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Copper-Catalyzed Double C−S Bonds Formation *via* Different Paths: Synthesis of Benzothiazoles from *N*-Benzyl-2-iodoaniline and Potassium Sulfide

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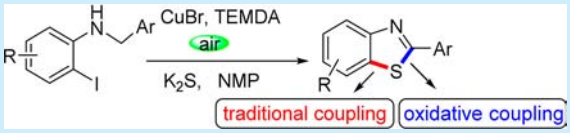
Supporting Information

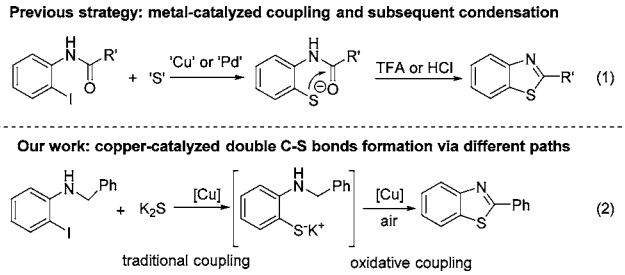
ABSTRACT: A new, highly efficient procedure for the synthesis of benzothiazoles from easily available *N*-benzyl-2-iodoaniline and potassium sulfide has been developed. The results show copper-catalyzed double C−S bond formation via a traditional cross-coupling reaction and an oxidative cross-coupling reaction.



The transition-metal-catalyzed C−S coupling reaction has recently attracted considerable attention, as it can provide a more efficient, practical, and straightforward approach to valuable sulfur-containing compounds.[1] In the past, this reaction has been less studied due to deactivation of the metal catalysts by the strong coordinating properties of sulfur compounds.[2] Recently, the problem has been successfully overcome, and a number of catalytic systems based on transition metals have been developed for C−S bond formation.[3−6] However, these methods have been mainly focused on the "traditional" cross-couplings of ArX (X═Cl, Br, I, OTf, and $B(OH)_2$) and sulfides.[3−5] With the aim for greener and more atom-economic C−S bond formation, transition-metal-catalyzed direct oxidative cross-coupling of C−H bonds and sulfides would be an ideal approach to realize this goal. In recent years, the direct C−S bond formation promoted by transition metals has attracted much attention.[6] However, the transition-metal-catalyzed C−S formation through $C(sp^3)$−H bond cleavage was seldom reported.[7] Therefore, catalytic direct thiolation of a $C(sp^3)$−H bond seems to represent a significantly bigger challenge.

Benzothiazoles are one of the most important classes of heterocycles in a myriad of natural products and biologically active compounds.[8] Thus, development of general methods for the synthesis of these compounds is valuable in drug discovery. Conventional methods for the construction of a benzothiazole framework focus on (1) the condensation of 2-amino-thiophenols with carboxylic acids, alcohols, ketone, nitriles, or aldehydes[9] and (2) transition-metal-catalyzed intramolecular cyclization of thiobenzanilides.[6a,b,10] However, these methods are suffering from difficulties in preparation of starting sulfur-containing materials, which limit their synthetic applications. To overcome this drawback, Itoh,[11] Ma,[12] and Sekar[13] et al. developed a novel and practical synthesis of benzothiazoles from 2-haloanilides and thiol surrogates via palladium or copper catalyzed double C−S bond formation (Scheme 1, reaction 1). General and efficient methods for the synthesis of benzothiazoles from simple and readily available precursors are of great value.

Scheme 1. Methods for the Synthesis of Benzothiazole



In our previous work on new methods for sulfur-heterocycle synthesis using potassium sulfide as a coupling partner,[14] we found that *N*-benzyl-2-iodoaniline could efficiently react with potassium sulfide to generate 2-benzylbenzothiazole through a copper-catalyzed coupling reaction (Scheme 1, reaction 2). We thought that double C−S bonds formed via different paths in this reaction. First, copper-catalyzed the coupling reactions of aryl halides with potassium sulfide form the intermediate aryl sulfide (traditional coupling). Then, the aryl sulfide transformed to benzothiazole by oxidative coupling via copper-catalyzed $C(sp^3)$−H bond activation (oxidative coupling). Direct oxidative intramolecular C−S bonds formation via $C(sp^3)$−H activation would no doubt be an attractive approach to synthesize benzothiazole. Herein, we wish to detail our results.

