

An efficient, one-pot synthesis of trithiocarbonates from alcoholic tosylates using the $\text{Cs}_2\text{CO}_3/\text{CS}_2$ system

Devdutt Chaturvedi¹, Nisha Mishra², Amit K. Chaturvedi², Virendra Mishra²

¹ Bio-Organic Chemistry Division, Indian Institute of Integrative Medicine, Jammu-Tawi, J&K, India

² Synthetic Research Laboratory, Department of Chemistry, B.S.A.P.G. College, Mathura, U.P., India

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Abstract A single-step novel protocol for the preparation of symmetrical trithiocarbonates from a corresponding variety of primary, secondary, and tertiary alcoholic tosylates using the $\text{Cs}_2\text{CO}_3/\text{CS}_2$ system, was developed. This protocol is mild and more efficient than the reported methods.

Keywords Alcoholic tosylates; Carbon disulfide; Cesium carbonate; Trithiocarbonates.

Introduction

Organic trithiocarbonates have received much attention due to their numerous remarkable industrial, synthesis, and medicinal applications [1]. They have extensively been used as pharmaceuticals [2], agrochemicals [3], intermediates in organic synthesis [4], for protection of thiol functionality [5], in free radical polymerization reactions [6], as lubricating additives [7], in material science [8], in froth floatation process [9], for the recovery of minerals from their ores, and for their metals absorption properties [10]. Moreover, their application as synthons for the synthesis of various kinds of useful compounds, such as sulfines [11], ketenes [12], trithiocarbonate-*S*-oxides [13], thiols [14], dithiocarboxylate derivatives [15],

thioacetates [16], olefins [17], nitro-1,3-benzodithiole-2-thiones [18], phosphite ylides [19], and various kinds of C–C bond forming reactions [20], *etc.* necessitates their preparation through a convenient and safe methodology.

Classical synthesis of trithiocarbonates involves the reaction of thiols with thiophosgene [21] or its derivatives [22]. These methods are associated with several drawbacks, such as use of costly, toxic, and corrosive reagents. Alternative routes for their synthesis involves reaction of metal xanthates with epoxides [23] or episulfides [24], the reaction of organic dihalides with sodium trithiocarbonates [25], reaction of sodium trithiocarbonates with epoxides [26], reaction of CS_2 with alkyl halides using KOH [27], reaction of alkyl halides with the hydroxide form of anion exchange resin [28], and by *S*-arylation of potassium carbonotrithiolates with diaryliodonium salts [29]. The application of phase transfer catalyst technique has had enormous impact on the synthesis of this class of compounds [30], but the method requires strongly basic conditions. Recently, a method for the synthesis of trithiocarbonates was achieved using $\text{Cs}_2\text{CO}_3/\text{CS}_2$ system [31]. Most of these methods suffer from the limitations of long reaction times, use of expensive strongly basic reagents, tedious work-up, and low yields. Consequently, there is continued interest in developing new and convenient methods for the synthesis of trithiocarbonates using mild reaction conditions.

Correspondence: Devdutt Chaturvedi, Bio-Organic Chemistry Division, Indian Institute of Integrative Medicine, Canal Road, Jammu-Tawi-18000, J&K, India. E-mail: ddchaturvedi002@yahoo.co.in

Our group [32] has been engaged from the past several years in the development of new and efficient protocols for the synthesis of carbamates, dithiocarbamates, and dithiocarbonates (xanthates) using cheap and abundantly available reagents like CO_2 and CS_2 . In the present paper, we report an efficient and novel protocol for the preparation of symmetrical trithiocarbonates from the corresponding alcoholic tosylates using a minimum amount of the $\text{Cs}_2\text{CO}_3/\text{CS}_2$ system. Alcoholic tosylates were prepared from the corresponding alcohols following the standard procedure [33].

Results and discussion

In order to attain easy operations and to maintain the base sensitive trithiocarbonate group, we conducted the reaction under very mild conditions (*i.e.*, at room temperature under an aerial atmosphere). Thus, an equimolar mixture of CS_2 and Cs_2CO_3 was taken

