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Introduction

Sulfur-containing organic molecules play a vital role in pharmaceuticals, biologically important molecules, and organic functional materials. The construction of the C–S bond is an effective way to synthesize sulfur-containing compounds.¹ Therefore, developing methodologies for the synthesis of the C–S bond is a persistently attractive research topic among synthetic chemists. Classically, the well-known nucleophilic substitution reaction² and the Ullmann reaction³ could provide approaches for C–S bond formation using halides with thiol compounds as starting materials, but these reactions are often accompanied by some side-reactions generating redundant compounds and the reactant halides also need to be prefunctionalized.⁴

Direct C-H functionalization has provided a streamlined synthetic route, and this strategy has been proven to be a promising synthetic approach for chemical bond construction with atomand step-economy.⁵ How to achieve the transformation of the C-H bond to the C-S bond is an attractive topic in synthetic chemistry.⁶ Traditionally, thiol⁷ and disulfide compounds⁸ are often introduced as sulfur sources to construct the C-S bond. The use of these sulfur reagents usually comes with some limitations, namely, lower reaction yields, unpleasant odor, and airsensitivity. Therefore, alternatives to these compounds have always been explored. Bunte salts are stable, relatively easy to prepare and odorless and have therefore gradually been preferred for C-S bond formation.9 Over the past few years, we have noticed that research on the construction of the C-S bond via C-H activation using Bunte salts as sulfur sources has been widely developed.^{9a-c,10} For example, in 2016, Ji and Yang's

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Ag–Cu copromoted direct C2–H bond thiolation of azoles with Bunte salts as sulfur sources†

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A direct C2–H thiolation of azoles with Bunte salts was achieved under the combined action of copper and silver salts. This protocol could furnish various substituted 2-thioazoles in moderate to good yields. This method has a broad substrate scope and shows good functional group tolerance.

> group developed an efficient tetra-*n*-butylammonium iodide (TBAI) promoted procedure for C3–H sulfenylation of indoles with Bunte salts under metal-free and oxidant-free conditions.¹¹ A similar synthesis of C3–H sulfenylated 4-anilinocoumarins *via* KI-catalyzed sulfenylation of 4-anilinocoumarins with Bunte salts was realized by Yang's group.¹² Recently, Wu's group has achieved the reaction of CuI-catalyzed thioamination of maleimides with secondary amines and Bunte salts with the formation of C–N, C–S bonds in one pot.¹³

> Substituted 2-thioazoles as an important class of sulfurcontaining heterocyclic compounds have received widespread attention because of their biological activities (Fig. 1).¹⁴ Over



antischistosomal agents

new class of AhR agonists

Fig. 1 Representative substituted 2-thio-azole molecules.

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the past few decades, considerable progress has been made in the synthesis of substituted 2-thioazoles.¹⁵ Liu and co-workers realized the copper-mediated reaction of thiazoles and thiols to afford substituted 2-thioazoles in the presence of Na₂CO₃ as a base (Scheme 1a, route 1).^{15b} Gao's group achieved the coupling of azoles and thiols without adding additional bases, by adding Lewis acids to increase the activity of the thiazole C2-H bond (Scheme 1a, route 2).^{15e} Bolm and co-workers found that disulfide compounds have the ability to couple with azoles (Scheme 1b).^{15f} In order to replace thiols and disulfides, Dong's group utilized tetramethylthiuram (TMTD) as the sulfur reagent and developed a one-pot synthesis of substituted 2-thioazoles through the cyclization of 2-aminothiophenols, 2-aminophenols, and 1,2-phenylenediamines with TMTD to give azoles followed by coupling with halides (Scheme 1c).^{15j} However, in this reaction, the raw materials are complex and difficult to obtain. Therefore, it is necessary to develop an efficient and novel protocol for preparing substituted 2-thioazoles from simple, easily available and odorless reagents. Herein, we report a direct C-H thiolation of azoles with Bunte salts as the source of sulfur.

