Taylor & Francis
Taylor & Francis Group

Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

Metal sulfide: An efficient promoter for the synthesis of 2-mercaptobenzothiazoles from 2-haloanilines and carbon disulfide

Tianmiao Zhang, Weijing Qin, Ning Zhu, Limin Han, Liubo Wang & Hailong Hong

To cite this article: Tianmiao Zhang, Weijing Qin, Ning Zhu, Limin Han, Liubo Wang & Hailong Hong (2017): Metal sulfide: An efficient promoter for the synthesis of 2-mercaptobenzothiazoles from 2-haloanilines and carbon disulfide, Synthetic Communications, DOI: 10.1080/00397911.2017.1356927

To link to this article: http://dx.doi.org/10.1080/00397911.2017.1356927

Metal sulfide: An efficient promoter for the synthesis of 2-mercaptobenzothiazoles from 2-haloanilines and carbon disulfide

Tianmiao Zhang

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, P. R. China

Weijing Qin

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, P. R. China

Ning Zhu

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, P. R. China

Limin Han*

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, P. R. China

Liubo Wang

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, P. R. China

Hailong Hong

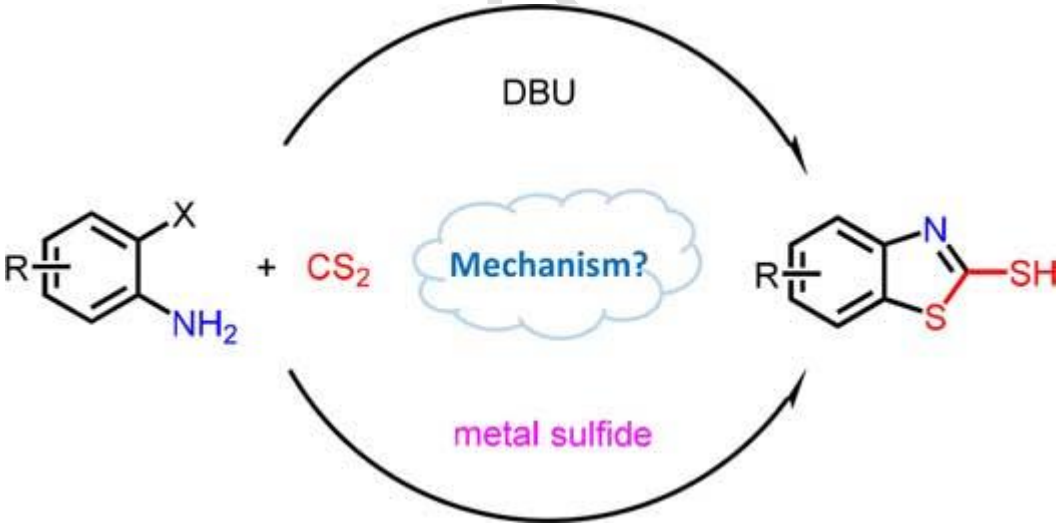
Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, P. R. China

Address correspondence to Limin Han. E-mail: hanlimin_442@hotmail.com

ABSTRACT

A convenient method has been developed for the preparation of a variety of 2-mercaptobenzothiazoles from 2-haloanilines and CS_2 mediated by metal sulfide. In this reaction, 2-haloanilines reacted with CS_2in the presence of $Na_2S \cdot 9H_2O$ to form 2-mercaptobenzothiazoles. $Na_2S \cdot 9H_2O$ functioned both as an activator of CS_2 and as a base. Furthermore, NMR analysis was used to identify the different reaction mechanisms of 2-haloanilines and CS_2 mediated by Na_2S or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which demonstrated that Na_2S interacted only with CS_2, while DBU reacted with both 2-iodoaniline and CS_2.

GRAPHICAL ABSTRACT



KEYWORDS: 2-haloanilines, 2-mercaptobenzothiazoles, carbon disulfide, metal sulfide, reaction mechanism

Introduction

2-Mercaptobenzothiazole derivatives (MBTs), which were prepared for the first time in 1887 by Hofmann,[1] have been widely studied for industrial use and medicinal researches (**Figure 1**). In industry, MBTs (**a** and **b**) can be used as corrosion inhibitors of coatings,[2] a fungicide and bactericide in leather processing,[3] and a vulcanization accelerator in the production of rubber[4, 5] and sulfurized carbon materials.[6] In medicinal research, MBTs have frequently been synthesized as important intermediates for preparing bioactive compounds[7] such as dual antagonists for the human CCR1 and CCR3 receptors (**c**),[8] heat shock protein-90 inhibitors (**d**),[9, 10] and protoporphyrinogen IX oxidase inhibitors (**e**).[11] Moreover, the tripodal benzothiazole derivative (**f**) has been developed as a sensitive chemosensor for the determination of Ba^{2+}.[12] Due to the significant application of 2-thio-substituted benzothiazoles, many research groups are exploring various efficient protocols for preparing MBTs (Scheme 1).

