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Efficient synthesis of benzothiazolone derivatives by a domino reaction of disulfide and COS under mild conditions

Bohao Zhou,[a] Hailong Hong,*[a] Hongcai Wang,[a] Tianmiao Zhang,[a] Limin Han,[a] Ning Zhu*[a]

Abstract: Carbonyl sulfide (COS), whose molecular structure is similar to CO_2 and CS_2, could be used as a better alternative carbonyl reagent due to its high chemical activity. However, the unfriendly by-product H_2S would be generated when COS is used as a carbonyl reagent in the carbonylation reaction. In this report, the odorless and stable disulfide was used to replace the traditional foul smelling and unstable *o*-aminobenzenethiol to react with COS for preparing benzothiazolone derivatives in excellent yield, in which coupling reaction of H_2S generation and S-S bond cleavage was firstly designed. Notably, the C=O of COS was converted into benzothiazolone derivatives by carbonylation reaction and the sulfur of COS was transformed into sulfur and sulfide after cleaving the S-S bond by a domino reaction of disulfide and COS under mild conditions. This efficient synthetic methodology provided a promising process for the utilization of COS.

Benzothiazolone and its derivatives are widely used heterocyclic compounds in medicine, pesticides and materials (Fig. 1). For instance, Tiaramide is a commonly used nonsteroidal anti-inflammatory and analgesic drug[1]. Sibenadet is a β_2-adrenergic receptor agonist which could be used to treat asthma[2]. Benazolin and chlobenthiazone as herbicides and fungicides are widely used in agriculture[3]. Hence, the study of synthetic methods for preparing benzothiazolone derivatives is one of the most attractive fields in synthetic chemistry.

So far, many synthetic approaches have been developed for the synthesis of benzothiazolones and its derivatives. Traditionally, benzothiazolones are prepared from the starting material *o*-aminobenzenethiol; however, the majority of *o*-aminobenzenethiol with different substitution groups could not be synthesized easily and often spontaneously oxidized into the corresponding disulfides[4]. Disulfide is an odorless, stable and convenient raw material, comparing with the foul smelling and unstable *o*-aminobenzenethiol. In reactions, the thiol compounds are regenerated from disulfides by reducing the S-S bond. Generally, the S-S bond could be broken by nucleophilic reagents[5], thiol[6], free radical reagents[7] and metal catalysts[8]. Although the S-S bond could be effectively cleaved by these methods, it is difficult to cleave the S-S bond of disulfide under mild conditions due to the inherent stability of the disulfides.

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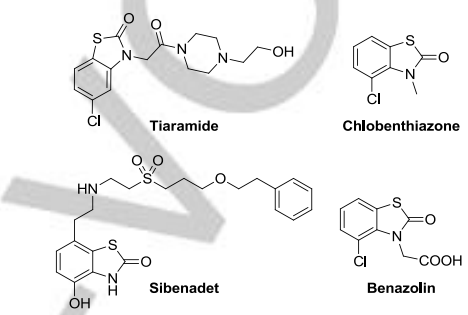
Fig. 1. Structures of bioactive benzothiazolones

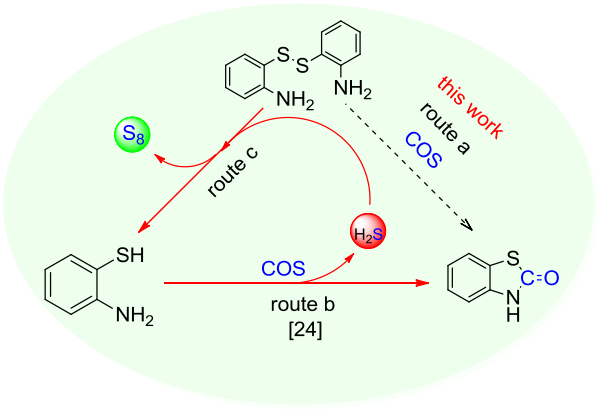


Recently, our group has reported an efficient way of cleaving S-S bond by the dynamic interchange reaction between metal sulfide and disulfide under mild conditions[9]. Moreover, carbonylation reagent is another important raw material for the synthesis of benzothiazolone from the disulfide 2,2'-disulfanediyldianiline. Commonly, urea[10], triphosgene[11], N,N'-carbonyldiimidazole[12], ethyl chlorocarbonate[13] and disuccinimido carbonate (DSC)[14] are used as carbonylation reagents for preparing carbonyl compounds. However, these common carbonylation reagents possess complex structures or produce many environment unfriendly byproducts. Therefore, there is still a need to find highly atomic economy carbonylation reagents.

CO is the simplest carbonylation reagent[15], which could be used for the synthesis of benzothiazolones[16]. However, the utilization of CO as a carbonylation reagent for the synthesis of benzothiazolone usually requires harsh reaction conditions due to the explosive nature of CO. CO_2 is abundant source of C1 resources with a simple structure, which has attracted much attention in the organic synthesis of carbonyl compounds[17]. Additionally, Liu and coworkers reported a method for preparing benzothiazolone through the carbonylation of *o*-aminobenzenethiol with CO_2, in which the chemically inert CO_2 was activated by costly ionic liquid catalyst[18]. Notably, the structure of CS_2 is similar to CO_2, which could easily react with disulfide to form 2-mercaptobenzothiazole[9]. The C=S bond of CS_2 is easily broken because of the weaker C=S bond energy of CS_2 (4.463 eV)[19]. The structure of COS is similar to that of CS_2 and CO_2[20]. Moreover, C=S bond energy of COS (3.12 eV) is lower than C=S bond energy of CS_2 (4.463 eV) and C=O bond energy of COS (6.81 eV) is higher than C=O bond energy of CO_2 (5.453 eV)[19], which clearly demonstrate that C=S bond of COS is more reactive and C=O bond of COS is more stable. Therefore, COS could be used as a better alternative carbonyl reagent. Moreover, COS, produced in the process of utilizing the fossil fuels[21], was the main molecule of the atmospheric sulfur

cycle, which could cause acid rain[22]. Thus, COS should be captured and chemically utilized. However, the study for COS utilization is limited.

