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Journal Name

COMMUNICATION

Synthesis of Symmetrical Disulfides by Reacting Organic Halides with Na₂S₂O₃·5H₂O in DMSO

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Mohammad Abbasi,^{a,*} Mohammad Reza Mohammadzadeh^a and Narges Saeedi^a

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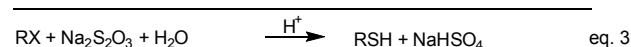
A one-pot, and scalable method to prepare symmetric disulfides from their corresponding primary, secondary, allylic, and benzylic halides has been developed. In this method, a disulfide is synthesized by reacting an alkyl halide with Na₂S₂O₃·5H₂O at 60-70 °C in DMSO.

The synthesis of organic disulfides (disulfanes) is a matter of interest for the industrial production of some pharmaceuticals and agrochemicals.¹ This goal can be achieved in the laboratory by means of numerous methods using diverse reagents and substrates.² Symmetrical disulfides can be obtained by reductive coupling of sulfonyl chlorides³ reaction of Sulfur monochloride (S₂Cl₂) with aromatic compounds,⁴ alkynes,⁵ and alkenes,⁵ treatment of organic thiocyanates with samarium,⁶ samarium diiodide,⁷ tetrabutylammonium fluoride⁸ or tetrathiomolybdate,⁹ and nucleophilic ring opening of thiiranes followed by oxidation.¹⁰ However, the most important method for the preparation of symmetrical disulfides is the oxidation of the appropriate thiols.² Thiols are foul-smelling compounds that are usually prepared from their corresponding alkyl halides in organic synthesis. In other words, thiols are intermediates in the synthesis of disulfides from alkyl halides. Even though a wide range of methods is available for the synthesis of disulfides from thiols in the literature, the search for a simple, rapid and inexpensive conversion of alkyl halides into disulfides is still a challenge and an interesting area of study.² In this regard, the treatment of alkyl halides with disulfide anion,¹¹ tetrathiomolybdate and tetrathiotungstate complexes,¹² a combination of borohydride reducing agents with sulfur,¹³ and sulfur element in strong alkaline media¹⁴ has been used to convert them into the related disulfides.

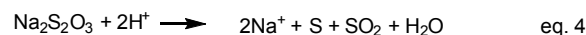
Also, the symmetric disulfides can be achieved when Bunte salts are treated with samarium in the presence of indium (III) chloride, or molecular iodine¹⁵ or when they are heated with thiourea,

substituted thioureas, iodide ion, or thiocyanate ion in the strong acidic solutions.¹⁶

The synthesis of organosulfur compounds *via in situ* generation of thiols has been of interest especially in recent years.¹⁷ In this regard, thia-Michael adducts have been synthesized by reacting Bunte salts with electron-deficient alkenes in acidic conditions^{18a} and by reaction of elemental sulfur, aryl halides and electron-deficient alkenes in the presence of copper ferrite nanoparticle very recently.^{18b} Also, the treatment of alkyl halides with thiourea as a thiol producing reagent in the presence of a suitable oxidant has been shown to be practical for the one-pot synthesis of disulfides.¹⁹ To establish a new strategy to *in situ* generation of thiols, we focused our attention on the reaction of alkyl halides with Na₂S₂O₃. Sodium *S*-alkyl thiosulfates (Bunte salts) are generally prepared from the reaction of alkyl halides with thiosulfate anion.²⁰ Their hydrolysis in acidic conditions is known as a suitable method for achieving thiols.²⁰ It can be said that the Bunte salts are intermediates in the synthesis of thiols from reaction of alkyl halides with sodium thiosulfate.



Theoretically, thiols can be synthesized by reacting alkyl halides with Na₂S₂O₃ in acidic conditions through hydrolysis of Bunte salt intermediates (eq. 3). As an important problem, the hydrolysis of Bunte salt intermediates to thiols is an acid-dependent reaction whereas Na₂S₂O₃ is an acid-degradable reagent which undergoes decomposition to elemental sulfur and SO₂ by reaction with acidic reagents rapidly.²¹



Thus, the synthesis of thiols via reaction presented by eq. 3 is not practically possible. However, our studies on the reaction of 2-phenylethyl bromide with Na₂S₂O₃·5H₂O in the various solvents led us to a simple and efficient route for the preparation of the

^a Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr, 75169, Iran. E-mail: abbassi@pqu.ac.ir and pqu.chem@gmail.com.

