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Sulfenylation

Sodium Iodide (NaI)-Catalyzed Cross-Coupling for C–S Bond Formation via Oxidative Dehydrogenation: Cheap, Direct Access to Unsymmetrical Aryl Sulfides

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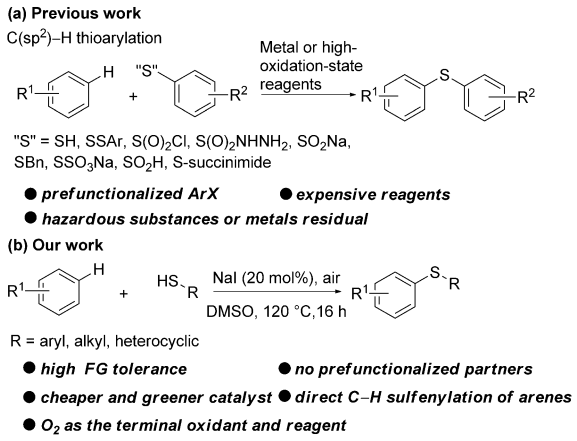
Abstract: A simple and practical NaI-catalyzed direct C–H sulfenylation of arenes has been developed under air. In this reaction, aryl sulfides were obtained in moderate to excellent yields with high regioselectivity from readily available aromatic compounds and aryl/alkyl thiols, even on gram scale. To demonstrate the practicability of this reaction, two bioactive compound skeletons were synthesized in good yields. This method can also be used to late-stage modification of curcumin.

Aryl sulfides are ubiquitous structural motifs existing in many natural products, biologically active compounds, and organic materials.[1] Thus, the formation of C–S bonds has garnered much attention.[2] Among them, C(sp^2)–S bond formation is one of the most important and fundamental reactions for the synthesis of these sulfide compounds (Scheme 1). Classical transition-metal-catalyzed cross-coupling reactions of prefunctionalized arenes[1c,3] (e.g., aryl halides) with various sulfur-based partners were mediated by palladium,[4] copper,[5] nickel,[6] iron,[7] cobalt,[8] rhodium[9] and gold.[10] Subsequently, direct C–H thioarylation was also achieved in the presence of suitable metal catalysts.[3c,11] Since thiol(ate) anions deactivate the catalysts[12] and disulfide formation in the presence of oxidants,[13] the general applicability of these metal-catalyzed procedures has been limited. Typically toxic matters[14] and heavy-metal-salt waste produced were also serious problems in those



Scheme 1. Examples of C–S bond formation reactions.

reactions. In recent years, with the emergence of the concepts of "atom economy"and "green chemistry", metal-free C–H thioarylation of electron rich arenes and heteroarenes using (thio)-succinimides,[15] sulfonyl hydrazines,[16] and other precursors[17] can circumvent some of the problems of transition-metal-mediated transformations. Considering the highly active oxidants and intermediates, these methodologies, however, often suffer from low functional-group tolerance and multistep preparations of the coupling precursors. In addition, the direct metal-free conversion of C–H bonds into C–S bonds using thiols has been reported as an efficient alternative approach,[18] but such approaches used toxic and volatile iodine, which limited the applicability. It is desirable in the medicinal industry that reactions are conducted under metal-free and non-toxic conditions. A metal-free electrophilic phosphination reaction has been recently achieved.[19] Therefore, developing a practical and economic approach to aryl sulfides directly from arenes and aryl/alkyl thiols is a challenging and urgent task. Herein, we report an efficient, metal-free, practical, and simple route for the synthesis of unsymmetrical aryl sulfides by oxidative dehydrogenation in the presence of inexpensive and environment friendly NaI, using air as the oxidant.