Traditionally, MBTs are obtained directly from the reaction of aniline, carbon disulfide and sulfur at high temperatures and pressures (route a), which is used in industry practice.[13, 14] MBTs are also prepared by the reaction of 2-aminothiophenol with carbon disulfide in the presence of organic/inorganic base[15, 16] or ZnO/Al_2O_3 catalyst[17] (route b). However, 2-aminothiophenols are readily oxidized to their corresponding disulfide and not always easily available. Thus, 2,2'-

disulfanediyldianiline is used as the staring material to react with carbon disulfide to prepare MBTs in our previously reported method (route c).[18], [19] Moreover, MBTs are prepared by the reaction of 2-chlorobenzothiazole with $Na_2S_2O_3$,[20] 1,2-ethanedithiol[21] or thiourea[22–24] (route d). But the raw material 2-chlorobenzothiazole was usually prepared from MBT, which suggests this methodology could not be used in practice. MBT could also be synthesized through the one-step reaction from 2-chloronitrobenzenes and carbon disulfide mediated by NaHS[25] or Na_2S /S[26] (route e). Recently, it is reported that 2-haloanilines (2-F, Cl or Br, route f) could react with potassium O-ethyl dithiocarbonate to produce MBTs under heat[27] or microwave irradiation.[28] However, the reactions of 2-iodoanilines and potassium O-ethyl dithiocarbonate are not reported. Thus, our group successfully has synthesized MBTs by the reaction of 2-iodoanilines with potassium O-ethyl dithiocarbonate catalyzed via copper[29] or iron.[30] Furthermore MBTs could be prepared by a three-component reaction via 2-iodoanilines, carbon disulfide and amines[31] or 2-iodoanilines, isocyanide and potassium sulfide.[32] Another way to prepare MBTs is the reaction of 2-haloanilines with carbon disulfide via recyclable copper ferrite ($CuFe_2O_4$) nanoparticles[33] or sodium hydride.[34] Xi's group successfully prepared a variety of MBTs by the addition of DBU to promote the tandem reaction of 2-haloanilines and carbon disulfide in the absence of any catalyst.[35] However, the underlying mechanism of DBU promoted tandem reaction of 2-haloanilines and carbon disulfide is still unclear. Encouraged by this highly efficient synthetic method, we investigated other low-cost and more easily available reagent to replace DBU in the synthesis of 2-mercaptobenzothiazoles.

$Na_2S \cdot 9H_2O$ is a widely available inorganic base, which could react with carbon disulfide to form sodium thiocarbonate (Na_2CS_3).[36], [37] Therefore, $Na_2S \cdot 9H_2O$ was used as an efficient promoter to synthesize 2-mercaptobenzothiazoles from 2-haloanilines and carbon disulfide in this work. Furthermore, the different reaction mechanisms of 2-haloanilines and carbon disulfide promoted by $Na_2S \cdot 9H_2O$ or DBU were also discussed.

Results and Discussion

Initially, we used 2-iodoaniline **1a** and carbon disulfide as the starting materials to prepare 2-mercaptobenzothiazole in DMF. However, little 2-mercaptobenzothiazole was obtained after the mixture solution was stirred for 12h at 110 °C (**Table 1**, entry 1). When 0.5 equiv. sodium sulfide was added, the yield of **2a** was improved significantly (entry 2). The experimental results demonstrated that sodium sulfide was important in the reaction of **1a** and carbon disulfide. Thus, sodium sulfide was selected as a promoter for the reaction of **1a** and carbon disulfide. The yield of **2a** increased with increasing amount of Na_2S (entries 3-5) and reached 76% when 2 equiv. Na_2S was used. Further increases in the amount of Na_2S did not affect the yield of **2a** notably (entries 5-6). Additionally, more CS_2 needed to be added to the reaction mixture due to the low boiling point and high-volatility of CS_2. When the amount of CS_2 was 5 equiv. to **1a**, the highest yield of **2a** was obtained (entries 5, 7). Therefore, the optimal feeding ratio of **1a**, sodium sulfide and carbon disulfide was 1: 2: 5. Moreover, we found that the higher or lower reaction temperature than 110 °C considerably reduced the yield of product **2a** (entries 5, 8-10). After investigating the

effect of solvents, DMF was found to give the highest yield compared with glycol, 1,4-dioxane or toluene (entries 11-13). We speculated the protic solvent glycol weakened the nucleophilicity of sulfur and 1,4-dioxane or toluene reduced the solubility of sodium sulfide, which reduced the yield of **2a**. Furthermore, to test the efficiency of other metal sulfides in this reaction process, we found that K_2S and NaHS could also promote the reaction of **1a** and CS_2 to form **2a** in moderate yields (entries 14-15), which demonstrated that most metal sulfide could promote this reaction smoothly. Finally, the optimal conditions for this transformation were identified as **1a**, Na_2S (2 equiv.) and CS_2 (5 equiv.) in DMF at 110 °C.

