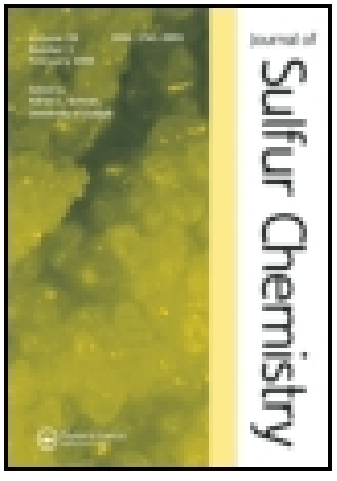

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4,4′-Azopyridine as an easily prepared and recyclable oxidant for synthesis of symmetrical disulfides from thiols or alkyl halides(tosylates)/thiourea

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4,4′-Azopyridine as an easily prepared and recyclable oxidant for synthesis of symmetrical disulfides from thiols or alkyl halides(tosylates)/thiourea

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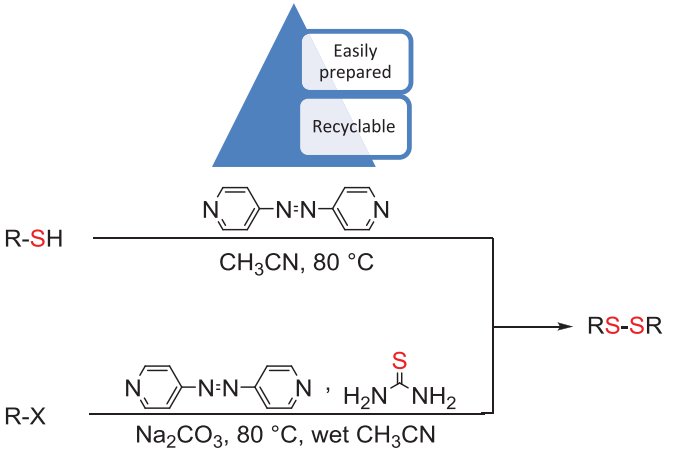
Heterocyclic azo compounds, prepared from corresponding amines in one step, are used as effective oxidants for the conversion of thiols into symmetrical disulfides in high yields. Among the studied azo compounds, 4,4′-azopyridine was found to be very efficient for the odorless conversion of alkyl halides into disulfides in the presence of thiourea. An attractive feature of this azo compound is that its obtained solid side product hydrazine is easily separated by filtration and can be recycled to its azo compound for further use.



Keywords: azopyridine; azo compounds; disulfide; thiol; alkyl halide

1. Introduction

The disulfide bond (S−S) is widely pervasive in both synthetic and naturally occurring compounds.[1–8] Owing to the increasing importance of the disulfides (disulfanes) in chemistry [9–14] and biology,[15–17] synthetic approaches for their preparation have been extensively studied.[18–22] According to the literature, disulfides can be obtained directly from

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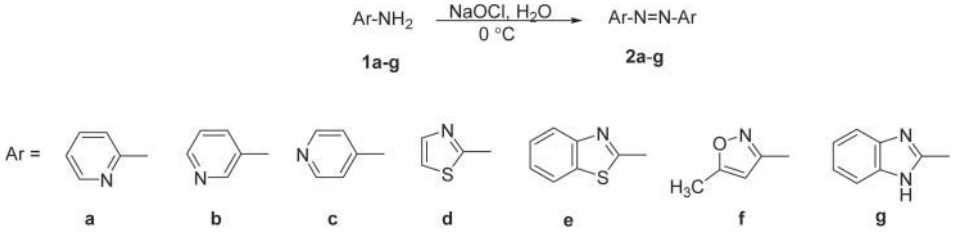


Scheme 1. Synthesis of heterocyclic azo compounds.

