

## Triethylamine-catalyzed one-pot synthesis of trithiocarbonates from carbon disulfide, thiols, and alkyl halides in water

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**Abstract** Symmetrical and unsymmetrical trithiocarbonates were prepared by a simple and efficient one-pot reaction of thiols, carbon disulfide, and alkyl halides in the presence of triethylamine in water at room temperature.

**Keywords** Trithiocarbonates; Thiols; Carbon disulfide; Triethylamine; Alkyl halides.

### Introduction

Organic reactions in aqueous media have attracted considerable attention in recent years, since they offer a powerful tool for minimizing waste production and harmful organic solvent dispersal [1]. Some particular properties of water make this solvent very attractive (*i.e.*, non-toxicity, non-inflammability, high heat capacity, possibility of controlling *pH*, isolating insoluble solid products by filtration and recycling inorganic catalysts and itself), allowing organic processes in aqueous medium to be safer, very efficient, and highly selective [2].

Much attention has been paid to the synthesis of both symmetrical and unsymmetrical dialkyl trithiocarbonates, since they represent an important class of key compounds that have been used for various

applications, especially for the preparation of pesticides, insecticides in agriculture, and as lubricating additives [3]. Additionally, radical polymerization with thiocarbonylthio RAFT (reversible addition-fragmentation chain transfer) agents [4–6] is arguably one of the most versatile processes for living free radical polymerization displaying superior flexibility with respect to monomers and reaction conditions. For instance, dibenzyl trithiocarbonate (*DBTTC*) derivatives are focused as RAFT agents [5–7], which enables controlled free-radical polymerization of various vinyl monomers to afford polymers with narrow polydispersities and controlled molecular weights.

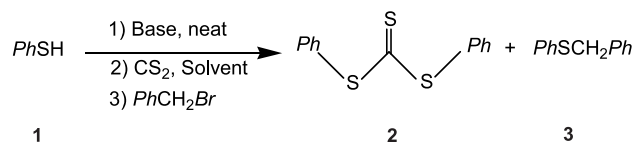
The usual syntheses of trithiocarbonates involve reactions of aryl chlorothioformates with alkanethiols [8], thiols with thiophosgene [9], benzenethiols and alkyl halides with carbon disulfide in the presence of a phase-transfer catalyst [10], sodium trithiocarbonates with alkyl halides [11], and dialkylation of the trithiocarbonate anion with halides using phase-transfer catalysts or at elevated temperature [12]. Another method involves the reaction of aliphatic thiols with 2-ethoxy-1,3-dithiolane to afford 2-alkylthio-1,3-dithiolanes. Removal of the trithioorthoformate proton at low temperature and subsequent addition of alkyl halides afforded unsymmetrical dialkyl trithiocarbonates [13]. However, various drawbacks, such as synthetic inconvenience, unavailability of starting materials, long reaction times, use of

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high or low temperatures, use of large excess of highly toxic or stinky chemicals, low yields of products, and formation of unwanted side products, such as sulfides, *etc.*, encountered in the reported procedures necessitate the development of a more efficient and convenient method. Very recently, Wood and co-workers have reported the synthesis of symmetrical trithiocarbonates using 1,1'-thiocarbonyl diimidazole (*TCDI*) and primary thiols [14]; this method, however, needs an inert atmosphere and elevated temperature (60°C) and gives moderate yields of the product. In a recent report, symmetrical trithiocarbonates have been obtained from various alkyl halides with carbon disulfide and cesium carbonate under ambient conditions [15]. In the course of our investigations on the chemistry of organosulfur compounds [16], we now describe a new, efficient, and convenient one-pot synthesis of a variety of trithiocarbonates from thiols, carbon disulfide, and alkyl halides in the presence of triethylamine in water at room temperature.