Scheme 1. The process of benzothiazolone formation from disulfide and COS.



Recently, Zhang utilized COS to prepare the sulfur-containing polymers[23], which showed that COS was completely incorporated into the polymers. We expected that COS as both carbonyl source and sulfur source to react with the starting material disulfide to synthesize benzothiazolone from the standpoint of atomic economy (**Scheme 1**, route a). Furthermore, according to the previous work, COS could react with *o*-aminobenzenethiol to form the target product benzothiazolone and the toxic byproduct H_2S[24] (Scheme 1, route b). In addition, the S-S bond of disulfide may be broken by the hydrogen sulfide according to our previous experiment[9]. Moreover, in the reaction of disulfide and COS, the disulfide needs to be reduced into *o*-aminobenzenethiol which would react with COS to generate H_2S. Therefore, we postulated that the H_2S generation and the S-S bond cleavage could be coupled in the same reaction process (Scheme 1, route c), in which the unfriendly gas H_2S could be converted into nontoxic byproduct (S_8). Our experimental results confirmed the proposed coupling process and we provided a new method for the efficient, highly atomic economy synthesis of benzothiazolone by the domino reaction of COS and disulfide, which demonstrated that COS was firstly used as both carbonylation reagent and S-S bond cleaving reagent (Scheme 1, red arrows).

Results and Discussion

To shed light on the reaction mechanism of disulfide and COS, we investigated the reaction intermediates by mixing the disulfide **1a** (2,2′-disulfanediyldianiline) and COS in DMF at room temperature for 20 minutes. The reaction products were monitored by liquid chromatography mass spectrometry (LC-MS). As illustrated in Fig. 2 and S1 in ESI, the LC-MS results showed that the reaction of **1a** with COS generated the target product benzothiazolone (**2a**), and several multisulfide intermediates such as trisulfide (A), tetrasulfide (B), pentasulfide (C), and hexasulfide (D). Meanwhile, after the reaction of **1a** and

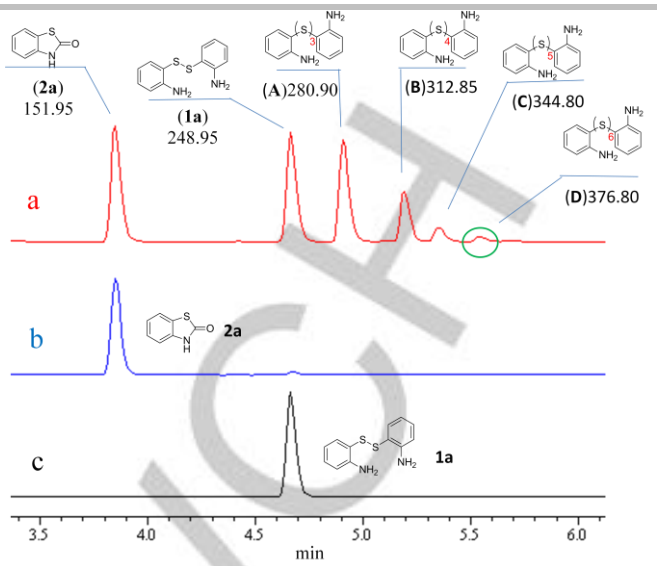


Fig. 2 (a) The reaction between disulfide **1a** and COS after 20 min in DMF at room temperature analyzed by LC-MS (the molecular weight is shown under molecular structure) (b) The LC chromatogram of benzothiazolone **2a** and (c) the LC chromatogram of disulfide **1a**

COS was completed, byproduct S_8 was isolated by column chromatography eluted with petroleum and was characterized according to our previous experiment[9]. In addition, the gas vented from the reactor reacted with the lead acetate test paper and the color turned black, which clearly indicated the formation of hydrogen sulfide (H_2S). Furthermore, the reaction process of **1a** and H_2S was monitored by ^{1}HNMR in deuterated methanol (Fig. 3 a, c and d, red rectangle and blue rectangle), which demonstrated that disulfides could be reduced into *o*-aminobenzenethiol by H_2S. Therefore, H_2S, S_8, *o*-aminobenzenethiol and multisulfide could be formed by the reaction process of **1a** with COS, which further demonstrated that a dynamic interchange reaction between **1a** and the product H_2S produced *in situ* took place in the reaction solution. Benzothiazolone could be formed through the tandem reaction of COS and *o*-aminobenzenethiol produced by the dynamic interchange reaction of **1a** and H_2S. However, **1a** could not react with COS completely to produce the target product **2a** according to the LC-MS results.

