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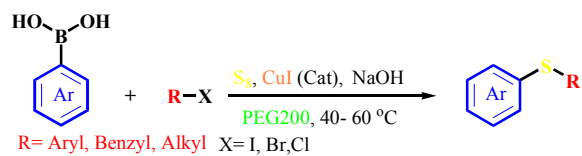
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Efficient one-pot, one-step synthesis of unsymmetrical sulfides has been reported under mild reaction conditions with good yields in green solvent.

COMMUNICATION

Ligand-free Cu-catalyzed odorless synthesis of unsymmetrical sulfides through cross-coupling reaction of aryl/benzyl/alkyl halides with aryl boronic acids/S₈ system as a thiolating agent in PEG

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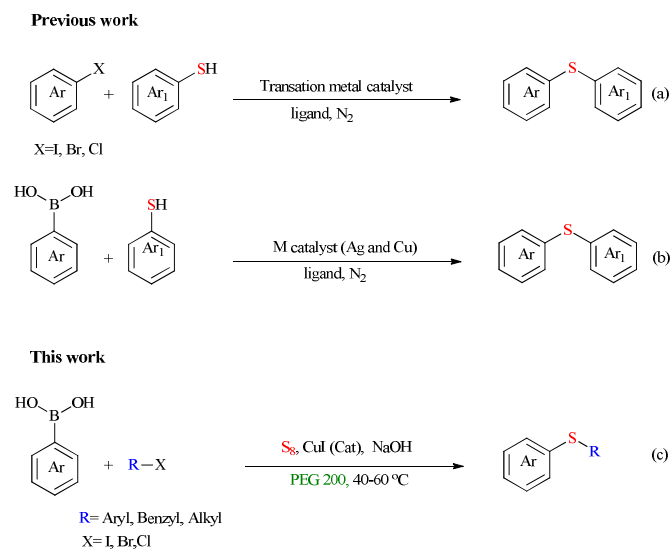
In this article, we have presented a novel, efficient and environmentally benign method for one-pot, one-step and odorless synthesis of a wide range of unsymmetrical sulfides from the reaction of aryl/benzyl/alkyl halides with aryl boronic acids in the presence of S₈, NaOH and catalytic amount of CuI in PEG200 as green solvent at 40-60 °C. The products were obtained in moderate to excellent yields. More importantly, this reaction is applicable for the gram-scale preparation of the desired sulfides.

Aryl alkyl sulfide and diaryl sulfide compounds are important and useful in chemistry, pharmaceutical industries and as intermediates in organic synthesis.¹⁻⁴ Numerous examples of drugs applied for diabetes, Alzheimer's and Parkinson's diseases, Inflammatory and immune diseases have sulfide moieties in their structure.⁵ Therefore, protocols leading to C-S bond generation, which are efficient, cheap and practical have attracted a great deal of attention.⁶ The cross-coupling reactions of aryl halides with thiols are one of the most synthetic methods for the preparation of these valuable materials. However, these reactions require elevated temperatures and high boiling point, toxic and polar solvents.⁷⁻⁸ To solve these drawbacks, a number of transition metal catalysts have been reported for the cross-coupling reactions between thiols and aryl halides (Scheme 1, eqn (a)).⁹⁻¹³ Chan-Lam type S-arylation of thiols with boronic acids is an efficient and valuable alternative to traditional cross-couplings in the construction of C-S bond (Scheme 1, eqn (b)).¹⁴

Although, these efforts have led to significant progress in improving reaction conditions and substrate scope, the main limitations of these protocols are still using of volatile and foul-smelling thiols as substrate can lead to the serious safety and environmental problems. In addition, thiols are prone to form undesired disulfides, and can act as metal deactivators. In order to overcome these difficulties, various sulfur reagents such as thiourea,¹⁵ thiolates,¹⁶ metal sulfides,¹⁷ ethyl xanthogenate,¹⁸ thiocyanate,¹⁹ carbon disulfide,²⁰ sulfur powder,²¹ sodium thiosulfate²² and thioimide²³ have been applied in the synthesis of sulfides. Among sulfur reagents, S₈ shows particular promise for S-arylation, due to its low cost and being odorless.

However, these procedures still require the use of Cu/N-ligand and Pd/P-ligand as the catalyst,¹⁷⁻²⁰ long reaction times,¹⁸ using harmful organic solvents,¹⁸ foul-smell of sulfur source^{17,20} and more importantly, limited to synthesis of symmetrical diaryl sulfides^{15b,18-21} or alkyl aryl thioethers.^{15a,17} Therefore, there is still a great interest to find a new reagent as an arenthiol alternative to afford unsymmetrical sulfides under ligand-free and mild reaction conditions.

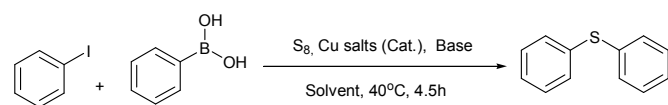
In the past years, aryl boronic acids were used as a source of aryl for C-C and C-hetroatom bond formation.²⁴ These reports prompted us to explore the prospects of this commercially available, easy workable, chemically stable and eco-friendly aryl group source for other demanding reactions. To the best of our knowledge there has been no report on the C-S cross-coupling reaction of aryl boronic acid/S₈ system as a thiolating agent with aryl halides catalyzed by copper.



