

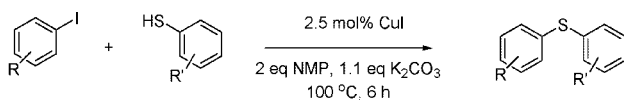
Ligand-Free Copper-Catalyzed C–S Coupling of Aryl Iodides and Thiols

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R = COMe, Me, NH₂, Br; R' = H
 or
 R' = Me, OMe, *t*-Bu, NO₂, CH₂NMe₂; R = H

A protocol for the copper-catalyzed aryl–sulfur bond formation between aryl iodides and thiophenols is reported. The reaction is catalyzed by a low amount (1–2.5 mol %) of readily available and ligand-free copper iodide salt. A variety of diaryl thioethers are synthesized under relatively mild reaction conditions with good chemoselectivity and functional group tolerance.

The formation of aryl–sulfur bonds represents a key step in the synthesis of many molecules that are of biological, pharmaceutical, and materials interest.¹ For example, a large variety of aryl sulfides are in use for diverse clinical applications such as the treatment of Alzheimer's and Parkinson's diseases,² treatment of cancer,³ and treatment of human immunodeficiency virus⁴ diseases. However, transition-metal-mediated C(aryl)–S

bond formation is a much less studied transformation than the corresponding C–N and C–O bond formations. The synthetic reaction involving sulfur-containing compounds poses special requirements because the sulfur functionality is known to be reactive and may act as a poison for metal-based catalysts because of its strong coordinative properties, often making the catalytic reaction ineffective.^{1b} In the last decades, transition-metal-catalyzed organosulfur chemistry received particular interest, which brought about important progress in the field. One of the first reports involving the coupling between aryl halides and thiols refers to Migita's system, using Pd(PPh₃)₄ as catalyst.⁵ Other efficient palladium catalysts are based on bidentate phosphines or diverse organophosphane derivatives.⁶ Nevertheless, these systems still suffer from some limitations because of the need to prepare and use environmentally unfriendly PR₃ ligands. Recently, the application of other metals in the catalytic carbon–sulfur bond formation resulted in synthetic protocols based on nickel⁷ and cobalt,⁸ but these were fraught with common problems such as metal toxicity, low turnover numbers, and reagents needed in excess. Consequently, there still is interest in further development of the classical Ullmann's coupling reaction,¹ applying cheap metals (e.g., copper) for the preparation of the diaryl thioether functionality. The major drawbacks related to this transformation are the use of large amounts of metal catalysts, their short lifetime (and hence low turnover numbers), harsh reaction conditions, and often the narrow scope. Therefore, different approaches have been studied in order to develop a general and more efficient system for the preparation of diaryl thioethers. Examples of attractive copper-catalyzed processes have recently been reported by Palomo,⁹ Buchwald,¹⁰ Venkataraman,¹¹ and others¹² and more recently also by Domínguez¹³ and Verma,¹⁴ mainly using copper halide salts as the metal source together with a suitable ligand. The general approach for the C–S bond coupling

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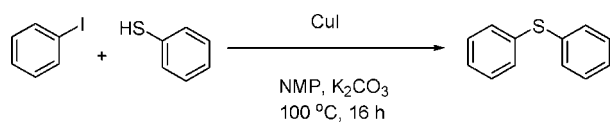
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SCHEME 1. Model Reaction for CuI-Catalyzed C–S Coupling


procedures is the employment of a catalytic amount of copper, usually between 5 and 10 mol %, always in the presence of a ligand (10–20 mol %) and a base (1.5–2.5 equiv), under relatively mild conditions (80–110 °C for 18–24 h).

Prompted by our current interest in carbon–carbon^{15–17} and carbon–heteroatom coupling reactions,¹⁸ we decided to investigate the copper-catalyzed carbon–sulfur bond formation via the utilization of commercially available copper(I) halide salts.

In this paper, we report a simple, inexpensive, and fast catalytic system for the synthesis of substituted diaryl thioethers under mild, ligand-free reaction conditions.

The influence of copper(I) iodide as catalyst on C–S bond formation was first investigated for the cross-coupling reaction of iodobenzene with thiophenol (Scheme 1). CuI was the chosen halide salt because of its stability to air. Catalytic tests performed with CuCl and CuBr, freshly prepared before use, gave the same results as obtained with commercially available CuI salt. Cu(II) salts tested (CuBr₂, CuSO₄·5H₂O, CuCl₂) were found to be less efficient as catalysts (yields 25–35%) than the Cu(I) salts. A low amount of 2.5 mol % of copper iodide salt was employed in these initial reactions.