To further investigate the synthetic process of benzothiazolone from disulfides and COS, control experiments were carried out. As shown in Scheme 2, when disulfide reacted with COS, **2a** was obtained in 26% yield (eqn (1)); however, product **2a** was formed only in 39% yield when the reaction time was extended to 24 hours (eqn (1)), which might indicate that the reaction rate gradually became slower as the reaction time increased due to the increase of H_2S. To verify our hypothesis, H_2S (0.2 MPa) was added to the reaction of disulfide and COS (eqn (2)), and the product **2a** could not be formed, which further confirmed that the reaction of disulfide and COS could be inhibited by H_2S. Similarly, after the hydrochloric acid (0.3 eq. to **1a**) was added

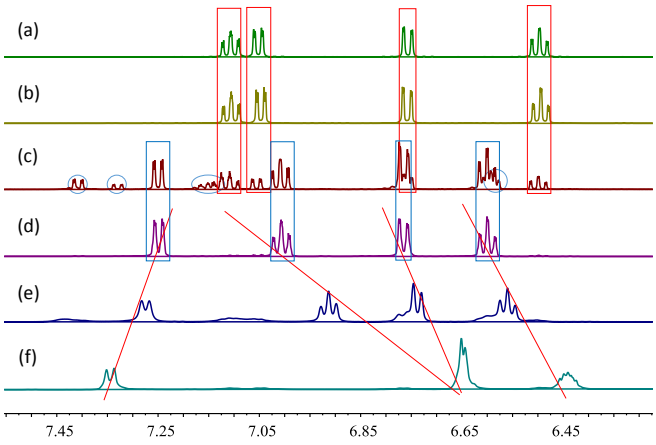
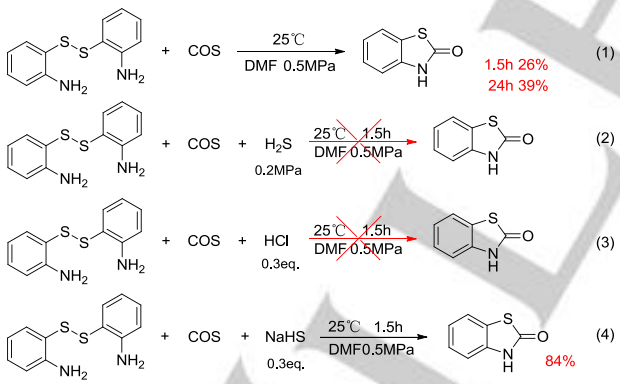


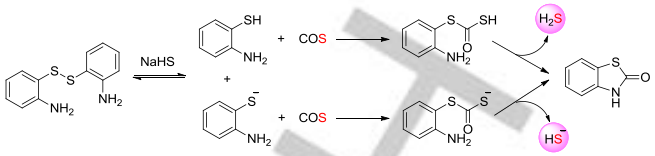
Fig. 3 (a) ^{1}HNMR spectra of **1a**; (b) **1a** and NaOH; (c) **1a** and H_2S; (d) *o*-aminobenzenethiol; (e) the mixture of NaOH, H_2S and **1a**; (f) *o*-aminobenzenethiol and NaOH in deuterated methanol.

into the reaction solution of disulfide and COS (eqn (3)), the target product **2a** also could not be found. Thus, the reaction of disulfide and COS could not take place spontaneously in acidic solution. Therefore, a base was needed to regulate pH in the acidic reaction solution caused by H_2S. According to our previous experiment, NaSH could be used as both an inorganic base and the S-S bond breakage reagent[9]. Interestingly, when NaSH was added in the reaction of COS and disulfide, the yield of **2a** increased dramatically to 84% (eqn (4)), which showed that NaSH could promote the reaction of COS and disulfide.



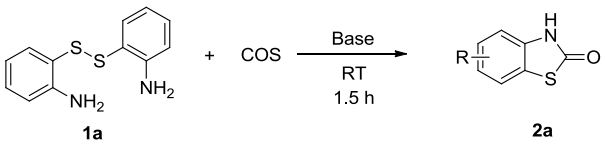
Scheme 2 Controlled experiments

Scheme 3 The reaction pathway of disulfide **1a** with COS mediated by NaSH



Inspired by the experimental results, the optimal conditions of synthesizing benzothiazolone from disulfide and COS were explored (Table 1). Initially, the optimal ratio of NaSH needed to improve the reaction yield of disulfide and COS was determined. When the base was not added in this reaction, product **2a** was obtained in only 26% yield (entry 1). However, the yield of **2a** increased rapidly with increasing ratio of NaSH (entries 2-4), which showed that 0.5 eq. of NaSH was the optimal ratio. These experimental results demonstrated that NaSH played an important role in the reaction system. Moreover, product **2a** could also be efficiently obtained from the reaction of **1a** and COS in excellent yields (entries 5 and 6) when K_2S or $Na_2S{\cdot}9H_2O$ was added, which indicated that metal sulfides could promote this reaction. However, according to the reaction mechanism of disulfide and CS_2 mediated by NaSH[9], the S-S bond of disulfide was broken through the dynamic interchange reaction to form one equivalent of *o*-aminobenzenethiol and one equivalent of *o*-aminobenzenethiolate when one equivalent of **1a** was mixed with one equivalent of NaSH. These intermediates subsequently reacted with two equivalents of COS to produce one equivalent of H_2S, one equivalent of SH^- and two equivalents of the target product **2a** (scheme 3). Obviously, the S-S bond of disulfide could be broken by one equivalent of SH^- to produce one equivalent of H_2S and one equivalent of SH^-, which indicated that 1.5 equivalents of H_2S and SH^- were left in the reaction solution after 0.5 equivalents of NaSH were consumed. Therefore, the H_2S and SH^- produced by the reaction of **1a** and COS were enough to break the S-S bond of disulfide, which clearly showed that the reaction of disulfide and COS promoted by metal sulfide had poor atom economy.