Scheme 1 Approaches to C-S bond formation

Herein, we present for the first time the cross-coupling reactions of aryl/benzyl/alkyl halides with aryl boronic acid/S₈ in the presence of copper as a catalyst *via* a process releasing from the unclean smell of thiols in environment-friendly solvent (Scheme 1, eqn (c)). Initially, the reaction between iodobenzene and phenyl boronic acid in the presence of S₈ at 40 °C, was selected as a model reaction, and various parameters were optimized to develop the scope of this reaction further (Table 1).

Table 1 Optimization of the reaction conditions between iodobenzene and phenyl boronic acid^a



Entry	Base	S-source	Solvent	Cu salts	GC Yield (%)
1	K ₂ CO ₃	S ₈	PEG200	CuI	0
2	Cs ₂ CO ₃	S ₈	PEG200	CuI	15
3	Et ₃ N	S ₈	PEG200	CuI	0
4	DABCO	S ₈	PEG200	CuI	0
5	KOAc	S ₈	PEG200	CuI	65
6	NaOtBu	S ₈	PEG200	CuI	78
7	NaOH	S ₈	PEG200	CuI	100
8	NaOH	S ₈	DMF	CuI	100
9	NaOH	S ₈	PEG200	Cu(OAc) ₂	89
10	NaOH	S ₈	PEG200	CuI	78 ^b
11	NaOH	S ₈	CH ₃ CN	CuI	36
12	NaOH	S ₈	dioxane	CuI	35
13	-	S ₈	<i>n</i> Bu ₄ NOH(20%aq)	CuI	78
14	NaOH	S ₈	<i>n</i> Bu ₄ NOH(20%aq)	CuI	75
15	NaOH	S ₈	<i>n</i> Bu ₄ NOH(20%aq)	CuI	65 ^c
16	NaOH	Na ₂ S	PEG200	CuI	57
17	NaOH	Na ₂ S ₂ O ₃	PEG200	CuI	0
18	NaOH	Thiourea	PEG200	CuI	0

^aReaction conditions: iodobenzene (1 mmol), phenyl boronic acid (1.1 mmol), S₈ (1 mmol), Cu salts (10 mol%), NaOH (4 mmol) and solvent (2 mL). ^bNaOH (3 mmol) was used. ^cThe reaction was occurred at 70 °C in 8h.

As shown in Table 1, the nature of the base was important affecting the yield of the desired product (Table 1, entries 1-7). Among organic and inorganic bases, the most effective one was found to be NaOH (Table 1, entries 7 and 8). It should be noted that the use of Cu(OAc)₂ in stead of CuI give lower yield of diphenyl sulfide (Table 1, entry 9). In order to optimize the solvent, we have conducted the reaction in PEG200, DMF, dioxane, CH₃CN and aqueous *n*Bu₄NOH (20%) (Table 1, entries 7-13). Among these solvents, PEG200 and DMF both gave the best yields compared with other solvent (Table 1, entries 7, 8). No improvement of the yield of the desired product was observed when other S-sources, such as Na₂S₂O₃, Na₂S and thiourea, were used as sulfur reagents (Table 1, entry 16-18). However, the results showed that when the reaction was conducted with CuI as the catalyst, NaOH as both inorganic base and sulfur activator and PEG200 or DMF as the solvent, the desired diphenyl sulfide was obtained in excellent yield (Table 1, entries 7 and 8).

In order to generalize the scope of the reaction, a series of structurally diverse aryl/benzyl/alkyl halides was subjected to reaction with aryl boronic acids under the optimized reaction conditions in PEG200 as the solvent. The reactions proceeded well to produce the corresponding unsymmetrical sulfides in moderate to excellent yields ranging from 65 to 98% (Table 2). It was observed that aryl halides with electron-withdrawing groups show greater activities than those having electron-donating groups (Table 2, entries 4-20). Also, *p*-tolyl boronic acid is less

reactive than phenyl boronic acid in these reactions (Table 2, entries 1-11).

Table 2 C-S bond formation of aryl/benzyl/alkyl halides with aryl boronic acids using S₈ catalyzed by CuI for the synthesis of unsymmetrical sulfides^a

Entry	RX	ArB(OH) ₂	Product	Time (h): Yield (%) ^b
1				4.3:93
2				5:90
3				9:89
4				11:85
5				9:89
6				10:85
7				12:78
8				1.3:94
9				3:98
10				2.3:95
11				4:97
12				13:93
13				20:89
14				23:79
15				5:91(89) ^c

^aReaction conditions: aryl/benzyl/alkyl halide (1 mmol), aryl boronic acid (1.1 mmol), CuI (10-20 mol %), S₈ (1 mmol), NaOH (4 mmol), 2 mL of PEG200, 40-60 °C. ^bIsolated yield after column chromatography. ^cIn parenthesis the yield of the reaction performed with 10 mmol of 1-bromo-4-nitrobenzene, 10 mol% of CuI, 11 mmol of phenyl boronic acid, 40 mmol of NaOH, 20 mL of PEG200.