Our first goal was to optimize reaction conditions and to achieve information about the role of additives and solvent polarity.

Since in previous studies of copper-catalyzed C–N and C–O coupling reactions¹⁸ *N*-methylpyrrolidinone (NMP) and potassium carbonate were found to be a preferred solvent and base, respectively, we used these conditions first.

It appeared that, by applying NMP and potassium carbonate, diphenyl thioether was obtained in quantitative yield using copper iodide as such, that is, without the use of added ligands. The need to use a polar solvent is highlighted by the screening results presented in Table 1, which show that, unlike toluene, DMF and DMA are excellent solvents for this coupling reaction (entries 3–5). Besides polarity, a weak coordination of these solvents to copper could also be a reason for their excellent performance.

It is noteworthy that an interesting yield of 60% was obtained by using water as solvent and NEt₃ as base (Table 1, entry 6).

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TABLE 1. Screening of Solvents for the Copper-Catalyzed C–S Coupling (reaction conditions: thiophenol (6.5 mmol), iodobenzene (5 mmol), K₂CO₃ (5.5 mmol), CuI (2.5 mol %), solvent (1 mL), 100 °C, 16 h)

entry	solvent	yield (%) ^a
1	toluene	11
2	DMSO	75
3	DMF	99
4	DMA	99
5	NMP	99
6	H ₂ O	60 ^c
7		10 ^b
8		98 ^c

^a Determined by GC using 100 μL of dihexyl ether as external standard.
^b K₂CO₃ as base. ^c NEt₃ (5.5 mmol) as base.

TABLE 2. Screening of Bases for the Copper Iodide-Catalyzed C–S Coupling (reaction conditions: thiophenol (6.5 mmol), iodobenzene (5 mmol), base (5.5 mmol), CuI (2.5 mol %), NMP (1 mL, 10.4 mmol), 100 °C, 16 h)

entry	base	yield (%) ^a
1	K ₂ CO ₃	99
2	NEt ₃	98
3	DIPEA	97
4	pyridine	37
5	2,6-lutidine	64
6	Cs ₂ CO ₃	85
7		5

^a Determined by GC using 100 μL of dihexyl ether as external standard.

Remarkably, apart from results in water, these findings also pointed to the possibility of performing the coupling reaction under neat conditions, that is, without using a solvent (Table 1, entry 8) but working with a homogeneous system.

Similarly, a series of bases were screened. Among inorganic bases, potassium carbonate gave quantitative results for the coupling reaction to diphenyl thioethers (Table 2), while, among organic bases, triethyl amine and Hunig's base (DIPEA) gave excellent results (entries 2 and 3) in a homogeneous reaction mixture. Notably, the required amount for the base is only 1.1 equiv (based on the aryl halide), while in common reports this usually is between 1.5 and 2.5 equiv.^{9–14}

Both Tables 1 and 2 refer to overnight reactions and a reaction temperature of 100 °C. Further experiments were performed to find the optimal reaction temperature and reaction time. An excellent yield of 95% was obtained after 6 h of reaction (see Supporting Information, Chart 1). It was noted that a small decrease in temperature of only 15 °C already caused a significant decrease in diaryl thioether yield to 75% (Supporting Information, Chart 2). Accordingly, at 100 °C, the reaction of iodobenzene with thiophenol is relatively fast (65 and 95% after 2 and 6 h, respectively).

Subsequently, different phenyl halides were tested. It appeared that under the above developed conditions fluoro-, chloro-, and bromobenzene hardly showed any reactivity, giving only traces (4–7%) of the C–S coupling product (see Table 3), whereas reactions of the corresponding iodo derivative gave rise to almost quantitative formation of diphenyl thioether.

Finally, the influence of the amount of CuI catalyst was evaluated. As shown in Table 4, lowering the amount of CuI to 1.5 mol % did not affect the efficiency of the coupling reaction, while only a slight decrease in yield from 99 to 96% was noticed when the amount of CuI was further lowered to 1 mol %.