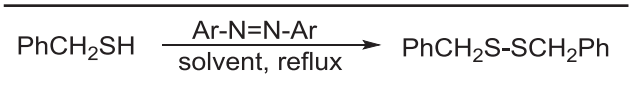
thiocyanates,[23–25] alcohols [26–28] and sulfonyl chlorides.[29] Alternatively, oxidative coupling of thiols represents one of the most convenient and straightforward methods for the synthesis of disulfides. Various oxidants and catalysts have been used to produce disulfides from thiols under controlled conditions.[30–54] Although these methods are efficient for the synthesis of disulfides, some of these procedures produce large amounts of toxic waste by-products, need expensive reagents and hazardous oxidants, and involve complicated work-up procedures.[55–62] Another commonly used method of disulfide formation involves the reaction of alkyl halides with sulfur transfer reagents in the presence of an oxidant.[63–74] The reaction was claimed to be the oxidation of *in situ*-generated thiols which are formed from alkyl halides and the sulfur transfer reagent. This strategy decreases often encountered problems such as unpleasant odor of thiols and tedious work-up that is confronted when using methods involving direct oxidation of thiols. In addition, the sensitivity of the disulfide bond to over-oxidation as a persistent challenge in this area restricts the choice of the oxidant for the transformation of thiols to disulfides. Azo compounds with activated −N=N− bonds have frequently been used for the oxidation of thiols to disulfides. In addition to diethyl azodicarboxylate (DEAD),[75,76] its analogues such as diisopropyl azo dicarboxylate,[75] diazenecarboxamide,[77] tetramethylazodicarboxamide [78] and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) [79] have also been used for this transformation. These azo reagents make purifications of the reaction mixtures rather difficult since removal of the hydrazine by-product is required. Recently, we have reported that heterocyclic azo compounds could act as acceptable alternative for traditional DEAD and its analogues in organic reactions.[80–84] In view of the helpful features associated with these azo compounds, herein we would like to report the potential of these compounds as recyclable oxidants in the synthesis of disulfides from thiols and also from alkyl halides/thiourea.

2. Results and discussion

We initiated the present study with the synthesis of heterocyclic azo compounds **2a**–**2g** by oxidative coupling of the corresponding amines **1a**–**1g** using sodium hypochlorite solution (bleach) as a cheap and readily available oxidant at low temperature (0°C) (1). Among the reported methods for the preparation of azo compounds,[85–92] this method has been found to be the most suitable.[93]

We then focused our attention to study whether these azo compounds could be employed for the oxidative coupling of thiols to generate symmetrical disulfides. This survey study was performed using benzyl mercaptan **3g** as the model substrate in the presence of the azo compounds under different conditions (Table 1). Generally, the procedure is based on the addition of benzyl mercaptan (2 mmol) to a solution of azo compounds **2a**–**2g** in an organic solvent. A blank run (in the absence of any azo compound) gave no conversion to disulfide in refluxing CH_3CN after 12 h (Table 1, Entry 1).

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



3g **4g**

Entry	Azo	Solvent	mmol of azo	Time (h)	Yield (%)[b]
1[c]	**–**	CH_3CN	–	12	N.R
2	**2a**	CH_3CN	1.1	2	93
3	**2b**	CH_3CN	1.1	6	71
4	**2c**	CH_3CN	1.1	2	**96**[d]
5[e]	**2c**	CH_3CN	1.1	2	57
6	**2c**	CH_3CN	1.0	2	81
7	**2c**	CH_3CN	1.2	2	94
8	**2c**	CH_2Cl_2	1.1	2	72
9	**2c**	Et_2O	1.1	2	75
10	**2c**	THF	1.1	2	84
11	**2d**	CH_3CN	1.1	5	77
12	**2e**	CH_3CN	1.1	5	83
13	**2f**	CH_3CN	1.1	5	86
14	**2g**	CH_3CN	1.1	5	85

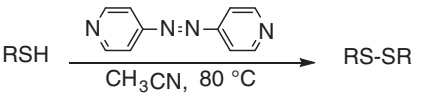
Note: THF, Tetrahydrofuran.
[a]Reaction conditions: benzyl bromide (2 mmol), azo compound, solvent (reflux, 3 mL).
[b]Isolated yields.
[c]Blank experiment in CH_3CN without azo compound.
[d]Bold value signifies best reaction conditions.
[e]The reaction temperature was 25°C.