To demonstrate the generality of this approach for the synthesis of 2-mercaptobenzothiazoles, various 2-haloaniline derivatives were used to react with CS_2 at 110 °C in DMF, which are summarized in **Table 2**. The results demonstrated that 2-F, or 2-Br substituted anilines could also produce the product **2a** (entries 2-3). Unfortunately, 2-chloroaniline could not produce the corresponding product (entry 4). Significantly, under the same reaction conditions, 2-iodoanilines bearing a weaker electron-withdrawing (3-Cl, 4-Cl, 4-F) or weaker electron-donating group (4-methyl) afforded better yields than strong electron-withdrawing (4-cyano, 4-trifluoromethyl) or strong electron-donating group (4-methoxyl) (entries 5-11). It is noteworthy that 2-bromo-4-chloroaniline reacted with CS_2 and produced the target product **2c** in an excellent yield (entry 12).

To verify how Na_2S promoted the reaction of 2-iodoanilines with CS_2, some control experiments were carried out. Firstly, we knew that 2-iodoaniline could not react with CS_2in the absence of Na_2S (**Table 1**, entry 1; Scheme 2a), which demonstrated that Na_2S was important to promote this reaction. Secondly, our experimental result indicated that 2-iodoaniline could not react with Na_2S directly at 110 °C to form the intermediate 2-aminobenzothiol or sodium 2-aminobenzothiolate, which indicated that Na_2S reacted with CS_2 (Scheme 2b). Therefore, the mixture solution of CS_2 and Na_2S in DMF was analyzed by ^{13}C NMR, and a new peak (214.6ppm) was present in the ^{13}C NMR spectrum compared to the ^{13}C NMR spectrum of CS_2 (**Figure 2a,b**). The ^{13}C NMR experiment showed that CS_2 might react with Na_2S to form sodium thiocarbonate, which was accordant with the corresponding report (Scheme 2c).[36]

In order to map out the different reaction mechanisms of 2-iodoaniline **1a** and CS_2 mediated by Na_2S or DBU,[35] NMR was employed to analyze the interactions between the raw materials and DBU or Na_2S . The ^1H NMR spectrum of **1a** showed the NH_2 proton signal was moved from δ = 5.28 to 5.32ppm after one equivalent (relative to **1a**) of DBU was added into the deuterated DMF solution of 2-iodoaniline (**Figure 3a,b**). Moreover, the ^1H NMR spectrum of DBU in the mixture solution of DBU and **1a** was also changed compared with the pure DBU (Figure S1 in SI), which further indicated some interaction existed between DBU and 2-iodoaniline. In contrast, no interaction between Na_2S and 2-iodoaniline was observed in the ^1H NMR spectrum of the mixture of Na_2S and 2-iodoaniline (**Figure 3a,c**). Thus, the ^1H NMR spectra

demonstrated that DBU could react with 2-iodoaniline, while Na_2S did not react with 2-iodoaniline directly. However, there was no new peak in the ^{13}C NMR spectrum of the mixture solution of CS_2 and DBU (Scheme 2c). It is well known that CS_2 is closely related to CO_2 molecule and exhibits similar reactivity.[38], [39] Considering bicyclic amidines (DBU, TBD, and DBN) are able to activate the CO_2 molecule and have been used as catalysts in reactions involving the use of CO_2,[38], [40] we speculated that DBU could still activate CS_2. A literature report also did not find a new carbon peak in the ^{13}C NMR spectrum of the TBD-CS_2 mixture solution.[38] Therefore, these results indicated that DBU showed interactions with both 2-iodoaniline and CS_2, while Na_2S only interacted with CS_2.

To investigate the mechanism of the formation of 2-mercaptobenzothiazole after $Na_2S \cdot 9H_2O$ reacted with CS_2 to form sodium thiocarbonate, a series of experiments were carried out. The three component reaction of $Na_2S \cdot 9H_2O$, CS_2 and iodobenzene or aniline were carried out to verify the site-selective reaction of 2-iodoaniline (Scheme 2d,e). However, no new benzo-containing product was detected by TLC or LCMS. Hence, the reaction mechanism was proposed as following (Scheme 3). $Na_2S \cdot 9H_2O$ reacts with CS_2 to form sodium thiocarbonate **3**, and **3** reacts with **1** via nucleophilic substitution and simultaneous nucleophilic addtion to form the cyclic intermediate **4**. Furthermore, the reduced electron density of 2-haloanilines would promote the nucleophilic substitution reaction of halo group with sodium thiocarbonate **3** while prevent the nucleophilic addtion reaction of the amino group with sodium thiocarbonate **3**. The increased

electron density of 2-haloanilines would show the opposite effects. Therefore, the simultaneous reactions of amino and halo group with sodium thiocarbonate **3** would take place smoothly when the electron density of benzene ring is in a suitable range. Additionally, these reactions of 2-haloanilines would be inhibited when the electron density is shifted out of the suitable range by the strong electron-withdrawing or electron-donating group in 2-iodoanilines (**Table 2**) and the yields of target products decreased. Finally, the intermediate **4** is converted into product **2** after HS^- is eliminated. Based on the proposed reaction mechanism, Na_2S is converted into NaHS and Na_2S acts not only as an activator of CS_2 but also as a base.