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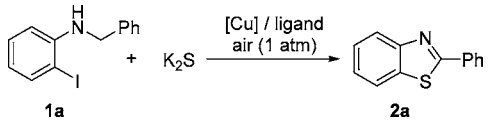
In this work, 2-phenyl benzothiazole was obtained in good yields from *N*-benzyl-2-iodoaniline **1a** and potassium sulfide in one pot, via a copper-catalyzed double sulfuration reaction. The results of the screening for optimal reaction conditions are shown in Table 1. Our investigation started by an attempted

Table 1. Optimization of Reaction Conditions[a]



1a **2a**

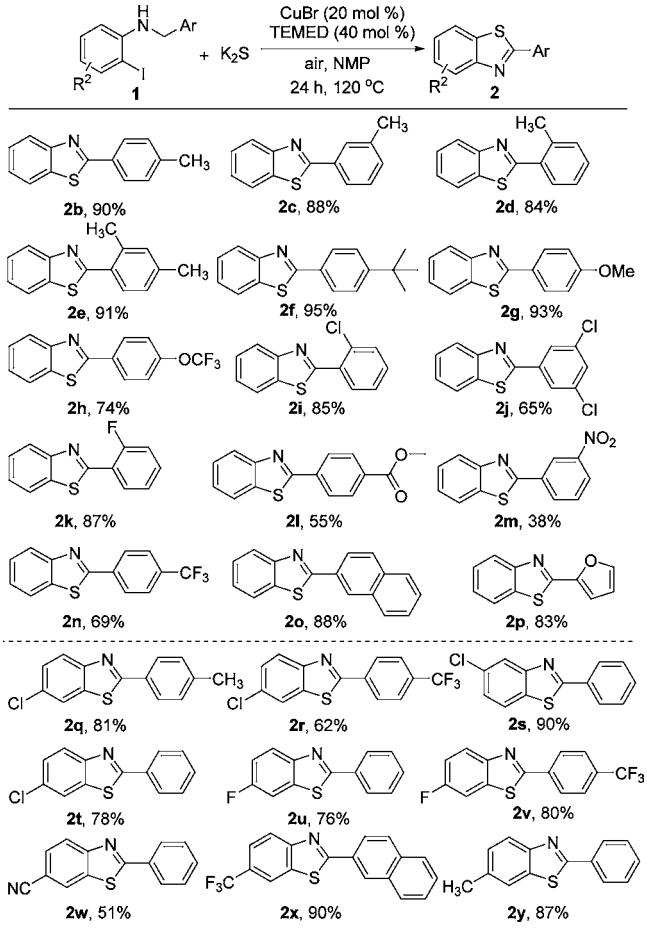
entry	catalyst	ligand	solvent	yield **2a** (%)[b]
1	CuI	pyridine	DMF	77
2	CuBr	pyridine	DMF	80
3	CuCl	pyridine	DMF	74
4	$CuBr_2$	pyridine	DMF	42
5	CuBr	1,10-Phen	DMF	67
6	CuBr	TEMED	DMF	83
7	CuBr	L-Proline	DMF	26
8	CuBr	DMEDA	DMF	60
9	CuBr	TEMED	DMSO	43
10	CuBr	TEMED	NMP	93
11[c]	CuBr	TEMED	NMP	88
12[d]	CuBr	TEMED	NMP	67

[a]Reaction conditions: **1a** (0.3 mmol), K_2S (0.9 mmol), Cu salt (20 mmol %), ligand (40 mmol %), solvent (1 mL), under air atmosphere in sealed Schlenk tube, at 120 °C for 24 h. [b]Isolated yields. [c]At 110 °C. [d]CuBr (10 mmol %), TEMED (20 mmol %).

sulfuration of substrate **1a** with K_2S in DMF at 120 °C in the presence of CuI as the catalyst and pyridine as the ligand, and the desired product **2a** was isolated in 77% yield (entry 1). This result encouraged us to develop an efficient catalytic system to synthesize benzothiazole using *N*-benzyl-2-iodoaniline as a starting substrate. A variety of copper catalysts, such as CuI, CuBr, CuCl, and $CuBr_2$, were screened (entries 1−4). The results indicated that CuBr is the best one for this coupling reaction. Subsequently, the effects of ligands (including pyridine, 1,10-phenanthroline, TEMED, L-proline, and DMEDA) are examined (entries 5−8). TEMED achieved the best result, and the product of benzothiazole was obtained in 83% yield. Solvents such as DMSO and NMP were also evaluated, and a 93% yield of benzothiazole was afforded when NMP was used (entry 10). Finally, the amount of catalyst and the reaction temperature were evaluated, and relatively low yields were found with any reduction in the reaction temperature or the amount of catalyst. Thus, the optimized reaction conditions were as follows: **1a** (0.3 mmol), K_2S (0.9 mmol), CuBr (20 mol %), TEMED (40 mol %), in NMP (1 mL) under an air atmosphere at 120 °C.

