K₂S as Sulfur Source and DMSO as Carbon Source for the Synthesis of 2-Unsubstituted Benzothiazoles

Xiaoming Zhu,* Fuxing Zhang, Daizhi Kuang, Guobo Deng, Yuan Yang, Jiangxi Yu,* and Yun Liang*



ABSTRACT: We describe a three-component reaction of *o*-iodoanilines with K_2S and DMSO that provides 2-unsubstituted benzothiazoles in moderate to good isolated yields with good functional group tolerance. Electron-rich aromatic amines and *o*-phenylenediamines instead of *o*-iodoanilines provided 2-unsubstituted benzothiazoles and 2-unsubstituted benzimidazoles with and without K_2S under similar conditions. Notably, DMSO plays three vital roles: carbon source, solvent, and oxidant.

T he 2-unsubstituted benzothiazoles are vital core structures for functional molecules applied in biology, pharmacy, and material science.¹ They are also very important precursors for synthesizing 2-substituted benzothiazoles via C2–H functionalization.² Accordingly, considerable efforts have been made toward the development of diverse synthetic methods for 2-unsubstituted benzothiazoles.^{3,4} Traditionally, synthetic strategies for 2-substituted benzothiazoles involved the condensation of *o*-aminobenzenethiols with suitable carbon sources such as DMF,^{3a–c} CH(OEt)₃,^{3d–f} CO₂,^{3g–i} CHOOH,^{3j,k} and CH₂O^{3l,m} and the deamination reaction of the 2-aminobenzothiazoles (Scheme 1, eq 1).⁴ However, their application is limited by instability and easy oxidation of *o*-





aminobenzenethiols as well as poor availability of starting materials and harsh reaction conditions. Recently, an efficient strategy involving inorganic sulfurating reagents was employed to assemble sulfur-containing heterocycles, particularly 2-substituted benzothiazoles.^{5,6} However, using easily available inorganic sulfurating reagents as sulfur source for a simple and effective method for the synthesis of 2-unsubstituted benzothiazoles has not been described.

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During this synthesis of thiobenzothiazoles, a small amount of benzothiazole formation was observed (Scheme 1, eqs 2 and 3).⁷ Based on this unexpected finding and our interest in synthesis of sulfur-containing heterocycles using inorganic sulfurating reagents,^{7,8} we studied the synthesis of 2-unsubstituted benzothiazoles from *o*-iodoanilines, K_2S , and DMSO (Scheme 1, eq 4).

The initial evaluation of the reaction used *o*-iodoaniline (1a), K_2S , and DMSO to optimize the reaction conditions, and the results are summarized in Table 1. The desired benzothiazole product 2a could be obtained in 83% yield using CuI, H_2O , and NH_4OAc at 140 °C under nitrogen atmosphere (entry 1). Some control experiments were carried out to investigate the role of each component in the reaction. The results showed that CuI, NH_4OAc , and K_2S were indispensable for this reaction (entries 2–4), and a small



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Table 1. Optimization of the Reaction Conditions^a

	$ \begin{array}{c} & & \\ & & $	S N 2a	S J J
entry	variation from the standard conditions	yield of 2a (%)	yield of 2ae (%)
1	none	83	0
2	without CuI	trace	0
3	without NH ₄ OAc	trace	29
4	without K ₂ S	0	0
5	without H ₂ O	44	0
6	K ₂ CO ₃ instead of K ₂ S	0	0
7	NMP instead of DMSO	0	0
8	KOAc instead of NH ₄ OAc	16	25
9	NH ₄ OOCH instead of NH ₄ OAc	72	0
10	NH ₄ I instead of NH ₄ OAc	0	0
11	HOAc (6.equiv) instead of NH ₄ OAc	0	0
12	NH ₃ ·H ₂ O (6 equiv) instead of NH ₄ OAc and H ₂ O	12	0
13	KOH (2 equiv)	60	0
14	HOAc (2 equiv)	44	0
15 ^b	none	32	0
16 ^c	none	trace	0
17 ^d	none	82	0

^{*a*}Reaction conditions: **1a** (0.2 mmol), K_2S (3 equiv), CuI (20 mol %), NH₄OAc (6 equiv), H₂O (80 μ L), and DMSO (2 mL) in a sealed Schlenk tube at 140 °C for 10 h under N₂ atmosphere; isolated yields. ^{*b*}Air. ^{*c*}O₂. ^{*d*}**1a** (5 mmol).