Table 2 (Continued)

Entry	RX	ArB(OH) ₂	Product	Time (h): Yield (%) ^b
16				6.3:89
17				35:65
18				17:89
19				18:86
20				21:79
21				X=Br 6: 84 X=Cl 11:72
22				X=Br 9: 87 X=Cl 14:76
23				12:89
24				14:88

^aReaction conditions: aryl/benzyl/alkyl halide (1 mmol), aryl boronic acid (1.1 mmol), CuI (10-20 mol %), S₈ (1 mmol), NaOH (4 mmol), 2 mL of PEG200, 40-60 °C. ^bIsolated yield after column chromatography. ^cIn parenthesis the yield of the reaction performed with 10 mmol of 1-bromo-4-nitrobenzene, 10 mol% of CuI, 11 mmol of phenyl boronic acid, 40 mmol of NaOH, 20 mL of PEG200.

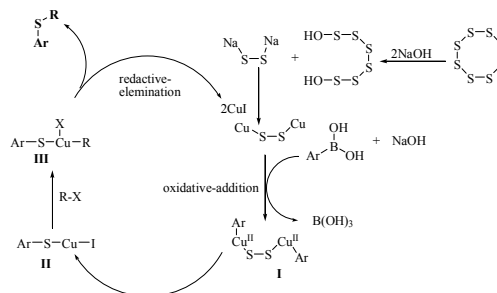
Among aryl halides the most reactive are aryl iodides (Table 2, entries 1-20). Interestingly, aryl bromides and chlorides which are relatively unreactive substrates were also converted to the corresponding unsymmetrical sulfides in moderate to good yields under the same reaction conditions (Table 2, entries 12-20).

Another important aspect of this method is the successful reaction of sterically demanding substrates to give the desired products in good yields (Table 2, entries 7 and 14), *ortho*-substituted aryl halides require longer reaction time and gave relatively lower product yields than *para*-substituted aryl halides (Table 2, entries 6 and 7). The reaction of 1-bromo-4-chlorobenzene as dihalogenated aryl halide was also subjected to investigate the selectivity of the method; the bromide showed more reactivity (Table 2, entry 20). This selectivity allows remaining an active halide site for further functionalization. Benzyl bromide and benzyl chloride as two model compounds for benzylic halides were satisfactorily subjected to C-S bond formation as well (Table 2, entries 21-22). The cross-coupling reactions of butyl bromide, as a model for alkyl halides, with phenyl boronic acid or *p*-tolyl boronic acid were also conducted. The reactions proceeded well to produce the corresponding unsymmetrical sulfides in good yields (Table 2, entries 23 and 24).

It was shown that the method was suitable for large scale reactions. For this purpose, the reaction of 1-bromo-4-nitrobenzene with phenyl boronic acid was scaled-up to 10 times under similar reaction conditions. The reaction proceeded well and the desired sulfide was isolated in 89% yield (Table 2, entry 15).

In order to prove our hypothesis that, in the synthesis of unsymmetrical diaryl sulfide, ArB(OH)₂/S₈ act as a thiolating agent, the reaction of iodobenzene with S₈ was studied under same reaction conditions. It was observed that the iodobenzene remained intact during the reaction. However, when the reaction temperature was increased to 100 °C two products including thiophenol and diphenyl sulfide from the coupling reaction of aryl halide and S₈ were obtained. The results showed that aryl halides require elevated temperatures to act as thiolating agent.

We have also proposed a mechanism for this reaction which is presented in Scheme 2. On the basis of obtained results (Table 1, entries 1, 5, 6, 8, and 16) and previously reported mechanism for the formation of a stable copper disulfide complex from the reaction of S₈ with CuI,²¹ⁱ as well as formation of aryl organocopper intermediate from the reaction of aryl boronic acid with copper disulfide,^{21h} we hypothesize that S₈ reacts with NaOH to give sodium disulfide. Then copper disulfide was formed from the reaction of sodium disulfide with CuI. Copper disulfide reacts with aryl boronic acid via oxidative-addition reaction to give aryl organocopper (intermediate I) which may convert to intermediate II. The intermediate II reacts with aryl/benzyl/alkyl halide to provide the key intermediate III. The desired product could obtain from reductive elimination of the key intermediate.

**Scheme 2** Proposed mechanism

Conclusions

In summary, we have developed new efficient methodology for the synthesis of unsymmetrical sulfides *via* C-S bond formation reaction of aryl boronic acid with aryl/benzyl/alkyl halides using S₈ as a sulfur surrogate, NaOH as both base and sulfur activator and CuI as catalyst in the PEG200 as a green solvent. This procedure offers several major advantages; first, the synthesis of structurally diverse unsymmetrical sulfides has been reported in moderate to high yields in green solvent. Second, release from the unclean smell of thiols makes this method more eco-friendly and practical for C-S bond formation. Third, commercially available, cheap and chemically stable sulfur source, starting material and catalyst have been used.

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Notes and references

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Electronic Supplementary Information (ESI) available: Detailed experimental methods, and copies of the ¹H NMR and ¹³C NMR spectra.

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