be versatile in the presence of different sulfur-containing reagents,¹⁶ most of them required the utilization of a transition metal or lower yields were obtained. Recently, the cross couplings of symmetrical diaryl disulfides with aromatic reagents¹⁷ such as arylboronic acids,¹⁸ aryl halides¹⁹ and arenediazonium tetrafluoroborates²⁰ provided efficient access to unsymmetrical arylsulfides. Despite these significant advances, the development of novel alternative methods that employs inexpensive reagents or promoters is highly desirable.

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⁺ Footnotes relating to the title and/or authors should appear here.

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In general, selective catalytic oxidation of sulfides to sulfoxides is one of the most efficient approaches in the presence of various oxidants.²¹ Such, the choice of oxidants and catalysts is crucial. The use of hydrogen peroxide (H₂O₂) or molecular O_2 as an oxidant is more attractive because it is a readily available, inexpensive, and environmentally friendly oxidizing agent.²² In terms of catalysts, many metal-based catalytic systems²³ and metal-free catalysts²⁴ have been well reported. However, these available protocols still suffer from one or more limitations, like high catalyst loading, the requirement of a promoter or a co-catalyst, difficult recycle of catalyst, relatively low yields, or high temperature. In addition, the reaction can be carried out without any catalyst.²⁵ Unfortunately, the complex operation and relatively low yields were observed. Therefore, it is of current interest to explore a more economic and environmental friendly method with the use of greener catalyst to finish this reaction.

Among the methodologies reported²⁶ such as DABSO-based sulfone synthesis²⁷, the preparation of arylsulfones from arylsulfinic acid salts²⁸ and promoter-mediated oxidation of sulphides²⁹, a reliable and straightforward route to sulfones involves the selective catalytic oxidation of sulfides using H₂O₂ or molecular O₂ as oxidant³⁰. Although transition-metal catalysts have been successfully reported,³¹ most procedures required complicated ligands. Such, the development of recyclable catalytic systems which utilized a recycled catalyst and readily available ligand to facilitate the oxidation is still of central importance. On the basis of the oxidation of sulfides to sulfoxides, we want to further investigate the oxidation of sulfides to sulfones. During several previous studies in our research group, we reported an aluminum hydroxidesupported nano-palladium catalyst which had been applied to some cross couplings.32

Herein, we will report the microwave-assisted synthesis of symmetrical diaryl sulfides *via* the coupling of arenediazonium tetrafluoroborates with Na₂S•9H₂O without any catalyst in the presence of H₂O as a solvent, and FeCl₃-promoted preparation of symmetrical diaryl disulfides *via* the coupling of arenediazonium tetrafluoroborates with Na₂S•9H₂O. K₂CO₃-mediated cross-coupling of symmetrical disulfides with arenediazonium salts for the construction of unsymmetrical sulfides has been elucidated. More importantly, we report our efforts in catalyst development for the nano-Pd catalyzed, highly selective oxidation of sulfides to sulfoxides and sulfones in the presence of H₂O₂ as an oxidant, respectively.

Results and discussion

Our initial studies focused on the reaction of arenediazonium tetrafluoroborates with $Na_2S \cdot 9H_2O$ for synthesis of symmetrical diaryl thioethers without any catalyst in the presence of H_2O as a solvent under microwave conditions. Optimization of reaction conditions was performed to make this transformation more efficient, as summarized in Table 1. Extensive screening showed that the optimal reaction conditions were 0.2 mmol scale of **1a** with 1.0 equivalent of $Na_2S \cdot 9H_2O$ under the power of 300 W in 1.0 mL H_2O at 100 °C (Table 1, entry 7).

[N ₂ BF ₄	+ Na ₂ S•9H ₂ O <u>T, Mw</u>		139/C8OB03209E
1a		2	3а	
Entry	T (°C)	Power (W)	t (min)	Yield (%) ^b
1	80	300	30	67
2	90	300	30	60
3	100	300	30	89
4	100	200	30	80
5	100	400	30	85
6	100	300	10	81
7	100	300	20	90
8	100	300	40	62

 Table 1 Optimization of reaction conditions under microwave irradiation^a Article Online

 o Reaction conditions: 1a (38.5 mg, 0.2 mmol), 2 (53.2 mg, 0.22 mmol), H_2O (1.0 mL). b Isolated yield.