3-3′-Azopyridine showed low reactivity in the oxidative coupling of benzyl mercaptan with only a 71% yield after 6 h reaction time (Entry 3). When 2,2′- (**2b**) and 4-4′-azopyridine (**2c**) were used as oxidants in refluxing acetonitrile, the reaction proceeded smoothly, and benzyl disulfide **4g** was obtained in excellent 93% and 96% yields, respectively (Table 1, Entries 2 and 4). This can be explained on the basis of the stabilization of the generated negative charge after reaction of the azo compound with RSH through the resonance effect of the nitrogen atom in the 2- and 4-positions of azopyridines. In contrast, azo compounds **2d**–**2g** gave the desired disulfide **4g** in comparatively lower yields (Table 1, Entries 11–14). The enhanced activity of azo **2a** and **2c** compared with azo compounds **2d**–**2g** could be due to the heterogeneity of azo compounds **2d**–**2g** in the reaction media.

Among the studied azo reagents, 2-2′- (**2a**) and 4,4′-azopyridine (**2c**) were found to be the most efficient for disulfide formation (Table 1, Entries 2 and 4). Despite their equal efficiency, **2c** was chosen as the reagent of choice since the yield for synthesis of **2c** (51% isolated yield) is much higher than that for **2a** (37%). In the reactions of azo compound **2c**, decreasing the temperature led to a decrease in the yield of the desired product (Table 1, Entry 5). The reaction also showed a considerable dependence on the amount of the azo compound used. When 1.0 and 1.1 equiv of 4,4′-azopyridine (**2c**) was used, the desired product was formed in 81% and 96% yields, respectively. A further increase in the amount of the azo compound did not lead to an increased product yield (Table 1, Entry 7). We also examined the effect of different solvents such as CH_2Cl_2, Et_2O and THF. Of all the solvents tested, CH_3CN was the best choice (Table 1, Entries 4, 8, 9 and 10).

After establishing the optimized reaction conditions, the range of thiols that could be coupled using this procedure was explored (Table 2). Aliphatic (Entries 1–4), alicyclic (Entries 5 and 6) and benzylic thiols (Entries 7 and 8) all smoothly participated in this reaction to afford the expected disulfides in excellent yields (85–97%; **4a**–**4h**). Notably, thiophenol (**3i**) and 4-methyl

Table 2. Oxidative coupling of thiols to disulfides by 4,4′-azopyridine (**2c**)[a].



	Entry	Thiol	Disulfide		Time (h)	Yield (%)[b]	Mp (°C)
1[c]	**3a**	*n*-C_3H_7SH	(*n*-$C_3H_7S-)_2$	**4a**	2	97	–
2	**3b**	*n*-C_4H_9SH	(*n*-$C_4H_9S-)_2$	**4b**	2	95	–
3	**3c**	*n*-$C_5H_{11}SH$	(*n*-$C_5H_{11}S-)_2$	**4c**	2	92	–
4	**3d**	*n*-$C_8H_{17}SH$	(*n*-$C_8H_{17}S-)_2$	**4d**	4	89	–
5	**3e**	*c*-C_5H_9 SH	(*c*-$C_5H_9-S-)_2$	**4e**	5	85	106–108
6	**3f**	*c*-C_6H_{11} SH	(*c*-$C_6H_{11}-S-)_2$	**4f**	5	86	–
7	**3g**	$PhCH_2SH$	$(PhCH_2S-)_2$	**4g**	2	96	69–71
8	**3h**	4-$CH_3-C_6H_4-CH_2SH$	(4-$CH_3-C_6H_4-CH_2S-)_2$	**4h**	2	94	–
9	**3i**	C_6H_5-SH	$(C_6H_5-S-)_2$	**4i**	2	91	50–52
10	**3j**	4-$CH_3-C_6H_4-SH$	(4-$CH_3-C_6H_4-S-)_2$	**4j**	2	93	46–48
11	**3k**	PhCOSH	$(PhCOS-)_2$	**4k**	4	90	133–135
12	**3l**	$OH-CH_2CH_2-SH$	$(OH-CH_2CH_2-S-)_2$	**4l**	2	91	–
13	**3m**	2-mercaptobenzothiazol	2,2'-dibenzothiazolyl disulfide	**4m**	4	88	178–180

[a]The reactions were carried out with 2 mmol of substrates with 1.1 mmol of 4,4′-azopyridine in refluxing acetonitrile.
[b]Isolated yields.
[c]Reaction was performed in a sealed tube.