To extend the substrate scope of the cyclization reaction, various benzothiazoles were synthesized and submitted to the CuBr/air/K_2S system. The results obtained under the optimized conditions are listed in Scheme 2. Initially, the substituent of benzyl was screened. The results demonstrated that both electron-rich and -deficient benzyl substituted 2-iodoanilines could be smoothly transformed into the desired products. Furthermore, substituents at different positions of the benzyl (para-, meta-, and ortho-positions) do not obviously affect the efficiency (**2b−2g**). It is noteworthy that halo-substituted benzyl survived well leading to halo-substituted products, which could be used for further modification (**2i−2k**). In addition, *N*-(2-iodophenyl)naphthalen-2-amine could react with K_2S and afford the expected product in 88% yield (**2o**). Importantly, a heterobenzyl-substituted 2-iodoaniline, *N*-(furan-2-ylmethyl)-2-iodoaniline, was also tolerated in this transformation generating **2p** in 83% yield. On the other hand, we also evaluated an aryl group linked with 2-iodoaniline. Different functional groups, including electron-withdrawing groups such as fluoro, chloro, and trifluoromethyl and electron-donating groups such as methyl groups on the benzene rings, all well-tolerated under the reaction conditions and proceeded with almost equal efficiency (**2q−2y**). These results indicated that electronic effect on the benzene ring did not play a significant role in regulating the reaction and revealed the inherent high reactivity of *N*-benzyl-2-iodoaniline.

Scheme 2. Synthesis of 2-Arylbenzothiazoles[a,b]



[a]Reaction conditions: **1** (0.3 mmol), K_2S (0.9 mmol), CuBr (20 mol %), TEMED (40 mol %), air, 120 °C, 24 h. [b] Isolated yields.

Having established the reaction of *N*-benzyl-2-iodoaniline **1** and potassium sulfide as a reliable and efficient synthetic process, we were curious about the possibility to apply this system to *N*-acyl-2-iodoaniline **3** and alkyl substituted 2-iodoaniline. As expected, under similar reaction conditions, 2-acylbenzothiazole products **4** were obtained in 71−82% yields (Scheme 3). Unfortunately, alkyl substituted 2-iodoaniline such as 2-iodo-*N*-methylaniline and 2-iodo-*N*-octylaniline did not work under these conditions due to its low reactive activity.

To shed light on the possible mechanism of the reaction, several control experiments were carried out, as shown in Scheme 4. According to the results of this transformation, first

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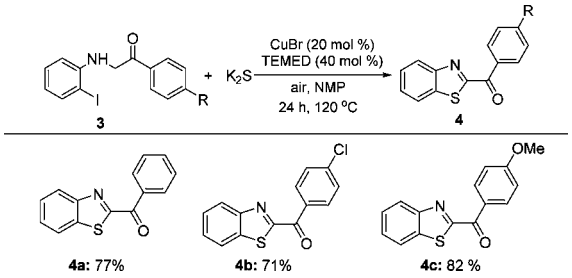
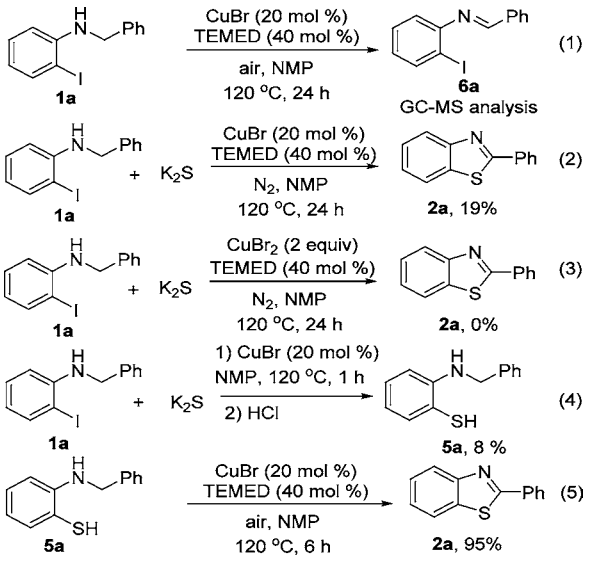
Scheme 3. Synthesis of 2-Acylbenzothzoles[a,b]



