



Efficient Cu-catalyzed one-pot odorless synthesis of sulfides from triphenyltin chloride, aryl halides and S₈ in PEG



Abed Rostami^a, Amin Rostami^{a,*}, Nasser Iranpoor^b, Mohammad Ali Zolfigol^c

^a Department of Chemistry, Faculty of Science, University of Kurdistan, 66177-15175 Sanandaj, Iran

^b Department of Chemistry, Shiraz University, Shiraz 71454, Iran

^c College of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran

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ABSTRACT

A novel method for the Cu(OAc)₂ catalyzed synthesis of unsymmetrical sulfides from triphenyltin chloride and aryl halides using S₈ as the sulfur source in PEG200 at 60–80 °C is reported. Triphenyltin chloride is capable of delivering all of its phenyl groups to the product. Also, the copper catalyzed synthesis of symmetrical diaryl sulfides from aryl halides using S₈ is described.

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Introduction

Symmetrical and unsymmetrical diaryl sulfides are found in numerous drugs displaying a broad spectrum of therapeutic activities such as anti-diabetes, anti-inflammatory, anti-Alzheimer's, anti-Parkinson's, anti-cancer, and anti-HIV.^{1,2}

Transition-metal-catalyzed cross-coupling reactions of aryl halides with thiols are the main synthetic methods for the preparation of diaryl sulfides.^{3–6} The main limitations of the aforementioned methodologies include the utilization of volatile and unpleasant smelling thiols that can act as metal deactivators due to their tendency to bind to transition metals. In addition, the oxidative coupling of thiols to disulfides is a known side-reaction.⁷

To overcome these drawbacks, recently, various sulfur sources^{8–15} have been employed for the conversion of aryl (pseudo) halides to aryl thioethers using transition metal catalysis. Although, these efforts have led to significant progress, disadvantages include the requirement for ligands, high reaction temperatures, and harmful organic solvents. Moreover, these methods are inefficient for the synthesis of unsymmetrical diaryl sulfides. To resolve these problems, sulfonyl hydrazides were recently reported as an aryl thiol surrogate for the synthesis of unsymmetrical sulfides.¹⁶ Although, this finding represents an interesting breakthrough for the synthesis of

unsymmetrical sulfides, this method employs harsh reaction conditions such as high temperature (130 °C), microwave irradiation,^{16a} and the use of sulfonyl hydrazides which are less readily available and expensive.¹⁶ Therefore, there is still interest in finding new reagents for the synthesis of symmetrical and unsymmetrical sulfides under mild reaction conditions.

Result and discussion

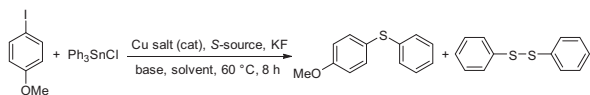
Recently, an efficient method for C–X (X = C, N, S, O) bond formation using triphenyltin chloride as a source of the phenyl group was developed by our research group.¹⁷ These investigations prompted us to further explore the prospective use of this phenyl group source for other reactions.

We report herein, the use of triphenyltin chloride in combination with S₈ as a thiolating agent in the reaction with aryl halides for the Cu(OAc)₂ catalyzed synthesis of phenyl aryl sulfides.

Optimization of the reaction conditions was performed upon the model reaction of 4-iodoanisole with triphenyltin chloride using various sulfur sources, KF as an activator, various Cu salts as catalysts and organic and inorganic bases in different solvents at 60 °C (Table 1). The nature of the base was found to be important and K₂CO₃ was found to be the most effective (Table 1, entries 1–6). When Et₃N in DMF was used as a base, diphenyl disulfide was the main product formed (Table 1, entry 1). The reaction was conducted in PEG200, DMF, dioxane, and CH₃CN, and among

* Corresponding author. Tel.: +98 918 373 0910; fax: +98 871 662 4004.
E-mail address: a.rostami@uok.ac.ir (A. Rostami).