Conclusions

In conclusion, we have developed an efficient reaction of 2-haloanilines, $Na_2S \cdot 9H_2O$, and CS_2 at 110 °C for the synthesis of 2-mercaptobenzothiazoles in one-pot procedure. In this system, $Na_2S \cdot 9H_2O$ acted not only as the CS_2 activator but also as a base. The protocol used simple and readily available starting materials, eliminated the need for any metal catalysts, and afforded the corresponding 2-mercaptobenzothiazoles under mild conditions in moderate to good yields.

Experimental

General procedure for synthesis of benzothiazole derivatives (2a-2i)

A sealed tube (50mL) was charged with 2-haloaniline **1a** (2mmol), CS_2 (10mmol), Na_2S (4mmol) and DMF (2mL) at room temperature under an argon gas atmosphere and the tube was

flushed with argon for three times and sealed. Then the mixture was stirred electromagnetically at 110 °C for 12hours . The reaction process was monitored by TLC on silica gel. After the reaction was completed, the reaction mixture was cooled to room temperature, 2mL HCl (3mol /L) was added and stirred for 30minutes . Then the reaction mixture solution was extracted by dichloromethane (3*20mL). Subsequently, the combined organic solution were dried by anhydrous magnesium sulfate and concentrated. The residue was purified by silica gel colum chromatography (eluent: petroleum ether / ethyl acetate) give the corresponding pure product **2a**.

Procedure for the reaction of CS2 with Na2S or DBU in a NMR tube

The CS_2 (10 μL) and Na_2S (30mg) or DBU(18 μL) dissolved in 0.6mL DMF in a NMR tube were detected by ^{13}C NMR at 25 °C, and the pure CS_2 and DBU were also detected respectively by ^{13}C NMR in 0.6mL DMF. The ^{13}C NMR results are shown in **Figure 2**.

Procedure for the reaction of 2-iodoaniline with DBU or Na2S in a NMR tube

The 2-iodoaniline (10.0mg) was dissolved with 0.5mL deuterated DMF in a NMR tube, which was detected by ^{1}H NMR at 25 °C. Then the DBU (18 μL) or Na_2S (30mg) was added into the NMR tube and then detected by ^{1}H NMR at 25 ºC. The ^{1}H NMR results are shown in **Figure 3** and Figure S1.

Acknowledgements

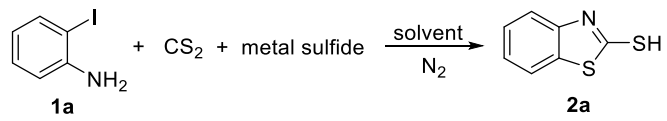
This work was supported by the National Natural Science Foundation of China (21362019), Natural Science Foundation of Inner Mongolia Autonomous Region of China (2016MS0207) and CAS "Light of West China" Program.

References

[1] Hofmann, A. *Chem. Ber.* **1887**, *20*, 1788–1797.
[2] Plawecka, M.; Snihirova, D.; Martins, B.; et al. *Electrochim. Acta* **2014**, *140*, 282–293.
[3] Ramadas, K.; Janarthanan, N. *Synth. Commun.* **1999**, *29*, 1003–1007.
[4] Aprem, A. S.; Joseph, K.; Thomas, S. *Rubber Chem. Technol.* **2005**, *78*, 458–488.
[5] Heideman, G.; Datta, R. N.; Noordermeer, J. W. M.; et al. *Rubber Chem. Technol.* **2004**, *77*, 512–541.
[6] Chen, H.; Wang, C.; Hu, C.; et al. *J. Mater. Chem.* **2015**, *3*, 1392–1395.
[7] Azam, M. A.; Suresh, B. *Sci. Pharm.* **2012**, *80*, 789–823.
[8] Naya, A.; Kobayashi, K.; Ishikawa, M.; et al. *Chem. Pharm. Bull.* **2003**, *51*, 697–701.
[9] Murru, S.; Mondal, P.; Yella, R.; et al. *Eur. J. Org. Chem.* **2009**, 5406–5413.
[10] He, G.; Huang, Y.; Tong, Y.; et al. *Tetrahedron Lett.* **2013**, *54*, 5318–5321.
[11] Zuo, Y.; Yang, S.-G.; Jiang, L.-L.; et al. *Biorg. Med. Chem.* **2012**, *20*, 296–304.
[12] Wu, F. L. M.; Hussein, W. P.; Ross, B. et al. *Curr. Org. Chem.* **2012**, *16*, 1555–1580.
[13] Sebrell, L.; Boord, C. *J. Am. Chem. Soc.* **1923**, *45*, 2390–2399.
[14] Galliford, C. V.; Voronin, K.; Hesk, D.; et al. *J. Labelled Compd. Radiopharm.* **2011**, *54*, 229–232.
[15] Harizi, A.; Romdhane, A.; Mighri, Z. *Tetrahedron Lett.* **2000**, *41*, 5833–5835.
[16] Samanta, S.; Lim, T. L.; Lam, Y. *ChemMedChem* **2013**, *8*, 994–1001.
[17] Ballabeni, M.; Ballini, R.; Bigi, F.; et al. *J. Org. Chem.* **1999**, *64*, 1029–1032.
[18] Zhu, N.; Zhang, F.; Liu, G. *J. Comb. Chem.* **2010**, *12*, 531–540.
[19] Lou, C.; Zhu, N.; Fan, R.; et al. *Green Chem.* **2017**, *19*, 1102–1108.
[20] Foye, W. O.; Abood, N.; Kauffman, J. M.; et al. *Phosphorus, Sulfur Silicon Relat. Elem.* **1980**, *8*, 205–207.
[21] Liu, Y.; Kim, J.; Seo, H.; et al. *Adv. Synth. Catal.* **2015**, *357*, 2205–2212.
[22] Prouillac, C.; Vicendo, P.; Garrigues, J. C.; et al. *Free Radical Biol. Med.* **2009**, *46*, 1139–1148.
[23] Cressier, D.; Prouillac, C.; Hernandez, P.; et al. *Biorg. Med. Chem.* **2009**, *17*, 5275–5284.
[24] Watt, G. W. *J. Org. Chem.* **1939**, *4*, 436–441.
[25] Teppema, J.; Sebrell, L. B.; *J. Am. Chem. Soc.*, **1927**, 1748–1758.
[26] Gatard, S.; Blanchard, S.; Schollhorn, B.; et al. *Chem. Eur. J.* **2010**, *16*, 8390–8399.