According to our previous work,[20] the bromide anion can be oxidized to bromine (Br_2) under air, and subsequently oxidize an S–H bond to an S–Br bond, while the umpolung of aryl thiols could be attacked by the nitrogen atom of an intra-

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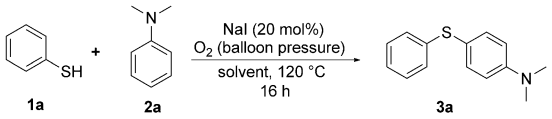
Table 1. Reaction optimizations.[a]

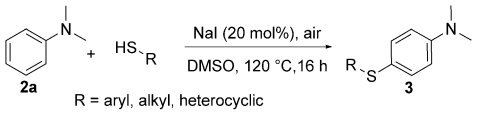


1a 2a 3a

Entry	Solvent	*T* [°C]	Catalyst [mol %]	Oxidant	Yield[a] [%]
1	DMF	120	KBr (10)	O_2	5
2	DMF	120	NaI (10)	O_2	26
3	DMF	120	NaI (10)	No	0
4	DMF	120	No	O_2	0
5	NMP	120	NaI (10)	O_2	0
6	toluene	120	NaI (10)	O_2	0
7	DMSO	120	NaI (10)	O_2	54
8[b]	DMSO	120	NaI (10)	O_2	60
9[c]	DMSO	120	NaI (10)	O_2	61
10	DMSO	120	KI (10)	O_2	57
11	DMSO	120	CuI (10)	O_2	23
12	DMSO	120	TBAI (10)	O_2	53
13[d]	DMSO	120	NaI (10)	O_2	60
14	DMSO	120	NaI (20)	O_2	90
15	DMSO	120	NaI (50)	O_2	93
16	DMSO	100	NaI (20)	O_2	20
17	DMSO	90	NaI (20)	O_2	trace
18	DMSO	120	NaI (20)	air	85

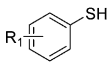
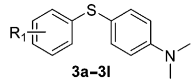
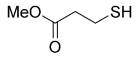
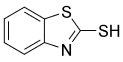
[a] Unless otherwise noted, the reactions were performed in a Schlenk tube with **1a** (0.1 mmol), **2a** (0.1 mmol), and O_2 (balloon pressure) in 1 mL (0.10 mmol mL^{-1}) solvent for 16 h. All yields listed are isolated yields. [b] 0.2 mmol mL^{-1}. [c] 0.5 mmol mL^{-1}. [d] 24 h.

Table 2. Substrate scope of thiols.[a,b]



2a 3

R = aryl, alkyl, heterocyclic

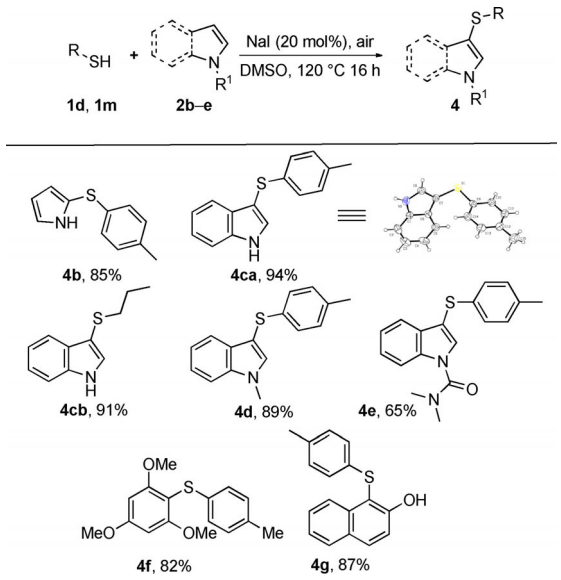
Entry	Thiol	Product	Yield[%][b]
–		 **3a–3l**	–
1[c]	R_1 = H	**1a**	**3a**	93
2	R_1 = 2-Me	**1b**	**3b**	80
3	R_1 = 3-Me	**1c**	**3c**	90
4	R_1 = 4-Me	**1d**	**3d**	87
5	R_1 = 2,6-dimethyl	**1e**	**3e**	70
6	R_1 = 4-F	**1f**	**3f**	94
7	R_1 = 4-Cl	**1g**	**3g**	93
8	R_1 = 4-Br	**1h**	**3h**	87
9	R_1 = 4-OMe	**1i**	**3i**	84
10	R_1 = 4-^{t}Bu	**1j**	**3j**	76
11	R_1 = 2-Cl	**1k**	**3k**	86
12	R_1 = 2-NH_2	**1l**	**3l**	78
13	R = Me 	**1m**	**3m**	71
14	R = Ph	**1m′**	**3m′**	75
15		**1n**	**3n**	83
16		**1o**	**3o**	86
17		**1p**	**3p**	92