Table 1
Optimization of the reaction conditions using 4-iodoanisole with triphenyltin chloride^a



Entry	Base	S-source	Solvent	Cu salts	GC yield ^{b,c} (%)
1	Et ₃ N	S ₈	DMF	Cu(OAc) ₂	0/100
2	DABCO	S ₈	DMF	Cu(OAc) ₂	20/80
3	NaOH	S ₈	DMF	Cu(OAc) ₂	35/45
4	Cs ₂ CO ₃	S ₈	DMF	Cu(OAc) ₂	78/22
5	K₂CO₃	S ₈	DMF	Cu(OAc)₂	100/0^d
6	K₂CO₃	S ₈	PEG200	Cu(OAc)₂	100/0^d
7	K ₂ CO ₃	S ₈	Dioxane	Cu(OAc) ₂	65/0
8	K ₂ CO ₃	S ₈	CH ₃ CN	Cu(OAc) ₂	76/0
9	K ₂ CO ₃	S ₈	PEG200	CuI	76/0
10	K ₂ CO ₃	S ₈	PEG200	CuCl ₂	81/0
11	K ₂ CO ₃	S ₈	PEG200	Cu(OAc) ₂	35/0 ^e
12	K ₂ CO ₃	S ₈	PEG200	Cu(OAc) ₂	78/0 ^f
13	K ₂ CO ₃	S ₈	PEG200	Cu(OAc) ₂	100/0 ^g
14	K ₂ CO ₃	S ₈	PEG200	Cu(OAc) ₂	78/0 ^h
15	K ₂ CO ₃	S ₈	PEG200	Cu(OAc) ₂	75/0 ⁱ
16	K ₂ CO ₃	S ₈	PEG200	Cu(OAc) ₂	NR/NR ^j
17	NaOH	S ₈	PEG200	Cu(OAc) ₂	58/21 ^j
18	K ₂ CO ₃	Na ₂ S·5H ₂ O	PEG200	Cu(OAc) ₂	48/52 ^j
19	K ₂ CO ₃	KSCN	PEG200	Cu(OAc) ₂	0/100 ^k
20	K ₂ CO ₃	Na ₂ S ₂ O ₃	PEG200	Cu(OAc) ₂	NR/NR ^j
21	K ₂ CO ₃	S ₈	PEG200	Cu(OAc) ₂	0/100 ^k

The bold letters represent the most effective reaction conditions.

^a Reactions conditions: 4-iodoanisole (1 mmol), triphenyltin chloride (0.35 mmol), S₈ (1.5 mmol), Cu salts (10 mol %), KF (3 mmol), base (2 mmol), solvent (2 mL).

^b 4-Methoxy diphenyl sulfide.

^c Diphenyl sulfide.

^d Optimal reaction conditions.

^e KF (2 mmol).

^f KF (1.5 mmol).

^g 70 °C.

^h S₈ (1 mmol).

ⁱ Cu(OAc)₂ (5 mol %).

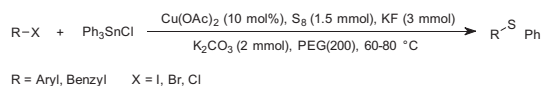
^j Without KF.

^k Without 4-iodoanisole.

these solvents the most effective were DMF and PEG200 (Table 1, entries 5–8). Among the copper salts tested, the most suitable was Cu(OAc)₂ (Table 1, entries 9 and 10). In the absence of KF, no product was observed (Table 1, entry 16). No improvement in yield was observed when other S-sources; Na₂S, KSCN, and Na₂S₂O₃, were used (Table 1, entries 18–20). The optimized reaction conditions were found to be S₈ (1.5 mmol), KF (3 mmol), K₂CO₃ (2 mmol) in the presence of catalytic Cu(OAc)₂ (10 mol %) in PEG200 or DMF.