^b Address here.

^c Address here.

† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

corresponding disulfide in excellent yield without needing to add any acidic reagents to reaction media. The results have been summarized in Table 1.

Table 1: The study on the reaction of 2-phenylethyl bromide with $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ under various conditions^a

Entry	Solvent	T	pH	Organic Product
1	THF	Reflux	Neutral	No
2	CH_3CN	Reflux	Neutral	No
3	CH_2Cl_2	Reflux	Neutral	No
4	H_2O	60-70 °C	Neutral	No
5	DMF	60-70 °C	Neutral	No
6	EtOH	Reflux	Neutral	No
7	DMSO	60-70 °C	(Acidic)	Yes (symmetric disulfide)

^aReaction conditions: 2-phenylethyl bromide (1 mmol), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (1 mmol), solvent (1-3 mL), H_2O (0.1 mL), 24h.

After 24 h, the reaction of 2-phenylethyl bromide with $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ to produce the corresponding Bunte salt in CH_3CN , THF, and CH_2Cl_2 was uncompleted and a considerable amount of starting alkyl halide was detected in the reaction mixture (Table 1, entries 1-3). The starting halide had been completely converted to the corresponding Bunte salt during this period in H_2O , DMF and EtOH (Table 1, entries 4-6). All reaction media were neutral to litmus paper test. No thiol or any organic products were found in the reaction mixtures. However, the similar reaction in DMSO yielded a different result (Table 1, entry 7). During this period the starting halide had been completely consumed to give the corresponding symmetric disulfide in 90% yield. Also, the reaction medium had been strongly acidified. The pH was below 3 as determined by using pH cooperative paper (Universalindikator pH 0–14 Merck, Merck KGaA, 64271 Darmstadt, Germany).

Then we decided to investigate this reaction in more details. In this line, a mixture of 2-phenylethyl bromide (2 mmol) and well-powdered $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (2 mmol) in wet DMSO (2 mL DMSO + 0.2 mL H_2O) was stirred magnetically at 60-70 °C. The reaction mixture was neutral to litmus paper at first. After stirring for 1 h, the starting halide was completely consumed and, the reaction medium was still neutral to wet litmus paper. After 2h, the reaction medium had been slightly acidified and the spot of disulfide was monitored on the TLC. Over time, the pink color of litmus paper gradually turned red which can be attributed to increasing NaHSO_4 in the reaction medium due to hydrolysis progressing of the Bunte salt. The litmus paper became completely red after 3h (pH<3) nevertheless, the reaction mixture was continuously stirred for another 2h under such conditions to ensure the reaction completion. After that, the reaction was worked up by dilution with water and extracted with EtOAc. The corresponding disulfide was obtained in 91% yield after chromatography on silica gel.

