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The synthesis of *N*,*N*′-disulfanediyl-bis(*N*′-((*E*)-benzylidene)acetohydrazide) from (*E*)-*N*′-benzylideneacetohydrazide and S_8†

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Herein we report an oxidative coupling reaction for N–S/S–S bond formation from (*E*)-*N*′-benzylideneacetohydrazide and S_8 to furnish substituted *N*,*N*′-disulfanediyl-bis(*N*′-((*E*)-benzylidene) acetohydrazide). It provides a direct approach for the synthesis of disulfides with good yields.

Introduction

Disulfide bonds are important structural units which were found prevalently in natural or endogenous peptides.[1] They have been applied in digital light processing 3D printing,[2] and as bioactive agrochemicals,[3] antimicrobials,[4] and synthetic intermediates.[5] In addition, it is well-established that the disulfide linkage can be cleaved with the tripeptide glutathione (GSH),[6] which is over-expressed in cancer cells associated with strong biomedical activities.[7] Especially, a number of *S*,*S*′-bis(heterosubstituted) disulfides with N–S–S–N units exhibit a wide spectrum of biological activity (Fig. 1).[8] Thus, developing an efficient and practical procedure for the synthesis of disulfides is highly desirable. Numerous strategies have been developed for the formation of disulfide bonds.[9] Among these pathways, the most common approach involves the substitution of a sulfenyl derivative with a thiol or thiol derivative and these

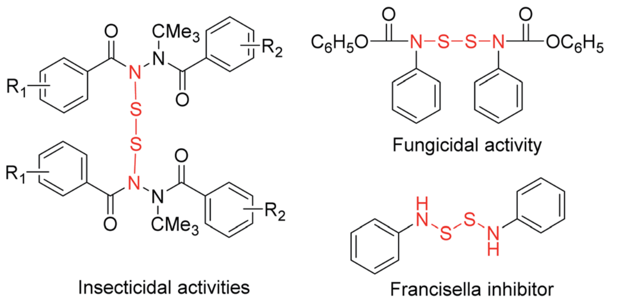
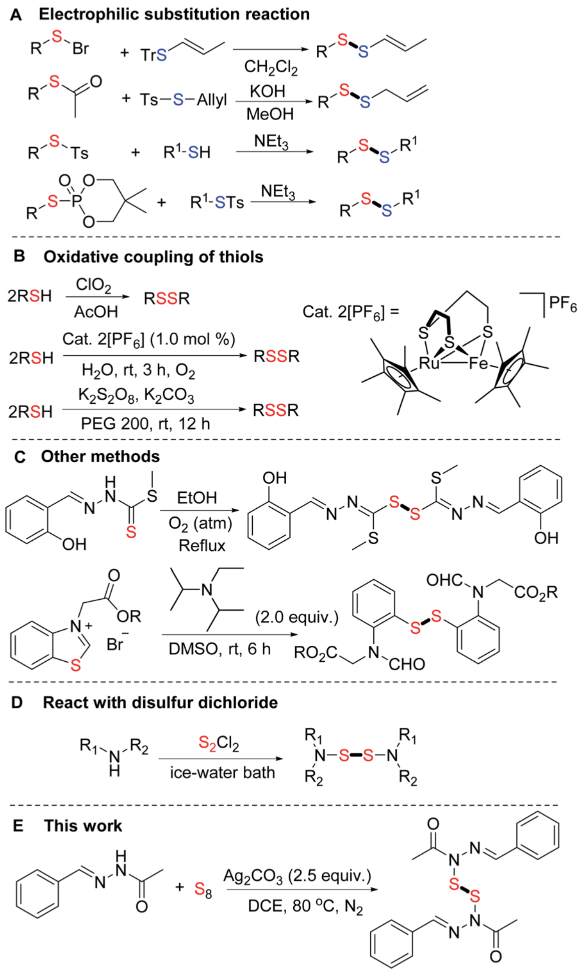


Fig. 1 Selected biologically active pharmaceuticals derived from *S*,*S*′-bis(heterosubstituted) disulfides.



Scheme 1 Strategies for the preparation of disulfides.