In order to examine the reaction scope, a series of structurally diverse aryl halides were reacted with triphenyltin chloride under the optimized reaction conditions in PEG200. The reactions produced the corresponding phenyl aryl sulfides in moderate to excellent yields ranging from 70% to 95% (Table 2). Interestingly, aryl bromides and chlorides which are relatively unreactive substrates, were also converted to the corresponding aryl phenyl sulfides in good yields (Table 2, entries 7–15). It was observed that aryl halides with electron-withdrawing groups showed greater activities than those with electron-donating groups (Table 2, entries 2–6), and sterically demanding substrates gave the desired products in good yields (Table 2, entries 4 and 9). The reaction of dihalogenated 1-bromo-4-chlorobenzene was also studied to investigate the selectivity of the reaction. The bromide functional group showed higher reactivity (Table 2, entry 15) and this selectivity allows the remaining active halide site to potentially undergo further functionalization. Benzyl bromide and benzyl chloride satisfactorily underwent C–S bond formation (Table 2, entries 16 and

Table 2
Synthesis of phenyl aryl/benzyl sulfides from the reaction of aryl/benzyl halides with triphenyltin chloride



Entry	RX	Product	T (°C)	Time (h)	Yield ^a (%)
1			60	3	95
2			70	7	89
3			70	5	87
4			70	5	86
5			60	1	95
6			60	1.5	95
7			80	10	83
8			80	17	80
9			80	17	80
10			60	4	91(89) ^b
11			60	5	92
12			80	29	70
13			60	14	83
14			60	16	81
15			70	10	79
16			80	2	85
17			80	5	74

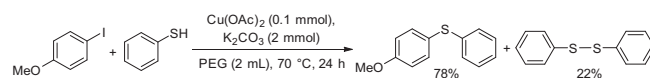
^a Isolated yield.

^b In parenthesis; yield performed using 1-bromo-4-nitrobenzene (10 mmol), Cu(OAc)₂ (10 mol %), triphenyltin chloride (3.5 mmol), S₈ (15 mmol), KF (30 mmol), PEG200 (20 mL), K₂CO₃ (20 mmol).

17). It was also shown that the method was suitable for large scale reactions. For this purpose, the reaction of 1-bromo-4-nitrobenzene with triphenyltin chloride was scaled-up 10 times and the desired sulfide was isolated in 89% yield (Table 2, entry 10).

To ascertain the nature of the reaction mechanism and illustrate the efficiency of this method, a control experiment was performed using thiophenol (instead of Ph₃SnCl/S₈) and 4-iodoanisole under same reaction conditions. It was observed that both the desired product and the diphenyl disulfide by-product were obtained after 24 h (Scheme 1). The results show that when thiophenol was used directly, both the deactivation of Cu(OAc)₂ (an extended time was required for complete conversion) and oxidation to diphenyl disulfide by air in the presence of Cu(OAc)₂ occur,⁷ while the Ph₃SnCl/S₈ system generates thiophenol or thiolate in situ relieving these difficulties.

Although the exact mechanism of this reaction is not clear, on the basis of preliminary results (Table 1, entries 1, 6, 16, 17, and 20), control experiment, and related studies,^{14h,17} we believe that potassium disulfide is initially produced from the reaction of S₈



Scheme 1. Control experiment.

with KF. Potassium disulfide then reacts with $\text{Cu}(\text{OAc})_2$ to generate copper sulfide which reacts with triphenyltin chloride by oxidative addition to form intermediate **1**. Intermediate **1** is transformed into intermediate **2** via phenyl group migration. Dissociation of intermediate **2** via reductive elimination gives two intermediates, **3** and **6**, of which intermediate **3** is transformed into intermediate **4** in the presence of K_2CO_3 . The aryl/benzyl halide reacts with intermediate **4** by oxidative addition to form compound **5**, which undergoes reductive elimination to afford the product and releases $\text{Cu}(\text{II})$ (Scheme 2). Intermediate **6** then reacts with potassium disulfide to give intermediate **7** which is capable of transfer to intermediate **3**. Intermediate **3** could also produce diphenyl disulfide when Et_3N was used instead of K_2CO_3 in DMF (Table 1, entry 1). Further studies regarding the mechanism are ongoing.

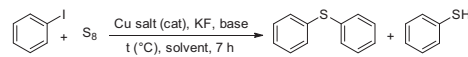
As shown in Scheme 1, in the synthesis of phenyl aryl/benzyl sulfide the $\text{Ph}_3\text{SnCl}/\text{S}_8$ system acts as a thiolating agent. To demonstrate this, the reaction of iodobenzene with S_8 was investigated under same reaction conditions. It was found that the reaction did not take place in the absence of Ph_3SnCl . Interestingly, upon increasing the reaction temperature to 100°C , two products, thiophenol and diphenyl sulfide, were detected.