Further studies indicated that, the molar ratio between substrate and sodium thiosulfate was crucial. When an equivalent of 2-phenylethyl bromide was treated with 1.2 equivalents of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ under reaction conditions, the starting halide was completely consumed within 30 min but the corresponding disulfide or any organic product was not found on the TLC even after 12 h. Meanwhile, the reaction medium was neutral to wet litmus paper during this period. However, this reaction gave the corresponding disulfide after 24 h in 90% yield. Conversely, when an equivalent of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was treated with 1.2 equivalents of 2-phenylethyl bromide, the reaction medium was acidified after 30 min (pH<3) and disulfide spot was detected on the TLC and gave the desired disulfide within 3 h in 91% yield. Considering these results, one can conclude that, the hydrolysis of the *in situ* generated Bunte salt is retarded or at least proceeds much slowly in the presence of $\text{Na}_2\text{S}_2\text{O}_3$. The hydrolysis of Bunte salt in DMSO in the absence of proton (acids) occurs but proceeds very slowly. This reaction is a non-catalyzed process at first but it produces acidic NaHSO_4 as by-product (eq. 2) which can accelerate the process. Hence, this reaction is a self-catalyzed reaction. However, in the presence of $\text{Na}_2\text{S}_2\text{O}_3$, proton undergoes reaction with this reagent very rapidly (eq. 4) and the hydrolysis process proceeds only *via* non-catalyzed process which is very slow and inappreciable. When thiosulfate is stoichiometric with respect to halide or is limiting reactant, sodium thiosulfate is consumed completely by reacting with alkyl halide and subsequently the self-catalyzed hydrolysis process proceeds exponentially by increasing proton in reaction media. When alkyl halide is limiting reactant, the proton-catalyzed hydrolysis process is retarded by unreacted thiosulfates and thus the hydrolysis proceeds *via* non-catalyzed hydrolysis very slowly until the remaining thiosulfate becomes completely decomposed by reaction with *in situ* generated proton. Because generation of protons by non-catalyzed hydrolysis is a very slow reaction, decomposition of remaining thiosulfates proceeds more slowly. On the other hand, the hydrolysis of S-alkylthiosulfate intermediate in the presence of $\text{Na}_2\text{S}_2\text{O}_3$ destroys this key reagent due to producing acidic NaHSO_4 which can cause yield loss or reaction failure. However, considering reaction yield, it can be concluded that, the non-catalyzed hydrolysis reaction of Bunte salt proceeds more slowly than the reaction between alkyl halide and sodium thiosulfate.

With these results in hand, the scope of the reaction was investigated using structurally diverse alkyl halides.²² The results are presented in Table 2. As shown in Table 2, various halides were efficiently treated with $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ generating the corresponding disulfides. Primary aliphatic bromides and iodides reacted efficiently providing the corresponding disulfides in excellent yields (entries 1–4). Also, secondary bromides, including *sec*-butyl, *iso*-propyl, cyclohexyl and cyclopentyl bromides (entries 15-18) offered similar results. However, longer reaction times were required for the desired transformations. Using this protocol, a variety of benzyl halides including electron-rich and electron-poor benzyl bromides and chlorides were also converted into the corresponding disulfides exclusively in excellent yields (entries 5-12). Exceptionally, *p*-nitrobenzyl bromide (entry 7) gave the corresponding disulfide in moderate yield. With this substrate, some unidentified side products were formed. Also, allyl disulfides were produced solely

when the corresponding halides were reacted with $\text{Na}_2\text{S}_2\text{O}_3$ at 50–60 °C in excellent yields (entries 13, 14).

Table 2: Conversion of alkyl halides to symmetric disulfides using $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in DMSO^a

Entry	Alkyl halide	$2 \text{RX} + 2 \text{Na}_2\text{S}_2\text{O}_3 \xrightarrow{\text{DMSO, 60-70 }^\circ\text{C}} \text{RS-SR}$		Entry	Alkyl halide		
		t^b (h)	Isolated Yield (%)			t^b (h)	Isolated Yield (%)
1	1-bromobutane	4	89	10	<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$	2.5	89
2	$\text{PhCH}_2\text{CH}_2\text{Br}$	3	91	11	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$	2	88
3	1-Bromo-3-methylbutane	3	86	12	<i>o</i> - $\text{ClC}_6\text{H}_4\text{CH}_2\text{Cl}$	4	92
4	1-Iododecane	5	91	13 ^c	$\text{CH}_2=\text{CHCH}_2\text{Br}$	1.5	91
5	PhCH_2Br	0.5	95	14 ^c	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$	3	88
6	<i>p</i> - $\text{BrC}_6\text{H}_4\text{CH}_2\text{Br}$	1	94	15	2-Bromobutane	8	88
7	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$	1	60	16 ^c	2-Bromopropane	10	86
8	PhCH_2Cl	3	90	17	Bromocyclohexane	10	89
9	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$	2.5	89	18	Bromocyclopentane	10	87

