Switchable Copper-Catalyzed Approach to Benzodithiole, Benzothiaselenole, and Dibenzodithiocine Skeletons

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ABSTRACT: A copper-catalyzed reaction between 2-bromo-benzothioamide and S₈ or Se involving sulfur rearrangement is reported, enabling access to benzodithioles 2 and benzothiaselenoles 6 in the presence of Cs₂CO₃. In the absence of S₈ or Se, the reaction affords dibenzodithiocines 7 via two consecutive C(sp²)−S Ullmann couplings.

Organosulfur compounds display prominent potential for diverse functionalization and exhibit attractive pharmacological properties. In this regard, copper-catalyzed cross-coupling reactions between aryl halides and carbon- or heteroatom-based nucleophiles represent an established synthetic strategy for forging carbon−carbon and carbon−heteroatom bonds. In recent years, elemental sulfur (S₈) has been demonstrated to be an effective sulfur source for C(sp²)−S bond formation under copper-catalyzed conditions. For example, Liu and coworkers disclosed a copper-catalyzed three-component reaction involving o-iodobenzamides, S₈, and CH₂Cl₂ to afford 2,3-dihydrobenzothiazinones in good yields (Figure 1). Similarly, the Shi group reported a copper-mediated C−S bond-forming protocol to access benzoisothiazolones from benzamides via C−H activation. Recently, a solvent-free method for the synthesis of 2-aclythiino[2,3-b]quinolines was described through dual copper/nitroxyl radical catalysis.

In this regard, benzodithiols (BDTs) and derivatives thereof, which contain a fused bicyclic molecule bearing a benzene ring connected to a five-membered 1,2- or 1,3-dithiol-containing ring, have been reported to possess promising bioactivity including anti-HBV, antitumor, antimicrobial, anti-Mycobacterium avium, and antibovine viral diarrhea virus activities. Therefore, numerous methods have been explored for accessing more potent and structurally diverse BDTs. Here 3H-benzo[c][1,2]dithiol-3-ones is an important member of 1,2-BDTs and has, for example, been utilized in the preparation of fluorescent probes.

In our recent study, 2-bromo-N-phenylbenzothioamide (1a) was subjected to a terminal alkyne in the presence of a copper catalyst to afford the corresponding 4H-thiochromen-4-imine. We reasoned that replacing the alkyne with S₈ as a sulfur source would furnish benzo[d]isothazole-3(2H)-thione through Caryl−Br thiolation. However, the reaction underwent an unexpected sulfur rearrangement, leading to 3H-benzo[c][1,2]dithiol-3-imine. As a continuation of our studies on construction of heterocycles catalyzed by copper(I) or silver(I), herein we disclose an efficient and modular approach to benzodithioles and benzothiaselenoles.
copper-catalyzed protocol for synthesis of benzodithiole derivatives 2 through the reaction of 2-bromo-benzothiazoles 1 with S₈ under alkaline conditions. Furthermore, this copper-mediated reaction provided benzothiazolene derivatives 6 when S₈ was replaced with Se powder.

As shown in Table 1, the model reaction of 2-bromo-N-phenylbenzothiazole (1a) and S₈ was performed in refluxing pyridine using 10 mol % Cu as a catalyst, affording 2a in 46% yield (Table 1, entry 1). To improve the yield, several reaction parameters were varied, including the copper source, base, ligand, and solvent. Using alternative copper precursors, such as CuBr₂, CuCl₂, and CuOAc, demonstrated that Cu was superior (cf. Table 1, entry 1 and entries 2–4). Furthermore, the use of copper(II) precursors, such as CuBr₂ and CuOAc, led to no desired product formation (Table 1, entries 5 and 6). The addition of frequently used ligands, such as Ph₃P, o-phen, and L-proline, revealed that a substantial increase in yield was possible when using o-phen, providing 2a in 68% yield (Table 1, entry 9). A survey of inorganic bases showed that Cs₂CO₃ furnished product 2a in 76% yield (Table 1, entry 10). Other carbonate bases, such as K₂CO₃, Na₂CO₃, and NaHCO₃, also promoted the reaction (Table 1, entries 11–13) but provided lower yields of 2a compared with Cs₂CO₃. Finally, the reaction also proceeded in common organic solvents, such as DMF, dioxane, DMSO, DMA, and toluene (Table 1, entries 14–20). Here DMF was found to be the best solvent for this reaction, leading to 2a in 85% yield (Table 1, entry 14).