[27] Zhu, L.; Zhang, M. B. *J. Org. Chem.* **2004**, *69*, 7371–7374.
[28] Huang, W.; Tan, Y.; Ding, M. W.; et al. *Synth. Commun.* **2007**, *37*, 369–376.
[29] Liu, L.; Zhu, N.; Gao, M.; et al. *Phosphorus, Sulfur Silicon Relat. Elem.* **2016**, *191*, 699–701.
[30] Gao, M.; Lou, C. Q.; Zhu, N.; et al. *Synth. Commun.* **2015**, *45*, 2378–2385.
[31] Shi, L.; Liu, X. Q.; Zhang, H.; et al. *J. Org. Chem.* **2011**, *76*, 4200–4204.
[32] Dang, P.; Zeng, W. L.; Liang, Y. *Org. Lett.* **2015**, *17*, 34–37.
[33] Satish, G.; Reddy, K. H. V.; Ramesh, K.; et al. *Eur. J. Chem.* **2014**, *5*, 291–295.
[34] Easmon, J.; Heinisch, G.; Hofmann, J.; et al. *Eur. J. Med. Chem.* **1997**, *32*, 397–408.
[35] Wang, F.; Cai, S.; Wang, Z.; et al. *Org. Lett.* **2011**, *13*, 3202–3205.
[36] William, E.; Messer, C. Conn., US Patent 2161741, 1937.
[37] Stueber, D.; Patterson, D.; Mayne, C. L.; et al. *Inorg. Chem.* **2001**, *40*, 1902–1911.
[38] Von Wolff, N.; Villiers, C.; Thuery, P.; et al. *Eur. J. Org. Chem.* **2016**, 676–686.
[39] Yu, T.; Cristiano, R.; Weiss, R. G. *Chem. Soc. Rev.* **2010**, *39*, 1435–1447.
[40] Perez, E. R.; Santos, R. H. A.; Gambardella, M. T. P.; et al. *J. Org. Chem.* **2004**, *69*, 8005–8011.

Table 1. Optimization of the reaction conditions[a].



1a 2a

Entry	Temp. (°C)	CS_2 (equiv.)	$Na_2S \cdot 9H_2O$ (equiv.)	Solvent	Yield of **2a** (%)[b]
1	110	5	–	DMF	5
2	110	5	0.5	DMF	53
3	110	5	1.0	DMF	62
4	110	5	1.5	DMF	65
5	110	5	2.0	DMF	76
6	110	5	2.5	DMF	78
7	110	4	2.0	DMF	55
8	120	5	2.0	DMF	58
9	100	5	2.0	DMF	67
10	90	5	2.0	DMF	43
11	110	5	2.0	1,4-dioxane	NR[c]

12	110	5	2.0	toluene	NR[c]
13	110	5	2.0	glycol	17
14[d]	110	5	2.0	DMF	58
15[e]	110	5	2.0	DMF	55

[a]The reactions were performed in a sealed tube with **1a** (0.5 mmol), carbon disulfide, and $Na_2S \cdot 9H_2O$ in solvent (2 mL) for 12 h.

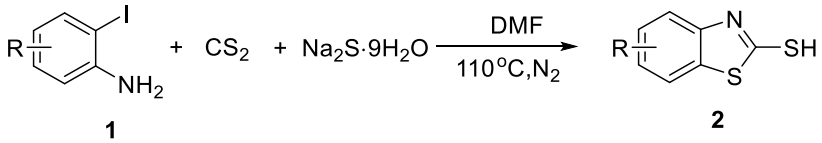
[b]Isolated yields.

[c]NR stand for no reaction.