[a] Conditions:**1** (0.1 mmol), **2a** (0.1 mmol), NaI (0.02 mmol), DMSO (1.0 mL), 120 °C, 16 h, under oxygen. [b] Isolated yield based on **2a**. [c] The reaction can also be performed on gram scale. **1a** (1.10 g) with **2a** (1.21 g) gave **3a** 1.87 g (82% yield).

molecularly formed amide S–N bond. Thus, 10 mol% KBr with equal amounts of **1a** and **2a** as starting materials were tested in DMF at 120 °C (Table 1, entry 1). Only 5% of the desired product **3a** was obtained in this trial. Therefore, we chose the more easily oxidized iodide as catalyst in this reaction. To our delight, when the reaction was carried out in the presence of 10 mol% NaI in DMF at 120 °C, the yield of **3a** slightly improved to 26%. The following control reactions in the absence of O_2 and NaI (Table 1, entries 3 and 4, respectively), showed no traces of **3a**, indicating that both NaI and oxygen are necessary in these transformations. Then various solvents were screened and the reaction proceeded well in highly polar DMSO (Table 1, entry 7). Subsequently, we tried to increase the yield of **3a** by enhancing the concentration of the reaction (Table 1, entries 8, 9) or prolonging the reaction time (Table 1, entry 13), and only a slightly increase occurred. A series of iodide salts (Table 1, entries 10, 11, 12) were also tested but failed to provide more favorable outcomes. However, when increasing the amount of NaI to 20 and 50 mol%, **3a** was obtained in 90 and 93% yield (Table 1, entries 14 and 15, respectively); for environmental concerns, 20 mol% NaI was used. The effect of temperature was also examined (Table 1, entries 16 and 17) and 120 °C was found to be the best. A similar yield was observed when the reaction was carried out under air (Table 1, entry 18).

With the optimized reaction conditions in hand, a range of arylthiols bearing an alkyl substituent were examined (Table 2) giving the corresponding products **3b**–**3d** in good to excellent yields (80–93%). Notably, when the arenes had two *ortho*-alkyl substituents, the yield of corresponding sulfenylated arene **3e** was 70%. Aryl thiols having electron-withdrawing halo groups at the 2 or 4 position **1f**–**h**, **1k** afforded the thiolated products **3f**–**3h**, **3k** in 86–94% yields. However, those having electron-donating groups at the 2 or 4 position **1i**, **1j**, and **1l** gave slightly lower yields than those with electron-withdrawing groups, which might be caused by the lower reactivity of sulfur cation intermediates. Moreover, alkylthiols **1m** and **1n** reacted smoothly and provided the desired products **3m**, **3m′** and **3n** in 71, 75 and 83% yield, respectively. Further investigations showed that heterocyclic thiols such as pyridine-2-thiol **1o** and benzo[d]thiazole-2-thiol **1p** also reacted well. In addition, this reaction also proceeded well on gram scale for **3a** (82% yield).