thiophenol (**3j**) also gave their corresponding products **4i** and **4j** in 91% and 93% yields, respectively. As shown in Table 2, thiobenzoic acid was also found to be adept in efficiently furnishing the desired product **4k** in 90% yield (Table 2, Entry 11). The carbonyl (in thiobenzoic acid) and hydroxyl (in 2-hydroxyethanethiol) functionalities (Entries 11 and 12) were also well tolerated under these reaction conditions and remained intact during the formation of the product disulfides. These results show that the selective oxidation of thiols can be achieved with heteroaryl azo compound **2c**.

Heterocyclic thiols, such as 2-mercaptobenzothiazole, can also be employed as substrates (Entry 13). Because this thiol is in equilibrium with its thioxo forms, the corresponding oxo compound might be produced as a by-product instead of the disulfides.[94,95] However, the oxidation of 2-mercaptobenzothiazole gave only 2,2'-dibenzothiazyl disulfide **4m** in 88% yield, and we did not detect the oxo product, 2-benzothiazolinone.

The major advantage of this method using 4,4'-azopyridine compared to that of DEAD and its derivatives is the ease of removal of the resultant hydrazine by-product of **2c** after the reaction. This simplification obviates the need for time-consuming chromatography and produces a very significant saving of time and effort. Furthermore, 4,4'-azopyridine was easily prepared in one step from the commercially available 4-aminopyridine. After the reaction, we were able to almost fully recover the hydrazine by-product in its azo form through the reaction with iodosobenzene diacetate $PhI(OAc)_2$ (73% yield), which was identified by its spectral data.

In analogy to previous reports of the oxidations of thiols with azo compounds,[79,96] we proposed an analogous two-step sequence for the oxidative coupling of thiols with 4,4'-azopyridine **2c**. This mechanism invokes an initial reaction of the thiol with 4,4'-azopyridine **2c** to form an intermediate **I**. This intermediate subsequently reacts with a second molecule of the thiol to generate the hydrazine derivative together with the respective symmetrical disulfide (Figure 1).

In order to further evaluate the use of our reagent, we extended our study to the one-pot and odorless synthesis of symmetrical disulfides using primary and secondary alkyl halides (tosylates) and thiourea as the sulfur source reagent under the same conditions utilized for the synthesis of disulfides from thiols. We were pleased to discover that a wide range of alkyl halides

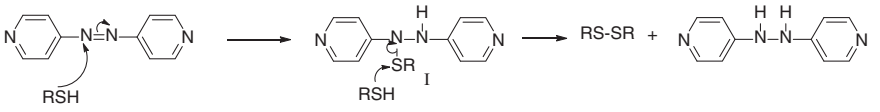
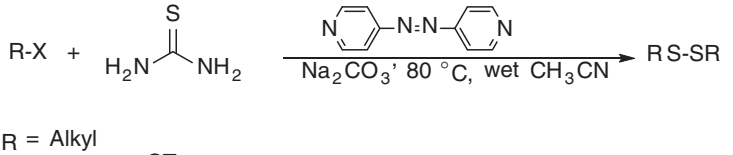


Figure 1. Proposed mechanism for the oxidative coupling of thiols.

Table 3. One-pot conversion of alkyl halides to their corresponding symmetrical disulfides in the presence of thiourea and 4,4′-azopyridine (**2c**).[a]