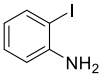
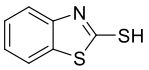
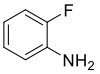
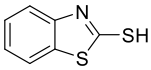
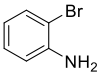
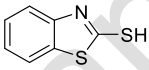
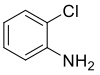
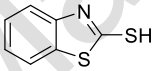
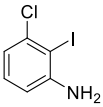
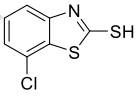
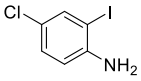
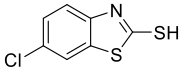
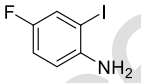
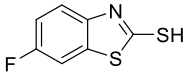
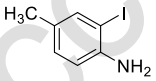
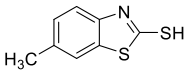
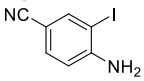
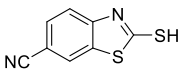
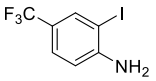
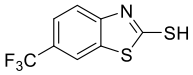
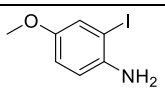
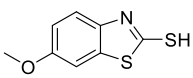
[d]K_2S was used to replace Na_2S .

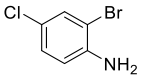
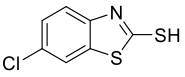
[e]NaHS was used to replace Na_2S .

Table 2. Synthesis of various 2-mercaptobenzothiazoles.<TS: Please take care of images in table.>



1 2

Entry	Substrate 1		Time(h)	Product		Yield(%)[a]
1		**1a**	12		**2a**	76
2		**1b**	12		**2a**	51
3		**1c**	12		**2a**	37
4		**1d**	12		**2a**	-
5		**1e**	12		**2b**	70
6		**1f**	12		**2c**	82
7		**1g**	12		**2d**	72
8		**1h**	7		**2e**	94
9		**1i**	12		**2f**	45
10		**1j**	15		**2g**	27
11		**1k**	12		**2h**	40

12		**1l**	15		**2c**	96

[a]Isolated yields.

Figure 1. Structures of representative 2-mercaptobenzothiazole derivatives.

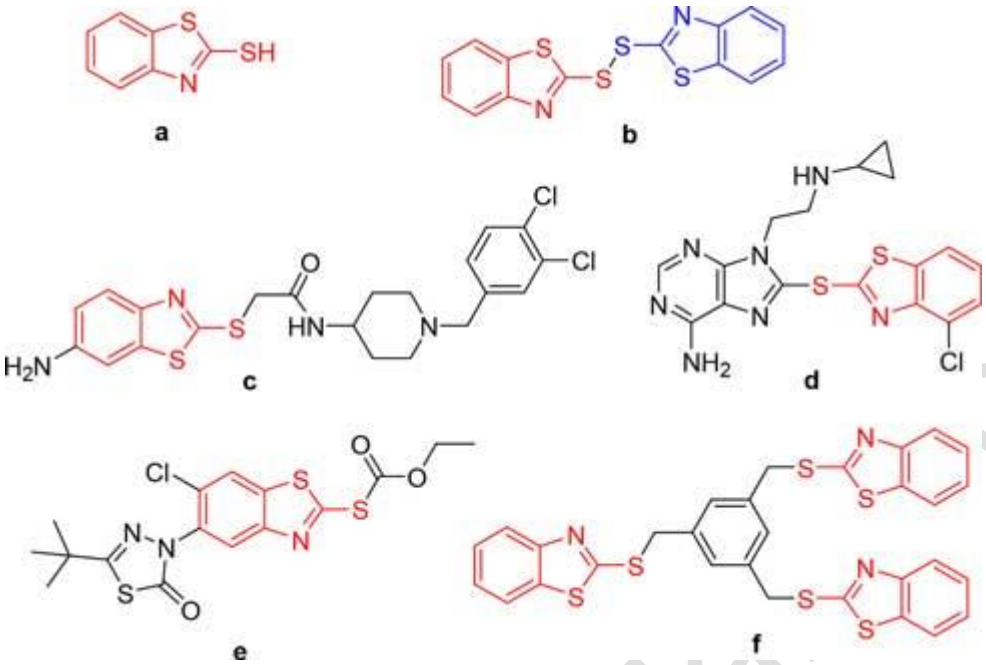


Figure 2. ^{13}C NMR spectra of (a) CS_2in DMF; (b) CS_2 and Na_2S in DMF; (c) CS_2 and DBU in DMF.