The above observation encouraged us to investigate the possible synthesis of symmetrical diaryl sulfides from the C–S coupling reaction of aryl halides and S_8 . Iodobenzene was chosen as a model substrate to optimize the reaction conditions (Table 3). Increasing the reaction temperature to 110°C led to an increased conversion to diphenyl sulfide (Table 3, entry 2). The base also affected the yield of the desired product. When Et_3N was used under the same reaction conditions, the yield of the desired product decreased to 30% (Table 3, entry 3). Cs_2CO_3 was found to be the most appropriate base and no undesired thiophenol was detected (Table 3, entry 4). When dioxane and Et_3N were used under the same reaction conditions, thiophenol was formed as the main product (Table 3, entry 7).

Further optimization of the reaction conditions revealed that PEG200 and $\text{Cu}(\text{OAc})_2$ were the most suitable solvent and catalyst, respectively. With optimized conditions in hand, a number of aryl halides were examined to explore the reaction scope (Table 4). Aryl halides possessing electron-donating and electron-withdrawing groups afforded the corresponding diaryl sulfides in good yields (Table 4). A steric effect was observed, for instance, *p*-iodotoluene and *p*-bromotoluene gave the desired products in 90% and 72% yields, respectively (entries 3 and 8), while 80% and 61% yields were obtained, respectively, in the cases of *o*-iodotoluene and

Table 3

Optimization of the reaction conditions for the conversion of iodobenzene to diphenyl sulfide using S_8 ^a



Entry	Base	Solvent	T (°C)	Cu salts	GC yield ^{b/c} (%)
1	K_2CO_3	PEG200	100	$\text{Cu}(\text{OAc})_2$	65/35
2	K_2CO_3	PEG200	110	$\text{Cu}(\text{OAc})_2$	80/20
3	Et_3N	PEG200	110	$\text{Cu}(\text{OAc})_2$	30/70
4	Cs_2CO_3	PEG200	110	$\text{Cu}(\text{OAc})_2$	100/0
5	Cs_2CO_3	DMF	110	$\text{Cu}(\text{OAc})_2$	100/0
6	Cs_2CO_3	dioxane	110	$\text{Cu}(\text{OAc})_2$	72/28
7	Et_3N	dioxane	110	$\text{Cu}(\text{OAc})_2$	0/100
8	Cs_2CO_3	PEG200	110	$\text{Cu}(\text{OAc})_2$	100/0 ^d
9	Cs_2CO_3	PEG200	110	CuI	96/0
10	Cs_2CO_3	PEG200	110	CuCl_2	96/0
11	Cs_2CO_3	PEG200	110	$\text{Cu}(\text{OAc})_2$	100/0 ^e
12	Cs_2CO_3	PEG200	110	$\text{Cu}(\text{OAc})_2$	93/0 ^f
13	Cs_2CO_3	PEG200	110	$\text{Cu}(\text{OAc})_2$	100/0 ^g
14	Cs_2CO_3	PEG200	110	$\text{Cu}(\text{OAc})_2$	70/30 ^h

The bold letters represent the most effective reaction conditions.

^a Reaction conditions: iodobenzene (1 mmol), S_8 (0.5 mmol), Cu salts (10 mol %), KF (1 mmol), base (2 mmol), solvent (1.5 mL).

^b Diphenyl sulfide,

^c Thiophenol,

^d KF (2 mmol), S_8 (1 mmol) and $\text{Cu}(\text{OAc})_2$ (15 mol %).

^e S_8 (1 mmol).

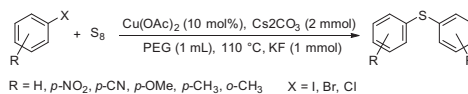
^f KF (1.5 mmol).

^g $\text{Cu}(\text{OAc})_2$ (0.2 mol %).

^h Cs_2CO_3 (1 mmol).