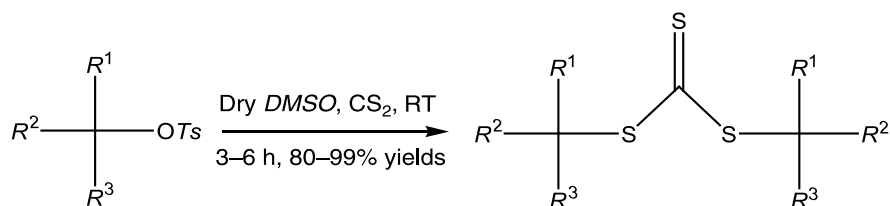
in dry *DMSO* and was vigorously stirred at room temperature for 15 min. The colorless mixture changed to a blood-red solution within a few minutes, indicating the formation of trithiocarbonate anion (CS_3^{2-}) [34]. After stirring for 15 min, an equimolar amount of the corresponding alcoholic tosylate was added. Stirring of the reaction mixture was continued at 25°C until the reaction was completed. The color of the reaction mixture immediately changed from red to pale yellow. The reaction was monitored periodically by NMR spectroscopy. After completion of the reaction, the mixture was poured into distilled water and extracted three times with ethyl acetate to afford the desired product. Thus, various trithiocarbonate derivatives were prepared in high yields (80–99%), and their spectroscopic confirmation was achieved from the reported values as mentioned in Table 1.

We have tried many solvents like *DMSO*, *DMF*, benzene, acetonitrile, dichloromethane, *n*-hexane,

Table 1 Conversion of alcoholic tosylates into trithiocarbonates^a

Entry	R^1	R^2	R^3	Time/h	Yields/%	Ref.
1	$\text{CH}_2=\text{CH}$	H	H	4	96	[31]
2	<i>Ph</i>	H	H	5	99	[31]
3	<i>Me</i>	H	H	4	98	[31]
4	<i>n</i> - C_3H_7	H	H	3	99	[31]
5	<i>n</i> - C_7H_{15}	H	H	3	99	[31]
6	<i>Et</i>	H	H	4	94	[35]
7	<i>Ph</i>	<i>Me</i>	H	5	96	[35]
9	<i>n</i> - C_4H_9	<i>n</i> - C_4H_9	H	5	85	[35]
10	<i>n</i> - C_4H_9	<i>n</i> - C_4H_9	<i>n</i> - C_4H_9	6	80	[28]
11	<i>n</i> - C_6H_{13}	H	H	3	94	[28]
12	<i>n</i> - C_7H_{15}	<i>Me</i>	H	4	85	[28]
13	<i>n</i> - C_8H_{17}	H	H	3	96	[18]
14	<i>n</i> - C_7H_{15}	H	H	4	98	[18]
15	<i>n</i> - C_5H_{11}	<i>Me</i>	H	5	90	[18]
16	2-Naphthyloxyethyl	H	H	5	86	[35]
17	3-(2-Naphthyloxy)prop-1-yl	H	H	5	92	[35]
18	<i>n</i> - C_6H_{13}	<i>Me</i>	<i>Me</i>	4	93	[18]
19	<i>n</i> - $\text{C}_{12}\text{H}_{25}$	H	H	3	99	[18]

^a All the products were characterized by IR, NMR, and mass spectral data



Scheme 1

heptane, methanol, chloroform, acetone. But, dry *DMSO* proved to be the most suitable solvent for carrying out this transformation. The overall reaction is shown in Scheme 1.

In conclusion, we developed a convenient and efficient protocol for the one-pot, three-component coupling of a variety of alcoholic tosylates *via* a CS_3^{2-} bridge. We have noted that equimolar amounts of cesium carbonate and carbon disulfide are necessary to give trithiocarbonates from a variety of alcoholic tosylates. This reaction generates the corresponding trithiocarbonates in excellent yields (80–99%) at room temperature. Furthermore, this method exhibits substrate versatility, mild reaction conditions, and experimental convenience. This synthetic protocol is believed to offer a more general method for the formation of C–S bonds essential to numerous organic syntheses.

Experimental

Chemicals were procured from Merck, Aldrich, and Fluka chemical companies. Reactions were carried out under an atmosphere of nitrogen. IR spectra ($4000\text{--}200\text{ cm}^{-1}$) were recorded on a Bomem MB-104–FTIR spectrophotometer whereas NMR spectra were scanned on an AC-300F NMR (300 MHz) instrument using CDCl_3 and some other deuterated solvents and *TMS* as internal standard. Elemental analysis were made by a Carlo-Erba EA 1110-CHNO-S analyzer and agreed favorably with calculated values.

General experimental procedure

A mixture of 5.0 mmol CS_2 and 5.0 mmol Cs_2CO_3 in 5 cm^3 dry *DMSO* was stirred at room temperature ($20\text{--}25^\circ\text{C}$) for 15 min, and then 5 mmol of the corresponding alcoholic tosylate in 2 cm^3 dry *DMSO* were added. Stirring of the reaction mixture was continued at room temperature until the reaction was completed (as monitored by TLC and ^1H NMR). The reaction was quenched by pouring into ice-water. The product was extracted with ethyl acetate, and the solution was dried over Na_2SO_4 , filtered, and evaporated to afford pure desired product.

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