TABLE 3. Aryl Halide Screening for C–S Coupling (reaction conditions: thiophenol (6.5 mmol), phenyl halide (5 mmol), K₂CO₃ (5.5 mmol), CuI (2.5 mol %), NMP (1 mL, 10.4 mmol), 100 °C, 16 h)

entry	phenyl halide	yield (%) ^a
1	fluorobenzene	7
2	chlorobenzene	4
3	bromobenzene	5
4	iodobenzene	99

^a Determined by GC using 100 μL of dihexyl ether as external standard.

TABLE 4. Copper Iodide Amount Screening for the C–S Coupling (Scheme 1) (reaction conditions: thiophenol (6.5 mmol), iodobenzene (5 mmol), K₂CO₃ (5.5 mmol), CuI, NMP (1 mL, 10.4 mmol), 100 °C, 16 h)

entry	Cu (mol %)	yield (%) ^a
1	0	2
2	0.5	76
3	1	96
4	1.5	99
5	2	99
6	2.5	99

^a Determined by GC using 100 μL of dihexyl ether as external standard.

Remarkable turnover numbers have been obtained (67–100) using 1–1.5 mol % of CuI only, but the turnover frequency was still low (6–13 h⁻¹, catalyst load 2.5 mol %).

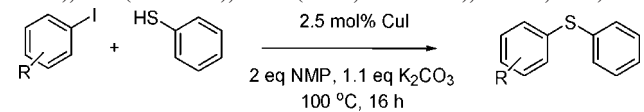
As a summary of the above-discussed results, the optimized system presented here involves the reaction between iodobenzene and thiophenol in a polar solvent (NMP, DMF, DMA) or under neat conditions at 100 °C, in the presence of 1.1 equiv of K₂CO₃ (or NEt₃) and only 1.5–2.5 mol % of CuI.

To determine the scope of the catalytic system, the present protocol was applied to reactions of a range of commercially available aryl iodides and thiophenols (Tables 5 and 6). As shown in Table 5, the coupling of thiophenol with different aryl iodide moieties was successful, leading to the desired products in good yields. The protocol is tolerant to electron-withdrawing and -donating functional groups and also to the presence of a functional group in the *ortho*-position of the aryl iodide (entries 5 and 6). Moreover, the reactions show interesting chemoselectivity; see entry 6 for preferred C–S coupling in the presence of an –NH₂ grouping. Since reaction conditions for the already optimized C–N and C–O bond formations are similar¹⁸ and these couplings present good chemoselectivity toward bromo derivatives, 1-bromo-4-iodobenzene is a suitable substrate for further development of one-pot N- and S- or O- and S-arylations.

Full selectivity toward the iodo derivative was found (entry 7), leading to 4-bromophenyl phenyl thioether as the only product through a clean and selective reaction. Results presented here also include an example of a double C–S bond formation reaction in good yield, starting from 1,3-diiodobenzene (entry 8). This coupling reaction could be an interesting option for applications in the field of material science and supramolecular chemistry for the preparation of poly(phenylene sulfide) oligomers and polymers.¹⁹

The carbon–sulfur bond formation reaction was also tested employing diverse commercially available thiols (Table 6), providing the corresponding diaryl thioethers in good to

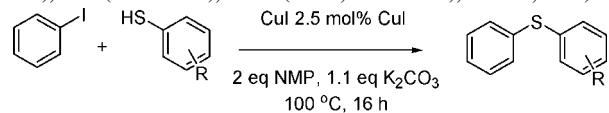
TABLE 5. Reaction of Aryl Iodides with Thiophenol (reaction conditions: thiophenol (6.5 mmol), aryl iodide (5 mmol), K₂CO₃ (5.5 mmol), CuI (2.5 mol %), NMP (1 mL, 10.4 mmol), 100 °C, 16 h)



entry	aryl iodide	product	yield (%) ^[a]
1			92
2			46
3			78
4			83
5			87
6			92
7			96
8			80

^a Determined by GC using 100 μL dihexyl ether as external standard.
^b Using 2.6 equiv of thiophenol and 2.2 equiv of base.

TABLE 6. Reaction of Iodobenzene with Various Thiols (reaction conditions: thiol (6.5 mmol), iodobenzene (5 mmol), K₂CO₃ (5.5 mmol), CuI (2.5 mol %), NMP (1 mL, 10.4 mmol), 100 °C, 16 h)



entry	thiol	product	yield (%) ^[a]
1			95
2			96
3			85
4			60
5			85
6			54

^a Determined by GC using 100 μL of dihexyl ether as external standard.