Results and discussion

At the outset of our study, the reaction of benzothiazole (1a) and sodium *S*-benzyl thiosulfate (2a) was exploited as a model reaction to optimize the reaction conditions. According to the reported research,^{9,10} we chose a cheap copper salt as the oxidant and accelerator, *N*,*N*-dimethylformamide (DMF) with good solubility for Bunte salts as the solvent, and 120 °C as the reaction temperature. We recognized that the silver salt could coordinate with the nitrogen atom of azoles to increase the activity of the C2–H bond.^{15e,16} So we initially introduced silver nitrate in this reaction. Gratifyingly, the desired 2-(benzylthio)benzo[*d*]thiazole (3a) was obtained in 62% isolated yield when Cu(OAc)₂ (2.0 equiv.) and AgNO₃ (20 mol%) were

employed (Table 1, entry 1). Then various copper salts were investigated, and the results of different reactions indicated that other copper salts could not provide a better yield of **3a**

Table 1 Optimization of the reaction conditions



| Entry | Cu salt | Lewis acid | Solvent | Temp. (°C) | Yield ^{b} (%) |
|------------------------|----------------------|-----------------------------------|---------|------------|-------------------------------------|
| 1 | $Cu(OAc)_2$ | AgNO ₃ | DMF | 120 | 62 |
| 2 | CuCl ₂ | AgNO ₃ | DMF | 120 | Trace |
| 3 ^c | CuI | AgNO ₃ | DMF | 120 | None |
| 4^c | CuBr | AgNO ₃ | DMF | 120 | None |
| 5 | _ | AgNO ₃ | DMF | 120 | None |
| 6 | $Cu(OAc)_2$ | _ | DMF | 120 | 53 |
| 7 | $Cu(OAc)_2$ | AgOAc | DMF | 120 | 50 |
| 8 | $Cu(OAc)_2$ | Ag_2SO_4 | DMF | 120 | 51 |
| 9 | $Cu(OAc)_2$ | AgCF ₃ SO ₃ | DMF | 120 | 60 |
| 10 | $Cu(OAc)_2$ | AgSbF ₆ | DMF | 120 | 57 |
| 11 | $Cu(OAc)_2$ | AgBF ₄ | DMF | 120 | 60 |
| 12 | $Cu(OAc)_2$ | AgNO ₃ | DMSO | 120 | 32 |
| 13 | $Cu(OAc)_2$ | AgNO ₃ | MeCN | 120 | 50 |
| 14 | $Cu(OAc)_2$ | AgNO ₃ | Dioxane | 120 | Trace |
| 15^d | $Cu(OAc)_2$ | AgNO ₃ | DMF | 120 | 53 |
| 16^e | $Cu(OAc)_2$ | AgNO ₃ | DMF | 120 | 27 |
| 17^{f} | $Cu(OAc)_2$ | AgNO ₃ | DMF | 120 | Trace |
| 18 | $Cu(OAc)_2$ | AgNO ₃ | DMF | 110 | 43 |
| 19 | $Cu(OAc)_2$ | AgNO ₃ | DMF | 130 | 56 |
| 20 ^g | Cu(OAc) ₂ | AgNO ₃ | DMF | 120 | 77 |
| 21 | $Cu(OAc)_2$ | FeCl ₃ | DMF | 120 | 46 |
| 22 | $Cu(OAc)_2$ | AlCl ₃ | DMF | 120 | 52 |
| 23 | $Cu(OAc)_2$ | $Zn(OAc)_2$ | DMF | 120 | 58 |
| $24^{g,h}$ | $Cu(OAc)_2$ | AgNO ₃ | DMF | 120 | 75 |
| $25^{g,i}$ | $Cu(OAc)_2$ | AgNO ₃ | DMF | 120 | 74 |
| $26^{c,i}$ | CuÌOAc) | AgNO ₂ | DMF | 120 | 41 |

^{*a*} Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Cu(OAc)_2$ (2 equiv.), Lewis acid (20 mol%) in DMF (2 mL) at 120 °C for 22 h under a nitrogen atmosphere in a sealed tube. ^{*b*} Isolated yields. ^{*c*} Under air. ^{*d*} Cu(OAc)₂ (1.5 equiv.). ^{*e*} Cu(OAc)₂ (1.2 equiv.). ^{*f*} Cu(OAc)₂ (1.0 equiv.). ^{*g*} **1a** (0.2 mmol), **2a** (0.3 mmol). ^{*h*} Run for 24 h. ^{*i*} Run for 20 h.