R = Alkyl
X = Cl, Br, I, OTs

Entry		R-X	RS-SR		Time (h)	Yield (%)[b]	Mp (°C)
1	**5a**	*n*–C_4H_9I	$(n\text{–}C_4H_9S\text{–})_2$	**4b**	3	93	–
2	**5b**	*n*-C_4H_9Br	$(n\text{-}C_4H_9S\text{–})_2$	**4b**	4	91	–
3	**5c**	*n*-$C_8H_{17}I$	$(n\text{-}C_8H_{17}S\text{–})_2$	**4d**	6	84	–
4	**5d**	*n*-$C_8H_{17}Br$	$(n\text{-}C_8H_{17}S\text{–})_2$	**4d**	8	81	–
5	**5e**	$PhCH_2Br$	$(PhCH_2S\text{–})_2$	**4g**	2	97	69–71
6	**5f**	$PhCH_2Cl$	$(PhCH_2S\text{–})_2$	**4g**	3	93	68–70
7	**5g**	4-Br–C_6H_4–CH_2Br	$(4\text{-Br–}C_6H_4CH_2S\text{–})_2$	**4n**	3	98	153–155
8[c]	**5h**	CH_2=$CHCH_2Br$	$(CH_2$=$CHCH_2S\text{–})_2$	**4o**	2	95	–
9[c]	**5i**	CH_2=$CHCH_2Cl$	$(CH_2$=$CHCH_2S\text{–})_2$	**4o**	3	92	–
10[c]	**5j**	CH_2=$C(CH_3)CH_2Cl$	$(CH_2$=$C(CH_3)CH_2S\text{–})_2$	**4p**	3	91	–
11	**5k**	$CH_3CH_2CH(CH_3)Br$	$(CH_3CH_2CH(CH_3)S\text{–})_2$	**4q**	12	80	–
12	**5l**	*c*-$C_6H_{11}Br$	$(c\text{-}C_6H_{11}\text{–S–})_2$	**4f**	12	77	–
13[c]	**5m**	*tert*-C_4H_9Br	$(tert\text{-}C_4H_9S\text{–})_2$	**4r**	24	21	–
14	**5n**	*n*-$C_8H_{17}OTs$	$(n\text{-}C_8H_{17}S\text{–})_2$	**4d**	6	83	–
15	**5o**	$PhCH_2OTs$	$(PhCH_2S\text{–})_2$	**4g**	2	92	69–70

[a]Reaction condition: 2 mmol of substrate, 1.1 mmol of 4,4′-azopyridine, 2.1 mmol of thiourea, 3 mmol of Na_2CO_3 in refluxing wet acetonitrile (3 mL).
[b]Isolated yields.
[c]Reaction was carried out in a sealed tube.

5 was transformed using these conditions into the corresponding symmetrical disulfides **4** in good to excellent yields. The results are listed in Table 3.

When butyl iodide (**5a**) was treated with thiourea (2.1 mmol) and 4,4'-azopyridine **2c** (1.1 mmol) in the presence of Na_2CO_3 (3 mmol) in refluxing CH_3CN for 3 h, butyl disulfide **4b** was formed in 74% isolated yield. It was also shown that addition of a few drops of water (0.2 mL) helped to facilitate the reaction and increased the isolated yield of **4b** to 93% (Table 3, Entry 1). This observation is similar to previous reports in which trace amounts of water can help to promote the conversion of alkyl halides into disulfides.[63,69,72]

Aliphatic alkyl halides were well tolerated in these optimized one-pot conditions, and the reactions of *n*-butyl bromide (**5b**), *n*-octyl iodide (**5c**) and *n*-octyl bromide (**5d**) with thiourea and 4,4'-azopyridine **2c** resulted in the desired products in 81–91% yields (Entries 2–4). Excellent yields were also obtained when benzylic (Entries 5–7) and allylic substrates (Entries 8–10) were used as starting materials. The effect of steric hindrance was also evident in these one-pot reactions. For example, sterically more hindered secondary alkyl halides were effective for this transformation, but required extended reaction times at 80°C. Treatment of 2-bromobutane (Table 3, Entry 11) and cyclohexyl bromide (Entry 12) with thiourea and the azo oxidant **2c** in the presence of sodium carbonate gave the target products **4q** and **4f** in 80% and 77% total yields in

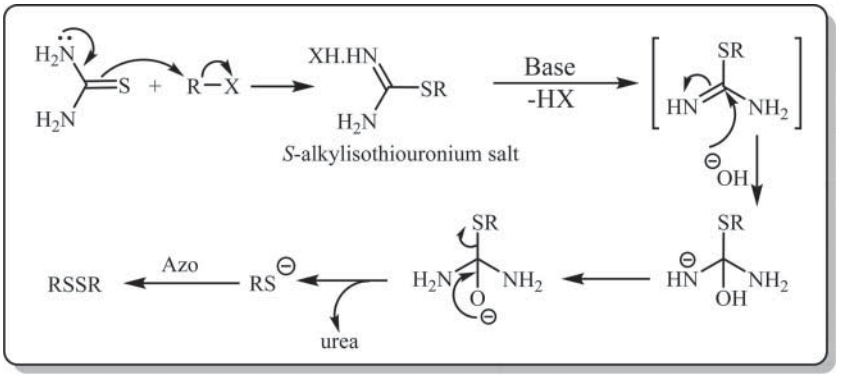


Figure 2. Plausible reaction mechanism of the azopyridine promoted disulfide formation from alkyl halides (tosylates).