Table 1 Optimization of the reaction conditions[a]



Entry	Base	Amount (equiv)	P_{COS} (MPa)	Solvent	Yield (%)
1	—	0	0.5	DMF	26
2	NaSH	0.3	0.5	DMF	84
3	NaSH	0.5	0.5	DMF	92
4	NaSH	1	0.5	DMF	91

5	$Na_2S.9H_2O$	0.5	0.5	DMF	91
6	K_2S	0.5	0.5	DMF	91
7	Et_3N	0.5	0.5	DMF	56
8	NaOH	0.5	0.5	DMF	94
9	NaOH	0.1	0.5	DMF	82
10	NaOH	0.2	0.5	DMF	87
11	NaOH	0.3	0.5	DMF	94
12	NaOH	0.3	0	DMF	NR
13[c]	NaOH	0.3	0.1	DMF	73
14	NaOH	0.3	0.3	DMF	84
15	NaOH	0.3	1	DMF	92
16	NaOH	0.3	0.5	EtOH	83
17	NaOH	0.3	0.5	THF	92
18	NaOH	0.3	0.5	DCM	5
19	NaOH	0.3	0.5	H_2O	3

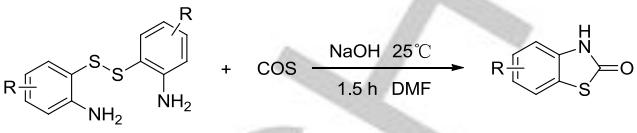
[a] Reaction conditions: **1a** (1 mmol), indicated amounts of base and solvent (1 mL) were stirred in the high pressure reactor (10 mL) for 1.5 hour at room temperature under the indicated pressure of COS.

[b] Isolated yield based on **1a** after column chromatography.

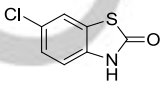
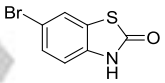
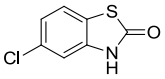
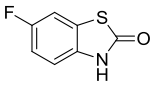
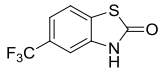
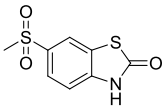
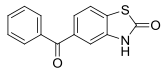
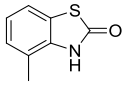
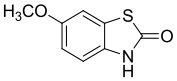
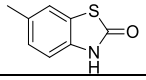
[c] 10 mL high pressure reactor was replaced by 50 mL reactor.

To increase the reaction atom economy, the metal sulfides should be replaced by some sulfur-free bases. When 0.5 eq. triethylamine were used to replace the metal sulfide in the reaction of disulfide and COS (entry 7), the yield of **2a** was reduced to 56%, which probably suggested the basicity of triethylamine was not strong enough. When 0.5 eq. NaOH were added to the reaction solution of **1a** and COS (entry 8), the target product was achieved in 94% yield, which demonstrated that NaOH could promote the reaction of disulfide and COS efficiently. The optimal ratio of NaOH was then determined (entries 8-11), which showed that 0.3 eq. NaOH could promote the reaction to produce the target product in excellent yield. Moreover, the influence of COS pressure on the reaction yield was investigated (entries 12-15). The product **2a** was not formed in the absence of COS, which demonstrated that COS was the only carbonyl source in this reaction. When 0.1 MPa COS was applied to the reactor (entry 13), the yield of **2a** was 73%, which demonstrated that **1a** could react with COS smoothly under low pressure; however, some raw material **1a** was left after 1.5 h. The highest yield of **2a** could be obtained after the pressure of COS reached 0.5 MPa**.** The effect of solvents was also investigated (entries 16-19 and 11). Polar aprotic solvents such as THF and DMF were found to give excellent yield of **2a**, and EtOH also provided a good yield of **2a**. However, water and DCM generated low yields of **2a**, because the raw material **1a** was poorly soluble in water at room temperature and DCM could react with *o*-aminobenzenethiol produced *in situ* to form some by-products under alkaline condition[25], which hindered the synthesis of benzothiazolone from disulfide and COS.

Table 2 Synthesis of benzothiazolone derivatives[a]



1 **2**

Entry	Substrate 1	Product 2		Yield[b] (%)
1	4,4′-Cl		**2b**	80
2	4,4′-Br		**2c**	90
3	3,3′-Cl		**2d**	87
4	4,4′-F		**2e**	87
5	3,3′-CF_3		**2f**	85
6	4,4′-SO_2CH_3		**2g**	65
7	4,4′-COC_6H_5		**2h**	85
8	2,2′-CH_3		**2i**	85
9	4,4′-OCH_3		**2j**	93
10	4,4′-CH_3		**2k**	89

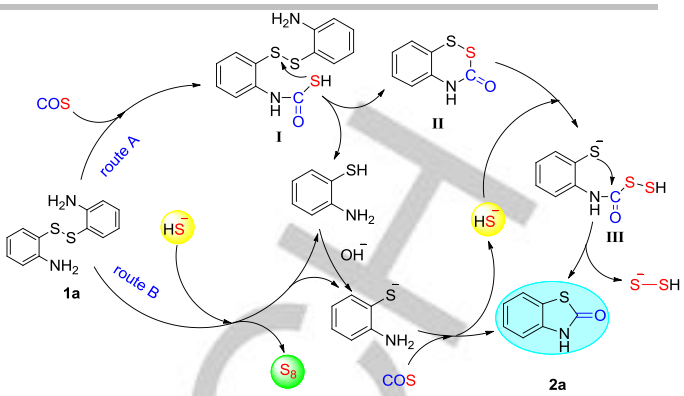
[a] Reaction conditions: **1** (1 mmol) and NaOH (0.3 mmol) were mixed in DMF (1 mL) at 25 °C under COS (0.5 MPa) for 1.5h.

[b] Isolated yield based on substrate **1** after column chromatography.

After obtaining the optimum conditions (Table 1, entry 11), a series of benzothiazolone derivatives were synthesized from diversely substituted 2,2'-disulfanediyldianilines and COS (Table 2). We found that this reaction could tolerate many functional groups such as fluoro, chloro, bromo, trifluoromethyl, benzoyl, methylsulfonyl, methyl and methoxy groups (entries 1 - 10). The disulfides bearing electron-donating or electron-withdrawing groups could provide the corresponding products **2** in excellent yields

under the optimal reaction conditions. The electron-donating groups (entries 8 - 10) on the disulfides produced higher yields of the corresponding products. In contrast, some disulfides with strong electron-withdrawing groups, such as methylsulfonyl (entry 6), could not react with COS completely within 1.5 h, suggesting strong electron-withdrawing groups could inhibit the reaction.