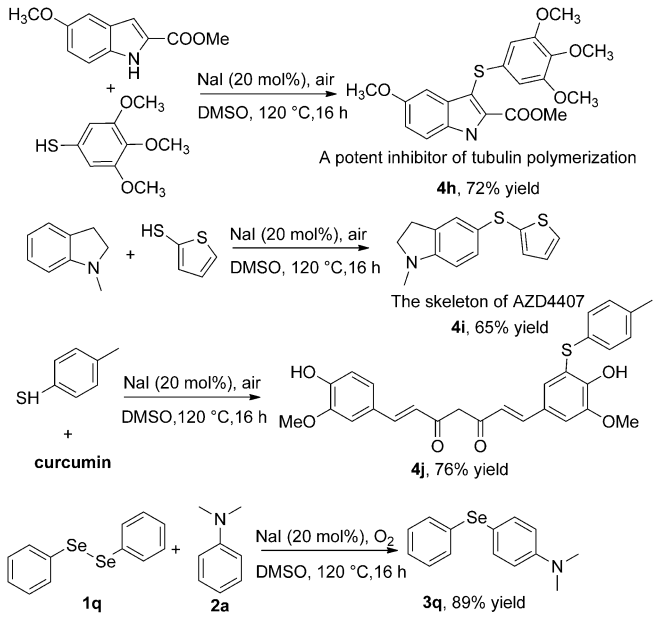
On the basis of the results obtained in the case of carbon nucleophile *N*,*N*-dimethylaniline **2a**, we further extended this strategy to investigate the nucleophile partners (Scheme 2). For this purpose, the arylthiolation of pyrrole **2b** was initially carried out under the aforementioned conditions, providing the corresponding sulfide **4b** in 85% yield. In addition, it is noteworthy that indoles could couple with aryl (alkyl) thiols, giving the expected products **4ca** and **4cb** in excellent yield. Furthermore, indoles with methyl group **2d** and moderate



Scheme 2. Substrate scope of the arene and heteroarene coupling partners. Conditions: **1 d** (0.1 mmol), **2** (0.1 mmol), NaI (0.02 mmol), DMSO (1.0 mL), 120 °C, 16 h, under oxygen. Isolated yields based on **1 d** or **1 m**.

electron-withdrawing acetyl group **2 e** substituents were tolerated and afforded the corresponding diaryl sulfides **4 d** and **4 e** in 89 and 65% yield rather than a iodination products.[21] The thiolation of 1,3,5-trimethoxybenzene **2 f** and 2-naphthol **2 g** also afforded the thiolated products **4 f** and **4 g** in 82 and 87% yield, respectively.

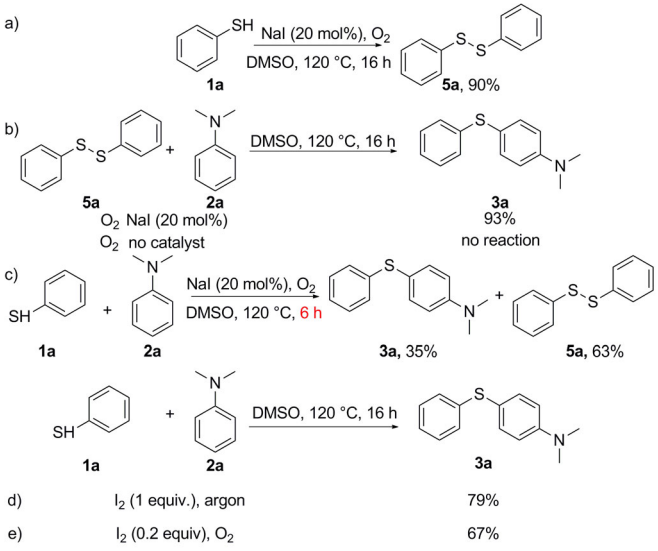
To demonstrate the practicability of this reaction, two complex bioactive compounds were synthesized using our approach (Scheme 3). AZD4407 is a known 5-lipoxygenase inhibitor.[22] Methyl 5-methoxy-3-((3,4,5-trimethoxyphenyl)thio)-1*H*-indole-2-carboxylate (**4 h**) shows excellent antitumor activities



Scheme 3. Syntheses of two bioactive compound skeletons.

as a potent inhibitor of tubulin polymerization.[23] Both of them were synthesized previously in low yields and many steps.[17d,22] Notably, by using the method we developed, the two bioactive compounds were successfully prepared in 65 and 72% yield, respectively. The metal-free protocol was also applied to late-stage modification of curcumin, an extensive pharmacologically active compound,[24] leading selectively to monosulfide **4 j** in 76% yield. In addition, when the reaction was conducted with diphenyl diselenide **1 q**,[25] it proceeded smoothly and gave the product in 89%.