12 h, respectively. A 21% yield of product **4r** was obtained after 24 h, when *t*-butyl bromide was used; this poor yield may be due to steric hindrance. In this system, the type of halide as a leaving group is an important factor that affects the results. For example when the good leaving group –I in the substrate was exchanged with −Br or −Cl, the yields of the desired product dropped (Table 3, Entries 1, 3, 5 and 8 compared with Entries 2, 4, 6 and 9, respectively). In addition, as the length of alkyl chain increases, the rate of the disulfide formation decreases (Table 3, Entries 1, 2 compared with Entries 3, 4, respectively). The preparation of symmetrical disulfides from alkyl tosylates was also explored using our standard conditions in order to evaluate the potential practical application of our method. Both *n*-octyl (**5n**) and benzyl tosylate (**5o**) could be efficiently converted using the general conditions and the desired disulfides **4d** and **4g** were isolated with excellent yields (Table 3, Entries 14 and 15). On the basis of the previous reports,[63,69] a plausible mechanism for this transformation is illustrated in Figure 2.

3. Experimental

General information: All chemicals used in this study were analytical grade, commercially available and used without further purification. Most of the products were purified by column chromatography using appropriate solvents and were identified by ^{1}H NMR, ^{13}C NMR and elemental analyses. Progress of the reactions was monitored by thin-layer chromatography (TLC) using silica gel polygrams SIL G/UV 254 plates. FT-IR spectra were recorded on a Shimadzu DR-8001 Spectrometer. NMR spectra were recorded on a Bruker Avance DPX 250 MHz Instrument in $CDCl_3$ or DMSO-d_6 solvents using tetramethylsilane as the internal standard. Chemical shifts were reported in ppm (δ) and coupling constants (J) in Hz. Elemental analyses were determined in our department using ThermoFinnigan Flash EA 1112 Series.

General procedure for the preparation of azo compounds (***2***)*:* Azo compounds (**2a–2g**) were prepared by oxidative coupling of their corresponding amines (**1a–1g**) by sodium hypochlorite solution. In a 250 mL round-bottomed flask, a solution of sodium hypochlorite (6–14%, 120 mL) was cooled to 0°C using an ice water bath. Then, 50 mL aliquot of a cold solution of heterocyclic aromatic amine **1** (25 mmol) in water was added dropwise over 30 min while keeping the temperature below 5°C. The mixture was stirred until a colored precipitate formed. Filtration was performed a few minutes after the end of addition. The resulting azo participates were collected and were used in our reactions without any purification.

Sample procedure for the synthesis of benzyl disulfide from benzyl mercaptan by oxidation with 4,4'-azopyridine: In a round-bottomed flask, a solution of benzyl mercaptan (2 mmol, 0.234 mL)

in refluxing CH_3CN (4 mL) was treated with 4,4'-azopyridine (1.1 mmol, 0.202 g). The resulting red solution was stirred at 80°C for 2 h. After decolorization of the red solution (indication of completion of the reaction) and disappearance of benzyl mercaptan on TLC, the reaction mixture was filtered to remove the hydrazine by-product. The filtrate was washed twice with 10% NaOH solution (8 mL), then with saturated brine and was dried over anhydrous Na_2SO_4. Removal of the volatile compounds and solvent afforded a viscous oil. The product was purified by short-column chromatography on silica gel eluted with *n*-hexane. Benzyl disulfide was obtained as white crystals and its ^{1}H NMR and ^{13}C NMR agreed well with the reported values.