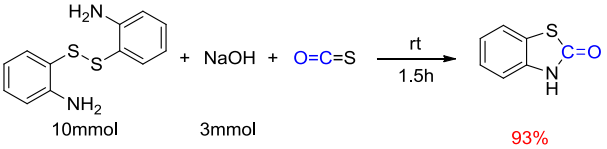
To shed light on the effect of NaOH in the reaction of disulfide and COS, several experiments were explored by ^{1}HNMR (Fig. 3). According to our experimental results, disulfide **1a** (Fig. 3 a and c red rectangle), *o*-aminobenzenethiol (Fig. 3 c and d blue rectangle) and some intermediates (Fig. 3 c blue circle) were found after the interchange reaction between **1a** and H_2S reached dynamic equilibrium, which demonstrated that disulfide could not be converted to *o*-aminobenzenethiol by H_2S completely. To further shed light on the effect of NaOH for cleaving the S-S bond of disulfide, a method was developed to calculate the relative amount of *o*-aminobenzenethiol by ^{1}HNMR (Fig. S2 in ESI). Notably, the total aromatic hydrogen on the benzene ring did not change during the dynamic interchange reaction between disulfide and H_2S. Thus, the relative amount of *o*-aminobenzenethiol could be calculated from the integral area of the aromatic hydrogen signals in ^{1}HNMR spectra, which indicated that 46% yield of *o*-aminobenzenethiol was converted from the dynamic interchange reaction between disulfide and H_2S (Fig. S2a in ESI). Moreover, the integral area ratio of *o*-aminobenzenethiol increased from 46% to 65% according to the ^{1}HNMR spectra (Fig. S2b in ESI) after 0.3 eq. NaOH was added into the reaction solution of **1a** and H_2S, which demonstrated that more disulfide **1a** could be converted into *o*-aminobenzenethiol through the interchange reaction between disulfide and H_2S promoted by NaOH. However, the S-S bond could not be broken when NaOH was mixed directly with the disulfide (Fig. 3 a and b, red rectangle). We were intrigued by the observation that the S-S bond of disulfide could be broken more efficiently in the mixture of disulfide and H_2S in the present of NaOH. Obviously, the base NaOH reacted with H_2S to form S^{2-} or SH^- which could break the S-S bond of disulfide easily according to the mechanism of thiol-disulfide interchange reaction[26]. To explore other functions of NaOH, *o*-aminobenzenethiol instead of disulfide was used to react with COS under the same reaction conditions. Product **2a** could be formed only in 38% yield without NaOH; however, the product **2a** could be obtained in 87% yield after the addition of 0.5eq. NaOH. This experimental result suggested that NaOH could also promote the reaction of COS and *o*-aminobenzenethiol. Furthermore, the reaction of *o*-aminobenzenethiol and excess NaOH were tested by ^{1}HNMR in deuterated methanol (Fig. 3 f), which showed that the chemical shift of *o*-aminobenzenethiol was changed greatly because *o*-aminobenzenethiol might react with NaOH to form *o*-aminobenzenethiolate[27], which easily reacted with COS. Moreover, the ^{1}HNMR chemical shift of *o*-aminobenzenethiol changed gradually with increasing amount of NaOH (Fig. 3 d, e and f, red lines), which indicated that the amount of *o*-aminobenzenethiolate would also increase with increasing amount of NaOH.



Scheme 4. The proposed mechanism for the reaction of disulfide **1a** with COS in the presence of NaOH.

The reaction mechanism of disulfide and COS in the presence of NaOH is proposed based on experimental results of this and previous works[9] (Scheme 4). The amino group of **1a** reacts with COS to generate intermediate **I** which cyclizes intramolecularly to form *o*-aminobenzenethiol and the intermediate **II** (route A). The newly formed *o*-aminobenzenethiol is converted into *o*-aminobenzenethiolate under the alkaline condition, and reacts with COS to form benzothiazolone **2a** and SH^-. Simultaneously, SH^- can break the S-S bond of intermediate **II** to form intermediate **III**, which would cyclize intramolecularly to form benzothiazolone **2a** and multisulfide. After the formation of SH^- and multisulfide, the S-S bond of disulfide **1a** can be efficiently cleaved to form *o*-aminobenzenethiol, followed by the formation of *o*-aminobenzenethiolate and S_8 by a dynamic interchange reaction under the alkaline condition (route B). Eventually, the *o*-aminobenzenethiolate reacts with COS to form the target product **2a**. In conclusion, the reaction of **1a** and COS is initiated by route A which generates SH^- or multisulfide, but benzothiazolone is mainly formed by the domino reaction of **1a** with COS mediated by SH^- or multisulfide through route B. Obviously, NaOH plays a key role through regulating the reaction pH. In this process, the C=O of COS can be efficiently converted into the highly valuable benzothiazolone derivatives and the sulfur atom of COS is converted into sulfur S_8 and sulfide anion by this coupling system under mild condition.

To demonstrate the practical value of this reaction, a gram-scale experiment was conducted by using 2,2′-disulfanediyldianiline **1a** (10 mmol) under optimum conditions (Scheme 5). The crude product was purified by column chromatography and the pure target product was obtained in 93% yield (2803 mg).



Scheme 5 A gram-scale reaction of COS and 1a. Reaction conditions: 2,2'-disulfanediyldianiline (10.0 mmol, 1.0 equiv.), NaOH (3.0 mmol, 0.3 equiv.), COS (0.5 MPa), DMF (10 mL), 25 °C, and stirred in a high

pressure reactor (50 mL) for 1.5 h; the yields of the target product are calculated according to the theoretical amount.