A wide range of substituted arenediazonium tetrafluoroborates were then used to react with sodium sulfide using this procedure. As shown in Scheme 1, good to excellent yields were obtained for all examined substrates (**3a-3q**). It's obvious that the electronic nature of substituents on the phenyl ring of arenediazonium salts had a significant effect



 a Reaction conditions: 1 (0.2 mmol), 2 (53.2 mg, 0.22 mmol), H_2O (1.0 mL), microwave (300 W), 100 o C. b Isolated yield. c 400 W and 25 min were adopted.

on the yield. For example, arenediazonium salts bearing electron-donating groups (Me and MeO) provided good to excellent yields, which were higher than those with electron-

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withdrawing groups (NO₂, Br, Cl, and F) (**3b-3g** vs. **3h-3q**). The steric hindrance on the phenyl ring also played an important role on yields, which *para*-substituted arenediazonium salts afforded the corresponding products with higher yields than *ortho-* and *meta*-substituted ones (**3b** vs. **3c** and **3d**, **3e** vs. **3f** and **3g**, **3h** vs. **3i** and **3j**, **3k** vs. **3l** and **3m**, **3n** vs. **3o** and **3p**).

Having identified the optimal conditions of the reaction of arenediazonium tetrafluoroborates with Na₂S·9H₂O leading to symmetrical diaryldisulfides in the presence of FeCl₃, we investigated the scope and generality of arenediazonium tetrafluoroborates. As listed in Scheme 2, phenyldiazonium tetrafluoroborate could smoothly offer the 73% yield (**4a**). Electron-donating groups such as Me and MeO were tolerated in various positions on the phenyl ring, forming the corresponding products **4b-4g** in good yields. In terms of electron-withdrawing groups such as F, Cl, Br, and NO₂, moderate to good yields could be obtained (**4h-4q**).



 a Reaction conditions: 1 (0.2 mmol), 2 (53.2 mg, 1.1 equiv), FeCl_3 (39.1 mg, 1.2 equiv) in CH_3OH (1.0 mL) at 0-25 °C. b Isolated yield.

Under the optimized experimental conditions, the results of an examination of the scope of the cross-coupling reaction of a series of arenediazonium tetrafluoroborates with symmetrical disulfides are presented in Scheme 3. With regard to various aryldiazonium salts, modest to good yields could be obtained. It was noteworthy that steric hindrance of substituents on the aromatic ring played an important role on the yield which *para*substituted substrates afforded the corresponding products with higher yields than *ortho*- and *meta*-substituted ones (**5b** *vs.* **5c**, **5d** *vs.* **5g** and **5h**, **5i** *vs.* **5j**). Interestingly, substrates bearing 4-F and 4-NO₂ groups indicated obvious higher yields





^a All reactions were performed with ArN₂BF₄ **1** (0.2 mmol), (ArS)₂ **4** (0.18 mmol) and K₂CO₃ (27.7 mg, 0.2 mmol) in CH₃CN (1.0 mL) under N₂ atmosphere at 25 °C. ^b The corresponding homocoupling products of arenediazonium tetrafluoroborates were also detected during these reactions. ^c Isolated yield. ^d 35 °C was used. ^e 20 °C was used.

On the basis of the above-described synthesis of the symmetrical and unsymmetrical sulfides, we started the research on the oxidation of sulfides using 30% aqueous hydrogen peroxide as an oxidant in the presence of nanopalladium catalyst Cat. 1. First, the selective oxidation of sulfides to sulfoxides was examined. Under the optimized conditions, a series of symmetrical sulfides was subjected to the oxidation, and the results are presented in Scheme 4. Diverse sulfides proved to be amenable to the reaction conditions, delivering the desired products 6a-6p in good to excellent yields. The electronic properties of substituents on the phenyl ring of sulfides had an obvious influence on the yield. Substrates bearing electron-donating groups supplied excellent yields which were higher than those with electron-withdrawing groups (6a-6f and 6n-6o vs. 6g-6m). It was noteworthy that ortho-substituted arylsulfides, which are sterically hindered,

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could give good yields (**6d**, **6f**, **6i**, **6l**, and **6o**). Interestingly, dibenzyl sulfide was also a suitable substrate giving the dibenzyl sulfoxide **6p** in 99% yield.