Typical procedure for direct conversion of benzyl chloride to benzyl disulfides using thiourea and 4,4′-azopyridine in CH_3CN: To a solution of thiourea (2.1 mmol, 0.160 g) and benzyl chloride (2 mmol, 0.23 mL) in wet CH_3CN (3 mL CH_3CN + 0.2 mL H_2O), 4,4′-azopyridine (1.1 mmol, 0.202 g) and Na_2CO_3 (3 mmol, 0.318 g) were added. The mixture was stirred magnetically at 80°C. The progress of the reaction was monitored by TLC or GC until the benzyl chloride was consumed. After completion of the reaction, the mixture was filtered through a sintered glass funnel to remove the produced pyridine hydrazine. The solvent was evaporated under reduced pressure and the so-obtained residue was purified by flash chromatography on silica gel with petroleum ether as eluent to provide benzyl disulfide.

Oxidation of 4,4′-pyridinehydrazine to 4,4′-azopyridine by iodosobenzene diacetate $PhI(OAc)_2$: To a 50 mL flask equipped with a magnetic stirrer containing pyridinehydrazine (0.186 g, 1.0 mmol) in DMSO (5 mL), iodosobenzene diacetate (0.322 g, 1.0 mmol) was added in one portion and the mixture was stirred for 6 h at room temperature. H_2O (20 mL) was then added and the reaction solution was extracted with EtOAc (4 × 15 mL). The organic extracts were combined together and dried over anhydrous sodium sulfate. Upon concentrating the solution under vacuum, azopyridine (**2c**) was precipitated as orange crystals (134 mg, 73%). All the products are known compounds and were characterized by the comparison of their physical and spectral data with those reported in the literature. Selected spectral data for representative disulfides:

Dipropyl disulfide (***4a***) yellow liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.96 (t, J = 7.1 Hz, 6H), 1.83 (sext, J = 7.1 Hz, 4H), 2.59 (t, J = 7.1 Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 41.5, 22.7, 13.0. Anal. Calcd. $C_6H_{14}S_2$: C, 47.95%; H, 9.39%; S, 42.66%. Found: C, 48.09%, H, 9.32%; S, 42.59%.

*Dibutyl disulfide (**4b**)* colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.93 (t, J = 7.5 Hz, 6H), 1.44–1.51 (m, 8H), 2.61 (t, J = 7.7 Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 39.2, 31.6, 21.4, 13.7. Anal. Calcd. $C_8H_{18}S_2$: C, 53.88%; H, 10.17%; S, 35.95%. Found: C, 54.02%; H, 10.20%; S, 35.78%.

*Dipentyl disulfide (**4c**)* colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.93 (t, J = 7.2 Hz, 6H), 1.36–1.41 (m, 8H), 1.61–1.1.68 (m, 4H), 2.66 (t, J = 7.4 Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 39.4, 29.5, 29.0, 22.1, 14.2. Anal. Calcd. $C_{10}H_{22}S_2$: C, 58.19%; H, 10.74%; S, 31.06%. Found: C, 58.10%; H, 10.67%; S, 31.23%.

Dioctyl disulfide (***4d***) colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.79–0.85 (t, J = 6.6 Hz, 6H), 1.09–1.37 (m, 20H), 1.53–1.68 (m, 4H), 2.62 (t, J = 7.4 Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 39.2, 33.9, 32.7, 31.9, 29.2, 28.8, 22.6, 14.0. Anal. Calcd. $C_{16}H_{34}S_2$: C, 66.14%; H, 11.79%; S, 22.07%. Found: C, 66.08%; H, 11.89%; S, 22.03%.

Dicyclohexyl disulfide (***4f***) colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.16–1.27 (m, 10H), 1.53–1.56 (m, 2H), 1.68–1.74 (m, 4H), 1.93–1.98 (m, 4H), 2.58–2.61 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 49.5, 33.1, 26.0, 25.6. Anal. Calcd. $C_{12}H_{22}S_2$: C, 62.55%; H, 9.62%; S, 27.83%. Found: C, 62.66%; H, 9.53%; S, 27.81%.