Conclusions

An efficient and highly atomic economy method for preparing benzothiazolone derivatives was developed by a tandem coupling reaction between the disulfide and COS. Benzothiazolone derivatives with various substitution groups were prepared efficiently by reacting *o*-aminophenyldisulfides with COS in the presence of NaOH under mild conditions. This new process provides an efficient and mild method for the preparation of benzothiazolone derivatives and the utilization of COS.

Experimental Section

General Procedures

All reagents were used without any previous purification, which were purchased from Aladdin, AMQUAR and other commercial sources. Most of the reactions were carried out in a high pressure reactor. Column chromatography separations were obtained on silica gel (200–300 mesh). Melting points were measured on XT4A melting point apparatus. The ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained in deuterated DMF, DMSO, MeOH or $CHCl_3$ on an Agilent 500 MHz DD2 spectrometer, which were analyzed using MestReNova software. The FTIR spectra of compounds were recorded using a PerkinElmer FT-IR spectrometer. Low-resolution mass spectra (ESI) were characterized by LCMS-2020 of Shimadzu and high resolution mass spectra (ESI) were obtained by Agilent Technologies LC/MSD TOF.

General procedure for the synthesis of benzothiazolone derivatives (2a–2k)

2,2′-disulfanediyldianiline or its corresponding derivatives (1 mmol), inorganic or organic base (0.3 mmol) and DMF (1 mL) were put into a high pressure reactor (10 mL), and then 0.5 MPa COS (gas purity: 99.99%) was added into the reactor. Most of the substituent disulfides were consumed completely after the reaction mixture was stirred at room temperature for 1.5 h. Then the reaction mixture was extracted with EA (ethyl acetate), and the organic solution was dried by anhydrous $MgSO_4$. The solvent of organic solution was removed under reduced pressure after the $MgSO_4$ was removed by filtration. The crude product was purified by column chromatography through a silica-gel column to afford the byproduct sulfur S_8 eluted by petroleum ether and the desired products eluted by EA and CH_2Cl_2.

The influence of hydrochloric acid, H_2S or NaSH on the reaction of 2,2′-disulfanediyldianiline and COS

2,2′-disulfanediyldianiline (1 mmol), and (0.3 mmol) hydrochloric acid, (0.3 mmol) NaSH or (0.2 MPa) H_2S in DMF (1 mL) were put into a high pressure reactor (10 mL), and then 0.5 MPa COS was charged into the reactor. The post processing of reaction was based on general procedure for the synthesis of benzothiazolone derivatives. All the raw materials were left when the hydrochloric acid or H_2S was added to the reaction of 2,2′-disulfanediyldianiline and COS, which monitored by LC-MS analysis and TLC. The desired products were obtained in 84% yield (254 mg) when (0.3 mmol) NaSH was added into the reaction mixture of 2,2′-disulfanediyldianiline and COS.

The *o*-aminobenzenethiol reacted with COS mediated by NaOH or without NaOH

The *o*-aminobenzenethiol (2 mmol), NaOH (0 mmol or 1 mmol) and DMF (1 mL) were put into a high pressure reactor (10 mL), and then 0.5 MPa COS was charged into the reactor. The reaction condition and post processing according to the general procedure for the synthesis of benzothiazolone derivatives, the desired product was obtained in 38% (114 mg) yield in the absence of NaOH or 87% (263 mg) yield in the presence of NaOH (1.0 mmol).

The reaction process of COS and 2,2′-disulfanediyldianiline detected by LC-MS

2,2′-disulfanediyldianiline (1 mmol), DMF (1 mL) and COS (0.5 MPa) were put into a high pressure reactor (10 mL). The reaction mixture was stirred at room temperature for 20 min and analyzed by LC-MS. The LC-MS results are shown in Fig. 2 (The original spectrometry is shown in Fig. S1).

^{1}HNMR spectra for the reaction of 2,2′-disulfanediyldianiline and H_2S in a high pressure NMR tube.

The 2,2′-disulfanediyldianiline (4 mg) was dissolved in a high pressure NMR tube by deuterated Methanol (0.15 mL), and the ^{1}HNMR spectra of 2,2′-disulfanediyldianiline were obtained. Then the ^{1}HNMR spectra of mixing 2,2′-disulfanediyldianiline and H_2S were acquired after H_2S (0.7 MPa) was charged into the high pressure NMR tube, which were shown in Fig. 2 c and S2a in ESI.

^{1}HNMR spectra for the mixture of 2,2′-disulfanediyldianiline, NaOH and H_2S

The 2,2′-disulfanediyldianiline (8 mg) and NaOH (4 mg) was dissolved in 0.15 mL of deuterated Methanol in a high pressure NMR tube, and the ^{1}HNMR spectra for the mixture of 2,2′-disulfanediyldianiline and NaOH were acquired. The ^{1}HNMR spectra for the mixture solution of 2,2′-disulfanediyldianiline, NaOH and H_2S were acquired after H_2S (0.7 MPa) was added into the mixture of 2,2′-disulfanediyldianiline and NaOH. The above ^{1}HNMR spectra were showed in Fig. 2 e and S2b in ESI.

^{1}HNMR spectra for the mixture of *o*-aminobenzenethiol and NaOH

The *o*-aminobenzenethiol (7 μL) was added in 0.5 mL of deuterated Methanol in a NMR tube, and the ^{1}HNMR spectra of *o*-aminobenzenethiol were obtained. Then NaOH (15 mg) was added into the NMR tube, and the ^{1}HNMR spectra of mixing *o*-aminobenzenethiol and NaOH were acquired. The above ^{1}HNMR spectra were showed in Fig. 2 f.