Scheme 4 Nano-Pd-catalyzed selective oxidation of symmetrical sulfides to sulfoxides with $H_2 O_2^{\alpha,b}$



^a All reactions were performed with sulfide **3** (0.2 mmol), nano-Pd catalyst **Cat. 1** (4.1 mg, 0.12 mol% Pd) and H₂O₂ (10 equiv) in MeOH (1.0 mL) at 60 °C. ^b Isolated yield. ^c 0.08 mol% nano-Pd catalyst and 5 equiv. of H₂O₂ were used. ^d 15 equiv. of H₂O₂ was utilized. ^e 5 equiv. H₂O₂ was used.

Next, we turned our attention to unsymmetrical sulfides under the same optimal conditions. This catalyst system also exhibited a remarkably broad substrate scope, and equally good results and a similar trend regarding the yield were also observed. As summarized in Scheme 5, diary sulfides underwent the reaction smoothly providing good to excellent yields (**7a–7g**). Notably, extremely excellent yields could be obtained for (hetero)aryl alkyl sulfides (**7h–7l**). Alkyl alkyl sulfides also provided high yields (**7m** and **7n**).

On the basis of the above study about the oxidation of sulfides to sulfoxides, we then sought to investigate the oxidation of sulfides to sulfones. It was found that the addition of diphenyl disulfide to the catalytic system is essential, which resulted in the formation of sulfones 8a with excellent yields. To evaluate the scope of the oxidation reaction under the optimized conditions, various sulfides were subjected to the reaction and the results are shown in Scheme 6. Symmetrical diaryl sulfides could be smoothly converted to sulfones 8a-8e with high yields. Unsymmetrical diaryl sulfides having electronwithdrawing groups (F) or electron-donating groups (OMe, Me) on the phenyl ring were well tolerated and gave the desired products 8g-8k in good to excellent yields. In addition, good yields were achieved for aryl alkyl sulfides (81 and 8m). Alkyl alkyl sulfide such as 3-(methylsulfonyl)prop-1-ene could also offered 83% yield (8n).

Scheme 5 Nano-Pd-catalyzed selective oxidation of unsymmetrical sulfides.tagedfoxides with H₂O₂^{a, b} DOI: 10.1039/C8OB03209B



^a All reactions were performed with sulfide 5 (0.2 mmol), nano-pd catalyst Cat. 1 (4.1 mg, 0.12 mol% Pd) and H₂O₂ (10 equiv) in MeOH (1.0 mL) at 60 °C. ^b Isolated yield.

Scheme 6 Nano-Pd-catalyzed selective oxidation of sulfides to sulfone with diphenyl disulfides and $H_2O_2{}^{\sigma,\,b}$



 a All reactions were performed with sulfide 3 or 5 (0.2 mmol), nano-pd catalyst Cat. 1 (4.1 mg, 0.12 mol% Pd), H_2O_2 (10 equiv) and (PhS)_2 (10 mol%) in MeOH (1.0 mL) at 100 °C. b Isolated yield.

Conclusions

In conclusion, we have developed one green and efficient approach for the synthesis of symmetrical diaryl sulfides and symmetrical diaryl disulfides via the coupling of arenediazonium tetrafluoroborates with sodium sulfide, respectively. A variety of arenediazonium salts are welltolerated, affording the corresponding products in moderate to good yields. Then we have also reported the reaction of arenediazonium tetrafluoroborates with symmetrical disulfides which could afford unsymmetrical sulfides in moderate to good yields under mild conditions. More importantly, on the basis of the above-described products, one highly effective and green

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methodology has been developed for the preparation of symmetrical or unsymmetrical sulfoxides and sulfones in the presence of H_2O_2 as an oxidant and nano-pd **Cat. 1** as a catalyst, respectively. The nano-Pd catalyst is highly active and highly selective, is widely applicable to various sulfide substrates, is capable of facile recycling, and the corresponding products are provided with good to excellent yields.

Experimental procedures

2.1 General procedure for the preparation of the nano-Pd catalyst

A mixture of Pd(PPh₃)₄ (260 mg, 0.225 mmol), tetra(ethylene glycol) (418 mg, 2.20 mmol), 1-butanol (3 mL, 32.7 mmol), and aluminum tri-sec-butoxide (9.50 g, 38.5 mmol) was stirred at 110 °C for 10 h. Then water was dropwise added and the system was stirred at 110 °C for another 0.5 h to form a black gel. Subsequently, filtering, washing with acetone, and drying the gel gave the nano-Pd catalyst 1 at room temperature as dark greyish-green powder.