With the optimized reaction conditions in hand, we examined the generality of the protocol (Scheme 1). Initially, substrates with various substituents on the imine nitrogen atom were investigated.

In addition to aliphatic groups, the reaction tolerated various aromatic substituents bearing either electron-donating (methyl, methoxy, iso-propyl) or electron-withdrawing substituents, such as nitro and chloro, as well as heteroaryl motifs. All of these substrates underwent the cascade coupling/cyclization smoothly to afford products 2a-o in good to excellent yields (62–90%, Scheme 1). The structure of product 2a was supported through single-crystal X-ray diffraction analysis of 2l, as shown in Scheme 1.

With respect to the substituents on the benzene ring, we were delighted to find that various groups, such as methyl, methoxy, chloro, and fluoro, at either the five- or seven-position could be employed, furnishing the corresponding benzodithiole products 2r-ad in 75–91% yields (Scheme 1). Additionally, a pyridine derivative was also an effective coupling/cyclization partner, affording product 2ae in 91% yield.

To evaluate possible further applications of the developed protocol, several benzodithioles were transformed into their corresponding BDT derivatives (3a–e) in high yields via acidic hydrolysis (Scheme 1). The developed protocol undoubtedly provides an efficient and practical method for the preparation of these valuable and medicinally relevant compounds. Furthermore, the synthetic conversion of 3a into the important compounds 4 and 5 was attained in good yield by reacting with m-CPBA and hydrogen peroxide, respectively.

Next, we reasoned that the corresponding selenium analogue of 2 would be accessible by replacing the sulfur source with an appropriate selenium source. Intriguingly, conducting the reaction under the optimized reaction conditions using Se powder instead of S₈ provided product 3a in 91% yield (Scheme 1). The structure of product 6u was supported by X-ray diffraction analysis. (See Scheme 2.) Gratifyingly, a variety of substituted aromatic motifs, such as alkylphenyl (e.g., methyl, isopropyl, and tert-butyl), alkoxyphenyl (e.g., methoxy and ethoxy), and mono- and dihalogenated phenyl (e.g., F and Cl) reacted smoothly to give the desired products under the optimized reaction conditions. A total of 30 benzothiazolenes were obtained in moderate to high yields (56–78%, Scheme 2).

A proposed mechanism for the synthesis of 2 and 6 is detailed in Scheme 3. According to the structure of the products 2 and 6, benzothietane-2-imine B is envisioned as a key intermediate. Initially, benzothioamide 1 is believed to be converted to anion A in the presence of a base. Then, benzothietane-2-imine B is produced via an intramolecular copper-catalyzed Ullmann coupling reaction to form thietane adduct B. Subsequent cleavage of the C=S bond occurs to give the ring-opened thiophenolate D. In the following step, intermediate D reacts with S₈ or Se to form an S=S or S–Se bond, which is similar to reacting Na₂S with S₈ to form Na₂S₂. Finally, intermediate E undergoes an addition/elimination process to give the target structure 2 or 6. An alternative mechanism involves the initial formation of a copper thiolate adduct (G), which undergoes oxidative addition into the C–Br bond to form the five-membered cupracycle H. The subsequent migration and insertion of sulfur or selenium