## Results and discussion

In order to optimize the reaction condition with respect to temperature, time, solvent, base, and molar ratios of the components, we first conducted the reaction of thiophenol, carbon disulfide, and benzyl bromide, as a model reaction, at various conditions under an aerial atmosphere (Scheme 1). The best molar ratios of thiophenol:carbon disulfide:benzyl



**Scheme 1**

bromide was found to be 1.5:3:1. The results are listed in Table 1. As seen from Table 1, in most cases the sulfide **3** is obtained either as the major product or as the side product; only triethylamine as the base and water at 25°C gives the expected trithiocarbonate **2** as the sole product within a short period of time and in high yield. It should be emphasized that when the reaction sequence is altered from that of shown in Scheme 1, in such a way that initially a mixture of thiophenol, CS<sub>2</sub>, and Et<sub>3</sub>N in water was stirred for 30 min at 25°C, and then benzyl bromide was added, trithiocarbonate **2** was formed as the sole product after 8 h in 83% yield. Upon examination of a broader array of thiols and alkyl halides, a series of symmetrical and unsymmetrical trithiocarbonates were prepared with a molar ratio of thiol:Et<sub>3</sub>N:CS<sub>2</sub>:alkyl halide = 1.5:2:3:1 (Table 2). The reaction sequence is summarized in Scheme 2.

The trithiocarbonate anion CS<sub>3</sub><sup>2-</sup> [17] is known to be prepared by reacting ammonium sulfide, strong aqueous ammonia, and aqueous alkali-metal hydroxide or alkali-metal sulfide with carbon disulfide. In our experiments when carbon disulfide and water were added, after 15 min to a vigorously stir-

**Table 1** Study of the influence of the base on the reaction between thiophenol, CS<sub>2</sub>, and benzyl bromide (1.5:3:1 mmol) (according to Scheme 1)

Entry	Base (mmol)	Solvent	Condition	Yield of product/% <sup>a</sup>	
				<b>2</b>	<b>3</b>
1	KF/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup> (2)	–	25°C; 2 h	0	93
2	KF/Al <sub>2</sub> O <sub>3</sub> (2)	CH <sub>3</sub> CN	25°C; 2 h	0	90
3	NaOH (5)	H <sub>2</sub> O	25°C; 3 h	15	70
4	Bu <sub>4</sub> N <sup>+</sup> OH <sup>-</sup> (1)	H <sub>2</sub> O	25°C; 2 h	25	70
5	DBU (1.5)	H <sub>2</sub> O	25°C; 4 h	60	20
6	DABCO (1.5)	H <sub>2</sub> O	25°C; 4 h	30	50
7	Et <sub>3</sub> N (2)	H <sub>2</sub> O	25°C; 50 min	85	0
8	Et <sub>3</sub> N (2)	H <sub>2</sub> O	35°C; 50 min	70	trace
9	Et <sub>3</sub> N (2)	H <sub>2</sub> O	50°C; 50 min	20	66
10	Et <sub>3</sub> N (2)	CH <sub>3</sub> CN	25°C; 11 h	76	0
11	Et <sub>3</sub> N (2)	DMF	25°C; 11 h	80	0
12	Et <sub>3</sub> N (2)	PhCH <sub>3</sub>	25°C; 20 h	70	0