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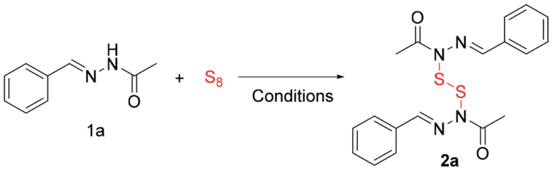
predecessor's work have been summarized by Witt (Scheme 1A).[10] In recent decades, oxidative coupling of thiols has developed into an efficient approach for producing disulfides. Many oxidants such as oxygen or air,[11,12] hydrogen peroxide,[13] halogens,[14] high-valent sulfur compounds[15] and other agents[16] were applied (Scheme 1B). In addition, methyl (*E*)-2-(2-hydroxybenzylidene)hydrazine-1-carbodithioate[17] and *N*-phenacylbenzothiazolium bromides[18] have also been used as starting materials to produce disulfides (Scheme 1C). Different from these C–S–S–C bonds, there are only a few reports in the literatures that describe N–S–S–N bond formation. In these cases, secondary amines reacted with disulfur dichloride to afford *S*,*S*′-bis(heterosubstituted) disulfides (Scheme 1D).[8,19] As part of our continuing efforts into the development of the C–S bonds formation,[20] herein we report an efficient method for generating *N*,*N*′-disulfanediyl bis(*N*′-((*E*)-benzylidene) acetohydrazide from (*E*)-*N*′-benzylideneacetohydrazide and S_8. To the best of our knowledge, it is the first example of the formation of N–S–S–N bonds from S_8 in moderate yields, and the reaction conditions are simple and mild (Scheme 1E).

Results and discussion

As an initial experiment, we treated the model substrate (*E*)-*N*′-benzylideneacetohydrazide **1a** and S_8 using Ag_2CO_3 as the oxidant in 1,2-dichloroethane at 80 °C (Table 1). First, the screening of the loading of Ag_2CO_3 was carried out, and it was found that 2.5 equiv. of Ag_2CO_3 provided the best result (Table 1, entries 1–5). After this, we only obtained 32% yield when it added 2.5 equiv. of $K_2S_2O_8$ and reduced the loading of Ag_2CO_3 to 0.5 equiv. (Table 1, entry 6). Meanwhile, we also evaluated the amount of S_8, and the use of 0.3 equiv. of the material gave the highest yield (Table 1, entries 3, 7–9). The temperature also played an important role in the reaction. Various temperatures, such as 60, 90, 100, 110 and 120 °C were also screened, but the yields are poor (Table 1, entries 10–14). Finally, there was no obvious improvement on shortening the reaction time to 2 h or prolonging the reaction time to 4, 6, or 12 h (Table 1, entries 15–18). Impressively, control experiments revealed that the reactions performed under O_2 and air atmosphere provided slightly decreased yields (Table 1, entry 19). And it has been shown that K_2CO_3 replaced Ag_2CO_3 has no reaction (Table 1, entry 20).

With the standard reaction conditions in hand (Table 1, entry 3), we subsequently investigated the scope of the benzoquinones (Table 2). Substrates derived from aromatic aldehydes with the *para*-substituted groups, such as 4-OMe (**2b**), 4-C$(CH_3)_3$ (**2c**), 4-C_2H_5 (**2d**), 4-Br (**2e**), 4-Cl (**2f**), afforded the corresponding products in good yields. Unfortunately, the product with an electron-withdrawing group such as 4-NO_2 (**2g**) could not be detected. Gratifyingly, the substrates with *meta*-substituted groups such as electron-withdrawing 3-Br (**2h**) and 3-CF_3 (**2j**) and electron-donating 3-OMe (**2i**) also give good yields. But, the product with a 3-NO_2 group (**2k**) could not be observed.

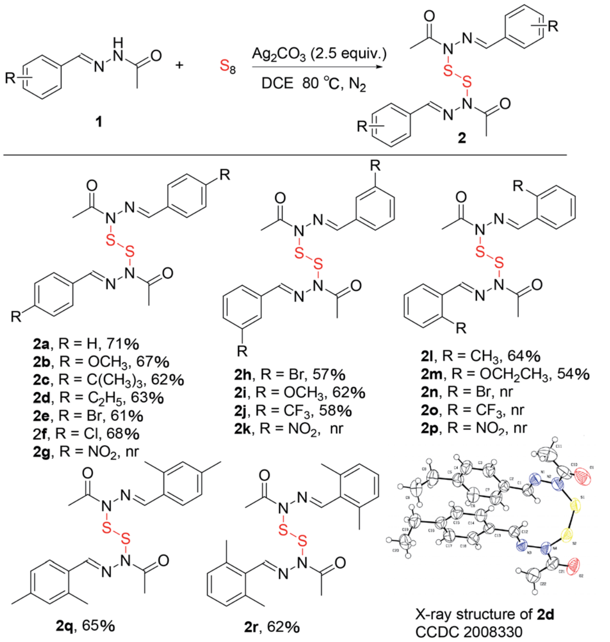
Table 1 Optimization of reaction conditions[a,b]