[a]Reaction conditions: **1** (0.3 mmol), K_2S (0.9 mmol), CuBr (20 mol %), TEMED (40 mol %), air, 120 °C, 24 h. [b] Isolated yields.

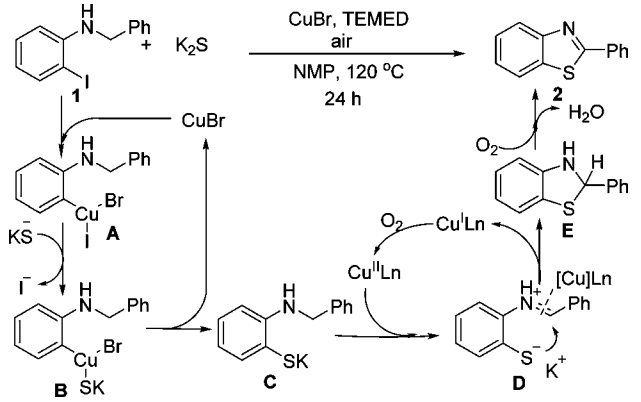
Scheme 4. Mechanistic Investigations



of all, we predicted that the imine may be a key intermediate before the cyclization reaction. Therefore, we conducted the first control experiment involving oxidation of **1a** in the absence of K_2S under standard conditions (Scheme 4, eq 1). The GC-MS trace analysis shows that **1a** does not convert into imine at all. Consequently, based on the present experimental results and the previous reported mechanism,[15,17b] we speculate it would be impossible for the copper-catalyzed cyclization to undergo the imine-type intermediate producing process through activation of the C(sp^3)−H adjacent to nitrogen. Subsequently, *N*-benzyl-2-iodoaniline was treated with K_2S in the presence of a copper(I) or copper(II) catalyst under N_2, respectively. However, only 19% of the desired product was obtained in the presence of 0.2 equiv of CuBr, and no desired product was observed in the presence of 2 equiv of $CuBr_2$. We therefore postulated that the dioxygen acted not only as the oxidant but also as an initiator to trigger this catalytic process.[16] Additionally, when *N*-benzyl-2-iodoaniline **1a** was reacted with K_2S under N_2 for 1 h, then hydrochloric acid was added to quench the reaction, and 2-(benzylamino)benzenethiol **5a** was formed in 8% yield (together with 2-phenylbenzothiazole and some unidentified side products) (Scheme 4, eq 4). Subsequently, **5a** can be transformed into the desired product benzothiazole in 95% yield under standard reaction conditions (Scheme 4, eq 5). This result indicated that potassium 2-(benzylamino)benzenethiolate should be the intermediate in the reaction of *N*-benzyl-2-iodoaniline with potassium sulfide.

On the basis of these observations, a tentative mechanism for the product formation is proposed in Scheme 5. First, the

Scheme 5. Plausible Mechanism



copper catalyzed coupling reaction of *N*-benzyl-2-iodoaniline with K_2S provides the intermediate **C**.[12] Then, the intermediate **C** undergoes a copper-assisted single-electron-transfer oxidation with oxygen to produce the imine-type intermediate **D**.[15−17] Subsequently, **D** undergoes an intramolecular nucleophilic attack as well as addition to produce intermediate **E**. Finally, an oxidative dehydrogenation sequence affords the desired product benzothiazole **2**.[18]

In summary, we have demonstrated a novel copper-catalyzed coupling reaction of *N*-benzyl-2-iodoaniline and potassium sulfide. This method provides an effective approach to synthesize benzothiazoles, which are ubiquitous structural units in a number of biologically active compounds. The experiment indicated that CuBr acts as a catalyst both for traditional cross-coupling reactions and for oxidative cross-coupling reactions. Molecular oxygen was found to act not only as the oxidant but also as an initiator to trigger this catalytic process.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and scanned NMR spectra of all new products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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