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excellent yields. Iodobenzene was maintained as arylating substrate, in order to analyze the influence of the different

substitution patterns on the reactivity of the aryl thiol. Interestingly, satisfactory results also with electron-deficient thiols and even with butanethiol were obtained.

The preparation of 2-[(dimethylamino)methyl]phenyl phenyl thioether (Table 6, entry 5, 85% yield) could also be achieved through reaction between bromobenzene and 2-[(dimethylamino)methyl]thiophenol but in much lower yield (30%). Nevertheless, since the halide screening (Table 3) showed no reactivity for bromobenzene in the model reaction, the result obtained here underlines a possible cooperative role played in the catalytic reaction by the *ortho*-NMe₂ group, which is not yet understood.

All the desired products here reported were formed in a clean and selective coupling reaction. The formation of only minute amounts (<2%) of the undesired symmetrical disulfides^{6b,20} was detected. Traces of diphenyldisulfides found at the end of the reaction were most likely due to the fact that the starting thiophenol was used in excess.

The present optimized catalytic process provides the arylation of thiophenols with aryl iodides, in the presence of K₂CO₃ or NEt₃ as a base in a polar solvent (NMP, DMF, or DMA) or under neat conditions. The use of the solvent can be avoided by using triethylamine, which can act both as solvent and as base for the system. Copper(I) iodide, in amounts between 1 and 2.5 mol %, is used as catalyst. To the best of our knowledge, this is the first report about aryl–sulfur bond formation in which a simple, commercially available copper halide salt is used without additional ligands.

The scope of the reaction is quite broad, ranging from electron-withdrawing to electron-donating substituents on both the thiophenol and aryl iodide. The present C–S coupling reactions are chemoselective toward the –SH functionality in the presence of an –NH₂ group. The chemoselectivity and tolerance of functional groups lead to an attractive opportunity to catalyze a variety of C–X coupling reactions in a tandem fashion by the same copper(I) catalyst.

In recent years, research efforts have been directed toward the design of more sustainable chemical processes, via the use of nontoxic chemicals and environmentally friendly solvents.²¹ In this respect, water seems to be a first choice for the development of “green” chemical protocols. With this idea in

mind, the observation that in the present study diphenylthioether was formed in 60% yield in the reaction of iodobenzene and thiophenol in water warrants further study.

In summary, a selective and efficient copper-catalyzed C–S bond-forming reaction of aryl iodides and various thiophenols was developed. This catalytic procedure offers general applicability and simplicity, avoiding the expensive and time-consuming preparation of suitable ligands and activated substrates. Interestingly, the experimental conditions proposed for the coupling reaction facilitate the easy workup of the reaction mixtures and isolation of the desired product. Because of these issues, we believe that this protocol could find large application in organic synthesis.

Experimental Section

General Procedure. A glass tube was charged with inorganic base (5.5 mmol) and solid substrate, if present. Liquid reagents (phenyl halide, 5 mmol; thiophenol, 6.5 mmol) and solvent (1 mL) were then added and finally the copper(I) salt. The reaction vessel, prepared under air, was closed and placed under stirring in a preheated oil bath at 100 °C. Subsequently, the reaction mixture was allowed to cool to room temperature and diluted with acetonitrile (5 mL), and dihexyl ether (100 μL, 0.425 mmol) was added as external standard. Samples were analyzed by gas chromatography. The reaction mixture was filtered through a plug of Celite and the solvent removed in vacuo to yield the crude product, which was purified by silica gel chromatography.

4-Phenylsulfanylacetophenone (Table 5, entry 1). Column chromatography (hexane/ethyl acetate 9:1), isolated as a yellow solid (89%): ¹H NMR (CDCl₃, 400 MHz) δ 2.55 (s, 3H), 7.19 (dt, *J* = 7.00, 1.75 Hz, 2H), 7.39–7.41 (m, 3H), 7.48–7.50 (m, 2H), 7.82 (dt, *J* = 7.00, 1.75 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 26.9, 127.7, 127.8, 129.0, 129.3, 129.9, 132.4, 134.1, 145.1, 197.3; HRMS (ES⁺) calcd for C₁₄H₁₂OS ([M + H]⁺) 229.0687, found 229.0654.

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Supporting Information Available: Representative experimental procedures with compound characterization data and additional charts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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