2.2 General procedure for the synthesis of symmetrical sulfides under microwave

The mixture of phenyl diazonium tetreafluoroborate (38.5 mg, 0.2 mmol), and Na₂S·9H₂O (53.2 mg, 0.22 mmol) in water (1.0 mL) was heated under microwave irradiation (300 W, 100 °C) until the starting material was consumed which was determined by TLC. The reaction system was then extracted with ethyl acetate (3 × 10 mL), and the combined organic phase was dried over anhydrous Na₂SO₄. At last, the organic extracts were concentrated in vacuum and the resulting mixture was purified by column chromatography on silica gel with petroleum ether as an eluent to afford the pure product **3a**.

2.3 General procedure for the synthesis of symmetrical disulfides promoted by \mbox{FeCl}_3

To the mixture system of phenyl diazonium tetrafluoroborate (38.5 mg, 0.2 mmol) and FeCl₃ (39.1 mg, 0.24 mmol, 1.2 equiv) in CH₃OH (1.0 mL) was added Na₂S·9H₂O (53.2 mg, 1.1 equiv.) slowly at 0 °C. The reaction mixture was then stirred, and the temperature rose to room temperature naturally. The stirring continued until no substrate could be detected by TLC. After the solvent CH₃OH was removed under reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether as an eluent to afford the direct cross-coupling product diphenyl disulfide **4a**.

2.4 General procedure for the synthesis of asymmetrical sulfides *via* the cross-coupling of disulfides with aryl diazonium tetrafluoroborate

To the mixture system of *p*-MeO-phenyl diazonium tetrafluoroborate (44.5 mg, 0.2 mmol) and K_2CO_3 (27.7 mg 0.2 mmol) in CH₃CN (1.0 mL) was added diphenyl disulfide (39.3 mg, 0.18 mmol) under N₂ atmosphere at 25 °C. The reaction mixture was then stirred until no substrate could be detected by TLC. The resulting mixture was purified by column chromatography on silica gel with petroleum ether as an eluent to afford the direct cross-coupling product (4-methoxyphenyl)(phenyl)sulfide **5a**.

2.5 General procedure for oxidation of symmetric sulfides to sulfoxides with $H_2 O_2$

The mixture of nano Pd catalyst (4.1 mg, 0.12 mol% Pd), symmetric diphenyl sulfide (0.2 mmol) and 30% H₂O₂ (0.2 mL, 10 equiv.) in methanol (1.0 mL) was stirred at 60 °C until the starting material was consumed which was determined by TLC. After the solvent CH₃OH was removed under reduced pressure, the resulting product was

purified by column chromatography on silica gel with ethyl acetate and petroleum ether as eluents to afford the pure product 68 DOI: 10.1039/COB03209B

2.6 General procedure for oxidation of asymmetric sulfides to sulfoxides with H_2O_2

The mixture of nano Pd catalyst (4.1 mg, 0.12 mol% Pd), asymmetric sulfide (0.2 mmol), 30% H₂O₂ (0.2 mL, 10 equiv.) in methanol (1.0 mL) was stirred at 60 °C until the starting material was consumed which was determined by TLC. After the solvent CH₃OH was removed under reduced pressure, the resulting mixture was purified by column chromatography on silica gel with ethyl acetate and petroleum ether as eluents to afford the pure product **7**.

2.7 General procedure for the symmetrical and asymmetric sulfides to sulfones

The mixture of nano Pd catalyst (4.1 mg, 0.12 mol% Pd), diphenyl disulfide (10 mol%) symmetric or asymmetric sulfide (0.2 mmol), 30% H_2O_2 (0.2 mL, 10 equiv.) in methanol (1.0 mL) was stirred at 100 °C until the starting material was consumed which was determined by TLC. After the solvent CH₃OH was removed under reduced pressure, the resulting mixture was purified by column chromatography on silica gel with ethyl acetate and petroleum ether as eluents to afford the pure product **8**.

Conflicts of interest

There are no conflicts to declare.

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