<sup>a</sup> Yields of pure isolated product

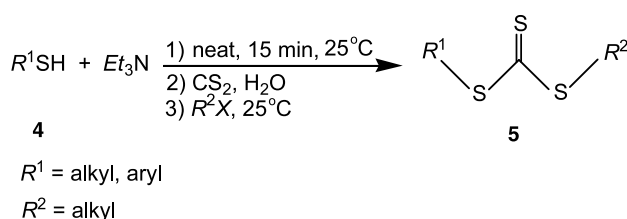
<sup>b</sup> 40% KF by weight

**Table 2** Synthesis of various trithiocarbonates<sup>a</sup>

Entry	R <sup>1</sup>	R <sup>2</sup> X	Time/h	Product	Yield <sup>b,c</sup> /%	Ref.
1	Ph	PhCH <sub>2</sub> Br	0.83	<b>5a</b>	85	[10]
2	Ph	PhCH <sub>2</sub> Cl	2.33	<b>5a</b>	82	[10]
3	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub> Br	1.83	<b>5b</b>	96	[10]
4	PhCH <sub>2</sub>	PhCH <sub>2</sub> Br	0.67	<b>5c</b>	97	[15]
5	Ph	CH <sub>3</sub> CH <sub>2</sub> I	2.67	<b>5d</b>	84	[8]
6	4-ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> CH <sub>2</sub> I	3	<b>5e</b>	80	[8]
7	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> CH <sub>2</sub> I	1.67	<b>5f</b>	86	[8]
8	2-naphthyl	CH <sub>3</sub> CH <sub>2</sub> I	2	<b>5g</b>	78	[8]
9	PhCH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> I	1.92	<b>5h</b>	91	[8]
10	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> CH <sub>2</sub> I	3	<b>5i</b>	83	[8]
11	2-ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> CH <sub>2</sub> I	1.83	<b>5j</b>	74	[8]
12	(CH <sub>3</sub> ) <sub>3</sub> C	CH <sub>3</sub> CH <sub>2</sub> I	13	<b>5k</b>	43	[8]
13	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> I	1.5	<b>5l</b>	80	[8]
14	Ph	CH <sub>3</sub> I	1.2	<b>5m</b>	92	[8]
15	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> I	1.2	<b>5n</b>	94	[8]
16	4-ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> I	1.67	<b>5o</b>	75	[8]
17	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> I	1	<b>5p</b>	95	[8]
18	PhCH <sub>2</sub>	CH <sub>3</sub> I	1	<b>5q</b>	96	[8]
19	Ph	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> Br	0.75	<b>5r</b>	94	[10]
20	Ph	(CH <sub>3</sub> ) <sub>2</sub> CHBr	2.67	<b>5s</b>	48	[10]
21	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> I	1.25	<b>5t</b>	78	[15]

<sup>a</sup> Reaction conditions: thiol (1.5 mmol), triethylamine (2 mmol), CS<sub>2</sub> (3 mmol), alkyl halide (1 mmol), H<sub>2</sub>O (1 cm<sup>3</sup>), 25°C in air;

<sup>b</sup> Isolated yield; <sup>c</sup> References for known compounds



red mixture of thiol and triethylamine at 25°C, the colorless mixture immediately changed to a blood-red solution indicating the formation of trithiocarbonate anion [17]; after 30 min the alkyl halide was added to the red solution to afford the desired trithiocarbonates within a short period of time in 43–97% yields (Table 2). The structures of all the products were established from their analytical and spectral properties. We found that this method is applicable for aliphatic as well as aromatic thiols and different alkyl halides (primary, secondary, and benzyl halides). The procedure worked fine with primary and benzyl halides, whereas secondary halides (Table 2, entry 20) react slowly, giving the product with low yield. Reaction of a bulky thiol such as 2-methyl-2-propanethiol with ethyl iodide (Table 2,

entry 12) took a long time giving 43% yield of the product.

This novel one-pot procedure provides high yields of both symmetrical and unsymmetrical dialkyl and aryl alkyl trithiocarbonates at room temperature under an aerial atmosphere. Our method has the advantages of operational simplicity, mild reaction conditions, fast reaction rates, simple reaction work-up, high yields of trithiocarbonates without using large excess amounts of toxic carbon disulfide, and use of a cheap basic catalyst.

## Experimental

All products were characterized by comparison of their spectral and physical data with those of known samples. IR spectra were obtained using an ABB FTLA 2000 instrument. NMR spectra were recorded on a Bruker DRX-500 Avance instrument at 500 MHz for <sup>1</sup>H and at 125 MHz for <sup>13</sup>C NMR in CDCl<sub>3</sub> solutions. Melting points and boiling points were determined by a Büchi B-540 melting point/boiling point capillary apparatus.

*Typical procedure exemplified by the preparation of benzyl phenyl trithiocarbonate (5a, C<sub>14</sub>H<sub>12</sub>S<sub>3</sub>)*

In a typical experiment, a mixture of 165 mg thiophenol (1.5 mmol) and 202 mg triethylamine (2 mmol) was vigorous-

ly stirred at 25°C for 15 min. Then 1 cm<sup>3</sup> H<sub>2</sub>O and 228 mg CS<sub>2</sub> (3 mmol) were added at once. After 30 min of stirring, 171 mg benzyl bromide (1 mmol) was added to the blood-red mixture. The color of the resulting reaction mixture changed from red to light-yellow. Stirring was continued at 25°C for 50 min in air atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, the organic materials were extracted with 3 × 15 cm<sup>3</sup> Et<sub>2</sub>O. The combined organic phases were washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was evaporated and the residue was subjected to preparative TLC (silica gel, eluent: *n*-hexane/CHCl<sub>3</sub> = 10/1) to afford 235 mg of the pure benzyl phenyl trithiocarbonate (85%) as a pale-yellow oil. Spectroscopic properties were found to be identical with that of an authentic sample.

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