**Table 1. Optimization of the Reaction Conditions**

| entry | catalyst | base | ligand | solvent | yield (%) |
|-------|----------|------|--------|---------|-----------|
| 1     | Cu       |      |        |         | 46        |
| 2     | CuBr     |      |        |         | 37        |
| 3     | CuCl     |      |        |         | 26        |
| 4     | CuOAc    |      |        |         | 39        |
| 5     | CuBr₂    |      |        |         | 25        |
| 6     | Cu(OAc)₂ |      |        |         | 51        |
| 7     | Cu       | PPh₃ |        | py      | 62        |
| 8     | Cu       | L-proline |   | py       | 58        |
| 9     | Cu       | o-phen |     | py       | 68        |
| 10    | Cu       | Cs₂CO₃ | o-phen | py      | 76        |
| 11    | Cu       | K₂CO₃ | o-phen | py      | 72        |
| 12    | Cu       | Na₂CO₃ | o-phen | py      | 73        |
| 13    | Cu       | NaHCO₃ | o-phen | py      | 69        |
| 14    | Cu       | Cs₂CO₃ | o-phen | DMF     | 85        |
| 15    | Cu       | Cs₂CO₃ | o-phen | DMF     | 37        |
| 16    | Cu       | Cs₂CO₃ | o-phen | DMF     | 86        |
| 17    | Cu       | Cs₂CO₃ | o-phen | dioxane | 76        |
| 18    | Cu       | Cs₂CO₃ | o-phen | DMSO    | 79        |
| 19    | Cu       | Cs₂CO₃ | o-phen | DMA     | 82        |
| 20    | Cu       | Cs₂CO₃ | o-phen | toluene | 69        |

*Reaction conditions: 1a (146 mg, 0.5 mmol), S₈ (154 mg, 0.6 mmol), catalyst (0.05 mmol), ligand (0.1 mmol), base (0.5 mmol), solvent (5.0 mL), 100 °C. *Isolated yield. *Reaction carried out with 1.0 mmol NaHCO₃ (100 mg, 1.2 mmol). *Reaction run with 5 mol % Cu (0.025 mmol). *Reaction run with 20 mol % Cu (0.1 mmol).
Scheme 1. Substrate Scope for Synthesis of Benzodithiole 2

Reaction conditions: 1 (0.5 mmol), S₈ (154 mg, 0.6 mmol), CuI (10 mg, 0.05 mmol), o-phen (18 mg, 0.1 mmol), Cs₂CO₃ (163 mg, 0.5 mmol), DMF (5.0 mL), 100 °C. Yields are of isolated products after purification by column chromatography.

Scheme 2. Substrate Scope for Synthesis of Benzothiaselenole 6

Reaction conditions: 1 (0.5 mmol), Se (48 mg, 0.6 mmol), CuI (10 mg, 0.05 mmol), o-phen (18 mg, 0.1 mmol), Cs₂CO₃ (163 mg, 0.5 mmol), DMF (5.0 mL), 100 °C. Yields are of isolated products after purification by column chromatography.
into the Cu−S or Cu−C bond of intermediate I affords the six-membered metallacycle J or J′, respectively, which upon reductive elimination delivers product 2 or 6 and regenerates the copper(I) catalyst.

Finally, conducting the reaction under standard conditions but in the absence of S8 or Se provided a new product, dibenzodithiocine 7a, derived from two consecutive C(sp2)−S coupling reactions (Scheme 4). The initial yield (42%) for this copper-catalyzed coupling product could be improved to 79% upon changing the ligand and base to PPh3 and K2CO3, respectively. A total of 20 dibenzodithiolenes (7a−o) were obtained in 72−85% yield, and the structure of 7n was supported by X-ray diffraction analysis (Scheme 4).

In conclusion, an efficient and switchable copper-catalyzed method for the synthesis of benzothioles and benzothiaseolenes using S8 or Se as the chalcogen source is disclosed. Conducting the reaction in the absence of S8 or Se affords eight-membered dibenzodithiocine annulation products via two consecutive C(sp2)−S coupling reactions. Considering the importance of sulfur and selenium compounds, this protocol may be of great value for synthetic chemists and pharmacologists in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00907.

Experimental details and NMR spectra of compounds 2−7 (PDF)

Accession Codes

CCDC 1950837 and 1950844−1950845 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(19) Conducting the reaction under the optimized conditions with the chloro and iodo analogues of substrate 1 afforded product 2 in 21 and 89% yield, respectively.

(20) Attempts were made to access product 3 through a C–H functionalization strategy. However, no reaction occurred for the substrate lacking the bromo group under the optimized reaction conditions.

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