Spectral Data:

Benzothiazolone 2a
This is a known compound. 2,2′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 285 mg, 94% yield. Mp: 138-140 °C; MS (EI): m/z 151.0 [C_7H_5NOS], calcd [M] 151.0. ^{1}H NMR (500 MHz, $CDCl_3$, 25℃): δ (ppm) = 9.85 (brs, 1 H, NH), 7.41 (d, 1H, *J* =7 Hz, CHarom), 7.30-7.26 (m, 1 H, CHarom), 7.17-7.14 (m, 2 H, CHarom).; ^{13}C NMR (125 MHz, $CDCl_3$, 25°C): δ (ppm) = 172.81, 135.26, 126.51, 123.92, 123.27, 122.56, 111.67. IR (ATR): ṽ= 3310, 3155, 3105, 2884, 1659, 1465, 1218, 1123, 736, 701 cm^{-1}. The NMR spectra are in agreement with previously reported data[18a].

6-chlorobenzo[d]thiazol-2(3H)-one 2b
This is a known compound. 2,2′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 297 mg, 80% yield. Mp: 213-215 °C; MS (EI): m/z 185.0 [C_7H_4ClNOS], calcd [M] 185.1. ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = 12.02 (brs, 1H, NH), 7.75 (s, 1H, CHarom), 7.32 (d, 1H, *J* =8.5, CHarom), 7.10 (d, 1H, *J* =8.5 Hz, CHarom); ^{13}C NMR, (125 MHz, DMSO-d_6, 25°C): δ (ppm) = 169.73, 135.24, 126.43, 125.15, 122.36, 122.70. IR (ATR): ṽ= 3676, 2989, 2902, 1671, 1597, 1466, 1210, 1054, 812, 800, 716, 651, 566 cm^{-1}. The NMR spectra are in agreement with previously reported data[28].

6-bromobenzo[d]thiazol-2(3H)-one 2c
This is a known compound. 2,2′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 413mg, 90% yield. Mp: 230-232 °C; MS (EI): m/z 228.9 [C_7H_4BrNOS], calcd [M] 228.9. ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = 12.03 (brs, 1H,NH), 7.86 (d, 1H, J = 2.0 Hz, CHarom), 7.44 (dd, 1H, J_1 =8.5, J_2 =2.0 Hz, CHarom), 7.06 (d, 1H, J = 8.5 Hz, CHarom); ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ (ppm) = 169.66, 135.60, 129.18, 125.56, 125.02, 113.96, 113.13. IR (ATR): ṽ= 3134, 3009, 1668, 1597, 1460, 1209, 809, 713, 647, 540 cm^{-1}. The NMR spectra are in agreement with previously reported data[29].

5-chlorobenzo[d]thiazol-2(3H)-one 2d
This is a known compound[30]. 6,6′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 324mg, 87% yield. Mp: 238-239 °C; MS (EI): m/z 185.0 [C_7H_4ClNOS], calcd [M] 184.9. ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = 12.04 (brs, 1H,NH), 7.61 (dd, 1H, J_1 =8.5, J_2 =1.5, CHarom), 7.19 (dd, 1H, J_1 =8.5, J_2 =2.5 Hz, CHarom), 7.12 (d, 1H, *J* =2.0 Hz, CHarom); ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ (ppm) = 170.07, 137.45, 130.79, 124.25, 122.42, 122.19, 111.20. IR (ATR): ṽ= 3666, 2989, 2902, 1672, 1577, 1408, 1302, 1078, 843, 793, 746, 718, 648, 578 cm^{-1}.

4-fluorobenzo[d]thiazol-2(3H)-one 2e
This is a known compound. 6,6′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 294mg, 87% yield. Mp: 173-175 °C; MS (EI): m/z 169.0 [C_7H_4FNOS], calcd [M] 169.0. ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = 12.40 (brs, 1H, NH), 7.42 (d, 1H, *J* =7.5 Hz, CHarom), 7.12-7.22 (m, 2H, CHarom); ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ (ppm) = 169.77, 147.18 (d, 1C, *J* =243.8 Hz), 125.64 (d, 1C, *J* =3.8 Hz), 124.40 (d, 1C, *J* =15.0 Hz), 123.14 (d, 1C, *J* =6.3 Hz), 118.73 (d, 1C, *J* =3.8 Hz), 112.79 (d, 1C, *J* =16.3 Hz) ; ^{19}F NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = -128.46 (brs, 1F). IR (ATR): ṽ= 3673, 2989, 2902, 1670, 1631, 1485, 1394, 1200, 1076, 1066, 1053, 764, 702 cm^{-1}. The NMR spectra are in agreement with previously reported data[28, 31].

5-(trifluoromethyl)benzo[d]thiazol-2(3H)-one 2f
This is a known compound. 6,6′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 374mg, 85% yield. Mp: 222-223 °C; ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = 12.23 (brs, 1H, NH), 7.85 (d, 1H, *J* =8.5 Hz, CHarom), 7.48 (d, 1H, *J*=8.0 Hz, CHarom), 7.33 (s, 1H, CHarom); ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ (ppm) = 169.75, 136.75, 128.42 (d, 1C, *J* =1.25 Hz), 126.94 (q, 1C, *J* =32.5 Hz), 124.04 (q, 1C, *J* =270.0 Hz), 123.78, 119.00 (q, 1C, *J* =3.8 Hz), 107.60 (q, 1C, *J* =3.8 Hz) ; ^{19}F NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = -60.77 (brs, 3F). IR (ATR): ṽ= 3676, 2991, 1689, 1640, 1333, 1164, 1148, 1115, 1154, 887, 771 cm^{-1}. HRMS (ESI): calcd for $C_8H_5ONF_3S$ [M + H]$^+$: 220.00385; found: 220.00325.