amount of water could promote the reaction (entry 5). Product 2a could not be obtained when the reaction was conducted using K₂CO₃ instead of K₂S (entry 6) and NMP instead of DMSO (entry 7). These results indicated that K₂S and DMSO served as the sulfur source and carbon source, respectively. The yield of 2a did not improve when KOAc, NH4OOCH, NH4I, or HOAc was used in place of NH4OAc and $NH_3 \cdot H_2O$ instead of NH_4OAc and H_2O (entries 8–12). These results implied that NH4OAc played an important role in this reaction. When KOH (2 equiv) or HOAc (2 equiv) was added, the yield of 2a was reduced to 60% and 44%, respectively (entries 13 and 14). These results showed the effect of acid on the reaction was greater than base. Conducting the reaction under air atmosphere or in the presence of oxygen did not improve the yield. However, 2a was formed in 82% yield when done on a 5 mmol scale (entry 17, see the Supporting Information (SI) for details).

With the optimal reaction conditions in hand, the substrate scope of *o*-iodoanilines (1) was next investigated (Scheme 2). The *o*-iodoanilines (1b–1i) with various functional groups were successfully applied to react with K_2S and DMSO, and the corresponding products were obtained in moderate to good yields (2b–2i). The efficiency of the three-component reaction was not affected by the electronic properties of the substituents. For example, the electron-rich groups such as methyl and electron-deficient groups such as ester-, cyano-, and nitryl-substituted benzothiazoles were obtained in excellent yields (2b–2e). However, the electron-withdrawing groups such as fluorine-, chlorine-, and bromine-substituted benzothiazoles led to only moderate yields (2f–2i). This might be due to the instability of these groups.

Substituents at different positions of the aromatic ring of *o*iodoaniline were also investigated. These results indicated that

Scheme 2. Synthesis of 2-Unsubstituted Benzothiazoles from o-Iodoanilines^a



"Reaction conditions: 1 (0.2 mmol), K_2S (3 equiv), CuI (20 mol %), NH₄OAc (6 equiv), H₂O (80 μ L), and DMSO (2 mL) in a sealed Schlenk tube at 140 °C for 10 h under N₂ atmosphere.

the electron-donating groups such as $-CH_3$ and $-OCH_3$ at the 4- and 5-positions of *o*-iodoaniline showed the same reactivity (**2b**, **2f**, **2j**, **2k**), whereas the response efficiency of electron-withdrawing groups such as fluorine and chlorine at 5position of *o*-iodoaniline (**1l**, **1m**) was higher than that at the 4-position of *o*-iodoaniline (**1g**, **1h**). Notably, the disubstituted *o*-iodoanilines (**1n**, **1o**) could give the corresponding products in moderate yields (**2n**, **2o**). Gratifyingly, 3-iodopyridin-2amine and 1-iodonaphthalen-2-amine could be smoothly transformed into the desired products in 52% and 95% yields, respectively.

In our preliminary work, 2-substituted benzothiazoles and 2substituted naphtho[2,1-*d*]thiazoles compounds could be synthesized by breaking the C(sp²)–H bond of electron-rich aromatic amines.^{8b} An ideal strategy would prepare the 2unsubstituted benzothiazoles via halogen-free aromatic amines instead of *o*-iodoanilines. To our delight, when the electronrich aromatic amines (0.3 mmol) were treated with K₂S (3 equiv), NH₄OAc (4 equiv), H₂O (80 μ L), and DMSO (2 mL) under transition-metal-free conditions, the corresponding 2unsubstituted benzothiazoles and 2-unsubstituted naphtho-[2,1-*d*]thiazoles products 4 were obtained in 30–92% yields (Scheme 3). Under these conditions, the naphtho[2,1*d*]thiazole and 6-bromonaphtho[1,2-*d*]thiazole were afforded in 92% and 69% yields (4a, 4b), respectively. Subsequently, the electron-rich anilines were examined. The results showed that

Scheme 3. Synthesis of 2-Unsubstituted Benzothiazoles from Halogen-Free Electron-Rich Aromatic Amines^a



"Reaction conditions 3 (0.3 mmol), K_2S (3 equiv), NH_4OAc (4 equiv), H_2O (80 μ L), and DMSO (2 mL) in a sealed Schlenk tube at 140 °C for 10 h under N_2 atmosphere.

electron-donating groups such as methyl- and methoxylsubstituted anilines could smoothly transform into the corresponding products in medium to good yields (4c-4e). Furthermore, when 2-aminoanthracene was employed as a substrate, the polycyclic anthra[2,1-d] thiazole 4f was obtained in moderate yield. Unfortunately, the other anilines without electron-rich substituents such as aniline and *p*-nitroaniline were unsuccessful (3g, 3h).