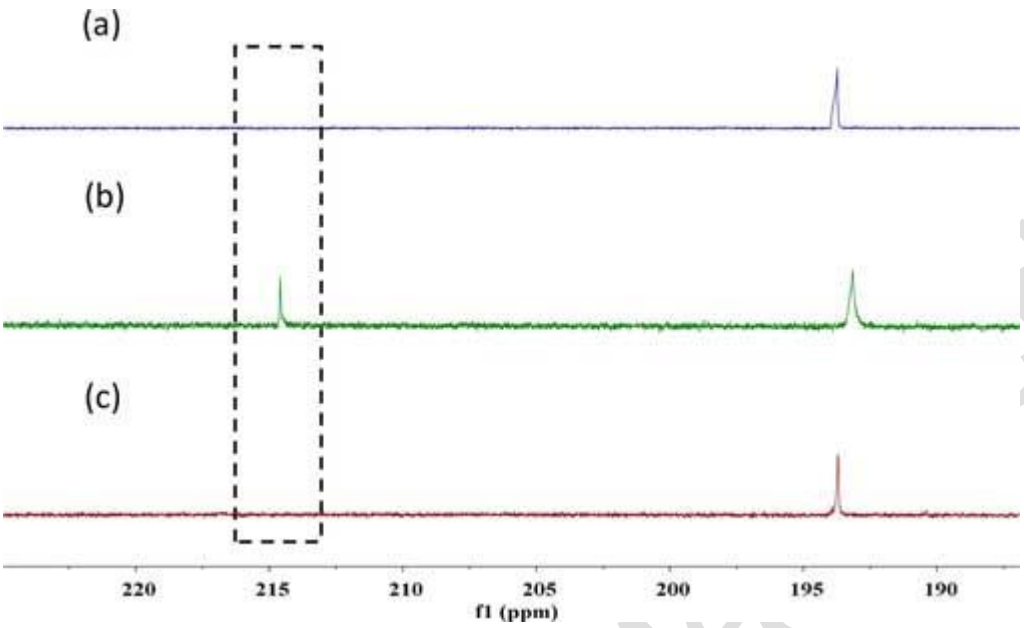
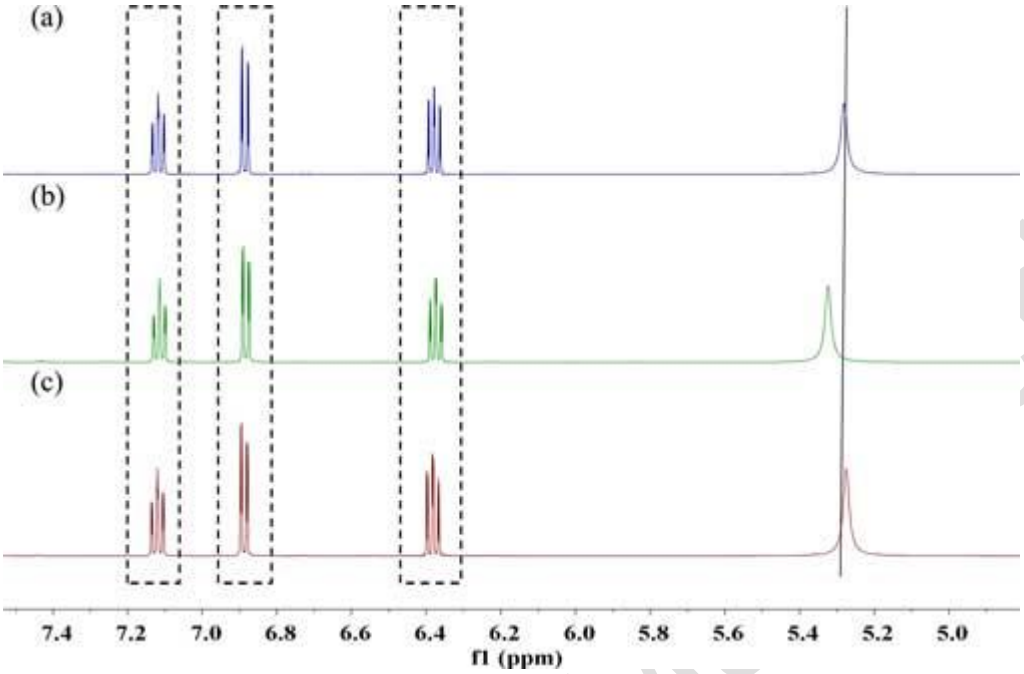
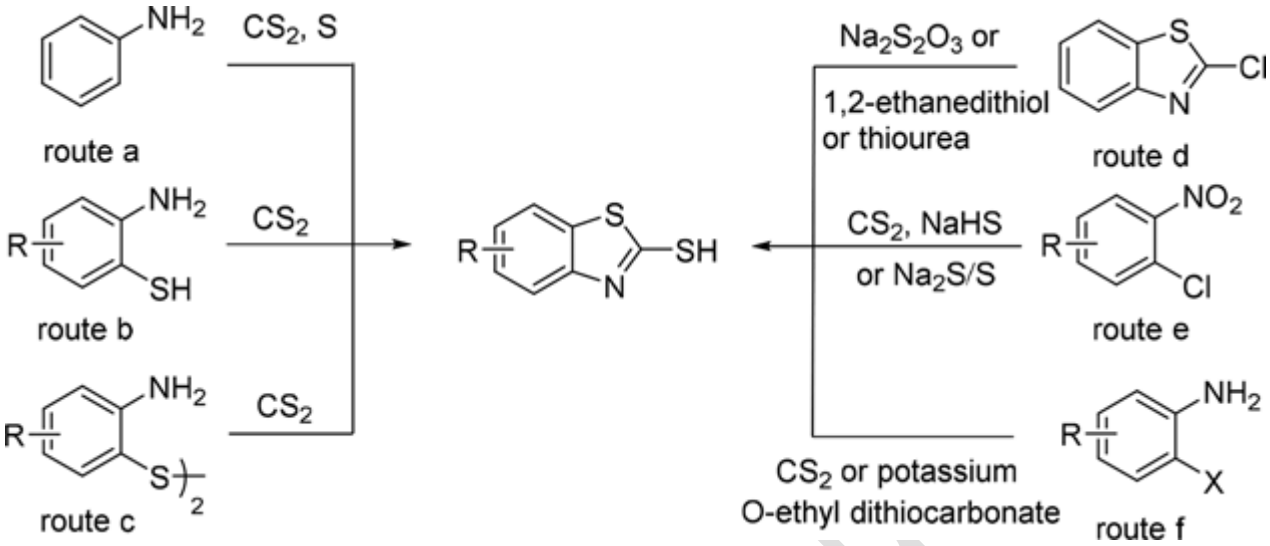