6-(methylsulfonyl)benzo[d]thiazol-2(3H)-one 2g
This is a known compound. 6,6′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1),, yield: 299mg, 65% yield. Mp: 242-243 °C; ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = 11.73 (brs, 1H,NH), 7.36 (s, 1H, CHarom), 7.08 (d, 1H, *J* = 8.5 Hz, CHarom), 7.00 (d, 1H, *J* = 8.0 Hz, CHarom), 2.30 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ (ppm) = 170.26, 140.44, 134.74, 125.71, 124.30, 122.25, 111.59, 43.95. IR (ATR): ṽ= 3667, 2989, 2902, 1693, 1405, 1291, 1261, 1143, 1131, 1098, 1077, 1061, 784 cm^{-1}. HRMS (ESI): calcd for $C_8H_8O_3NS_2$ [M + H]$^+$: 229.99401; found: 229.99358.

5-benzoylbenzo[d]thiazol-2(3H)-one 2h
This is a known compound. 6,6′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 432mg, 85% yield. Mp: 192-194 °C; MS (EI): m/z 255.95 [$C_{14}H_9NO_2S$], calcd [M] 255.3. ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) 12.09 (brs, 1 H, NH), 7.78-7.75 (m, 3 H, CHarom), 7.70-7.67 (m, 1 H, CHarom), 7.57 (t, 2 H, J =2.5 Hz, CHarom) , 7.51-7.49 (m, 1 H, CHarom), 7.44 (d, *J* = 1.5 Hz, 1 H, CHarom); ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ (ppm) = 194.92, 169.67, 137.08, 136.43, 134.96, 132.60, 129.51, 128.97, 128.55, 124.09, 122.80, 112.19. IR (ATR): ṽ= 3673, 2973, 2902, 1718, 1649, 1604, 1285, 1069, 701 cm^{-1}. The NMR spectra are in agreement with previously reported data[31].

4-methylbenzo[d]thiazol-2(3H)-one 2i
This is a known compound. 6,6′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 281mg, 85% yield. Mp: 210-212 °C; ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = 11.73 (brs, 1H, NH), 7.37 (d, 1H, J =7.5Hz, CHarom), 7.09 (d, 1H, J =7.5Hz, CHarom), 7.03 (t, 1H, J =7.5 Hz, CHarom), 2.32 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ (ppm) = 170.42, 135.03, 127.57, 122.84, 122.47, 121.30, 119.98, 17.44. IR (ATR): ṽ= 3679, 2988, 2902, 1665, 1408, 1381, 1074 cm^{-1}. HRMS (ESI): calcd for C_8H_8ONS [M + H]$^+$: 166.03211; found: 166.03181.

6-methoxybenzo[d]thiazol-2(3H)-one 2j
This is a known compound. 6,6′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 336mg, 93% yield. Mp: 160-161 °C; MS (EI): m/z 181.0 [C8H7NO2S], calcd [M] 180.9. ^{1}H NMR (500 MHz, DMSO-d6, 25°C): δ (ppm) = 11.66 (brs, 1H), 7.23 (d, 1H, *J* =2.5 Hz, CHarom), 7.02 (d, 1H, *J* =9.0 Hz, CHarom), 6.86 (dd, 1H, J_1 = 8.5 Hz, J_2 =2.5 Hz, CHarom), 3.73 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, DMSO-d6, 25°C): δ (ppm) = 169.74, 155.22, 129.87, 124.32, 113.22, 112.10, 107.74, 55.59. IR (ATR): ṽ= 3667, 2989, 2902, 1670, 1409, 1063, 791 cm^{-1}. The NMR spectra are in agreement with previously reported data[28].

6-methylbenzo[d]thiazol-2(3H)-one 2k
This is a known compound. 2,2′-Disulfanediyldianiline reacted with COS under the general procedure to produce a white solid. The crude product was eluted by EA and CH_2Cl_2 (20:1), yield: 295mg, 89% yield. Mp: 171-172 °C; MS (EI): m/z 165.0 [C_8H_7NOS], calcd [M] 165.0. ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ (ppm) = 11.73 (brs, 1H, NH), 7.36 (s, 1H, CHarom), 7.08 (d, 1H, *J* = 8.5 Hz, CHarom), 7.00 (d, 1H, *J* = 8 Hz, CHarom), 2.30 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ (ppm) = 169.87, 133.94, 131.77, 127.07, 123.22, 122.61, 111.18, 20.60. IR (ATR): ṽ= 3145, 3014, 2913, 1656, 1485, 1449, 1393, 1285, 1230, 1195, 1063, 1042, 800 cm^{-1}. The NMR spectra are in agreement with previously reported data[29].

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Keywords: synthesis design • domino reaction • COS • benzothiazolone derivatives • reaction mechanism

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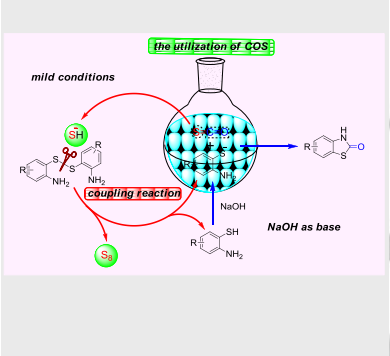
An efficient method for preparing benzothiazolone derivatives was developed by a domino coupling reaction between the disulfide and COS in the present of NaOH. Notably, the C=O of COS was converted into benzothiazolone by carbonylation reaction and the sulfur of COS was transformed into sulfur and sulfide after cleaving the S-S bond under mild conditions. This efficient synthetic methodology could provide a promising process for the utilization of COS.



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Efficient synthesis of benzothiazolone derivatives by a domino reaction of disulfide and COS under mild conditions.

Key Topic: Heterocyclic synthesis