The 2-unsubstituted benzimidazoles are useful intermediates in fine chemicals¹⁰ and privileged scaffolds in medicinal chemistry.¹¹ Accordingly, we were curious about the possibility of applying this method to the synthesis of 2-unsubstituted benzimidazoles. Our further study indicated that the corresponding product **6** was obtained in 35-86% yields (Scheme 4) when the *o*-phenylenediamines (0.2 mmol) were

Scheme 4. Synthesis of 2-Unsubstituted Benzimidazoles from *o*-Phenylenediamines^{*a*}



^{*a*}Reaction conditions: **5** (0.2 mmol), NH₄OAc (6 equiv), H₂O (80 μ L), and DMSO (2 mL) in a sealed Schlenk tube at 140 °C for 10 h under N₂ atmosphere.

treated with NH₄OAc (6 equiv), H₂O (80 μ L), and DMSO (2 mL). Fortunately, an array of substituents such as $-CH_3$, $-OCH_3$, -F, -Cl, -Br, $-COOCH_3$, -CN, $-NO_2$, and -COPh on the phenyl ring at *o*-phenylenediamine were well tolerated, and the corresponding products were afforded in moderate to good yields (**6b**-**6k**). In addition, the disubstituted *o*-phenylenediamines could smoothly transformed into the target products in moderate yields (**6l** and **6m**). Importantly, the *N*-substituted-benzene-1,2-diamines, such as *N*-methylbenzene-1,2-diamine, *N*-benzylbenzene-1,2-diamine, and *N*-phenylbenzene-1,2-diamine, were also competent substrates; the corresponding *N*-substituted-2-unsubstituted benzimidazoles were obtained in moderate to good yields (**6n**-**6p**).

Some control experiments were performed to investigate the possible reaction mechanism (Scheme 5). The benzothiazole (2a), o-aminobenzenethiol (B), dimethyl trisulfide (E), and a small amount of 2-methylbenzothiazole (K) could be detected from the reaction mixture by GC-MS analysis when oiodoaniline (1a) was reacted with K₂S and DMSO for 1.5 h (eq 1, see the SI). Subsequently, the benzothiazole (2a) could be synthesized from o-aminobenzenethiol (B) in the absence of CuI and K_2S (eq 2), but the 2-(methylthio)benzo[d]thiazole (k) could not be reacted with K_2S and DMSO under standard conditions (eq 3). The results showed that oaminobenzenethiol (B) may be the intermediate of the reaction and CuI only worked in the early stages of the reaction. The 2-mercaptobenzothiazole (J) could be obtained in 29% and 25% yields in the absence of NH₄OAc (Table 1, entries 3 and 8)—here, 2-(methylthio)benzo[d]thiazole (I)

Scheme 5. Controlled Experiments



(eq 4) and 2-mercaptobenzothiazole (J) (eq 5) are possible intermediates, respectively. Product **2a** was not obtained. These results indicated that the reaction underwent different mechanisms from our previous report^{7b} perhaps because of the acid–base effect of NH_4OAC .

We subsequently performed a 13 C labeling experiment with CH¹³COOH, and **2a** was not marked by 13 C (eq 6). In addition, the naphtho[2,1-*d*]thiazole **4a** could be isolated in 40% yield in the absence of NH₄OAc (eq 7). This result showed that the carbon source was derived from DMSO. Furthermore, we used methyl phenyl sulfoxide instead of DMSO, and benzothiazole (**2a**) and methyl(phenyl)sulfide (L) could be isolated in 50% yield and 62.0 mg weight along with benzenethiol (**M**) and diphenyl disulfide (**N**) by GC–MS (eq 8, see the SI). These results indicated that DMSO is concurrently the carbon source and oxidant.