Table 4

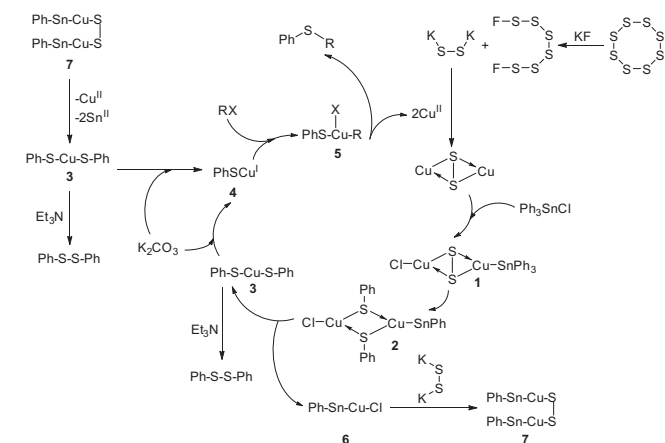
The reaction of various aryl halides with S_8 for the synthesis of symmetrical diaryl sulfides^a



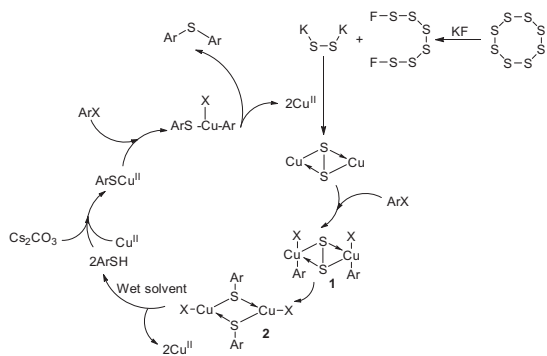
Entry	ArX	Product	Time (h)	Yield ^b (%)
1			7	92
2			15	87
3			12	87
4			16	90
5			2	80
6			2.5	92
7			18	78
8			25	72
9			30	61
10			9	89
11			10	90
12			48	60
13			20	83
14			20	84

^a Reactions conditions: aryl halide (1 mmol), S_8 (0.5 mmol), KF (1 mmol), $\text{Cu}(\text{OAc})_2$ (0.1 mmol), Cs_2CO_3 (2 mmol), PEG200 (1.5 mL).

^b Isolated yield after column chromatography.



Scheme 2. Proposed mechanism for the synthesis of phenyl aryl/benzyl sulfides catalyzed by $\text{Cu}(\text{OAc})_2$.



Scheme 3. Proposed mechanism.

o-bromotoluene (Table 4, entries 4 and 9). Aryl chlorides could also be transformed into diaryl sulfides under the same reaction conditions in moderate to good yields (Table 4, entries 12–14).

On the basis of our observations (Table 3, entries 4, 6, and 7) and previously reported mechanism^{14h} we believe that the synthesis of the symmetrical diaryl sulfides proceeds through a mechanism similar to that suggested for the synthesis of phenyl aryl/benzyl sulfide (Scheme 3). Copper sulfide reacts with the aryl halide by oxidative addition to give intermediate **1** and gives intermediate **2** via aryl group migration. The thiol can be generated by the reaction of intermediate **2** with wet-PEG. The thiol then reacts with Cu(II) in the presence of Cs₂CO₃ to form an organocopper species which undergoes oxidative addition with the aryl halide. Finally, reductive elimination occurs to produce the symmetrical diaryl sulfide.

Conclusions

In summary, we have developed an efficient methodology for the synthesis of phenyl aryl/benzyl sulfides via the C–S bond formation reaction of triphenyltin chloride with aryl/benzyl halides using S₈ as a sulfur surrogate and Cu(OAc)₂ as catalyst. Additionally, symmetrical diaryl sulfides were obtained from the copper-catalyzed reaction of aryl halides and S₈. These procedures offer several advantages. First, the synthesis of structurally diverse symmetrical and unsymmetrical sulfides in good to high yields has been reported. Second, the in situ release of thiol makes the methods more practical for C–S bond formation. Third, commercially available, inexpensive and chemically stable sulfur sources, starting materials, and catalyst have been used. Further studies on additional applications for this methodology are currently underway in our laboratory.

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Supplementary data

Supplementary data including experimental details and ¹H NMR and ¹³C NMR spectra of products associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2015.11.093>.

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