Dibenzyl disulfide (***4g***) white crystal; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.65 (s, 4H), 7.16–7.54 (m, 10H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 137.3, 129.8, 128.2, 128.0, 43.9. Anal. Calcd. $C_{14}H_{14}S_2$: C, 68.25%; H, 5.73%; S, 26.02%. Found: C, 68.41%; H, 5.79%; S, 25.80%.

1,2-Diphenyldisulfide (***4i***) white solid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.22–7.25 (m, 2H), 7.30–7.37 (m, 4H), 7.58 (d, $J = 7.6$ Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 137.5, 129.4, 128.2, 127.9. Anal. Calcd. $C_{12}H_{10}S_2$: C, 66.02%; H, 4.62%; S, 29.37%. Found: C, 65.91%; H, 4.70%; S, 29.39%.

Bis(*4-methylphenyl*) *disulfide* (***4j***) white solid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.33 (6H, s), 7.11 (d, $J = 7.5$ Hz, 4H), 7.41 (d, $J = 7.5$ Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 137.4, 133.9, 131.1, 129.3, 21.1. Anal. Calcd. $C_{14}H_{14}S_2$: C, 68.25%; H, 5.73%; S, 26.02%. Found: C, 68.13%; H, 5.85%; S, 26.02%.

Dibenzoyl disulfide (***4k***) white solid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49–7.67 (m, 6H), 8.10 (dd, $J = 8.1$, 1.2 Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 184.4, 135.7, 134.5, 129.3, 128.5. Anal. Calcd. $C_{14}H_{10}O_2S_2$: C, 61.29%; H, 3.67%; S, 23.37%. Found: C, 61.17%; H, 3.78%; S, 23.26%.

Di[*2-*(*hydroxy*)*ethyl*] *disulfide* (***4l***) colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.12 (br s, 2H), 2.80 (t, $J = 6.2$ Hz, 4H), 3.89 (t, $J = 6.2$ Hz, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 60.5, 40.8. Anal. Calcd. $C_4H_{10}O_2S_2$: C, 31.15%; H, 6.54%; S, 41.57%. Found: C, 31.31%; H, 6.43%; S, 41.50%.

Bis(*4-bromobenzyl*) *disulfide* (***4n***) white solid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.53 (s, 4H); 7.07 (d, $J = 7.5$ Hz, 4H), 7.35 (d, $J = 8.3$ Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 136.3, 133.0, 131.2, 121.5, 42.5. Anal. Calcd. $C_{14}H_{12}Br_2S_2$: C, 41.60%; H, 2.99%; S, 15.86%. Found: C, 41.48%; H, 3.11%; S, 15.69%.

Diallyl disulfide (***4o***) colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.36 (d, $J = 7.5$ Hz, 2H), 5.26 (m, 2H), 5.73 (m, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 133.1, 118.4, 42.7. Anal. Calcd. $C_6H_{10}S_2$: C, 49.27%; H, 6.89%; S, 43.84%. Found: C, 49.18%; H, 7.05%; S, 43.77%.

Bis(*2-methyl-2-propenyl*) *disulfide* (***4p***) colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.70 (s, 6H), 3.18 (s, 4H), 4.82–4.88 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 141.9, 113.3, 47.0, 21.3. Anal. Calcd. $C_8H_{14}S_2$: C, 55.12%; H, 8.09%; S, 36.79%. Found: C, 55.24%; H, 8.00%; S, 36.76%.

t-Butyl disulfide (***4r***) colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.28 (s, 18H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 30.7, 45.8. Anal. Calcd. $C_8H_{18}S_2$: C, 53.88%; H, 10.17%; S, 35.95%. Found: C, 54.02%; H, 10.11%; S, 35.87%.

4. Conclusion

In summary, we have developed a practical and efficient procedure for the oxidation of thiols to their corresponding disulfides utilizing 4,4′-azopyridine as an inexpensive oxidant. Odorless synthesis of symmetrical alkyl disulfides from readily available alkyl halides (tosylates) and thiourea can also be achieved with 4,4′-azopyridine. Apart from the stability, ease of handling and synthesis of 4,4′-azopyridine, our method allows for the isolation of the parent pyridine hydrazine by simple filtration from the reaction mixture, which can be reoxidized to the corresponding 4,4′-azopyridine by known oxidation procedure.

Disclosure statement

No potential conflict of interest was reported by the authors.

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