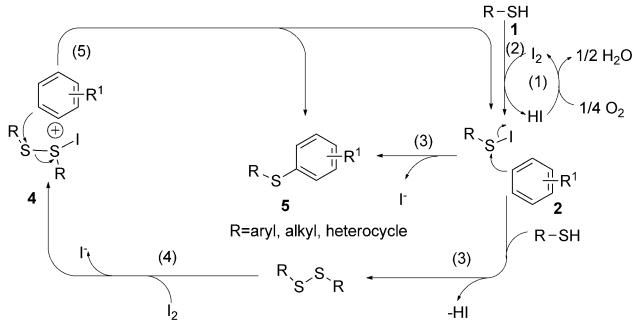
A primary mechanism research was also conducted. Previous results indicated NaI and oxygen are necessary in these transformations. Then, to further elucidate the mechanism, some control experiments were carried out (Scheme 4). Thiols could



Scheme 4. Control experiments.

be absolutely transferred to disulfide **5 a** in the absence of aromatics (Scheme 4 a). Disulfide **5 a** reacted well with **2 a** giving the product in 93% yield. However, the reaction could not conduct in the absence of NaI (Scheme 4 b). On the other hand, when the reaction time was shortened to 6 h, disulfide **5 a** and product **3 a** were observed in 63 and 35% yield, respectively (Scheme 4 c). All of these reactions indicated that both thiols and disulfides could be converted to the desired products. Besides, when using I_2 as oxidant or catalyst (Scheme 4 d,e), **3 a** was obtained in a slightly lower yield (79 and 67% respectively), which uncovered that I_2 is a very important oxidant intermediate.

A proposed mechanism for the formation of sulfides is shown as follows (Scheme 5): (1) I^- is oxidized to I_2 by molecular oxygen; (2) the nucleophilic arylthiol attacks the electrophilic iodine leading to the formation of electrophilic intermediate Ar–SI via elimination of one molecule of HI; (3) the species Ar–SI is attacked by electron-rich arenes or arylthiols forming desired compounds or disulfides, upon elimination of HI; (4) the disulfide is oxidized by I_2 to an activated intermediate **4**; (5) **4**



Scheme 5. Proposed mechanism.

is then converted into the desired product and **2** by a direct nucleophilic substitution.

In summary, an operationally simple and environmentally friendly method of direct C–H thioarylation of arenes and heteroarenes with high regioselectivity was developed. In this reaction, cheap and safe NaI was used as catalyst and air as oxidant, affording sulfenylated arenes in good to excellent yields, even on gram scale. The reaction had high functional group tolerance and a broad substrate scope. The developed method was also successfully utilized in the syntheses of two biologically active compounds and late-stage modification of the pharmacologically active compound curcumin. Further studies on sulfur cations and applications of this reaction are under investigation.

Experimental Section

General procedure for the synthesis of *N,N*-dimethyl-4-(phenylthio)aniline (3 a):

A mixture of thiophenol (11.0 mg, 0.1 mmol) with *N,N*-dimethylaniline (12.1 mg, 0.1 mmol), NaI (2.98 mg, 0.02 mmol) and DMSO (1.0 mL) was stirred at 120 °C in a Schlenk tube for 16 h under dry air conditions. The mixture was then cooled to room temperature, diluted with water, extracted with ethyl acetate, dried over sodium sulfate and concentrated. The crude products were purified by column chromatography on silica gel to give the corresponding products.

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Keywords: aryl sulfides · C–H sulfenylation · cross-coupling · regioselectivity · sodium iodide

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