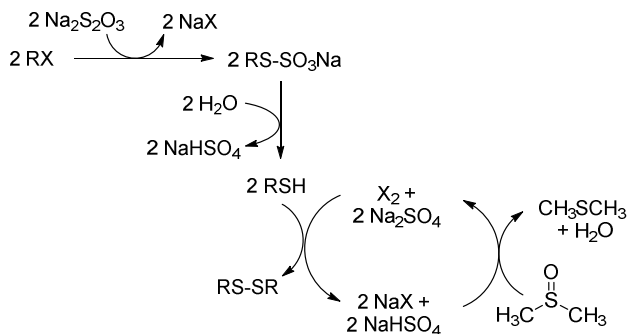
^aReaction conditions: alkyl halide (2–2.1 mmol), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (2 mmol), DMSO (2 mL), H_2O (0.2 mL), 60–70 °C.

^b t refers to the time required to change the color of litmus paper from yellow to red (pH<3).

^cThe reaction was conducted at 50–60 °C.

A proposed pathway for whole process is presented in Scheme 1. DMSO plays a dual role: It acts as a suitable solvent for the reaction and as a proper thiol oxidizing reagent. Dimethylsulfoxide is among employed reagents for the oxidation of thiols to disulfides.²² Because of its low oxidizing power, the conversion of thiols to disulfides with DMSO is not synthetically useful. This drawback has been circumvented by using dimethylsulfoxide in conjunction with a variety of co-reagents such as halogens and hydrogen halides,²³ oxophile reagents,²⁴ rhenium,²⁵ or dichlorodioxomolybdenum catalysts.²⁶

As proposed in Scheme 1, conversion of an alkyl halide to disulfide consists of three steps. At first, the alkyl halide undergoes a nucleophilic substitution reaction with thiosulfate to yield the *S*-alkylthiosulfate. Next, the thiol and sodium bisulfate as its co-product is formed from the hydrolysis of salt. This stage is a self-catalyzed reaction since the hydrolysis of Bunte salts is catalyzed by acidic reagents.²⁰ Finally, the *in situ* generated mercaptan undergoes oxidative coupling by DMSO producing the corresponding disulfide. This process can be catalyzed by molecular halogen which is generated *via* deoxygenating of DMSO by hydrogen halide.



Scheme 1: A proposed reaction pathway for the preparation of disulfides from organic halides and $\text{Na}_2\text{S}_2\text{O}_3$ in DMSO.

In conclusion, a new one-pot process for the formation of disulfides from alkyl halides is described. This method is suitable for scale-up. As structurally diverse organic halides, sodium thiosulfate and DMSO are readily available the preparation of structurally diverse disulfides becomes more practical than alternative protocols.

Experimental section

A typical scale-up procedure: A mixture of well-powdered $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (30 mmol, 7.445 g) and *o*-chlorobenzyl chloride (30.75 mmol, 4.952 g) in wet DMSO (30 mL DMSO + 3 mL H_2O) was stirred magnetically at 60–70 °C. The progress of the reaction was checked by litmus paper. After stirring for 4h, the color of litmus paper changed from yellow to red. The stirring was continued for further 2h under such conditions. Then the reaction was worked up by adding H_2O (10 mL) and extracted with 1:1 *n*-hexane/EtOAc (3×15 mL). The product was further purified by recrystallization from 20:1 *n*-hexane/EtOAc to afford pure bis(2-chlorobenzyl) disulfide in 4.162 g, 88% yield.

Bis(2-chlorobenzyl) disulfide (Table 2, entry 12): Yellow crystals; m.p. 70–72 °C (Lit.²⁷ 74 °C); $^1\text{H NMR}$ (250 MHz, CDCl_3): δ 7.40–7.18 (m, 8H), 3.79 (s, 4H); $^{13}\text{C NMR}$ (62.5 MHz, CDCl_3): δ 135.0, 134.1, 131.6, 129.7, 128.9, 126.7, 41.1. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{S}_2$: C, 53.34; H, 3.84; S, 20.34%. Found: C, 53.44; H, 3.96; S, 20.19%.

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Graphical Abstract:

Symmetrical disulfides were prepared by heating organic halides with $\text{Na}_2\text{S}_2\text{O}_3$ in DMSO in high yields and good purities.