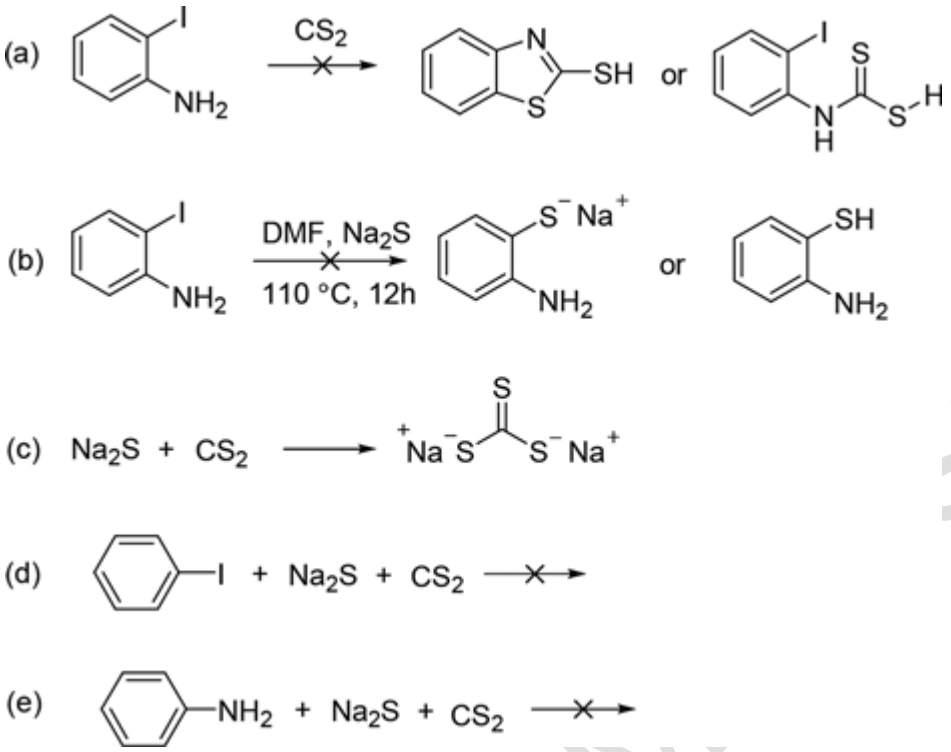
Figure 3. ^{1}H NMR spectra of (a) 2-iodoaniline; (b) 2-iodoaniline and DBU; (c) 2-iodoaniline and Na_2S in deuterated DMF.



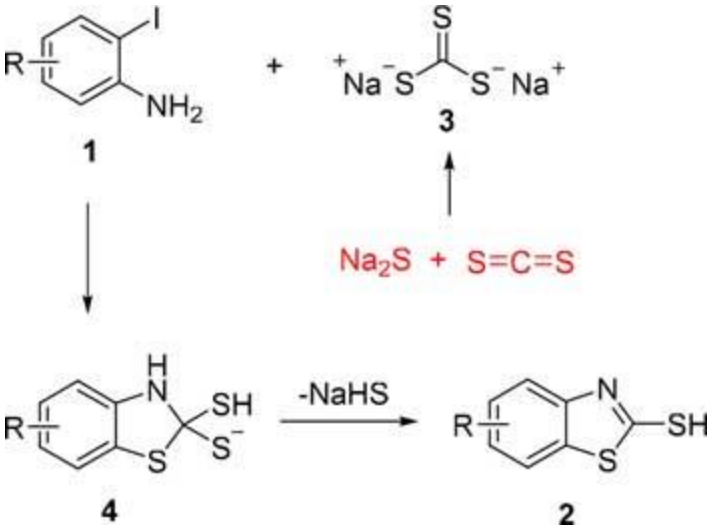
Scheme 1. Representative synthetic methods for preparing 2-mercaptobenzothiazoles.



Scheme 2. Control experiment.



Scheme 3. The mechanism for the reaction of 1, CS_2 and Na_2S .



Supplementary Materials

Experimental procedures, characterization data and NMR spectra of all compounds could be obtained in Supplementary Materials.