Scheme 1 Synthesis routes of substituted 2-thioazoles.

(Table 1, entries 2-5). We noted that CuCl₂ could only provide a trace amount of the product, and this may be attributed to the chlorine anion which impedes the C2-H activation of azoles. Subsequently, an examination of diverse silver salts revealed that AgNO₃ in combination with copper salts was still a better choice (Table 1, entries 1 and 6-11). Afterwards, different solvents were tested in this reaction, and it was found that DMF could furnish a more satisfactory result (Table 1, entries 1 and 12-14). Then other influencing factors of the reaction were examined in this system. Reducing the amount of $Cu(OAc)_2$ could evidently reduce the yield of the target product (Table 1, entries 15-17). Interestingly, when one equivalent of $Cu(OAc)_2$ was employed in this reaction, only a trace amount of the product was observed (Table 1, entry 17). Next, raising or lowering the reaction temperature could not improve the reaction (Table 1, entries 18 and 19). We found that the yield of 3a could increase to 77% when the amount of 2a was reduced to 1.5 equivalents (Table 1, entry 20). We speculated that the concentration of the Bunte salt could affect the selfpolymerization reaction of the Bunte salt forming the disulfide. Considering the role of silver salts, other Lewis acids were also investigated and the reactions could not give a better result (Table 1, entries 21-23). Next, adjusting the reaction time had an inconspicuous effect on this reaction (Table 1,



entries 24 and 25). Finally, we carried out the reaction under an air atmosphere, and the yield of 3a was reduced to only 41% (Table 1, entry 26).

With the optimized conditions in hand, the generality of this protocol was further investigated. The scope of Bunte salts was first evaluated (Scheme 2). Sodium S-benzyl thiosulfate with -Me and -Cl at the 4-position of the benzene ring could afford the desired compounds in yields of 41% and 60% (3b and 3c). Phenethyl Bunte salt could react well in this system to provide the expected product (3d). Alkyl Bunte salts also could furnish the target products in moderate to good yields, and we noted that the yield of the corresponding products increased with the growth of the carbon chain of Bunte salts (3e-3i). We believe that this could be attributed to the improved solubility



Scheme 2 Substrate scope of Bunte salts. Standard conditions: 1a (0.20 mmol), 2 (0.30 mmol), Cu(OAc)₂ (2.0 equiv.), AqNO₃ (20 mol%), DMF (2.0 mL), under N₂ at 120 °C for 22 h, isolated yield. ^a Reaction at 130 °C. ^b Reaction at 110 °C.

Scheme 3 Substrate scope of azoles. Standard conditions: 1 (0.20 mmol), 2a (0.30 mmol), Cu(OAc)₂ (2.0 equiv.), AgNO₃ (20 mol%), DMF (2.0 mL), under N₂ at 120 °C for 22 h, isolated yield. ^a Reaction at 110 °C.



Scheme 4 Scale-up reaction



Scheme 5 Mechanistic experiments.

of Bunte salts bearing larger organic groups. Isopropyl Bunte salt could provide the expected product with a moderate yield (**3j**). Aryl Bunte salts with electron-donating groups such as methyl and methoxyl on the benzene ring were smoothly converted to the desired products in moderate yields (**3k**-**3m**).

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Unfortunately, we did not observe the corresponding product when aryl Bunte salts bearing electron-withdrawing groups such as -Cl and -NO₂ were employed in this system.

After examining the scope of Bunte salts, we further evaluated the substrate scope of azoles (Scheme 3). Benzothiazole with 5-Cl and 5-Br could give the desired sulfides in 80% and 62% yields, respectively (4a and 4b). Interestingly, benzothiazole bearing the electron-withdrawing -NO2 group could provide the desired product in 53% yield (4c). The reactions with thiazole and 4,5-dimethylthiazole also proceeded well, giving the products in 61% and 64% yields, respectively (4d and 4e). Thiazoles with sensitive functional groups, namely, -CO₂CH₃ and -CHO, were all compatible (4f and 4g). Benzoxazoles and differently substituted benzoxazoles such as 5-Cl, 5-Br, 5-Me and 6-Me were well tolerated, affording the desired products in moderate to good yields (4h-41). Oxazole and imidazole were successfully transformed to afford the target products in 44% and 30% yields, respectively (4m and 4n). Additionally, benzoxazole could also react with different Bunte salts to produce the target products in moderate yields (40-4q). The reactions of oxazole and imidazole with arylsubstituted Bunte salts were not successful and only provided the desired product in less than 10% yield.