To our surprise, when DMSO was replaced by DMSO- d_6 in the standard reaction, only 5% of deuterium labeling product **2a-D1** was obtained (Scheme 6, eq 1). To further verify the reaction process and the hydrogen source of **2a**, we performed several deuterium-labeling experiments (Scheme 6, eqs 2–4). When D₂O or ND₄OOCCD₃ was used, 74% and 19% of the

Scheme 6. Deuterium Labeling Experiments



deuterium-substituted products **2a-D2** and **2a-D3** were obtained, respectively (eqs 2 and 3). These results showed that the hydrogen source of the product **2a** came from DMSO, H_2O , and NH_4^+ , which reacted with water to complete hydrogen exchange from H_2O . Finally, the benzothiazole **2a**, which had not been deuterium labeled, was used as a substrate to react with D_2O under standard conditions (eq 4). The **2a-D4** was deuterized with only 60% of hydrogen, which was lower than the deuterium-substituted percentage ratio of 74% in **2a-D2** (eq 2). This result indicated that both benzothiazole **2a** and the reaction intermediate might lead to the exchange of deuterium and hydrogen from D_2O before the formation of **2a-D2**.

Based on the controlled experimental results and previous reports, 7a,b,8e,b,9,12 we proposed a plausible reaction mechanism for the formation of 2a (Scheme 7). The intermediate **B** was

Scheme 7. Possible Reaction Mechanism



first formed via acidification of **A** produced by a coppercatalyzed coupling reaction of *o*-iodoaniline.^{7a,8e} The NH₄OAc activated DMSO to generate **C** via the Pummerer reaction.^{12a-d} The imine **F** was then generated via the elimination of methane thiol from **D**, ^{12b,d-f} which was obtained via intermolecular nucleophilic addition from **C** and **B**.^{12b,e} Alternatively, the formaldehyde was formed by decomposition of DMSO.^{12b,i} **F** was also provided by condensation of *o*-aminobenzenethiol **B** and formaldehyde. Meanwhile, **F** reacted with water to decompose into **B** and formaldehyde, and this process possibly completed the exchange of hydrogen between **F** and water. Finally, the target product **2a** was formed via cyclization and oxidation of **F**.

Another possible reaction pathway was also proposed. Here, **D** was oxidized to generate imine G, ^{7b,8b} which formed **H** via intramolecular nucleophilic addition.^{7b} Under the action of NH₄OAc, **H** was more likely to form **2a** by the elimination reaction of demethylmercaptan^{7b} rather than providing **I** by aromatization reaction. Thus, the synthesis of **J** was completely inhibited. A more comprehensive reaction mechanism requires further study.

In conclusion, we report an efficient and practical protocol for 2-unsubstituted benzothiazoles from *o*-iodoanilines with K_2S and DMSO under the promotion of NH₄OAc. Furthermore, the controlled experimental results indicate that the K_2S provides the sulfur source and DMSO acts as the carbon source, oxidant, and solvent for the reaction. Notably, the advantages of this protocol are tolerance to a wide range of functional groups and readily available starting materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00994.

Experimental details, NMR spectra, and details of the experiments (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Xiaoming Zhu Key Laboratory of Functional Metal–Organic Compounds of Hunan Province, Hunan Province Universities Key Laboratory of Functional Organometallic Materials, College of Chemistry and Material Science, Hengyang Normal University, Hengyang, Hunan 421008, China; Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha, Hunan 410081, China; ◎ orcid.org/0000-0003-4086-4674; Email: zxmhnhy@163.com
- Jiangxi Yu Key Laboratory of Functional Metal–Organic Compounds of Hunan Province, Hunan Province Universities Key Laboratory of Functional Organometallic Materials, College of Chemistry and Material Science, Hengyang Normal University, Hengyang, Hunan 421008, China; Email: hnhyyjx@126.com
- Yun Liang Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha, Hunan 410081, China;
 orcid.org/0000-0002-2550-9220; Email: yliang@hunnu.edu.cn

Authors

- Fuxing Zhang Key Laboratory of Functional Metal–Organic Compounds of Hunan Province, Hunan Province Universities Key Laboratory of Functional Organometallic Materials, College of Chemistry and Material Science, Hengyang Normal University, Hengyang, Hunan 421008, China
- **Daizhi Kuang** Key Laboratory of Functional Metal–Organic Compounds of Hunan Province, Hunan Province Universities Key Laboratory of Functional Organometallic Materials, College of Chemistry and Material Science, Hengyang Normal University, Hengyang, Hunan 421008, China
- Guobo Deng Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha, Hunan 410081, China;
 orcid.org/0000-0002-5470-5706
- Yuan Yang Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha, Hunan 410081, China;
 orcid.org/0000-0002-9061-1758

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c00994

Notes

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