Entry	Additive (equiv.)	S_8 (equiv.)	Temp (°C)	Time (h)	Yield[b] (%)
1	Ag_2CO_3 (1.0)	S_8 (0.3)	80	3	46
2	Ag_2CO_3 (2.0)	S_8 (0.3)	80	3	61
3	Ag_2CO_3 (2.5)	S_8 (0.3)	80	3	71
4	Ag_2CO_3 (3.0)	S_8 (0.3)	80	3	66
5	Ag_2CO_3 (4.0)	S_8 (0.3)	80	3	64
6	Ag_2CO_3 (0.5)	S_8 (0.3)	80	3	32[c]
7	Ag_2CO_3 (2.5)	S_8 (0.2)	80	3	42
8	Ag_2CO_3 (2.5)	S_8 (0.4)	80	3	63
9	Ag_2CO_3 (2.5)	S_8 (0.6)	80	3	60
10	Ag_2CO_3 (2.5)	S_8 (0.3)	60	3	40
11	Ag_2CO_3 (2.5)	S_8 (0.3)	90	3	49
12	Ag_2CO_3 (2.5)	S_8 (0.3)	100	3	52
13	Ag_2CO_3 (2.5)	S_8 (0.3)	110	3	53
14	Ag_2CO_3 (2.5)	S_8 (0.3)	120	3	50
15	Ag_2CO_3 (2.5)	S_8 (0.3)	80	2	41
16	Ag_2CO_3 (2.5)	S_8 (0.3)	80	4	68
17	Ag_2CO_3 (2.5)	S_8 (0.3)	80	6	61
18	Ag_2CO_3 (2.5)	S_8 (0.3)	80	12	59
19	Ag_2CO_3 (2.5)	S_8 (0.3)	80	3	46[d], 48[e]
20	K_2CO_3 (2.5)	S_8 (0.3)	80	3	0

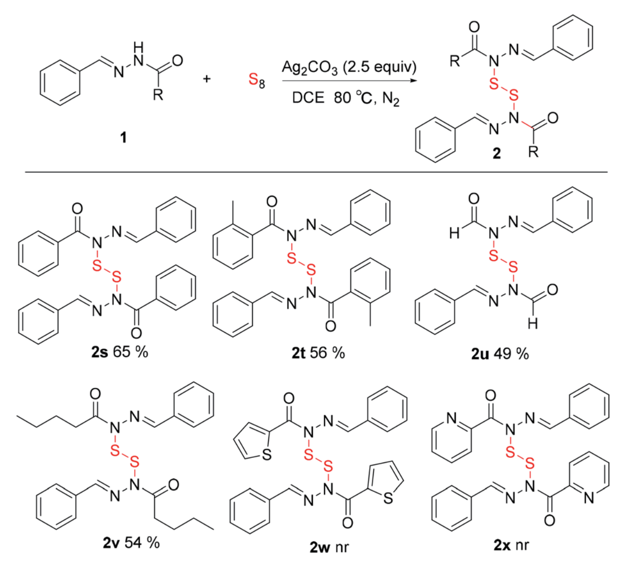
[a] Reaction conditions: **1a** (0.2 mmol), S_8 (0.3 mmol), Ag_2CO_3 (2.5 equiv.) in CH_2ClCH_2Cl (2.0 mL) was stirred at sealed tube, N_2, 80 °C for 3 h. [b] Isolated yields. [c] Added $K_2S_2O_8$ (2.5 equiv.). [d] Air. [e] O_2.

Table 2 Scope of various substituents on the benzene ring of the aromatic aldehyde **1**[a,b]



[a] Reaction conditions: **1a** (0.2 mmol), S_8 (0.3 mmol), Ag_2CO_3 (2.5 equiv.) in CH_2ClCH_2Cl (2.0 mL) was stirred at sealed tube, N_2, 80 °C for 3 h. [b] Isolated yields.

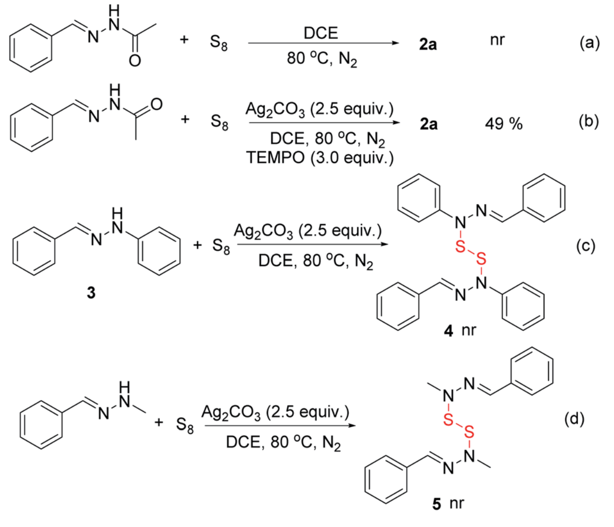
Table 3 Scope of various substituents of caprylic hydrazide 1[a,b]