Next, we carried out a scale-up reaction of benzothiazole (1a, 2 mmol) with sodium *S*-benzyl thiosulfate (2a) under the optimal reaction conditions to demonstrate the synthetic utility of this transformation as shown in Scheme 4. The reaction afforded the corresponding product 3a in 64% yield.

To probe the mechanism of this transformation, some experiments were carried out. The thiolation of benzothiazole with benzenethiol and Cu^{II} thiolate was carried out and the corresponding products were obtained, which proved that benzenethiol and Cu^{II} thiolate could be involved in this reaction process (Scheme 5a and b). The reaction of benzothiazole (**1a**) with tolyl Bunte salt (**2k**) and benzyl Bunte salt (**2b**) in one pot provided **3b** in 34% yield and **3k** in 17% yield (Scheme 5c). It showed that benzyl Bunte salts could perform better in this system.



Scheme 6 Plausible mechanism.

On the basis of our experiments and related literature precedents, a plausible reaction mechanism for this transformation is proposed as shown in Scheme 6. First, Bunte salt 2 reacts with Cu^{II} and releases SO_3 to afford Cu thiolate intermediate A.^{9h,17} The nitrogen atom of azoles 1 is coordinated with Ag^I to generate intermediate **B** to increase the acidity of C2–H.^{15e,16} Next, intermediate **C** is delivered through a concerted metalation–deprotonation process and RSH intermediate **D** is released.^{7g,15b,15e} RSH could react with Cu^{II} to afford Cu thiolate intermediate **A**. Then a disproportionation reaction between **C** and the Cu^{II} salt affords Cu^{III} intermediate **E**.^{13,15e,18} Finally, **E** undergoes reductive elimination to produce the corresponding product **3**.

Conclusions

In summary, we have achieved a direct C–H thiolation of azoles with Bunte salts using a combination of copper and silver salts. This protocol employs Bunte salts as sulfur sources, avoiding the use of air-sensitive and smelly thiols, disulfides and other sulfur reagents. Various substituted 2-thioazoles have been obtained in moderate to good yields. This method has a broad substrate scope and possesses good functional group tolerance.

Experimental

General information

All reagents were purchased and used without further purification. DMF was distilled from CaH2 under nitrogen and stored over 4 Å molecular sieves under nitrogen. ¹H NMR (400 MHz) and ¹³C NMR (101 MHz) spectra were obtained using a Bruker spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in units (ppm) by assigning the TMS resonance in the ¹H NMR spectra as 0.00 ppm (chloroform, 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constant (J values) in Hz and integration. Chemical shifts for the ¹³C NMR spectra are recorded in ppm relative to tetramethylsilane using the central peak of CDCl₃ (77.05 ppm) as the internal standard. Melting points were recorded using an X-5 Micro melting point instrument. Flash column chromatography was performed using 300-400 mesh silica with the indicated solvent system according to standard techniques. Analytical thin layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. The yields of the products reported are the isolated yields and the average of two runs.

General procedure for the thiolation of azoles with Bunte salts

In a glove box, a 25 mL Schlenk tube equipped with a stir bar was charged with the Bunte salt (0.3 mmol, 1.5 equiv.), $Cu(OAc)_2$ (0.4 mmol, 2.0 equiv.), and AgNO₃ (0.04 mmol,

20 mol%). The tube was fitted with a rubber septum and taken out of the glove box. Then azole (0.2 mmol) was added through the rubber septum using a syringe under an atmosphere of N₂. DMF (2 mL) was added to the Schlenk tube through the rubber septum using a syringe. The septum was replaced by a Teflon screwcap under N₂ flow. The mixture was stirred at 120 °C (preheated to 120 °C) for 22 h. After cooling, the mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of silica gel, followed by washing of the pad of silica gel with ethyl acetate (20 mL). The organic phase was concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

Conflicts of interest

There are no conflicts to declare.

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