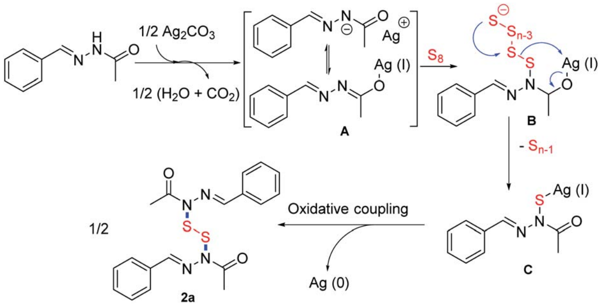
[a] Reaction conditions: **1a** (0.2 mmol), S_8 (0.3 mmol), Ag_2CO_3 (2.5 equiv.) in CH_2ClCH_2Cl (2.0 mL) was stirred at sealed tube, N_2, 80 °C for 3 h. [b] Isolated yields.

Subsequently, many components with the electron-donating groups such as 2-CH_3 (**2l**) and 2-OC_2H_5 (**2m**) at the *ortho* position on the benzene ring gave good yields. However, the substrates with a halogen group such as 2-Br (**2n**) and electron-withdrawing groups such as 2-CF_3 (**2o**), 2-NO_2 (**2p**) at the *ortho*-position did not to provide the corresponding products. To our delight, many disubstituted substrates such as **2q** and **2r** also gave the related products in 62–65% yields. In addition, the structure of the product (**2d**) was confirmed by X-ray crystallography. Notably, the gram-scale synthesis was achieved under the standard conditions, giving the product **2a** in 46% yield.

Various acyl hydrazides were also examined to explore the limits of the reaction. As shown in Table 3, benzohydrazide (**2s**), 2-methylbenzohydrazide (**2t**) all afforded good yields. Furthermore, the alkyl hydrazide such as formyl hydrazide (**2u**), valeryl hydrazide (**2v**) also afforded the corresponding products in 49–54% yields. Surprisingly, thiophene-2-carbohydrazide (**2w**) picolinohydrazide (**2x**) failed to produce the requisite disulfides.



Scheme 2 Mechanistic studies.



Scheme 3 Postulated reaction mechanism.

To understand the mechanism of the reaction, several control experiments were carried out (Scheme 2). First, product **2a** was not obtained without Ag_2CO_3 (Scheme 2a), which indicated that Ag_2CO_3 was crucial to facilitate this reaction. Second, we found that the desired product **2a** was only slightly decreased when the radical scavenger such as TEMPO was added to the reaction mixture (Scheme 2b). The result indicates that a free radical pathway might be ruled out in this transformation. Third, replacing (*E*)-*N*′-benzylideneacetohydrazide with (*E*)-*N*′-benzylidenebenzohydrazide produced the desired compound **2s** in 65% yield under the standard conditions. Additionally, the product **4** was not observed when (*E*)-1-benzylidene-2-phenylhydrazine **3** was used as the substrate under the standard reaction conditions (Scheme 2c). Furthermore, when (*E*)-1-benzylidene-2-methylhydrazine was used in the reaction, the target product **5** was not detected (Scheme 2d). Based on these results, we knew that the acetyl group was essential for the reaction and an oxygen atom of acetyl group was also necessary. Additionally, the reactions carried out under O_2 and air atmosphere have slightly decreased the yields of the product and the by-products increased (Table 1, entries 18 and 19).

On basis of these preliminary studies and previous reports,[21–28] a plausible pathway for the preparation of **2a** from (*E*)-*N*′-benzylideneacetohydrazide is proposed in (Scheme 3). Initially, Ag_2CO_3 react with **1** to produce the intermediate (**A**). Next, **A** reacts with S_8 to provide the intermediate **B.** The intermediate **C** is then produced through an electrophilic attack of elemental sulfur.[21,22] Finally, **2a** was obtained *via* facile oxidative coupling of the intermediate **C**.

Conclusions

In summary, we have developed a silver-mediated oxidative coupling reaction for N–S/S–S bond formation using (*E*)-*N*′-benzylideneacetohydrazide and S_8 as the starting materials under neutral conditions. In these processes, *N*,*N*′-disulfanediyl bis(*N*′-((*E*)-benzylidene) acetohydrazides have been successfully synthesized. Moreover, this method provides a direct way to form the disulfides in moderate yields.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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